

Stereoselective Synthesis of Methylene Oxindoles via Palladium(II)-Catalyzed Intramolecular Cross-Coupling of Carbamoyl Chlorides

Christine M. Le,[†] Theresa Sperger,[‡] Rui Fu,[†] Xiao Hou,[†] Yong Hwan Lim,[†] Franziska Schoenebeck^{*,‡} and Mark Lautens^{*,†}

[†]Department of Chemistry, University of Toronto, Lash Miller Laboratories, 80 St. George St., Toronto M5S 3H6, Canada.

[‡]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

* E-mails: franziska.schoenebeck@rwth-aachen.de, mlautens@chem.utoronto.ca

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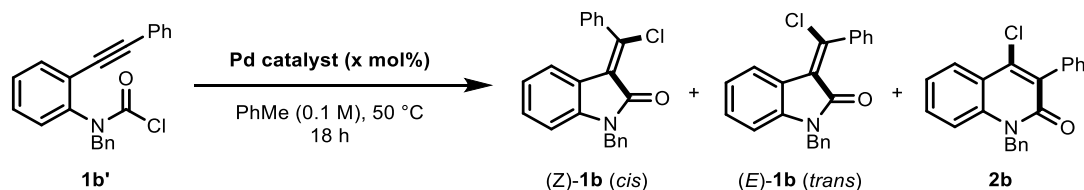
1 General Considerations

Commercial reagents were purchased from Sigma Aldrich, Combi-Blocks, Strem or Alfa Aesar and used without further purification. Unless otherwise stated, all catalytic reactions were carried out under air without rigorous exclusion of oxygen and moisture, whereas the work-up and isolation of the products from the catalytic reactions were conducted on the bench-top using standard techniques. Solvents and solutions were transferred by syringe or cannula. Tetrahydrofuran was distilled from sodium and benzophenone ketal, toluene was distilled over sodium, and triethylamine and diisopropylamine were distilled from potassium hydroxide. Reactions were monitored by Thin Layer Chromatography (TLC) using EM Separations pre-coated silica gel 0.2 mm layer UV 254 fluorescent sheets, and visualization was accomplished with 250 nm UV light followed by immersion in KMnO₄ stain. Organic solutions were concentrated by rotary evaporation at reduced pressure (15 – 30 torr, house vacuum) at 25-50 °C. Unless otherwise stated, flash chromatography was performed using Ultra Pure 230-400 mesh silica gel purchased from Silicycle. NMR characterization data was collected at 296 K on a Varian Mercury 300, Varian Mercury 400, Agilent DD2 500, Agilent DD2 600, or a Bruker Advance III spectrometer operating at 300, 400, 500, or 600 MHz for ¹H NMR, and 75, 100, 125, or 150 MHz for ¹³C NMR. ¹H NMR spectra were internally referenced to the residual solvent signal (CDCl₃ = 7.26 ppm) or TMS (0 ppm). ¹³C NMR spectra were internally referenced to the residual solvent signal (CDCl₃ = 77.16 ppm) and are reported as observed. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (Hz), integration. Melting point ranges were determined on a Fisher-Johns Melting Point Apparatus and are reported uncorrected. IR spectra were obtained on either a Shimadzu FTIR-8400S FT-IR spectrometer on NaCl plates or on a PerkinElmer Spectrum 100 instrument equipped with a single-bounce diamond / ZnSe ATR accessory in the solid state. All reported Z:E ratios are obtained from ¹H NMR analysis of the crude reaction mixtures using a 5 second relaxation delay. NMR yields for the optimization section were obtained by ¹H NMR analysis of the crude reaction mixture using a 10 second relaxation delay and 1,3,5-trimethoxybenzene as an internal standard. High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI) or a JEOL AccuTOF medel JMS-T1000LC mass spectrometer

equipped with an IONICS® Direct Analysis in real Time (DART) ion source at Advanced Instrumentation for Molecular Structure (AIMS) in the Department of Chemistry at the University of Toronto.

2 Full Reaction Optimization

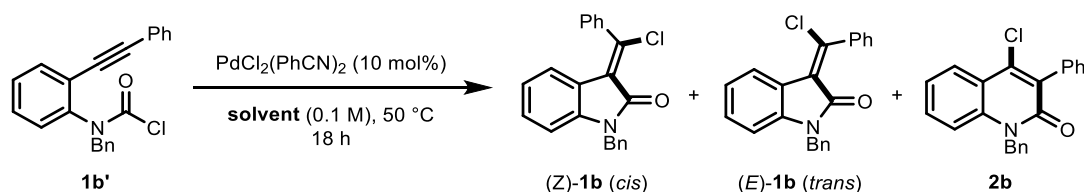
Table S1. Screening of Pd Catalysts



Entry ^a	Pd catalyst [x]	Conv. (%)	NMR yields (%)				Z:E ratio
			Z-1b	E-1b	2b	Combined	
1	PdCl ₂ [10]	25	17	1	5	23	94:6
2	PdCl ₂ (MeCN) ₂ [10]	100	73	3	15	91	>95:5
3	PdCl ₂ (PhCN) ₂ [10]	100	77	3	15	96	>95:5
4	Na ₂ PdCl ₄ [10]	25	22	<2	5	22	90:10
5	PdCl ₂ (PPh ₃) ₂ [10]	2	0	0	0	0	N/A
6	PdCl ₂ (phen) [10]	0	-	-	-	-	N/A
7	PdBr ₂ [10]	4	0	0	0	0	N/A
8	PdBr ₂ (PhCN) ₂ [10]	4	0	0	0	0	N/A
9	Pd(OAc) ₂	100	53	12	15	80	82:18
10 ^b	Pd ₂ dba ₃ /PA-Ph [1.25/5.0]	8	0	0	0	0	N/A
11	PdL ₂ [5.0] (L = PtBu ₂ Ph, PtBu ₃ , QPhos)	9-19	0	0	0	0	N/A
12	None	-	-	-	-	-	N/A

N/A = not applicable. ^a Conversions, NMR yields, and Z:E ratios determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard. ^b Reaction concentration = 0.2 M

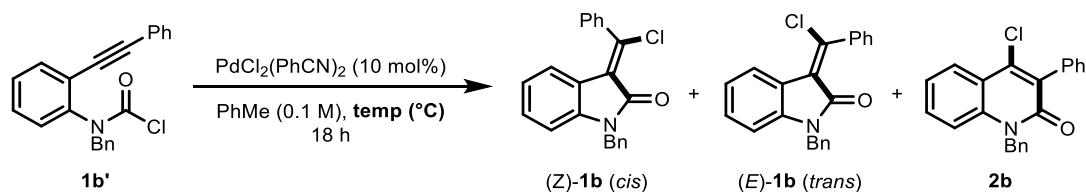
Table S2. Solvent Screen



Entry ^a	Solvent	Conv. (%)	NMR yields (%)				Z:E ratio
			Z-1b	E-1b	2b	Combined	
1 ^b	PhMe	100	77	3	15	96	>95:5
2	THF	100	65	8	16	89	89:11
3	1,4-dioxane	6	5	0	0	6	N.D.
4	DCE	100	79	8	13	100	91:9
5	MeCN	10	5	2	2	9	71:29

N.D. = not determined. ^a Conversions, NMR yields, and Z:E ratios determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard. ^b Same as Entry 3 in Table S1.

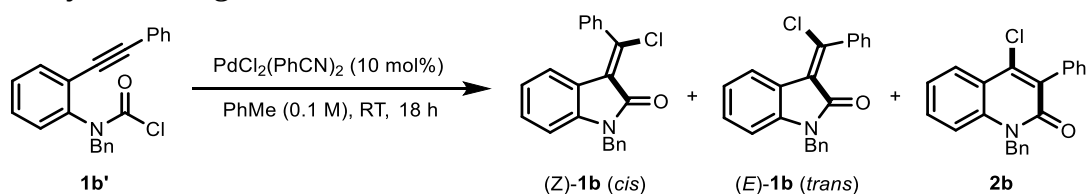
Table S3. Temperature Screen



Entry ^a	Temperature (°C)	Conv. (%)	NMR yields (%)			Z:E ratio
			Z-1b	E-1b	2b	
1	100	100	33	49	16	40:60
2	80	100	56	18	11	76:24
3 ^b	50	100	77	3	15	>95:5
4	40	100	80	2	15	>95:5
5	30	100	82	2	16	>95:5
6	RT	100	83	<1	16	>95:5

^a Conversions, NMR yields, and Z:E ratios determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard. ^b Same as Entry 3 in Table S1.

Table S4. Catalyst Loading and Additive Screen

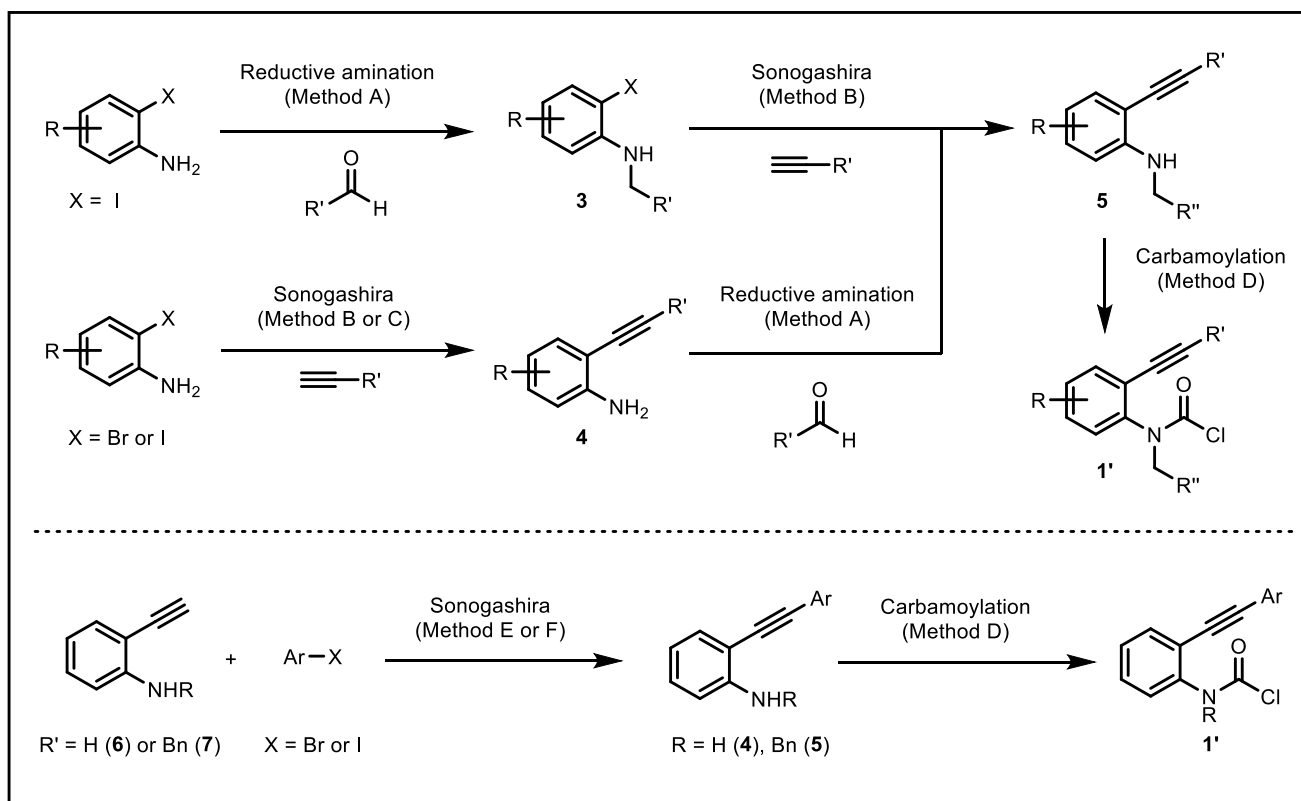


Entry ^a	Deviations	Conv. (%)	NMR yields (%)			Z:E ratio
			Z-1b	E-1b	2b	
1 ^b	none	100	83	<1	16	>95:5
2	5 mol% Pd	98	78	3	17	>95:5
3	5 mol% Pd, PhMe (0.2 M), under air	100	81	1	16	>95:5
4	LiCl (1.0 equiv)	84	70	1	13	>95:5
5	CuCl (1.0 equiv)	100	82	2	15	>95:5
6	CuCl ₂ (1.0 equiv)	100	81	2	16	>95:5

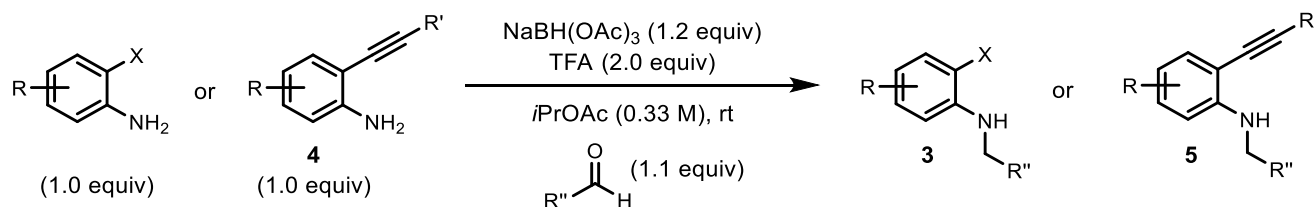
^a Conversions, NMR yields, and Z:E ratios determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard. ^b Same as Entry 6 in Table S3.

3 General Procedures and Characterization Data for Starting Materials

3.1 General synthetic scheme for the synthesis of carbamoyl chlorides **1'**

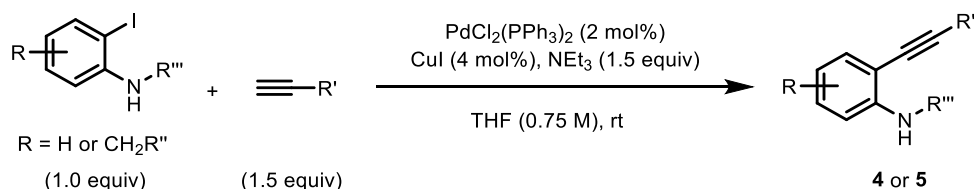


General procedure for reductive amination (**Method A**):



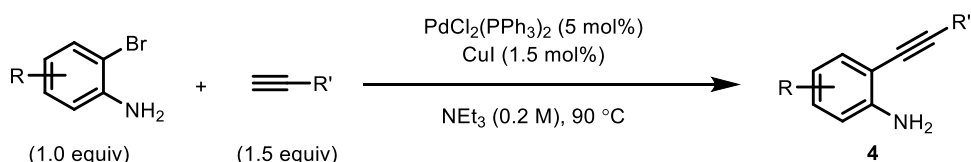
Following a modified literature procedure described by McLaughlin and co-workers,¹ a two-neck round bottom flask was sequentially charged with the aniline (1.0 equiv), $iPrOAc$ and the aldehyde (1.1 equiv). To this solution, TFA (2.0 equiv) was added dropwise. After stirring for 10 minutes, $NaBH(OAc)_3$ (1.2 equiv) was added portionwise under argon to the reaction mixture (slightly exothermic). Upon full consumption of the starting material (typically overnight), the reaction was quenched by the addition of 10% (w/w) aqueous NaOH until a pH of 8-9 was reached. The aqueous phase was extracted with Et_2O (3x). The combined organics were washed with brine (1x), dried over Na_2SO_4 , and concentrated *in vacuo*. The crude material was purified by flash chromatography using the indicated eluent.

General procedure for Sonogashira cross-coupling (**Method B**):



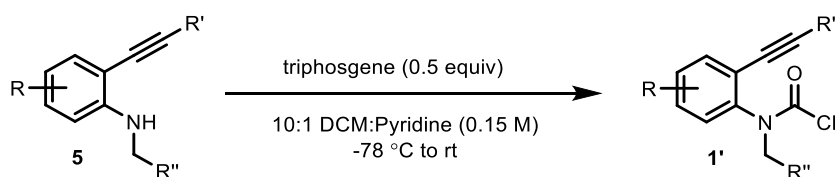
To solution of aryl iodide (1.0 equiv), PdCl₂(PPh₃)₂ (0.02 equiv) and CuI (0.04 equiv) in anhydrous THF was added NEt₃ (1.5 equiv) dropwise at rt under argon. After stirring for 5 minutes, the terminal alkyne (1.5 equiv) was added neat and dropwise to the reaction mixture (slightly exothermic). Upon full consumption of the starting material, the reaction mixture was filtered through a pad of celite, eluting with EtOAc (3x). The combined organics were sequentially washed with H₂O (2x) and brine (1x), dried over Na₂SO₄ and concentrated *in vacuo*. The resulting crude mixture was purified by flash chromatography using the indicated eluent.

General procedure for Sonogashira cross-coupling (**Method C**):



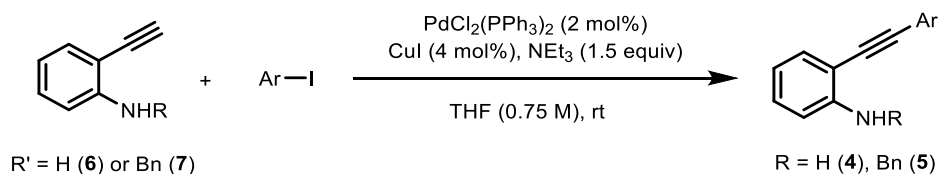
To solution of aryl bromide (1.0 equiv), PdCl₂(PPh₃)₂ (0.05 equiv) and CuI (0.015 equiv) in anhydrous NEt₃ (0.2 M) was added the terminal alkyne (1.5 equiv) neat and dropwise under argon. The flask was equipped with a reflux condenser and heated to 90 °C. Upon full or nearly full consumption of the starting material (typically overnight), the reaction mixture was filtered through a pad of celite, eluting with EtOAc (3x). The combined organics were sequentially washed with H₂O (2x) and brine (1x), dried over Na₂SO₄ and concentrated *in vacuo*. The crude mixture was purified by flash chromatography using the indicated eluent.

General procedure for carbamoylation (**Method D**):



Following a literature procedure,² a solution of triphosgene (0.5 equiv) in anhydrous DCM was cooled to -78 °C. Pyridine was added dropwise under argon, resulting in the formation of a yellow precipitate. After stirring for 5 minutes, a solution of **5** in DCM was added and the reaction mixture was subsequently warmed to rt. The final reaction concentration was 0.15 M with respect to **5**. The reaction became a homogeneous solution after 10-15 minutes. Upon full consumption of the starting material, the reaction was quenched by the addition of 1M HCl and the aqueous layer was extracted with DCM (3x). The combined organics were washed with brine (1x), dried over Na₂SO₄ and concentrated *in vacuo*. The crude material was purified by flash chromatography using the indicated eluent.

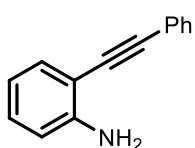
General procedure for Sonogashira cross-coupling (**Method E**):



To solution of aryl iodide (1.0 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.02 equiv) and CuI (0.04 equiv) in anhydrous THF was added NEt_3 (1.5 equiv) dropwise at rt under argon. After stirring for 5 minutes, terminal alkyne **6** or **7** (1.2 equiv) was added as a solution in THF (slightly exothermic). The final reaction concentration was 0.75 M with respect to the aryl iodide. Upon full consumption of the starting material, the reaction mixture was filtered through a pad of celite, eluting with EtOAc (3x). The combined organics were sequentially washed with H_2O (2x) and brine (1x), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude mixture was purified by flash chromatography using the indicated eluent.

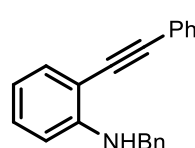
3.2 Characterization Data for Starting Materials

2-(phenylethynyl)aniline (**4b**)



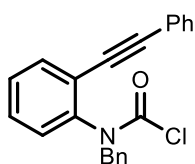
The title compound was prepared according to **Method B** (20.0 mmol scale) using 2-iodoaniline and phenylacetylene. The crude material was purified by flash chromatography (15% EtOAc /hexanes) and the desired product was isolated as an orange solid (3.81 g, 19.7 mmol, 98%). The spectral data is consistent with literature values.³

N-benzyl-2-(phenylethynyl)aniline (**5b**)



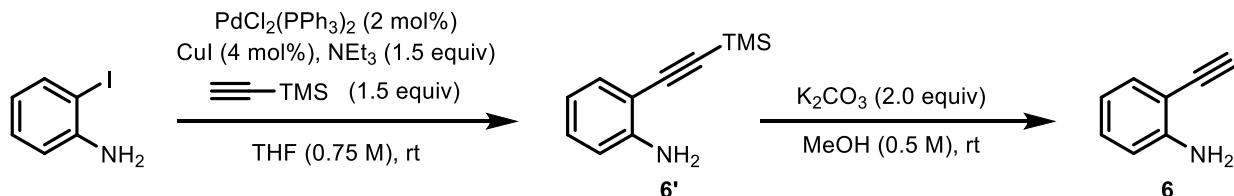
The title compound was prepared according to **Method A** (5.00 mmol scale) using **4b** and benzaldehyde. The crude material was purified by flash chromatography (5% Et_2O /hexanes) and the desired product was isolated as a light yellow oil (1.20 g, 4.24 mmol, 85%). The spectral data is consistent with literature values.⁴

benzyl(2-(phenylethynyl)phenyl)carbamic chloride (**1b'**)



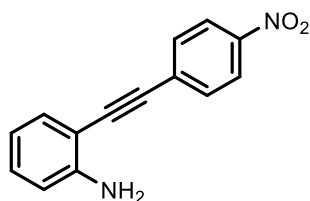
The title compound was prepared according to **Method D** (7.20 mmol scale) using **5b**. The crude material was purified by flash chromatography (5% Et_2O /hexanes) and the desired product was isolated as a white solid (2.34 g, 6.77 mmol, 94%). **MP** = 69-71 °C. **¹H NMR** (400 MHz, CDCl_3) δ 7.60 (dd, J = 7.7, 1.6 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.42 – 7.30 (m, 4H), 7.29 – 7.17 (m, 6H), 6.87 (dd, J = 7.9, 1.3 Hz, 1H), 5.38 (d, J = 14.3 Hz, 1H), 4.52 (d, J = 14.3 Hz, 1H). **¹³C NMR** (126 MHz, CDCl_3) δ 150.2, 142.7, 135.5, 132.9, 131.9, 129.7, 129.5, 129.1, 129.0, 128.9, 128.7, 128.6, 128.3, 123.3, 122.6, 95.4, 84.9, 55.8. **IR** (CHCl_3 , cm^{-1}) 3063, 3032, 2218, 1736, 1497, 1452, 1375, 1225, 1194. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{17}\text{ClNO}]^+$ $[\text{M}+\text{H}]^+$ 346.09987 found 346.10033.

2-ethynylaniline (**6**)



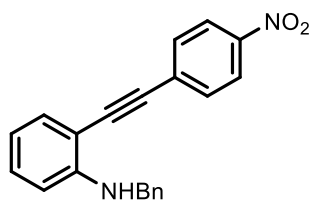
To solution of 2-iodoaniline (2.33 g, 10.0 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (140 mg, 0.20 mmol) and CuI (76.2 mg, 0.40 mmol) in anhydrous THF (13.3 mL) was added NEt_3 (2.09 mL, 15.0 mmol) dropwise at rt under argon. After stirring for 5 minutes, ethynyltrimethylsilane (2.12 mL, 15.0 mmol) was added neat and dropwise to the reaction mixture. The reaction was stirred at rt overnight, diluted with EtOAc and filtered through a pad of celite. The combined organics were sequentially washed with H_2O (2x) and brine (1x), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude mixture was purified by flash chromatography (10% Et₂O/hexanes) and **6'** was isolated as brown oil (1.61 g, 8.50 mmol, 85%). To a stirring solution of **6'** (1.42 g, 7.50 mmol) in MeOH (15.0 mL), solid K_2CO_3 (2.07 g, 15.0 mmol) was added. After stirring at rt for 1 h, the solvent was removed under reduced pressure, water was added and aqueous phase was extracted with EtOAc (3x). The combined organics were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography (20% Et₂O/hexanes) and **6** was isolated as a yellow oil (520 mg, 4.44 mmol, 59%). The spectral data is consistent with literature values.⁵

2-((4-nitrophenyl)ethynyl)aniline (**4c**)



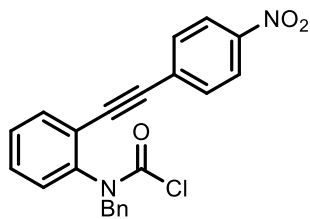
The title compound was prepared according to **Method E** (3.75 mmol scale) using 1-iodo-4-nitrobenzene and 2-ethynylaniline (**6**). The crude material was purified by flash chromatography (10→25% EtOAc/hexanes) and the desired product was isolated as an orange solid (625 mg, 2.63 mmol, 70%). The spectral data is consistent with literature values.⁶

N-benzyl-2-((4-nitrophenyl)ethynyl)aniline (**5c**)



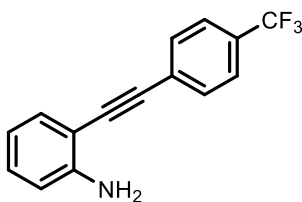
The title compound was prepared according to **Method A** (2.16 mmol scale) using **4c** and benzaldehyde. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as an orange solid (296 mg, 0.90 mmol, 42%). **MP** = 108–110 °C. **¹H NMR** (500 MHz, CDCl_3) δ 8.23 – 8.16 (m, 2H), 7.61 – 7.55 (m, 2H), 7.44 – 7.33 (m, 5H), 7.34 – 7.26 (m, 1H), 7.22 (ddd, J = 8.3, 7.5, 1.6 Hz, 1H), 6.69 (td, J = 7.5, 1.1 Hz, 1H), 6.62 (ddd, J = 8.3, 1.1, 0.5 Hz, 1H), 5.05 (bs, 1H), 4.47 (d, J = 5.2 Hz, 2H). **¹³C NMR** (126 MHz, CDCl_3) δ 149.2, 146.9, 139.0, 132.7, 132.0, 131.3, 130.4, 128.9, 127.6, 127.2, 123.8, 117.0, 110.4, 106.4, 93.8, 92.0, 47.9. **IR** (CHCl_3 , cm^{-1}) 3065, 3032, 2920, 2247, 1697, 1607, 1468, 1344, 1175, 1103. **HRMS** (DART) Calc'd for $[\text{C}_{21}\text{H}_{17}\text{N}_2\text{O}_2]^+ [\text{M}+\text{H}]^+$ 329.12900 found 329.12832.

benzyl(2-((4-nitrophenyl)ethynyl)phenyl)carbamic chloride (1c')



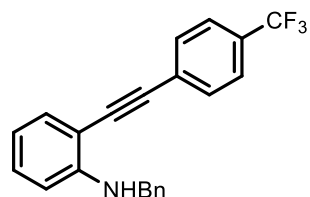
The title compound was prepared according to **Method D** (0.73 mmol scale) using **5c**. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a yellow solid (256 mg, 0.66 mmol, 90%). **MP** = 117-119 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.28 – 8.17 (m, 2H), 7.67 – 7.53 (m, 3H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.34 (td, *J* = 7.6, 1.6 Hz, 1H), 7.28 – 7.14 (m, 5H), 7.05 – 6.93 (m, 1H), 5.23 (d, *J* = 14.2 Hz, 1H), 4.61 (d, *J* = 14.2 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.1, 147.5, 143.0, 135.2, 133.2, 132.6, 130.3, 129.6, 129.6, 129.4, 129.1, 128.7, 128.5, 123.8, 122.6, 92.9, 89.9, 56.2. **FTIR** (neat, cm⁻¹) 2218, 1742, 1589, 1513, 1378, 1338, 1229, 1198. **HRMS** (DART) Calc'd for [C₂₂H₁₆ClN₂O₃]⁺ [M+H]⁺ 391.08494 found 391.08495.

2-((4-(trifluoromethyl)phenyl)ethynyl)aniline (4d)



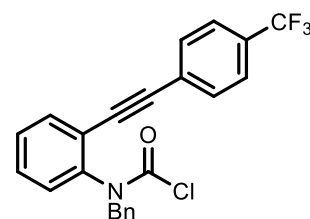
The title compound was prepared according to **Method E** (5.00 mmol scale) using 4-iodobenzotrifluoride and 2-ethynylaniline (**6**). The crude material was purified by flash chromatography (20% Et₂O/hexanes) and the desired product was isolated as an off-white solid (1.19 g, 4.56 mmol, 91%). The spectral data is consistent with literature values.⁷

N-benzyl-2-((4-(trifluoromethyl)phenyl)ethynyl)aniline (5d)



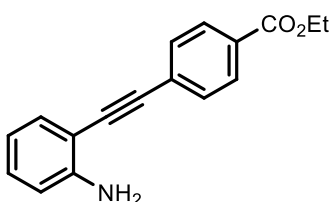
The title compound was prepared according to **Method A** (4.00 mmol scale) using **4d** and benzaldehyde. The crude material was purified by flash chromatography (2% Et₂O/hexanes) and the desired product was isolated as a light yellow solid (745 mg, 2.12 mmol, 53%). The spectral data is consistent with literature values.⁸

benzyl(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)carbamic chloride (1d')



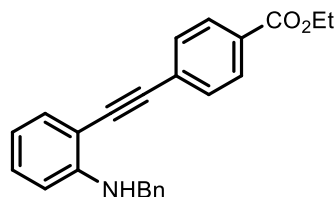
The title compound was prepared according to **Method D** (1.61 mmol scale) using **5d**. The crude material was purified by flash chromatography (1→10% EtOAc/hexanes) and the desired product was isolated as a white solid (330 mg, 0.80 mmol, 50%). **MP** = 85-87 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.67 – 7.52 (m, 5H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 (ddd, *J* = 7.5, 1.6 Hz, 1H), 7.29 – 7.19 (m, 5H), 6.93 (ddd, *J* = 7.9, 1.3, 0.5 Hz, 1H), 5.30 (d, *J* = 14.3 Hz, 1H), 4.57 (d, *J* = 14.3 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.0, 142.8, 135.1, 132.9, 132.0, 130.5 (q, *J* = 32.7 Hz), 129.6, 129.4, 129.4, 128.8, 128.6, 128.2, 126.2 (q, *J* = 1.6 Hz), 125.4 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.3 Hz), 122.7, 93.5, 87.1, 55.9. **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.9. **FTIR** (neat, cm⁻¹) 1726, 1614, 1484, 1453, 1373, 1231, 1171, 1110, 1065. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClF₃NO]⁺ [M+H]⁺ 414.08725 found 414.08616.

ethyl 4-((2-aminophenyl)ethynyl)benzoate (4e)



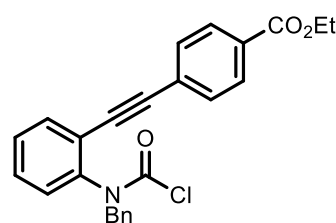
The title compound was prepared according to **Method E** (4.13 mmol scale) using ethyl 4-iodobenzoate and 2-ethynylaniline (**6**). The crude material was purified by flash chromatography (10→20% EtOAc/hexanes) and the desired product was isolated as a yellow solid (909 mg, 3.43 mmol, 83%). The spectral data is consistent with literature values.⁹

ethyl 4-((2-(benzylamino)phenyl)ethynyl)benzoate (5e)



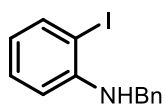
The title compound was prepared according to modified procedure of **Method A** (3.01 mmol scale) using **4e** and benzaldehyde [Modification: *after stirring the reaction for 19 h at rt, another 0.5 equiv of NaBH(OAc)₃ was added and the reaction was heated to 60 °C until complete consumption of the starting material was observed by TLC*]. The crude material was purified by flash chromatography (25→50% DCM/hexanes) and the desired product was isolated as a white solid (558 mg, 1.57 mmol, 52%). **MP** = 97-99 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.07 – 7.94 (m, 2H), 7.57 – 7.48 (m, 2H), 7.47 – 7.26 (m, 6H), 7.24 – 7.14 (m, 1H), 6.68 (td, *J* = 7.5, 1.0 Hz, 1H), 6.60 (d, *J* = 8.2 Hz, 1H), 5.11 (bt, *J* = 5.5 Hz, 1H), 4.47 (d, *J* = 5.5 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.0, 148.9, 139.0, 132.3, 131.2, 130.5, 129.7, 129.5, 128.7, 127.8, 127.3, 127.0, 116.7, 110.1, 106.9, 94.7, 89.1, 61.1, 47.7, 14.3. **IR** (CHCl₃, cm⁻¹) 3065, 3032, 2220, 1738, 1589, 1456, 1416, 1265, 1221, 1194. **HRMS** (DART) Calc'd for [C₂₄H₂₂NO₂]⁺ [M+H]⁺ 356.16505 found 356.16451.

ethyl 4-((2-(benzyl(chlorocarbonyl)amino)phenyl)ethynyl)benzoate (1e')



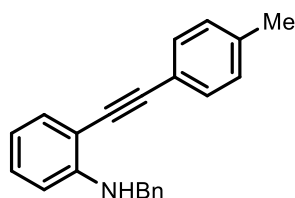
The title compound was prepared according to **Method D** (1.26 mmol scale) using **5e**. The crude material was purified by flash chromatography (20% EtOAc/hexanes) and the desired product was isolated as a light yellow solid (506 mg, 1.21 mmol, 96%). **MP** = 75-77 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.14 – 7.95 (m, 2H), 7.61 (ddd, *J* = 7.6, 1.6, 0.5 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 – 7.19 (m, 6H), 6.92 (ddd, *J* = 7.9, 1.3, 0.5 Hz, 1H), 5.31 (d, *J* = 14.2 Hz, 1H), 4.57 (d, *J* = 14.2 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.1, 150.1, 142.8, 135.3, 133.1, 131.8, 130.6, 129.7, 129.7, 129.6, 129.5, 128.9, 128.7, 128.4, 127.0, 123.0, 94.4, 87.6, 61.4, 56.0, 14.5. **IR** (CHCl₃, cm⁻¹) 2982, 2205, 1713, 1605, 1485, 1452, 1308, 1273, 1225. **HRMS** (DART) Calc'd for [C₂₅H₂₁ClNO₃]⁺ [M+H]⁺ 418.12100 found 418.12116.

N-benzyl-2-iodoaniline (3f)



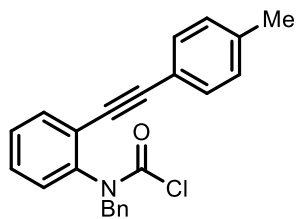
The title compound was prepared according to **Method A** (25.0 mmol scale) using 2-iodoaniline and benzaldehyde. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a white solid (6.74 g, 21.8 mmol, 87%). The spectral data is consistent with literature values.¹⁰

N-benzyl-2-(p-tolylethynyl)aniline (5f)



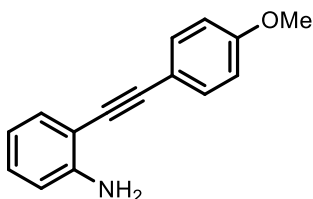
The title compound was prepared according to a modified procedure of **Method B** (2.50 mmol scale) using *N*-benzyl-2-iodoaniline (**3f**) (1.0 equiv) and 4-ethynyltoluene (1.2 equiv). The crude material was purified by flash chromatography (2% Et₂O/10% DCM/88% hexanes) and the desired product was isolated as a yellow solid (623 mg, 2.09 mmol, 84%). The spectral data is consistent with literature values.¹¹

benzyl(2-(p-tolylethynyl)phenyl)carbamic chloride (1f')



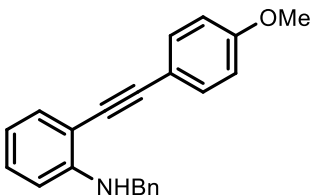
The title compound was prepared according to **Method D** (1.65 mmol scale) using **5f**. The crude material was purified by flash chromatography (1→10% EtOAc/hexanes) and the desired product was isolated as a yellow solid (310 mg, 0.86 mmol, 52%). **MP** = 75-77 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.58 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.14 (m, 8H), 6.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.38 (d, *J* = 14.3 Hz, 1H), 4.50 (d, *J* = 14.3 Hz, 1H), 2.38 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.2, 142.6, 139.3, 135.5, 132.8, 131.8, 129.7, 129.5, 129.4, 128.8 (2 overlapping signals), 128.7, 128.3, 123.5, 119.5, 95.8, 84.3, 55.7, 21.7. **IR** (CHCl₃, cm⁻¹) 3030, 2218, 1728, 1512, 1485, 1452, 1375, 1225, 1194. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO]⁺ [M+H]⁺ 360.11552 found 360.11524.

2-((4-methoxyphenyl)ethynyl)aniline (4g)



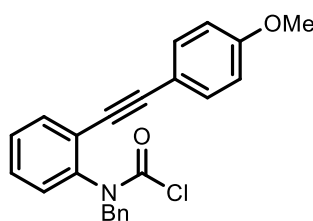
The title compound was prepared according to **Method E** (3.63 mmol scale) using 4-iodoanisole and 2-ethynylaniline (**6**). The crude material was purified by flash chromatography (20% EtOAc/hexanes) and the desired product was isolated as a yellow solid (761 mg, 3.41 mmol, 94%). The spectral data is consistent with literature values.⁶

N-benzyl-2-((4-methoxyphenyl)ethynyl)aniline (5g)



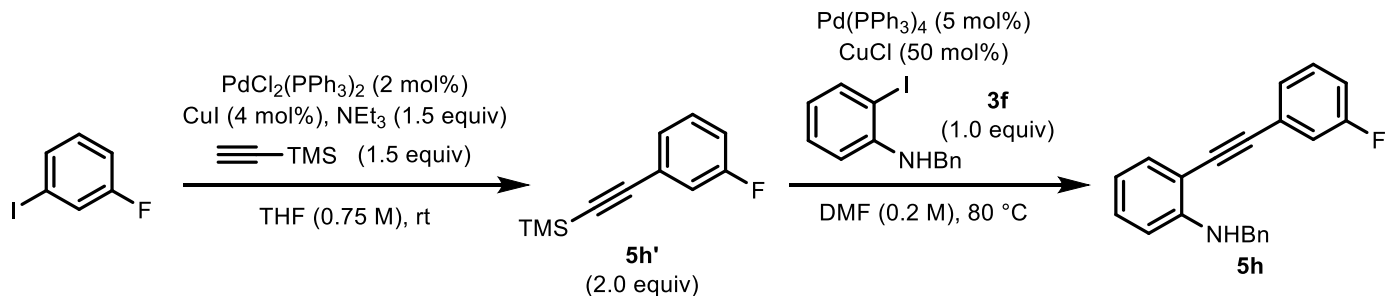
The title compound was prepared according to **Method A** (2.86 mmol scale) using **4g** and benzaldehyde. The crude material was purified by flash chromatography (10→15% EtOAc/hexanes) and the desired product was isolated as a yellow solid (375 mg, 1.20 mmol, 42%). The spectral data is consistent with literature values.¹²

benzyl(2-((4-methoxyphenyl)ethynyl)phenyl)carbamic chloride (1g')



The title compound was prepared according to **Method D** (1.06 mmol scale) using **5g**. The crude material was purified by flash chromatography (12% EtOAc/hexanes) and the desired product was isolated as a viscous yellow oil (279 mg, 0.74 mmol, 70%). **¹H NMR** (500 MHz, CDCl₃) δ 7.57 (ddd, *J* = 7.6, 1.5, 0.5 Hz, 1H), 7.52 – 7.42 (m, 2H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.24 – 7.14 (m, 3H), 6.97 – 6.88 (m, 2H), 6.85 (ddd, *J* = 8.0, 1.2, 0.5 Hz, 1H), 5.38 (d, *J* = 14.3 Hz, 1H), 4.50 (d, *J* = 14.3 Hz, 1H), 3.85 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.3, 150.3, 142.5, 135.6, 133.5, 132.7, 129.6, 129.5, 128.8, 128.7, 128.6, 128.2, 123.7, 114.7, 114.3, 95.7, 83.8, 55.7, 55.5. **IR** (CHCl₃, cm⁻¹) 3032, 2957, 2837, 2216, 1728, 1607, 1512, 1452, 1290. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO₂]⁺ [M+H]⁺ 376.11043 found 376.10949.

N-benzyl-2-((3-fluorophenyl)ethynyl)aniline (5h)

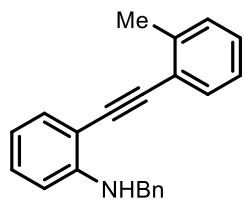


To solution of 1-fluoro-3-iodobenzene (0.47 mL, 4.00 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (56.2 mg, 0.08 mmol) and CuI (30.5 mg, 0.16 mmol) in anhydrous THF (5.3 mL) was added NEt_3 (0.84 mL, 6.00 mmol) dropwise at rt under argon. After stirring for 5 minutes, ethynyltrimethylsilane (0.85 mL 6.00 mmol) was added neat and dropwise to the reaction mixture (slightly exothermic). After 18 h, the reaction mixture was filtered through a pad of celite, washing EtOAc (3x). The combined organics were sequentially washed with H_2O (2x) and brine (1x), dried over Na_2SO_4 and concentrated *in vacuo*. The crude material was used immediately in the next step without further purification (**5h'** unstable to silica gel chromatography). Following a modified literature procedure,¹³ a round bottom flask was charged with **3f** (618 mg, 2.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 0.10 mmol) and CuCl (10 mg, 1.00 mmol). The flask was purged with argon for 15 minutes and then dissolved in anhydrous DMF (5.0 mL). A solution of **5h'** (769 mg, 4.00 mmol) in DMF (5 mL) was added dropwise to the reaction mixture. The reaction was heated to 80 °C overnight, cooled to rt, diluted with EtOAc, and quenched with H_2O . The layers were separated and the aqueous phase was extracted with a 1:1 mixture of EtOAc:hexanes (3x). The combined organics were washed with sat. NH_4Cl and brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and **5h** was isolated as an orange oil (214 mg, 0.72 mmol, 36%). **¹H NMR** (500 MHz, CDCl_3) δ 7.47 – 7.36 (m, 5H), 7.33 – 7.26 (m, 3H), 7.23 – 7.14 (m, 2H), 7.09 – 7.00 (m, 1H), 6.70 (td, J = 7.5, 1.0 Hz, 1H), 6.62 (dd, J = 8.4, 1.0 Hz, 1H), 5.11 (bs, 1H), 4.48 (s, 2H). **¹³C NMR** (126 MHz, CDCl_3) δ 162.5 (d, J = 246.6 Hz), 148.9, 139.2, 132.4, 130.5, 130.1 (d, J = 8.6 Hz), 128.9, 127.4, 127.4, 127.2, 125.3 (d, J = 9.4 Hz), 118.3 (d, J = 22.8 Hz), 116.8, 115.6 (d, J = 21.2 Hz), 110.2, 107.1, 94.1 (d, J = 3.3 Hz), 87.2, 47.8. **¹⁹F NMR** (564 MHz, CDCl_3) δ -112.92 (q, J = 8.2 Hz). **FTIR** (neat, cm^{-1}) 3413, 3071, 3035, 1601, 1577, 1509, 1486, 1455, 1323. **HRMS** (DART) Calc'd for $[\text{C}_{21}\text{H}_{17}\text{FN}]^+$ $[\text{M}+\text{H}]^+$ 302.13450 found 302.13397.

benzyl(2-((3-fluorophenyl)ethynyl)phenyl)carbamic chloride (1h')

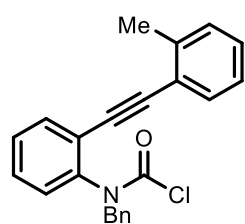
The title compound was prepared according to **Method D** (0.37 mmol scale) using **5h**. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as a yellow solid (104 mg, 0.29 mmol, 79%). **MP** = 48-51 °C. **¹H NMR** (600 MHz, CDCl_3) δ 7.60 (ddd, J = 7.7, 1.6, 0.5 Hz, 1H), 7.39 – 7.25 (m, 7H), 7.24 – 7.21 (m, 2H), 7.20 (ddd, J = 9.2, 2.6, 1.2 Hz, 1H), 7.08 (tdd, J = 8.3, 2.6, 1.2 Hz, 1H), 6.90 (ddd, J = 8.0, 1.2, 0.5 Hz, 1H), 5.32 (d, J = 14.4 Hz, 1H), 4.55 (d, J = 14.4 Hz, 1H). **¹³C NMR** (126 MHz, CDCl_3) δ 162.5 (d, J = 246.9 Hz), 150.2, 142.8, 135.4, 133.1, 130.2 (d, J = 8.6 Hz), 129.6, 129.5, 129.5, 128.9, 128.7, 128.3, 127.9 (d, J = 3.1 Hz), 124.4 (d, J = 9.5 Hz), 123.0, 118.6 (d, J = 22.9 Hz), 116.4 (d, J = 21.2 Hz), 93.9 (d, J = 3.4 Hz), 85.8, 55.9. **¹⁹F NMR** (564 MHz, CDCl_3) δ -112.6 (dd, J = 9.2, 8.3 Hz). **FTIR** (neat, cm^{-1}) 1736, 1607, 1575, 1495, 1451, 1426, 1377, 1224, 1191. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{ClFNO}]^+$ $[\text{M}+\text{H}]^+$ 364.09044 found 364.08999.

N-benzyl-2-(*o*-tolylethynyl)aniline (**5i**)



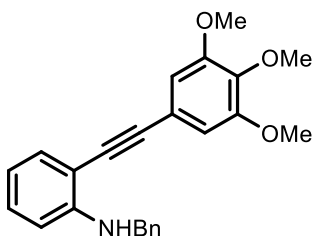
The title compound was prepared according to **Method B** (2.50 mmol scale) using *N*-benzyl-2-iodoaniline (**3f**) and 1-ethynyl-2-methylbenzene. The crude material was purified by flash chromatography (5→10% DCM/hexanes) and the desired product was isolated as a white solid (700 mg, 2.35 mmol, 94%). **MP** = 45-47 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.52 – 7.46 (m, 1H), 7.45 – 7.40 (m, 3H), 7.40 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.25 – 7.12 (m, 4H), 6.71 (td, *J* = 7.5, 1.1 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.10 (t, *J* = 5.6 Hz, 1H), 4.46 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 148.7, 139.6, 139.1, 132.1, 131.8, 130.1, 129.6, 128.8, 128.3, 127.5, 127.5, 125.8, 123.2, 116.8, 110.0, 108.1, 94.4, 90.1, 48.1, 21.0. **IR** (CHCl₃, cm⁻¹) 3404, 3028, 2851, 2203, 1597, 1574, 1559, 1508, 1452, 1323. **HRMS** (DART) Calc'd for [C₂₂H₂₀N]⁺ [M+H]⁺ 298.15957 found 298.15993.

benzyl(2-(*o*-tolylethynyl)phenyl)carbamic chloride (**1i'**)



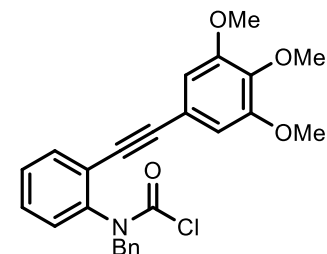
The title compound was prepared according to **Method D** (2.00 mmol scale) using **5i**. The crude material was purified by flash chromatography (5% Et₂O/hexanes) and the desired product was isolated as a white solid (674 mg, 1.87 mmol, 94%). **MP** = 58-61 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.35 (td, *J* = 7.7, 1.3 Hz, 1H), 7.30 – 7.16 (m, 9H), 6.81 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.44 (d, *J* = 14.3 Hz, 1H), 4.46 (d, *J* = 14.3 Hz, 1H), 2.53 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.1, 142.2, 140.5, 135.5, 133.2, 132.5, 129.9, 129.7, 129.5, 129.1, 128.9, 128.9, 128.7, 128.3, 125.8, 123.4, 122.4, 94.3, 88.7, 55.7, 21.0. **IR** (CHCl₃, cm⁻¹) 3065, 3030, 2943, 2214, 1732, 1495, 1452, 1375, 1225, 1194. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO]⁺ [M+H]⁺ 360.11552 found 360.11466.

N-benzyl-2-((3,4,5-trimethoxyphenyl)ethynyl)aniline (**5j**)



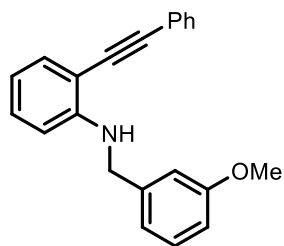
The title compound was prepared according to **Method B** (2.00 mmol scale) using *N*-benzyl-2-iodoaniline (**3f**) and 5-ethynyl-1,2,3-trimethoxybenzene. The crude material was purified by flash chromatography (25% EtOAc/hexanes) and the desired product was isolated as a brown oil (740 mg, 1.98 mmol, 99%). The spectral data is consistent with literature values.¹⁴

benzyl(2-((3,4,5-trimethoxyphenyl)ethynyl)phenyl)carbamic chloride (**1j'**)



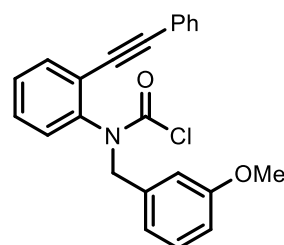
The title compound was prepared according to **Method D** (1.11 mmol scale) using **5j**. The crude material was purified by flash chromatography (20% EtOAc/hexanes) and the desired product was isolated as a viscous yellow oil (433 mg, 0.99 mmol, 89%). **¹H NMR** (500 MHz, CDCl₃) δ 7.59 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.35 (td, *J* = 7.6, 1.2 Hz, 1H), 7.31 – 7.18 (m, 6H), 6.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.76 (s, 2H), 5.36 (d, *J* = 14.3 Hz, 1H), 4.51 (d, *J* = 14.3 Hz, 1H), 3.91 (s, 6H), 3.89 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 153.3, 150.4, 142.8, 139.5, 135.5, 132.7, 129.6, 129.5, 129.0, 128.9, 128.7, 128.3, 123.3, 117.6, 109.1, 95.7, 84.2, 61.2, 56.4, 55.9. **FTIR** (neat, cm⁻¹) 2936, 2846, 2218, 1712, 1575, 1504, 1449, 1355, 1228, 1186, 1123. **HRMS** (DART) Calc'd for [C₂₅H₂₃ClNO₄]⁺ [M+H]⁺ 436.13156 found 436.13214.

N-(3-methoxybenzyl)-2-(phenylethynyl)aniline (5k)



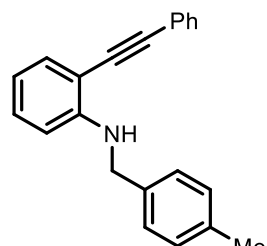
The title compound was prepared according to **Method A** (3.00 mmol scale) using **4b** and *m*-anisaldehyde. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as a light yellow oil (767 mg, 2.45 mmol, 82%). **¹H NMR** (500 MHz, CDCl₃) δ 7.56 – 7.47 (m, 2H), 7.40 (ddd, *J* = 7.5, 1.6, 0.5 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.30 – 7.24 (m, 1H), 7.17 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H), 6.99 (ddd, *J* = 7.6, 1.6, 0.9, 1H), 6.96 – 6.94 (m, 1H), 6.82 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 6.67 (td, *J* = 7.5, 1.1 Hz, 1H), 6.59 (ddd, *J* = 8.3, 1.1, 0.5 Hz, 1H), 5.15 (bs, 1H), 4.45 (s, 2H), 3.79 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 160.1, 148.8, 141.0, 132.3, 131.6, 130.1, 129.9, 128.5, 128.3, 123.4, 119.4, 116.8, 112.8, 112.7, 110.1, 107.7, 95.4, 86.1, 55.4, 47.9. **FTIR** (neat, cm⁻¹) 3407, 3059, 2834, 2204, 1595, 1507, 1488, 1455, 1321, 1260, 1153, 1042. **HRMS** (DART) Calc'd for [C₂₂H₂₀NO]⁺ [M+H]⁺ 314.15449 found 314.15433.

(3-methoxybenzyl)(2-(phenylethynyl)phenyl)carbamic chloride (1k')



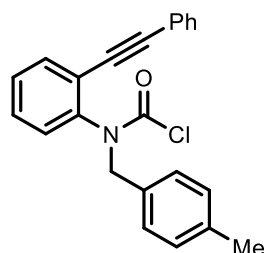
The title compound was prepared according to **Method D** (1.01 mmol scale) using **5k**. The crude material was purified by flash chromatography (20% EtOAc/hexanes) and the desired product was isolated as an orange oil (275 mg, 0.73 mmol, 72%). **¹H NMR** (500 MHz, CDCl₃) δ 7.60 (ddd, *J* = 7.7, 1.6, 0.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.32 (m, 4H), 7.25 (ddd, *J* = 7.9, 7.5, 1.6 Hz, 1H), 7.21 – 7.14 (m, 1H), 6.92 (ddd, *J* = 7.9, 1.2, 0.5 Hz, 1H), 6.84 – 6.73 (m, 3H), 5.34 (d, *J* = 14.3 Hz, 1H), 4.49 (d, *J* = 14.3 Hz, 1H), 3.71 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 159.8, 150.3, 142.7, 137.0, 132.9, 131.9, 129.7, 129.6, 129.1, 129.0, 128.9, 128.6, 123.4, 122.6, 121.8, 114.8, 114.0, 95.4, 84.9, 55.8, 55.3. **FTIR** (neat, cm⁻¹) 2942, 2836, 2219, 1729, 1492, 1373, 1262, 1221, 1191, 1153, 1044. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO₂]⁺ [M+H]⁺ 376.11043 found 376.10944.

N-(4-methylbenzyl)-2-(phenylethynyl)aniline (5l)



The title compound was prepared according to **Method A** (2.97 mmol scale) using **4b** and *p*-tolualdehyde. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a light yellow solid (561 mg, 1.89 mmol, 64%). **MP** = 56-58 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.45 (m, 2H), 7.40 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 – 7.11 (m, 3H), 6.67 (td, *J* = 7.5, 1.0 Hz, 1H), 6.61 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.18 (bs, 1H), 4.43 (s, 2H), 2.35 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 148.8, 136.8, 136.0, 132.1, 131.4, 130.0, 129.4, 128.4, 128.1, 127.0, 123.3, 116.5, 109.9, 107.5, 95.2, 86.0, 47.5, 21.1. **FTIR** (neat, cm⁻¹) 3409, 2830, 2200, 1592, 1570, 1506, 1455, 1325, 1280. **HRMS** (DART) Calc'd for [C₂₂H₂₀N]⁺ [M+H]⁺ 298.15957 found 298.16055.

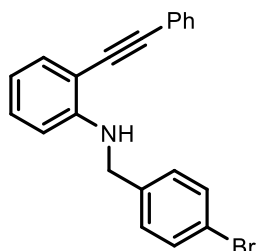
(4-methylbenzyl)(2-(phenylethynyl)phenyl)carbamic chloride (1l')



The title compound was prepared according to **Method D** (1.00 mmol scale) using **5l**. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as a colourless oil (309 mg, 0.86 mmol, 86%). **¹H NMR** (500 MHz, CDCl₃) δ 7.60 (ddd, *J* = 7.8, 1.6, 0.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.41 – 7.31 (m, 4H), 7.28 – 7.21 (m, 1H), 7.14 – 7.08 (m, 2H), 7.09 – 7.02 (m, 2H),

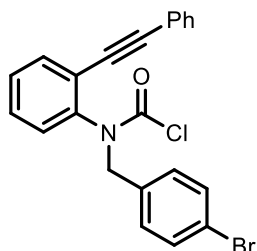
6.87 (dd, $J = 7.8, 1.1$ Hz, 1H), 5.33 (d, $J = 14.2$ Hz, 1H), 4.48 (d, $J = 14.2$ Hz, 1H), 2.30 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 150.1, 142.7, 138.0, 132.9, 132.5, 131.9, 129.7, 129.5, 129.4, 129.0, 129.0, 128.8, 128.6, 123.3, 122.6, 95.4, 85.0, 55.6, 21.3. **FTIR** (neat, cm^{-1}) 3057, 2931, 2219, 1729, 1515, 1496, 1480, 1450, 1442, 1374, 1221, 1192. **HRMS** (DART) Calc'd for $[\text{C}_{23}\text{H}_{19}\text{ClNO}]^+ [\text{M}+\text{H}]^+$ 360.11552 found 360.11432.

***N*-(4-bromobenzyl)-2-(phenylethynyl)aniline (5m)**



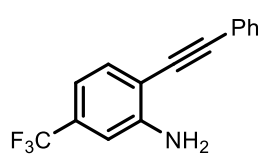
The title compound was prepared according to **Method A** (3.00 mmol scale) using **4b** and 4-bromobenzaldehyde. The crude material was purified by flash chromatography (25% DCM/hexanes) and the desired product was isolated as a yellow solid (728 mg, 2.01 mmol, 67%). **MP** = 53-55 °C. **^1H NMR** (500 MHz, CDCl_3) δ 7.57 – 7.43 (m, 4H), 7.40 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.39 – 7.30 (m, 3H), 7.30 – 7.23 (m, 2H), 7.15 (ddd, $J = 8.3, 7.5, 1.6$ Hz, 1H), 6.68 (td, $J = 7.5, 1.1$ Hz, 1H), 6.52 (d, $J = 8.3$ Hz, 1H), 5.17 (bs, 1H), 4.42 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 148.33, 138.24, 132.37, 131.90, 131.60, 130.12, 128.86, 128.56, 128.44, 123.29, 121.10, 117.21, 110.27, 107.98, 95.52, 85.91, 47.37. **IR** (CHCl_3 , cm^{-1}) 3416, 3077, 1595, 1574, 1508, 1489, 1323, 1071, 1011. **HRMS** (DART) Calc'd for $[\text{C}_{21}\text{H}_{17}\text{BrN}]^+ [\text{M}+\text{H}]^+$ 362.05444 found 362.05355.

(4-bromobenzyl)(2-(phenylethynyl)phenyl)carbamic chloride (1m')



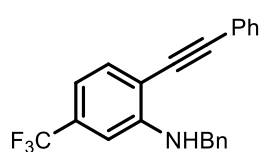
The title compound was prepared according to **Method D** (1.15 mmol scale) using **5m**. The crude material was purified by flash chromatography (40% DCM/hexanes) and the desired product was isolated as a white solid (432 mg, 1.02 mmol, 88%). **MP** = 72-74 °C. **^1H NMR** (400 MHz, CDCl_3) δ 7.60 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.53 – 7.45 (m, 2H), 7.41 – 7.33 (m, 6H), 7.32 – 7.24 (m, 1H), 7.19 – 7.05 (m, 2H), 6.91 (dd, $J = 7.8, 1.3$ Hz, 1H), 5.23 (d, $J = 14.4$ Hz, 1H), 4.55 (d, $J = 14.4$ Hz, 1H). **^{13}C NMR** (126 MHz, CDCl_3) δ 150.3, 142.5, 134.5, 133.1, 131.9, 131.9, 131.2, 129.5, 129.2, 129.1, 129.0, 128.6, 123.4, 122.5, 122.5, 95.5, 84.8, 55.2. **IR** (CH_2Cl_2 , cm^{-1}) 3061, 2218, 1732, 1593, 1497, 1489, 1373, 1225, 1194. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{BrClNO}]^+ [\text{M}+\text{H}]^+$ 424.01038 found 424.00993.

2-(phenylethynyl)-5-(trifluoromethyl)aniline (4n)



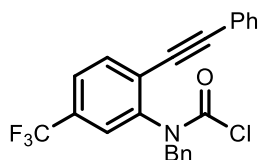
The title compound was prepared according to **Method C** (6.00 mmol scale) using 2-bromo-5-(trifluoromethyl)aniline and phenylacetylene. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as an orange solid (1.18 g, 4.50 mmol, 75%). The spectral data is consistent with literature values.¹⁵

***N*-benzyl-2-(phenylethynyl)-5-(trifluoromethyl)aniline (5n)**



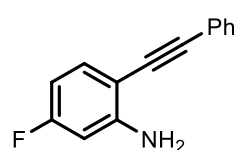
The title compound was prepared according to **Method A** (3.06 mmol scale) using **4n** and benzaldehyde. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a yellow solid (873 mg, 2.48 mmol, 81%). The characterization data is consistent with the literature.¹¹

benzyl(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)carbamic chloride (1n')



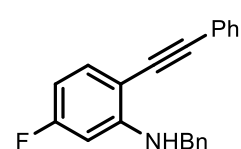
The title compound was prepared according to **Method D** (2.00 mmol scale) using **5n**. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a white solid (731 mg, 1.77 mmol, 88%). **MP** = 54-57 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.70 (dt, *J* = 8.1, 0.7 Hz, 1H), 7.60 (ddd, *J* = 8.1, 2.0, 0.7 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 – 7.36 (m, 3H), 7.31 – 7.22 (m, 3H), 7.22 – 7.14 (m, 2H), 7.07 (dt, *J* = 2.0, 0.7 Hz, 1H), 5.35 (d, *J* = 14.2 Hz, 1H), 4.54 (d, *J* = 14.2 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.8, 142.7, 134.8, 133.3, 132.1, 130.9 (q, *J* = 33.5 Hz), 129.7, 129.6, 128.9, 128.7, 128.7, 127.5 (q, *J* = 1.3 Hz), 126.8 (q, *J* = 3.8 Hz), 125.6 (q, *J* = 3.7 Hz), 123.2 (q, *J* = 272.5 Hz), 121.9, 97.9, 83.8, 55.8. **¹⁹F NMR** (375 MHz, CDCl₃) δ -63.0 (s). **FTIR** (neat, cm⁻¹) 2221, 1738, 1432, 1363, 1324, 1195, 1173, 1117, 1070. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClF₃NO]⁺ [M+H]⁺ 414.08725 found 414.08741.

5-fluoro-2-(phenylethynyl)aniline (4o)



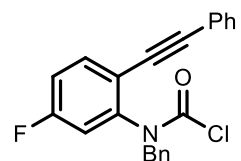
The title compound was prepared according to **Method C** (5.03 mmol scale) using 2-bromo-5-fluoroaniline and phenylacetylene. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a yellow solid (796 mg, 3.77 mmol, 75%). **MP** = 79-81 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.57 – 7.48 (m, 2H), 7.39 – 7.29 (m, 4H), 6.48 – 6.36 (m, 2H), 4.38 (bs, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 163.8 (d, *J* = 247.2 Hz), 149.5 (d, *J* = 11.8 Hz), 133.7 (d, *J* = 10.4 Hz), 131.4, 128.4, 128.3, 123.1, 105.3 (d, *J* = 22.7 Hz), 104.0 (d, *J* = 2.6 Hz), 101.0 (d, *J* = 25.5 Hz), 94.3 (d, *J* = 1.6 Hz), 84.9 (d, *J* = 0.9 Hz). **¹⁹F NMR** (376 MHz, CDCl₃) δ -109.9 (ddd, *J* = 10.3, 8.6, 6.4 Hz). **FTIR** (neat, cm⁻¹) 3477, 3378, 2204, 1613, 1579, 1499, 1442, 1284, 1262, 1167. **HRMS** (DART) Calc'd for [C₁₄H₁₁FN]⁺ [M+H]⁺ 212.08755 found 212.08692.

N-benzyl-5-fluoro-2-(phenylethynyl)aniline (5o)



The title compound was prepared according to **Method A** (2.20 mmol scale) using **4o** and benzaldehyde. The crude material was purified by flash chromatography (3% EtOAc/hexanes) and the desired product was isolated as a pale yellow solid (581 mg, 1.93 mmol, 88%). **MP** = 44-46 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.50 – 7.42 (m, 2H), 7.41 – 7.28 (m, 9H), 6.36 (td, *J* = 8.5, 2.5 Hz, 1H), 6.28 (dd, *J* = 11.5, 2.5 Hz, 1H), 5.25 (bs, 1H), 4.43 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 164.5 (d, *J* = 246.7 Hz), 150.6 (d, *J* = 11.8 Hz), 138.5, 133.6 (d, *J* = 10.6 Hz), 131.5, 128.9, 128.5, 128.4, 127.6, 127.2, 123.3, 103.8 (d, *J* = 2.5 Hz), 103.7 (d, *J* = 22.8 Hz), 97.5 (d, *J* = 26.9 Hz), 95.0 (d, *J* = 1.4 Hz), 85.2 (d, *J* = 1.1 Hz), 47.8. **¹⁹F NMR** (564 MHz, CDCl₃) δ -108.5 – -108.6 (m). **FTIR** (neat, cm⁻¹) 3419, 1583, 1517, 1490, 1440, 1297, 1272, 1166. **HRMS** (DART) Calc'd for [C₂₁H₁₇FN]⁺ [M+H]⁺ 302.13450 found 302.13373.

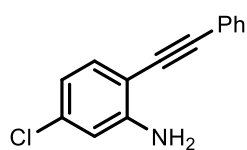
benzyl(5-fluoro-2-(phenylethynyl)phenyl)carbamic chloride (1o')



The title compound was prepared according to **Method D** (1.00 mmol scale) using **5o**. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a white solid (298 mg, 0.83 mmol, 83%). **MP** = 68-70 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.58 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.40 – 7.36 (m, 3H), 7.33 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 7.08 (ddd, *J* = 8.7, 7.9, 2.6 Hz, 1H), 6.62 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.36 (d, *J* = 14.4 Hz, 1H), 4.52 (d, *J* = 14.4 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.8 (d, *J* = 252.6 Hz), 149.7, 143.8 (d, *J* = 10.2 Hz), 134.9, 134.0 (d, *J* = 9.1 Hz), 131.7, 129.3, 129.0, 128.7,

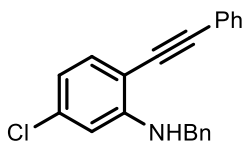
128.5, 128.4, 122.2, 119.6 (d, $J = 3.9$ Hz), 117.3 (d, $J = 23.2$ Hz), 116.3 (d, $J = 21.8$ Hz), 95.0 (d, $J = 1.7$ Hz), 83.8 (d, $J = 1.2$ Hz), 55.6. **FTIR** (neat, cm^{-1}) 2215, 1736, 1497, 1435, 1363, 1281, 1195, 1166, 1158. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{ClFNO}]^+ [\text{M}+\text{H}]^+$ 364.09044 found 364.08904.

5-chloro-2-(phenylethynyl)aniline (4p)



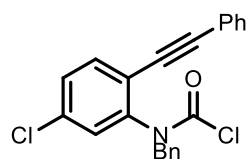
The title compound was prepared according to **Method B** (3.52 mmol scale) using 5-chloro-2-iodoaniline and phenylacetylene. The crude material was purified by flash chromatography (25% EtOAc/hexanes) and the desired product was isolated as a beige solid (705 mg, 3.10 mmol, 88%). The spectral data is consistent with literature values.⁶

N-benzyl-5-chloro-2-(phenylethynyl)aniline (5p)



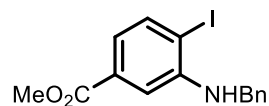
The title compound was prepared according to **Method A** (2.70 mmol scale) using **4p** and benzaldehyde. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a light yellow solid (524 mg, 1.65 mmol, 61%). **MP** = 80-81 °C. **¹H NMR** (500 MHz, CDCl_3) δ 7.52 – 7.42 (m, 2H), 7.39 – 7.27 (m, 9H), 6.64 (dd, $J = 8.1, 2.0$ Hz, 1H), 6.57 (d, $J = 2.0$ Hz, 1H), 5.16 (bt, $J = 5.6$ Hz, 1H), 4.42 (d, $J = 5.6$ Hz, 2H). **¹³C NMR** (126 MHz, CDCl_3) δ 149.6, 138.5, 136.0, 133.0, 131.6, 129.0, 128.6, 128.5, 127.6, 127.2, 123.1, 116.9, 110.1, 106.3, 96.1, 85.1, 47.8. **IR** (CHCl_3 , cm^{-1}) 3416, 1562, 1505, 1490, 1422, 1453, 1274, 1260, 1095. **HRMS** (DART) Calc'd for $[\text{C}_{21}\text{H}_{17}\text{ClN}]^+ [\text{M}+\text{H}]^+$ 318.10495 found 318.10466.

benzyl(5-chloro-2-(phenylethynyl)phenyl)carbamic chloride (1p')



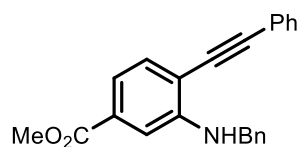
The title compound was prepared according to **Method D** (1.52 mmol scale) using **5p**. The crude material was purified by flash chromatography (35% DCM/hexanes) and the desired product was isolated as a light yellow solid (536 mg, 1.41 mmol, 93%). **MP** = 57-60 °C. **¹H NMR** (500 MHz, CDCl_3) δ 7.55 – 7.47 (m, 3H), 7.43 – 7.35 (m, 3H), 7.33 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.31 – 7.27 (m, 3H), 7.25 – 7.20 (m, 2H), 6.90 (d, $J = 2.0$ Hz, 1H), 5.31 (d, $J = 14.3$ Hz, 1H), 4.54 (d, $J = 14.3$ Hz, 1H). **¹³C NMR** (126 MHz, CDCl_3) δ 149.9, 143.4, 135.0, 134.4, 133.6, 131.9, 129.9, 129.4, 129.3, 129.3, 128.8, 128.6, 128.5, 122.3, 122.2, 96.4, 84.0, 55.8. **IR** (CHCl_3 , cm^{-1}) 3080, 3065, 3032, 2220, 1738, 1553, 1495, 1221, 1194. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{NO}]^+ [\text{M}+\text{H}]^+$ 380.06089 found 380.06147.

methyl 3-(benzylamino)-4-iodobenzoate (3q)



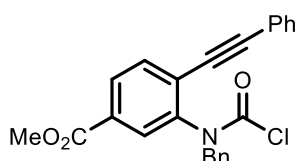
The title compound was prepared according to **Method A** (5.00 mmol scale) using methyl-3-amino-4-iodobenzoate and benzaldehyde. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a white solid (1.37 g, 3.73 mmol, 75%). **MP** = 80-82 °C. **¹H NMR** (500 MHz, CDCl_3) δ 7.75 (d, $J = 8.1$ Hz, 1H), 7.41 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 7.12 – 7.09 (m, 1H), 4.68 (bs, 1H), 4.44 (s, 2H), 3.87 (s, 3H). **¹³C NMR** (126 MHz, CDCl_3) δ 167.2, 147.3, 139.2, 138.2, 131.5, 128.9, 127.7, 127.6, 119.6, 111.2, 91.3, 52.3, 48.5. **IR** (CHCl_3 , cm^{-1}) 3406, 3032, 2920, 1721, 1589, 1570, 1497, 1437, 1420, 1296, 1254, 1107, 1007. **HRMS** (DART) Calc'd for $[\text{C}_{15}\text{H}_{15}\text{INO}_2]^+ [\text{M}+\text{H}]^+$ 368.01475 found 368.01589.

methyl 3-(benzylamino)-4-(phenylethynyl)benzoate (5q)



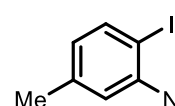
The title compound was prepared according to **Method B** (2.50 mmol scale) using **3q** and phenylacetylene. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as a yellow solid (835 mg, 2.45 mmol, 98%). **MP** = 79-83 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.50 – 7.46 (m, 2H), 7.45 (dd, *J* = 7.9, 0.5 Hz, 1H), 7.43 – 7.40 (m, 2H), 7.39 – 7.33 (m, 6H), 7.33 – 7.28 (m, 2H), 5.17 (bs, 1H), 4.51 (s, 2H), 3.88 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 167.2, 148.6, 138.8, 132.1, 131.7, 131.2, 128.9, 128.8, 128.6, 127.6, 127.4, 122.8, 117.9, 112.2, 110.6, 97.8, 85.4, 52.3, 47.9. **IR** (CHCl₃, cm⁻¹) 3406, 3032, 2920, 1717, 1605, 1566, 1516, 1435, 1296, 1252, 1107. **HRMS** (DART) Calc'd for [C₂₃H₂₀NO₂]⁺ [M+H]⁺ 342.14940 found 342.14880.

methyl 3-(benzyl(chlorocarbonyl)amino)-4-(phenylethynyl)benzoate (1q')



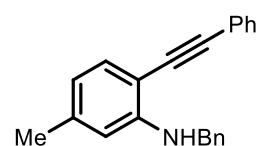
The title compound was prepared according to **Method D** (2.12 mmol scale) using **5q**. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a yellow solid (832 mg, 2.06 mmol, 97%). **MP** = 91-93 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.00 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.43 – 7.34 (m, 3H), 7.30 – 7.18 (m, 5H), 5.25 (d, *J* = 14.4 Hz, 1H), 4.65 (d, *J* = 14.4 Hz, 1H), 3.88 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 149.9, 142.6, 135.0, 132.9, 132.1, 130.6, 130.5, 129.7, 129.5, 129.5, 128.8, 128.7, 128.4, 128.2, 122.0, 98.3, 84.6, 56.0, 52.6. **IR** (CHCl₃, cm⁻¹) 3065, 3032, 2951, 2220, 1728, 1607, 1497, 1439, 1366, 1292, 1238, 1219, 1196, 1103. **HRMS** (DART) Calc'd for [C₂₄H₁₉ClNO₃]⁺ [M+H]⁺ 404.10535 found 404.10490.

N-benzyl-2-iodo-5-methylaniline (3r)



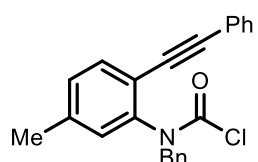
The title compound was prepared according to **Method A** (7.00 mmol scale) using 2-iodo-5-methylaniline and benzaldehyde. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a white solid (1.94 g, 6.01 mmol, 86%). **MP** = 42-44 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.35 – 7.24 (m, 1H), 6.39 (d, *J* = 1.9 Hz, 1H), 6.33 – 6.29 (m, 1H), 4.56 – 4.49 (m, 1H), 4.39 (d, *J* = 5.5 Hz, 2H), 2.22 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 147.0, 139.7, 138.9, 138.8, 128.8, 127.4, 127.4, 120.2, 112.0, 81.6, 48.5, 21.6. **FTIR** (neat, cm⁻¹) 3392, 3054, 3019, 2921, 1569, 1495, 1445, 1407, 1355, 1292, 1266, 1003. **HRMS** (DART) Calc'd for [C₁₄H₁₅IN]⁺ [M+H]⁺ 324.02492 found 324.02420.

N-benzyl-5-methyl-2-(phenylethynyl)aniline (5r)



The title compound was prepared according to **Method B** (4.50 mmol scale) using **3r** and phenylacetylene. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a beige solid (1.33 g, 4.47 mmol, 99%). The spectral data is consistent with literature values.¹¹

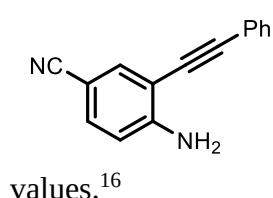
benzyl(5-methyl-2-(phenylethynyl)phenyl)carbamic chloride (1r')



The title compound was prepared according to **Method D** (3.00 mmol scale) using **5r**. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a light yellow solid (1.06 g, 2.94 mmol, 98%). **MP** = 77-78 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.55 – 7.48 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H),

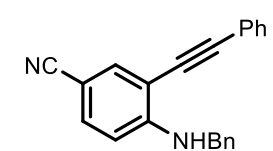
7.40 – 7.34 (m, 3H), 7.29 – 7.21 (m, 5H), 7.16 (ddd, $J = 7.8, 1.8, 0.8$ Hz, 1H), 6.71 (dt, $J = 1.8, 0.6$ Hz, 1H), 5.33 (d, $J = 14.4$ Hz, 1H), 4.55 (d, $J = 14.4$ Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 150.2, 142.6, 139.7, 135.5, 132.6, 131.8, 130.1, 129.6, 129.5, 128.8, 128.6, 128.5, 128.2, 122.8, 120.2, 94.6, 85.1, 55.9, 21.4. **FTIR** (neat, cm^{-1}) 1736, 1504, 1432, 1372, 1269, 1234, 1199. **HRMS** (DART) Calc'd for $[\text{C}_{23}\text{H}_{19}\text{ClNO}]^+ [\text{M}+\text{H}]^+$ 360.11552 found 360.11546.

4-amino-3-(phenylethynyl)benzonitrile (4s)



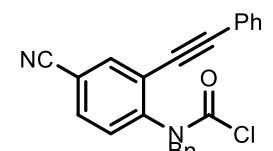
The title compound was prepared according to **Method B** (4.60 mmol scale) using 4-amino-3-iodobenzonitrile and phenylacetylene. The crude material was purified by flash chromatography (50% EtOAc/hexanes) and the desired product was isolated as a brown oil (995 mg, 4.56 mmol, 99%). The spectral data is consistent with literature values.¹⁶

4-(benzylamino)-3-(phenylethynyl)benzonitrile (5s)



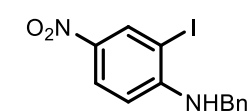
The title compound was prepared according to **Method A** (4.54 mmol scale) using **4s** and benzaldehyde. The crude material was purified by flash chromatography (10→15% EtOAc/hexanes) and the desired product was isolated as a white solid (491 mg, 1.59 mmol, 35%). **MP** = 107-109 °C. **^1H NMR** (400 MHz, CDCl_3) δ 7.65 (d, $J = 2.0$ Hz, 1H), 7.52 – 7.45 (m, 2H), 7.43 – 7.29 (m, 9H), 6.57 (d, $J = 8.7$ Hz, 1H), 5.63 (bt, $J = 5.5$ Hz, 1H), 4.51 (d, $J = 5.5$ Hz, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 151.2, 137.6, 136.0, 133.9, 131.7, 129.1, 129.1, 128.7, 127.9, 127.0, 122.4, 119.7, 109.9, 108.5, 99.1, 96.9, 83.5, 47.4. **IR** (CHCl_3 , cm^{-1}) 3401, 2218, 1597, 1566, 1522, 1456, 1339. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{17}\text{N}_2]^+ [\text{M}+\text{H}]^+$ 309.13917 found 309.13921.

benzyl(4-cyano-2-(phenylethynyl)phenyl)carbamic chloride (1s')



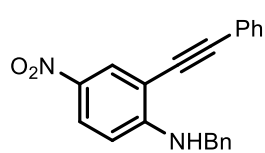
The title compound was prepared according to **Method D** (1.10 mmol scale) using **5s**. The crude material was purified by flash chromatography (20% EtOAc/hexanes) and the desired product was isolated as a light yellow viscous oil (368 mg, 0.99 mmol, 90%). **^1H NMR** (500 MHz, CDCl_3) δ 7.88 (dd, $J = 1.9, 0.5$ Hz, 1H), 7.57 – 7.51 (m, 2H), 7.50 (dd, $J = 8.2, 1.9$ Hz, 1H), 7.46 – 7.37 (m, 3H), 7.32 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 6.97 (dd, $J = 8.2, 0.5$ Hz, 1H), 5.37 (d, $J = 14.4$ Hz, 1H), 4.53 (d, $J = 14.4$ Hz, 1H). **^{13}C NMR** (126 MHz, CDCl_3) δ 149.3, 145.8, 136.4, 134.7, 132.1, 132.1, 130.8, 129.8, 129.4, 128.9, 128.7, 128.7, 125.4, 121.6, 117.3, 113.4, 98.0, 82.8, 55.6. **IR** (CHCl_3 , cm^{-1}) 2233, 2214, 1740, 1497, 1375, 1225, 1194. **HRMS** (DART) Calc'd for $[\text{C}_{23}\text{H}_{16}\text{ClN}_2\text{O}]^+ [\text{M}+\text{H}]^+$ 371.09512 found 371.09462.

N-benzyl-2-iodo-4-nitroaniline (3t)



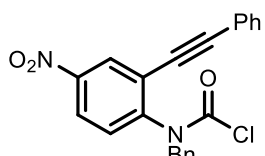
The title compound was prepared according to **Method A** (7.02 mmol scale) using 2-iodo-4-nitroaniline and benzaldehyde. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as a yellow solid (1.99 g, 5.62 mmol, 80%). **MP** = 97-99°C. **^1H NMR** (400 MHz, CDCl_3) δ 8.60 (d, $J = 2.6$ Hz, 1H), 8.08 (dd, $J = 9.2, 2.6$ Hz, 1H), 7.47 – 7.30 (m, 5H), 6.49 (d, $J = 9.2$ Hz, 1H), 5.40 (bt, 5.4 Hz, 1H), 4.51 (d, $J = 5.4$ Hz, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 151.8, 138.7, 136.8, 135.4, 129.2, 128.1, 127.2, 126.2, 108.6, 82.5, 48.3. **FTIR** (neat, cm^{-1}) 3377, 3068, 2867, 1577, 1484, 1313, 1276, 1113, 1019. **HRMS** (DART) Calc'd for $[\text{C}_{13}\text{H}_{12}\text{IN}_2\text{O}_2]^+ [\text{M}+\text{H}]^+$ 354.99434 found 354.99457.

N-benzyl-4-nitro-2-(phenylethynyl)aniline (5t)



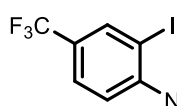
The title compound was prepared according to **Method B** (3.00 mmol scale) using **3t** and phenylacetylene. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a yellow solid (939 mg, 2.86 mmol, 95%). **MP** = 123-125 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.32 (d, *J* = 2.7 Hz, 1H), 8.07 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.42 – 7.31 (m, 8H), 6.57 (d, *J* = 9.2 Hz, 1H), 5.84 (bs, 1H), 4.56 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 152.9, 137.8, 137.2, 131.8, 129.2, 128.7 (2 overlapping signals), 128.6, 128.0, 127.1, 126.6, 122.2, 108.8, 107.6, 97.0, 83.5, 47.6. **FTIR** (neat, cm⁻¹) 3391, 1606, 1594, 1574, 1525, 1489, 1455, 1433, 1298, 1277, 1139, 1094. **HRMS** (DART) Calc'd for [C₂₁H₁₇N₂O₂]⁺ [M+H]⁺ 329.12900 found 329.12863.

benzyl(4-nitro-2-(phenylethynyl)phenyl)carbamic chloride (1t')



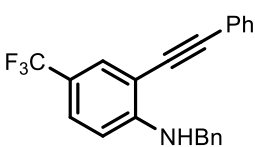
The title compound was prepared according to **Method D** (2.02 mmol scale) using **5t**. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a white solid (410 mg, 1.05 mmol, 52%). **MP** = 92-93 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.44 (dd, *J* = 2.6, 0.4 Hz, 1H), 8.06 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.47 – 7.37 (m, 3H), 7.35 – 7.24 (m, 3H), 7.23 – 7.17 (m, 2H), 7.03 (d, *J* = 8.7 Hz, 1H), 5.39 (d, *J* = 14.4 Hz, 1H), 4.56 (d, *J* = 14.4 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.2, 147.5, 147.2, 134.6, 132.1, 130.9, 129.9, 129.5, 129.0, 128.8, 128.8, 127.9, 125.4, 123.6, 121.5, 98.2, 83.0, 55.6. **FTIR** (neat, cm⁻¹) 2209, 1734, 1530, 1495, 1441, 1351, 1219, 1193, 1080. **HRMS** (DART) Calc'd for [C₂₂H₁₆ClN₂O₃]⁺ [M+H]⁺ 391.08494 found 391.08479.

N-benzyl-2-iodo-4-(trifluoromethyl)aniline (3u)



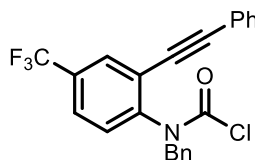
The title compound was prepared according to **Method A** (5.00 mmol scale) using 2-iodo-4-(trifluoromethyl)aniline and benzaldehyde. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a light yellow oil (1.65 g, 4.37 mmol, 87%). The spectral data is consistent with literature values.¹⁷

N-benzyl-2-(phenylethynyl)-4-(trifluoromethyl)aniline (5u)



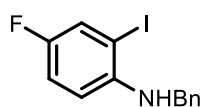
The title compound was prepared according to **Method B** (3.42 mmol scale) using **3u** and phenylacetylene. The crude material was purified by flash chromatography (5→10% EtOAc/hexanes) and the desired product was isolated as a yellow solid (1.02 g, 2.91 mmol, 85%). **MP** = 55-57 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 2.2 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.44 – 7.27 (m, 9H), 6.61 (d, *J* = 8.7 Hz, 1H), 5.47 (bs, 1H), 4.51 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.6 (q, *J* = 1.0 Hz), 138.1, 131.5, 129.3 (q, *J* = 3.8 Hz), 128.9, 128.7, 128.5, 127.5, 126.9, 126.9 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 270.6 Hz), 122.6, 118.5 (q, *J* = 32.9 Hz), 109.3, 107.5, 96.2, 84.5, 47.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ -61.3 (s). **FTIR** (neat, cm⁻¹) 3404, 3044, 2852, 1611, 1572, 1525, 1490, 1329, 1270, 1137, 1106, 1063. **HRMS** (DART) Calc'd for [C₂₂H₁₇F₃N]⁺ [M+H]⁺ 352.13131 found 352.13186.

benzyl(2-(phenylethynyl)-4-(trifluoromethyl)phenyl)carbamic chloride (1u')



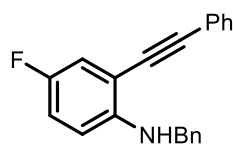
The title compound was prepared according to **Method D** (2.57 mmol scale) using **5u**. The crude material was purified by flash chromatography (5% Et₂O/10% DCM/85% hexanes) and the desired product was isolated as a light yellow solid (1.05 g, 2.54 mmol, 99%). **MP** = 67-69 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.88 (dt, *J* = 2.2, 0.7 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.49 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.33 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2H), 7.00 (dt, *J* = 8.3, 0.7 Hz, 1H), 5.40 (d, *J* = 14.4 Hz, 1H), 4.54 (d, *J* = 14.4 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.7, 145.2 (q, *J* = 1.6 Hz), 135.0, 132.1, 131.3 (q, *J* = 33.3 Hz), 130.3, 130.0 (q, *J* = 3.8 Hz), 129.6, 129.4, 128.9, 128.7, 128.6, 125.7 (q, *J* = 3.6 Hz), 124.6, 123.3 (q, *J* = 272.8 Hz), 121.9, 97.1, 83.6, 55.7. **¹⁹F NMR** (564 MHz, CDCl₃) δ -62.9 (s). **FTIR** (neat, cm⁻¹) 2220, 1739, 1497, 1381, 1335, 1229, 1123, 1115, 1072. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClF₃NO]⁺ [M+H]⁺ 414.08725 found 414.08694.

N-benzyl-4-fluoro-2-iodoaniline (3v)



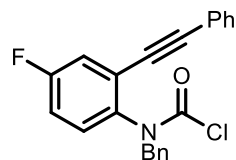
The title compound was prepared according to **Method A** (6.00 mmol scale) using 4-fluoro-2-iodoaniline and benzaldehyde. The crude material was purified by flash chromatography (10% DCM/hexanes) and the desired product was isolated as a white solid (1.29 g, 3.94 mmol, 66%). The spectral data is consistent with literature values.⁴

N-benzyl-4-fluoro-2-(phenylethynyl)aniline (5v)



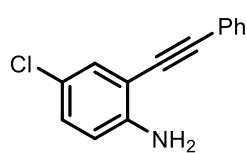
The title compound was prepared according to **Method B** (1.20 mmol scale) using **3v** and phenylacetylene. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a beige wax (335 mg, 1.11 mmol, 93%). **MP** = 30-32 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.56 – 7.49 (m, 2H), 7.45 – 7.35 (m, 7H), 7.34 – 7.29 (m, 1H), 7.16 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.92 (ddd, *J* = 9.0, 8.3, 3.0 Hz, 1H), 6.52 (dd, *J* = 9.0, 4.6 Hz, 1H), 5.04 (bs, 1H), 4.46 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 154.6 (d, *J* = 234.9 Hz), 145.5 (d, *J* = 1.6 Hz), 139.1, 131.6, 128.8, 128.6, 128.6, 127.4, 127.1, 122.9, 118.2 (d, *J* = 23.8 Hz), 117.0 (d, *J* = 22.4 Hz), 110.9 (d, *J* = 7.9 Hz), 108.3 (d, *J* = 9.1 Hz), 96.0, 85.1 (d, *J* = 3.1 Hz), 48.3. **¹⁹F NMR** (470 MHz, CDCl₃) δ -128.5. **FTIR** (neat, cm⁻¹) 3377, 3035, 2846, 1741, 1591, 1501, 1444, 1421, 1298, 1261, 1188, 1140. **HRMS** (DART) Calc'd for [C₂₁H₁₇FN]⁺ [M+H]⁺ 302.13450 found 302.13425.

benzyl(4-fluoro-2-(phenylethynyl)phenyl)carbamic chloride (1v')



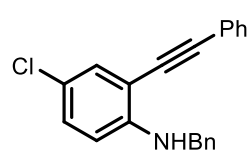
The title compound was prepared according to **Method D** (1.78 mmol scale) using **5v**. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a yellow solid (466 mg, 1.28 mmol, 72%). **MP** = 101-104 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.57 – 7.51 (m, 2H), 7.46 – 7.36 (m, 3H), 7.35 – 7.25 (m, 4H), 7.24 – 7.18 (m, 2H), 6.93 (ddd, *J* = 8.8, 7.8, 3.0 Hz, 1H), 6.80 (dd, *J* = 8.8, 5.2 Hz, 1H), 5.38 (d, *J* = 14.3 Hz, 1H), 4.48 (d, *J* = 14.3 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.9 (d, *J* = 250.0 Hz), 150.3 (d, *J* = 1.2 Hz), 138.8 (d, *J* = 3.4 Hz), 135.3, 132.0, 131.4 (d, *J* = 9.4 Hz), 129.5, 129.4, 128.8, 128.7, 128.4, 125.3 (d, *J* = 10.6 Hz), 122.1, 119.5 (d, *J* = 24.3 Hz), 116.3 (d, *J* = 22.8 Hz), 96.4, 83.9 (d, *J* = 3.0 Hz), 55.8. **¹⁹F NMR** (377 MHz, CDCl₃) δ -111.5 (td, *J* = 7.8, 5.2 Hz). **FTIR** (neat, cm⁻¹) 2209, 1727, 1609, 1582, 1500, 1382, 1229, 1189. **HRMS** (DART) Calc'd for [C₂₂H₁₆ClFNO]⁺ [M+H]⁺ 364.09044 found 364.08951.

4-chloro-2-(phenylethynyl)aniline (4w)



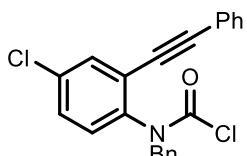
The title compound was prepared according to **Method B** (5.00 mmol scale) using 4-chloro-2-iodoaniline and phenylacetylene. The crude material was purified by flash chromatography (35% Et₂O/hexanes) and the desired product was isolated as a beige solid (1.01 g, 4.43 mmol, 89%). The spectral data is consistent with literature values.⁶

N-benzyl-4-chloro-2-(phenylethynyl)aniline (5w)



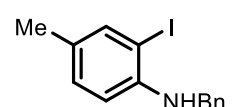
The title compound was prepared according to **Method A** (3.50 mmol scale) using **4w** and benzaldehyde. The crude material was purified by flash chromatography (10→25% DCM/hexanes) and the desired product was isolated as a light yellow solid (477 mg, 1.50 mmol, 43%). The spectral data is consistent with literature values.¹¹

benzyl(4-chloro-2-(phenylethynyl)phenyl)carbamic chloride (1w')



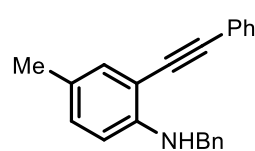
The title compound was prepared according to **Method D** (1.20 mmol scale) using **5w**. The crude material was purified by flash chromatography (25% DCM/hexanes) and the desired product was isolated as a light yellow solid (394 mg, 1.04 mmol, 86%). **MP** = 91-93 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.44 – 7.35 (m, 3H), 7.29 – 7.24 (m, 3H), 7.23 – 7.14 (m, 3H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.36 (d, *J* = 14.3 Hz, 1H), 4.48 (d, *J* = 14.3 Hz, 1H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.0, 141.0, 135.2, 134.7, 132.6, 132.0, 130.8, 129.5, 129.4, 129.2, 128.8, 128.7, 128.5, 125.0, 122.1, 96.6, 83.7, 55.7. **IR** (CHCl₃, cm⁻¹) 3065, 3032, 2930, 2220, 1732, 1495, 1373, 1225, 1194. **HRMS** (DART) Calc'd for [C₂₂H₁₆Cl₂NO]⁺ [M+H]⁺ 380.06089 found 380.06083.

N-benzyl-2-iodo-4-methylaniline (3x)



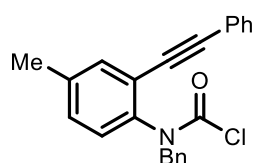
The title compound was prepared according to **Method A** (7.00 mmol scale) using 2-iodo-4-methylaniline and benzaldehyde. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a colourless oil (1.76 g, 5.46 mmol, 78%). The spectral data is consistent with literature values.¹⁷

N-benzyl-4-methyl-2-(phenylethynyl)aniline (5x)



The title compound was prepared according to **Method D** (4.50 mmol scale) using **3x** and phenylacetylene. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a yellow solid (1.30 g, 4.36 mmol, 97%). The spectral data is consistent with literature values.¹¹

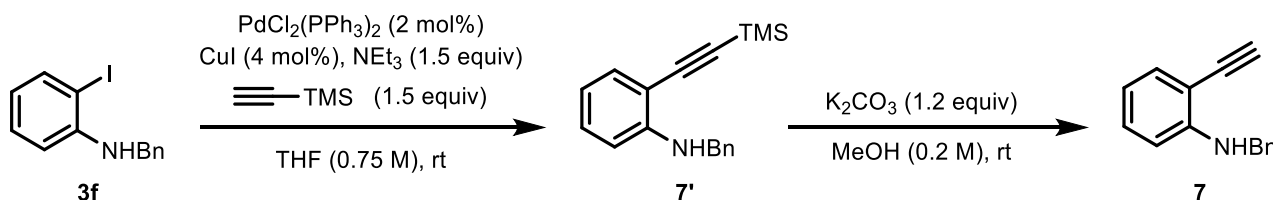
benzyl(4-methyl-2-(phenylethynyl)phenyl)carbamic chloride (1x')



The title compound was prepared according to **Method D** (3.00 mmol scale) using **5x**. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a light yellow solid (1.04 g, 2.89 mmol, 96%). **MP** = 82-83 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.57 – 7.49 (m, 2H), 7.43 – 7.41 (m, 1H), 7.40 – 7.35 (m, 3H), 7.28 – 7.22 (m, 5H), 7.06 – 7.01 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.37 (d, *J* = 14.3 Hz, 1H),

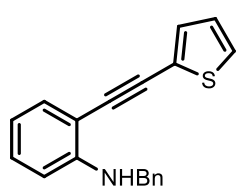
4.50 (d, $J = 14.3$ Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 150.4, 140.2, 139.0, 135.6, 133.4, 131.9, 129.9, 129.5, 129.3, 128.9, 128.6, 128.6, 128.2, 122.9, 122.7, 95.0, 85.1, 55.8, 21.2. **FTIR** (neat, cm^{-1}) 1729, 1497, 1455, 1440, 1375, 1222, 1191, 1079. **HRMS** (DART) Calc'd for $[\text{C}_{23}\text{H}_{19}\text{ClNO}]^+ [\text{M}+\text{H}]^+$ 360.11552 found 360.11574.

N-benzyl-2-ethynylaniline (**7**)



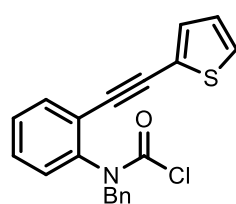
To solution of *N*-benzyl-2-iodoaniline (**3f**) (3.09 g, 10.0 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (140 mg, 0.2 mmol) and CuI (76.2 mg, 0.4 mmol) in anhydrous THF (13.3 mL) was added NEt_3 (2.09 mL, 15.0 mmol) dropwise at rt under argon. After stirring for 5 minutes, ethynyltrimethylsilane (2.12 mL, 15.0 mmol) was added neat and dropwise to the reaction mixture. The reaction was stirred at rt overnight, diluted with EtOAc and filtered through a pad of celite. The combined organics were sequentially washed with H_2O (2x) and brine (1x), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting crude mixture was purified by flash chromatography (15% DCM/hexanes) and **7'** was isolated as an orange solid (2.63 g, 9.41 mmol, 94%). To a stirring solution of **7'** (2.62 g, 9.40 mmol) in MeOH (47 mL), solid K_2CO_3 (1.56 g, 11.3 mmol) was added. After stirring at rt for 3 h, the solvent was removed under reduced pressure, water was added and aqueous phase was extracted with EtOAc (3x). The combined organics were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography (12% Et₂O/hexanes) and **7** was isolated as an orange oil (1.83 g, 8.80 mmol, 94%). The spectral data is consistent with literature values.¹⁸

N-benzyl-2-(thiophen-2-ylethynyl)aniline (**5y**)



The title compound was prepared according to a modified procedure of **Method B** (2.00 mmol scale) using 2-bromothiophene (1.2 equiv) and *N*-benzyl-2-ethynylaniline (**7**) (1.0 equiv). The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as a yellow oil (233 mg, 0.81 mmol, 40%). **^1H NMR** (500 MHz, CDCl_3) δ 7.42 – 7.33 (m, 5H), 7.30 – 7.27 (m, 2H), 7.24 (dd, $J = 3.6, 1.2$ Hz, 1H), 7.16 (ddd, $J = 8.3, 7.5, 1.6$ Hz, 1H), 7.03 – 6.99 (m, 1H), 6.67 (td, $J = 7.5, 1.1$ Hz, 1H), 6.58 (ddd, $J = 8.3, 1.1, 0.5$ Hz, 1H), 5.10 (bs, 1H), 4.47 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 148.8, 139.2, 132.3, 131.8, 130.4, 128.8, 127.4, 127.3, 127.3, 127.1, 123.4, 116.8, 110.2, 107.3, 89.8, 88.3, 47.8. **FTIR** (neat, cm^{-1}) 3408, 3033, 2859, 2190, 1600, 1573, 1503, 1451, 1322, 1277, 1161. **HRMS** (DART) Calc'd for $[\text{C}_{19}\text{H}_{16}\text{NS}]^+ [\text{M}+\text{H}]^+$ 290.10034 found 290.09976.

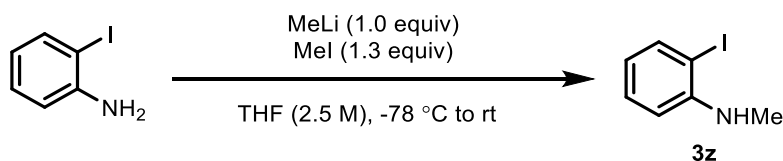
benzyl(2-(thiophen-2-ylethynyl)phenyl)carbamic chloride (**1y'**)



The title compound was prepared according to **Method D** (0.76 mmol scale) using **5y**. The crude material was purified by flash chromatography (10→15% EtOAc/hexanes) and the desired product was isolated as a light yellow solid (219 mg, 0.62 mmol, 82%). **MP** = 58–61 °C. **^1H NMR** (500 MHz, CDCl_3) δ 7.57 (ddd, $J = 7.8, 1.6, 0.5$ Hz, 1H), 7.34 – 7.30 (m, 3H), 7.30 – 7.25 (m, 3H), 7.25 – 7.21 (m, 3H), 7.04 (dd, $J = 5.1, 3.7$ Hz, 1H), 6.88 (ddd, $J = 7.9, 1.3, 0.5$ Hz, 1H), 5.33 (d, $J = 14.4$ Hz, 1H), 4.54 (d, $J = 14.4$ Hz, 1H). **^{13}C NMR** (126 MHz,

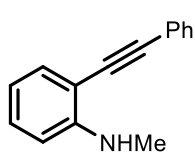
CDCl₃) δ 150.0, 142.3, 135.4, 133.0, 132.7, 129.7, 129.5, 129.2, 128.9, 128.7 (2 overlapping signals), 128.3, 128.3, 127.4, 123.1, 122.4, 88.6, 55.8. **FTIR** (neat, cm⁻¹) 3108, 2202 1720, 1484, 1453, 1423, 1380. 1356, 1239. **HRMS** (DART) Calc'd for [C₂₀H₁₅ClNOS]⁺ [M+H]⁺ 352.05629 found 352.05605.

2-iodo-*N*-methylaniline (**3z**):



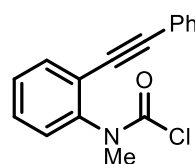
The title compound was prepared according to literature procedure (4.20 mmol scale).¹⁹ The crude material was purified by flash chromatography (10% EtOAc/hexanes) to afford the desired product as a pale yellow oil (970 mg, 4.16 mmol, 99%). The characterization data are consistent with the literature.²⁰

N-methyl-2-(phenylethynyl)aniline (**5z**)



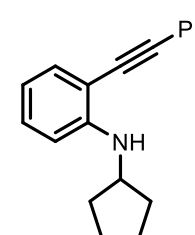
The title compound was prepared according to **Method B** (5.00 mmol scale) using 2-iodo-*N*-methylaniline (**3z**) and phenylacetylene. The crude material was purified by flash chromatography (30% DCM/hexanes) and the desired product was isolated as a pale yellow solid (950 mg, 4.58 mmol, 92%). The spectral data is consistent with literature values.²¹

methyl(2-(phenylethynyl)phenyl)carbamic chloride (**1z'**)



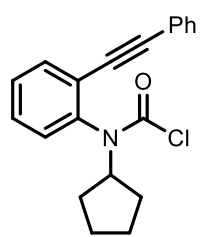
The title compound was prepared according to **Method D** (4.25 mmol scale) using **5z**. The crude material was purified by flash chromatography (10% EtOAc/hexanes) and the desired product was isolated as an orange oil (893 mg, 3.31 mmol, 78%). **¹H NMR** (500 MHz, CDCl₃) δ 7.70 – 7.59 (m, 1H), 7.58 – 7.50 (m, 2H), 7.47 – 7.39 (m, 2H), 7.39 – 7.34 (m, 3H), 7.33 – 7.28 (m, 1H), 3.41 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.7, 144.5, 133.0, 131.9, 129.7, 129.0, 128.9, 128.6, 128.3, 122.9, 122.5, 95.2, 84.6, 39.4. **IR** (CHCl₃, cm⁻¹) 3063, 2934, 2220, 1748, 1497, 1481, 1451, 1354, 1263, 1236. **HRMS** (DART) Calc'd for [C₁₆H₁₃ClNO]⁺ [M+H]⁺ 270.06857 found 270.06891.

N-cyclopentyl-2-(phenylethynyl)aniline (**5ab**)



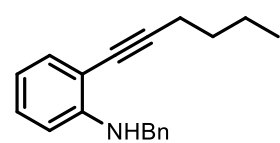
The title compound was prepared according to **Method A** (3.00 mmol scale) using **4b** and cyclopentanone. The crude material was purified by flash chromatography (25% DCM/hexanes) and the desired product was isolated as a yellow oil (635 mg, 2.43 mmol, 81%). **¹H NMR** (500 MHz, CDCl₃) δ 7.55 – 7.47 (m, 2H), 7.42 – 7.30 (m, 4H), 7.23 – 7.17 (m, 1H), 6.71 – 6.53 (m, 2H), 4.68 (bs, 1H), 3.92 – 3.78 (m, 1H), 2.19 – 1.96 (m, 2H), 1.86 – 1.73 (m, 2H), 1.72 – 1.61 (m, 2H), 1.60 – 1.50 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 148.6, 132.0, 131.3, 129.9, 128.4, 128.1, 123.5, 115.9, 110.3, 107.3, 94.9, 86.2, 54.3, 33.6, 24.1. **IR** (CH₂Cl₂, cm⁻¹) 3404, 2957, 2868, 2204, 1595, 1506, 1456, 1327, 1279. **HRMS** (DART) Calc'd for [C₁₉H₂₀N]⁺ [M+H]⁺ 262.15957 found 262.15919.

cyclopentyl(2-(phenylethynyl)phenyl)carbamic chloride (1ab')



The title compound was prepared according to **Method D** (2.00 mmol scale) using **5ab**. The crude material was purified by flash chromatography (15% EtOAc/hexanes) and the desired product was isolated as a white solid (589 mg, 1.82 mmol, 91%). **MP** = 65-67 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.69 – 7.58 (m, 1H), 7.57 – 7.48 (m, 2H), 7.43 – 7.30 (m, 5H), 7.24 – 7.14 (m, 1H), 4.59 (p, *J* = 8.3 Hz, 1H), 2.21 – 1.89 (m, 2H), 1.77 – 1.34 (m, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.2, 141.3, 132.7, 131.7, 129.8, 129.0, 128.8, 128.7, 128.5, 124.9, 122.6, 94.9, 85.6, 63.3, 30.6, 29.2, 22.9, 22.8. **IR** (CHCl₃, cm⁻¹) 2961, 2874, 2220, 1728, 1495, 1481, 1450, 1223. **HRMS** (DART) Calc'd for [C₂₀H₁₉ClNO]⁺ [M+H]⁺ 324.11552 found 324.11519.

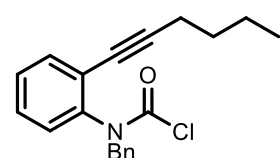
N-benzyl-2-(hex-1-yn-1-yl)aniline (5ac)



values.¹¹

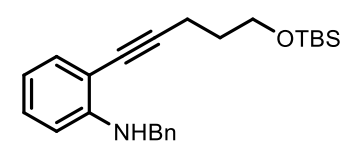
The title compound was prepared according to **Method B** (3.00 mmol scale) using *N*-benzyl-2-iodoaniline (**3f**) and 1-hexyne. The crude material was purified by flash chromatography (20% DCM/hexanes) and the desired product was isolated as a yellow oil (632 mg, 2.40 mmol, 80%). The spectral data is consistent with literature

benzyl(2-(hex-1-yn-1-yl)phenyl)carbamic chloride (1ac')



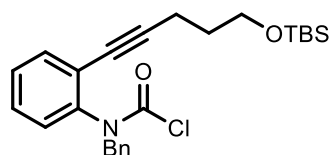
The title compound was prepared according to **Method D** (2.10 mmol scale) using **5ac**. The crude material was purified by flash chromatography (40% DCM/hexanes) and the desired product was isolated as a light yellow oil (613 mg, 1.88 mmol, 90%). **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.22 – 7.15 (m, 2H), 7.13 (td, *J* = 7.8, 1.5 Hz, 1H), 6.78 – 6.71 (m, 1H), 5.32 (d, *J* = 14.3 Hz, 1H), 4.38 (d, *J* = 14.3 Hz, 1H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.52 – 1.42 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.1, 142.6, 135.7, 133.1, 129.6, 129.5, 128.7, 128.6, 128.2, 128.2, 123.9, 97.0, 76.3, 55.5, 30.7, 22.1, 19.4, 13.7. **IR** (CH₂Cl₂, cm⁻¹) 2959, 2932, 2872, 1730, 1489, 1451, 1377, 1219, 1194. **HRMS** (DART) Calc'd for [C₂₀H₂₁ClNO]⁺ [M+H]⁺ 326.13117 found 326.13123.

N-benzyl-2-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)aniline (5ad)



The title compound was prepared according to **Method B** (3.00 mmol scale) using *N*-benzyl-2-iodoaniline (**3f**) and *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane, which was prepared according to a literature procedure.²² The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a yellow oil (1.05 g, 2.77 mmol, 92%). **¹H NMR** (500 MHz, CDCl₃) δ 7.41 – 7.31 (m, 4H), 7.31 – 7.23 (m, 2H), 7.11 (ddd, *J* = 8.3, 7.3, 1.6 Hz, 1H), 6.62 (td, *J* = 7.3, 1.1 Hz, 1H), 6.54 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.05 (bs, 1H), 4.43 (s, 2H), 3.74 (t, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 7.0 Hz, 2H), 1.80 (tt, *J* = 7.0, 6.0 Hz, 2H), 0.91 (s, 9H), 0.07 (s, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 148.7, 139.4, 132.1, 129.2, 128.8, 127.3, 127.2, 116.6, 109.8, 108.7, 95.9, 77.3, 61.7, 47.9, 32.2, 26.1, 18.5, 16.3, -5.2. **FTIR** (neat, cm⁻¹) 3425, 2952, 2929, 2856, 1601, 1576, 1508, 1453, 1323, 1253, 1101. **HRMS** (DART) Calc'd for [C₂₄H₃₄NOSi]⁺ [M+H]⁺ 380.24097 found 380.24050.

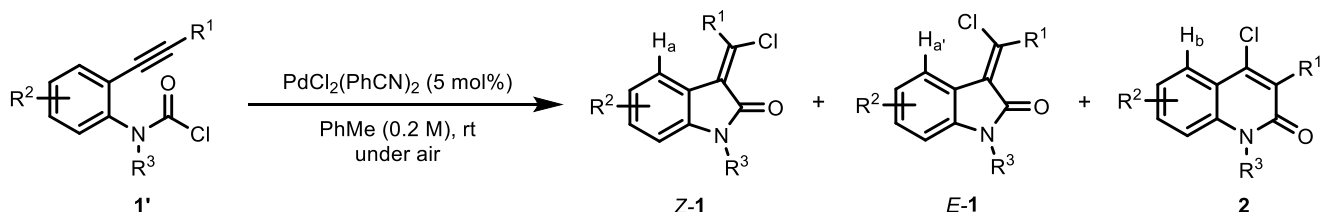
benzyl(2-(5-((tert-butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl)carbamic chloride (**1ad**)



The title compound was prepared according to **Method D** (1.60 mmol scale) using **5ad**. The crude material was purified by flash chromatography (5% EtOAc/hexanes) and the desired product was isolated as a light yellow oil (627 mg, 1.42 mmol, 89%). **¹H NMR** (500 MHz, CDCl₃) δ 7.46 (ddd, J = 7.8, 1.6, 0.5 Hz, 1H), 7.34 – 7.25 (m, 4H), 7.24 – 7.17 (m, 2H), 7.16 (td, J = 7.8, 1.6 Hz, 1H), 6.77 (ddd, J = 7.8, 1.3, 0.5 Hz, 1H), 5.32 (d, J = 14.3 Hz, 1H), 4.40 (d, J = 14.3 Hz, 1H), 3.75 (t, J = 6.0 Hz, 2H), 2.51 (t, J = 7.1 Hz, 2H), 1.81 (tt, J = 7.1, 6.0 Hz, 2H), 0.91 (s, 9H), 0.12 – 0.06 (m, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.1, 142.6, 135.7, 133.2, 129.6, 129.5, 128.7, 128.6, 128.3, 128.2, 123.9, 96.6, 76.3, 61.7, 55.6, 31.9, 26.1, 18.5, 16.2, -5.1, -5.2. **FTIR** (neat, cm⁻¹) 2953, 2930, 2857, 2230, 1735, 1489, 1376, 1252, 1220, 1192, 1102. **HRMS** (DART) Calc'd for [C₂₅H₃₃ClNO₂Si]⁺ [M+H]⁺ 442.19691 found 442.19620.

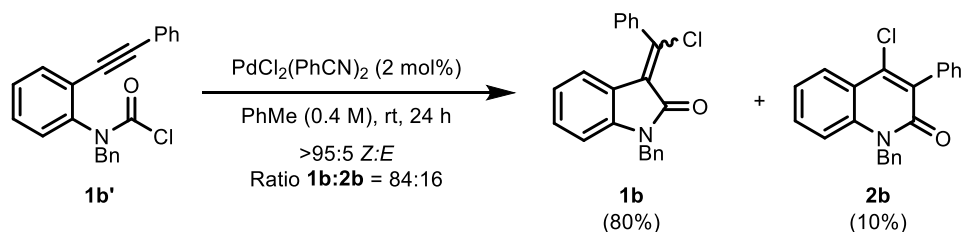
4 General Procedures and Characterization Data for Methylene Oxindoles

4.1 General Procedure for Cyclization



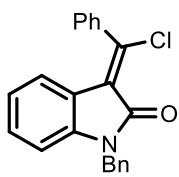
A 2 dram vial equipped with a stir bar was sequentially charged with PdCl₂(PhCN)₂ (4.8 mg, 0.0125 mmol), carbamoyl chloride **1'** (0.25 mmol) and anhydrous PhMe (1.25 mL) under air. The vial was sealed with a plastic screw cap and stirred at rt until full consumption of the starting material was observed by TLC (between 4.5-39 h). The reaction was diluted with EtOAc (1.0 mL) and passed through a plug of silica gel, washing with EtOAc (5 mL). The solvent was removed under reduced pressure and the resulting crude mixture was purified by flash chromatography using the indicated eluent. The isomeric and regiomer ratios were obtained by ¹H NMR analysis of the crude reaction mixtures using a 5 second relaxation delay. Characteristic downfield δ values observed for H_{a'} and H_b in ¹H NMR spectrum (in the range of 9.20 – 7.80 ppm) due to halogen anisotropy. In all cases, the H_{a'} resonance appears slightly downfield from that of H_b.

4.2 General Procedure and Characterization Data for Gram-Scale Reaction



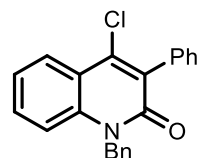
A 25 mL round bottom flask equipped with a stir bar was sequentially charged with PdCl₂(PhCN)₂ (22.4 mg, 0.0584 mmol), **1b'** (1.009 g, 2.92 mmol) and anhydrous PhMe (7.3 mL) under air. The flask was capped with a rubber septum and stirred at rt for 24 h. The reaction was diluted with EtOAc (5 mL), filtered across a pad of silica gel and concentrated under reduced pressure. The crude mixture was purified by flash chromatography (10% EtOAc/10% DCM/80% hexanes), yielding **1b** as a bright yellow solid (806 mg, 2.33 mmol, 80%) and **2b** as a light yellow solid (105 mg, 0.30 mmol, 10%).

(Z)-1-benzyl-3-(chloro(phenyl)methylene)indolin-2-one (1b)



MP = 158-160 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.61 – 7.48 (m, 5H), 7.41 – 7.20 (m, 5H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.65 (td, *J* = 7.8, 1.2 Hz, 1H), 6.34 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 5.01 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.7, 142.8, 141.3, 138.8, 136.1, 130.5, 129.5, 129.4, 128.9, 128.3, 127.8, 127.6, 124.3, 122.9, 121.9, 121.8, 108.9, 43.8. **IR** (CHCl₃, cm⁻¹) 3036, 2937, 1695, 1600, 1478, 1455, 1465, 1342. **HRMS** (DART) Calc'd for [C₂₂H₁₇ClNO]⁺ [M+H]⁺ 346.09987 found 346.10027.

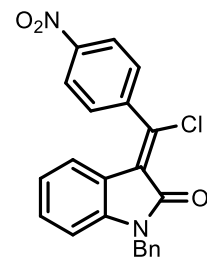
1-benzyl-4-chloro-3-phenylquinolin-2(1H)-one (2b)



MP = 187-188 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.60 – 7.37 (m, 6H), 7.38 – 7.19 (m, 7H), 5.58 (CH₂Bn, bs, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 161.1, 142.2, 138.6, 136.3, 134.9, 131.9, 131.6, 130.2, 129.0, 128.4, 128.3, 127.6, 127.0, 126.9, 122.9, 119.8, 115.2, 47.0. **IR** (CHCl₃, cm⁻¹) 3065, 3032, 1643, 1609, 1589, 1495, 1454, 1310. **HRMS** (DART) Calc'd for [C₂₂H₁₇ClNO]⁺ [M+H]⁺ 346.09987 found 346.09914.

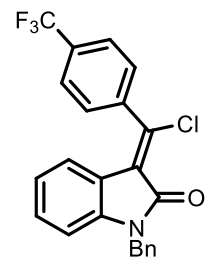
4.3 Characterization Data for Cyclized Products

(Z)-1-benzyl-3-(chloro(4-nitrophenyl)methylene)indolin-2-one (1c)



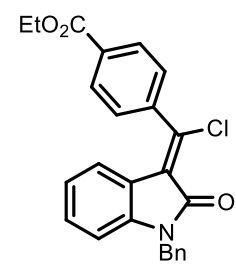
The title compound was prepared according to the General Procedure (0.109 mmol scale, 26 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 75:25). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and the desired product was isolated as a yellow solid (30.8 mg, 0.079 mmol, 72%). **MP** = 155-156 °C. **¹H NMR** (600 MHz, CDCl₃) δ 8.43 – 8.37 (m, 2H), 7.74 – 7.70 (m, 2H), 7.39 – 7.31 (m, 4H), 7.30 – 7.26 (m, 1H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 6.74 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.68 (td, *J* = 7.8, 1.0 Hz, 1H), 6.27 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 5.01 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.2, 148.8, 144.6, 141.7, 138.6, 135.8, 130.5, 129.8, 129.0, 127.9, 127.6, 125.6, 124.8, 122.8, 122.1, 121.0, 109.4, 43.9. **FTIR** (neat, cm⁻¹) 3035, 2924, 1707, 1601, 1590, 1517, 1466, 1344. **HRMS** (DART) Calc'd for [C₂₂H₁₆ClN₂O₃]⁺ [M+H]⁺ 391.08494 found 391.08457.

(Z)-1-benzyl-3-(chloro(4-(trifluoromethyl)phenyl)methylene)indolin-2-one (1d)



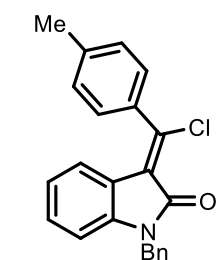
The title compound was prepared according to the General Procedure (0.250 mmol scale, 32 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 80:20). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and the desired product was isolated as a yellow solid (72.8 mg, 0.176 mmol, 70%). **MP** = 130-131 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.27 (m, 5H), 7.13 (td, *J* = 7.8, 1.2 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.69 (td, *J* = 7.8, 1.2 Hz, 1H), 6.30 (d, *J* = 7.8, 1H), 5.01 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.2, 141.9 (q, *J* = 1.5 Hz), 141.4, 140.0, 135.8, 132.2 (q, *J* = 32.8 Hz), 130.0, 128.8 (2 overlapping signals), 127.7, 127.5, 126.4 (q, *J* = 3.7 Hz), 125.0, 123.6 (q, *J* = 272.6 Hz), 122.7, 121.8, 121.1, 109.1, 43.7. **¹⁹F NMR** (470 MHz, CDCl₃) δ -62.84 (s). **IR** (CHCl₃, cm⁻¹) 3063, 1709, 1601, 1468, 1323, 1173, 1128, 1109, 1069. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClF₃NO]⁺ [M+H]⁺ 414.08725 found 414.08673.

ethyl (Z)-4-((1-benzyl-2-oxoindolin-3-ylidene)chloromethyl)benzoate (1e)



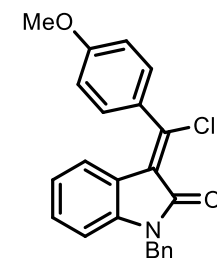
The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 83:17). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and the desired product was isolated as a yellow solid (71.1 mg, 0.170 mmol, 68%). **MP** = 144-146 °C. **¹H NMR** (500 MHz, CDCl₃) δ 8.26 – 8.13 (m, 2H), 7.73 – 7.55 (m, 2H), 7.44 – 7.30 (m, 4H), 7.31 – 7.27 (m, 1H), 7.11 (td, *J* = 7.8, 1.2 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.65 (td, *J* = 7.8, 1.2 Hz, 1H), 6.31 (ddd, *J* = 7.8, 1.2, 0.5 Hz, 1H), 5.01 (s, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.9, 165.4, 142.7, 141.4, 140.9, 136.0, 132.2, 130.7, 129.9, 128.9, 128.5, 127.8, 127.6, 124.8, 123.0, 121.9, 121.4, 109.1, 61.6, 43.8, 14.5. **IR** (CHCl₃, cm⁻¹) 2967, 1713, 1601, 1454, 1362, 1261, 1076. **HRMS** (DART) Calc'd for [C₂₅H₂₁ClNO₃]⁺ [M+H]⁺ 418.12100 found 418.12048.

(Z)-1-benzyl-3-(chloro(*p*-tolyl)methylene)indolin-2-one (1f)



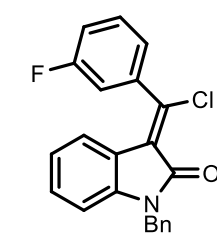
The title compound was prepared according to the General Procedure (0.250 mmol scale, 4.5 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 87:13). The crude material was purified by flash chromatography (10% DCM/10% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (69.2 mg, 0.192 mmol, 77%). **MP** = 123-125°C. **¹H NMR** (500 MHz, CDCl₃) δ 7.45 – 7.39 (m, 2H), 7.40 – 7.29 (m, 6H), 7.30 – 7.23 (m, 1H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.67 (td, *J* = 7.8, 1.2 Hz, 1H), 6.49 – 6.44 (m, 1H), 5.01 (s, 2H), 2.47 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.8, 143.3, 141.2, 140.9, 136.2, 135.9, 130.0, 129.4, 128.9, 128.4, 127.7, 127.6, 124.0, 122.9, 122.0, 121.7, 108.9, 43.8, 21.7. **IR** (CHCl₃, cm⁻¹) 3030, 2922, 1705, 1607, 1468, 1346, 1177. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO]⁺ [M+H]⁺ 360.11552 found 360.11501.

(Z)-1-benzyl-3-(chloro(4-methoxyphenyl)methylene)indolin-2-one (1g)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 6.5 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 91:9). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and the desired product was isolated as a yellow solid (82.5 mg, 0.220 mmol, 88%). **MP** = 101-104 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.54 – 7.46 (m, 2H), 7.41 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.75 – 6.62 (m, 2H), 6.57 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 5.01 (s, 2H), 3.91 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.9, 161.4, 143.3, 141.1, 136.2, 131.0, 130.4, 129.3, 128.9, 127.7, 127.6, 123.7, 122.7, 122.2, 121.7, 114.6, 108.9, 55.6, 43.8. **IR** (CHCl₃, cm⁻¹) 2932, 2837, 1701, 1605, 1508, 1468, 1346, 1252, 1173. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO₂]⁺ [M+H]⁺ 376.11043 found 376.10982.

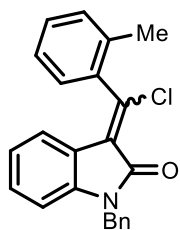
(Z)-1-benzyl-3-(chloro(3-fluorophenyl)methylene)indolin-2-one (1h)



The title compound was prepared according to the General Procedure (0.100 mmol scale, 26 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 79:21). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (29.9 mg, 0.082 mmol, 82%). **MP** = 93-96 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.51 (dtd, *J* = 7.6, 5.7, 2.7 Hz, 1H), 7.41 – 7.19 (m, 8H), 7.12 (td, *J* = 7.8, 1.2 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.68 (td, *J* = 7.8, 1.2 Hz, 1H), 6.36 (dd, *J* = 7.8, 1.2

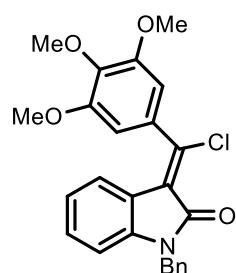
Hz, 1H), 5.01 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.48, 163.07 (d, *J* = 249.1 Hz), 141.44, 140.48 (d, *J* = 7.9 Hz), 140.47, 135.98, 131.27 (d, *J* = 8.2 Hz), 129.89, 128.93, 127.81, 127.62, 124.83, 124.09 (d, *J* = 3.2 Hz), 122.95, 121.94, 121.46, 117.55 (d, *J* = 21.0 Hz), 115.55 (d, *J* = 22.8 Hz), 109.10, 43.84. **¹⁹F NMR** (564 MHz, CDCl₃) δ -110.58 (td, *J* = 8.5, 5.7 Hz). **FTIR** (neat, cm⁻¹) 1703, 1598, 1581, 1466, 1343, 1281, 1264, 1174. **HRMS** (DART) Calc'd for [C₂₂H₁₆ClFNO]⁺ [M+H]⁺ 364.09044 found 364.09083.

1-benzyl-3-(chloro(*o*-tolyl)methylene)indolin-2-one (1i)



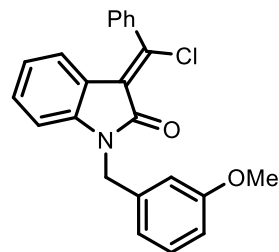
The title compound was prepared according to the General Procedure (0.250 mmol scale, 24.5 h, 72:28 *Z:E* selectivity, ratio of **1:2** = 85:15). The crude material was purified by flash chromatography (10% DCM/10% Et₂O/80% hexanes) and the desired product was isolated as a yellow solid (50.6 mg, 0.141 mmol, 56%). The purified sample (mixture of *Z:E*-isomers) was triturated with hexanes in order to obtain clean spectral data for the (***Z***)-**isomer**: **MP** = 130-134 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.46 – 7.39 (m, 1H), 7.40 – 7.22 (m, 8H), 7.08 (td, *J* = 7.8, 1.1 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.63 (td, *J* = 7.8, 1.1 Hz, 1H), 5.94 (dd, *J* = 7.8, 1.1 Hz, 1H), 5.06 (d, *J* = 15.6 Hz, 1H), 4.96 (d, *J* = 15.6 Hz, 1H), 2.31 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 142.3, 141.3, 138.1, 136.1, 135.3, 131.2, 130.2, 129.5, 128.9, 127.8, 127.7, 127.6, 127.2, 124.9, 122.7, 122.2, 121.8, 108.9, 43.8, 19.1. **IR** (CHCl₃, cm⁻¹) 3048, 2924, 1705, 1622, 1603, 1468, 1344, 1175. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO]⁺ [M+H]⁺ 360.11552 found 360.11466.

(*Z*)-1-benzyl-3-(chloro(3,4,5-trimethoxyphenyl)methylene)indolin-2-one (1j)



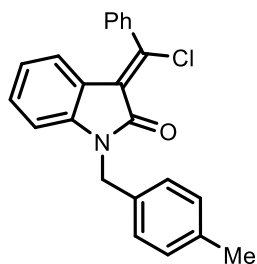
The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 93:7). The crude material was purified by flash chromatography (20% DCM/20% Et₂O/60% hexanes) and the desired product was isolated as a yellow solid (97.5 mg, 0.224 mmol, 89%). **MP** = 127-130 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.27 (m, 1H), 7.11 (td, *J* = 7.7, 1.2 Hz, 1H), 6.74 – 6.68 (m, 4H), 6.53 (ddd, *J* = 7.7, 1.2, 0.6 Hz, 1H), 5.01 (s, 2H), 3.95 (s, 3H), 3.85 (s, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.7, 154.0, 142.5, 141.3, 139.8, 136.2, 133.7, 129.6, 128.9, 127.8, 127.7, 124.2, 123.2, 121.9, 121.8, 108.9, 105.4, 61.3, 56.5, 43.8. **IR** (CHCl₃, cm⁻¹) 3011, 2924, 2838, 1705, 1582, 1479, 1468, 1454, 1414, 1339, 1242, 1175, 1126. **HRMS** (DART) Calc'd for [C₂₅H₂₃ClNO₄]⁺ [M+H]⁺ 436.13156 found 436.13117.

(*Z*)-3-(chloro(phenyl)methylene)-1-(3-methoxybenzyl)indolin-2-one (1k)



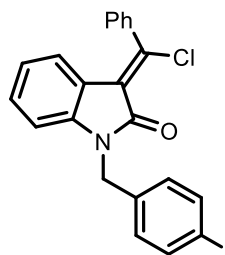
The title compound was prepared according to the General Procedure (0.150 mmol scale, 15 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 84:16). The crude material was purified by flash chromatography (10% DCM/10% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (44.9 mg, 0.119 mmol, 80%). **MP** = 90-92 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.56 – 7.49 (m, 5H), 7.24 (dd, *J* = 8.2, 7.6 Hz, 1H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 6.94 (ddt, *J* = 7.6, 1.6, 1.0 Hz, 1H), 6.89 (dd, *J* = 2.5, 1.6 Hz, 1H), 6.81 (ddd, *J* = 8.2, 2.5, 1.0 Hz, 1H), 6.71 (dd *J* = 7.8, 1.0 Hz, 1H), 6.65 (td, *J* = 7.8, 1.0 Hz, 1H), 6.33 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 4.98 (s, 2H), 3.79 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.6, 160.1, 142.8, 141.3, 138.7, 137.7, 130.5, 129.9, 129.5, 129.4, 128.3, 124.3, 122.9, 121.8, 121.8, 119.9, 113.5, 112.9, 109.0, 55.4, 43.8. **FTIR** (neat, cm⁻¹) 3005, 2918, 2843, 1698, 1603, 1589, 1469, 1349, 1263, 1279, 1145. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO₂]⁺ [M+H]⁺ 376.11043 found 376.10964.

(Z)-3-(chloro(phenyl)methylene)-1-(4-methylbenzyl)indolin-2-one (1l)



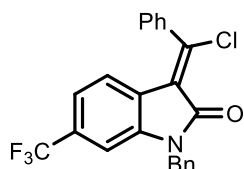
The title compound was prepared according to the General Procedure (0.150 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 84:16). The crude material was purified by flash chromatography (10% DCM/10% Et₂O/80% hexanes) and the desired product was isolated as a yellow solid (43.5 mg, 0.121 mmol, 81%). **MP** = 55-56 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.56 – 7.48 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.64 (td, *J* = 7.8, 1.2 Hz, 1H), 6.32 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.97 (s, 2H), 2.32 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.7, 142.7, 141.3, 138.8, 137.5, 133.1, 130.5, 129.6, 129.5, 129.4, 128.3, 127.7, 124.4, 122.9, 121.9, 121.7, 109.0, 43.6, 21.3. **FTIR** (neat, cm⁻¹) 3051, 2920, 1703, 1598, 1466, 1344, 1174, 1104. **HRMS** (DART) Calc'd for [C₂₃H₁₉ClNO]⁺ [M+H]⁺ 360.11552 found 360.11553.

(Z)-1-(4-bromobenzyl)-3-(chloro(phenyl)methylene)indolin-2-one (1m)



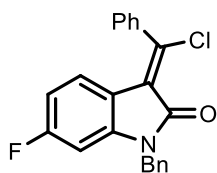
The title compound was prepared according to the General Procedure (0.250 mmol scale, 21 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 88:12). The crude material was purified by flash chromatography (10% DCM/10% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (78.6 mg, 0.185 mmol, 74%). **MP** = 56-59 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.58 – 7.49 (m, 5H), 7.48 – 7.42 (m, 2H), 7.26 – 7.22 (m, 2H), 7.10 (td, *J* = 7.7, 1.2 Hz, 1H), 6.69 – 6.63 (m, 2H), 6.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.96 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.7, 143.2, 140.9, 138.7, 135.2, 132.1, 130.6, 129.6, 129.4, 129.4, 128.3, 124.2, 123.0, 122.0, 121.9, 121.7, 108.7, 43.2. **IR** (CHCl₃, cm⁻¹) 3030, 2922, 1705, 1603, 1468, 1348, 1175. **HRMS** (DART) Calc'd for [C₂₂H₁₆BrClNO]⁺ [M+H]⁺ 424.01038 found 424.00995.

(Z)-1-benzyl-3-(chloro(phenyl)methylene)-6-(trifluoromethyl)indolin-2-one (1n)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 91:9). The crude material was purified by flash chromatography (10% DCM/10% Et₂O/80% hexanes) and the desired product was isolated as a yellow solid (88.1 mg, 0.213 mmol, 85%). **MP** = 120-123 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.60 – 7.51 (m, 3H), 7.53 – 7.48 (m, 2H), 7.42 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.00 – 6.83 (m, 2H), 6.42 (dd, *J* = 8.5, 0.9 Hz, 1H), 5.04 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.3, 146.3, 141.5, 138.2, 135.4, 131.2 (q, *J* = 32.6 Hz), 131.0, 129.6, 129.1, 128.1, 128.1, 127.7, 125.0 (q, *J* = 1.5 Hz), 123.8 (q, *J* = 272.4 Hz), 123.4, 123.0, 118.8 (q, *J* = 4.0 Hz), 105.4 (q, *J* = 3.9 Hz), 44.0. **¹⁹F NMR** (564 MHz, CDCl₃) δ -62.8 (s). **FTIR** (neat, cm⁻¹) 1711, 1606, 1591, 1456, 1316, 1267, 1162, 1117. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClF₃NO]⁺ [M+H]⁺ 414.08725 found 414.08670.

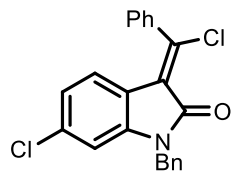
(Z)-1-benzyl-3-(chloro(phenyl)methylene)-6-fluoroindolin-2-one (1o)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 85:15). The crude material was purified by flash chromatography (10% DCM/15% Et₂O/75% hexanes) and the desired product was isolated as a yellow solid (74.4 mg, 0.204 mmol, 82%). **MP** = 127-129 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.57 – 7.47 (m, 5H), 7.37 – 7.27 (m, 5H), 6.43 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.33 (ddd, *J* = 9.3, 8.6, 2.4 Hz, 1H), 6.27 (dd, *J* = 8.6, 5.5 Hz, 1H), 4.98 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.9, 163.6 (d, *J* = 248.8 Hz), 142.9 (d, *J* = 11.5 Hz), 142.3 (d, *J* = 3.5 Hz), 138.5, 135.6, 130.6, 129.5, 129.0, 128.2, 128.0,

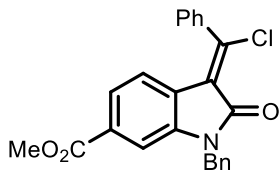
127.6, 124.3 (d, $J = 9.6$ Hz), 123.5 (d, $J = 2.1$ Hz), 117.8 (d, $J = 3.2$ Hz), 108.2 (d, $J = 22.6$ Hz), 97.5 (d, $J = 27.7$ Hz), 44.0. **^{19}F NMR** (564 MHz, CDCl_3) δ -108.8 – -108.9 (m). **FTIR** (neat, cm^{-1}) 1706, 1601, 1488, 1456, 1375, 1338, 1264, 1154, 1104. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{ClFNO}]^+ [\text{M}+\text{H}]^+$ 364.09044 found 364.09077.

(Z)-1-benzyl-6-chloro-3-(chloro(phenyl)methylene)indolin-2-one (1p)



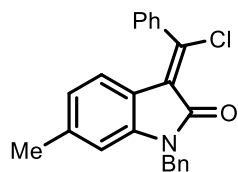
The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 85:15). The crude material was purified by flash chromatography (10% DCM/15% Et_2O /75% hexanes) and the desired product was isolated as a yellow solid (66.5 mg, 0.175 mmol, 70%). **MP** = 120-123 °C. **^1H NMR** (500 MHz, CDCl_3) δ 7.57 – 7.45 (m, 5H), 7.38 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 6.62 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.24 (d, $J = 8.4$ Hz, 1H), 4.98 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 165.6, 143.5, 142.3, 138.5, 135.6, 135.2, 130.7, 129.5, 129.1, 128.2, 128.0, 127.6, 123.7, 123.5, 121.8, 120.3, 109.4, 43.9. **FTIR** (neat, cm^{-1}) 2934, 1626, 1707, 1600, 1477, 1441, 1114. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{NO}]^+ [\text{M}+\text{H}]^+$ 380.06089 found 380.06215.

methyl (Z)-1-benzyl-3-(chloro(phenyl)methylene)-2-oxoindoline-6-carboxylate (1q)



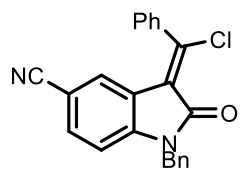
The title compound was prepared according to the General Procedure (0.250 mmol scale, 19 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 90:10). The crude material was purified by flash chromatography (15% EtOAc /20% DCM /65% hexanes) and the desired product was isolated as a yellow solid (62.3 mg, 0.154 mmol, 62%). The isolated yield for **1q** was lower than expected due difficulties fully separating **2q** from the product using silica gel chromatography. **MP** = 170-173 °C. **^1H NMR** (600 MHz, CDCl_3) δ 7.60 – 7.49 (m, 5H), 7.41 – 7.38 (m, 3H), 7.37 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 – 7.26 (m, 1H), 6.39 (dd, $J = 8.2, 0.6$ Hz, 1H), 5.05 (s, 2H), 3.84 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 166.5, 165.4, 146.0, 141.3, 138.4, 135.8, 130.9, 130.8, 129.5, 129.0, 128.3, 127.9, 127.7, 126.0, 123.9, 123.5, 122.6, 109.3, 52.4, 43.9. **IR** (CHCl_3 , cm^{-1}) 1711, 1605, 1487, 1454, 1374, 1339, 1263, 1242, 1175, 1103. **HRMS** (DART) Calc'd for $[\text{C}_{24}\text{H}_{19}\text{ClNO}_3]^+ [\text{M}+\text{H}]^+$ 404.10535 found 404.10615.

(Z)-1-benzyl-3-(chloro(phenyl)methylene)-6-methylindolin-2-one (1r)



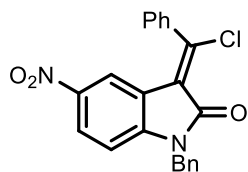
The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 82:18). The crude material was purified by flash chromatography (10% DCM/10% EtOAc /80% hexanes) and the desired product was isolated as a yellow solid (72.5 mg, 0.201 mmol, 81%). **MP** = 155-158 °C. **^1H NMR** (400 MHz, CDCl_3) δ 7.51 (s, 5H), 7.39 – 7.30 (m, 4H), 7.27 (m, 1H), 6.53 (d, $J = 1.5$ Hz, 1H), 6.46 (ddq, $J = 8.0, 1.5, 0.8$ Hz, 1H), 6.22 (d, $J = 8.0$ Hz, 1H), 4.99 (s, 2H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 166.0, 141.5, 141.2, 140.1, 138.8, 136.2, 130.3, 129.3, 128.9, 128.3, 127.7, 127.5, 124.3, 122.7, 122.5, 119.3, 109.6, 43.7, 22.0. **FTIR** (neat, cm^{-1}) 2918, 1702, 1613, 1453, 1442, 1372, 1339, 1123. **HRMS** (DART) Calc'd for $[\text{C}_{23}\text{H}_{19}\text{ClNO}]^+ [\text{M}+\text{H}]^+$ 360.11552 found 360.11506.

(Z)-1-benzyl-3-(chloro(phenyl)methylene)-2-oxoindoline-5-carbonitrile (1s)



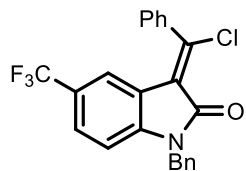
The title compound was prepared according to the a modified version of the General Procedure (0.250 mmol scale, RT for 18 h then 50 °C for 24 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 85:15). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and the desired product was isolated as a yellow solid (30.6 mg, 0.083 mmol, 33% [85% *brsm*]). **MP** = 190-193 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.64 – 7.54 (m, 3H), 7.53 – 7.46 (m, 2H), 7.39 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.39 – 7.26 (m, 5H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 1.5 Hz, 1H), 5.04 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.3, 147.0, 144.3, 137.8, 135.1, 133.9, 131.5, 129.8, 129.1, 128.2, 128.0, 127.6, 126.2, 122.5, 122.5, 119.1, 109.4, 105.1, 44.0. **FTIR** (neat, cm⁻¹) 2219, 1716, 1600, 1485, 1340, 1181, 1121. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClN₂O]⁺ [M+H]⁺ 371.09512 found 371.09515.

(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-nitroindolin-2-one (1t)



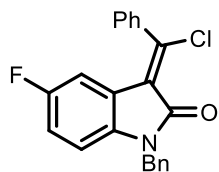
The title compound was prepared according to the General Procedure (0.250 mmol scale, 17.5 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 93:7). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (77.4 mg, 0.198 mmol, 79%). **MP** = 194-195 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.68 – 7.57 (m, 3H), 7.55 – 7.49 (m, 2H), 7.41 – 7.28 (m, 5H), 7.24 (d, *J* = 2.2 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 5.07 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.6, 147.5, 145.8, 142.9, 137.6, 135.0, 131.6, 129.8, 129.2, 128.3, 128.0, 127.6, 125.8, 122.6, 122.1, 118.6, 108.5, 44.2. **FTIR** (neat, cm⁻¹) 1713, 1594, 1509, 1482, 1441, 1323, 1297, 1282, 1168, 1075, 1056. **HRMS** (DART) Calc'd for [C₂₂H₁₆ClN₂O₃]⁺ [M+H]⁺ 391.08494 found 391.08455.

(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (1u)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 16 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 91:9). The crude material was purified by flash chromatography (10% DCM/10% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (78.3 mg, 0.189 mmol, 76%). **MP** = 123-125 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.63 – 7.47 (m, 5H), 7.39 – 7.25 (m, 6H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.54 (s, 1H), 5.05 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 145.5, 143.6 (q, *J* = 1.4 Hz), 138.0, 135.5, 131.1, 129.6, 129.1, 128.1, 128.0, 127.6, 126.7 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 32.6 Hz), 124.1 (q, *J* = 271.6 Hz), 123.3, 122.0, 119.9 (q, *J* = 4.1 Hz), 108.7, 44.0. **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.2 (s). **FTIR** (neat, cm⁻¹) 3038, 2966, 1707, 1613, 1498, 1453, 1387, 1326, 1175, 1153, 1107. **HRMS** (DART) Calc'd for [C₂₃H₁₆ClF₃NO]⁺ [M+H]⁺ 414.08725 found 414.08761.

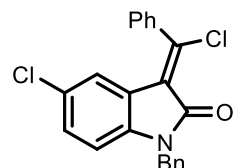
(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-fluoroindolin-2-one (1v)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 19 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 88:12). The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and the desired product was isolated as a yellow solid (70.2 mg, 0.193 mmol, 77%). **MP** = 118-120 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.66 – 7.44 (m, 5H), 7.39 – 7.26 (m, 5H), 6.79 (td, *J* = 8.6, 2.6 Hz, 1H), 6.60 (dd, *J* = 8.6, 4.4 Hz, 1H), 6.03 (dd, *J* = 9.3, 2.6 Hz, 1H), 5.00 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 158.3 (d, *J* = 238.6 Hz), 144.6 (d, *J* = 1.4 Hz), 138.2, 137.3 (d, *J* = 1.8 Hz), 135.8, 130.9, 129.6, 129.0, 128.1, 127.9, 127.6,

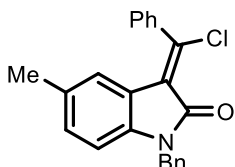
124.1 (d, $J = 3.0$ Hz), 122.8 (d, $J = 9.2$ Hz), 115.8 (d, $J = 24.1$ Hz), 110.6 (d, $J = 26.9$ Hz), 109.3 (d, $J = 8.3$ Hz), 43.9. **^{19}F NMR** (564 MHz, CDCl_3) δ -121.0 (td, $J = 8.6, 4.4$ Hz). **FTIR** (neat, cm^{-1}) 3032, 2913, 1700, 1600, 1478, 1453, 1343, 1168, 1144. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{ClFNO}]^+ [\text{M}+\text{H}]^+$ 364.09044 found 364.09028.

(Z)-1-benzyl-5-chloro-3-(chloro(phenyl)methylene)indolin-2-one (1w)



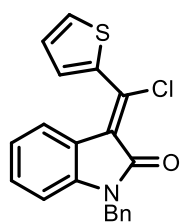
The title compound was prepared according to the General Procedure (0.250 mmol scale, 17 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 81:19). The crude material was purified by flash chromatography (10% DCM/15% Et_2O /75% hexanes) and the desired product was isolated as a yellow solid (79.8 mg, 0.210 mmol, 84%). **MP** = 138-141 °C. **^1H NMR** (400 MHz, CDCl_3) δ 7.64 – 7.46 (m, 5H), 7.39 – 7.26 (m, 5H), 7.05 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.27 (d, $J = 2.0$ Hz, 1H), 5.00 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 165.3, 144.8, 139.7, 138.2, 135.7, 131.0, 129.6, 129.2, 129.0, 128.1, 127.9, 127.6, 127.2, 123.6, 123.2, 123.1, 109.8, 43.9. **FTIR** (neat, cm^{-1}) 2921, 2855, 1712, 1593, 1474, 1429, 1336, 1168. **HRMS** (DART) Calc'd for $[\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{NO}]^+ [\text{M}+\text{H}]^+$ 380.06089 found 380.06096.

(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-methylindolin-2-one (1x)



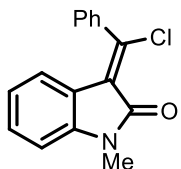
The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 82:18). The crude material was purified by flash chromatography (10% DCM/10% EtOAc /80% hexanes) and the desired product was isolated as a yellow solid (74.3 mg, 0.206 mmol, 83%). **MP** = 124-125 °C. **^1H NMR** (600 MHz, CDCl_3) δ 7.56 – 7.49 (m, 5H), 7.38 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 6.89 (ddd, $J = 8.0, 1.6, 0.8$ Hz, 1H), 6.59 (d, $J = 8.0$ Hz, 1H), 6.11 (dd, $J = 1.6, 0.8$ Hz, 1H), 4.99 (s, 2H), 1.99 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 165.7, 142.3, 139.1, 138.8, 136.2, 131.1, 130.4, 129.9, 129.3, 128.9, 128.3, 127.7, 127.6, 124.5, 123.7, 121.9, 108.7, 43.8, 21.2. **FTIR** (neat, cm^{-1}) 3062, 3032, 2924, 1710, 1602, 1591, 1485, 1433, 1378, 1342, 1183, 1123. **HRMS** (DART) Calc'd for $[\text{C}_{23}\text{H}_{19}\text{ClNO}]^+ [\text{M}+\text{H}]^+$ 360.11552 found 360.11558.

(Z)-1-benzyl-3-(chloro(thiophen-2-yl)methylene)indolin-2-one (1y)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 17 h, >95:5 *Z:E* selectivity, ratio of **1:2** = >99:1). The crude material was purified by flash chromatography (10% DCM/10% EtOAc /80% hexanes) and the desired product was isolated as a yellow solid (76.2 mg, 0.217 mmol, 87%). **MP** = 155-156 °C. **^1H NMR** (500 MHz, CDCl_3) δ 7.62 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.42 (dd, $J = 3.6, 1.2$ Hz, 1H), 7.38 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 7.17 – 7.11 (m, 2H), 6.86 (dd, $J = 8.1, 1.0$ Hz, 1H), 6.77 – 6.70 (m, 2H), 5.00 (s, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 165.5, 141.4, 140.2, 136.1, 135.1, 130.4, 129.9 (2 overlapping signals), 128.9, 127.8, 127.6 (2 overlapping signals), 125.3, 122.6, 121.9, 121.8, 109.0, 43.8. **FTIR** (neat, cm^{-1}) 3416, 3401, 3029, 2846, 1705, 1612, 1596, 1574, 1525, 1491, 1332, 1270, 1102. **HRMS** (DART) Calc'd for $[\text{C}_{20}\text{H}_{15}\text{ClNOS}]^+ [\text{M}+\text{H}]^+$ 352.05629 found 352.05584.

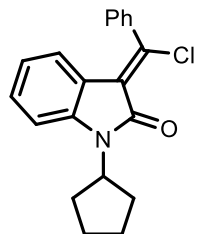
(Z)-3-(chloro(phenyl)methylene)-1-methylindolin-2-one (1z)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 85:15). The crude material was purified by flash chromatography (10% DCM/20% EtOAc /70% hexanes) and the desired product was isolated

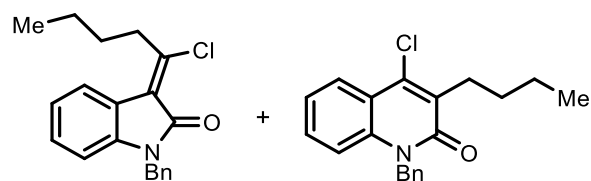
as a yellow solid (50.7 mg, 0.188 mmol, 75%). **MP** = 98-100 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.64 – 7.38 (m, 5H), 7.20 (td, *J* = 7.8, 1.2 Hz, 1H), 6.79 (d, *J* = 7.8, 1H), 6.68 (td, *J* = 7.8, 1.2 Hz, 1H), 6.33 (ddd, *J* = 7.8, 1.2, 0.6 Hz, 1H), 3.29 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.6, 142.3, 142.1, 138.7, 130.4, 129.6, 129.4, 128.3, 124.5, 122.8, 121.8, 121.7, 107.9, 26.2. **IR** (CHCl₃, cm⁻¹) 3055, 2932, 1705, 1605, 1470, 1371, 1337, 1269, 1099. **HRMS** (DART) Calc'd for [C₁₆H₁₃ClNO]⁺ [M+H]⁺ 270.06857 found 270.06907.

(Z)-3-(chloro(phenyl)methylene)-1-cyclopentylindolin-2-one (1ab)



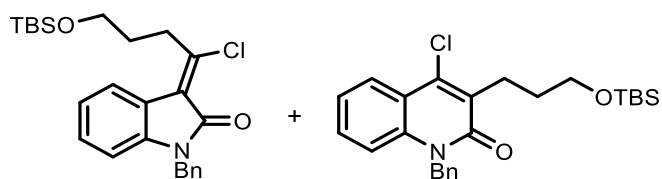
The title compound was prepared according to the General Procedure (0.250 mmol scale, 18 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 94:6). The crude material was purified by flash chromatography (10% DCM/10% EtOAc/80% hexanes) and the desired product was isolated as a yellow solid (66.1 mg, 0.204 mmol, 82%). **MP** = 131-133 °C. **¹H NMR** (600 MHz, CDCl₃) δ 7.54 – 7.49 (m, 3H), 7.51 – 7.45 (m, 2H), 7.16 (td, *J* = 7.8, 1.3 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.65 (td, *J* = 7.8, 1.0 Hz, 1H), 6.32 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 4.88 (p, *J* = 8.8 Hz, 1H), 2.25 – 2.05 (m, 2H), 2.04 – 1.88 (m, 4H), 1.83 – 1.67 (m, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.5, 142.0, 140.8, 138.9, 130.3, 129.4, 129.2, 128.3, 124.6, 123.1, 122.2, 121.2, 109.4, 52.3, 27.8, 25.5. **IR** (CHCl₃, cm⁻¹) 2957, 2922, 1703, 1599, 1464, 1356, 1261, 1215, 1165. **HRMS** (DART) Calc'd for [C₂₀H₁₉ClNO]⁺ [M+H]⁺ 324.11552 found 324.11519.

(Z)-1-benzyl-3-(1-chloropentylidene)indolin-2-one (1ac) and 1-benzyl-3-butyl-4 chloroquinolin-2(1H)-one (2ac)



The title compound was prepared according to the General Procedure (0.250 mmol scale, 20 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 73:27). The crude material was purified by flash chromatography (5% EtOAc/10% CHCl₃/85% hexanes), providing the product as an inseparable mixture of regioisomers (72.0 mg, 0.221 mmol, 88%, final ratio of **1:2** = 74:26). **1ac**: **¹H NMR** (400 MHz, CDCl₃) δ 7.49 – 7.42 (m, 1H), 7.35 – 7.20 (m, 5H), 7.24 – 7.15 (m, 1H), 7.02 (td, *J* = 7.6, 1.0 Hz, 1H), 6.76 (dd, *J* = 7.6, 1.0 Hz, 1H), 4.98 (s, 2H), 3.09 – 2.98 (m, 2H), 1.91 – 1.75 (m, 2H), 1.59 – 1.44 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).

(Z)-1-benzyl-3-(4-((tert-butyldimethylsilyl)oxy)-1-chlorobutylidene)indolin-2-one (1ad) and 1-benzyl-3-(3-((tert-butyldimethylsilyl)oxy)propyl)-4-chloroquinolin-2(1H)-one (2ad)

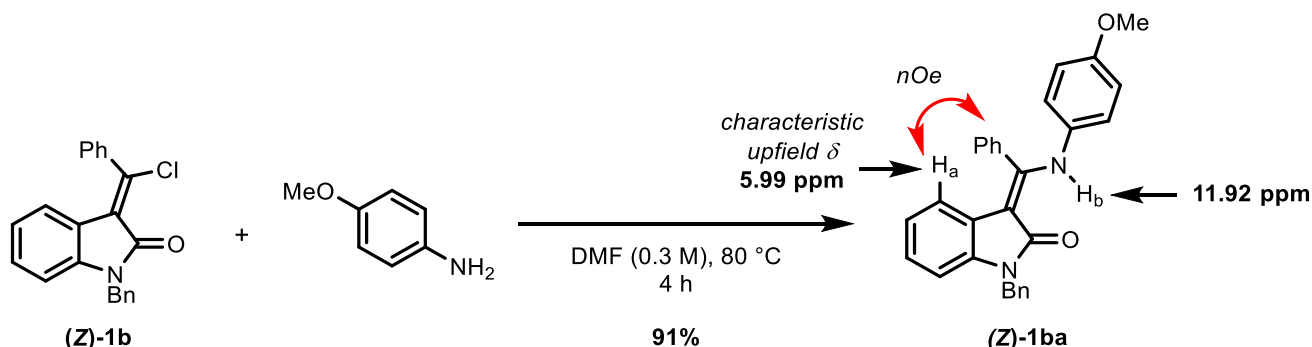


The title compound was prepared according to the General Procedure (0.25 mmol scale, 20 h, >95:5 *Z:E* selectivity, ratio of **1:2** = 72:28). The crude material was purified by flash chromatography (5% EtOAc/10% DCM/85% hexanes), providing the product as a mixture of regioisomers that could not be fully separated (86.1 mg, 0.195 mmol, 78%, final ratio of **1:2** = 77:23). **1ad**: **¹H NMR** (500 MHz, CDCl₃) δ 7.68 (ddd, *J* = 7.8, 1.2, 0.5 Hz, 1H), 7.34 – 7.23 (m, 5H), 7.19 (td, *J* = 7.8, 1.2 Hz, 1H), 7.00 (td, *J* = 7.8, 1.2 Hz, 1H), 6.75 (ddd, *J* = 7.8, 1.2, 0.5 Hz, 1H), 4.98 (s, 2H), 3.81 – 3.75 (m, 2H), 3.21 – 3.08 (m, 2H), 2.06 – 1.97 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H).

5 Derivatization Studies

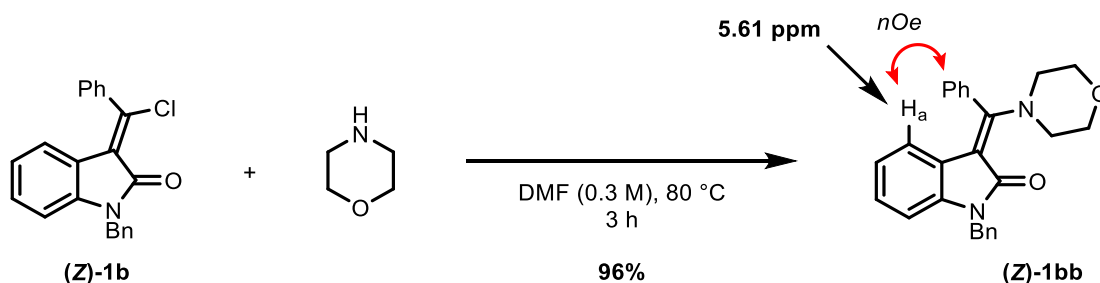
5.1 General Procedures and Characterization Data for Methylene Oxindole Derivatives

(Z)-1-benzyl-3-(((4-methoxyphenyl)amino)(phenyl)methylene)indolin-2-one (**1ba**)



A 2 dram vial equipped with a stir bar was charged with (Z)-**1b** (51.9 mg, 0.15 mmol, 1.0 equiv) and *p*-anisidine (44.3 mg, 0.36 mmol, 2.4 equiv). After purging the vial with Ar for 15 minutes, anhydrous DMF (0.5 mL) was added. The vial was sealed with a Teflon-lined cap and placed in a pre-heated oil bath at 80 °C for 4 h. The reaction was cooled to rt, diluted with EtOAc (1.0 mL), and quenched by the addition of a 10% NaOH(w/w) solution (1.0 mL). The aqueous layer was extracted with EtOAc (3x) and the combined organics were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. ¹H NMR analysis of the crude reaction mixture showed that the (Z)-isomer was formed exclusively. The stereochemistry of the product confirmed by 1D and 2D NOESY experiments. Characteristic chemical shift values for H_a (upfield due to magnetic anisotropy, H_a points towards center of phenyl ring) and H_b (downfield due to internal hydrogen bonding with carbonyl group) provide further evidence for the assigned stereochemistry. The crude material was purified by flash chromatography (10% DCM/20% EtOAc/70% hexanes) and (Z)-**1ba** was isolated as a yellow solid (59 mg, 0.136 mmol, 91%). **MP** = 184-185 °C. **¹H NMR** (600 MHz, CDCl₃) δ 11.92 (bs, 1H), 7.52 – 7.44 (m, 3H), 7.43 – 7.39 (m, 2H), 7.37 – 7.34 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.23 (m, 1H), 6.91 (td, J = 7.8, 1.2 Hz, 1H), 6.79 (d, J = 7.8, 1H), 6.77 – 6.73 (m, 2H), 6.67 – 6.61 (m, 3H), 5.99 (ddd, J = 7.8, 1.2, 0.5 Hz, 1H), 5.13 (s, 2H), 3.71 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 169.3, 157.8, 156.8, 137.4, 137.2, 133.2, 131.9, 129.9, 129.3, 129.0, 128.8, 127.4, 127.4, 125.1, 124.3, 123.3, 120.9, 118.6, 114.1, 108.4, 96.7, 55.5, 43.4. **FTIR** (neat, cm⁻¹) 1645, 1572, 1512, 1455, 1344, 1242, 1183, 1159, 1105. **HRMS** (ESI) Calc'd for [C₂₉H₂₅N₂O₂]⁺ [M+H]⁺ 433.1911 found 433.1911.

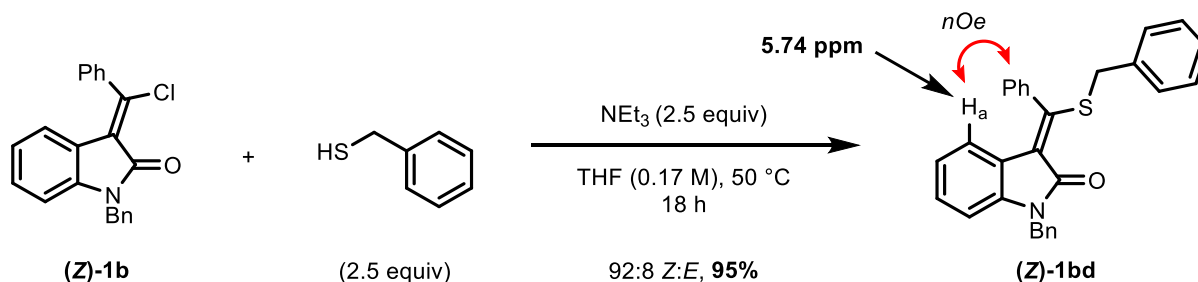
(Z)-1-benzyl-3-(morpholino(phenyl)methylene)indolin-2-one (**1bb**)



A 2 dram vial equipped with a stir bar was charged with (Z)-**1b** (51.9 mg, 0.15 mmol, 1.0 equiv) and morpholine (26.2 μ L, 0.30 mmol, 2.0 equiv). After purging the vial with Ar for 15 minutes, anhydrous DMF (0.5 mL) was added. The vial was sealed with a Teflon-lined cap and placed in a pre-heated oil bath at 80 °C for 3 h. The reaction was cooled to rt, diluted with EtOAc (1.0 mL), and quenched by the addition of a 10%

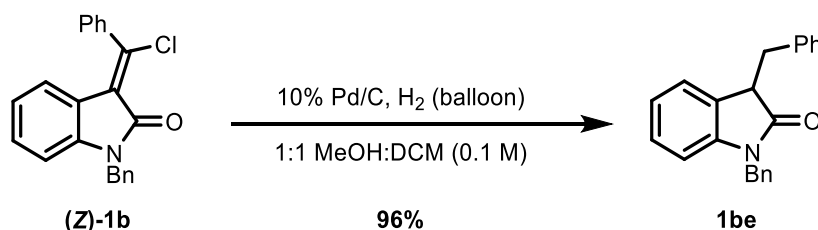
NaOH(w/w) solution (1.0 mL). The aqueous layer was extracted with EtOAc (3x) and the combined organics were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. ¹H NMR analysis of the crude reaction mixture showed that the (Z)-isomer was formed exclusively. The stereochemistry of the product confirmed by 1D NOESY experiments. Characteristic upfield chemical shift value for H_a provides further evidence for the assigned stereochemistry. The crude material was purified by flash chromatography (4% MeOH/DCM) and (Z)-**1bb** was isolated as an orange solid (57 mg, 0.144 mmol, 96%). **MP** = 191-193 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.62 – 7.55 (m, 1H), 7.55 – 7.45 (m, 4H), 7.34 – 7.25 (m, 4H), 7.26 – 7.18 (m, 1H), 6.82 (td, *J* = 7.5, 1.2 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 6.52 (td, *J* = 7.5, 1.2 Hz, 1H), 5.61 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.08 (s, 2H), 3.99 – 3.79 (m, 4H), 3.63 (bs, 4H). **¹³C NMR** (126 MHz, CDCl₃) δ 165.2, 161.2, 138.2, 137.6, 135.6, 131.2, 130.6, 129.6, 128.7, 127.3, 127.2, 126.7, 122.9, 120.3, 119.2, 107.9, 98.5, 67.9 (2 overlapping signals), 43.5. **FTIR** (neat, cm⁻¹) 2903, 2855, 1647, 1522, 1482, 1431, 1348, 1258, 1166, 1102, 1009. **HRMS** (ESI) Calc'd for [C₂₆H₂₅N₂O₂]⁺ [M+H]⁺ 397.1911 found 397.1913.

(Z)-1-benzyl-3-((benzylthio)(phenyl)methylene)indolin-2-one (**1bc**)



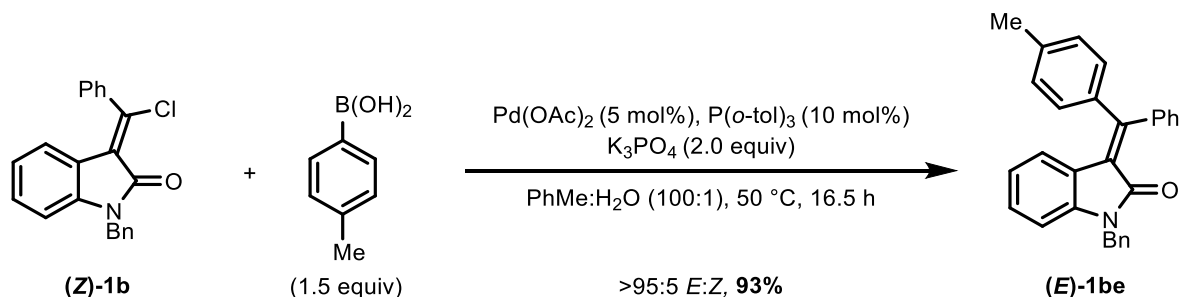
A 2 dram vial equipped with a stir bar was charged with (Z)-**2a** (51.9 mg, 0.15 mmol, 1.0 equiv) and purged with argon for 15 minutes. Neat NEt₃ (52 μL, 0.375 mmol, 2.5 equiv) and benzyl mercaptan (44 μL, 0.375 mmol, 2.5 equiv) were sequentially added to the reaction vessel. The vial was sealed with a Teflon-lined cap and placed in a pre-heated oil bath at 50 °C for 18 h. The reaction mixture was diluted with DCM (1.0 mL), washed with H₂O (2x) and brine (1x). The combined organics were dried over Na₂SO₄ and concentrated under reduced pressure. The Z:E ratio was determined by analysis of the crude reaction mixture by ¹H NMR using a 5 s relaxation delay. The stereochemistry of the product confirmed by 1D NOESY experiments and by X-Ray crystallographic analysis (see Section 6). Characteristic upfield chemical shift value for H_a provides further evidence for the assigned stereochemistry. The crude material was purified by flash chromatography (10% DCM/15% EtOAc/75% hexanes) and (Z)-**1bd** was isolated as a yellow solid (62 mg, 0.143 mmol, 95%). **MP** = 211-214 °C. **¹H NMR** (500 MHz, CDCl₃) δ 7.58 – 7.48 (m, 3H), 7.40 – 7.34 (m, 2H), 7.33 – 7.17 (m, 8H), 7.15 – 7.08 (m, 2H), 6.98 (td, *J* = 7.8, 1.2 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.57 (td, *J* = 7.8, 1.2 Hz, 1H), 5.74 (dd, *J* = 7.8, 1.2 Hz, 1H), 5.01 (s, 2H), 3.64 (s, 2H). **¹³C NMR** (126 MHz, CDCl₃) δ 167.0, 157.2, 140.9, 136.6, 136.4, 136.2, 129.7, 129.3, 129.2, 128.8, 128.5, 127.8, 127.7, 127.5, 127.4, 127.2, 122.8, 121.4, 121.4, 119.8, 108.6, 43.6, 37.0. **IR** (CHCl₃, cm⁻¹) 3028, 2924, 1682, 1607, 1568, 1478, 1466, 1454, 1352, 1175. **HRMS** (ESI) Calc'd for [C₂₉H₂₄NOS]⁺ [M+H]⁺ 434.15786 found 434.15800.

1,3-dibenzylindolin-2-one (**1bd**)



Following a literature procedure,²³ to a stirring solution of (*Z*)-**1b** (51.9 mg, 0.15 mmol) in a 1:1 mixture of MeOH:DCM (0.75 mL:0.75 mL), 10% Pd/C (7.9 mg) was added in one portion. The reaction flask was sealed with a rubber septum, evacuated and refilled with H₂ gas (3x) from a balloon. After stirring at rt for 14 h, the reaction mixture was filtered through a pad of celite, washing with EtOAc. The crude material was purified by flash chromatography (25% EtOAc/hexanes) and the desired product was isolated as a white solid (45.2 mg, 0.144 mmol, 96%). The spectral data is consistent with literature values.²⁴

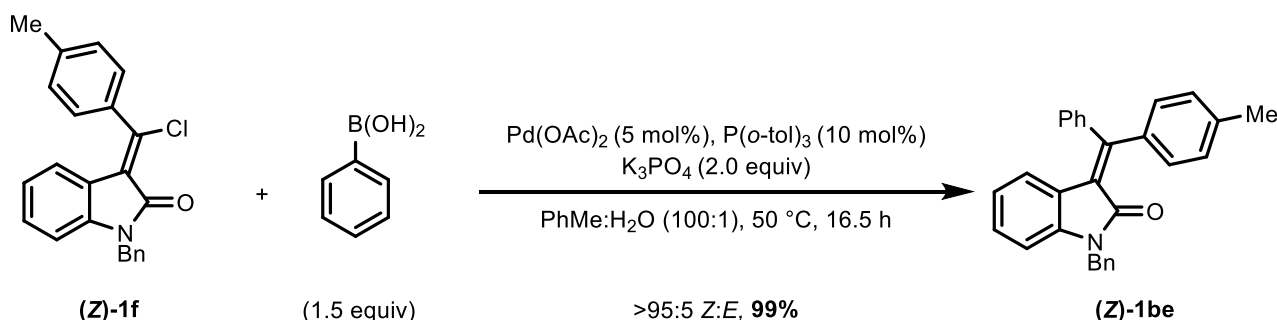
(*E*)-1-benzyl-3-(phenyl(*p*-tolyl)methylene)indolin-2-one (1be**)**



A 2 dram vial equipped with a stir bar was charged with (*Z*)-**1b** (34.6 mg, 0.1 mmol, 1.0 equiv), Pd(OAc)₂ (1.1 mg, 0.005 mmol, 0.05 equiv), P(*o*-tol)₃ (3.0 mg, 0.01 mmol, 0.1 equiv), K₃PO₄ (42.5 mg, 0.2 mmol, 2.0 equiv) and *p*-tolylboronic acid (20.4 mg, 0.15 mmol, 1.5 equiv). After purging the vial with argon for 15 minutes, anhydrous PhMe (1.1 mL) and degassed H₂O (11 μL) was added. The reaction vial was sealed with a Teflon-lined cap and heated to 50 °C for 16.5 h. The reaction was diluted with EtOAc (1 mL), filtered through a pad of silica and concentrated under reduced pressure. The *Z*:*E* ratio was determined by analysis of the crude reaction mixture by ¹H NMR. The crude material was purified by flash chromatography (10% EtOAc/10% DCM/80% hexanes) and (*E*)-**1be** was isolated as an orange solid (37.3 mg, 0.093 mmol, 93%). The spectral data is consistent with literature values.²⁵ ¹H NMR (500 MHz, CDCl₃) δ 7.49 – 7.40 (m, 3H), 7.37 – 7.21 (m, 9H), 7.21 – 7.17 (m, 2H), 7.04 (td, *J* = 7.7, 1.2 Hz, 1H), 6.68 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.63 (td, *J* = 7.7, 1.2 Hz, 1H), 6.38 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.93 (s, 2H), 2.38 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.0, 155.5, 142.4, 141.7, 139.7, 137.0, 136.6, 130.6, 129.6, 129.3, 129.0, 128.8, 128.7, 128.5, 127.6, 127.5, 123.8, 123.7, 123.2, 121.5, 108.7, 43.6, 21.7.

Note: Using Pd₂dba₃ (2.5 mol%) instead of Pd(OAc)₂ provided **1be** in 96% yield by NMR (90:10 *E*:*Z*).

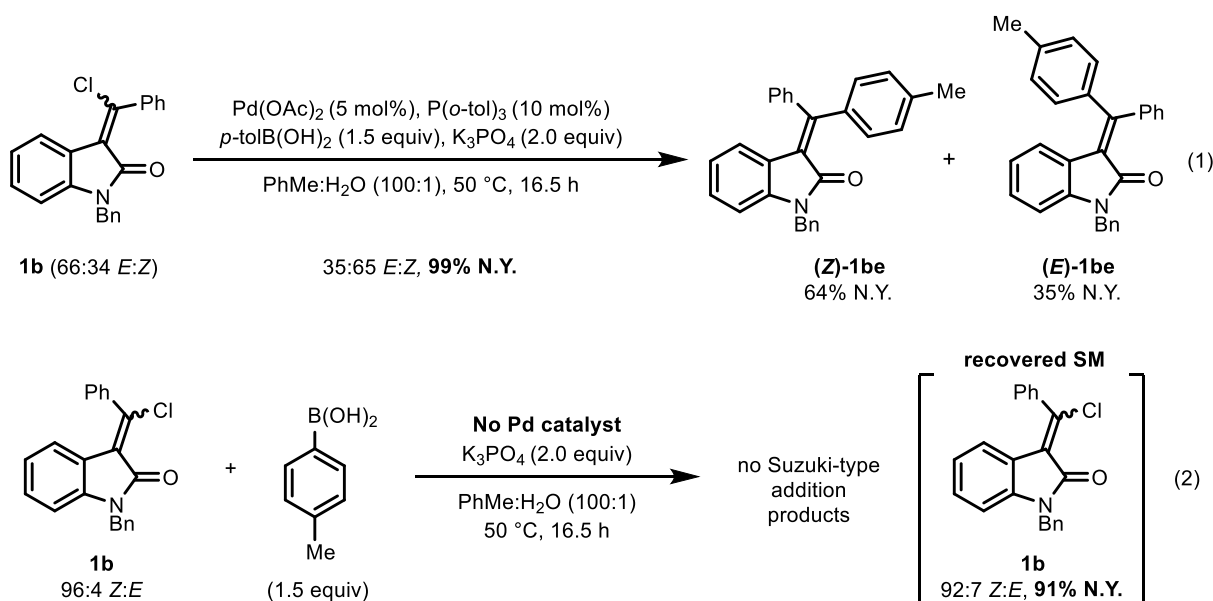
(*Z*)-1-benzyl-3-(phenyl(*p*-tolyl)methylene)indolin-2-one (1be**)**



A 2 dram vial equipped with a stir bar was charged with (*Z*)-**1b** (34.0 mg, 0.1 mmol, 1.0 equiv), Pd(OAc)₂ (1.1 mg, 0.005 mmol, 0.05 equiv), P(*o*-tol)₃ (3.0 mg, 0.01 mmol, 0.1 equiv), K₃PO₄ (42.5 mg, 0.2 mmol, 2.0 equiv) and phenylboronic acid (18.3 mg, 0.15 mmol, 1.5 equiv). After purging the vial with argon for 15

minutes, anhydrous PhMe (1.1 mL) and degassed H₂O (11 μ L) was added. The reaction vial was sealed with a Teflon-lined cap and heated to 50 °C for 16.5 h. The reaction was diluted with EtOAc (1 mL), filtered through a pad of silica and concentrated under reduced pressure. The *Z:E* ratio was determined by analysis of the crude reaction mixture by ¹H NMR. The crude material was purified by flash chromatography (10% EtOAc/10% DCM/80% hexanes) and (*Z*)-**1be** was isolated as an orange solid (39.8 mg, 0.099 mmol, 99%). The spectral data is consistent with literature values.²⁵ ¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.34 (m, 5H), 7.36 – 7.27 (m, 4H), 7.25 – 7.22 (m, 5H), 7.06 (td, *J* = 7.7, 1.2 Hz, 1H), 6.72 – 6.65 (m, 2H), 6.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.93 (s, 2H), 2.44 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.0, 155.5, 142.5, 140.3, 139.6, 138.5, 136.5, 130.4, 129.7, 129.7, 129.3, 128.8, 128.6, 127.9, 127.6, 127.5, 123.8, 123.7, 123.2, 121.5, 108.8, 43.6, 21.6.

5.2 Control Experiments for Stereoinvertive Suzuki Reaction



A 66:34 *E:Z* mixture of **1b** was synthesized under the standard conditions but at 100 °C instead of RT to increase the amount of the *E*-isomer formed. Subjecting this mixture to the standard Suzuki conditions resulted in a 35:65 *E:Z* of **1be**, which follows the same stereoinversion trend as previously described. In other words, the stereospecificity of the reaction is such that *E*-**1b** leads to *Z*-**1be** and *Z*-**1b** leads to *E*-**1be**.

A control experiment without Pd(OAc)₂/P(*o*-tol)₃ using a 96:4 *Z:E* mixture of **1b** resulted in 91% recovery of the starting material as a 92:7 *Z:E* mixture. No Suzuki-type addition products were observed in the crude ¹H NMR, which means that the reaction is indeed catalyzed by Pd. Additionally, the extent of *Z*-**1b** → *E*-**1b** isomerization is minimal under the reaction conditions without the Pd catalyst, suggesting that this stereoinversion process occurs during the Suzuki cross-coupling.

It is possible that the reaction involves *syn*-carbopalladation of the alkene in **1b** by an in situ generated [ArPd^{II}X] species, followed by a stereospecific *syn*- β -Cl elimination, which would necessitate C–C bond rotation and would formally lead to the stereoinverted Suzuki product. However, the reaction still proceeds when a Pd⁰ pre-catalyst is used (2.5 mol% Pd₂dba₃), although slightly lower *E:Z* selectivity is observed (90:10 *E:Z*) when starting with stereochemically pure *Z*-**1b**. Overall, we cannot rule out the intermediacy of a vinyl

Pd^{II} intermediate (formed via oxidative addition into the C–Cl bond of **1b**) undergoing isomerization prior to C–C bond reductive elimination.

6 Crystallographic Data

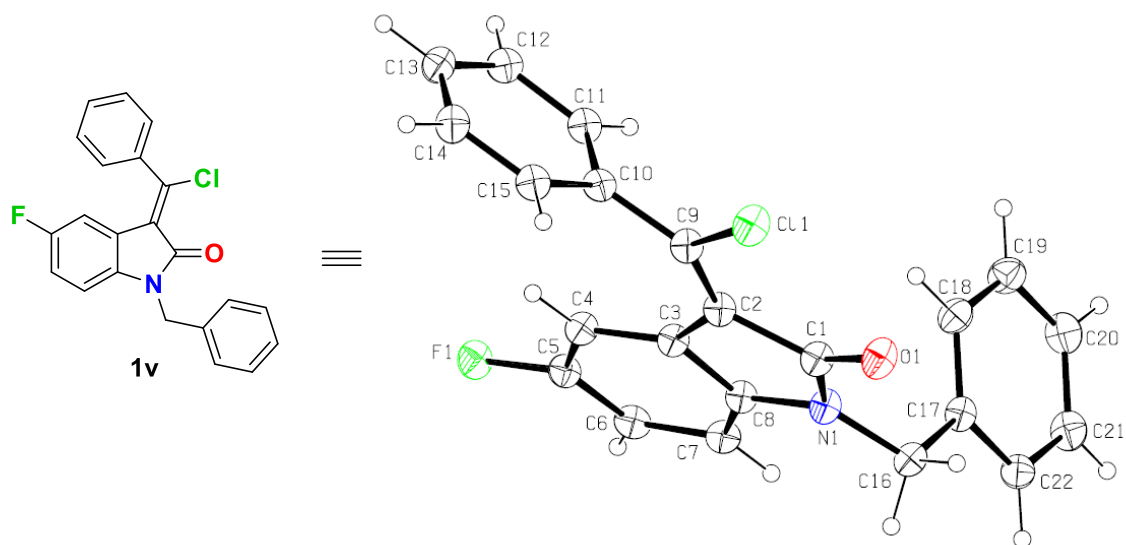


Table S5. Crystal data and structure refinement for **1v**

Identification code	d1613_a
Empirical formula	C ₂₂ H ₁₅ Cl F N O
Formula weight	363.80
Temperature	147(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 9.4120(7) Å α = 90°. b = 10.3695(8) Å β = 98.188(5)°. c = 17.6799(11) Å γ = 90°.
Volume	1707.9(2) Å ³
Z	4
Density (calculated)	1.415 Mg/m ³
Absorption coefficient	2.155 mm ⁻¹
F(000)	752
Crystal size	0.140 x 0.040 x 0.020 mm ³
Theta range for data collection	4.747 to 67.276°.
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -21 ≤ l ≤ 21
Reflections collected	29249
Independent reflections	3051 [R(int) = 0.0791]
Completeness to theta = 67.276°	99.3 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7529 and 0.6039
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3051 / 0 / 235
Goodness-of-fit on F ²	1.011
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1032
R indices (all data)	R1 = 0.0546, wR2 = 0.1137
Extinction coefficient	n/a
Largest diff. peak and hole	0.199 and -0.347 e.Å ⁻³

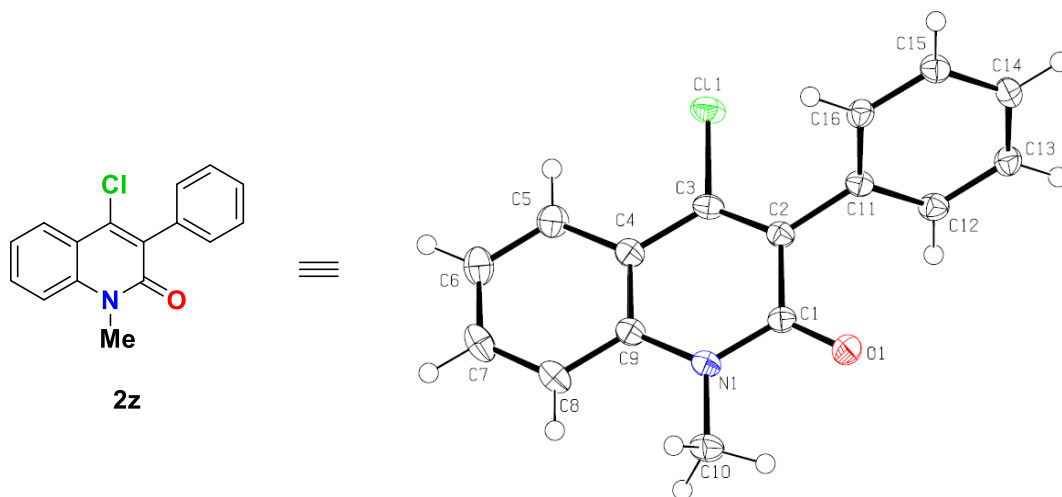


Table S6. Crystal data and structure refinement for **2z**

Identification code	d15140
Empirical formula	C ₁₆ H ₁₂ Cl N O
Formula weight	269.72
Temperature	147(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pna2 ₁
Unit cell dimensions	a = 12.0485(3) Å α = 90°. b = 19.1202(5) Å β = 90°. c = 5.4934(1) Å γ = 90°.
Volume	1265.51(5) Å ³
Z	4
Density (calculated)	1.416 Mg/m ³
Absorption coefficient	2.580 mm ⁻¹
F(000)	560
Crystal size	0.200 x 0.130 x 0.040 mm ³
Theta range for data collection	4.337 to 67.358°.
Index ranges	-14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -6 ≤ l ≤ 6

Reflections collected	47275
Independent reflections	2250 [R(int) = 0.0351]
Completeness to theta = 67.358°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.6628
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2250 / 1 / 174
Goodness-of-fit on F ²	1.098
Final R indices [I>2sigma(I)]	R1 = 0.0213, wR2 = 0.0553
R indices (all data)	R1 = 0.0216, wR2 = 0.0555
Absolute structure parameter	0.009(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.119 and -0.184 e.Å ⁻³

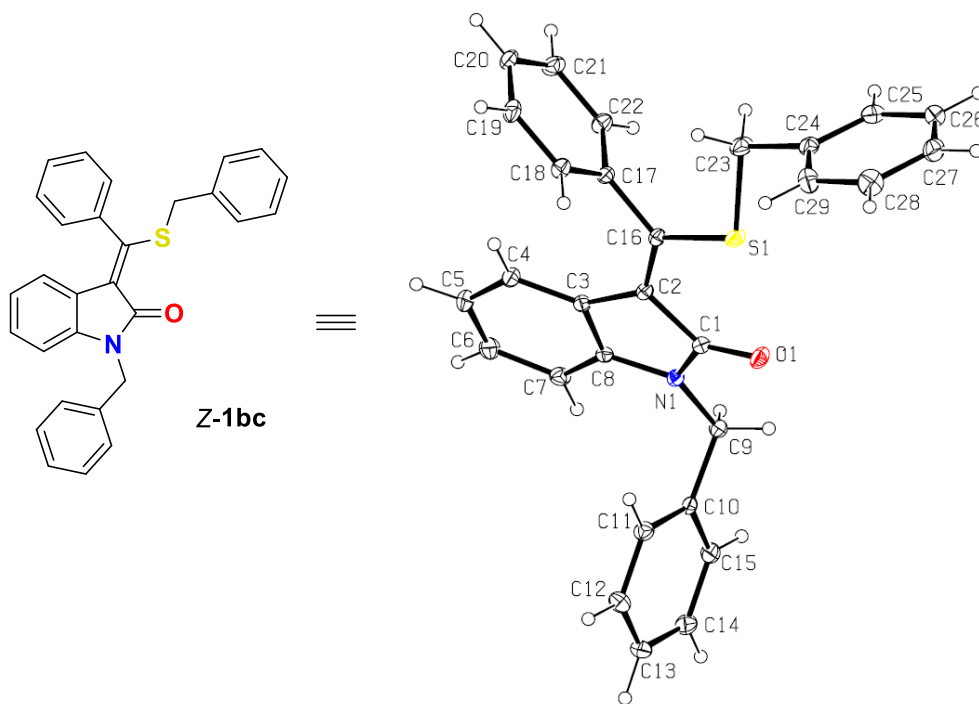
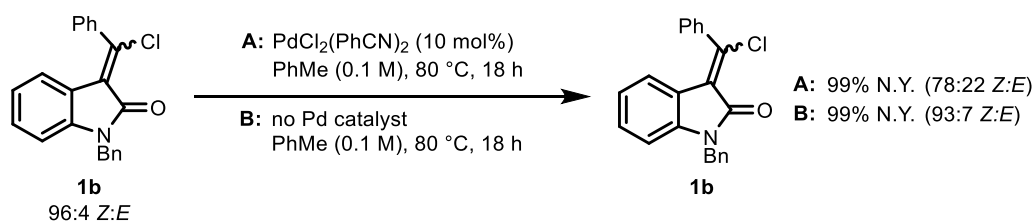


Table S7. Crystal data and structure refinement for **Z-1bc**.

Identification code	d1682
Empirical formula	C ₂₉ H ₂₃ N O S
Formula weight	433.54
Temperature	147(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 21.2078(16) Å α = 90°.

	$b = 5.8592(4) \text{ \AA}$	$\beta = 100.455(2)^\circ$.
	$c = 18.1652(13) \text{ \AA}$	$\gamma = 90^\circ$.
Volume	$2219.7(3) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.168 mm^{-1}	
F(000)	912	
Crystal size	$0.320 \times 0.260 \times 0.150 \text{ mm}^3$	
Theta range for data collection	$1.953 \text{ to } 27.611^\circ$.	
Index ranges	$-27 \leq h \leq 27, -7 \leq k \leq 7, -23 \leq l \leq 22$	
Reflections collected	39484	
Independent reflections	5138 [R(int) = 0.0383]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6944	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5138 / 0 / 289	
Goodness-of-fit on F^2	1.050	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0393, wR2 = 0.0904$	
R indices (all data)	$R1 = 0.0545, wR2 = 0.0980$	
Extinction coefficient	n/a	
Largest diff. peak and hole	$0.360 \text{ and } -0.348 \text{ e.\AA}^{-3}$	

7 Isomerization Study



To a 2 dram vial containing $\text{PdCl}_2(\text{PhCN})_2$ (1.9 mg, 0.005 mmol), 0.5 mL of a stock solution of **1b** (69.2 mg, 0.20 mmol, 96:4 Z:E) in anhydrous PhMe (2.0 mL) was added. To a separate 2 dram vial, 0.5 mL of the same stock solution was added. The remaining stock solution was evaporated under reduced pressure and re-dissolved in CDCl_3 for accurate analysis of the initial Z:E ratio by ^1H NMR using a 10 s relaxation delay. Both vials were sealed with a Teflon-lined screw cap and placed in a pre-heated oil bath at 80°C . After stirring for 18 h, the reaction was diluted with EtOAc (1.0 mL) and passed through a plug of silica gel, washing with EtOAc (5 mL). The NMR yields and Z:E ratios were obtained by ^1H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard and 10 s relaxation delay for the NMR experiment.

8 Computational Details

Full reference for Gaussian 09 Revision D.01

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

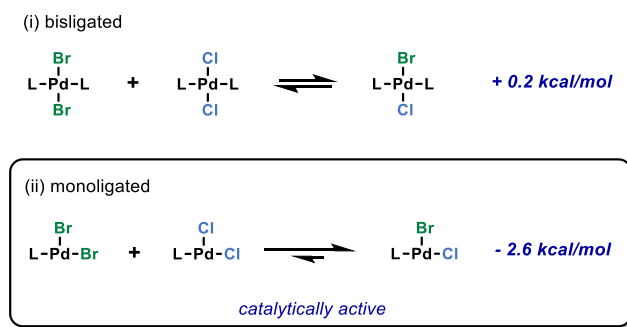
General Computational Details

DFT calculations were performed using Gaussian 09, Revision D.01. Geometry optimization was conducted in the gas-phase at the B3LYP/6-31G(d) level of theory employing LANL2DZ as an ECP for Pd. Frequencies were calculated at the same level of theory and used to verify the nature of all stationary points as either minima (no imaginary frequencies) or transition states (one imaginary frequency). Additionally, transition states were confirmed by following the intrinsic reaction coordinate (IRC) to their corresponding intermediates. Single point energies were calculated at the M06L/def2-TZVP level of theory employing the CPCM solvation model for toluene, unless noted otherwise (THF). All energies were corrected to 1m standard state (addition of 1.89 kcal/mol to every species). Images were created using the CYLview software.²⁶

Calculations employing PdBr₂(PhCN)₂ as a catalyst

Halide scrambling: While calculations suggest that there is no clear preference for either PdBr₂, PdCl₂ or the mixed PdBrCl in the bisligated form (0.2 kcal/mol in favor of PdBr₂ and PdCl₂) the monoligated form favors the formation of mixed LPdBrCl (L = PhCN; see Scheme S1). Since one ligand needs to dissociate in order for the PdX₂ species (X = Br or Cl) to coordinate to the substrate and react further, the monoligated form can be considered the catalytically active species.

Scheme S1. Halide scrambling on Pd(II) favors mixed LPdBrCl (L = PhCN) as the catalytically active species.^a



^aEnergies were calculated at CPCM (toluene) M06L/def2-TZVP//B3LYP/6-31G(d)(LANL2DZ).

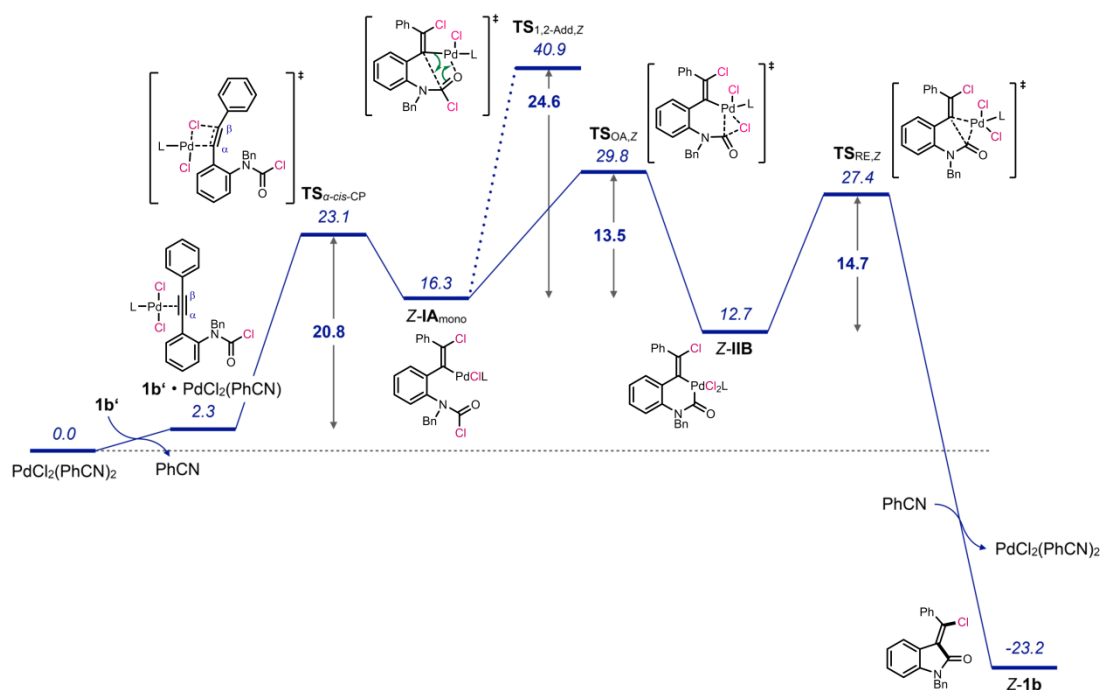
Note: Calculations were also performed in THF (since experiments with PdBr₂ were conducted in THF) and qualitatively agree with the results obtained in toluene.

In addition to the mixed monoligated LPdBrCl being more stable than LPdBr₂ it is also slightly more reactive (activation barrier towards chloro/bromopalladation is $\Delta\Delta G^\ddagger = 0.5$ kcal/mol in favor of LPdBrCl). The mixed LPdBrCl can transfer either Br or Cl *i.e.* bromopalladation versus chloropalladation can take place. However, calculations suggest chloride insertion to be slightly more favorable (by $\Delta\Delta G^\ddagger = 0.3$ kcal/mol).

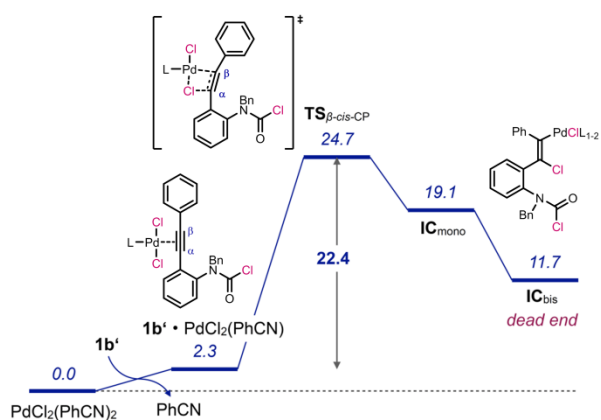
In summary, calculations suggest that bromide will be incorporated initially but since every turnover will liberate chloride from the substrate, more mixed species will be formed which is (i) slightly more reactive and (ii) preferentially transfers chloride over bromide. This is in line with the observation of minor amounts of bromide incorporation.

Full energetic pathways

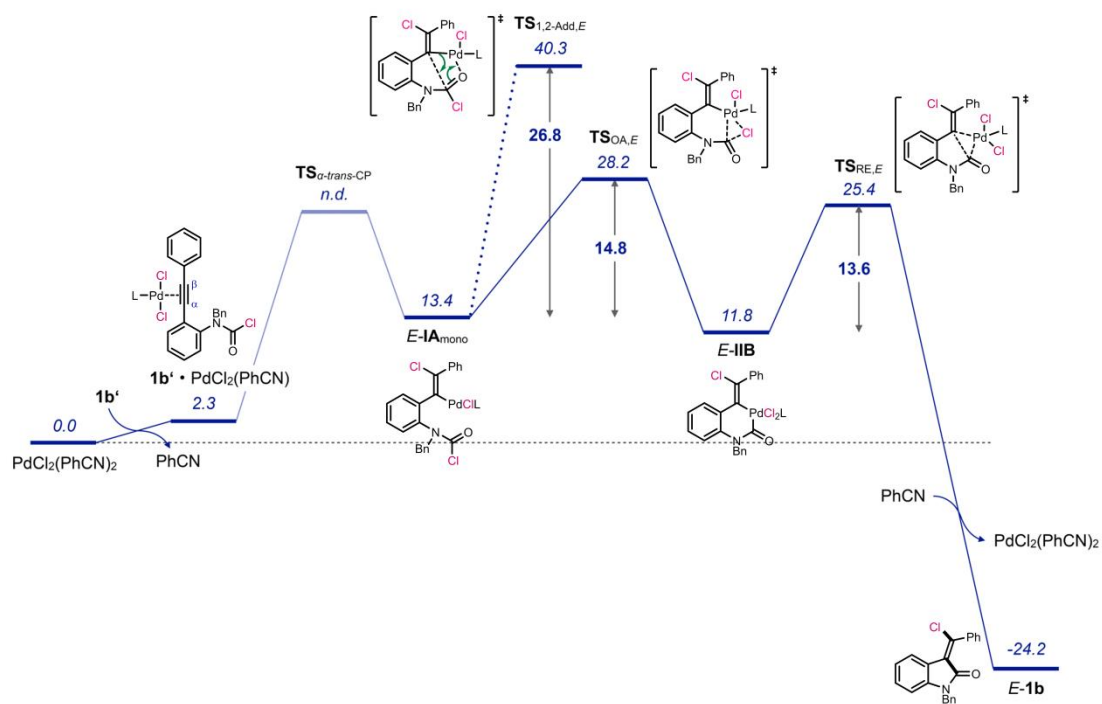
(i) α -*cis*-addition (leading to major product **Z-1b**)



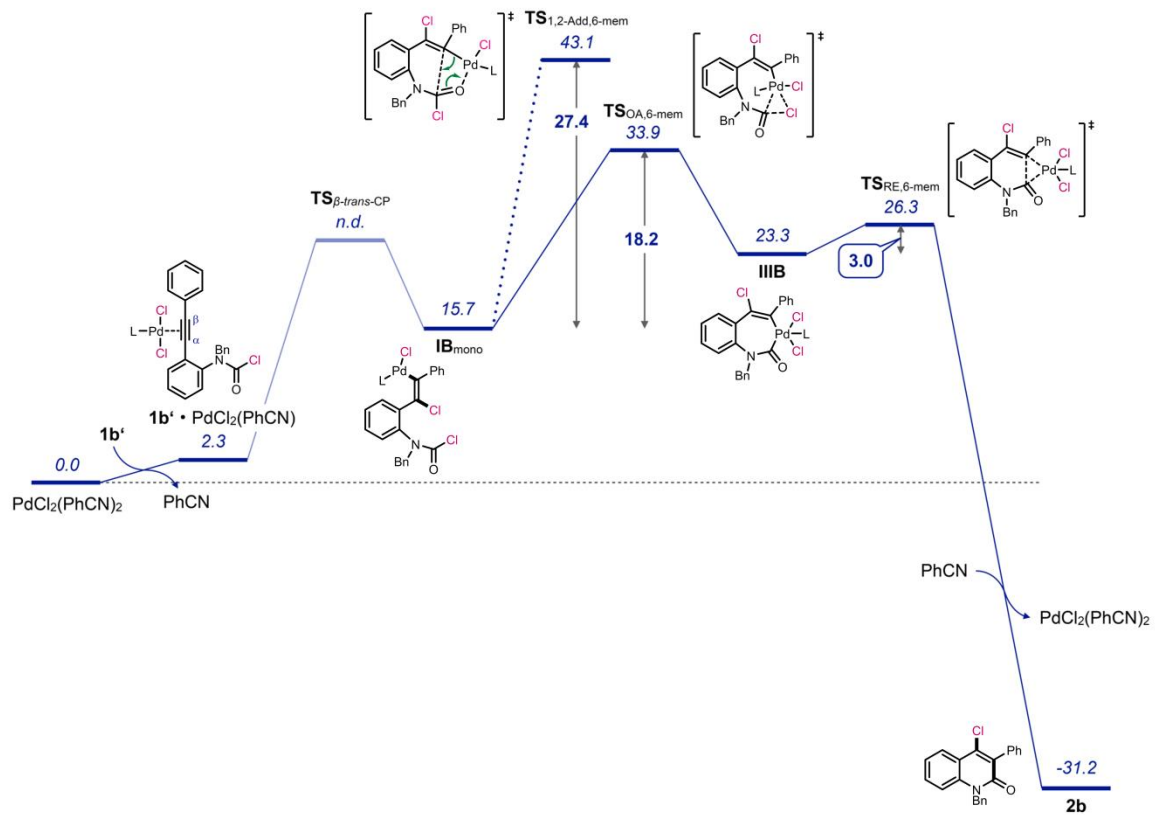
(ii) β -*cis*-addition (leading to unproductive intermediate **IC**, back reaction due to reversible chloropalladation and eventually to major product **Z-1b**)



(iii) α -*trans*-addition (leading to minor product *E*-**1b**)

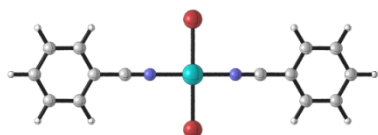


(iv) β -*trans*-addition (leading to side product **2b**)



XYZ Coordinates and Energies for Optimized Structures

PdBr₂(PhCN)₂



Pd	-0.00000100	-0.00001100	-0.00005600
N	-1.98942600	0.00007100	-0.00001200
C	-3.14634400	0.00009900	-0.00000200
C	-4.57325700	0.00007800	0.00005600
C	-5.26744300	-1.22321500	0.00016300
C	-5.26748600	1.22334500	-0.00000200
C	-6.65925700	-1.21361400	0.00021300
H	-4.71361600	-2.15635400	0.00020500
C	-6.65930000	1.21369500	0.00004900
H	-4.71369400	2.15650500	-0.00008600
C	-7.35322900	0.00002800	0.00015600
H	-7.20284400	-2.15341700	0.00029500
H	-7.20292100	2.15347800	0.00000400
H	-8.43950700	0.00000900	0.00019600
N	1.98942300	-0.00010600	-0.00016800
C	3.14634000	-0.00017500	-0.00019600
C	4.57325400	-0.00008600	-0.00001700
C	5.26753300	-1.22332500	0.00030300
C	5.26739000	1.22323500	-0.00019100
C	6.65934600	-1.21361800	0.00045100
H	4.71377700	-2.15650700	0.00042400
C	6.65920400	1.21369100	-0.00003900
H	4.71352600	2.15635200	-0.00044300
C	7.35322600	0.00007700	0.00028300
H	7.20300500	-2.15337900	0.00069700
H	7.20275400	2.15351600	-0.00017200
H	8.43950400	0.00014000	0.00040100
Br	0.00012200	2.55880600	-0.00030100
Br	-0.00011500	-2.55883200	0.00015700

Zero-point correction= 0.203962 (Hartree/Particle)

Thermal correction to Energy= 0.223944

Thermal correction to Enthalpy= 0.224888

Thermal correction to Gibbs Free Energy= 0.145886

Sum of electronic and zero-point Energies= -801.962115

Sum of electronic and thermal Energies= -801.942133

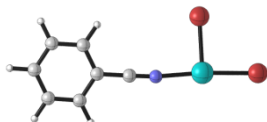
Sum of electronic and thermal Enthalpies= -801.941189

Sum of electronic and thermal Free Energies= -802.020191

E(RM06L; toluene) = -5925.39111397

E(RM06L; THF) = -5925.39872825

PdBr₂(PhCN)



Pd	-1.15840900	-0.57770600	-0.00000800
N	0.89996000	-0.62122900	0.00035300
C	2.05482000	-0.51377100	0.00055200
C	3.47244600	-0.34976300	0.00031700
C	4.01004800	0.95075100	0.00030000
C	4.31363400	-1.47701600	0.00012500
C	5.39221200	1.11344600	0.00010200
H	3.34534500	1.80840600	0.00044900
C	5.69330900	-1.29516000	-0.00007200
H	3.88369200	-2.47333100	0.00014000
C	6.23132100	-0.00471100	-0.00008500
H	5.81476200	2.11339800	0.00009300
H	6.34933000	-2.16011600	-0.00021400
H	7.30907700	0.12987300	-0.00024100

Br -3.59116000 -0.73887000 -0.00044500

Br -1.17232100 1.90921800 0.00016600

Zero-point correction= 0.102387 (Hartree/Particle)

Thermal correction to Energy= 0.114759

Thermal correction to Enthalpy= 0.115703

Thermal correction to Gibbs Free Energy= 0.056277

Sum of electronic and zero-point Energies= -477.532696

Sum of electronic and thermal Energies= -477.520323

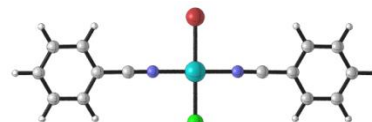
Sum of electronic and thermal Enthalpies= -477.519379

Sum of electronic and thermal Free Energies= -477.578806

E(RM06L; toluene) = -5600.78114477

E(RM06L; THF) = -5600.79040982

PdBrCl(PhCN)₂



Pd	0.00001100	-0.21887900	0.00003100
Cl	0.00012700	-2.59133200	0.00013100
N	-1.99183300	-0.21801400	0.00003700
C	-3.14845500	-0.23455800	0.00003600
C	-4.57545200	-0.25022100	-0.00003000
C	-5.25664700	-1.48072600	-0.00008500
C	-5.28275700	0.96550600	-0.00003000
C	-6.64850500	-1.48599000	-0.00014100
H	-4.69304300	-2.40797800	-0.00008200
C	-6.67440500	0.94108200	-0.00008600
H	-4.73901600	1.90455700	0.00001500
C	-7.35541700	-0.27985800	-0.00014300
H	-7.18202300	-2.43154900	-0.00018400
H	-7.22795300	1.87505700	-0.00008600
H	-8.44163400	-0.29144600	-0.00018700
N	1.99185400	-0.21782000	-0.00000400
C	3.14847800	-0.23425700	-0.00002400
C	4.57547300	-0.25006100	-0.00005500
C	5.25655200	-1.48063000	0.00002900
C	5.28289300	0.96559900	-0.00016700
C	6.64841000	-1.48602600	0.00000000
H	4.69286100	-2.40782900	0.00011500
C	6.67453900	0.94104400	-0.00019500
H	4.73924000	1.90470200	-0.00023000
C	7.35543600	-0.27996000	-0.00011200
H	7.18183900	-2.43163600	0.00006400
H	7.22817400	1.87496600	-0.00028200
H	8.44165100	-0.29165100	-0.00013500
Br	-0.00010700	2.33625800	0.00009000

Zero-point correction= 0.204286 (Hartree/Particle)

Thermal correction to Energy= 0.224039

Thermal correction to Enthalpy= 0.224983

Thermal correction to Gibbs Free Energy= 0.147324

Sum of electronic and zero-point Energies= -1248.979277

Sum of electronic and thermal Energies= -1248.959524

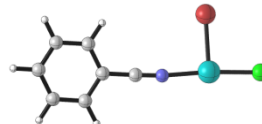
Sum of electronic and thermal Enthalpies= -1248.958580

Sum of electronic and thermal Free Energies= -1249.036240

E(RM06L; toluene) = -3811.53221058

E(RM06L; THF) = -3811.54027201

PdBrCl(PhCN)



Pd	-1.56721000	-0.74386100	0.00001700
N	0.47921100	-0.66987100	-0.00022000

C	1.62808500	-0.51157600	-0.00035100
C	3.03683300	-0.28474000	-0.00017800
C	3.51594300	1.03849300	-0.00011000
C	3.92738000	-1.37348500	-0.00009100
C	4.88947300	1.26255400	0.00003600
H	2.81369900	1.86568800	-0.00017900
C	5.29755500	-1.13030100	0.00005500
H	3.54231200	-2.38798900	-0.00014500
C	5.77753000	0.18285000	0.00012000
H	5.26707200	2.28032300	0.00008500
H	5.99145800	-1.96516600	0.00011800
H	6.84821900	0.36528700	0.00023500
Br	-1.69889200	1.74106500	-0.00005500
Cl	-3.80594900	-1.01714600	0.00033300

Zero-point correction= 0.102825 (Hartree/Particle)

Thermal correction to Energy= 0.114922

Thermal correction to Enthalpy= 0.115866

Thermal correction to Gibbs Free Energy= 0.057977

Sum of electronic and zero-point Energies= -924.552331

Sum of electronic and thermal Energies= -924.540234

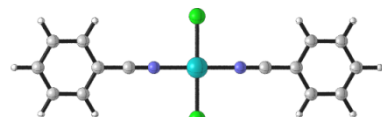
Sum of electronic and thermal Enthalpies= -924.539290

Sum of electronic and thermal Free Energies= -924.597179

E(RM06L; toluene) = -3486.92294824

E(RM06L; THF) = -3486.93266631

PdCl₂(PhCN)₂



Pd	-0.00001500	0.00034800	0.00010500
Cl	0.00028000	-2.36897100	0.00043900
N	1.99463100	0.00052400	-0.00012500
C	3.15118200	0.00030600	-0.00012100
C	4.57842100	0.00002100	-0.00013100
C	5.27249400	-1.22324900	-0.00020400
C	5.27317000	1.22289400	-0.00004000
C	6.66434300	-1.21411200	-0.00024000
H	4.71863600	-2.15635900	-0.00019300
C	6.66501400	1.21298000	-0.00007200
H	4.71984600	2.15632100	0.00001700
C	7.35875000	-0.00075700	-0.00018900
H	7.20756800	-2.15413100	-0.00034300
H	7.20876300	2.15269700	0.00001100
H	8.44502700	-0.00105500	-0.00021500
Cl	-0.00022000	2.36959200	-0.00004300
N	-1.99460800	0.00007400	0.00036000
C	-3.15116800	0.00014500	0.00019400
C	-4.57843400	-0.00010300	-0.00004200
C	-5.27257000	-1.22333200	-0.00048400
C	-5.27311700	1.22281400	0.00023000
C	-6.66443000	-1.21411500	-0.00059700
H	-4.71878700	-2.15648200	-0.00078500
C	-6.66495900	1.21297500	0.00010300
H	-4.71973900	2.15620700	0.00051000
C	-7.35876400	-0.00073100	-0.00028200
H	-7.20770500	-2.15410700	-0.00092100
H	-7.20867000	2.15271300	0.00030600
H	-8.44504000	-0.00096400	-0.00033500

Zero-point correction= 0.204610 (Hartree/Particle)

Thermal correction to Energy= 0.224139

Thermal correction to Enthalpy= 0.225083

Thermal correction to Gibbs Free Energy= 0.148738

Sum of electronic and zero-point Energies= -1695.996844

Sum of electronic and thermal Energies= -1695.977316

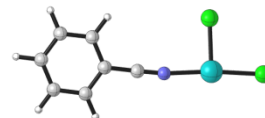
Sum of electronic and thermal Enthalpies= -1695.976372

Sum of electronic and thermal Free Energies= -1696.052716

E(RM06L; toluene) = -1697.67352896

E(RM06L; THF) = -1697.68202598

PdCl₂(PhCN)



Pd	1.83086700	-0.38046600	-0.00002800
Cl	4.08595900	-0.49646600	-0.00000100
Cl	1.75173100	1.91284300	0.00010900
N	-0.22217100	-0.46273200	-0.00005100
C	-1.37705000	-0.35926700	-0.00003700
C	-2.79529800	-0.20222400	-0.00001900
C	-3.33869600	1.09591200	-0.00010800
C	-3.63109400	-1.33350500	0.00009000
C	-4.72160800	1.25207000	-0.00009000
H	-2.67794900	1.95660500	-0.00018800
C	-5.01155900	-1.15801100	0.00010700
H	-3.19662400	-2.32785600	0.00016000
C	-5.55546600	0.12998700	0.00001700
H	-5.14879600	2.25003300	-0.00015800
H	-5.66359100	-2.02596600	0.00019000
H	-6.63382900	0.25957500	0.00003100

Zero-point correction= 0.103109 (Hartree/Particle)

Thermal correction to Energy= 0.115024

Thermal correction to Enthalpy= 0.115968

Thermal correction to Gibbs Free Energy= 0.059464

Sum of electronic and zero-point Energies= -1371.567692

Sum of electronic and thermal Energies= -1371.555777

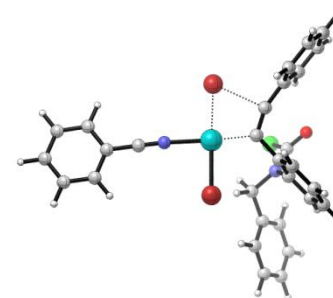
Sum of electronic and thermal Enthalpies= -1371.554833

Sum of electronic and thermal Free Energies= -1371.611337

E(RM06L; toluene) = -1373.06038212

E(RM06L; THF) = -1373.07094865

TS_{α-cis-BP}(PdBr₂(PhCN))



C	-0.85590300	-1.04309400	0.68378500
C	-1.16431700	-2.23943500	0.31303200
C	-1.86985400	-0.18019100	1.35336200
C	-2.58421000	0.79876700	0.63896500
C	-2.15170300	-0.36462000	2.71342300
C	-3.56012300	1.56379700	1.27937400
C	-3.12066500	0.40722800	3.35099900
H	-1.59259300	-1.11086000	3.26849900
C	-3.82974800	1.37103100	2.63412400
H	-4.10473300	2.30589700	0.70612100
H	-3.32088600	0.25216500	4.40738600
H	-4.59047800	1.97217100	3.12338800
N	-2.29356300	1.05416300	-0.75544500
C	-2.91341700	0.24919400	-1.65087400
O	-3.65907600	-0.66611600	-1.41265400
Cl	-2.54076000	0.62696800	-3.40608700

C	-1.89670800	-3.44852700	0.20982600
C	-1.78583200	-4.41985200	1.23256900
C	-2.76666900	-3.67242900	-0.88162200
C	-2.53538100	-5.58664300	1.16411800
C	-3.51799800	-4.84098000	-0.93117800
C	-3.40015200	-5.79705500	0.08312000
H	-2.45067400	-6.33309400	1.94826400
H	-4.19784900	-5.00858700	-1.76103600
H	-1.10456700	-4.24193600	2.05836800
H	-2.86243100	-2.91192900	-1.64701800
H	-3.98605300	-6.71093400	0.03312600
Pd	1.09740800	-0.58659900	0.36070800
N	3.13865900	-0.23352600	-0.00485700
C	4.25917500	0.02196500	-0.15059100
C	5.63766100	0.36244900	-0.31053400
C	6.15557400	1.47194700	0.38162600
C	6.46060400	-0.40702000	-1.15150200
C	7.49842100	1.80451900	0.22646100
H	5.50476800	2.05361500	1.02641000
C	7.80117500	-0.06059000	-1.29552300
H	6.04542700	-1.26002100	-1.67840300
C	8.31922500	1.04149400	-0.60909600
H	7.90466700	2.65974700	0.75788900
H	8.44212400	-0.65056800	-1.94360200
H	9.36620100	1.30652900	-0.72585000
C	-1.38589500	2.19215100	-1.04984300
H	-0.53935100	2.09664700	-0.36598300
H	-1.01017900	2.05676600	-2.06375400
C	-2.03012000	3.55685300	-0.88589400
C	-1.57854700	4.42033300	0.11950500
C	-3.06168600	3.98362000	-1.73557600
C	-2.14444300	5.68846200	0.27394800
H	-0.78265800	4.09271700	0.78374400
C	-3.63116800	5.24700000	-1.57784300
H	-3.41666600	3.32539300	-2.52422400
C	-3.17289800	6.10368500	-0.57248200
H	-1.78322300	6.34780500	1.05884100
H	-4.42865800	5.56620900	-2.24390000
H	-3.61557900	7.08910900	-0.45258500
Br	1.04222000	-2.80195600	-0.98020500
Br	1.11624000	1.47819500	1.86690400

Zero-point correction= 0.421936 (Hartree/Particle)

Thermal correction to Energy= 0.456447

Thermal correction to Enthalpy= 0.457391

Thermal correction to Gibbs Free Energy= 0.345133

Sum of electronic and zero-point Energies= -1915.317336

Sum of electronic and thermal Energies= -1915.282825

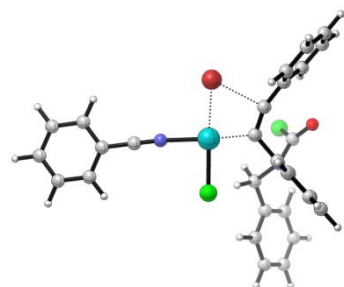
Sum of electronic and thermal Enthalpies= -1915.281881

Sum of electronic and thermal Free Energies= -1915.394139

E(RM06L; toluene) = -7039.14016115

E(RM06L; THF) = -7039.14734207

TS_{α-cis-BP}(PdBrCl(PhCN))



C	-0.82440100	-0.99976400	0.73471500
C	-1.13611000	-2.18415700	0.33055200

C	-1.83028900	-0.14005200	1.41859700
C	-2.51677500	0.87613700	0.72958600
C	-2.12936300	-0.36212800	2.76922500
C	-3.48404800	1.63933100	1.38496500
C	-3.08896600	0.40856400	3.42239000
H	-1.59162100	-1.13786200	3.30477100
C	-3.77161600	1.40864100	2.73011200
H	-4.00744300	2.41066400	0.83083600
H	-3.30307200	0.22369000	4.47126000
H	-4.52537700	2.00895500	3.23106900
N	-2.20723800	1.17129700	-0.65282900
C	-2.83867500	0.41274100	-1.57939800
O	-3.60640000	-0.49357700	-1.37882700
Cl	-2.44641600	0.84400800	-3.31854300
C	-1.88362200	-3.37712800	0.16593100
C	-1.79011900	-4.40088800	1.13810000
C	-2.75305000	-3.53250600	-0.93773700
C	-2.55556800	-5.55172600	1.00798300
C	-3.52106600	-4.68625100	-1.04871000
C	-3.41993800	-5.69439000	-0.08464500
H	-2.48396700	-6.33847700	1.75307900
H	-4.20059600	-4.80120300	-1.88775200
H	-1.10869500	-4.27537100	1.97332600
H	-2.83676500	-2.73236200	-1.66317100
H	-4.01846300	-6.59611900	-0.18268700
Pd	1.13260700	-0.53942500	0.46342900
Cl	1.05730600	1.39668800	1.83087600
N	3.18792200	-0.16777400	0.15195000
C	4.30672800	0.10822000	0.03339900
C	5.68388500	0.46605000	-0.10012600
C	6.17331000	1.59121600	0.58722800
C	6.53429700	-0.30391700	-0.91294300
C	7.51487300	1.93896000	0.45581100
H	5.50225700	2.17368700	1.21010600
C	7.87318500	0.05765100	-1.03355500
H	6.14111600	-1.16911900	-1.43681200
C	8.36278600	1.17541300	-0.35167900
H	7.89892500	2.80650700	0.98376800
H	8.53497000	-0.53276500	-1.65993000
H	9.40856500	1.45233500	-0.45007600
C	-1.26466800	2.29292800	-0.90015200
H	-0.42439300	2.14444600	-0.21837000
H	-0.89188100	2.18741900	-1.91857600
C	-1.86970900	3.66753000	-0.68176600
C	-1.40716700	4.46812400	0.36974900
C	-2.87505700	4.16551700	-1.52399400
C	-1.93680900	5.74438000	0.57679400
H	-0.63164200	4.08389800	1.02772200
C	-3.40837400	5.43710600	-1.31406400
H	-3.23782000	3.55612000	-2.34768900
C	-2.93944400	6.23070100	-0.26285600
H	-1.56776000	6.35464400	1.39698900
H	-4.18573000	5.81209400	-1.97487300
H	-3.35381000	7.22264000	-0.10219700
Br	1.11883300	-2.75274200	-0.87349900

Zero-point correction= 0.422334 (Hartree/Particle)

Thermal correction to Energy= 0.456581

Thermal correction to Enthalpy= 0.457525

Thermal correction to Gibbs Free Energy= 0.346493

Sum of electronic and zero-point Energies= -2362.336559

Sum of electronic and thermal Energies= -2362.302312

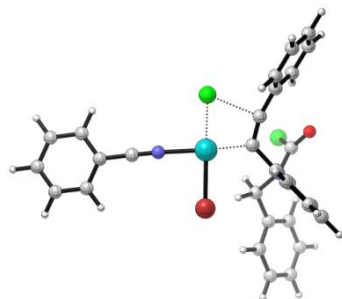
Sum of electronic and thermal Enthalpies= -2362.301368

Sum of electronic and thermal Free Energies= -2362.412400

E(RM06L; toluene) = -4925.28222348

E(RM06L; THF) = -4925.28966398

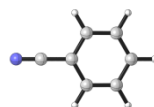
TS_{a-cis-CP}(PdBrCl(PhCN))



C	-0.81824300	1.18788100	-0.66499800
C	-1.06647800	2.38368900	-0.26991900
C	-1.83936300	0.35107900	-1.35012600
C	-2.57812500	-0.61724900	-0.64696800
C	-2.10442300	0.54802400	-2.71156700
C	-3.56307100	-1.36012100	-1.29945500
C	-3.08241000	-0.20215600	-3.36125300
H	-1.52586900	1.28589400	-3.25776900
C	-3.81641000	1.15556900	-2.65560300
H	-4.12696300	-2.09424600	-0.73467000
H	-3.27002300	-0.03824500	-4.41860200
H	-4.58395100	-1.73959500	-3.15483200
N	-2.30326800	-0.88419200	0.74819300
C	-2.89298700	-0.05521600	1.64191200
O	-3.59891000	0.89081000	1.40133500
Cl	-2.54798100	-0.45275300	3.39788800
C	-1.65847200	3.64907700	-0.06819000
C	-1.45591200	4.67656100	-1.02029100
C	-2.48626800	3.88078900	1.05488400
C	-2.07156500	5.90869600	-0.84907800
C	-3.10520900	5.11607600	1.20589600
C	-2.89508500	6.12743900	0.26253300
H	-1.91540400	6.69998300	-1.57610300
H	-3.75218300	5.29363700	2.05954600
H	-0.80836400	4.48831300	-1.87043000
H	-2.65370900	3.07807900	1.76284000
H	-3.37709000	7.09280300	0.39197900
Pd	1.13813800	0.70636100	-0.32695700
N	3.16554600	0.32506200	0.05559900
C	4.28279600	0.07135200	0.22589200
C	5.65844600	-0.26408600	0.41797800
C	6.19901600	-1.36839200	-0.26497900
C	6.45639700	0.50636000	1.28186000
C	7.53926400	-1.69491300	-0.07773800
H	5.56754900	-1.95108600	-0.92780300
C	7.79473600	0.16605000	1.45783800
H	6.02371100	1.35525200	1.80124600
C	8.33525900	-0.93090100	0.78059600
H	7.96286000	-2.54617800	-0.60194700
H	8.41639400	0.75683600	2.12373800
H	9.38035000	-1.19116900	0.92233700
C	-1.42166300	-2.04229200	1.04326200
H	-0.56842900	-1.96152100	0.36549900
H	-1.04976500	-1.91935800	2.06015900
C	-2.09352400	-3.39214100	0.86953100
C	-1.64699400	-4.26536800	-0.12958200
C	-3.14567100	-3.79607500	1.70497400
C	-2.23803300	-5.52101700	-0.29174400
H	-0.83514300	-3.95528500	-0.78286000
C	-3.74021800	-5.04682400	1.53943800
H	-3.49706000	-3.12981300	2.48851900
C	-3.28677000	-5.91356300	0.54048900
H	-1.88047700	-6.18825800	-1.07161300
H	-4.55358100	-5.34847400	2.19439000

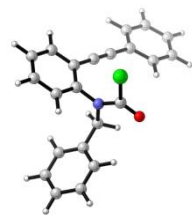
H -3.74902300 -6.88918700 0.41450900
 Br 1.14000000 -1.34821600 -1.84399300
 Cl 1.12109900 2.72927300 0.97628200
 Zero-point correction= 0.422310 (Hartree/Particle)
 Thermal correction to Energy= 0.456646
 Thermal correction to Enthalpy= 0.457590
 Thermal correction to Gibbs Free Energy= 0.346265
 Sum of electronic and zero-point Energies= -2362.336273
 Sum of electronic and thermal Energies= -2362.301937
 Sum of electronic and thermal Enthalpies= -2362.300993
 Sum of electronic and thermal Free Energies= -2362.412318
 E(RM06L; toluene) = -4925.28246777

PhCN



C	-2.04529100	0.00002900	-0.00001400
N	-3.20860700	-0.00001400	0.00001800
C	-0.61057000	0.00000900	-0.00001300
C	0.09137800	1.21765500	-0.00000100
C	0.09134500	-1.21763700	-0.00000900
C	1.48420100	1.21113500	-0.00000100
H	-0.45907000	2.15293500	0.00000100
C	1.48418100	-1.21114800	0.00000600
H	-0.45910800	-2.15291600	-0.00000600
C	2.18118100	-0.00002000	0.00000500
H	2.02618400	2.15231100	0.00000300
H	2.02612500	-2.15234600	0.00001400
H	3.26756600	-0.00002200	0.00001400
Zero-point correction= 0.099473 (Hartree/Particle)			
Thermal correction to Energy= 0.105570			
Thermal correction to Enthalpy= 0.106515			
Thermal correction to Gibbs Free Energy= 0.069198			
Sum of electronic and zero-point Energies= -324.385247			
Sum of electronic and thermal Energies= -324.379149			
Sum of electronic and thermal Enthalpies= -324.378205			
Sum of electronic and thermal Free Energies= -324.415521			
E(RM06L) = -324.567008780			

1b'



C	1.47534400	1.15975200	-0.48373100
C	2.52139000	0.53873700	-0.49629600
C	0.24540800	1.87413500	-0.46058300
C	-0.91050400	1.30281800	0.12358800
C	0.14829100	3.16757300	-1.01008400
C	-2.11606400	2.00233000	0.13736900
C	-1.05658600	3.86390200	-0.98104700
H	1.03293600	3.61372500	-1.45305300
C	-2.19126200	3.28477500	-0.40752900
H	-2.98779300	1.53411300	0.58242700
H	-1.11045600	4.86152100	-1.40763900
H	-3.13245200	3.82609300	-0.38631600
N	-0.85209600	-0.03691500	0.63110700
C	-1.02762800	-1.14722300	-0.34309000
H	-0.48637500	-0.86260300	-1.24927300
H	-0.53477400	-2.01952800	0.08980700

C	-2.47930800	-1.44609700	-0.65567500
C	-3.03699100	-1.07388200	-1.88412900
C	-3.28645200	-2.10057800	0.28759000
C	-4.37664300	-1.34803300	-2.17042400
H	-2.41856700	-0.56889300	-2.62275700
C	-4.62475600	-2.37082100	0.00449200
H	-2.85743900	-2.39692400	1.24103700
C	-5.17322800	-1.99564100	-1.22559400
H	-4.79520200	-1.05569500	-3.12983900
H	-5.23935000	-2.88080300	0.74159000
H	-6.21533000	-2.21107500	-1.44623600
C	-0.62659300	-0.37760900	1.92670300
O	-0.58335200	-1.49276400	2.37999500
Cl	-0.37156200	1.05062400	3.01923200
C	3.74033400	-0.19891100	-0.49295000
C	3.85475300	-1.37788900	0.27209100
C	4.84689500	0.23579600	-1.25007900
C	5.04574000	-2.09886700	0.27482000
C	6.03343400	-0.49258600	-1.24070300
C	6.13721200	-1.66054700	-0.48019900
H	5.12321200	-3.00488000	0.86944600
H	6.88024100	-0.14814600	-1.82801600
H	3.00587800	-1.71165300	0.86098900
H	4.76179900	1.14380000	-1.83912200
H	7.06500300	-2.22594800	-0.47494500

Zero-point correction= 0.319009 (Hartree/Particle)

Thermal correction to Energy= 0.340348

Thermal correction to Enthalpy= 0.341292

Thermal correction to Gibbs Free Energy= 0.262797

Sum of electronic and zero-point Energies= -1437.773120

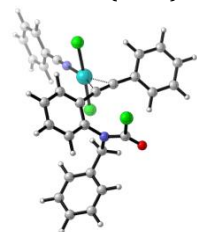
Sum of electronic and thermal Energies= -1437.751781

Sum of electronic and thermal Enthalpies= -1437.750837

Sum of electronic and thermal Free Energies= -1437.829332

E(RM06L) = -1438.34989257

1b' • PdCl₂(PhCN)



C	0.60315800	0.83885300	0.82479200
C	0.28769200	1.82977900	0.14318000
C	1.34138000	-0.08165900	1.64389000
C	2.63216400	-0.50504600	1.24761800
C	0.80902300	-0.54857600	2.85911700
C	3.35256900	-1.38633100	2.05273000
C	1.54332200	-1.42158200	3.65699100
H	-0.17564100	-0.20632700	3.16063800
C	2.81256400	-1.84337500	3.25571400
H	4.33804800	-1.70270700	1.72869000
H	1.12225600	-1.77159000	4.59489600
H	3.38494600	-2.52653200	3.87640100
N	3.17518000	-0.08494500	-0.01048200
C	2.91689300	-0.95177900	-1.19716400
H	1.86087700	-1.23039600	-1.17191000
H	3.07520400	-0.32012800	-2.07272400
C	3.80924100	-2.17427100	-1.24504300
C	3.27423900	-3.45218400	-1.04672900
C	5.18399300	-2.04363400	-1.49580400
C	4.09472700	-4.58218800	-1.09531700
H	2.20878100	-3.56175200	-0.85903600

C	6.00470500	-3.17005100	-1.53842800
H	5.60433300	-1.05519800	-1.66368200
C	5.46155100	-4.44294400	-1.33815300
H	3.66490000	-5.56868000	-0.94260400
H	7.06739500	-3.05649300	-1.73612900
H	6.10153100	-5.32055800	-1.37615600
C	3.90933000	1.04022200	-0.20299200
O	4.37277200	1.43233100	-1.24423000
Cl	4.16983900	2.00750500	1.31508100
C	0.15911100	3.04720400	-0.59486400
C	-0.84468500	3.98255800	-0.27073400
C	1.07103400	3.32237400	-1.63431200
C	-0.92853600	5.17467700	-0.98279000
C	0.97816400	4.52408500	-2.33050700
C	-0.02091400	5.44764300	-2.01112900
H	-1.70263300	5.89477500	-0.73356900
H	1.68679400	4.73804000	-3.12518200
H	-1.53846500	3.75505600	0.53235800
H	1.84984400	2.60623900	-1.87434000
H	-0.09136400	6.38129800	-2.56252900
Pd	-1.48004800	0.42036700	0.26801800
Cl	-0.77892000	-0.71832000	-1.68562200
N	-3.36283100	-0.39043300	0.01516100
C	-4.41148000	-0.85617800	-0.13598100
C	-5.70447000	-1.43139000	-0.32532400
C	-5.93941100	-2.25772700	-1.43894000
C	-6.72688100	-1.16511200	0.60299800
C	-7.20248300	-2.81485900	-1.61664800
H	-5.13802700	-2.45118100	-2.14452900
C	-7.98386700	-1.73072600	0.40971400
H	-6.52678100	-0.52476100	1.45589500
C	-8.22133900	-2.55271200	-0.69594200
H	-7.39218600	-3.45366300	-2.47373600
H	-8.77859900	-1.53016000	1.12164400
H	-9.20473800	-2.99076800	-0.84075900
Cl	-2.24783700	1.51418000	2.23518700

Zero-point correction= 0.423155 (Hartree/Particle)

Thermal correction to Energy= 0.458214

Thermal correction to Enthalpy= 0.459159

Thermal correction to Gibbs Free Energy= 0.345706

Sum of electronic and zero-point Energies= -2809.381042

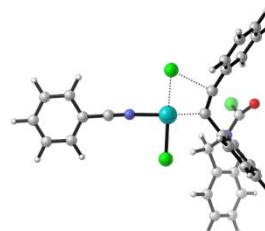
Sum of electronic and thermal Energies= -2809.345983

Sum of electronic and thermal Enthalpies= -2809.345039

Sum of electronic and thermal Free Energies= -2809.458491

E(RM06L) = -2811.45616716

TS_{α-cis-CP}

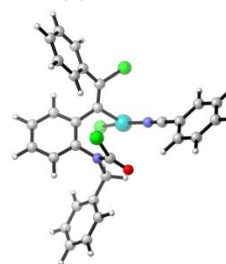


C	0.77964700	1.14915100	0.72331000
C	1.03094600	2.33350700	0.29806000
C	1.79249800	0.31406100	1.42106900
C	2.50503300	-0.68965500	0.74117000
C	2.07294700	0.54565500	2.77384300
C	3.48112200	-1.43192200	1.40738500
C	3.04131200	-0.20463500	3.43786400
H	1.51448800	1.31165500	3.30208100
C	3.75049700	-1.19251600	2.75475600
H	4.02525700	-2.19370300	0.86011200

H	3.24136000	-0.01326400	4.48832700
H	4.51093300	-1.77661600	3.26468400
N	2.21318500	-0.99309800	-0.64303300
C	2.81396500	-0.20524300	-1.56535800
O	3.54061400	0.73352600	-1.35945200
Cl	2.45038900	-0.65084800	-3.30657400
C	1.63450500	3.58249700	0.03734100
C	1.44063200	4.65787600	0.93707100
C	2.46717100	3.74995800	-1.09351100
C	2.06899200	5.87355600	0.70664400
C	3.09963200	4.97004900	-1.30340500
C	2.89762400	6.02880300	-0.41212200
H	1.91909900	6.70150900	1.39303600
H	3.75053100	5.09826400	-2.16289900
H	0.78840100	4.51875000	1.79301400
H	2.62936400	2.91145100	-1.76012700
H	3.38975200	6.98169700	-0.58768400
Pd	-1.18063300	0.66120000	0.43636400
Cl	-1.08496100	-1.27310300	1.80246300
N	-3.22141500	0.25960600	0.10723100
C	-4.33766900	-0.01444400	-0.03548700
C	-5.71270700	-0.36740100	-0.20040200
C	-6.22300500	-1.49021600	0.47540400
C	-6.54054600	0.40615000	-1.03290500
C	-7.56266200	-1.83211900	0.31281400
H	-5.56937200	-2.07564500	1.11383400
C	-7.87785200	0.05043000	-1.18462700
H	-6.13119200	1.26944200	-1.54744400
C	-8.38818000	-1.06501000	-0.51426000
H	-7.96271600	-2.69787600	0.83176400
H	-8.52222700	0.64365200	-1.82632800
H	-9.43259900	-1.33734600	-0.63695500
Cl	-1.21590600	2.69578700	-0.84043300
C	1.30054400	-2.13812400	-0.89539400
H	0.45290300	-2.01098200	-0.21806200
H	0.93022300	-2.04165800	-1.91563200
C	1.93915600	-3.49696500	-0.67507700
C	1.48288400	-4.31568100	0.36506300
C	2.96939300	-3.96314800	-1.50532100
C	2.04300800	-5.57878300	0.57264800
H	0.68803800	-3.95613600	1.01387700
C	3.53315000	-5.22140200	-1.29473600
H	3.32774900	-3.33931100	-2.32011100
C	3.07020200	-6.03340700	-0.25497000
H	1.67846200	-6.20344000	1.38396100
H	4.32970700	-5.57174800	-1.94613200
H	3.50835500	-7.01498100	-0.09379900

Zero-point correction= 0.422700 (Hartree/Particle)
 Thermal correction to Energy= 0.456775
 Thermal correction to Enthalpy= 0.457719
 Thermal correction to Gibbs Free Energy= 0.347566
 Sum of electronic and zero-point Energies= -2809.355763
 Sum of electronic and thermal Energies= -2809.321688
 Sum of electronic and thermal Enthalpies= -2809.320744
 Sum of electronic and thermal Free Energies= -2809.430897
 E(RM06L) = -2811.45616716

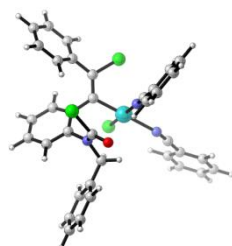
Z-IA_{mono}



C	0.52710900	1.81126900	-0.15160000
C	1.51470700	1.00397800	-0.76650200
C	0.67204700	3.20948800	-0.27285800
C	2.54900900	1.58251800	-1.50773900
C	1.70529400	3.78040200	-1.00734100
H	-0.04995200	3.84520000	0.22601300
C	2.64361600	2.96587400	-1.64196100
H	3.28132100	0.93181500	-1.97280800
H	1.77820300	4.86188300	-1.07851100
H	3.45291900	3.39978700	-2.22179300
N	1.56509400	-0.42293400	-0.56506300
C	2.47025300	-0.91920300	0.51902500
H	2.34885500	-0.23167200	1.35881500
H	2.08574700	-1.89657900	0.81543700
C	3.92806000	-1.00938000	0.11529700
C	4.85312100	-0.08660600	0.61980800
C	4.37733700	-2.02065200	-0.74843000
C	6.20211500	-0.16638100	0.26642500
H	4.51427500	0.69540500	1.29499500
C	5.72327300	-2.09619700	-1.10618900
H	3.66875700	-2.74818000	-1.13406300
C	6.63906300	-1.16946200	-0.59967900
H	6.90874600	0.55460500	0.66864500
H	6.05992300	-2.88459300	-1.77432100
H	7.68835200	-1.23359200	-0.87540900
C	1.00323500	-1.35589700	-1.36097600
O	1.07206500	-2.55773900	-1.23624600
Cl	0.05172500	-0.67811300	-2.75379800
C	-0.63713000	1.30603000	0.60457900
C	-1.90405700	1.72367300	0.43135700
Pd	-0.26099400	0.08369000	2.13357000
Cl	0.89148900	1.68040100	3.33741600
N	-1.20044100	-1.53417700	1.24511700
C	-1.72391400	-2.43832600	0.73948500
C	-2.38305700	-3.55039000	0.13211700
C	-3.65521400	-3.93452700	0.59582300
C	-1.75594300	-4.24399500	-0.91959100
C	-4.29605800	-5.01793400	0.00328500
H	-4.12398700	-3.38449500	1.40540100
C	-2.41512400	-5.32496700	-1.49950400
H	-0.77686600	-3.92554200	-1.26328600
C	-3.67762200	-5.71178000	-1.04152400
H	-5.27774900	-5.32046200	0.35485500
H	-1.94090900	-5.86599600	-2.31272600
H	-4.18336400	-6.55650000	-1.50078400
C	-2.43157200	2.59484300	-0.65337700
C	-3.24177000	3.70157900	-0.34416800
C	-2.13667900	2.32778800	-1.99915800
C	-3.72645300	4.52828000	-1.35571600
H	-3.48723900	3.91215200	0.69201300
C	-2.62733700	3.15572900	-3.00867000
H	-1.52804000	1.46713800	-2.25044300
C	-3.42130500	4.25921600	-2.69233300
H	-4.34543300	5.38363300	-1.09841900
H	-2.39320000	2.93063600	-4.04574700

H -3.80474500 4.90163800 -3.48046900
 Cl -3.15786200 1.23570500 1.59747900
 Zero-point correction= 0.424609 (Hartree/Particle)
 Thermal correction to Energy= 0.458457
 Thermal correction to Enthalpy= 0.459401
 Thermal correction to Gibbs Free Energy= 0.352173
 Sum of electronic and zero-point Energies= -2809.366466
 Sum of electronic and thermal Energies= -2809.332618
 Sum of electronic and thermal Enthalpies= -2809.331674
 Sum of electronic and thermal Free Energies= -2809.438902
 E(RM06L) = -2811.44026221

Z-IA_{bis}

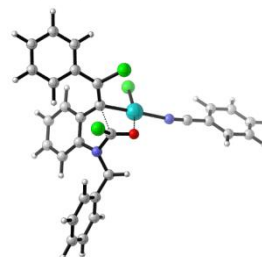


C	1.30854700	1.29116700	-1.39320700
C	1.24709000	2.15955800	-0.27771600
C	1.67655400	1.86790900	-2.62687800
C	1.59229700	3.50986200	-0.39564500
C	2.01326000	3.21201300	-2.74375100
H	1.68882300	1.23212000	-3.50423200
C	1.98705600	4.04013000	-1.62098900
H	1.54236600	4.13765900	0.48755000
H	2.29239000	3.61181400	-3.71476800
H	2.25376500	5.09024500	-1.69798400
N	0.72670900	1.72409200	0.99603800
C	-0.72610300	1.97065800	1.24982400
H	-1.23990400	1.76015000	0.30976600
H	-1.04200300	1.23033900	1.98664400
C	-1.04070200	3.37602700	1.72223100
C	-1.64081500	4.29175800	0.84842200
C	-0.75490000	3.77788300	3.03648800
C	-1.94724900	5.58619300	1.27447500
H	-1.86837200	3.98669500	-0.17009100
C	-1.05593900	5.07224500	3.46027500
H	-0.29762900	3.07077500	3.72266200
C	-1.65316500	5.97970200	2.58068700
H	-2.41448700	6.28481700	0.58538400
H	-0.83085700	5.37135200	4.48077000
H	-1.89103400	6.98643200	2.91431900
C	1.45099700	1.25607300	2.03122300
O	1.04057900	0.93084700	3.12333700
Cl	3.23401700	1.11821400	1.69703500
C	0.99412600	-0.15722900	-1.36229800
C	1.79902600	-1.08323000	-1.91457200
Pd	-0.79312000	-0.74187700	-0.65458500
C	3.16899800	-0.91717700	-2.46972000
C	3.49420200	-1.42554300	-3.73976100
C	4.16586600	-0.25596700	-1.73519500
C	4.77381800	-1.25823300	-4.26556500
H	2.73685700	-1.95048000	-4.31362500
C	5.44676800	-0.09330000	-2.26296400
H	3.93297400	0.12537200	-0.74780400
C	5.75637400	-0.59097600	-3.52969300
H	5.00396200	-1.65165600	-5.25234200
H	6.20578100	0.41808500	-1.67661300
H	6.75561600	-0.46582100	-3.93848900
Cl	1.21611900	-2.77225500	-2.05046200
N	-2.83145900	-1.36256500	-0.04953000

C	-3.97166800	-1.44985500	-0.24426000
C	-5.35901800	-1.49255000	-0.58503800
C	-5.76595400	-0.84155600	-1.76431600
C	-6.28914900	-2.16209200	0.22714800
C	-7.11138400	-0.86787900	-2.12184800
H	-5.02407500	-0.33239600	-2.37239300
C	-7.63041800	-2.17770600	-0.14581100
H	-5.95762600	-2.65895900	1.13330200
C	-8.04062400	-1.53285600	-1.31652800
H	-7.43462200	-0.36884700	-3.03041500
H	-8.35620500	-2.69288000	0.47625300
H	-9.08875200	-1.54914200	-1.60187500
N	0.11649000	-1.69099600	0.95719500
C	0.63931000	-2.22410600	1.84397100
C	1.27918900	-2.90287500	2.92767900
C	1.76429800	-2.16761200	4.02442700
C	1.41721500	-4.30211300	2.87772200
C	2.38540200	-2.84775600	5.06931500
H	1.65306400	-1.08791600	4.03686700
C	2.04051400	-4.96280700	3.93196100
H	1.04202000	-4.85067200	2.01979200
C	2.52302800	-4.23773000	5.02580300
H	2.76517600	-2.28870400	5.91923500
H	2.15211000	-6.04243900	3.89955600
H	3.01000000	-4.75871700	5.84547800
Cl	-1.81094300	0.40336000	-2.45210400

Zero-point correction= 0.525328 (Hartree/Particle)
 Thermal correction to Energy= 0.567101
 Thermal correction to Enthalpy= 0.568045
 Thermal correction to Gibbs Free Energy= 0.439805
 Sum of electronic and zero-point Energies= -3133.773581
 Sum of electronic and thermal Energies= -3133.731809
 Sum of electronic and thermal Enthalpies= -3133.730865
 Sum of electronic and thermal Free Energies= -3133.859105
 E(RM06L) = -3136.03081834

TS_{1,2-Add,Z}

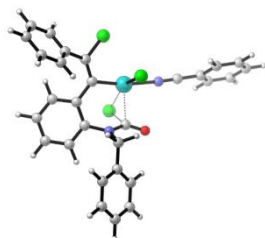


C	0.92163300	1.02958400	0.04120200
C	1.25195200	2.20087100	-0.59814200
C	1.64687900	0.46357000	1.18040600
C	1.89526000	-0.92041500	1.05603100
C	2.03663100	1.13120800	2.34930300
C	2.54172700	-1.62686400	2.07631400
C	2.67909700	0.43070600	3.36635200
H	1.81304400	2.18680600	2.45835600
C	2.93079800	-0.94015300	3.22557300
H	2.74050300	-2.68726200	1.97010000
H	2.97440600	0.94726100	4.27485700
H	3.43318800	-1.48236200	4.02204400
N	1.37750200	-1.51097300	-0.10841500
C	0.72454000	-2.83099600	-0.02464800
H	0.16448200	-2.89894800	0.91680700
H	-0.00807300	-2.86510700	-0.83576600
C	1.68842400	-3.99985300	-0.14243000
C	1.49340200	-5.14021300	0.64647900
C	2.74138800	-3.98618800	-1.06675200

C	2.32684600	-6.25260100	0.51009700
H	0.68359800	-5.15814400	1.37307500
C	3.57767000	-5.09485800	-1.19938000
H	2.90714000	-3.10074700	-1.67381100
C	3.37246500	-6.23224800	-0.41391000
H	2.16244700	-7.12959200	1.13072400
H	4.39208600	-5.07026600	-1.91871800
H	4.02607300	-7.09412100	-0.51865300
C	0.90196700	-0.60385600	-1.08951600
O	-0.26515000	-0.69840400	-1.56196600
Cl	2.22540200	-0.29457700	-2.38696100
C	2.46486300	3.01487900	-0.41619200
C	2.40449400	4.42117400	-0.45647700
C	3.71518900	2.39327800	-0.22621300
C	3.55827300	5.18278400	-0.29118300
C	4.86739800	3.16101200	-0.08749400
C	4.79353600	4.55657200	-0.11050500
H	3.49219100	6.26693300	-0.30827000
H	5.82686100	2.66707800	0.03701800
H	1.44745100	4.91103200	-0.59985900
H	3.78162500	1.31208300	-0.21848500
H	5.69456600	5.15204200	0.00861400
Pd	-1.11348600	0.55409600	-0.04972700
Cl	0.16613800	2.81115200	-1.83271500
N	-3.14830600	0.02407100	-0.21509500
C	-4.29966900	-0.10062900	-0.17458300
C	-5.72044000	-0.22627100	-0.08766600
C	-6.40756400	0.48701800	0.91127700
C	-6.41653500	-1.04993200	-0.98941700
C	-7.79184300	0.36932500	1.00055200
H	-5.85219100	1.11882400	1.59690100
C	-7.80067800	-1.15628500	-0.88605100
H	-5.87209700	-1.59261700	-1.75542700
C	-8.48687700	-0.44929900	0.10567500
H	-8.32856400	0.91739500	1.76891600
H	-8.34449000	-1.79041600	-1.57964100
H	-9.56705800	-0.53636900	0.18083500
Cl	-1.65594900	2.01552500	1.71767100

Zero-point correction= 0.422448 (Hartree/Particle)
 Thermal correction to Energy= 0.455570
 Thermal correction to Enthalpy= 0.456514
 Thermal correction to Gibbs Free Energy= 0.350044
 Sum of electronic and zero-point Energies= -2809.329734
 Sum of electronic and thermal Energies= -2809.296612
 Sum of electronic and thermal Enthalpies= -2809.295668
 Sum of electronic and thermal Free Energies= -2809.402138
 E(RM06L) = -2811.39898867

TS_{0A,Z}



C	-2.22495200	-0.19831700	0.76175100
C	-1.99247000	1.19601500	0.70776000
C	-3.40711000	-0.60694200	1.42160000
C	-2.92183700	2.11059600	1.21414200
C	-4.33892300	0.30063000	1.90884700
H	-3.58709400	-1.66598500	1.55360500
C	-4.10650700	1.67221500	1.79678400
H	-2.69268300	3.16874700	1.16213100

H	-5.23777100	-0.06712900	2.39595200
H	-4.81913700	2.39226100	2.18800700
N	-0.80628300	1.76094100	0.12952700
C	-0.91707900	2.51598300	-1.16227300
H	0.02036900	2.34743900	-1.69748800
H	-1.71027600	2.02349100	-1.72893800
C	-1.20636000	3.99435900	-1.00761500
C	-0.27070300	4.85424800	-0.41163900
C	-2.40743600	4.52896600	-1.48943100
C	-0.54064200	6.21699400	-0.29443700
H	0.66827100	4.45159000	-0.04272600
C	-2.67476100	5.89563200	-1.37960500
H	-3.13811500	3.87134700	-1.95479100
C	-1.74242000	6.74191500	-0.77890800
H	0.19145600	6.87242100	0.16964200
H	-3.61049100	6.29543900	-1.76101100
H	-1.94804400	7.80527200	-0.69018400
C	0.44693200	1.52280000	0.54784700
O	1.48808000	2.04313800	0.30119600
Cl	0.42634500	0.49166000	2.50266000
Pd	0.70687800	-0.78537000	0.37588700
C	-1.25284100	-1.20979700	0.31104500
C	-1.55621400	-2.48301600	-0.01452300
Cl	-0.23747700	-3.68328000	-0.04762900
C	-2.86462600	-3.04861500	-0.41690900
C	-3.62702100	-2.39319900	-1.39922000
C	-3.35274300	-4.24640700	0.13302300
C	-4.85698500	-2.91032800	-1.80189700
H	-3.23644000	-1.48718700	-1.85120500
C	-4.58497500	-4.75839700	-0.26993500
H	-2.76240900	-4.77140400	0.87778800
C	-5.34250600	-4.09164300	-1.23624400
H	-5.43102000	-2.39642800	-2.56829500
H	-4.95258600	-5.68193000	0.16931600
H	-6.29985300	-4.49609300	-1.55371500
Cl	0.78106300	-0.94508200	-2.00106100
N	2.91964300	-0.66303600	0.43301900
C	4.06454900	-0.64967600	0.25821200
C	5.47273400	-0.64018200	0.00989400
C	5.94475200	-0.96825900	-1.27344900
C	6.36894300	-0.30523400	1.03945200
C	7.31536200	-0.95945500	-1.51779200
H	5.23747200	-1.22209800	-2.05635100
C	7.73652800	-0.30137900	0.77880200
H	5.98863100	-0.05274500	2.02393000
C	8.20913100	-0.62763100	-0.49561100
H	7.68607400	-1.21153900	-2.50670600
H	8.43393400	-0.04340000	1.57004500
H	9.27741100	-0.62280300	-0.69274100

Zero-point correction= 0.422952 (Hartree/Particle)

Thermal correction to Energy= 0.456477

Thermal correction to Enthalpy= 0.457421

Thermal correction to Gibbs Free Energy= 0.349524

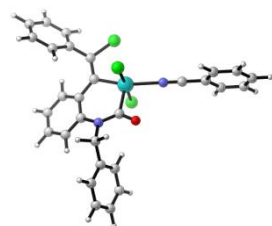
Sum of electronic and zero-point Energies= -2809.339861

Sum of electronic and thermal Energies= -2809.306336

Sum of electronic and thermal Enthalpies= -2809.305392

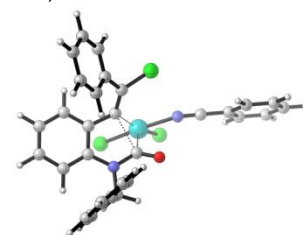
Sum of electronic and thermal Free Energies= -2809.413289

E(RM06L) = -2811.41606154

Z-IIIB

C	-2.38201500	0.33754800	0.35880000
C	-1.96785200	1.62566700	-0.06539800
C	-3.60749100	0.24222500	1.05656100
C	-2.81873400	2.72405300	0.14055100
C	-4.44363000	1.33122300	1.24731000
H	-3.89595300	-0.72374400	1.45021600
C	-4.04945500	2.58064900	0.77135200
H	-2.50344100	3.71530400	-0.15489900
H	-5.38284900	1.20725900	1.77793200
H	-4.67716200	3.45495800	0.91664500
N	-0.70540100	1.88912900	-0.68246500
C	-0.53261400	3.12656800	-1.48806400
H	0.26251000	2.90547600	-2.20442300
H	-1.45575100	3.26149800	-2.05802800
C	-0.19079600	4.39132600	-0.71510900
C	0.40944500	4.36869600	0.54848900
C	-0.45094000	5.62777700	-1.32219400
C	0.74229100	5.56328200	1.19067900
H	0.61113000	3.42318100	1.04177400
C	-0.11131000	6.82047900	-0.68332100
H	-0.92170100	5.65783200	-2.30311000
C	0.48708900	6.79098700	0.57801400
H	1.20311700	5.52968400	2.17408000
H	-0.32028300	7.77045700	-1.16800100
H	0.74832200	7.71817500	1.08073000
C	0.44299700	1.18737600	-0.52791000
O	1.55281600	1.53256900	-0.82269700
Cl	0.42512000	-0.07369000	2.38532200
Pd	0.40612700	-0.72980000	0.11448600
C	-1.58544100	-0.87039700	0.19052100
C	-2.00321500	-2.14842100	0.17989800
Cl	-0.75648600	-3.40575100	0.41935100
C	-3.35725300	-2.68489600	-0.07441100
C	-4.08566500	-2.22835900	-1.18625500
C	-3.92283400	-3.66677400	0.75656200
C	-5.36044100	-2.72808300	-1.44585800
H	-3.63695000	-1.49329500	-1.84669600
C	-5.19872000	-4.16217900	0.49276800
H	-3.36000000	-4.03604400	1.60856200
C	-5.92224400	-3.69329500	-0.60663700
H	-5.91036600	-2.37200100	-2.31272800
H	-5.62744400	-4.91708400	1.14623800
H	-6.91455100	-4.08495200	-0.81320100
Cl	0.33281300	-1.27012600	-2.21732800
N	2.67563400	-1.10753300	0.14788500
C	3.82005500	-1.27943500	0.10961500
C	5.23355900	-1.49154000	0.05321000
C	5.83820800	-1.81125800	-1.17497600
C	6.00429100	-1.37786400	1.22319100
C	7.21442200	-2.01613900	-1.22450400
H	5.22836200	-1.89400400	-2.06870200
C	7.37934800	-1.58577900	1.15702800
H	5.52215200	-1.12942800	2.16307600
C	7.98335200	-1.90411900	-0.06264300
H	7.68713400	-2.26313800	-2.17027500
H	7.97996100	-1.49916700	2.05743600

H 9.05672500 -2.06517600 -0.10782700
 Zero-point correction= 0.424232 (Hartree/Particle)
 Thermal correction to Energy= 0.458172
 Thermal correction to Enthalpy= 0.459116
 Thermal correction to Gibbs Free Energy= 0.349804
 Sum of electronic and zero-point Energies= -2809.359557
 Sum of electronic and thermal Energies= -2809.325617
 Sum of electronic and thermal Enthalpies= -2809.324673
 Sum of electronic and thermal Free Energies= -2809.433985
 E(RM06L) = -2811.44368431

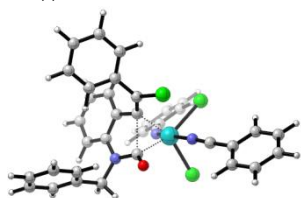
TS_{REZ}

C	0.55960300	0.95998300	0.54321600
C	0.40726200	1.98963000	-0.32327000
C	1.85139500	0.65164300	1.15466600
C	2.25823200	-0.69425700	1.13602200
C	2.64540900	1.58694000	1.83192600
C	3.45494000	-1.09392900	1.73181600
C	3.84204500	1.19767900	2.42516000
H	2.31529600	2.61881200	1.88429700
C	4.24654000	-0.13917500	2.36824300
H	3.77517300	-2.12807600	1.70713300
H	4.45714800	1.93266800	2.93557700
H	5.17925500	-0.44685000	2.83196600
N	1.38755900	-1.57883700	0.47092600
C	1.81303900	-2.94004900	0.06156300
H	2.22405200	-3.44052800	0.94270300
H	0.89910500	-3.46791000	-0.21690300
C	2.80812000	-2.94733300	-1.08244100
C	4.05413500	-3.56573300	-0.93683800
C	2.47716000	-2.36467700	-2.31523300
C	4.96068800	-3.60027900	-1.99924600
H	4.31840000	-4.02905000	0.01129200
C	3.38451400	-2.39163300	-3.37361000
H	1.50184200	-1.90340000	-2.44502800
C	4.62915200	-3.00917700	-3.21832300
H	5.92474700	-4.08472800	-1.87062700
H	3.11639400	-1.93864000	-4.32432800
H	5.33369600	-3.03185700	-4.04523300
C	0.14637500	-1.18102900	0.09017200
O	-0.53655600	-1.64194500	-0.78488800
Cl	-3.05159500	-0.59879000	2.77435400
C	1.52547100	2.76112200	-0.93241500
C	1.52680200	4.16612900	-0.92181600
C	2.58393000	2.08588200	-1.56322300
C	2.57476900	4.87586600	-1.50491200
C	3.62290500	2.79976900	-2.15707300
C	3.62542800	4.19603400	-2.12554800
H	2.56807300	5.96201200	-1.47715600
H	4.42955000	2.26258800	-2.64819100
H	0.70718900	4.69873500	-0.44975700
H	2.58595200	1.00105800	-1.59392300
H	4.43795800	4.75113700	-2.58626900
Pd	-1.11132800	-0.05446300	1.47697300
Cl	-1.16732900	2.58246500	-0.84555900
N	-2.57433300	0.09516400	-0.05172700
C	-3.57411000	-0.06780000	-0.61037000

C	-4.84726900	-0.27574800	-1.22217500
C	-5.01366300	-0.13297600	-2.60995400
C	-5.93021400	-0.62924200	-0.39658800
C	-6.27119100	-0.34460700	-3.16831400
H	-4.16611600	0.13873300	-3.23078800
C	-7.18063500	-0.83701300	-0.97237100
H	-5.77196700	-0.73596200	0.67210600
C	-7.35128600	-0.69509100	-2.35259500
H	-6.40934300	-0.23651800	-4.23987800
H	-8.02225800	-1.11052100	-0.34329200
H	-8.32987200	-0.85878300	-2.79505700
Cl	0.08183100	-0.34202200	3.44452800

Zero-point correction= 0.423483 (Hartree/Particle)
 Thermal correction to Energy= 0.456642
 Thermal correction to Enthalpy= 0.457586
 Thermal correction to Gibbs Free Energy= 0.351839
 Sum of electronic and zero-point Energies= -2809.332994
 Sum of electronic and thermal Energies= -2809.299836
 Sum of electronic and thermal Enthalpies= -2809.298891
 Sum of electronic and thermal Free Energies= -2809.404639
 E(RM06L) = -2811.42230145

TS_{RE,Z,bis}

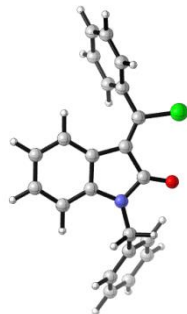


C	-0.42270900	-0.46150800	0.84572700
C	-0.15788100	-1.38644400	1.79586800
C	-1.74680900	0.14684100	0.67728900
C	-2.28173000	0.07027300	-0.62674300
C	-2.44460700	0.85717900	1.66058300
C	-3.51339400	0.65554700	-0.92774400
C	-3.67489100	1.44255200	1.36448500
H	-2.01727800	0.93965900	2.65457100
C	-4.20699900	1.33452900	0.07604200
H	-3.93673100	0.58184300	-1.92268300
H	-4.21954500	1.97756700	2.13689700
H	-5.16956700	1.78278900	-0.15451600
N	-1.49049000	-0.62510000	-1.55658100
C	-2.03376900	-1.16489500	-2.82036200
H	-2.52407100	-0.34769500	-3.35852800
H	-1.16498100	-1.46718900	-3.40879400
C	-2.98583200	-2.33041500	-2.62929200
C	-4.30155300	-2.26295700	-3.09875000
C	-2.54743300	-3.50606100	-2.00057200
C	-5.17130300	-3.34519300	-2.94183100
H	-4.64981700	-1.36047500	-3.59685300
C	-3.41675500	-4.58411200	-1.83718600
H	-1.51963600	-3.57362400	-1.65433200
C	-4.73146800	-4.50655200	-2.30682300
H	-6.19055200	-3.27733500	-3.31268900
H	-3.06496300	-5.49010300	-1.35087200
H	-5.40633400	-5.34895700	-2.18111300
C	-0.19944100	-0.95807300	-1.21491900
O	0.44641000	-1.87099300	-1.66177600
Cl	2.04546500	1.60710100	-2.41885500
C	-1.16427600	-1.96876900	2.72538800
C	-0.93664700	-1.97013100	4.11178100
C	-2.34257800	-2.54815800	2.22755500
C	-1.87966500	-2.51623000	4.98030100
C	-3.27651200	-3.10575400	3.09980500

C	-3.05176600	-3.08694900	4.47774500
H	-1.69634500	-2.49907500	6.05119700
H	-4.17906500	-3.55903500	2.69908100
H	-0.02209800	-1.53527000	4.50316900
H	-2.51979600	-2.57273300	1.15711400
H	-3.78241200	-3.51925100	5.15606400
Pd	1.01777500	0.67741800	-0.34696800
Cl	1.44589800	-2.05559000	2.03935100
N	-0.21650700	2.25403900	-0.46049200
C	-0.53847100	3.35976700	-0.36720200
C	-0.82403000	4.74217700	-0.16859800
C	0.08292200	5.47559700	0.61961700
C	-1.95573100	5.35037900	-0.73535500
C	-0.15745700	6.83046000	0.83207200
H	0.94641600	4.96899400	1.04218300
C	-2.17770500	6.70577100	-0.51022100
H	-2.64147100	4.76347600	-1.33759700
C	-1.28144100	7.44307100	0.27016300
H	0.53489200	7.40868400	1.43637100
H	-3.04832700	7.18844600	-0.94394800
H	-1.46067900	8.50107400	0.44021500
N	2.61433900	-0.51714500	-0.29907200
C	3.68778700	-0.93098000	-0.38942200
Cl	2.22435800	2.13198000	1.43902200
C	5.02166600	-1.43170800	-0.43965000
C	5.32868300	-2.55583400	-1.22540100
C	6.01808800	-0.77571900	0.30571400
C	6.63958900	-3.02246300	-1.25819100
H	4.54598900	-3.04364600	-1.79699600
C	7.32372100	-1.25609300	0.25976900
H	5.75643000	0.09421100	0.89943100
C	7.63379700	-2.37550400	-0.51812100
H	6.88664500	-3.88973400	-1.86296500
H	8.10013100	-0.75528500	0.83004800
H	8.65517100	-2.74437400	-0.54962000

Zero-point correction= 0.524012 (Hartree/Particle)
 Thermal correction to Energy= 0.565283
 Thermal correction to Enthalpy= 0.566227
 Thermal correction to Gibbs Free Energy= 0.439291
 Sum of electronic and zero-point Energies= -3133.700519
 Sum of electronic and thermal Energies= -3133.659247
 Sum of electronic and thermal Enthalpies= -3133.658303
 Sum of electronic and thermal Free Energies= -3133.785239
 E(RM06L) = -3135.98012018

Z-1b



C	-1.24330000	2.14400800	-0.34606600
C	-0.50886400	0.96710500	-0.50223700
C	0.87093400	1.05781300	-0.80440200
C	1.52518300	2.28015700	-0.91200200
C	0.77095400	3.44536500	-0.73335100
C	-0.59771600	3.37993200	-0.46249900
H	-2.30543000	2.11035000	-0.13704400
H	2.58867400	2.33129400	-1.11833500

H	1.26167100	4.41178800	-0.80981500
H	-1.16948900	4.29467200	-0.33691600
N	1.40058200	-0.22181000	-0.99037500
C	0.42147900	-1.20038400	-0.83592300
O	0.62911400	-2.39832200	-0.94217500
C	-0.85560200	-0.46520800	-0.49331600
C	2.77170300	-0.54369300	-1.36231400
H	3.07321700	0.10735300	-2.19149600
H	2.73371700	-1.57138800	-1.73663800
C	3.76701200	-0.43538500	-0.21967400
C	3.59626800	-1.20749100	0.93817400
C	4.87711700	0.40976600	-0.31308000
C	4.51553600	-1.12564800	1.98287300
H	2.74424700	-1.87866600	1.01038600
C	5.80184300	0.49080900	0.73161800
H	5.02457400	1.00614300	-1.21152700
C	5.62082000	-0.27500200	1.88316500
H	4.37334300	-1.73043100	2.87463200
H	6.65911100	1.15317900	0.64461900
H	6.33690300	-0.21313700	2.69824200
C	-2.04756200	-1.05673400	-0.23914600
Cl	-2.27528600	-2.78244400	-0.47441800
C	-3.26320400	-0.37900900	0.26997000
C	-4.46948900	-0.42290600	-0.44696000
C	-3.22800900	0.27742200	1.51067600
C	-5.60904400	0.20324300	0.05475600
C	-4.37430200	0.89052600	2.01611100
C	-5.56533300	0.85960300	1.28758100
H	-6.53377400	0.17369800	-0.51477100
H	-4.33686800	1.38791800	2.98133300
H	-2.30082800	0.29935400	2.07523500
H	-6.45742900	1.33894200	1.68122600
H	-4.50729700	-0.94600200	-1.39771800

Zero-point correction= 0.321132 (Hartree/Particle)

Thermal correction to Energy= 0.341220

Thermal correction to Enthalpy= 0.342164

Thermal correction to Gibbs Free Energy= 0.268827

Sum of electronic and zero-point Energies= -1437.816772

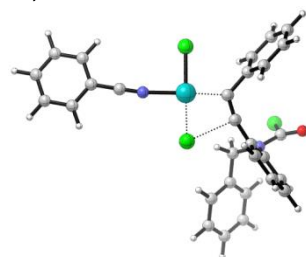
Sum of electronic and thermal Energies= -1437.796684

Sum of electronic and thermal Enthalpies= -1437.795740

Sum of electronic and thermal Free Energies= -1437.869077

E(RM06L) = -1438.39297003

TS _{β -cis-CP}



C	-0.23130800	1.64271600	0.55626600
C	-1.05396200	0.85388000	1.14451100
C	-0.61165100	3.02319300	0.15017900
C	-0.61166900	3.40302800	-1.19976000
C	-1.01995300	3.94154200	1.12938600
C	-1.03040800	4.68226500	-1.55948500
C	-1.42050900	5.22580900	0.76174700
H	-1.01072700	3.64874200	2.17511700
C	-1.43242100	5.59741800	-0.58337900
H	-1.03187600	4.96733200	-2.60777100
H	-1.72801800	5.93213400	1.52815400
H	-1.74938600	6.59632300	-0.87037600

C	-2.22116100	0.26147200	1.67547100
C	-2.44619500	0.28866700	3.07184300
C	-3.20806200	-0.30656200	0.82535400
C	-3.62395900	-0.21144400	3.60641100
C	-4.38738900	-0.80034300	1.37665300
C	-4.59517900	-0.75189300	2.75583900
H	-3.79012300	-0.18357600	4.67878900
H	-5.13792100	-1.22542600	0.71979300
H	-1.67256400	0.70228900	3.70968300
H	-5.51897200	-1.14659900	3.16892800
Pd	1.60269800	0.73837100	0.37561000
Cl	2.54830000	2.47892200	-0.88992500
N	3.45954900	-0.23700900	0.24034300
C	4.52915700	-0.65870700	0.10067300
C	5.85789600	-1.14831000	-0.09087500
C	6.77646900	-0.36860800	-0.81657300
C	6.23610800	-2.39318200	0.44152200
C	8.07180100	-0.84267000	-1.00484500
H	6.46573100	0.58990200	-1.21945700
C	7.53534200	-2.85238900	0.24401000
H	5.51541900	-2.98232200	0.99931800
C	8.45092100	-2.08018400	-0.47682800
H	8.78587300	-0.24574600	-1.56398200
H	7.83397000	-3.81301900	0.65261700
H	9.46328500	-2.44417700	-0.62740000
Cl	0.58679100	-1.03420400	1.67509300
N	-2.99061600	-0.38596400	-0.59157000
C	-3.77127500	0.43834300	-1.35050100
C	-2.06148100	-1.44361400	-1.06840700
H	-1.82389000	-1.22071000	-2.10765700
H	-1.13853100	-1.34844100	-0.49202700
O	-4.57281800	1.23451500	-0.94632200
Cl	-3.50987000	0.27657000	-3.14933000
C	-2.62805400	-2.84299600	-0.91675300
C	-3.72024600	-3.26890400	-1.68715300
C	-2.05389300	-3.73272400	-0.00124000
C	-4.22834100	-4.55926400	-1.54070200
H	-4.16857800	-2.58995700	-2.40823500
C	-2.55996000	-5.02721700	0.14267300
H	-1.20584700	-3.40863600	0.59725500
C	-3.64865300	-5.44219500	-0.62471000
H	-5.07224800	-4.87895500	-2.14640700
H	-2.10312000	-5.70832700	0.85576000
H	-4.04342400	-6.44868700	-0.51379900
H	-0.27368900	2.70282400	-1.95442000

Zero-point correction= 0.422260 (Hartree/Particle)

Thermal correction to Energy= 0.456477

Thermal correction to Enthalpy= 0.457421

Thermal correction to Gibbs Free Energy= 0.345531

Sum of electronic and zero-point Energies= -2809.348582

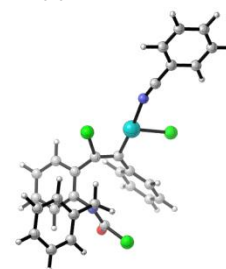
Sum of electronic and thermal Energies= -2809.314365

Sum of electronic and thermal Enthalpies= -2809.313421

Sum of electronic and thermal Free Energies= -2809.425311

E(RM06L) = -2811.42030269

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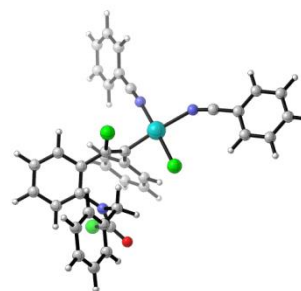


C	0.00305300	1.04208100	0.65533400
C	-0.70391700	0.12562500	1.31577500
C	-0.51587800	2.36041500	0.26255700
C	-0.43575400	2.81363600	-1.06589500
C	-1.12087800	3.18614800	1.22829800
C	-0.97488200	4.04779500	-1.41986500
C	-1.64484000	4.42642100	0.87029000
H	-1.17321300	2.84987100	2.25932800
C	-1.57852500	4.85834000	-0.45530800
H	-0.91660000	4.38044800	-2.45229600
H	-2.10942100	5.05251800	1.62717700
H	-1.99255800	5.82303200	-0.73570500
C	-2.08690800	-0.03388700	1.78789900
C	-2.32429500	-0.19045200	3.16638300
C	-3.19233900	-0.04824800	0.91070700
C	-3.61454200	-0.32538100	3.66621900
C	-4.48704500	-0.18184800	1.42026500
C	-4.70183200	-0.31330700	2.78913600
H	-3.77213600	-0.43385900	4.73536900
H	-5.32253400	-0.18732900	0.72911200
H	-1.47457000	-0.19304400	3.84269000
H	-5.71446800	-0.41775400	3.16753900
Pd	1.84981200	0.28158900	0.45993800
Cl	2.78453000	2.07000900	-0.71910600
N	3.79169800	-0.68842900	0.35961800
C	4.90962700	-0.90006900	0.13624500
C	6.29117200	-1.09435100	-0.17261500
C	6.97347800	-0.07883000	-0.86732300
C	6.95289800	-2.27385600	0.20946800
C	8.31982700	-0.25365900	-1.17534500
H	6.44231400	0.82373400	-1.15236800
C	8.29932900	-2.43214600	-0.10665400
H	6.41247400	-3.04776900	0.74496000
C	8.98117900	-1.42560000	-0.79686000
H	8.85315100	0.52559600	-1.71118800
H	8.81726200	-3.34069100	0.18529000
H	10.03182100	-1.55536400	-1.04045200
Cl	0.39892900	-1.33490900	1.75600400
N	-3.00798400	0.02737800	-0.51743400
C	-3.56224300	1.10977100	-1.13675200
C	-2.41634500	-1.16143100	-1.17415900
H	-2.14283200	-0.87527800	-2.18864300
H	-1.48959600	-1.39516100	-0.64508200
O	-4.12981800	2.02885700	-0.61831200
Cl	-3.39551500	1.10016200	-2.96637600
C	-3.33454800	-2.37014200	-1.17342600
C	-4.51413600	-2.38066400	-1.93230100
C	-3.00734400	-3.50115500	-0.41737700
C	-5.34665700	-3.49925900	-1.93071600
H	-4.77658300	-1.51176500	-2.53011200
C	-3.83793200	-4.62445800	-0.41740400
H	-2.09500800	-3.50322200	0.17483700
C	-5.01041800	-4.62495800	-1.17313800
H	-6.25594000	-3.49529600	-2.52601100
H	-3.56887400	-5.49521000	0.17461200
H	-5.65894900	-5.49698600	-1.17488100
H	0.05657700	2.19825700	-1.80962500

Zero-point correction= 0.423527 (Hartree/Particle)
 Thermal correction to Energy= 0.457822
 Thermal correction to Enthalpy= 0.458766
 Thermal correction to Gibbs Free Energy= 0.347556
 Sum of electronic and zero-point Energies= -2809.356673
 Sum of electronic and thermal Energies= -2809.322378
 Sum of electronic and thermal Enthalpies= -2809.321434
 Sum of electronic and thermal Free Energies= -2809.432644

E(RM06L) = -2811.43117235

IC_{bis}

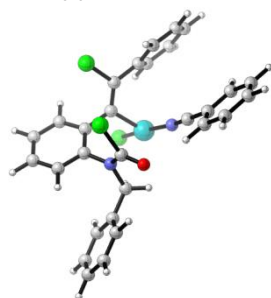


C	0.18182700	1.34403000	1.30168300
C	0.04026700	0.68661100	2.53898800
C	0.38179000	2.73881400	1.30059800
C	0.10783300	1.40335600	3.73242800
C	0.44324400	3.45122500	2.49825600
H	0.49730700	3.25674200	0.35298700
C	0.30291700	2.78661700	3.71893700
H	0.01015100	0.87698500	4.67801500
H	0.61157400	4.52551100	2.47797400
H	0.35233900	3.34127500	4.65222900
C	0.03374400	0.61320200	0.02700100
C	0.88965500	0.66895500	-0.99931900
Pd	-1.71815100	-0.34680700	-0.12474200
N	-2.61062600	1.47125000	-0.57962000
C	-3.02215000	2.55034600	-0.68512300
C	-3.50216500	3.89323600	-0.77514100
C	-2.98035900	4.86312200	0.10068800
C	-4.48109400	4.23601600	-1.72414400
C	-3.44467800	6.17300900	0.01911800
H	-2.22378300	4.57900100	0.82566400
C	-4.93431000	5.55051900	-1.79170600
H	-4.87280700	3.47694800	-2.39347100
C	-4.41841100	6.51673800	-0.92311300
H	-3.04659400	6.92643300	0.69203100
H	-5.68999700	5.82165800	-2.52269400
H	-4.77628600	7.54071000	-0.98105200
C	2.23657400	1.30228400	-1.06533500
C	2.43576000	2.37073100	-1.95789200
C	3.34725600	0.83521800	-0.32971700
C	3.67994800	2.97309800	-2.11113200
H	1.58841400	2.71978900	-2.54083900
C	4.60575000	1.42226100	-0.51635200
C	4.77390900	2.49323500	-1.38761900
H	3.79868200	3.80365700	-2.80154300
H	5.45165000	1.02294400	0.03255800
H	5.75679700	2.93860900	-1.51215400
Cl	0.44082500	-0.09687100	-2.55874500
N	-3.60007700	-1.52768700	-0.21905800
C	-4.13879100	-2.55019500	-0.11614100
C	-4.68856800	-3.85991400	0.04294700
C	-6.05481100	-4.10967000	-0.16657300
C	-3.81307700	-4.89575600	0.41814800
C	-6.54308400	-5.40263400	0.00109600
H	-6.71547400	-3.29852800	-0.45566500
C	-4.31932000	-6.18266000	0.58112300
H	-2.76169900	-4.67135600	0.57294600
C	-5.67830900	-6.43614200	0.37377000
H	-7.59795100	-5.60488700	-0.15877700
H	-3.65150800	-6.98849100	0.87038700
H	-6.06581200	-7.44286000	0.50288400
Cl	-0.62814000	-2.34004500	0.53509500
H	-0.11717100	-0.38724300	2.54721900

N	3.23258300	-0.29243400	0.54868000
C	3.52163300	-0.28299300	1.87804300
O	3.59342800	-1.23842300	2.60679800
Cl	3.79243600	1.37831800	2.58039900
C	3.02477000	-1.63730900	-0.06869600
H	2.25437700	-1.52595100	-0.83127900
H	2.61705600	-2.27746900	0.71305300
C	4.29381000	-2.21312800	-0.66285300
C	5.27350200	-2.79213700	0.15869700
C	4.50831700	-2.17375300	-2.04628300
C	6.44261700	-3.31379700	-0.39519600
H	5.11099100	-2.82997400	1.23198600
C	5.67745100	-2.69837900	-2.60199600
H	3.75111800	-1.73404500	-2.69123600
C	6.64801300	-3.26839600	-1.77698000
H	7.19191200	-3.76279300	0.25190900
H	5.82753500	-2.66298500	-3.67805400
H	7.55772500	-3.67943500	-2.20733000

Zero-point correction= 0.524858 (Hartree/Particle)
 Thermal correction to Energy= 0.566850
 Thermal correction to Enthalpy= 0.567794
 Thermal correction to Gibbs Free Energy= 0.437785
 Sum of electronic and zero-point Energies= -3133.768286
 Sum of electronic and thermal Energies= -3133.726294
 Sum of electronic and thermal Enthalpies= -3133.725350
 Sum of electronic and thermal Free Energies= -3133.855359
 E(RM06L) = -3136.02802614

E-IA_{mono}

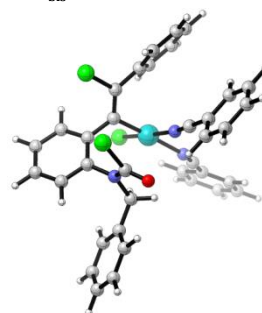


C	1.12999100	-1.74734300	0.89375600
C	2.07377400	-0.70273400	1.01093200
C	1.51983900	-3.03311600	1.31580400
C	3.33613800	-0.94223300	1.55922900
C	2.77939900	-3.26947700	1.85623500
H	0.81148200	-3.84681300	1.20734700
C	3.69064000	-2.22039800	1.98742300
H	4.03372600	-0.11647400	1.64573300
H	3.04833100	-4.27286300	2.17361800
H	4.67490200	-2.39395900	2.41255600
N	1.80212400	0.61211100	0.48955600
C	2.32633000	0.92341500	-0.87214000
H	2.16002400	0.02919700	-1.47857800
H	1.69984400	1.72521600	-1.26619200
C	3.78915300	1.31832600	-0.89926100
C	4.74593900	0.44476300	-1.43031500
C	4.20447400	2.56601600	-0.40830900
C	6.09479100	0.80600400	-1.46981100
H	4.43265200	-0.52276300	-1.81541300
C	5.55188500	2.92405500	-0.44183200
H	3.46640900	3.25322600	-0.00408400
C	6.50045600	2.04522500	-0.97312500
H	6.82552000	0.11861600	-1.88747700
H	5.86174000	3.89329800	-0.05996900
H	7.54931900	2.32824300	-1.00272600
C	1.20092200	1.61760900	1.16407300

O	0.99666400	2.73842200	0.75015700
Cl	0.67268300	1.17901700	2.83328300
C	-0.23854400	-1.57519100	0.38020700
C	-1.39092300	-1.79694400	1.02770000
Cl	-1.34508800	-2.10811000	2.78939000
C	-2.76447300	-1.80819900	0.46680200
C	-3.78366400	-1.03638800	1.04888500
C	-3.06653300	-2.60131500	-0.65315000
C	-5.06634900	-1.03234400	0.50358100
H	-3.56442500	-0.43978700	1.92922600
C	-4.35483500	-2.59877600	-1.19183500
H	-2.29399800	-3.22587700	-1.09009600
C	-5.35600500	-1.81173900	-0.62072300
H	-5.84333100	-0.42633400	0.96245300
H	-4.57456600	-3.22316200	-2.05356600
H	-6.35918800	-1.81520800	-1.03891300
Pd	-0.39025700	-1.07339600	-1.55156000
Cl	0.50907300	-3.05969700	-2.31525500
N	-1.28447200	0.74243700	-1.12150600
C	-1.87007900	1.70051000	-0.82722900
C	-2.62004700	2.86595700	-0.48267100
C	-3.97528800	2.94180100	-0.85645200
C	-2.00356400	3.91402200	0.22555000
C	-4.70866100	4.07627400	-0.52405500
H	-4.43455300	2.11636100	-1.39060300
C	-2.75671000	5.03982900	0.54956400
H	-0.96126500	3.82528800	0.51490100
C	-4.10073000	5.12347600	0.17576200
H	-5.75432400	4.14370600	-0.80865300
H	-2.29174200	5.85349500	1.09787300
H	-4.67894500	6.00651400	0.43303500

Zero-point correction= 0.424557 (Hartree/Particle)
 Thermal correction to Energy= 0.458448
 Thermal correction to Enthalpy= 0.459392
 Thermal correction to Gibbs Free Energy= 0.351833
 Sum of electronic and zero-point Energies= -2809.370621
 Sum of electronic and thermal Energies= -2809.336730
 Sum of electronic and thermal Enthalpies= -2809.335786
 Sum of electronic and thermal Free Energies= -2809.443345
 E(RM06L) = -2811.44448251

E-IA_{bis}



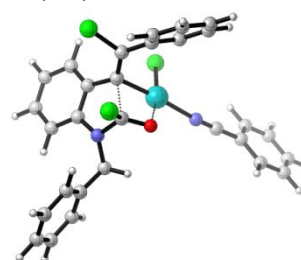
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C	-1.18197400	-2.37982300	-1.17696900
C	-0.77042900	-1.69779600	-3.44956000
C	-1.33357200	-3.70062800	-1.60958700
C	-0.91385600	-3.01330700	-3.87873700
H	-0.53940300	-0.91475800	-4.16275600
C	-1.20587100	-4.02169400	-2.95895100
H	-1.55375300	-4.46872200	-0.87596100
H	-0.79783800	-3.24967500	-4.93288900
H	-1.32716500	-5.05076200	-3.28499200
N	-1.22435200	-2.13105100	0.24281700
C	0.02708300	-2.38156000	1.01307600

H	0.84918500	-2.02661100	0.38683400
H	-0.02292300	-1.74862400	1.90051500
C	0.24076300	-3.83227100	1.39695100
C	1.20975500	-4.60099900	0.74026100
C	-0.51541700	-4.42276500	2.42149100
C	1.42125400	-5.93523600	1.09574600
H	1.79983100	-4.15144200	-0.05486400
C	-0.30815200	-5.75644500	2.77303700
H	-1.26441500	-3.83027200	2.93925600
C	0.66119900	-6.51610300	2.11170400
H	2.17790200	-6.51859700	0.57766700
H	-0.89942200	-6.20234000	3.56869400
H	0.82394400	-7.55411500	2.38988900
C	-2.31954500	-1.77789800	0.94937600
O	-2.37684200	-1.60380200	2.14870100
Cl	-3.80732000	-1.55456400	-0.04846400
C	-0.76800100	0.08147900	-1.72552300
C	-1.54598500	1.07949400	-2.16952900
Cl	-3.02552100	0.70933100	-3.12232300
C	-1.35071500	2.53661800	-1.96507000
C	-2.39155000	3.34614100	-1.47994900
C	-0.11228400	3.13226300	-2.25979000
C	-2.18896200	4.70813600	-1.26194700
H	-3.36020100	2.90064000	-1.27452500
C	0.08497600	4.49814100	-2.04517600
H	0.68651500	2.52197100	-2.66896700
C	-0.94794700	5.28954700	-1.54042600
H	-3.00477000	5.31868400	-0.88276600
H	1.04667700	4.94352000	-2.28641100
H	-0.79429000	6.35365000	-1.37990500
Pd	0.78160000	0.57497200	-0.53378700
N	2.57750300	1.04653600	0.67436200
C	3.72118400	1.15207300	0.83705500
C	5.14427600	1.24572500	0.93202700
C	5.90653100	0.88058500	-0.19297100
C	5.76631500	1.68856200	2.11120500
C	7.29481600	0.96319600	-0.12621700
H	5.39951900	0.54156100	-1.09135700
C	7.15560200	1.76480700	2.16014200
H	5.16318200	1.96580000	2.96983400
C	7.91783200	1.40343700	1.04523000
H	7.89087800	0.68351500	-0.98961800
H	7.64432100	2.10587800	3.06783600
H	9.00151000	1.46522700	1.09012300
Cl	2.25891000	-0.03323200	-2.27379600
N	-0.53942700	1.18431400	0.95055800
C	-1.32166500	1.61320400	1.69110700
C	-2.27283600	2.17969600	2.59565200
C	-3.12944900	1.34173600	3.33211800
C	-2.33892300	3.57933800	2.72786500
C	-4.04626600	1.91941800	4.20742100
H	-3.07154400	0.26618100	3.19822000
C	-3.26155900	4.13576500	3.60846500
H	-1.68150200	4.20769200	2.13582400
C	-4.11182500	3.30813700	4.34842100
H	-4.71413700	1.28140100	4.77837000
H	-3.31994400	5.21480300	3.71575900
H	-4.83094800	3.74855000	5.03353600

Zero-point correction= 0.525280 (Hartree/Particle)
 Thermal correction to Energy= 0.567085
 Thermal correction to Enthalpy= 0.568029
 Thermal correction to Gibbs Free Energy= 0.439379
 Sum of electronic and zero-point Energies= -3133.777689
 Sum of electronic and thermal Energies= -3133.735884
 Sum of electronic and thermal Enthalpies= -3133.734940

Sum of electronic and thermal Free Energies= -3133.863590
 E(RM06L) = -3136.03536793

TS_{1,2-Add,E}

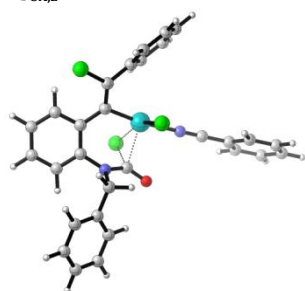


C	-0.92106500	-1.32458500	0.62688700
C	-0.96806500	-2.65409600	0.25935400
C	-1.77558200	-0.68595100	1.63041000
C	-2.37162600	0.50735900	1.17203900
C	-1.98989700	-1.10279500	2.95017800
C	-3.17650800	1.27801400	2.01776200
C	-2.79030800	-0.33880700	3.79495300
H	-1.50768000	-2.00456800	3.31111500
C	-3.37827600	0.84336500	3.32689700
H	-3.64091400	2.18883900	1.65756400
H	-2.95013600	-0.65635100	4.82105000
H	-4.00324300	1.43499100	3.99042700
N	-2.02715700	0.86239500	-0.14024700
C	-1.75371300	2.27169600	-0.47115600
H	-1.21748800	2.74391000	0.36266800
H	-1.07020200	2.26149000	-1.32487000
C	-2.99745100	3.07722800	-0.80945800
C	-3.09378200	4.40922400	-0.38822400
C	-4.03126900	2.53374000	-1.58321100
C	-4.19633100	5.19059600	-0.74074700
H	-2.30067400	4.83825400	0.22092300
C	-5.13565300	3.31215000	-1.93068300
H	-3.97006300	1.49733600	-1.90229800
C	-5.22136500	4.64298800	-1.51347100
H	-4.25633600	6.22249300	-0.40463900
H	-5.93217200	2.87725000	-2.52880100
H	-6.08354800	5.24649600	-1.78450000
C	-1.32077300	-0.13716100	-0.86478600
O	-0.20249200	0.12054700	-1.40900800
Cl	-2.50674700	-1.05507500	-1.99841000
Pd	0.91283800	-0.37239000	0.32012000
N	2.69398200	0.71246200	-0.08596700
C	3.72172800	1.24547700	-0.13776200
C	4.99662300	1.89083000	-0.16369200
C	5.82181800	1.81959400	0.97328200
C	5.41514100	2.58550400	-1.31202500
C	7.06444200	2.44688400	0.95217800
H	5.48143900	1.27840000	1.85018300
C	6.66072000	3.20708600	-1.31630600
H	4.76720000	2.63096700	-2.18139400
C	7.48333200	3.13849900	-0.18810300
H	7.70632900	2.39584800	1.82635000
H	6.99001200	3.74517100	-2.20000200
H	8.45414800	3.62573100	-0.19782400
Cl	1.82060800	-1.05247900	2.39656200
C	-0.07278000	-3.36020000	-0.66320900
C	1.32726700	-3.30303400	-0.50731100
C	-0.60928700	-4.12368800	-1.72305000
C	2.16207900	-3.95990300	-1.41314800
H	1.75019100	-2.80677100	0.35877900
C	0.23091400	-4.75642100	-2.62979100
H	-1.68455600	-4.18090300	-1.84723500

C	1.62062800	-4.67548600	-2.47964900
H	3.23805600	-3.92082400	-1.26882400
H	-0.19653900	-5.31498900	-3.45759100
H	2.27366600	-5.18246800	-3.18496400
Cl	-2.31925100	-3.63641000	0.82567100

Zero-point correction= 0.422523 (Hartree/Particle)
 Thermal correction to Energy= 0.455565
 Thermal correction to Enthalpy= 0.456510
 Thermal correction to Gibbs Free Energy= 0.350696
 Sum of electronic and zero-point Energies= -2809.332037
 Sum of electronic and thermal Energies= -2809.298995
 Sum of electronic and thermal Enthalpies= -2809.298050
 Sum of electronic and thermal Free Energies= -2809.403864
 E(RM06L) = -2811.40059983

TS_{OA,E}

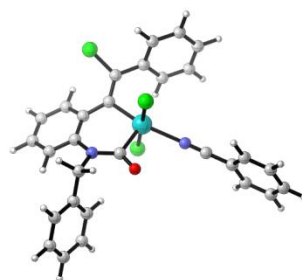


C	2.13927600	1.61736400	0.65071000
C	2.73703000	0.33795300	0.60719600
C	2.87241200	2.62690200	1.31268000
C	4.01721000	0.11065200	1.11971300
C	4.14982200	2.40676500	1.81443200
H	2.41869500	3.60156000	1.43608800
C	4.73819600	1.14627100	1.70676200
H	4.42940700	-0.89074500	1.07186300
H	4.67804200	3.21970100	2.30485400
H	5.73157600	0.95964200	2.10396300
N	2.06961500	-0.79906600	0.03868800
C	2.56052400	-1.35681200	-1.26636100
H	1.68301700	-1.76034300	-1.77705500
H	2.91057800	-0.49816600	-1.84346800
C	3.65072000	-2.39823200	-1.13242000
C	3.38548600	-3.64714400	-0.54945600
C	4.93765500	-2.13534600	-1.61734400
C	4.39271500	-4.60564900	-0.44805600
H	2.38809500	-3.86421900	-0.17747200
C	5.94502300	-3.09845600	-1.52312200
H	5.15227000	-1.17121600	-2.07244400
C	5.67471800	-4.33463600	-0.93553700
H	4.17547200	-5.56884100	0.00578100
H	6.93810500	-2.88061700	-1.90674400
H	6.45675600	-5.08530500	-0.85944000
C	0.91460100	-1.30974700	0.48415600
O	0.33852000	-2.32745500	0.27402200
Cl	0.39648400	-0.40430900	2.46880100
Pd	-0.62235500	0.45339500	0.35934700
C	0.77531400	1.89998100	0.18186400
C	0.28787500	3.06095800	-0.29809800
Cl	-0.93161000	0.44023700	-2.00135600
N	-2.35413100	-0.91567500	0.54650900
C	-3.26763200	-1.61824400	0.43132500
C	-4.39680800	-2.47764200	0.25501500
C	-5.02489600	-2.53456900	-1.00184800
C	-4.86691600	-3.25520700	1.32728900
C	-6.12363800	-3.37155700	-1.17676600
H	-4.64538300	-1.92925600	-1.81865800

C	-5.96694000	-4.08684000	1.13595800
H	-4.36941600	-3.20200900	2.29023900
C	-6.59418200	-4.14515900	-0.11188600
H	-6.61248500	-3.42065700	-2.14504100
H	-6.33456600	-4.69035900	1.96034500
H	-7.45186900	-4.79631200	-0.25497200
Cl	1.37389800	4.37572200	-0.85886100
C	-1.14338600	3.41403100	-0.41624800
C	-1.99723500	3.18276600	0.67825300
C	-1.67782700	3.99018800	-1.57999700
C	-3.35802900	3.48825300	0.59647000
H	-1.58166000	2.80157300	1.60720000
C	-3.03330900	4.29369700	-1.65731100
H	-1.02748600	4.17644800	-2.42784700
C	-3.88002300	4.04076300	-0.57217200
H	-4.00104500	3.30949800	1.45416100
H	-3.43502200	4.72514700	-2.57018100
H	-4.93695600	4.28527600	-0.63684200

Zero-point correction= 0.422884 (Hartree/Particle)
 Thermal correction to Energy= 0.456420
 Thermal correction to Enthalpy= 0.457364
 Thermal correction to Gibbs Free Energy= 0.349481
 Sum of electronic and zero-point Energies= -2809.341865
 Sum of electronic and thermal Energies= -2809.308329
 Sum of electronic and thermal Enthalpies= -2809.307385
 Sum of electronic and thermal Free Energies= -2809.415268
 E(RM06L) = -2811.41859441

E-IIB

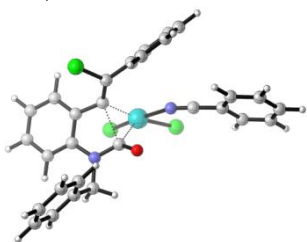


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C	-2.90758200	-0.46978800	-0.10518900
C	-3.10445900	-2.60702900	1.00943500
C	-4.27357600	-0.25964700	0.13596300
C	-4.45468000	-2.39233600	1.24440800
H	-2.63592700	-3.50795000	1.38335900
C	-5.04582200	-1.21579600	0.78768400
H	-4.73601800	0.67639400	-0.14714200
H	-5.03413500	-3.13139900	1.78944400
H	-6.09951400	-1.01891500	0.96247900
N	-2.18160700	0.59131200	-0.73074000
C	-2.91318800	1.59223200	-1.54904900
H	-2.19256200	1.96331100	-2.28252100
H	-3.68217900	1.04236300	-2.09831300
C	-3.52629800	2.76298100	-0.79456100
C	-3.13433100	3.12561300	0.49818300
C	-4.50041500	3.52926700	-1.44980500
C	-3.70747600	4.23627600	1.12196700
H	-2.39044500	2.54011700	1.02924500
C	-5.06766000	4.64178800	-0.82881900
H	-4.81656800	3.25413300	-2.45431900
C	-4.67163400	4.99895000	0.46205700
H	-3.39586900	4.50242800	2.12827700
H	-5.82185500	5.22464500	-1.35083600
H	-5.11468500	5.86267600	0.95024300
C	-0.87511500	0.89418800	-0.55190000
O	-0.31592700	1.91622300	-0.83181400

Cl	-0.16675800	-0.07657600	2.39198800
Pd	0.43040400	-0.50667000	0.13648400
C	-0.90680000	-2.01224900	0.06903600
C	-0.30151900	-3.19689600	-0.12939500
Cl	0.96008800	-0.82121100	-2.17635500
N	2.26090000	0.87996000	0.31626700
C	3.14984900	1.61987400	0.26111400
C	4.24923200	2.53081200	0.17366700
C	4.90691600	2.70226600	-1.05704100
C	4.66054100	3.24600900	1.31157200
C	5.97581400	3.59046000	-1.14075500
H	4.57401400	2.14377200	-1.92583100
C	5.73119300	4.13038300	1.21144200
H	4.14076300	3.10415900	2.25354900
C	6.38758400	4.30244900	-0.01058800
H	6.48718000	3.72778000	-2.08870200
H	6.05305900	4.68623100	2.08690100
H	7.22204100	4.99426900	-0.08251200
Cl	-1.23527700	-4.64808600	-0.58082800
C	1.15546100	-3.43164200	-0.02887300
C	1.86228900	-4.13491600	-1.01861200
C	1.85722300	-2.92894800	1.08421200
C	3.23850600	-4.30189100	-0.91249100
H	1.32860400	-4.52774400	-1.87723100
C	3.24304100	-3.09604400	1.18054400
H	1.31275800	-2.45267500	1.89449000
C	3.93594000	-3.77837300	0.18356100
H	3.77510500	-4.83672400	-1.69139100
H	3.76816300	-2.70767500	2.04880300
H	5.01122700	-3.91526700	0.25998500

Zero-point correction= 0.424330 (Hartree/Particle)
 Thermal correction to Energy= 0.458197
 Thermal correction to Enthalpy= 0.459141
 Thermal correction to Gibbs Free Energy= 0.350542
 Sum of electronic and zero-point Energies= -2809.360834
 Sum of electronic and thermal Energies= -2809.326967
 Sum of electronic and thermal Enthalpies= -2809.326023
 Sum of electronic and thermal Free Energies= -2809.434622
 E(RM06L) = -2811.44586231

TS_{RE,F}

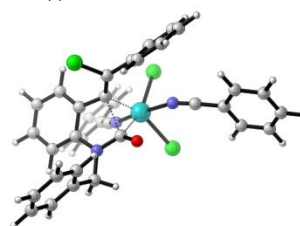


C	0.76356000	-1.21921000	0.56149600
C	0.16262200	-1.31443600	1.77103500
C	2.15788100	-1.54886900	0.28904200
C	2.90192300	-0.60291900	-0.43604400
C	2.75595100	-2.77417700	0.61017800
C	4.22763100	-0.84513800	-0.79596000
C	4.07814300	-3.02583900	0.25693800
H	2.17532900	-3.52474700	1.13561000
C	4.81114200	-2.05954200	-0.43808700
H	4.80619400	-0.10598300	-1.33568500
H	4.53728400	-3.97392700	0.52019500
H	5.84409400	-2.25268700	-0.71262300
N	2.21552900	0.58525200	-0.74529700
C	2.89672600	1.77016300	-1.31947100
H	3.45276000	1.43651300	-2.20078900
H	2.10154800	2.43242000	-1.66821300

C	3.80646500	2.49238500	-0.34501200
C	5.13245300	2.77008000	-0.69368200
C	3.32093800	2.93313200	0.89399700
C	5.96520800	3.47400500	0.17926000
H	5.51744500	2.43851900	-1.65588100
C	4.15369300	3.62839000	1.76939900
H	2.28800400	2.73536200	1.16694100
C	5.47797200	3.90101700	1.41457400
H	6.99316700	3.68177800	-0.10496700
H	3.76754500	3.96256600	2.72855000
H	6.12486900	4.44402200	2.09816100
C	0.88719900	0.69372900	-0.49595500
O	0.24313000	1.68729600	-0.30278600
Cl	-1.99094300	-1.00203300	-3.05133700
Pd	-0.46745400	-0.90854200	-1.20303600
N	-2.06517400	0.16982100	-0.32451100
C	-3.03739300	0.79414700	-0.26406300
C	-4.24914400	1.54888100	-0.29437300
C	-4.75462100	2.15722100	0.86649200
C	-4.92017300	1.66871300	-1.52512900
C	-5.93519700	2.89069600	0.78910400
H	-4.22530300	2.04438900	1.80668100
C	-6.10062800	2.40478900	-1.58323700
H	-4.50815200	1.18424300	-2.40504600
C	-6.60600400	3.01480000	-0.43148400
H	-6.33353400	3.36556400	1.68073200
H	-6.62601900	2.50237500	-2.52839600
H	-7.52703400	3.58849600	-0.48438600
Cl	0.97678400	-2.17349800	-2.49911100
Cl	1.18919500	-1.56579100	3.21956600
C	-1.27080600	-1.31950100	2.12041700
C	-1.78331400	-0.48129200	3.12511600
C	-2.12997000	-2.23546700	1.49000100
C	-3.13385700	-0.53128100	3.45997300
H	-1.11908100	0.20956000	3.63505000
C	-3.47891500	-2.29391000	1.83963500
H	-1.73254900	-2.90514000	0.73356100
C	-3.98593400	-1.43785800	2.81814400
H	-3.52139800	0.12603700	4.23404200
H	-4.13005200	-3.01010800	1.34684300
H	-5.03665500	-1.48396200	3.09139100

Zero-point correction= 0.423288 (Hartree/Particle)
 Thermal correction to Energy= 0.456545
 Thermal correction to Enthalpy= 0.457489
 Thermal correction to Gibbs Free Energy= 0.351767
 Sum of electronic and zero-point Energies= -2809.336297
 Sum of electronic and thermal Energies= -2809.303040
 Sum of electronic and thermal Enthalpies= -2809.302096
 Sum of electronic and thermal Free Energies= -2809.407818
 E(RM06L) = -2811.42534866

TS_{RE,E,bis}



C	0.33123800	0.59955000	1.24981500
C	-0.50887500	1.06961500	2.20070000
C	1.77624900	0.82719000	1.20569500
C	2.25689000	1.39416000	0.00786800
C	2.68842500	0.44472900	2.19470700

C	3.62227600	1.61341200	-0.18395800
C	4.05359500	0.65922100	2.00902100
H	2.31988300	-0.01782400	3.10441200
C	4.51344500	1.24744000	0.82673100
H	3.99115800	2.07467200	-1.09242100
H	4.75664100	0.37482500	2.78628900
H	5.57598000	1.42617700	0.68640100
N	1.26416400	1.70372100	-0.93371900
C	1.51092400	2.54871800	-2.11976600
H	2.36553300	2.13037900	-2.66152700
H	0.63191700	2.42632000	-2.75640400
C	1.74313200	4.01328600	-1.80085100
C	2.90086600	4.66127300	-2.24375600
C	0.78174300	4.74680000	-1.09098900
C	3.10258900	6.01855700	-1.98146600
H	3.64918900	4.10381300	-2.80374200
C	0.98499700	6.09944100	-0.82263300
H	-0.12755400	4.25357400	-0.75868500
C	2.14599500	6.73928400	-1.26667200
H	4.00730800	6.50814700	-2.33181800
H	0.23380900	6.65757500	-0.27025200
H	2.30161800	7.79409800	-1.05701200
C	-0.01879400	1.27223700	-0.70013500
O	-1.03372900	1.76205600	-1.11934800
Cl	-0.50912700	-1.86688400	-2.53252400
Pd	-0.20517100	-0.92422300	-0.23360000
N	1.68839500	-1.55793100	-0.38424600
C	2.56914600	-2.30578000	-0.38948500
C	3.57110900	-3.31817900	-0.33317900
C	3.19433500	-4.56297300	0.20566000
C	4.87690700	-3.08847700	-0.79607700
C	4.14413000	-5.57883100	0.27285600
H	2.17525900	-4.70095900	0.55661900
C	5.81100500	-4.11730900	-0.71943700
H	5.14422500	-2.11910100	-1.20382600
C	5.44552200	-5.35809100	-0.18758800
H	3.86694300	-6.54439400	0.68479300
H	6.82379700	-3.95309200	-1.07487400
H	6.17997100	-6.15678000	-0.13213600
N	-2.19182500	-0.69529400	-0.28732300
C	-3.27149500	-0.77942100	-0.68816500
Cl	-0.45112900	-3.13676700	1.16555600
C	-4.56484000	-0.93291900	-1.26885500
C	-5.71486200	-0.43405600	-0.63506600
C	-4.64567000	-1.60244000	-2.50423600
C	-6.95258500	-0.60990200	-1.24743200
H	-5.62508000	0.07607400	0.31814900
C	-5.89311600	-1.76878200	-3.09929500
H	-3.73632500	-1.97379400	-2.96725300
C	-7.04187700	-1.27474000	-2.47424700
H	-7.84915700	-0.22890300	-0.76761500
H	-5.96827800	-2.28457000	-4.05177000
H	-8.01190400	-1.40841600	-2.94501500
Cl	0.15035000	2.22054000	3.40843100
C	-1.93967000	0.79821900	2.43872900
C	-2.86773800	1.85322900	2.49885700
C	-2.36602700	-0.51491300	2.69738700
C	-4.20455900	1.59572600	2.78882400
H	-2.53592000	2.87062800	2.31604500
C	-3.70353400	-0.76200300	3.01078200
H	-1.65866700	-1.33720600	2.63931400
C	-4.62423000	0.28664100	3.05590700
H	-4.91615200	2.41630800	2.82419400
H	-4.02006700	-1.78014000	3.21884300
H	-5.66304500	0.09037500	3.31032000

Zero-point correction= 0.524057 (Hartree/Particle)

Thermal correction to Energy= 0.565304

Thermal correction to Enthalpy= 0.566248

Thermal correction to Gibbs Free Energy= 0.440689

Sum of electronic and zero-point Energies= -3133.705454

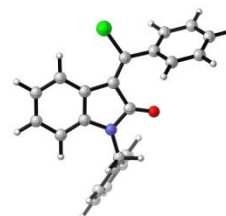
Sum of electronic and thermal Energies= -3133.664207

Sum of electronic and thermal Enthalpies= -3133.663263

Sum of electronic and thermal Free Energies= -3133.788822

E(RM06L) = -3135.98304318

E-1b



C	-0.07330200	3.25230700	0.25655200
C	0.01490200	1.90537800	-0.10431100
C	1.25761500	1.40595300	-0.56519100
C	2.39117100	2.20362600	-0.65616100
C	2.27691600	3.54876200	-0.28451200
C	1.06058500	4.06770700	0.16152600
H	-1.00670200	3.67207500	0.60614200
H	3.33954000	1.79663700	-0.98937200
H	3.15094300	4.19156400	-0.34357600
H	0.98900300	5.11381000	0.44415100
N	1.12923500	0.05502400	-0.90183700
C	-0.16682900	-0.39788800	-0.68629900
O	-0.52663500	-1.54933500	-0.88139200
C	-0.94366600	0.79228300	-0.15349900
C	2.17497100	-0.80320600	-1.44360100
H	2.68292300	-0.26666600	-2.25362600
H	1.64826000	-1.65656600	-1.88157300
C	3.18500900	-1.27999900	-0.41383900
C	2.76018600	-2.01822200	0.69991000
C	4.54908100	-1.01649900	-0.57254700
C	3.68466100	-2.47369500	1.63854700
H	1.70300700	-2.24026700	0.82059800
C	5.47792100	-1.47549100	0.36529800
H	4.89057500	-0.45255500	-1.43855900
C	5.04655600	-2.20266100	1.47454800
H	3.34352100	-3.04570500	2.49737900
H	6.53472800	-1.26165300	0.22889200
H	5.76578000	-2.55913500	2.20705500
C	-2.23616100	0.69201500	0.24589800
Cl	-2.99167500	2.06026800	1.07850600
C	-3.15989500	-0.44802700	0.07013600
C	-3.89771000	-0.94238700	1.15909400
C	-3.35545800	-1.01604000	-1.19879200
C	-4.78957600	-1.99814100	0.98642700
C	-4.26076600	-2.06019700	-1.37070500
C	-4.97628500	-2.55784700	-0.27962200
H	-5.34300500	-2.37965100	1.83997200
H	-4.40691200	-2.48552100	-2.35958700
H	-5.67987700	-3.37467300	-0.41597200
H	-2.80075600	-0.63234800	-2.04736700
H	-3.76369300	-0.50078600	2.14171200

Zero-point correction= 0.321165 (Hartree/Particle)

Thermal correction to Energy= 0.341214

Thermal correction to Enthalpy= 0.342158

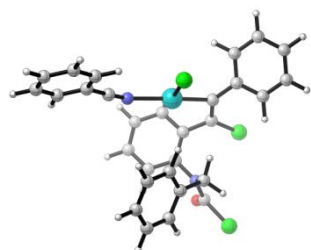
Thermal correction to Gibbs Free Energy= 0.269241

Sum of electronic and zero-point Energies= -1437.819159

Sum of electronic and thermal Energies= -1437.799110

Sum of electronic and thermal Enthalpies= -1437.798166
 Sum of electronic and thermal Free Energies= -1437.871083
 E(RM06L) = -1438.39497284

IB_{mono}



C	-1.39714500	1.88268300	0.34023900
C	-2.17238800	0.92922000	0.87537100
C	-1.75231300	3.11475200	-0.36370500
C	-2.73462200	3.11042600	-1.37115400
C	-1.13082400	4.33166900	-0.03133100
C	-3.09576100	4.29375500	-2.01254800
C	-1.50402300	5.51377200	-0.66465800
H	-0.34789600	4.33776400	0.72019200
C	-2.48681400	5.49921900	-1.65801600
H	-3.85448200	4.27303700	-2.79028600
H	-1.01859100	6.44673300	-0.39145500
H	-2.77084700	6.42141900	-2.15796900
C	-1.44947100	-0.17271500	1.56358800
C	-0.58985100	0.18995800	2.63728600
C	-1.55025600	-1.54540100	1.21404600
C	0.14850000	-0.79201900	3.33016800
C	-0.82001300	-2.49420500	1.91395700
C	0.02897800	-2.12292200	2.97055700
H	0.78564000	-0.49486900	4.15760500
H	-0.90935200	-3.53679100	1.62804000
H	-0.64917000	1.20066700	3.03162000
H	0.58301900	-2.88967800	3.50366800
Pd	0.45671900	1.14264900	0.66362200
Cl	1.41493200	2.26423500	-1.18252500
N	2.44356800	0.28113400	1.00378100
C	3.56914100	0.11581700	0.77777700
C	4.94523000	-0.01511200	0.41609300
C	5.41952400	0.75220100	-0.66412100
C	5.80136200	-0.88269900	1.11485200
C	6.75657000	0.64321000	-1.03676200
H	4.73592700	1.41391400	-1.18737100
C	7.13530900	-0.97895000	0.72838000
H	5.41921300	-1.46795100	1.94506600
C	7.61184900	-0.21850300	-0.34373000
H	7.13118600	1.23167500	-1.86877500
H	7.80377200	-1.64695200	1.26307800
H	8.65396800	-0.29823100	-0.63987600
Cl	-3.94034000	0.93644300	0.96543000
N	-2.38499900	-1.95325000	0.11410300
C	-3.49808100	-2.66747000	0.45166700
C	-1.90328700	-1.63620200	-1.25137900
H	-2.73936000	-1.78618700	-1.93364100
H	-1.65447700	-0.57243500	-1.26995200
O	-3.85806300	-2.95657700	1.55860400
Cl	-4.50336500	-3.21632200	-0.97490400
C	-0.69864600	-2.45726500	-1.67342600
C	-0.76674900	-3.85672100	-1.73833300
C	0.49315300	-1.81654000	-2.03232000
C	0.33850400	-4.60047700	-2.14993500
H	-1.69088400	-4.36443200	-1.47334600
C	1.59912900	-2.56233400	-2.45052500

H	0.56080400	-0.73168900	-1.98838700
C	1.52558000	-3.95412400	-2.50778700
H	0.27150400	-5.68420700	-2.19938700
H	2.51605900	-2.05016800	-2.72975100
H	2.38513400	-4.53455700	-2.83283000
H	-3.21208700	2.17634000	-1.64841200

Zero-point correction= 0.423703 (Hartree/Particle)

Thermal correction to Energy= 0.457963

Thermal correction to Enthalpy= 0.458907

Thermal correction to Gibbs Free Energy= 0.348023

Sum of electronic and zero-point Energies= -2809.361608

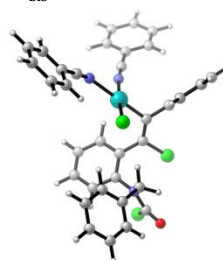
Sum of electronic and thermal Energies= -2809.327348

Sum of electronic and thermal Enthalpies= -2809.326404

Sum of electronic and thermal Free Energies= -2809.437289

E(RM06L) = -2811.43707934

IB_{bis}

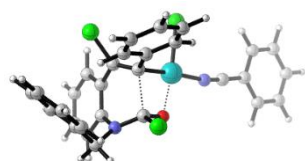


C	1.41335000	-1.58202500	1.95241900
C	1.30325200	-0.91470300	3.18589300
C	2.33525600	-2.64105100	1.84011600
C	2.08318200	-1.30476700	4.27473400
C	3.11645900	-3.02358000	2.93015100
H	2.41661700	-3.17442200	0.89760300
C	2.99482600	-2.35548800	4.15213800
H	1.97718900	-0.78408800	5.22285600
H	3.80960100	-3.85586300	2.83066700
H	3.60137900	-2.65632600	5.00233800
C	0.61774300	-1.15133600	0.78538500
C	-0.26875900	-1.88038700	0.09285900
Pd	1.11169100	0.71894100	0.23141900
N	2.88180900	-0.03290700	-0.58495400
C	3.91556700	-0.48656900	-0.85230900
C	5.18976300	-1.06526000	-1.14079100
C	5.76890200	-1.94056700	-0.20353600
C	5.85113300	-0.76082000	-2.34363700
C	7.01038600	-2.50657800	-0.47965200
H	5.24153800	-2.16371000	0.71873100
C	7.09188300	-1.33575000	-2.60328100
H	5.39128500	-0.08428600	-3.05675800
C	7.67036400	-2.20610200	-1.67471100
H	7.46337500	-3.18320900	0.23851400
H	7.60764500	-1.10574900	-3.53058400
H	8.63855300	-2.65195900	-1.88368600
C	-0.98520100	-1.47385900	-1.14391900
C	-0.22834300	-1.01043600	-2.23472700
C	-2.38860800	-1.52916600	-1.29728600
C	-0.82987000	-0.58459200	-3.41751700
H	0.85215000	-1.00611900	-2.14845000
C	-2.98834800	-1.08376000	-2.47901800
C	-2.21827200	-0.61486100	-3.54072200
H	-0.21187600	-0.23709200	-4.24110000
H	-4.07033900	-1.11474400	-2.55156900
H	-2.70119700	-0.28009300	-4.45430700
Cl	-0.61810100	-3.55507700	0.63085800
N	1.60417400	2.83210000	-0.26569500
C	1.36818300	3.96751300	-0.22835800

C	0.98227600	5.33939300	-0.11900200
C	1.74947200	6.36060900	-0.70370600
C	-0.19324900	5.63765000	0.59462800
C	1.33523700	7.68316600	-0.57147900
H	2.65360300	6.11290700	-1.25062200
C	-0.59232100	6.96598200	0.71689500
H	-0.76670100	4.82810300	1.03616600
C	0.16811600	7.98533000	0.13651100
H	1.92233400	8.47871500	-1.02038300
H	-1.49793700	7.20539100	1.26596700
H	-0.14947200	9.01945100	0.23599500
Cl	-0.79740000	1.54844300	1.34551300
H	0.59961500	-0.09305700	3.27598000
N	-3.23906900	-1.97218800	-0.22970700
C	-3.92052600	-3.14620100	-0.21594800
O	-4.71150300	-3.51271200	0.61436300
Cl	-3.53855500	-4.24619700	-1.62103200
C	-3.53871400	-1.01370700	0.87487200
H	-2.62279000	-0.45105200	1.06460600
H	-3.76673300	-1.61753700	1.75483200
C	-4.68275500	-0.07328500	0.54597300
C	-6.01633200	-0.49732700	0.65716400
C	-4.41985500	1.23492600	0.11786400
C	-7.06273000	0.36875200	0.33898500
H	-6.22578900	-1.50964800	0.98956100
C	-5.46891600	2.10154400	-0.19853800
H	-3.38978700	1.57468300	0.04945600
C	-6.79205600	1.67065500	-0.09094100
H	-8.09106300	0.02840100	0.43175300
H	-5.25060900	3.11516200	-0.52598400
H	-7.60874500	2.34559800	-0.33508000

Zero-point correction= 0.525118 (Hartree/Particle)
 Thermal correction to Energy= 0.567025
 Thermal correction to Enthalpy= 0.567969
 Thermal correction to Gibbs Free Energy= 0.438665
 Sum of electronic and zero-point Energies= -3133.771389
 Sum of electronic and thermal Energies= -3133.729481
 Sum of electronic and thermal Enthalpies= -3133.728537
 Sum of electronic and thermal Free Energies= -3133.857842
 E(RM06L) = -3136.02928732

TS_{1,2-Add,6-mem}

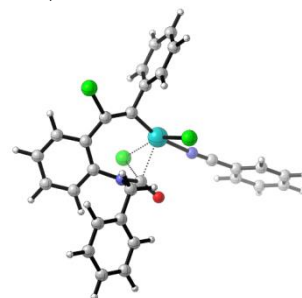


C	0.82894800	0.61561000	0.31134600
C	0.96687300	-1.79480600	1.04119100
C	1.25330500	-2.36481500	-0.23008100
C	0.63338600	-2.65616900	2.10419400
C	1.21332600	-3.75666700	-0.39043800
C	0.57730000	-4.03083000	1.92588300
H	0.40721400	-2.22142300	3.07168200
C	0.87739300	-4.58392800	0.67468700
H	1.41796600	-4.17975000	-1.36902700
H	0.29731400	-4.67272100	2.75571000
H	0.83080300	-5.65896100	0.52573800
N	1.62903400	-1.53664900	-1.31900800
C	2.96680500	-1.72736600	-1.92442600
H	3.11052800	-2.81092200	-1.96834000
H	2.92131500	-1.36879500	-2.95246100
C	4.14187100	-1.09378300	-1.19612000
C	4.56662900	-1.58133900	0.04910800

C	4.85322400	-0.04151500	-1.78524300
C	5.66378900	-1.01415900	0.69779600
H	4.04024500	-2.41078900	0.51353900
C	5.96017400	0.51895500	-1.14410900
H	4.53440200	0.34552100	-2.74875000
C	6.36466300	0.03783400	0.10190200
H	5.97588700	-1.39896800	1.66482800
H	6.50173700	1.33339500	-1.61768900
H	7.22303500	0.47508800	0.60476700
C	0.80245300	-0.42341700	-1.49025600
O	-0.46220700	-0.62093400	-1.56421400
Cl	1.46656000	0.78008000	-2.68738300
Pd	-1.24288600	0.31771900	0.06247600
N	-3.28898200	-0.01059700	-0.33880700
C	-4.44424000	-0.06275400	-0.40860100
C	-5.87205000	-0.10472100	-0.44966700
C	-6.60018400	0.45341100	0.61664000
C	-6.53432500	-0.69378300	-1.54063500
C	-7.99146700	0.41726000	0.58254300
H	-6.06995300	0.90435000	1.44925700
C	-7.92603400	-0.72174000	-1.55869900
H	-5.95799500	-1.11916600	-2.35584500
C	-8.65306500	-0.16814500	-0.50078500
H	-8.55969700	0.84668600	1.40204300
H	-8.44389500	-1.17498700	-2.39856100
H	-9.73890400	-0.19278500	-0.52112000
Cl	-1.90317600	1.39352100	2.06497300
C	1.37075100	1.98705700	0.28802000
C	2.76323600	2.18812400	0.36971900
C	0.54421600	3.11035800	0.11333300
C	3.30354500	3.46934900	0.30293100
H	3.42363300	1.33507300	0.48108500
C	1.08809500	4.39238100	0.05267800
H	-0.52971700	2.97504600	0.05002100
C	2.46827700	4.57840400	0.14710300
H	4.38059200	3.59925300	0.36920100
H	0.42869600	5.24750600	-0.06894300
H	2.89075600	5.57860300	0.09519800
C	1.13330200	-0.35298000	1.23691600
Cl	1.93572700	0.07209800	2.75656400

Zero-point correction= 0.423147 (Hartree/Particle)
 Thermal correction to Energy= 0.455798
 Thermal correction to Enthalpy= 0.456743
 Thermal correction to Gibbs Free Energy= 0.352813
 Sum of electronic and zero-point Energies= -2809.322967
 Sum of electronic and thermal Energies= -2809.290315
 Sum of electronic and thermal Enthalpies= -2809.289371
 Sum of electronic and thermal Free Energies= -2809.393301
 E(RM06L) = -2811.39823545

TS_{0A,6-mem}

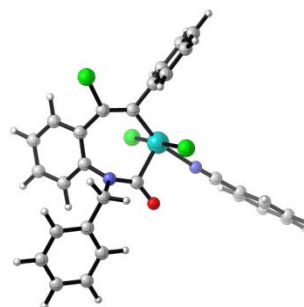


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C	2.67355200	-0.31401200	0.84933200
C	3.87530500	1.60684100	1.62044100
C	3.50466000	-1.13160600	1.62311300

C	4.70187900	0.79606000	2.39030200
H	4.02589600	2.67838200	1.64166000
C	4.52302800	-0.58650900	2.39675900
H	3.33567400	-2.20276500	1.60283500
H	5.48420800	1.25236400	2.99029900
H	5.16120200	-1.23115100	2.99357700
N	1.70022900	-1.00343800	0.05047100
C	2.08380100	-1.50053100	-1.31512700
H	1.15182600	-1.61009800	-1.87454400
H	2.64425900	-0.68225500	-1.77411500
C	2.89687600	-2.77470500	-1.29742800
C	2.28346300	-4.01282600	-1.05086700
C	4.27591300	-2.73636700	-1.53810900
C	3.03919500	-5.18460500	-1.03919800
H	1.21347200	-4.05380200	-0.86655900
C	5.03218900	-3.91023100	-1.53322700
H	4.75927400	-1.78218200	-1.73381600
C	4.41507200	-5.13628800	-1.28146800
H	2.55293900	-6.13765600	-0.84910000
H	6.10063600	-3.86545700	-1.72608400
H	5.00129000	-6.05131800	-1.27796100
C	0.46280100	-1.30009000	0.45707600
O	-0.28799900	-2.20378700	0.31245800
Cl	0.04702700	-0.07629100	2.42140300
Pd	-0.78271300	0.64769700	0.21299900
C	1.94694200	2.03338400	0.10532200
C	0.62313200	2.03720300	-0.11313200
Cl	-1.06450800	0.37015700	-2.16601800
N	-2.71646700	-0.42049200	0.51282700
C	-3.74821500	-0.94543900	0.47302100
C	-5.02139400	-1.59175200	0.39199800
C	-5.64598200	-1.72274100	-0.86100300
C	-5.63552800	-2.08895700	1.55433800
C	-6.88531100	-2.35197300	-0.94196500
H	-5.15556700	-1.33443500	-1.74775700
C	-6.87499300	-2.71544000	1.45640500
H	-5.13979300	-1.98139500	2.51365900
C	-7.49881400	-2.84675500	0.21242100
H	-7.37248600	-2.45645900	-1.90669000
H	-7.35435300	-3.10169600	2.35085000
H	-8.46590500	-3.33660700	0.14250900
C	-0.17399400	3.21730400	-0.50996400
C	-0.36377700	3.60132800	-1.85056200
C	-0.77458000	3.98188000	0.51039100
C	-1.12051000	4.72841300	-2.15423100
H	0.07858000	3.00515800	-2.63934900
C	-1.54353200	5.10281800	0.19693200
H	-0.62073900	3.69606700	1.54731300
C	-1.71688700	5.47972600	-1.13535300
H	-1.25288100	5.02031000	-3.19257600
H	-1.99864900	5.68376700	0.99462000
H	-2.31203500	6.35515100	-1.38159900
Cl	2.81612900	3.53091500	-0.41360000

Zero-point correction= 0.422424 (Hartree/Particle)
 Thermal correction to Energy= 0.456183
 Thermal correction to Enthalpy= 0.457127
 Thermal correction to Gibbs Free Energy= 0.348300
 Sum of electronic and zero-point Energies= -2809.332631
 Sum of electronic and thermal Energies= -2809.298872
 Sum of electronic and thermal Enthalpies= -2809.297927
 Sum of electronic and thermal Free Energies= -2809.406754
 E(RM06L) = -2811.40830651

IIIB

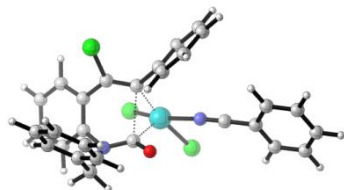


C	2.67691400	-1.12597000	-0.92740700
C	2.56432600	0.25868700	-0.71709300
C	3.51027300	-1.55636900	-1.97803900
C	3.22012300	1.16515700	-1.56014900
C	4.18340700	-0.65684000	-2.79563100
H	3.60880900	-2.61986700	-2.15997900
C	4.03298500	0.71533900	-2.59529100
H	3.08717300	2.22680400	-1.38960800
H	4.81051700	-1.03024400	-3.60018000
H	4.53645600	1.43050000	-3.23898400
N	1.82833700	0.82861700	0.38335700
C	2.57654100	1.45117500	1.52523800
H	1.84995300	1.54098700	2.33689000
H	3.31672400	0.70364000	1.82412300
C	3.25118300	2.77837700	1.25039200
C	2.49973900	3.95374100	1.09431000
C	4.64800700	2.85220700	1.17901800
C	3.13719400	5.17163800	0.85959500
H	1.41625200	3.90792900	1.15311800
C	5.28707200	4.07287500	0.95247100
H	5.23907600	1.94765600	1.30166200
C	4.53193200	5.23489100	0.78901300
H	2.54477500	6.07472900	0.73970900
H	6.37179400	4.11398800	0.90269900
H	5.02613600	6.18630100	0.61157900
C	0.50563000	1.05859100	0.33664700
O	-0.15407600	1.99406900	0.67369100
Cl	-0.45102500	-0.59883500	-2.42778200
Pd	-0.70675400	-0.59294900	-0.08501000
C	1.88830700	-2.13622600	-0.19383500
C	0.58822400	-2.13005600	0.11171800
Cl	-0.99748200	-0.58797900	2.30763200
N	-2.63922900	0.63033200	-0.29395700
C	-3.65022400	1.19368800	-0.33494200
C	-4.89778700	1.89270600	-0.37311400
C	-5.53906600	2.23116300	0.83130300
C	-5.47105800	2.23384100	-1.61036000
C	-6.75356600	2.91067400	0.78959500
H	-5.08230100	1.96000300	1.77755400
C	-6.68593700	2.91350600	-1.63515100
H	-4.96318300	1.96531500	-2.53099700
C	-7.32599100	3.25117400	-0.43928700
H	-7.25366600	3.17452900	1.71655100
H	-7.13360800	3.17964300	-2.58791300
H	-8.27387000	3.78123800	-0.46516300
C	-0.25064400	-3.27718800	0.49855900
C	-1.06844400	-3.86808100	-0.48488900
C	-0.26322000	-3.79704600	1.80640500
C	-1.87410500	-4.96174900	-0.16529600
H	-1.05689400	-3.46626900	-1.49397700
C	-1.05912400	-4.89565300	2.11191900
H	0.34984300	-3.33061400	2.56852100
C	-1.87006800	-5.47797900	1.13081200
H	-2.49858100	-5.41157000	-0.93231900

H	-1.05548200	-5.29639900	3.12188800
H	-2.49557100	-6.33121800	1.37959500
Cl	2.78494600	-3.65637800	0.12728700

Zero-point correction= 0.423376 (Hartree/Particle)
 Thermal correction to Energy= 0.457624
 Thermal correction to Enthalpy= 0.458568
 Thermal correction to Gibbs Free Energy= 0.349031
 Sum of electronic and zero-point Energies= -2809.345848
 Sum of electronic and thermal Energies= -2809.311600
 Sum of electronic and thermal Enthalpies= -2809.310656
 Sum of electronic and thermal Free Energies= -2809.420193
 E(RM06L) = -2811.42591522

TS_{RE,6-mem}

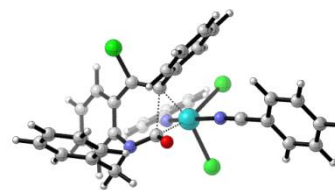


C	0.46795300	-0.16362300	1.21985700
C	2.89320300	-0.75050700	0.80024600
C	2.92379000	-0.89326000	-0.60067300
C	3.93341400	-1.32664100	1.54834000
C	3.94248100	-1.63371800	-1.21037900
C	4.95403600	-2.04504300	0.93854500
H	3.91786800	-1.21799300	2.62691600
C	4.95351500	-2.20862200	-0.44843000
H	3.92608200	-1.78085200	-2.28529900
H	5.73829600	-2.48939400	1.54403500
H	5.73001400	-2.79037700	-0.93613000
N	1.97048300	-0.24320100	-1.44041000
C	2.48780600	0.65747800	-2.53254900
H	3.36270200	0.16134400	-2.95157100
H	1.71294500	0.69194000	-3.29897800
C	2.84025900	2.04415900	-2.04344400
C	4.09576600	2.29713300	-1.47227700
C	1.91862500	3.09529500	-2.15311500
C	4.42055500	3.57283500	-1.01099000
H	4.82117000	1.49185800	-1.38882400
C	2.24515900	4.37245400	-1.69449200
H	0.94569800	2.90771800	-2.59742900
C	3.49525600	4.61318500	-1.12081300
H	5.39676900	3.75516600	-0.57024900
H	1.52457000	5.18027400	-1.79017700
H	3.74968400	5.60800800	-0.76529200
C	0.65619700	-0.11033700	-1.19044800
O	-0.12430900	0.62850900	-1.72937500
Cl	-1.67820300	-3.21876200	-1.30995300
Pd	-0.41751500	-1.57398600	-0.08582600
N	-2.25875200	-0.45683900	-0.27633600
C	-3.34696000	-0.09897600	-0.43765100
C	-4.69560400	0.31096200	-0.66837900
C	-5.22501000	1.41894000	0.01551200
C	-5.47883400	-0.41428900	-1.58397200
C	-6.54243500	1.79886200	-0.22571800
H	-4.60446900	1.95863800	0.72363000
C	-6.79442700	-0.02025600	-1.81238100
H	-5.05024900	-1.27037700	-2.09506300
C	-7.32456200	1.08285200	-1.13688700
H	-6.96060300	2.65313500	0.29820300
H	-7.40658300	-0.57517200	-2.51677600
H	-8.35204800	1.38462000	-1.31963400
Cl	1.07667700	-3.25996000	0.43346900

C	-0.58127000	0.61280800	1.90757700
C	-0.82576200	1.95152200	1.55622800
C	-1.35926600	0.01791700	2.91605100
C	-1.82148000	2.67900300	2.20725200
H	-0.22997900	2.41525200	0.77600400
C	-2.35233800	0.74951200	3.56530900
H	-1.17355100	-1.01694800	3.18941000
C	-2.58805600	2.08145400	3.21275300
H	-1.99176800	3.71798900	1.93646100
H	-2.93971100	0.28063900	4.35009700
H	-3.35667900	2.65345700	3.72617500
C	1.78231900	-0.06320300	1.47574200
Cl	2.30810900	0.99573800	2.81882700

Zero-point correction= 0.423792 (Hartree/Particle)
 Thermal correction to Energy= 0.456838
 Thermal correction to Enthalpy= 0.457783
 Thermal correction to Gibbs Free Energy= 0.353024
 Sum of electronic and zero-point Energies= -2809.334871
 Sum of electronic and thermal Energies= -2809.301824
 Sum of electronic and thermal Enthalpies= -2809.300880
 Sum of electronic and thermal Free Energies= -2809.405638
 E(RM06L) = -2811.42511503

TS_{RE,6-mem,bis}



C	-0.21284300	0.54836000	1.15200700
C	2.09406600	1.47156300	0.74815600
C	2.02121400	1.67827500	-0.65144100
C	3.35848500	1.47265500	1.36446700
C	3.20811200	1.83686700	-1.38515300
C	4.52455700	1.64671800	0.63150800
H	3.40925300	1.32427600	2.43749300
C	4.44642400	1.82465800	-0.75440800
H	3.16050800	1.94788100	-2.46255100
H	5.48734600	1.64131600	1.13391600
H	5.34931300	1.95167000	-1.34550400
N	0.77858000	1.77135400	-1.31884300
C	0.55615000	2.87665400	-2.30557300
H	1.44589700	2.94127600	-2.93190000
H	-0.27332800	2.55480900	-2.93479300
C	0.26366200	4.21422400	-1.65794300
C	1.30445900	5.10404000	-1.35935500
C	-1.05395000	4.58416700	-1.34979500
C	1.03803200	6.33467600	-0.75720500
H	2.32953500	4.83303500	-1.59985700
C	-1.32079300	5.81541800	-0.74982500
H	-1.86443300	3.89952400	-1.58027500
C	-0.27591900	6.69272900	-0.45045400
H	1.85565200	7.01435000	-0.53245200
H	-2.34650500	6.09206800	-0.52054600
H	-0.48511500	7.65210100	0.01516600
C	-0.35069500	1.09313300	-0.94572100
O	-1.47481500	1.37246900	-1.28817200
Cl	0.02338400	-2.08772300	-2.58980800
Pd	-0.06836400	-1.00217200	-0.35951600
N	1.91718300	-1.22003400	-0.30252000
C	2.89776200	-1.82595900	-0.21860000
C	4.03474500	-2.67028600	-0.05883100
C	3.80797200	-3.95488200	0.47090800

C	5.32428000	-2.24566100	-0.41890600
C	4.89274900	-4.81234400	0.63427000
H	2.79552600	-4.24448600	0.73940500
C	6.39422100	-3.11884300	-0.24740600
H	5.47141300	-1.24865700	-0.82060200
C	6.17897400	-4.39759700	0.27675000
H	4.73261100	-5.80639200	1.04054500
H	7.39634000	-2.80400700	-0.52270700
H	7.01935600	-5.07382100	0.40688900
N	-2.05091900	-1.25861100	-0.47257700
C	-3.15944400	-1.54611000	-0.61162400
Cl	0.01548400	-3.18031300	1.08876400
C	-4.52582800	-1.90857800	-0.80351700
C	-5.50802200	-1.44132100	0.08715300
C	-4.86559100	-2.73585500	-1.88867800
C	-6.83523900	-1.80777500	-0.11832800
H	-5.22160000	-0.80731000	0.92012300
C	-6.19802800	-3.09170400	-2.07713400
H	-4.08859500	-3.08558300	-2.56058300
C	-7.17967400	-2.62925600	-1.19579900
H	-7.60212900	-1.45318100	0.56375400
H	-6.47019300	-3.73091400	-2.91148300
H	-8.21764500	-2.91130000	-1.34864900
C	-1.49561700	0.53130700	1.88249500
C	-1.85195200	-0.56146700	2.69208500
C	-2.36933600	1.62836200	1.78420400
C	-3.05103000	-0.54169000	3.40315100
H	-1.19607600	-1.42564800	2.73549200
C	-3.57181900	1.63615700	2.49075900
H	-2.10137900	2.47201300	1.15689100
C	-3.91483000	0.55396900	3.30595500
H	-3.31115700	-1.38756900	4.03396300
H	-4.23619700	2.49276400	2.41095400
H	-4.84619000	0.56714300	3.86698500
C	0.87446100	1.25246200	1.52917600
Cl	0.86459600	2.06941600	3.11439400

Zero-point correction= 0.524888 (Hartree/Particle)

Thermal correction to Energy= 0.565715

Thermal correction to Enthalpy= 0.566659

Thermal correction to Gibbs Free Energy= 0.442732

Sum of electronic and zero-point Energies= -3133.707076

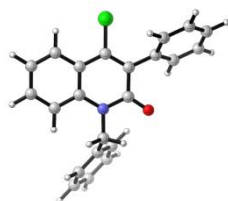
Sum of electronic and thermal Energies= -3133.666249

Sum of electronic and thermal Enthalpies= -3133.665305

Sum of electronic and thermal Free Energies= -3133.789232

E(RM06L) = -3135.98671399

2b



C	-0.04782800	3.41344300	0.47335200
C	-0.17637600	2.05995800	0.10124400
C	0.95827800	1.37774100	-0.41847200
C	2.18028300	2.07096600	-0.52948500
C	2.27308100	3.40343000	-0.15508900
C	1.15636400	4.08459800	0.34502500
H	-0.91597600	3.92928200	0.86484700
H	3.06586800	1.55822700	-0.87803900
H	3.22799100	3.91325700	-0.24705200
H	1.23182600	5.12734600	0.63732300
N	0.84528300	0.04430700	-0.80016900

C	-0.32712700	-0.70803700	-0.63283800
O	-0.33650700	-1.90950600	-0.89897800
C	1.97294000	-0.65656100	-1.44748100
H	2.39944800	0.01070600	-2.20195900
H	1.51871300	-1.50576600	-1.96119900
C	3.05221800	-1.14996000	-0.50055300
C	2.72451700	-1.94250300	0.60849100
C	4.39893000	-0.86546700	-0.75394100
C	3.72530500	-2.42314900	1.45221400
H	1.68502400	-2.19450900	0.79485800
C	5.40303500	-1.35193900	0.08665200
H	4.66797800	-0.26293900	-1.61984300
C	5.06728700	-2.12847100	1.19567600
H	3.45761100	-3.03605100	2.30888000
H	6.44364500	-1.12028300	-0.12450400
H	5.84494100	-2.50532700	1.85450500
C	-1.41048800	1.31536200	0.21707700
C	-1.52490900	0.00480100	-0.14210300
Cl	-2.79671000	2.16017300	0.89707100
C	-2.78284500	-0.78721000	-0.07974200
C	-2.84595800	-1.96879600	0.67454600
C	-3.91879800	-0.38089500	-0.79554100
C	-4.02514500	-2.70983500	0.73123900
H	-1.96725400	-2.30688300	1.21277500
C	-5.09473400	-1.12902300	-0.74693400
H	-3.87694100	0.52078400	-1.39907200
C	-5.15303700	-2.29323200	0.02090900
H	-4.06010700	-3.61853800	1.32615800
H	-5.96381900	-0.80206400	-1.31151100
H	-6.06974800	-2.87560100	0.06117200

Zero-point correction= 0.322201 (Hartree/Particle)

Thermal correction to Energy= 0.341812

Thermal correction to Enthalpy= 0.342756

Thermal correction to Gibbs Free Energy= 0.271917

Sum of electronic and zero-point Energies= -1437.829979

Sum of electronic and thermal Energies= -1437.810368

Sum of electronic and thermal Enthalpies= -1437.809423

Sum of electronic and thermal Free Energies= -1437.880263

E(RM06L) = -1438.40879646

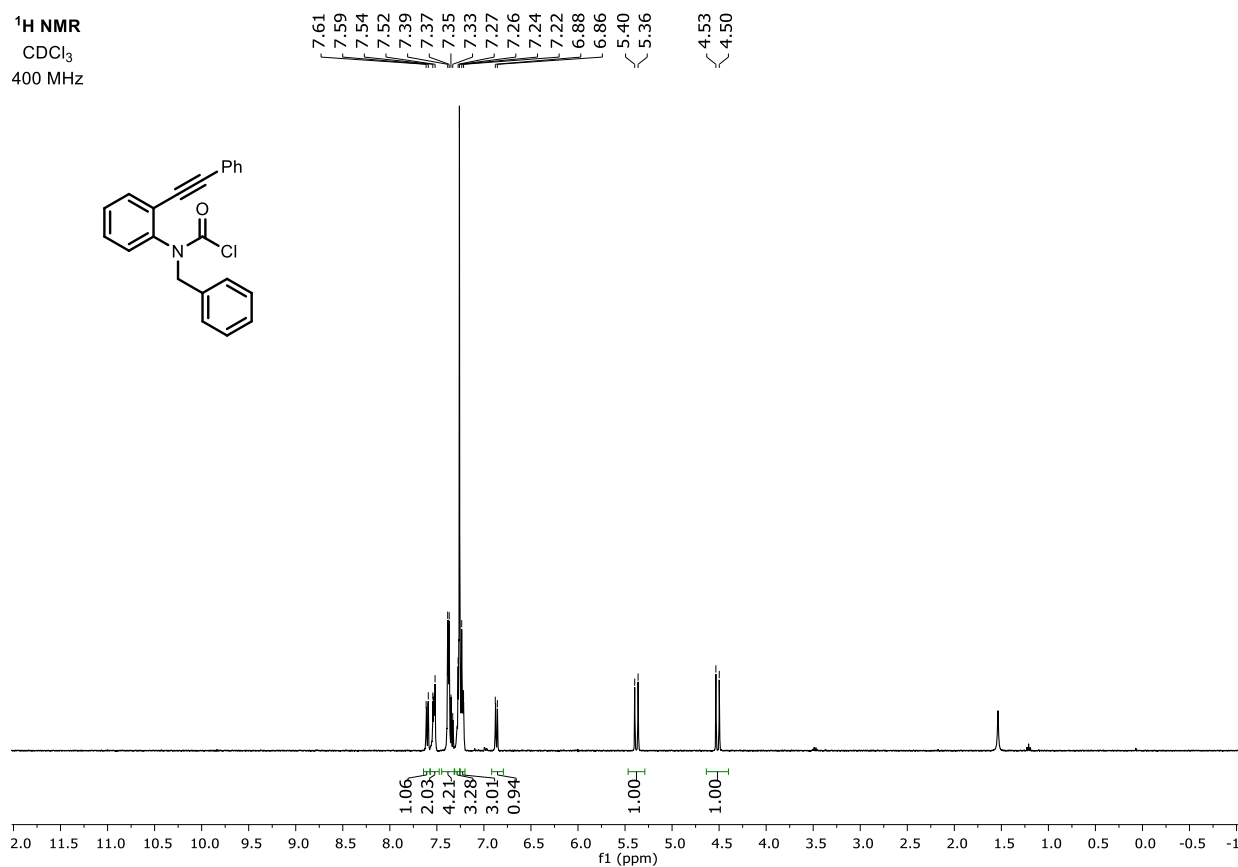
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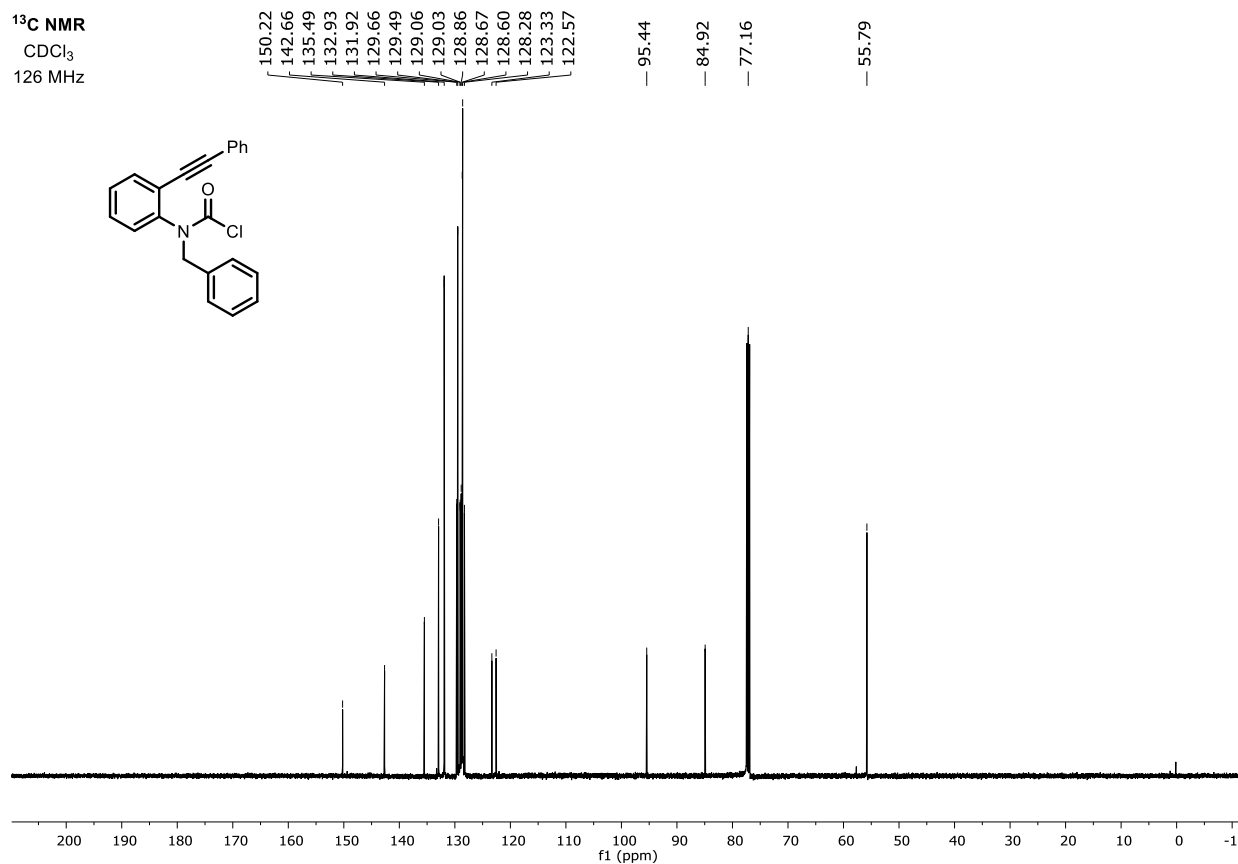
NMR Spectra for New Compounds

benzyl(2-(phenylethynyl)phenyl)carbamic chloride (1b')

¹H NMR
CDCl₃
400 MHz

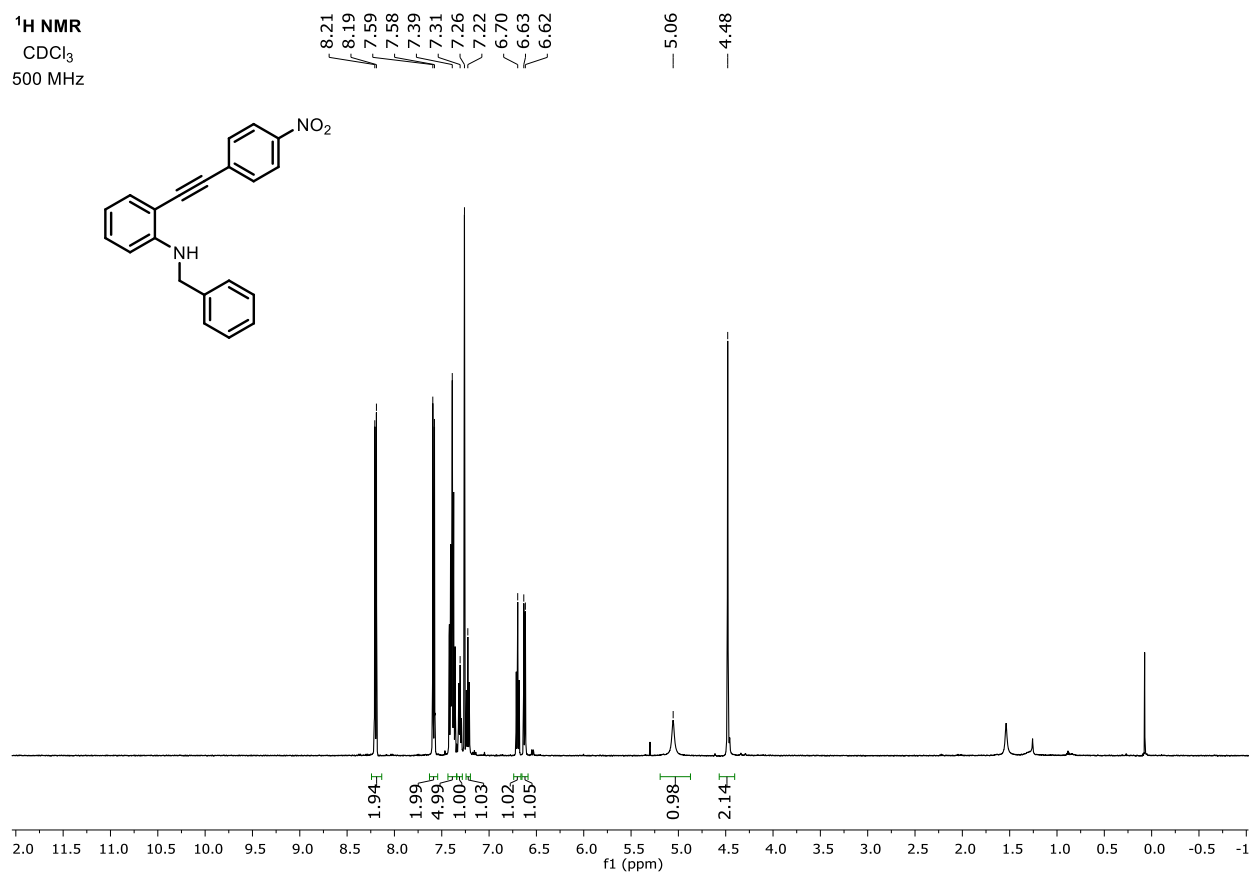


¹³C NMR
CDCl₃
126 MHz

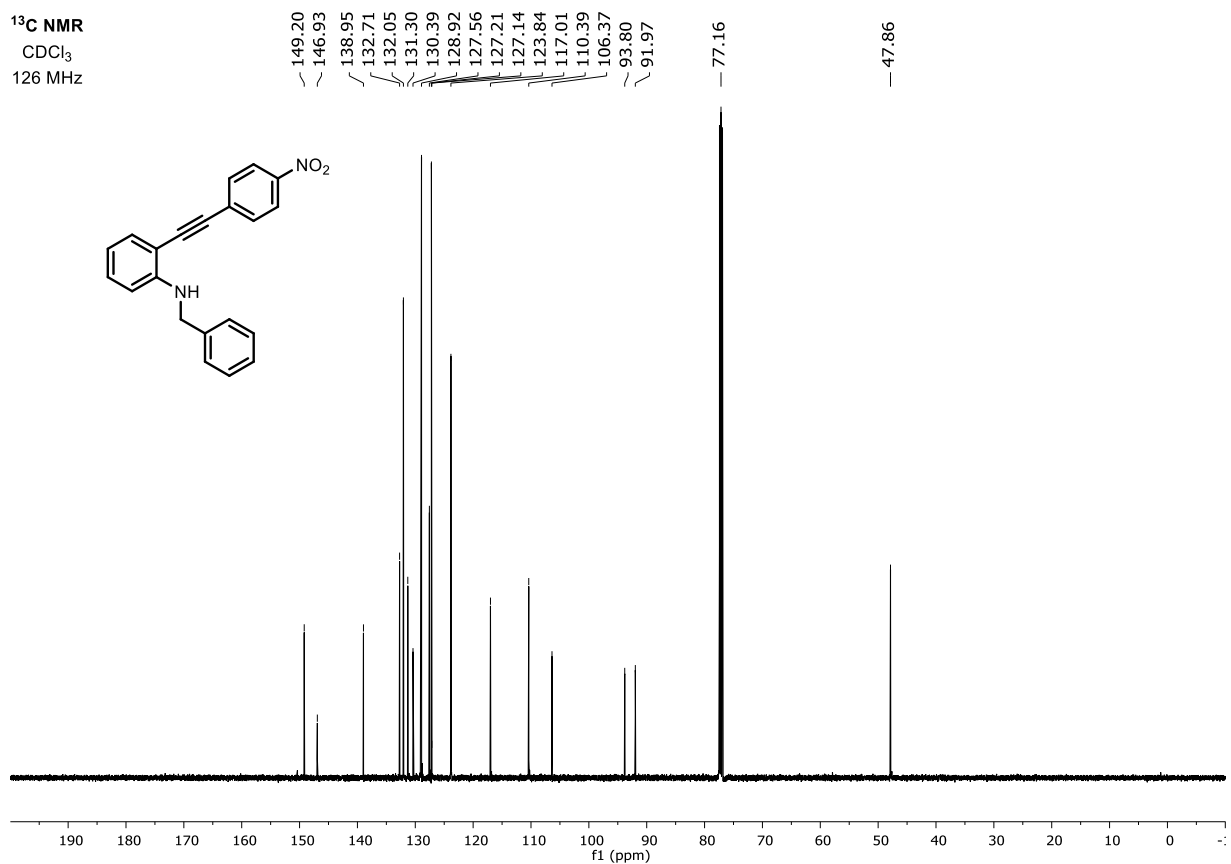


***N*-benzyl-2-((4-nitrophenyl)ethynyl)aniline (5c)**

¹H NMR
CDCl₃
500 MHz

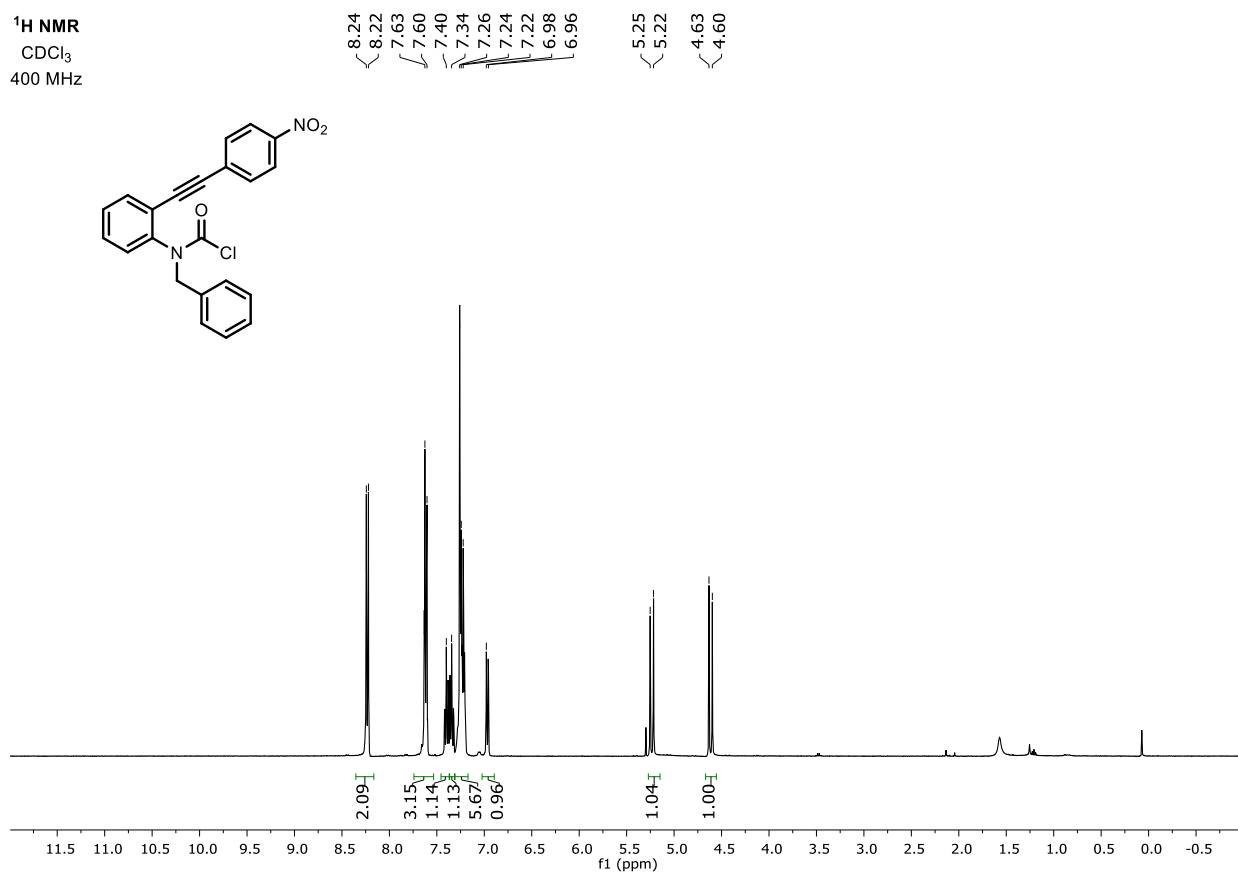


¹³C NMR
CDCl₃
126 MHz

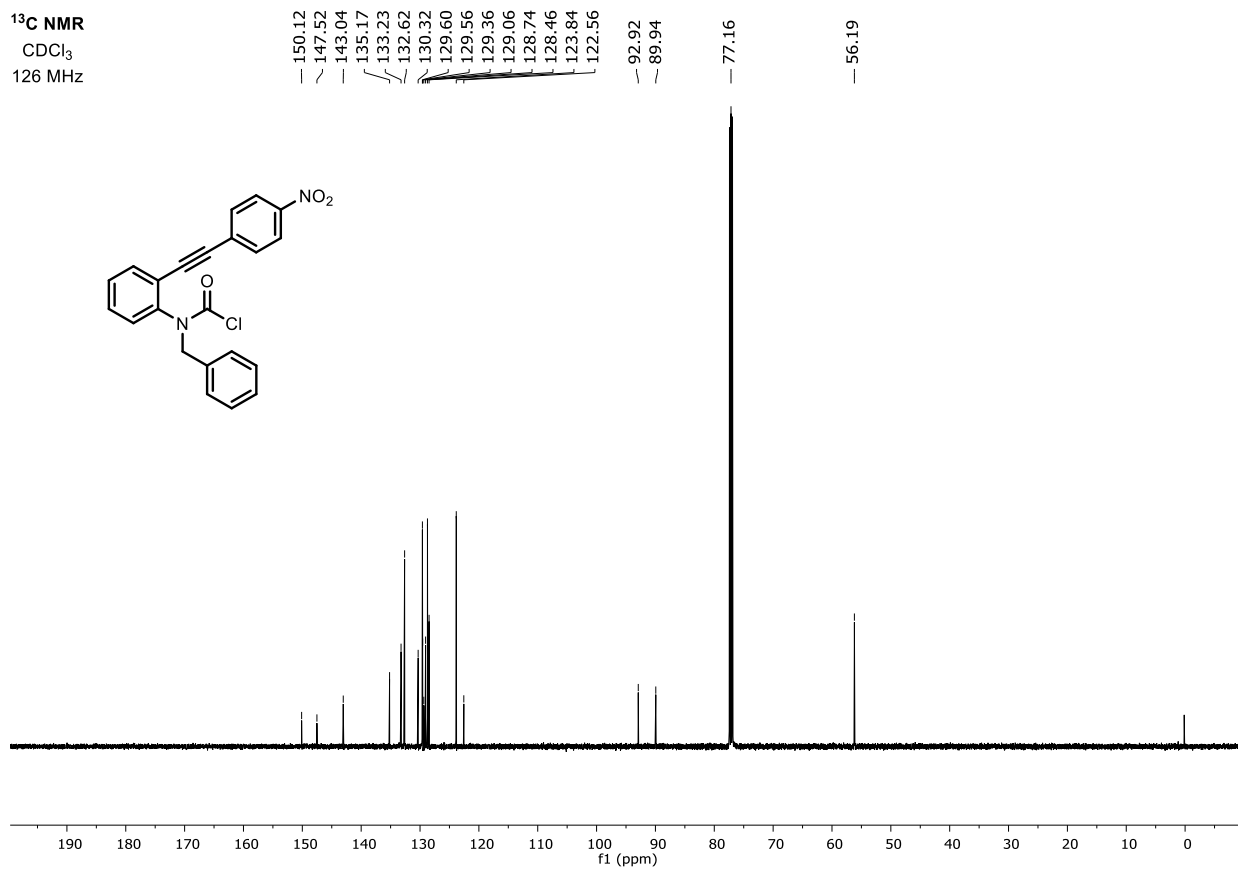


benzyl(2-((4-nitrophenyl)ethynyl)phenyl)carbamic chloride (1c')

¹H NMR
CDCl₃
400 MHz

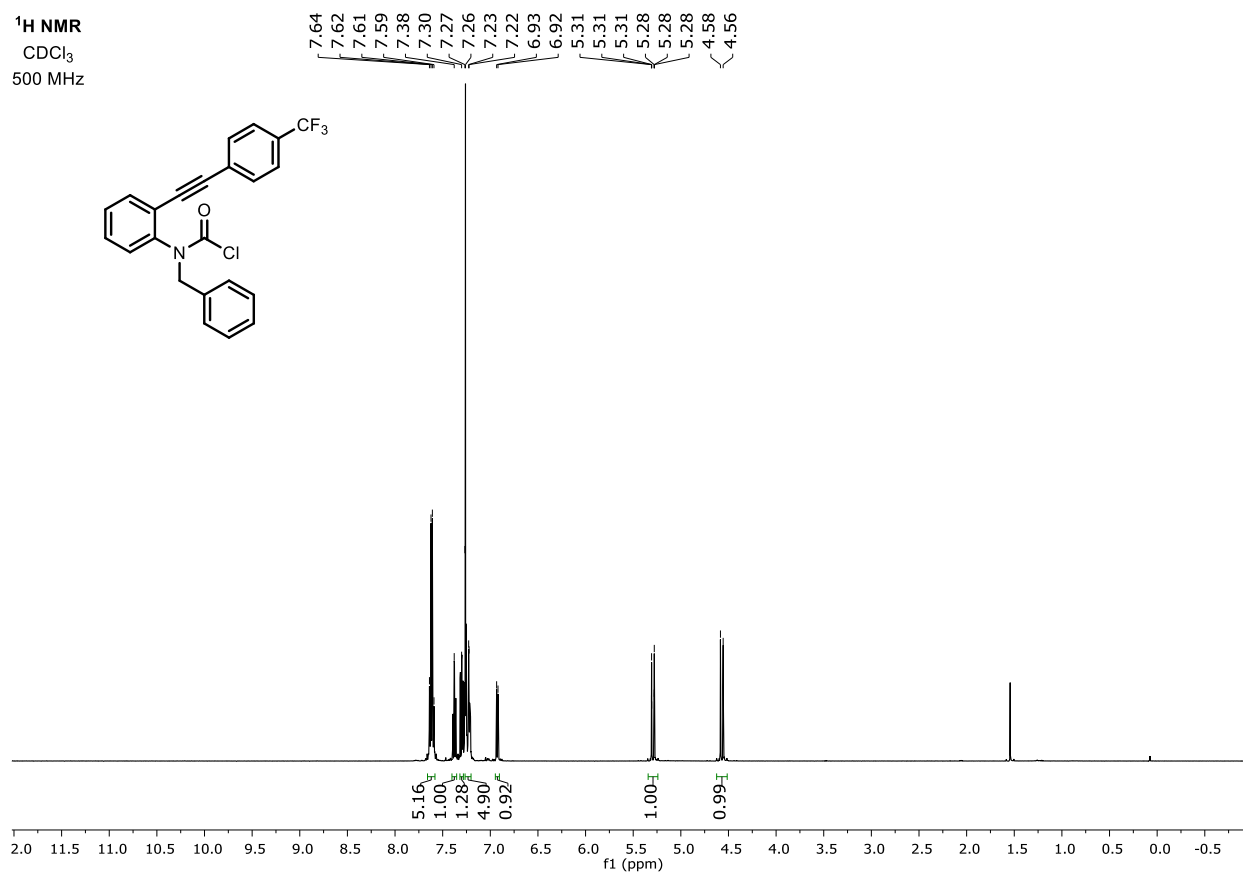


¹³C NMR
CDCl₃
126 MHz

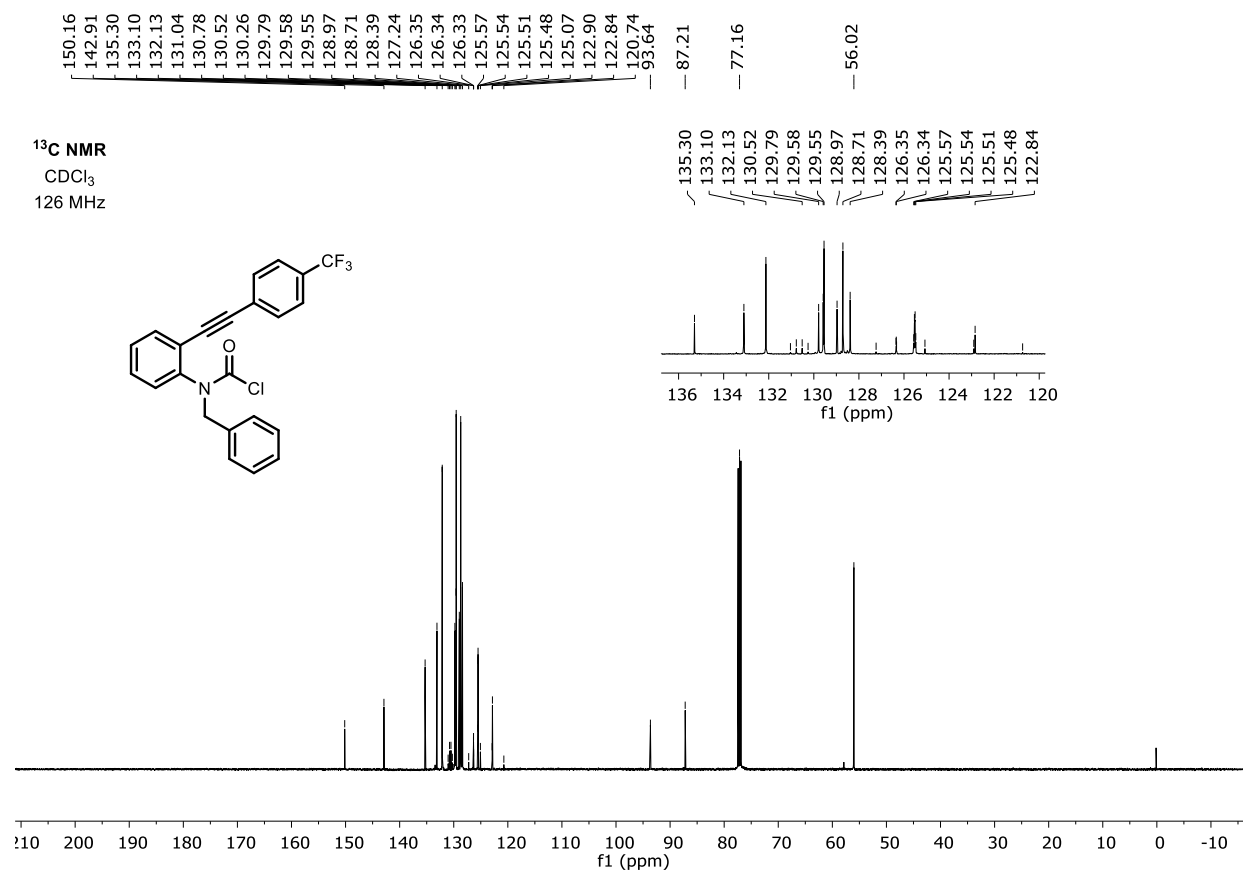


benzyl(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)carbamic chloride (1d')

¹H NMR
CDCl₃
500 MHz

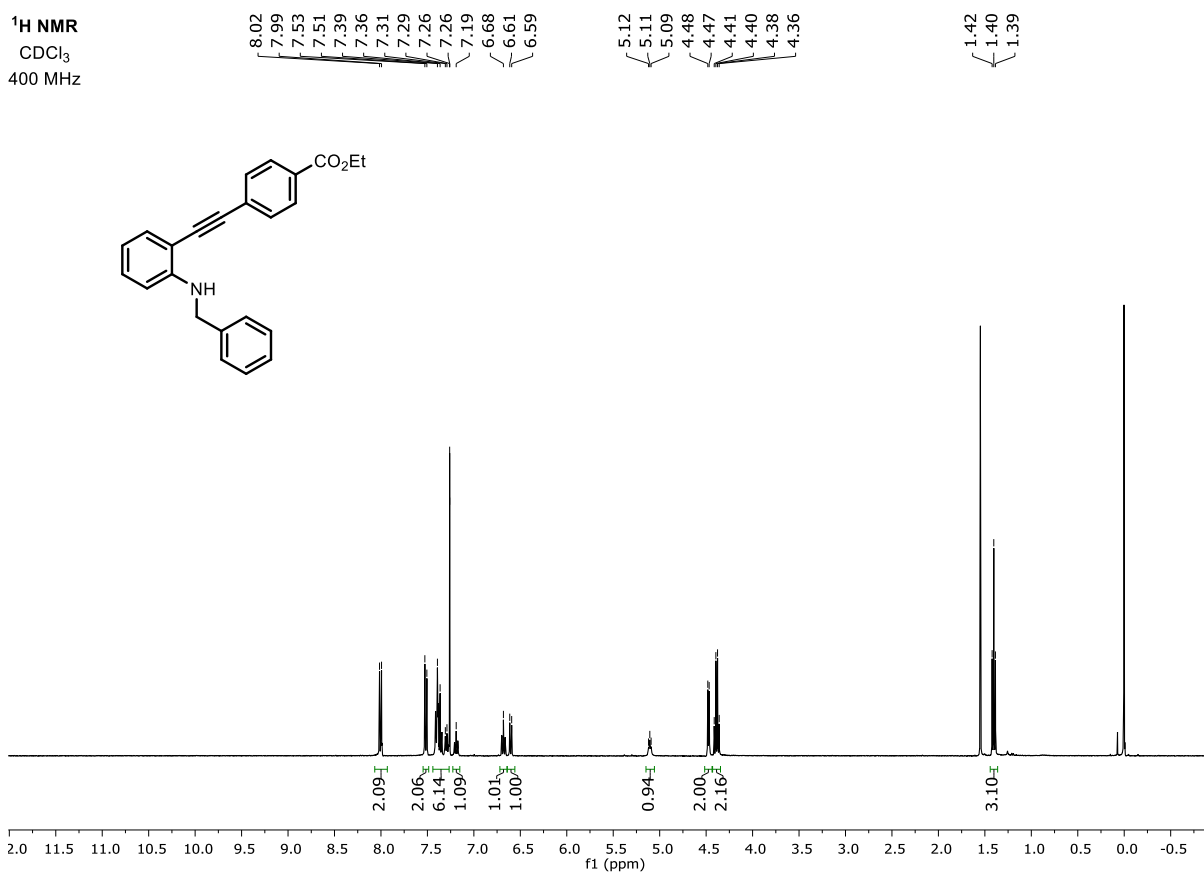


¹³C NMR
CDCl₃
126 MHz

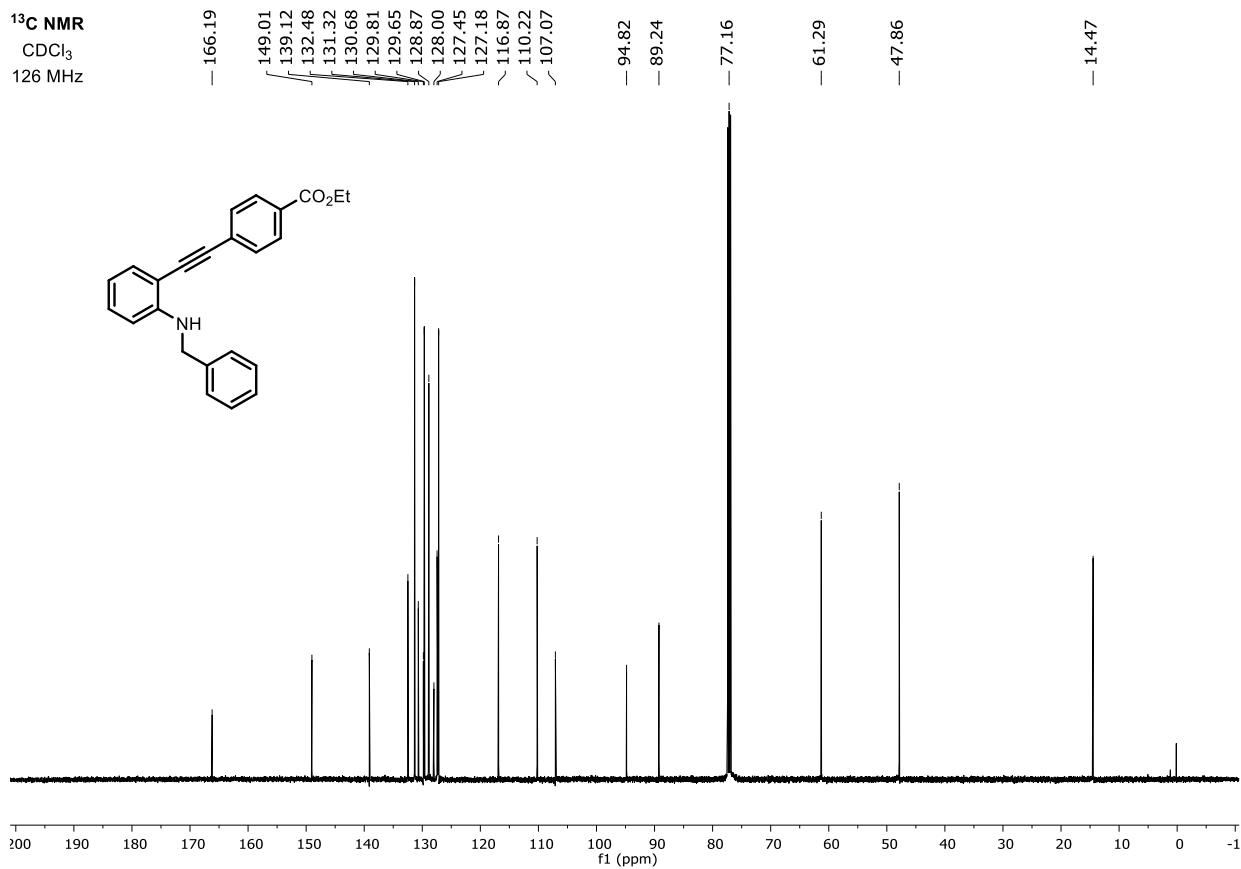


ethyl 4-((2-(benzylamino)phenyl)ethynyl)benzoate (5e)

¹H NMR
CDCl₃
400 MHz

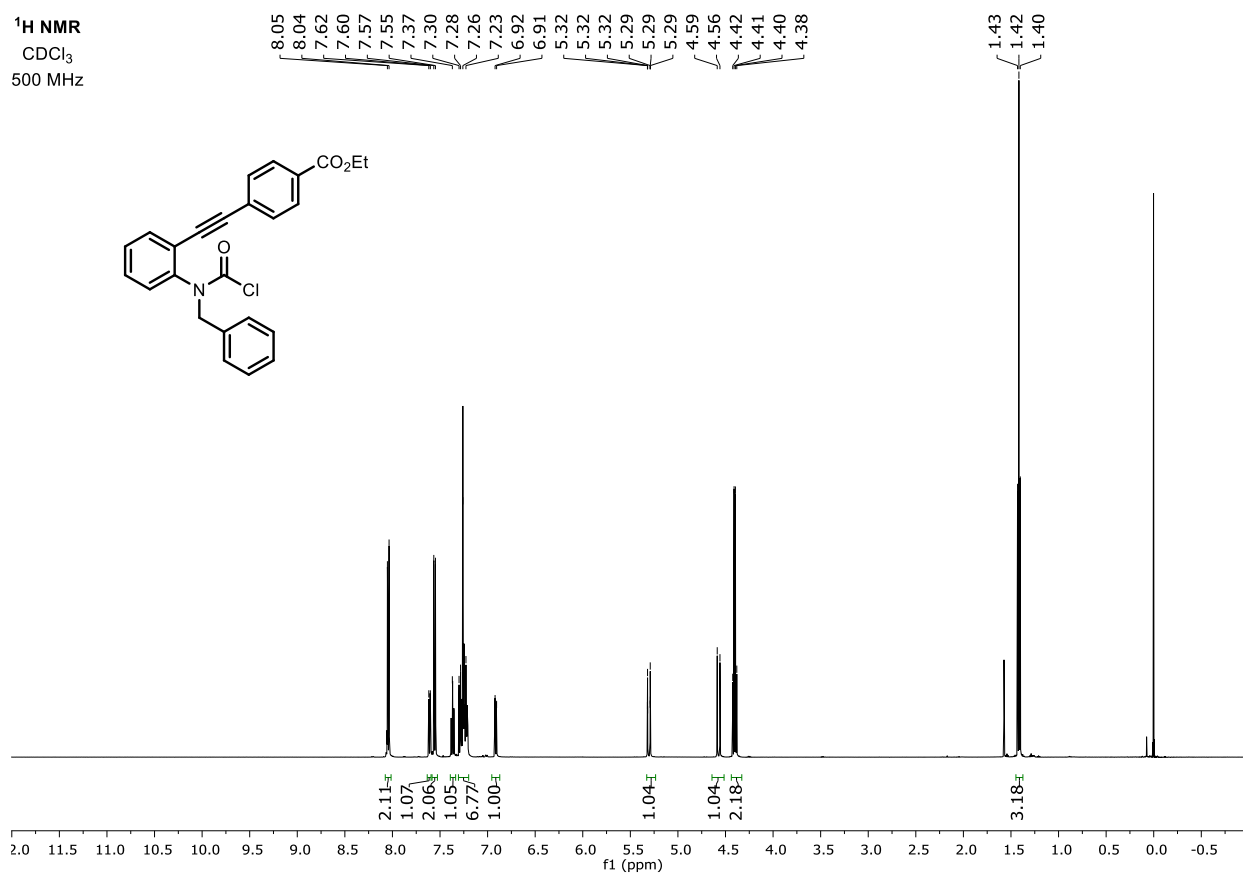


¹³C NMR
CDCl₃
126 MHz

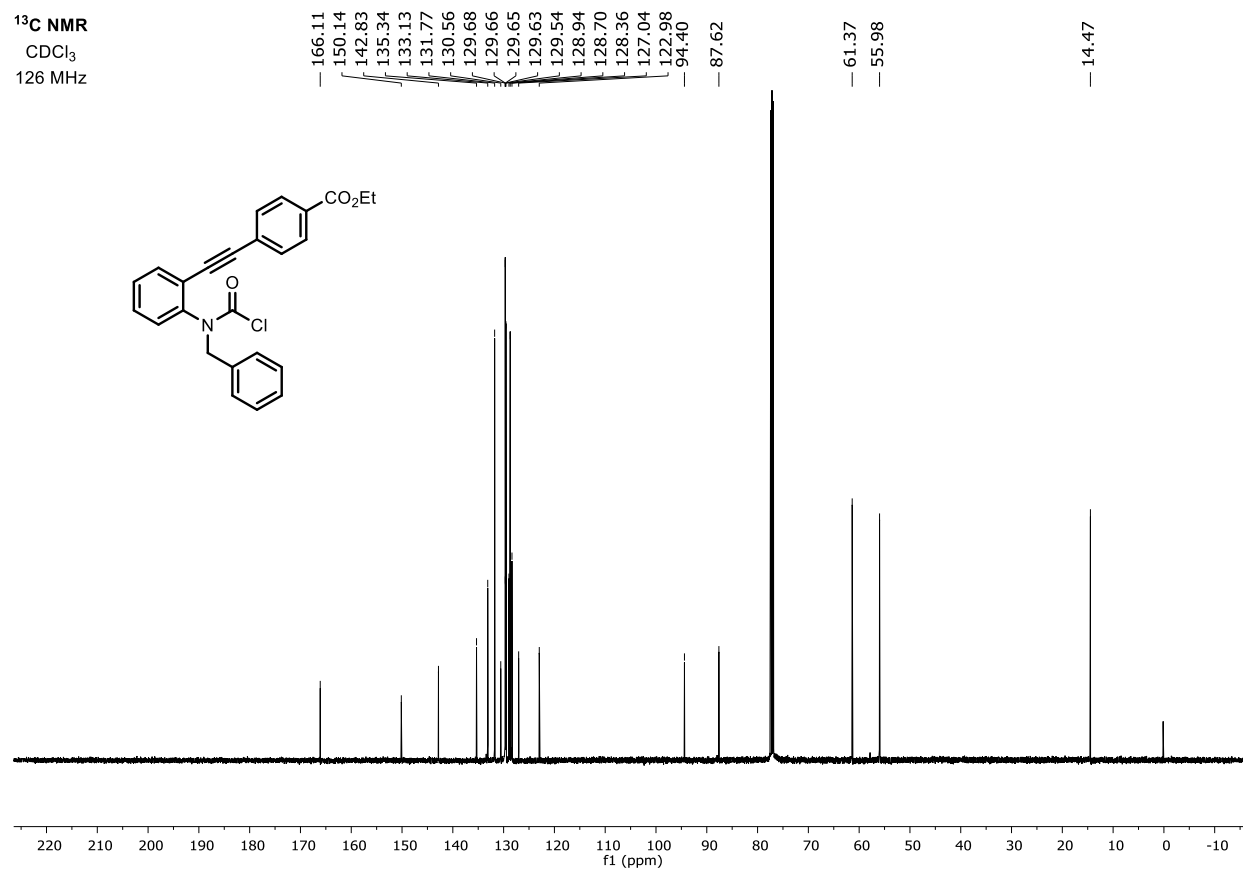


ethyl 4-((2-(benzyl(chlorocarbonyl)amino)phenyl)ethynyl)benzoate (1e')

¹H NMR
CDCl₃
500 MHz

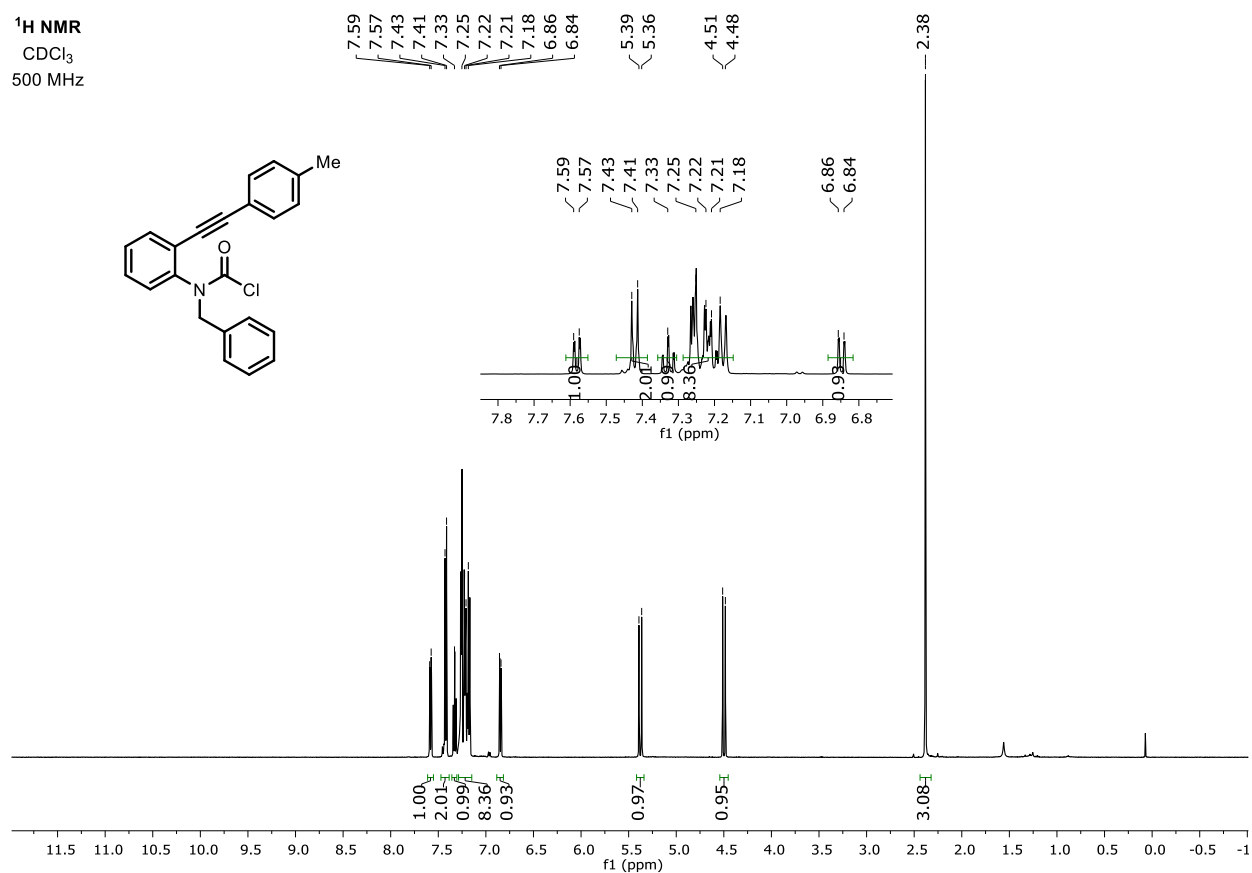


¹³C NMR
CDCl₃
126 MHz

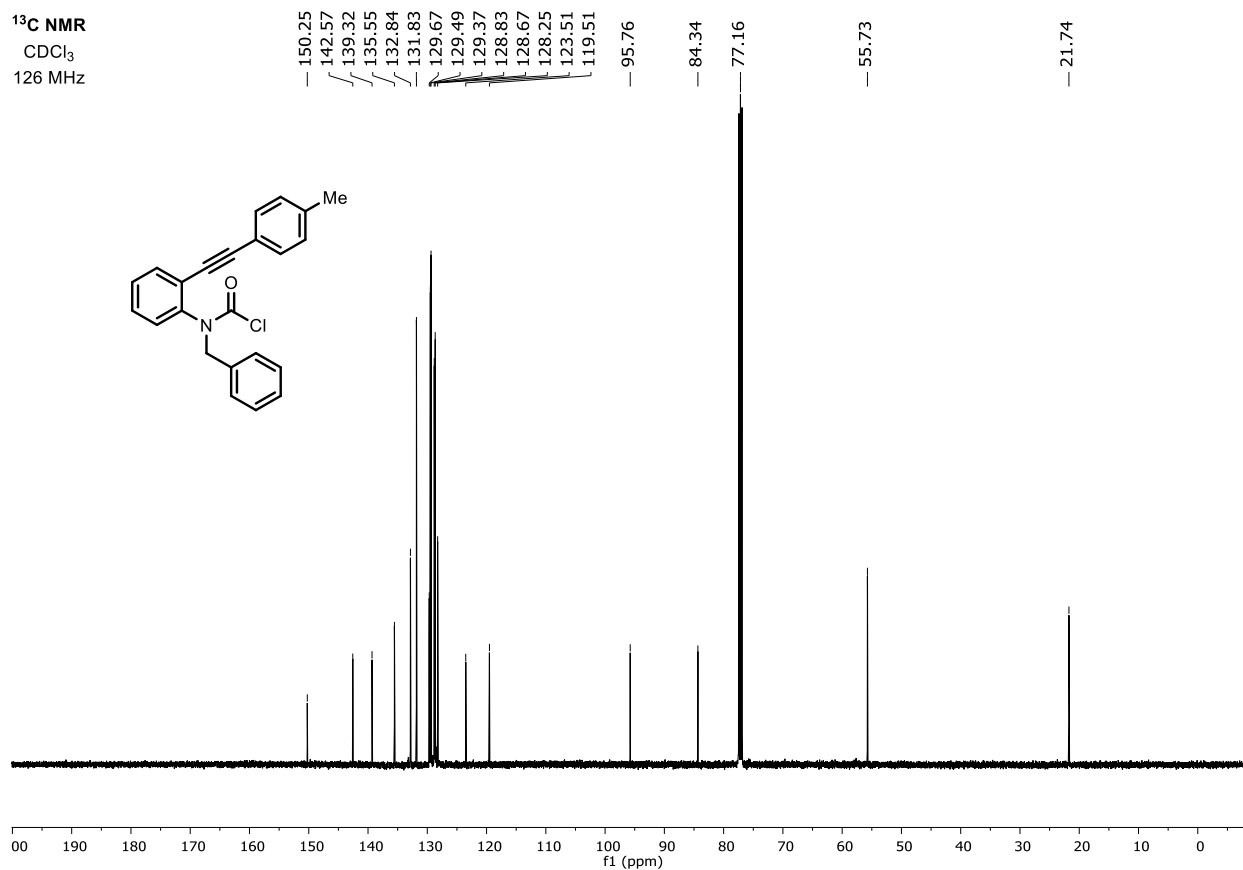


benzyl(2-(p-tolylethynyl)phenyl)carbamate (1f')

¹H NMR
CDCl₃
500 MHz



¹³C NMR
CDCl₃
126 MHz



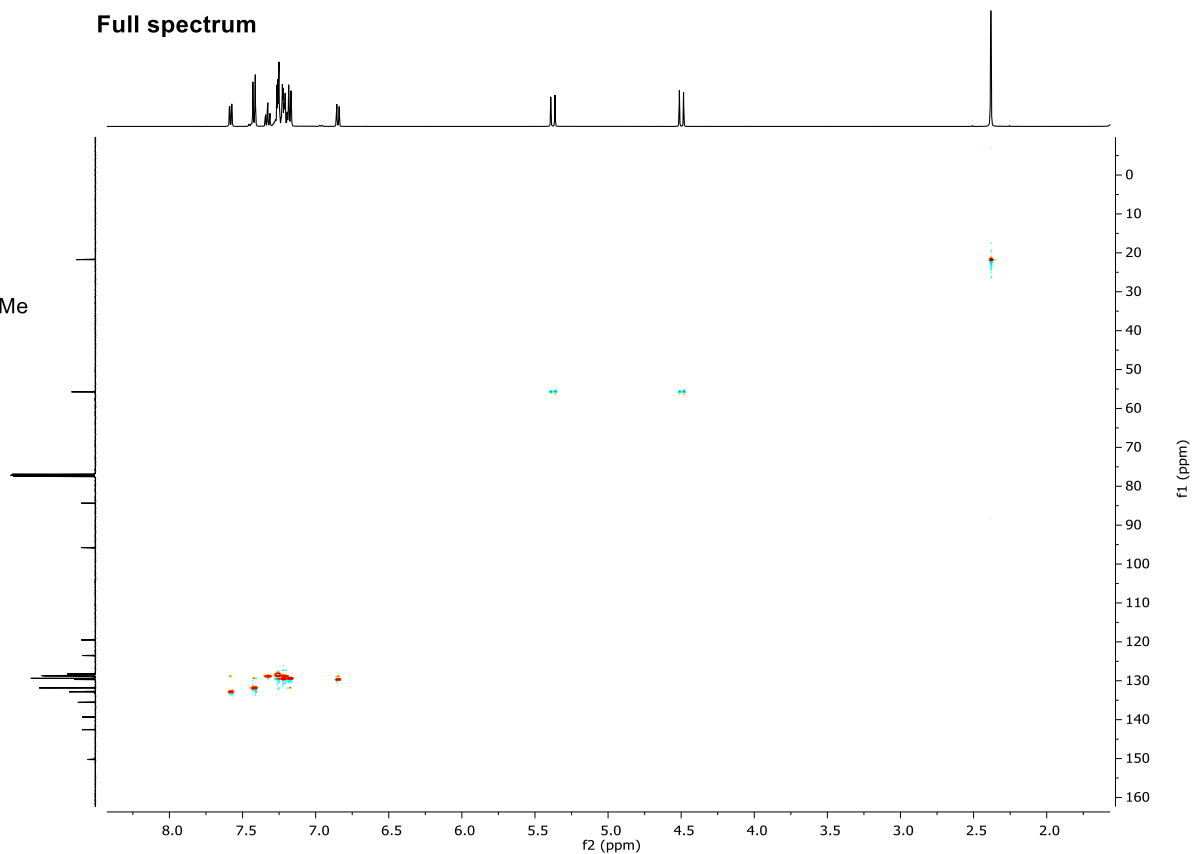
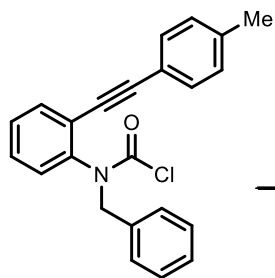
Full spectrum

¹H-¹³C HSQC

CDCl₃

500 MHz (¹H)

126 MHz (¹³C)



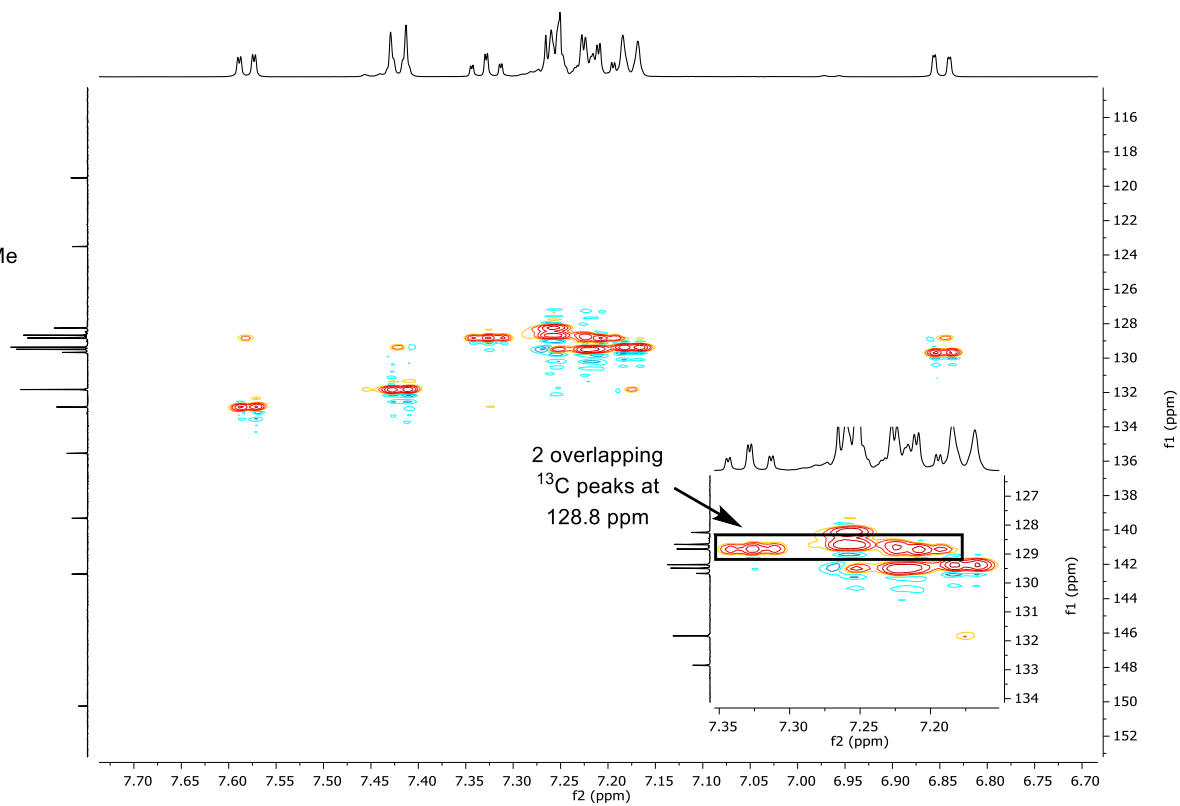
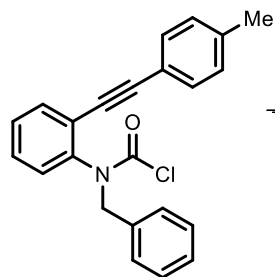
Zoom in

¹H-¹³C HSQC

CDCl₃

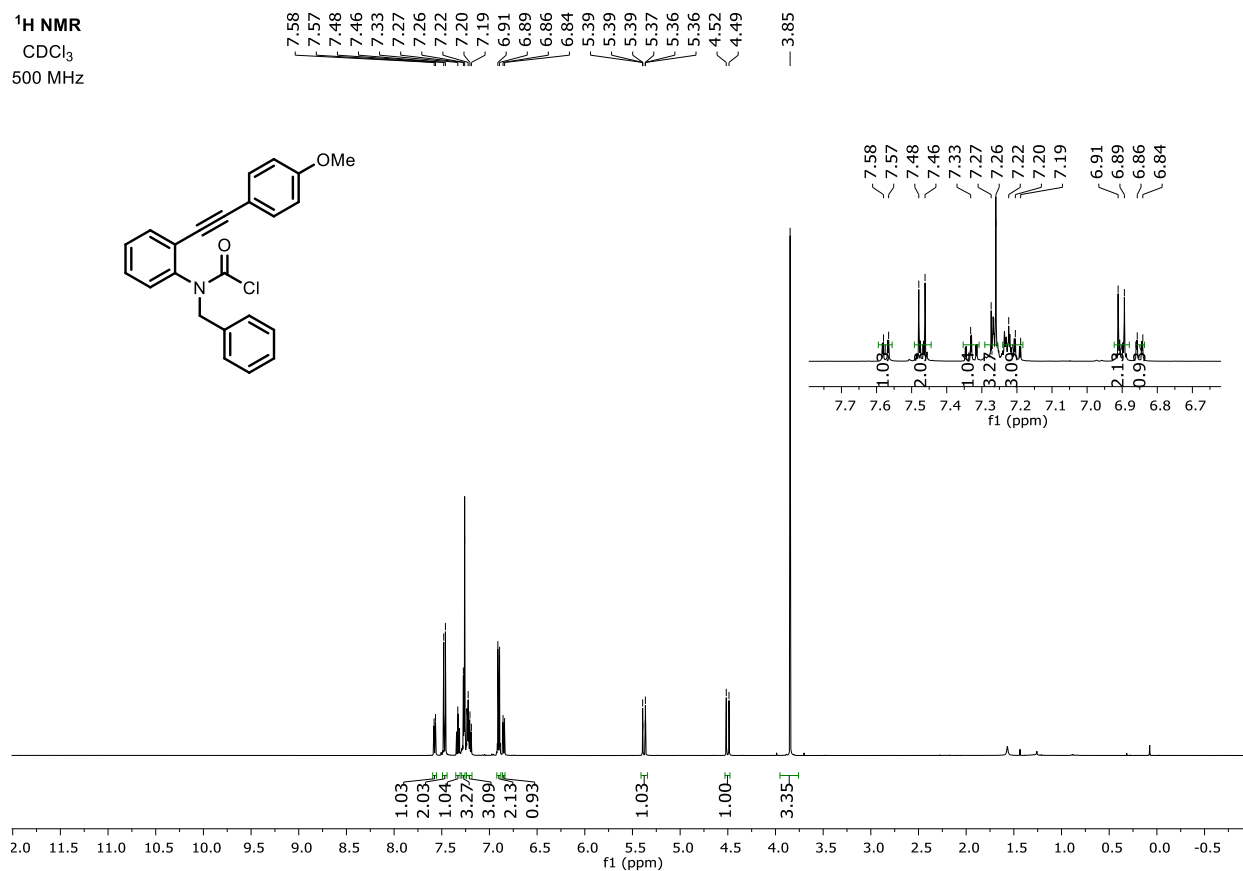
500 MHz (¹H)

126 MHz (¹³C)

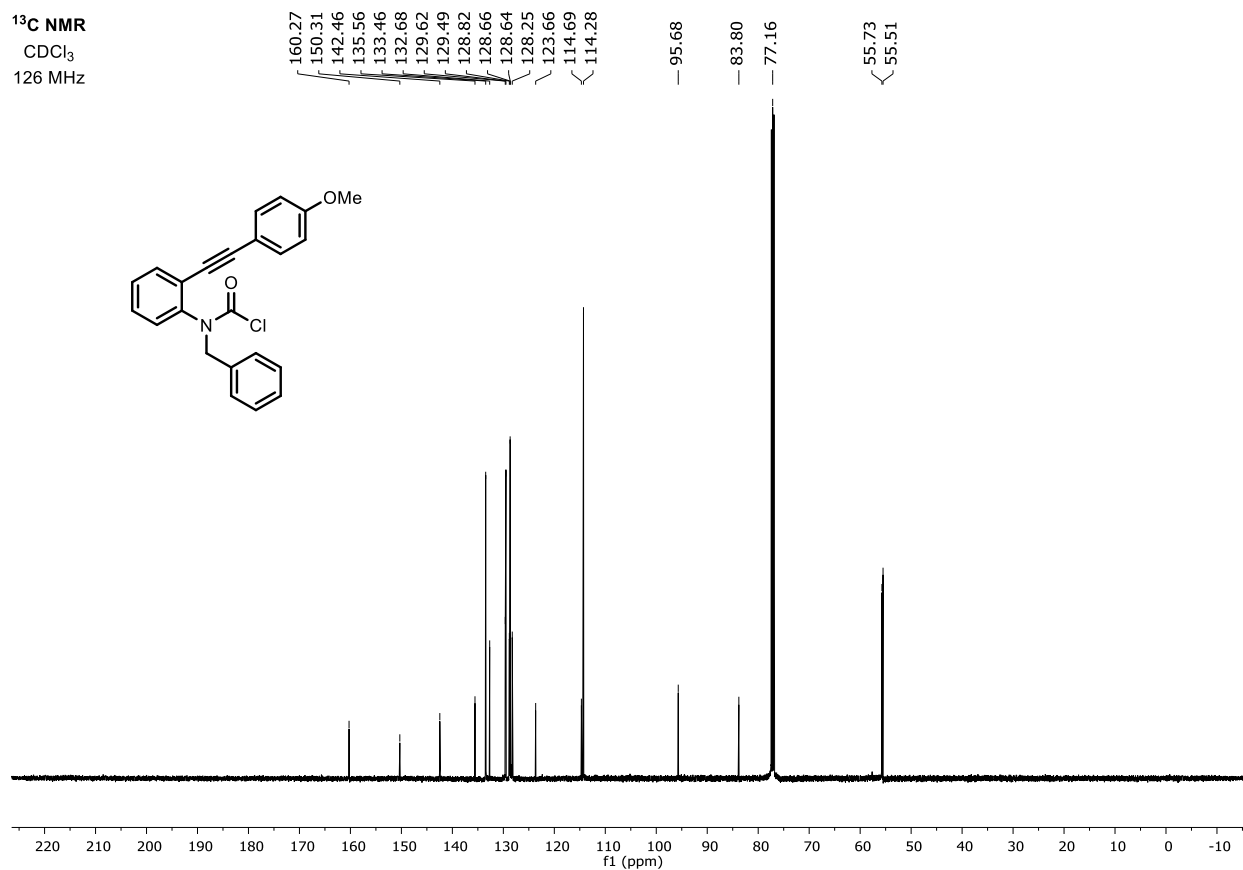


benzyl(2-((4-methoxyphenyl)ethynyl)phenyl)carbamic chloride (1g')

¹H NMR
CDCl₃
500 MHz

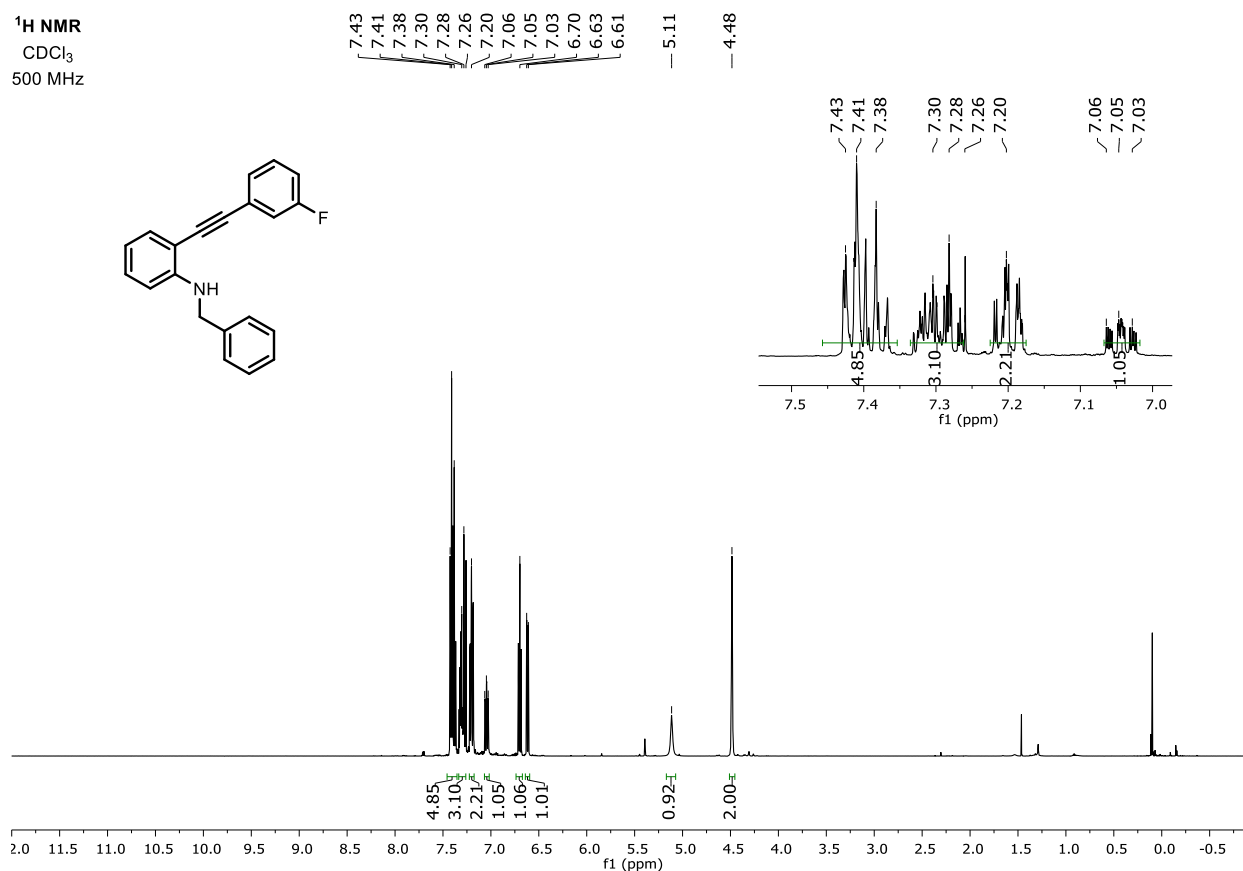


¹³C NMR
CDCl₃
126 MHz

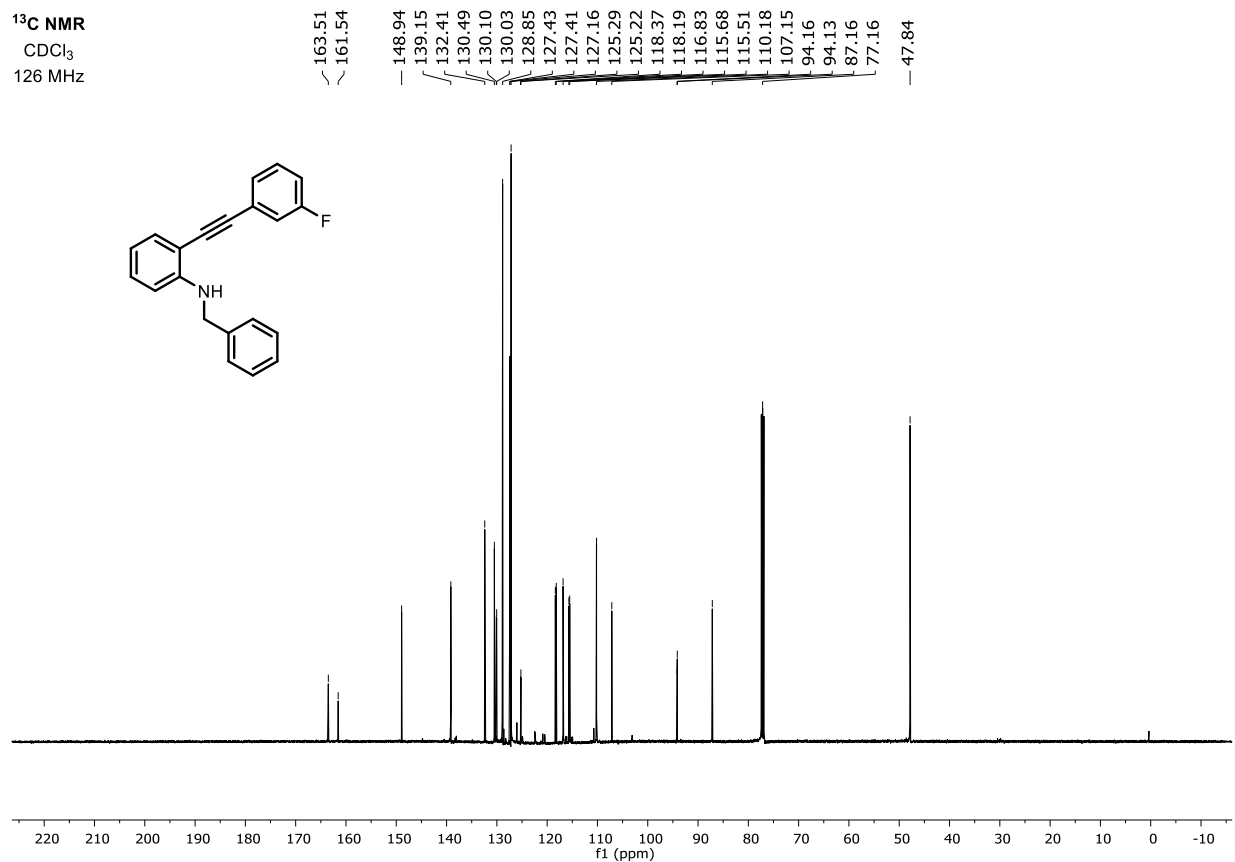


***N*-benzyl-2-((3-fluorophenyl)ethynyl)aniline (5h)**

¹H NMR
CDCl₃
500 MHz

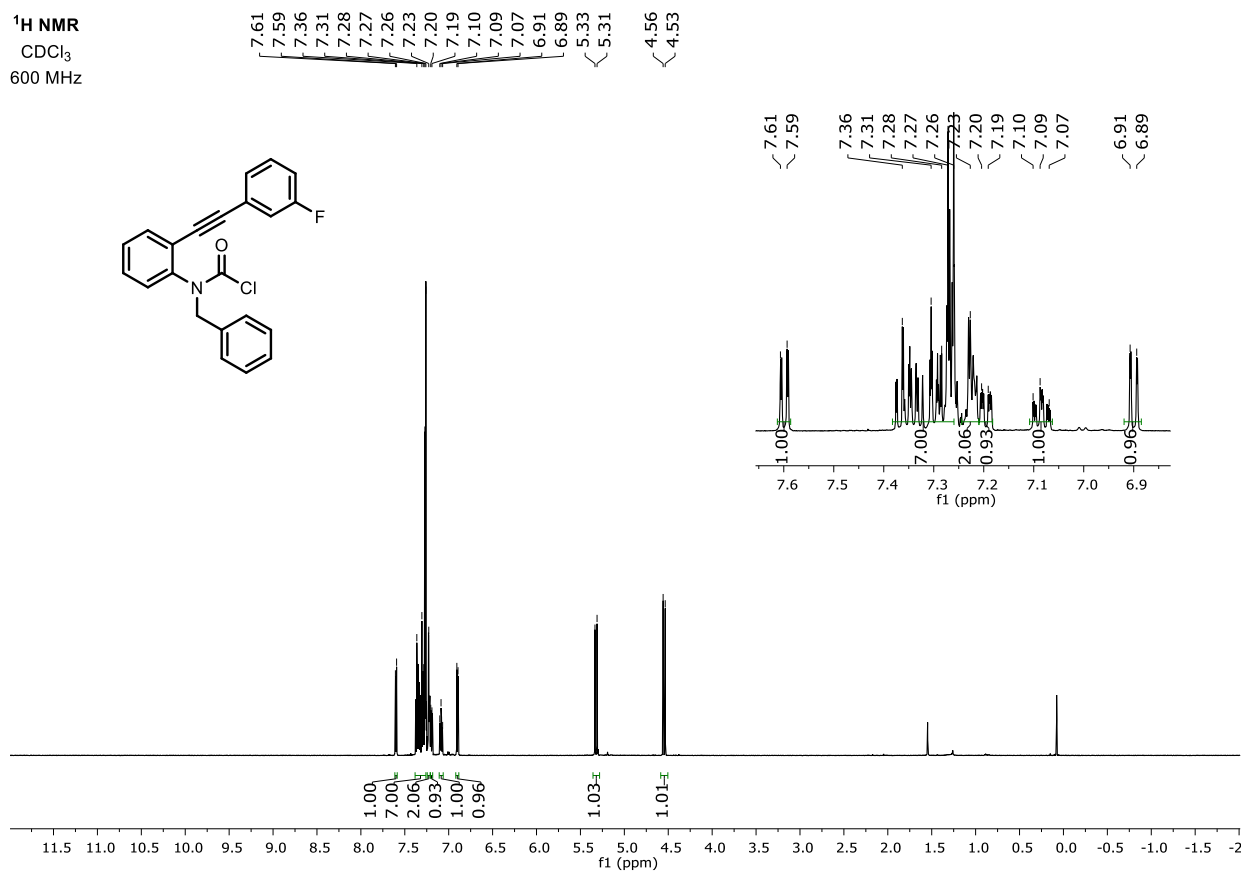


¹³C NMR
CDCl₃
126 MHz

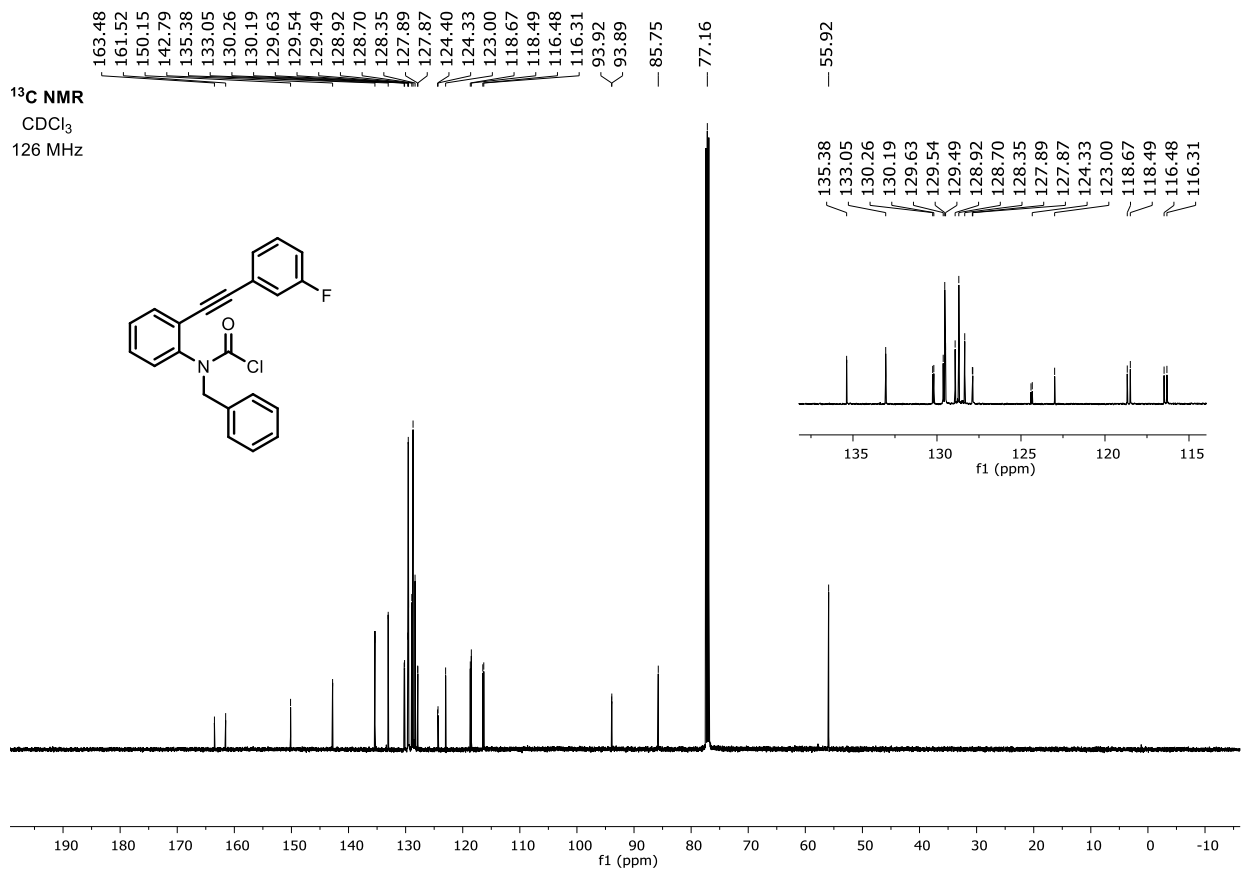


benzyl(2-((3-fluorophenyl)ethynyl)phenyl)carbamic chloride (1h')

¹H NMR
CDCl₃
600 MHz

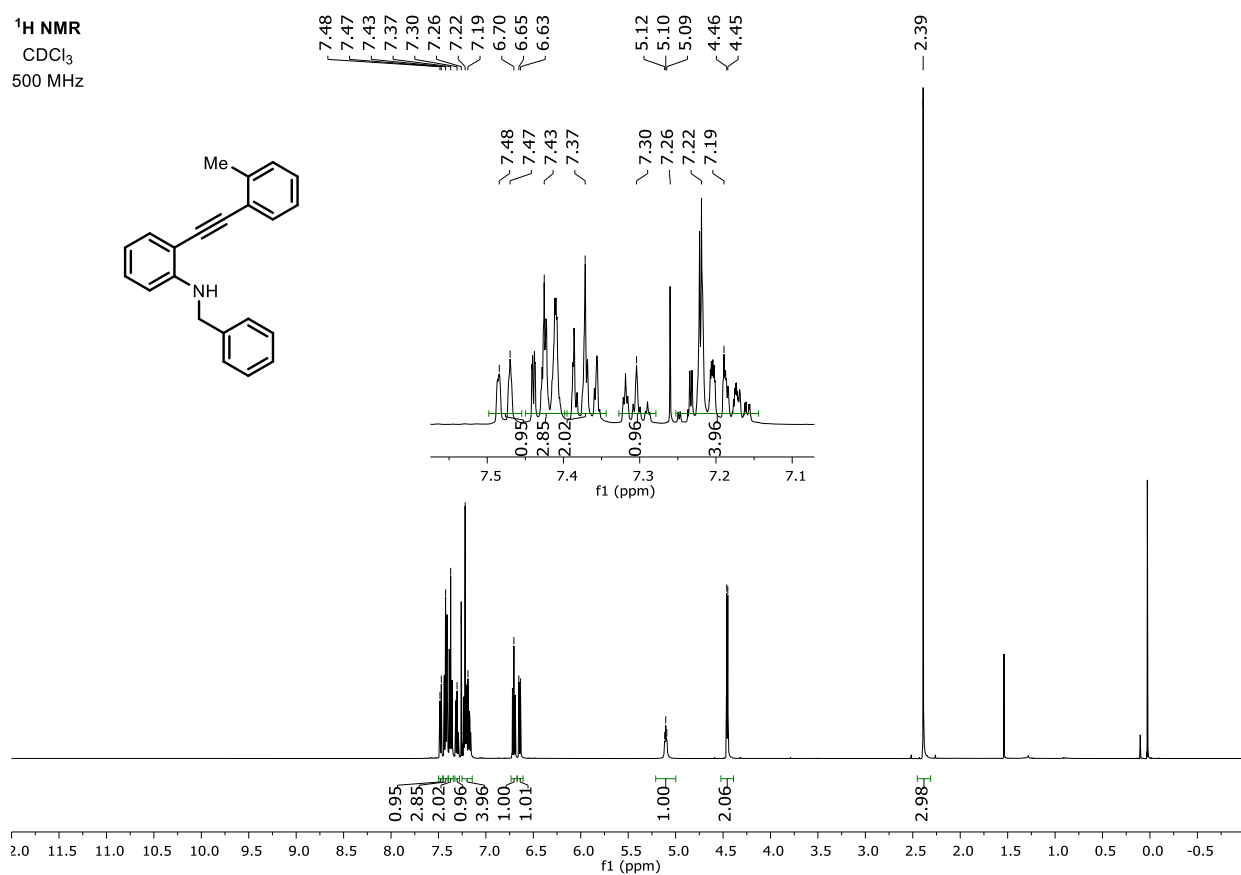


¹³C NMR
CDCl₃
126 MHz

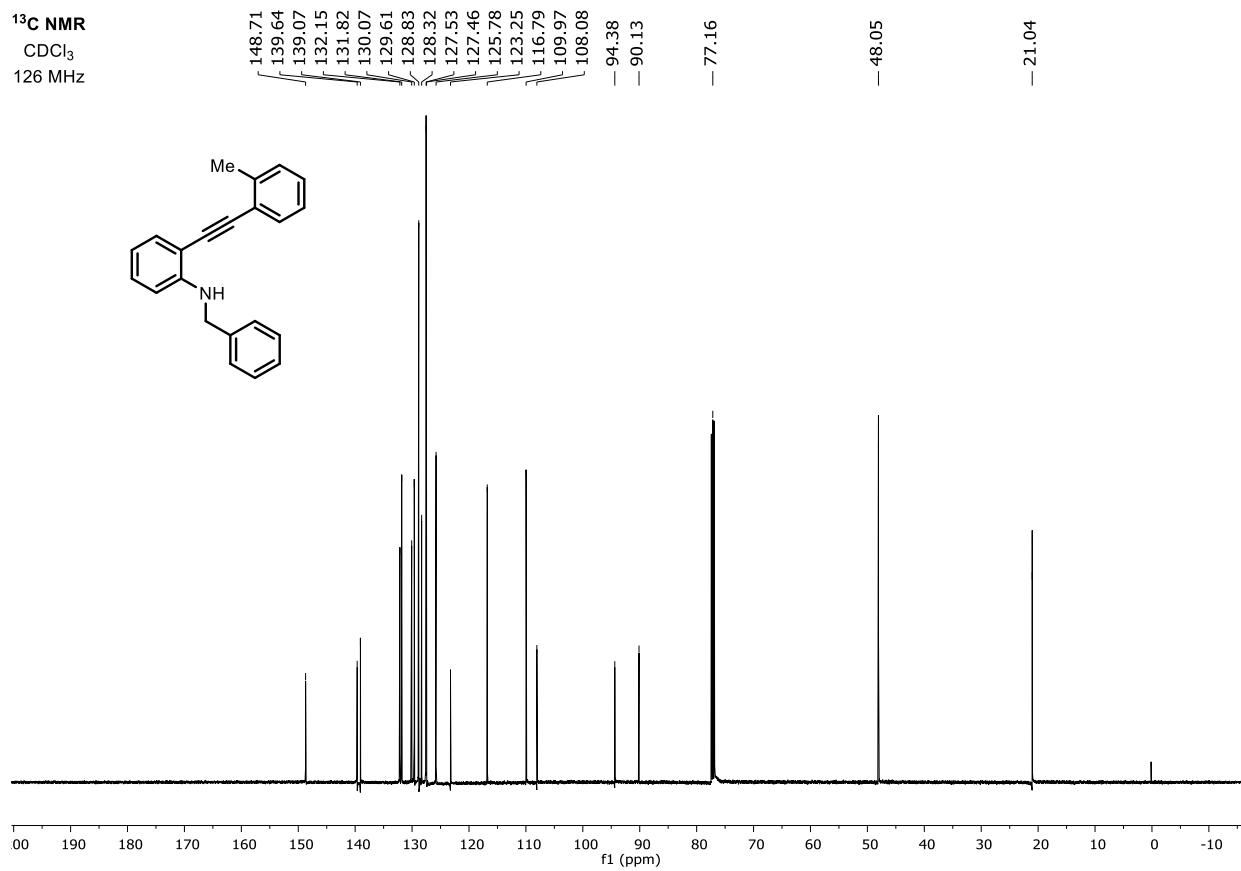


***N*-benzyl-2-(*o*-tolylethynyl)aniline (5i)**

¹H NMR
CDCl₃
500 MHz

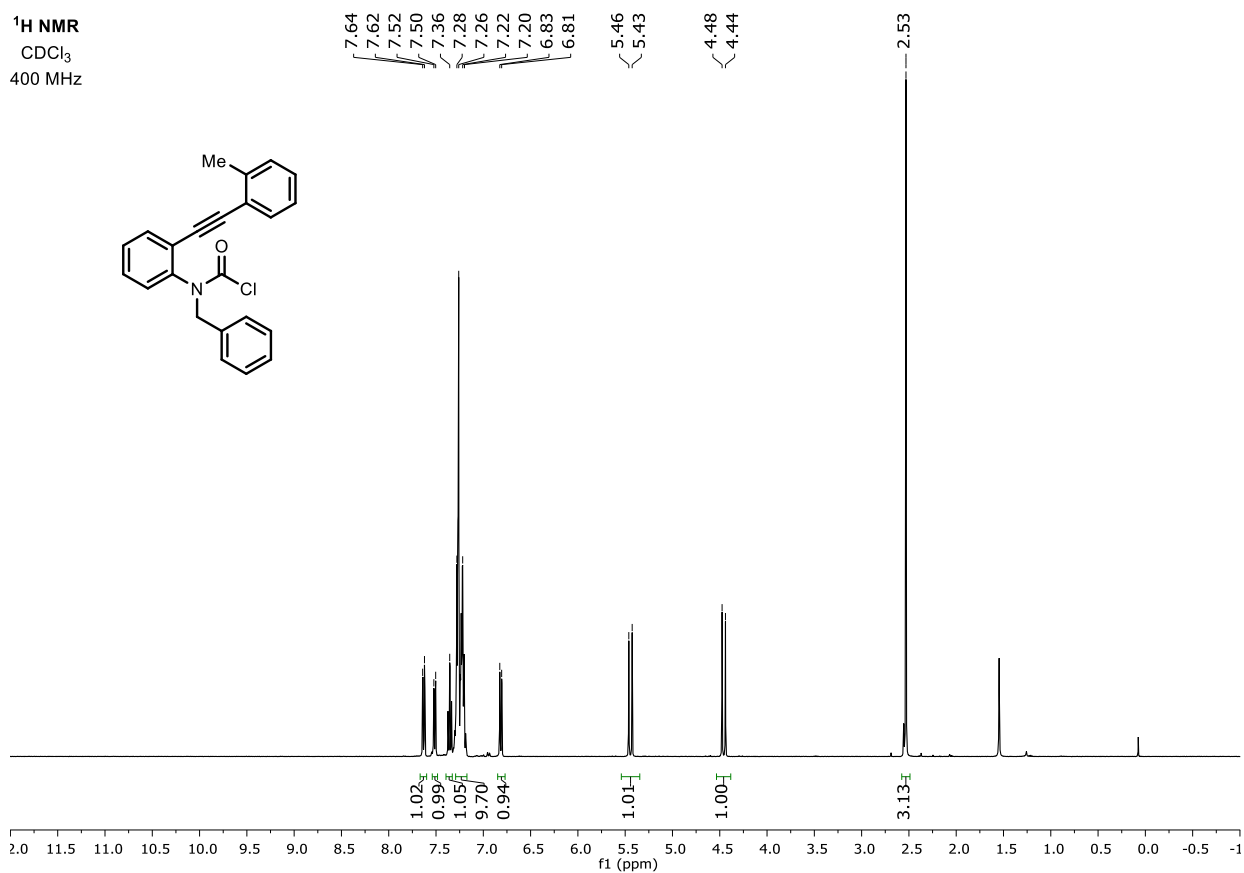


¹³C NMR
CDCl₃
126 MHz

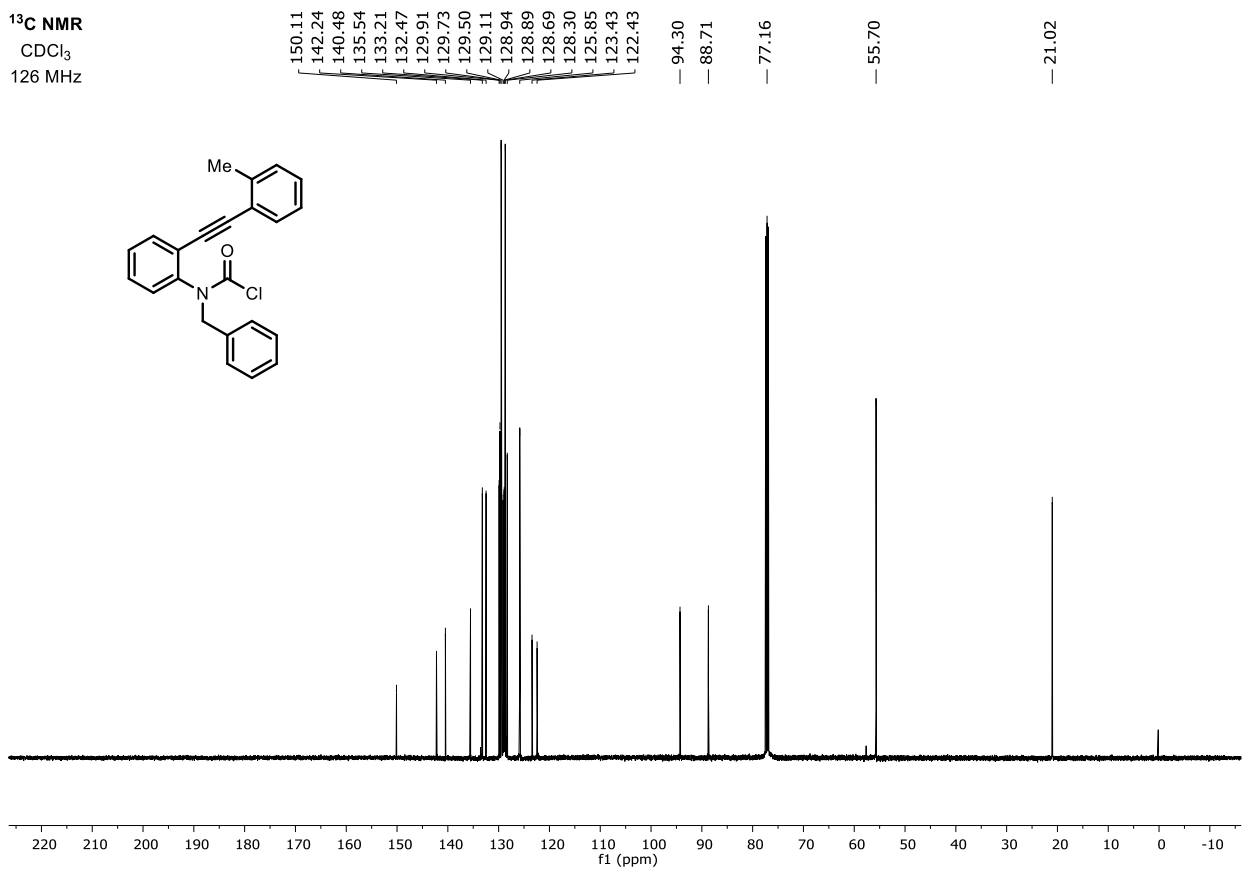


benzyl(2-(*o*-tolylethynyl)phenyl)carbamic chloride (1i')

¹H NMR
CDCl₃
400 MHz

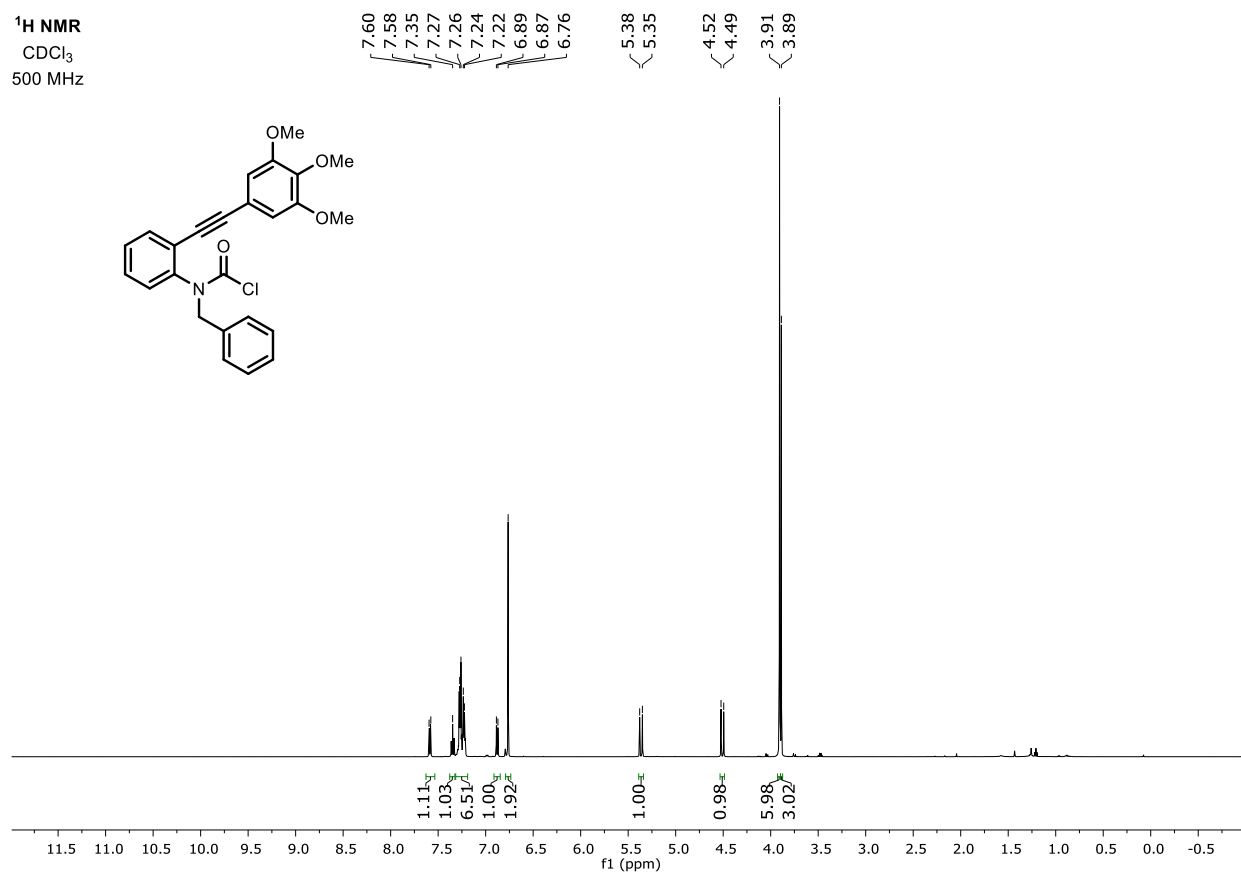


¹³C NMR
CDCl₃
126 MHz

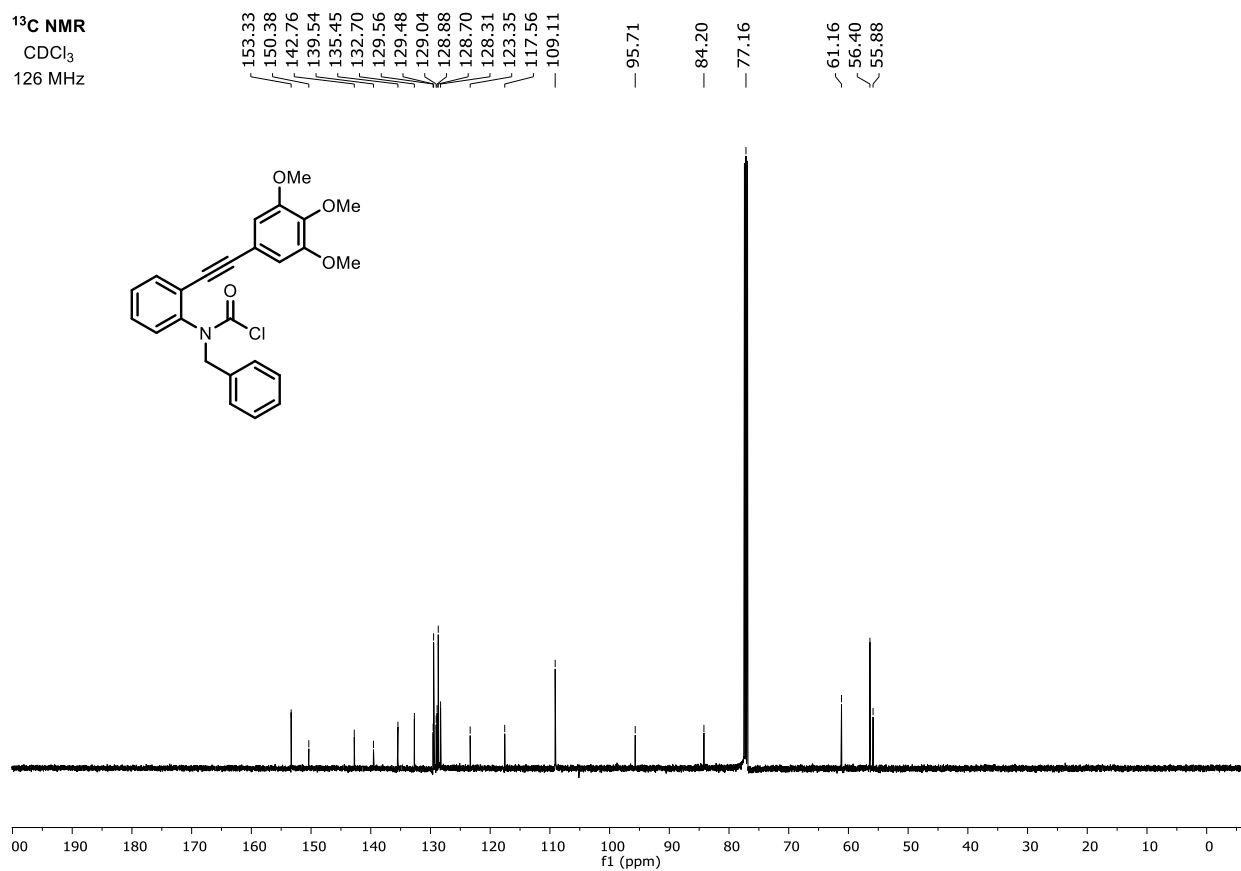


benzyl(2-((3,4,5-trimethoxyphenyl)ethynyl)phenyl)carbamate (1j')

¹H NMR
CDCl₃
500 MHz

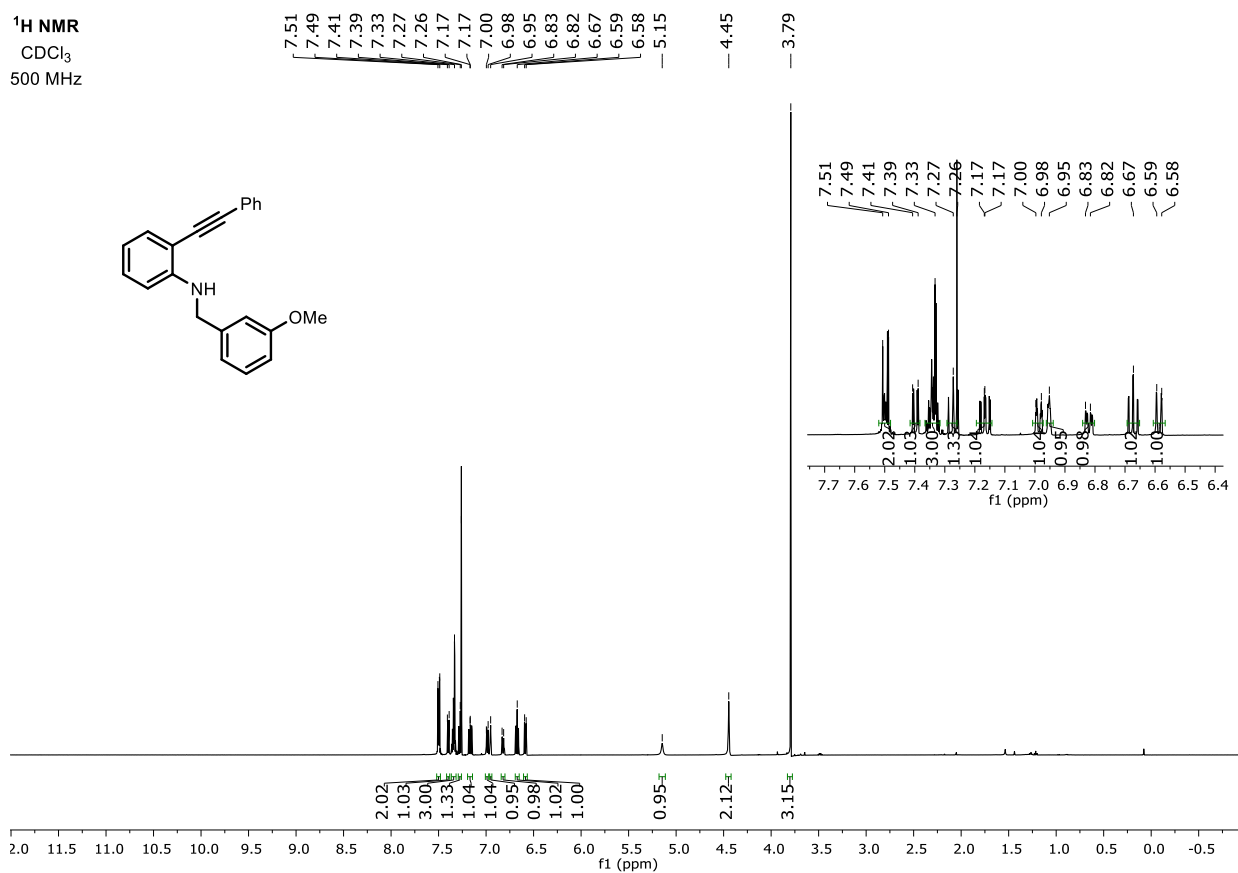


¹³C NMR
CDCl₃
126 MHz

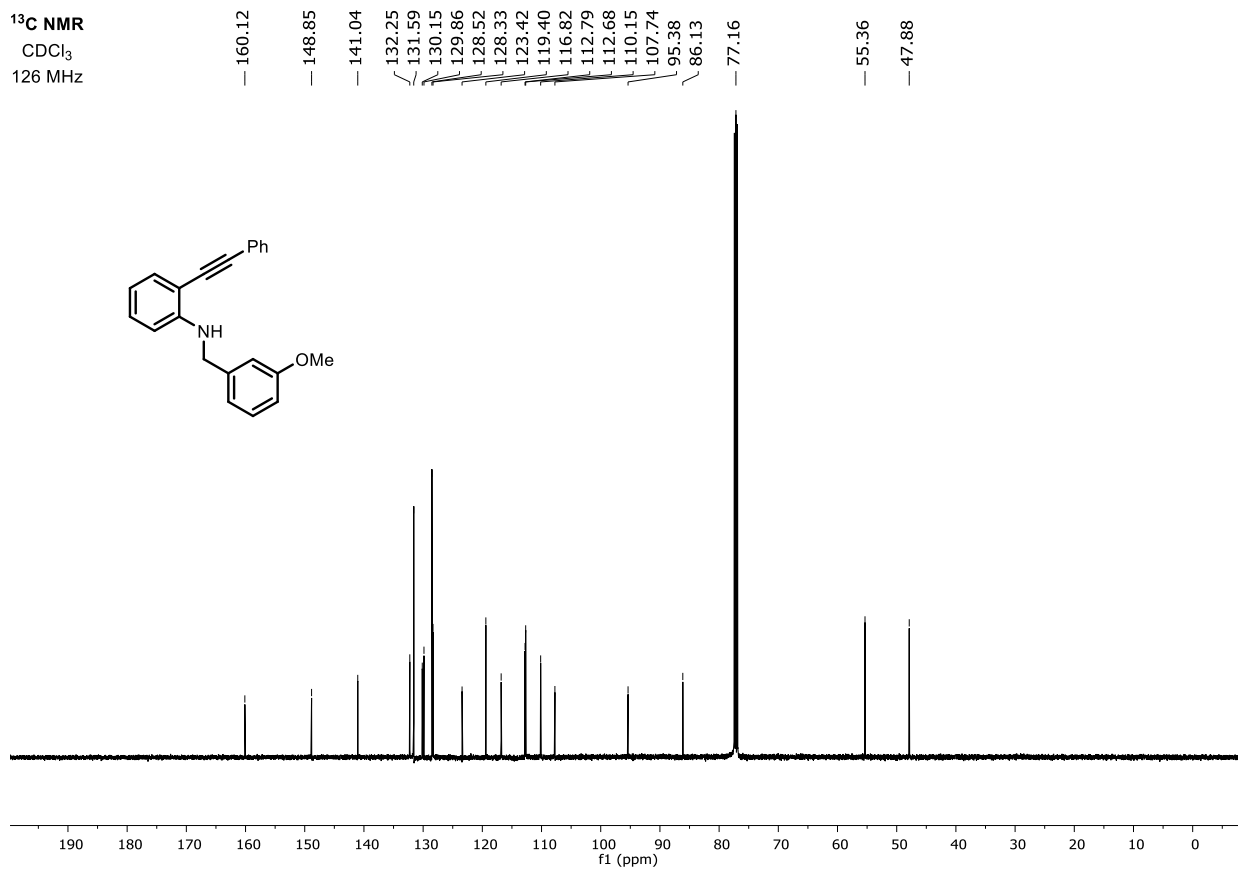


***N*-(3-methoxybenzyl)-2-(phenylethynyl)aniline (5k)**

¹H NMR
CDCl₃
500 MHz

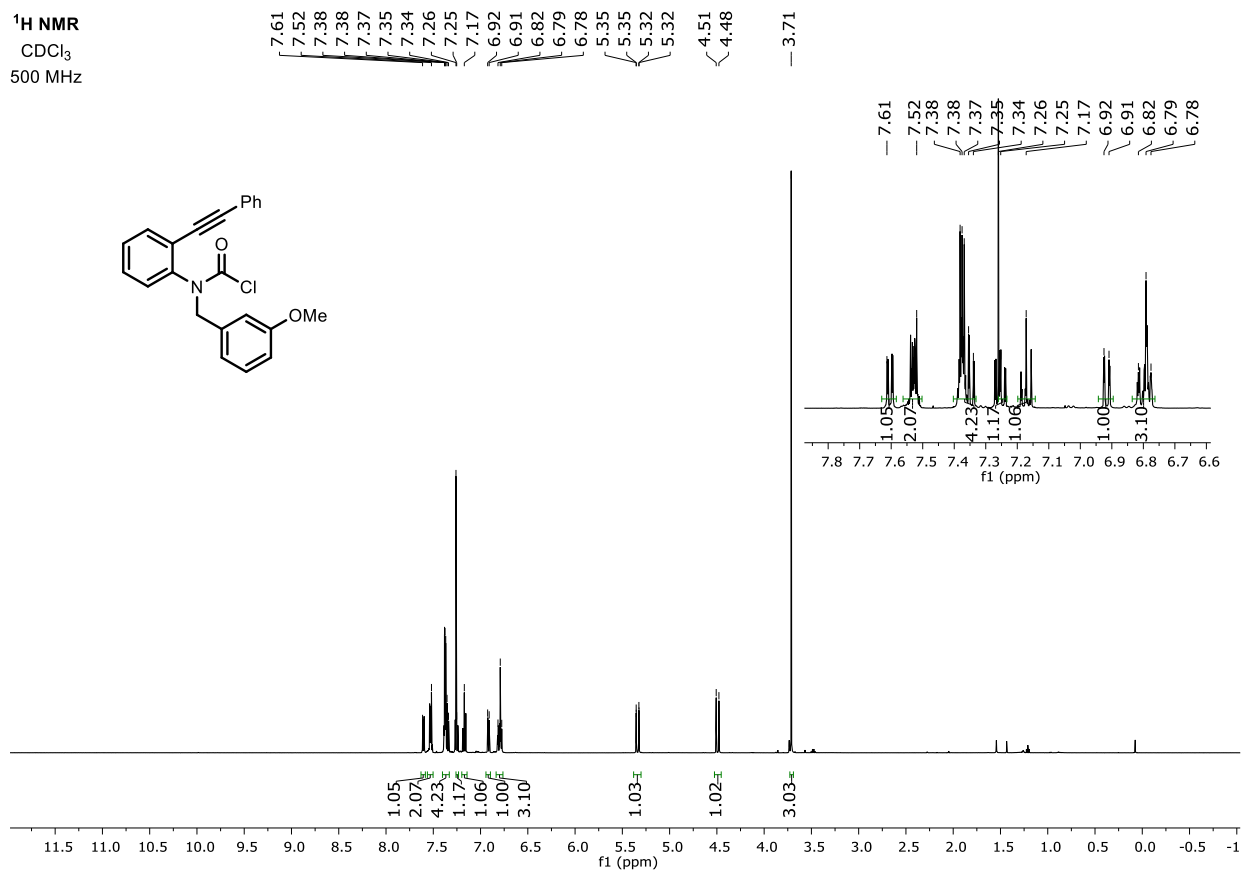


¹³C NMR
CDCl₃
126 MHz

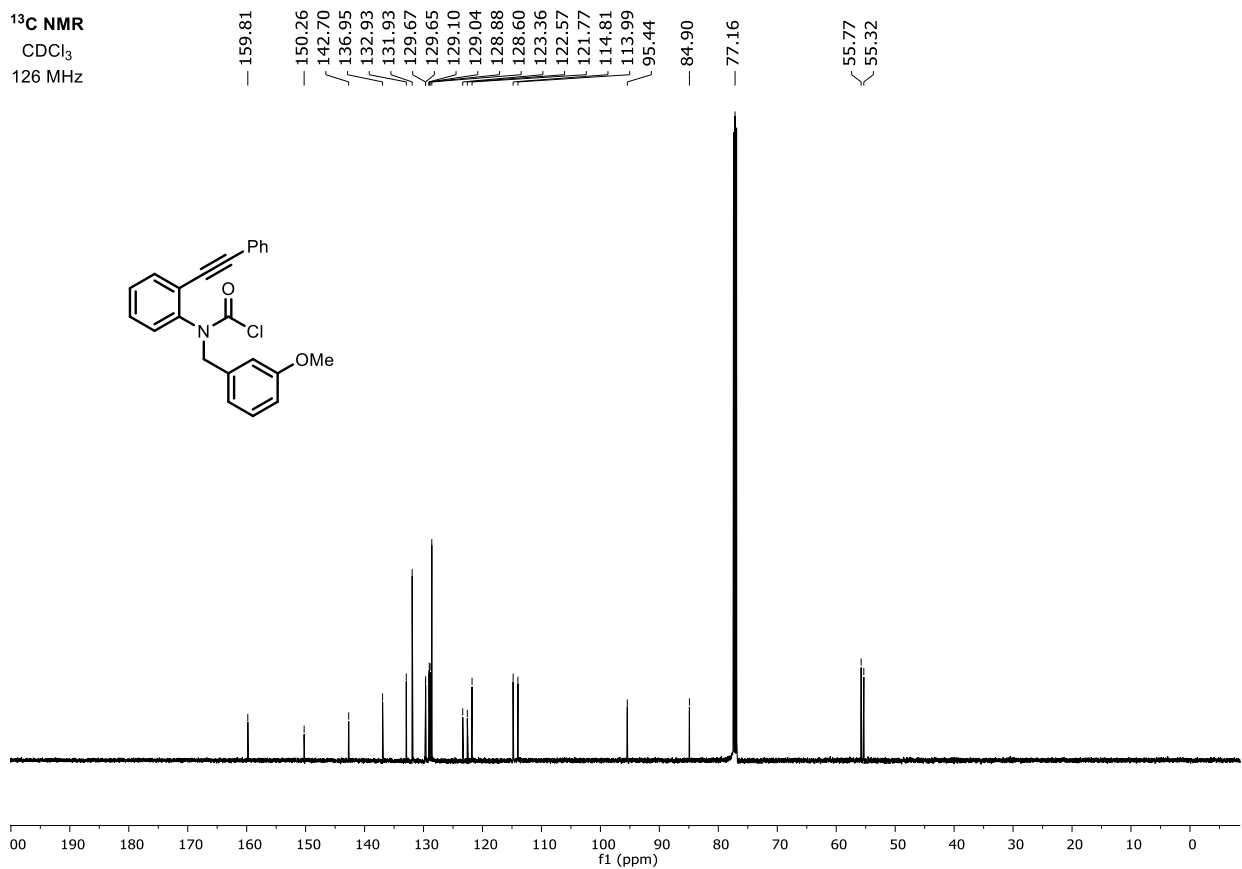


(3-methoxybenzyl)(2-(phenylethynyl)phenyl)carbamic chloride (1k')

¹H NMR
CDCl₃
500 MHz

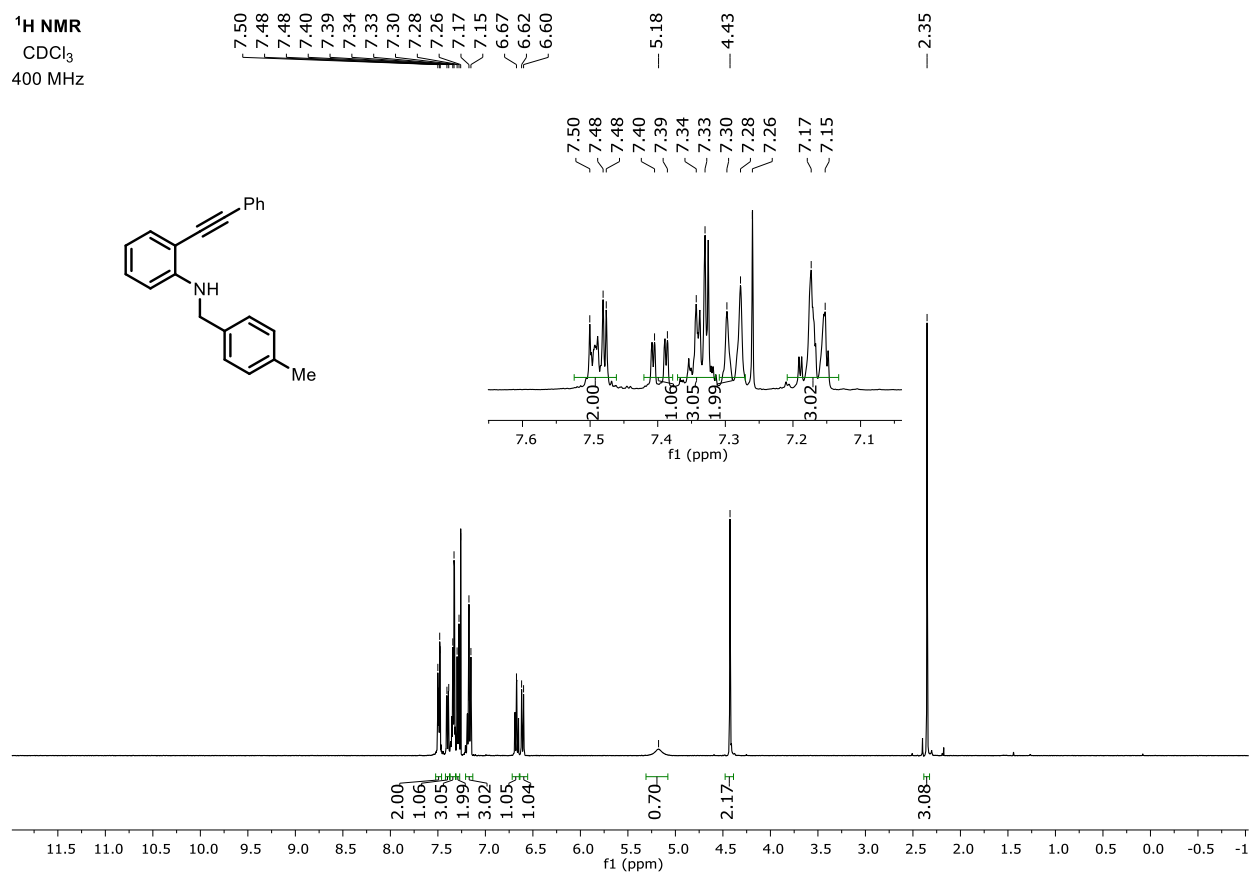


¹³C NMR
CDCl₃
126 MHz

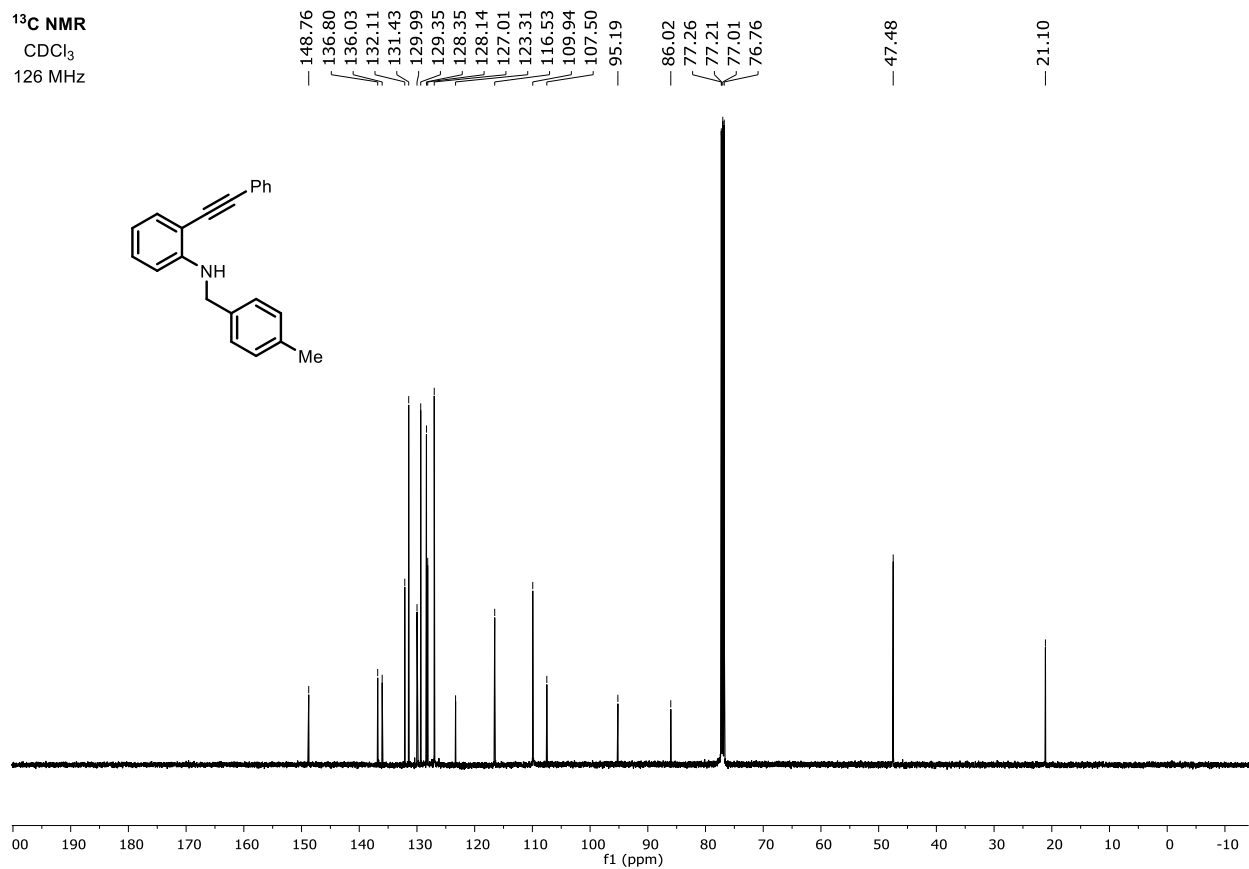


***N*-(4-methylbenzyl)-2-(phenylethynyl)aniline (5l)**

¹H NMR
CDCl₃
400 MHz

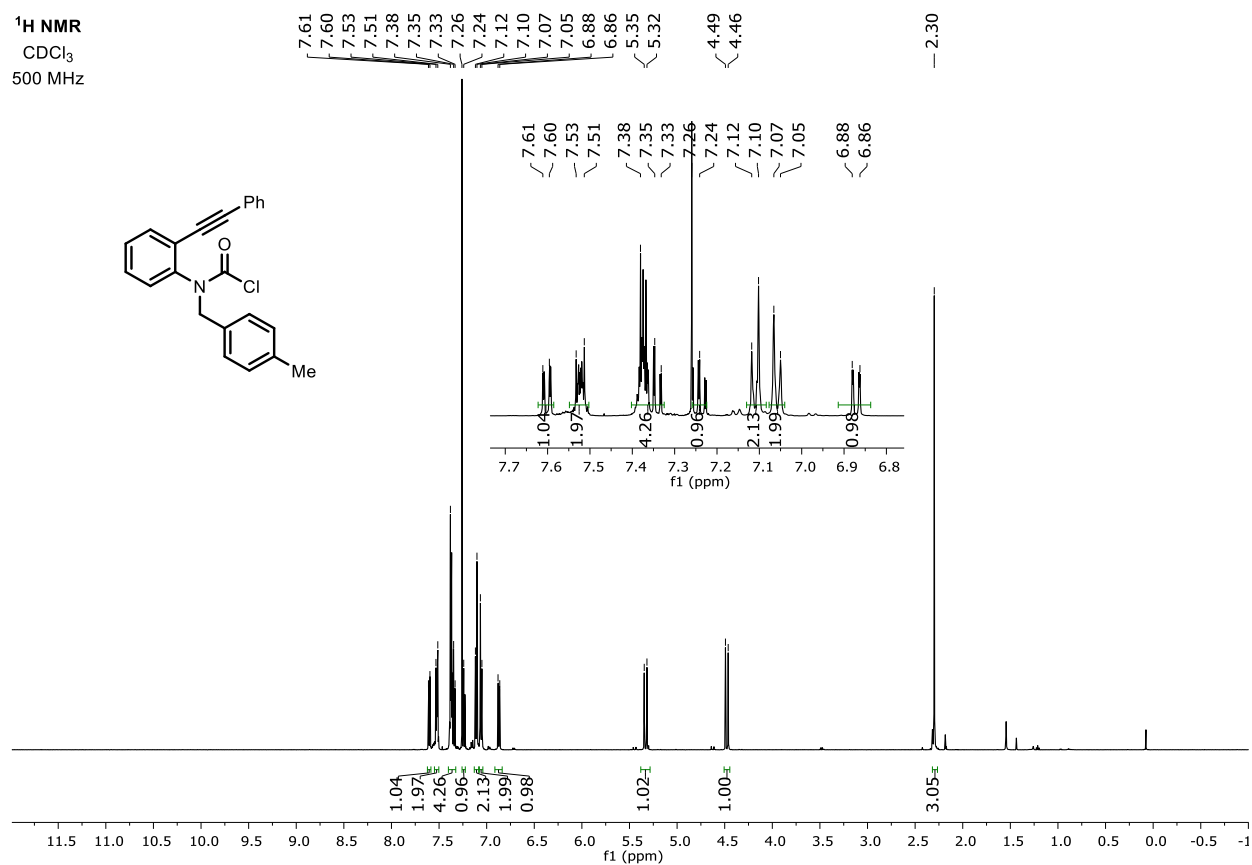


¹³C NMR
CDCl₃
126 MHz

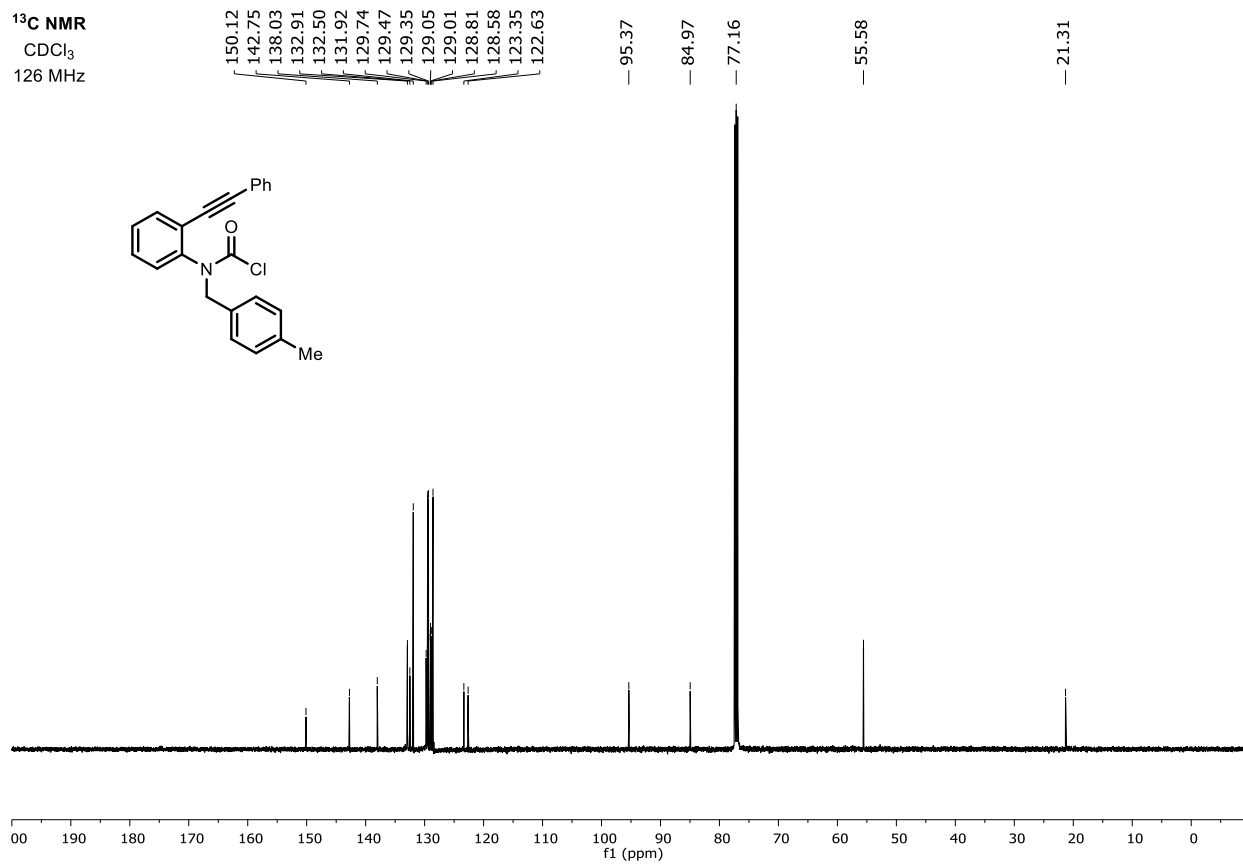


(4-methylbenzyl)(2-(phenylethynyl)phenyl)carbamic chloride (11')

¹H NMR
CDCl₃
500 MHz

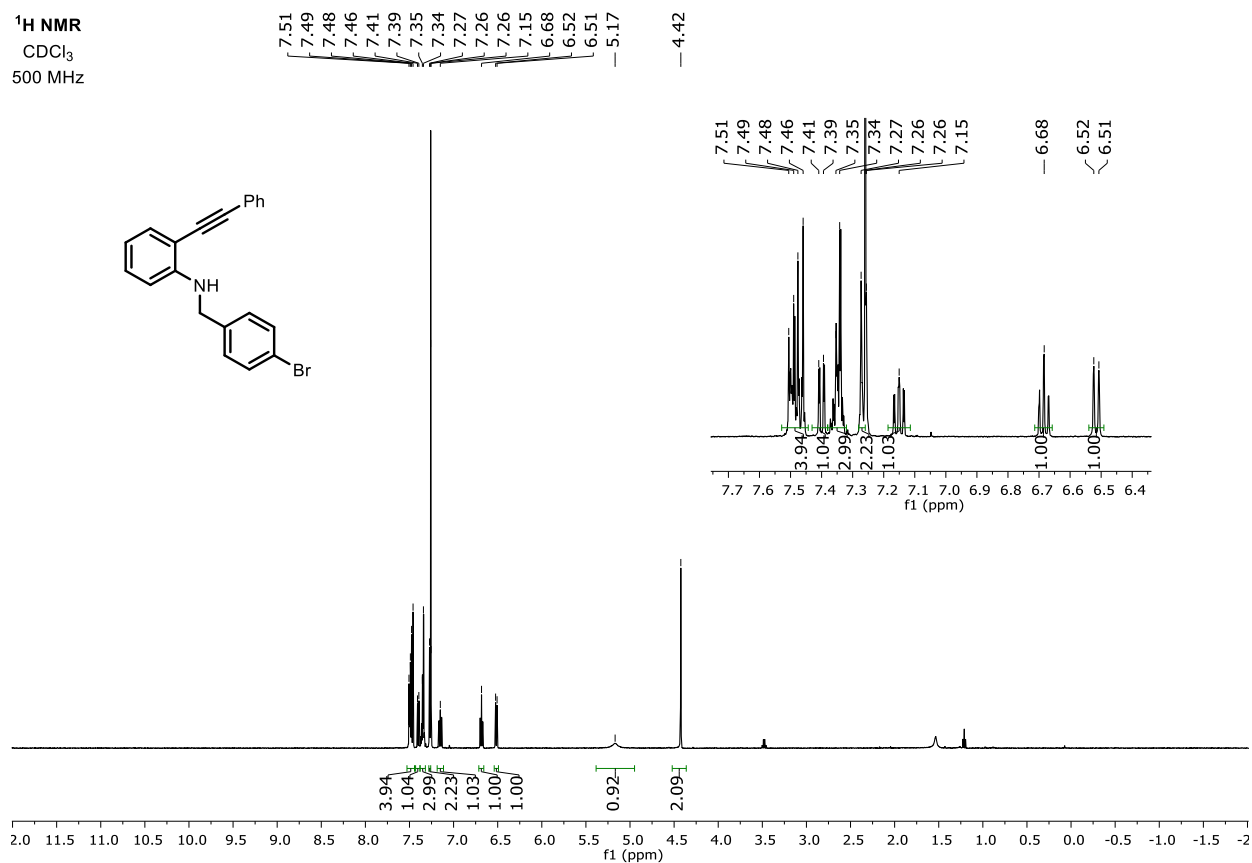


¹³C NMR
CDCl₃
126 MHz

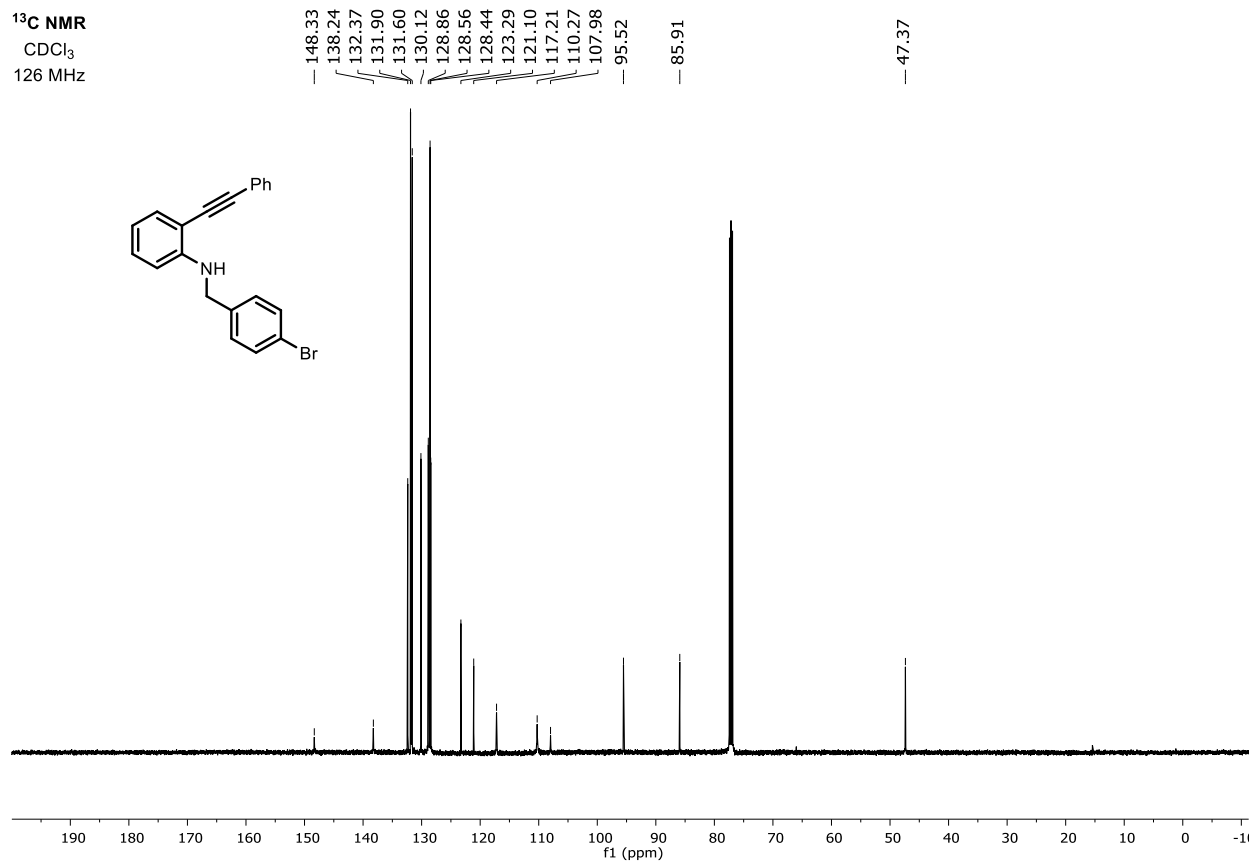


***N*-(4-bromobenzyl)-2-(phenylethynyl)aniline (5m)**

¹H NMR
CDCl₃
500 MHz

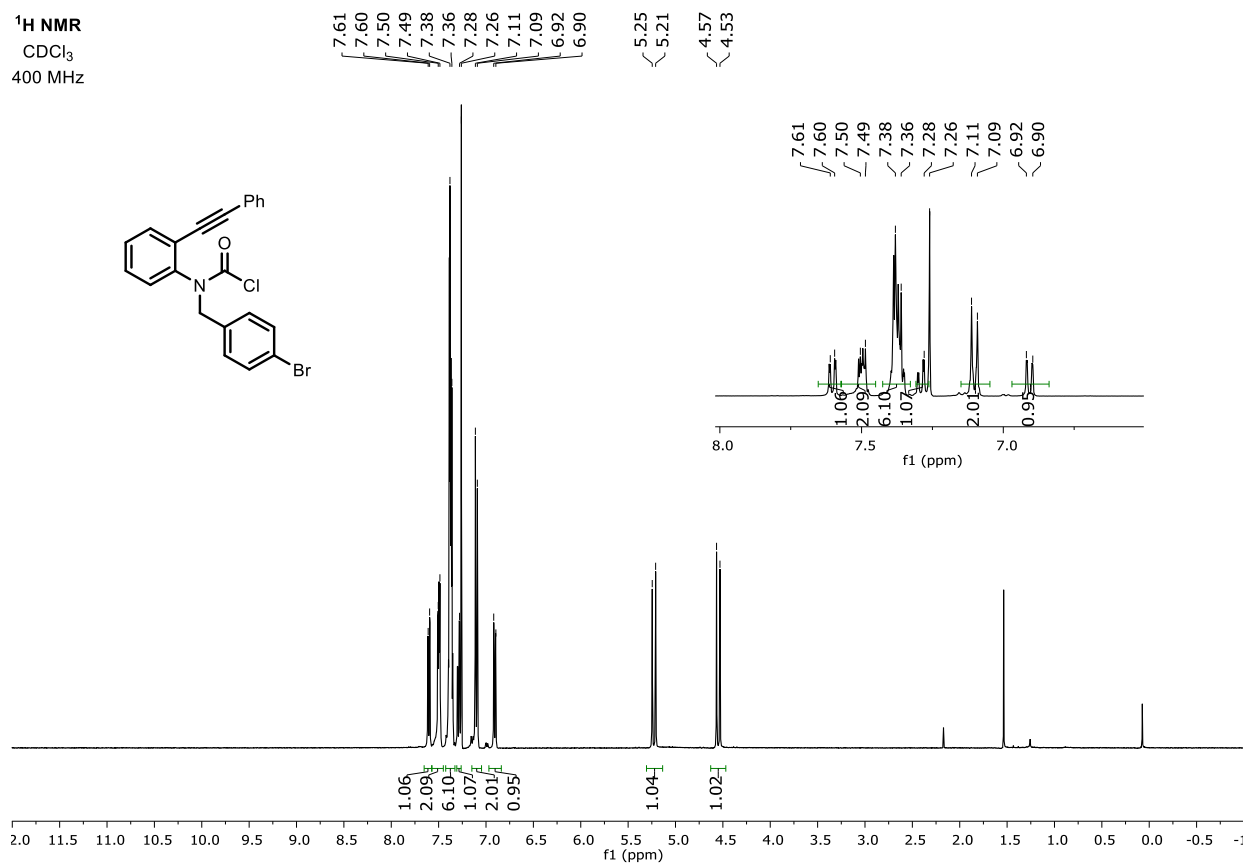


¹³C NMR
CDCl₃
126 MHz

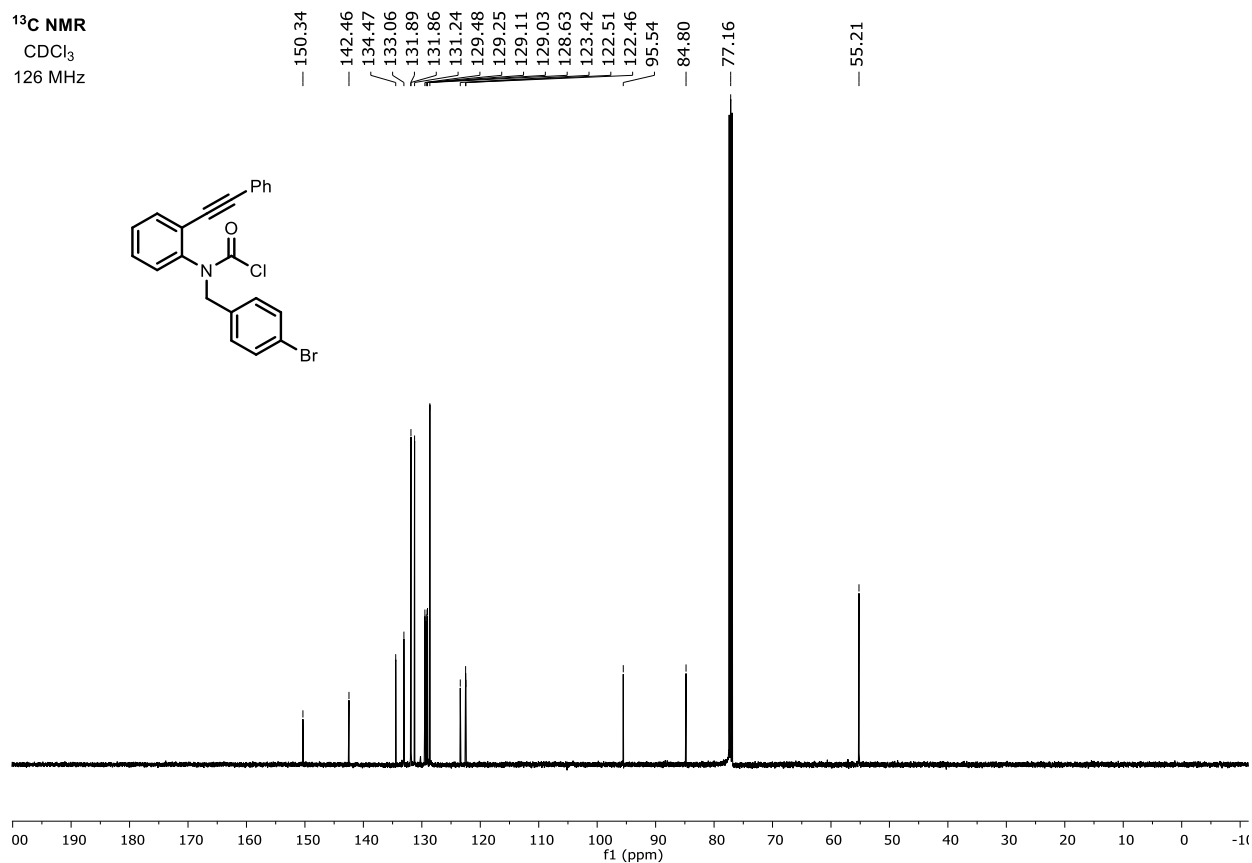


(4-bromobenzyl)(2-(phenylethynyl)phenyl)carbamic chloride (1m')

¹H NMR
CDCl₃
400 MHz



¹³C NMR
CDCl₃
126 MHz

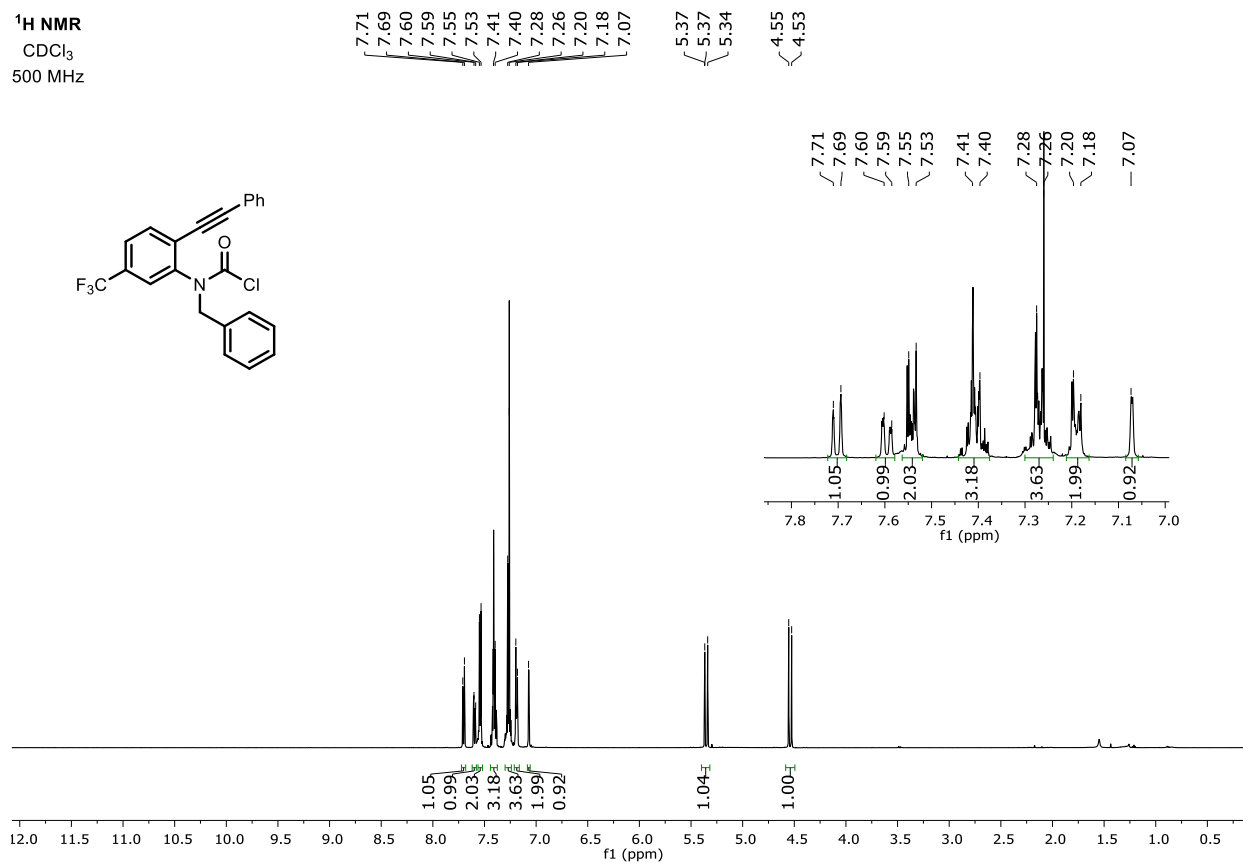
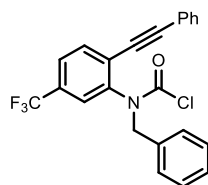


benzyl(2-(phenylethynyl)-5-(trifluoromethyl)phenyl)carbamate (1n')

¹H NMR

CDCl₃

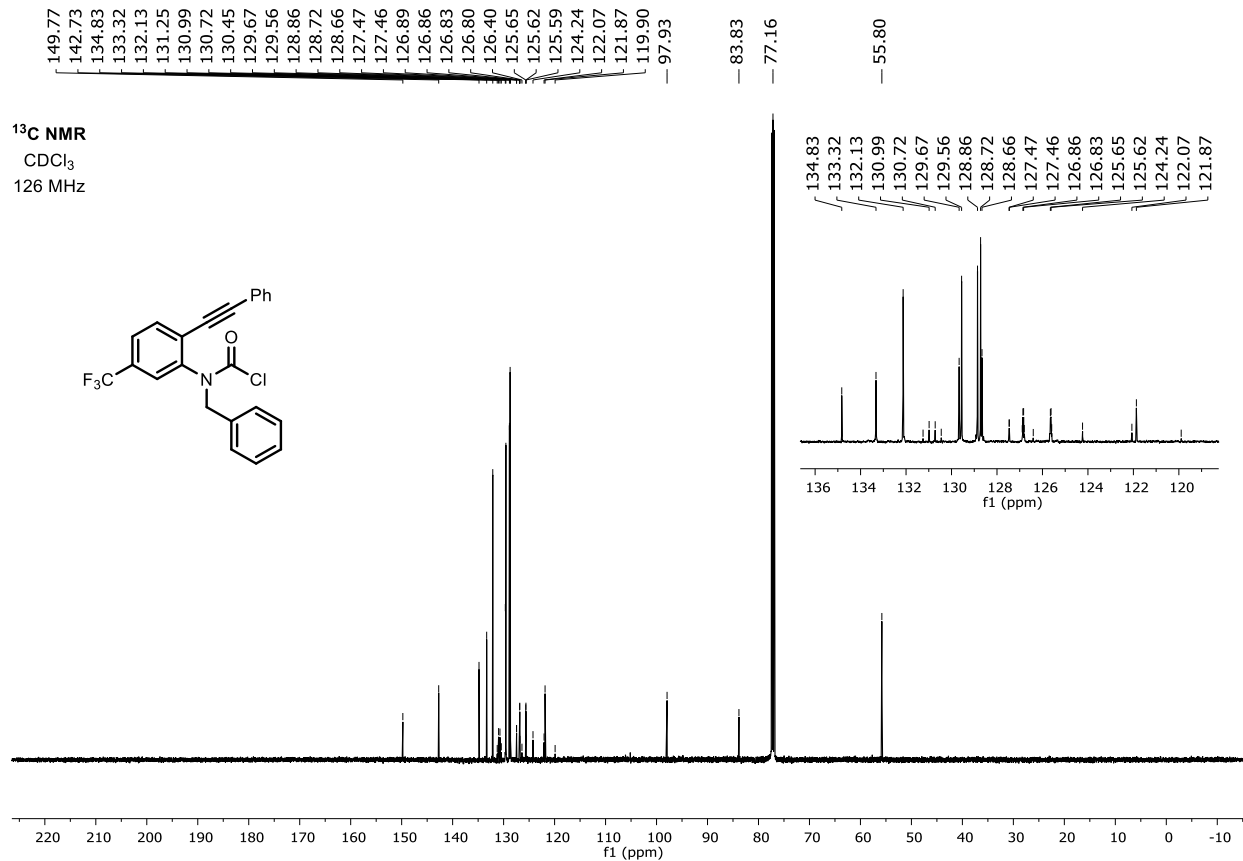
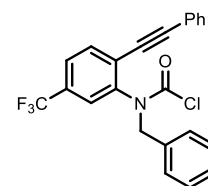
500 MHz



¹³C NMR

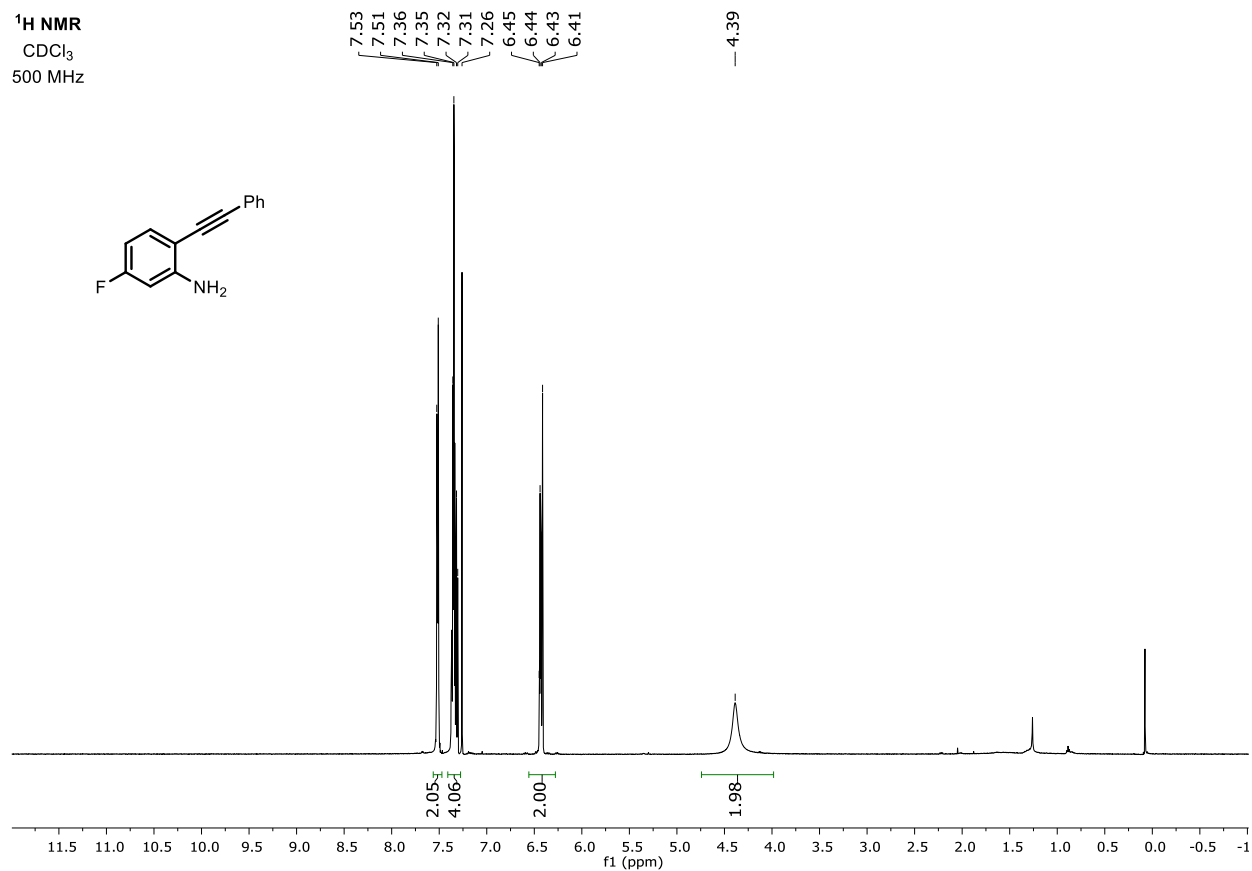
CDCl₃

126 MHz

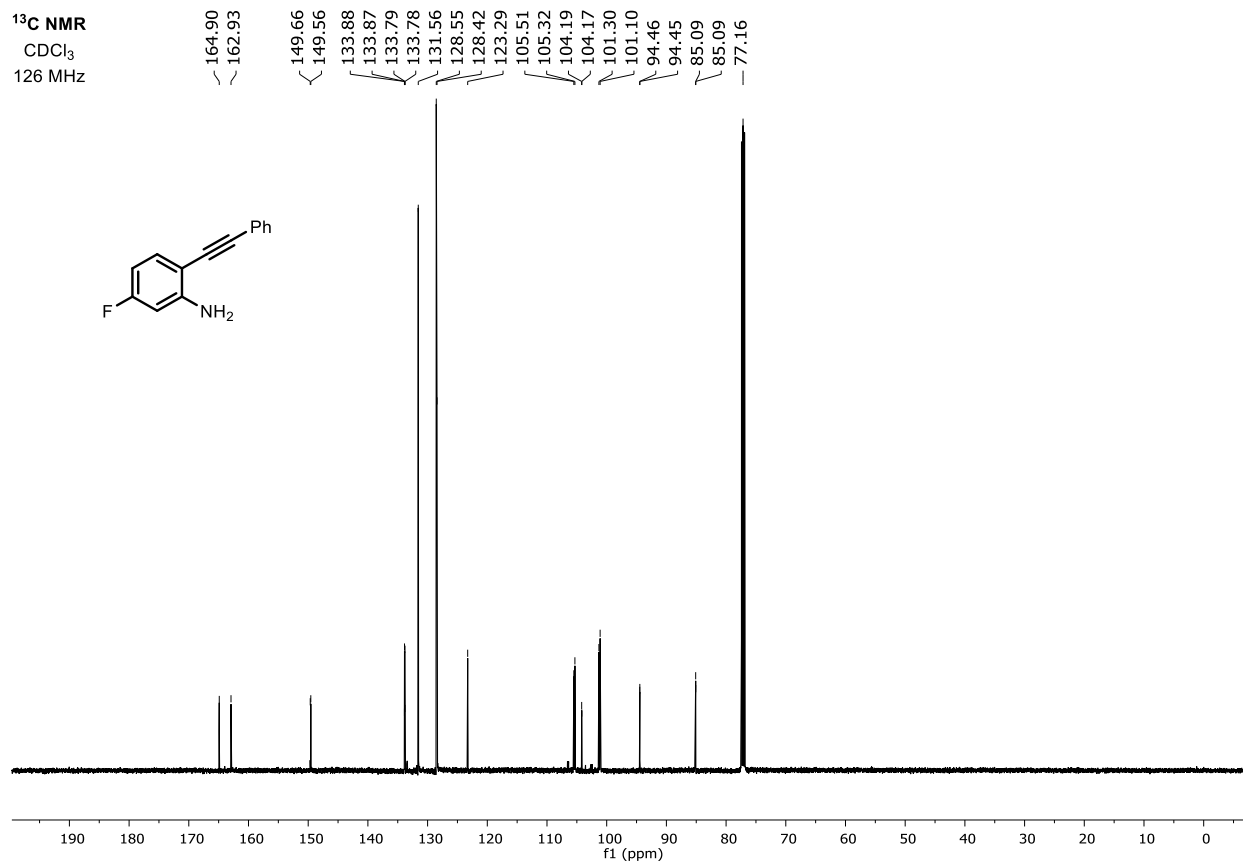


5-fluoro-2-(phenylethynyl)aniline (4o)

¹H NMR
CDCl₃
500 MHz

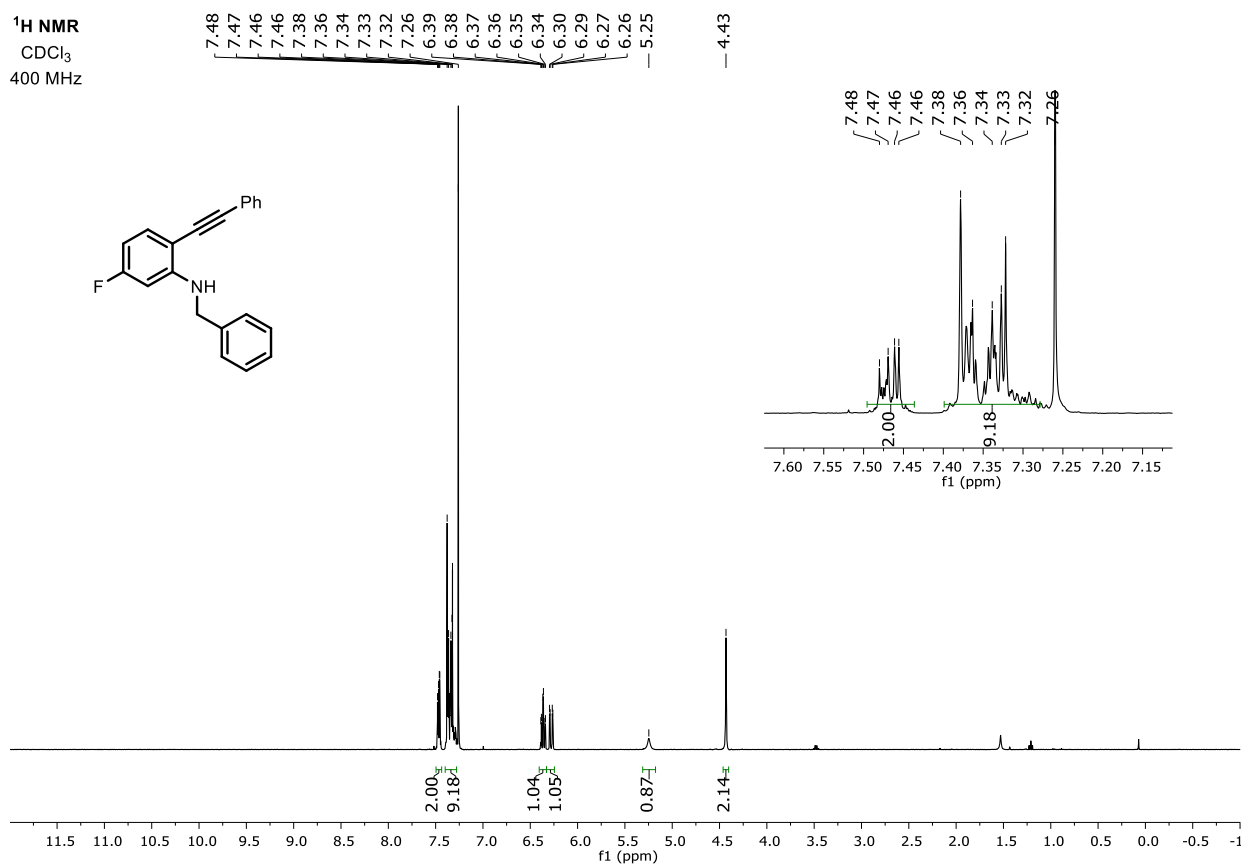


¹³C NMR
CDCl₃
126 MHz

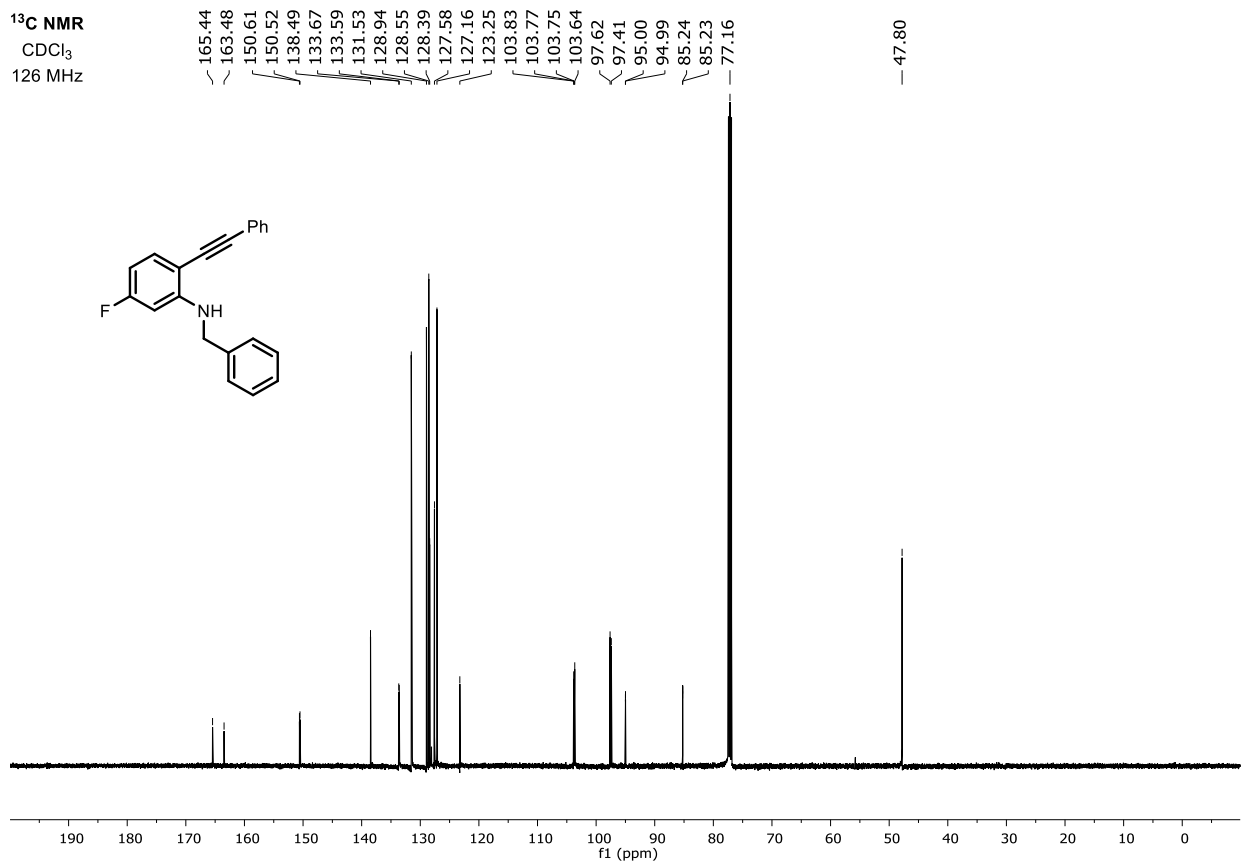


***N*-benzyl-5-fluoro-2-(phenylethynyl)aniline (5o)**

¹H NMR
CDCl₃
400 MHz

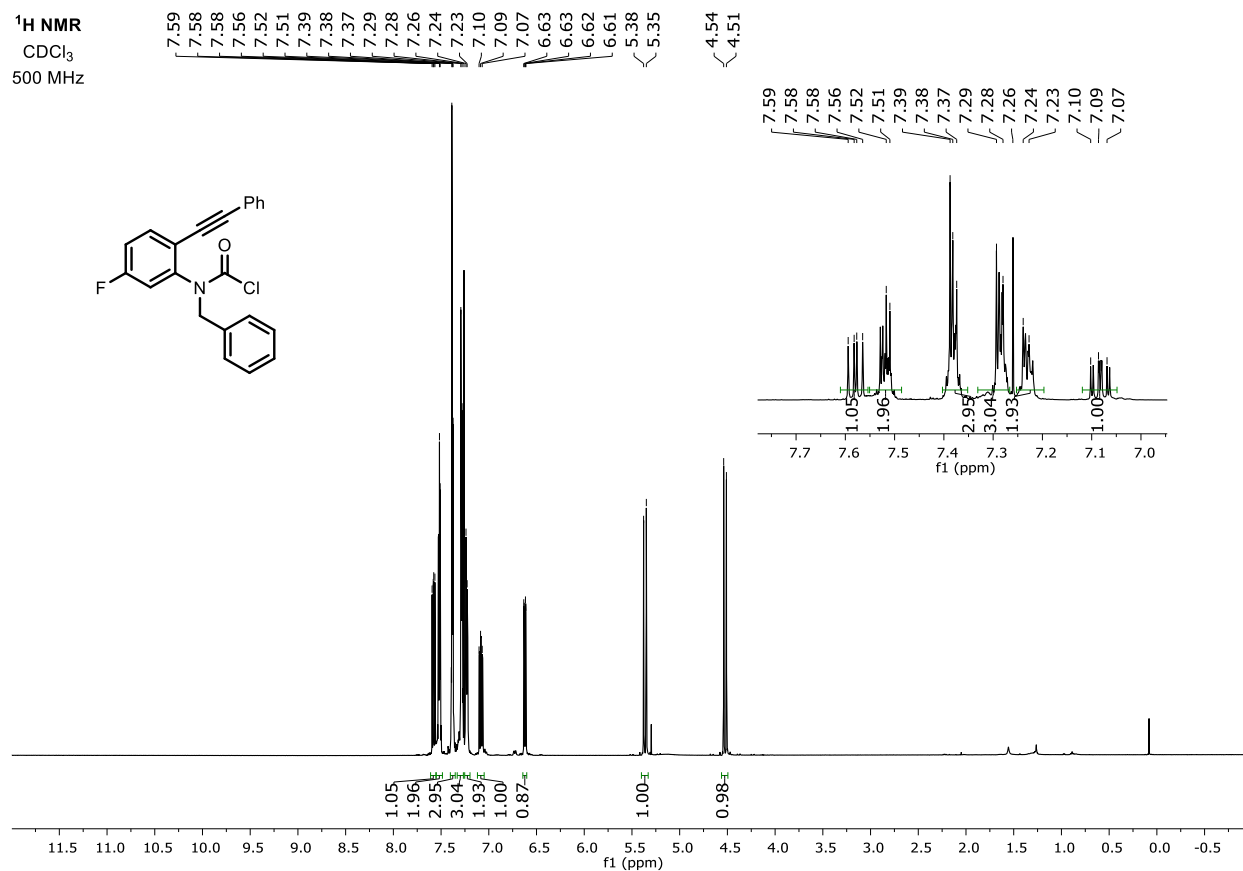


¹³C NMR
CDCl₃
126 MHz

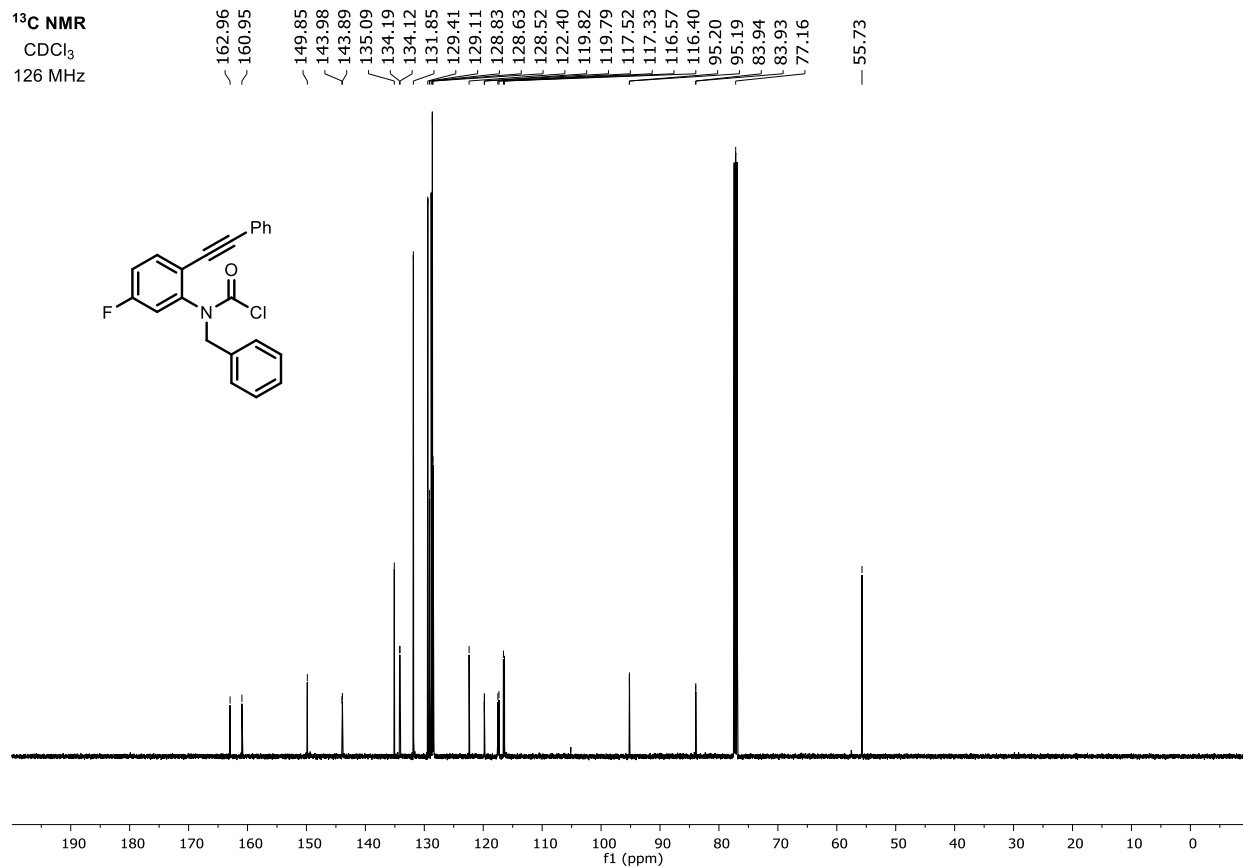


benzyl(5-fluoro-2-(phenylethynyl)phenyl)carbamic chloride (10')

¹H NMR
CDCl₃
500 MHz



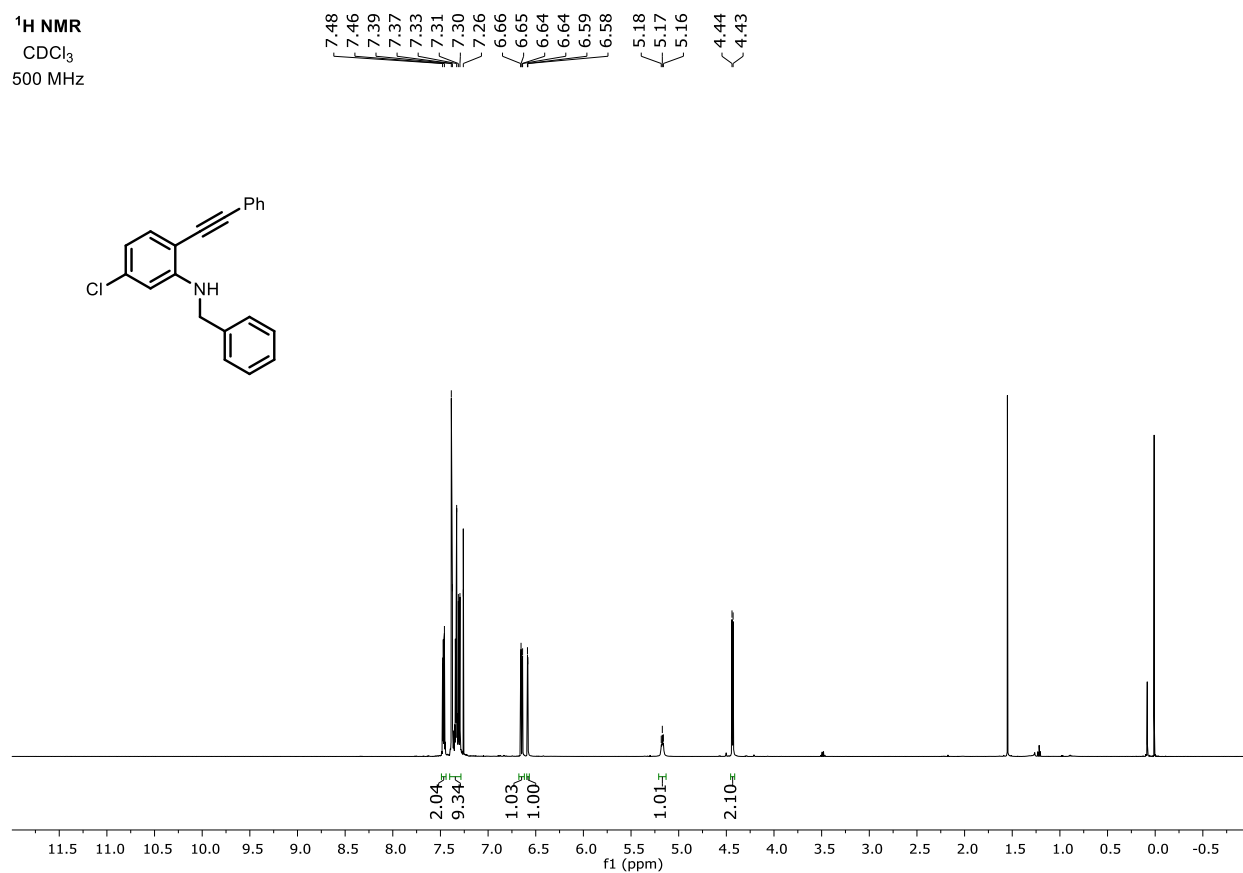
¹³C NMR
CDCl₃
126 MHz



***N*-benzyl-5-chloro-2-(phenylethynyl)aniline (5p)**

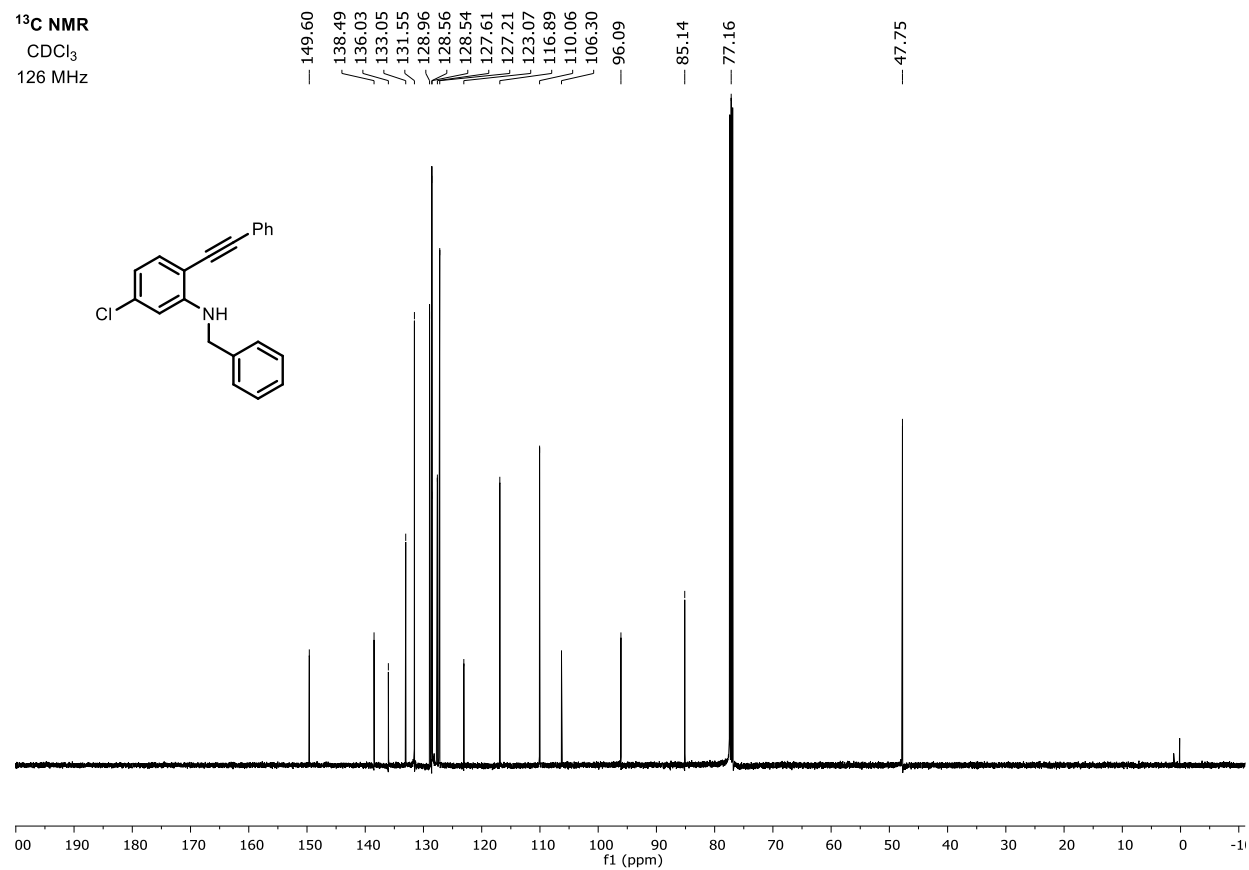
¹H NMR

CDCl₃
500 MHz



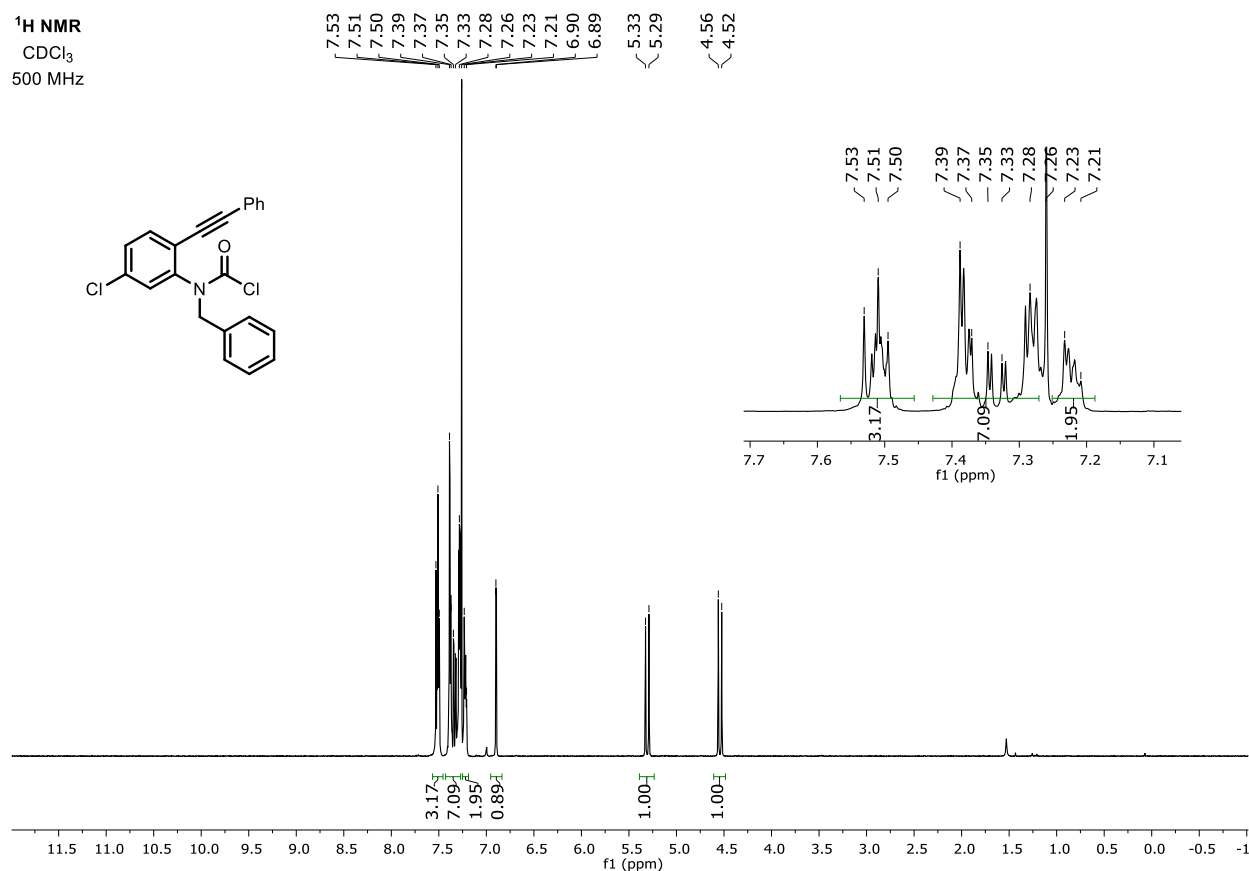
¹³C NMR

CDCl₃
126 MHz

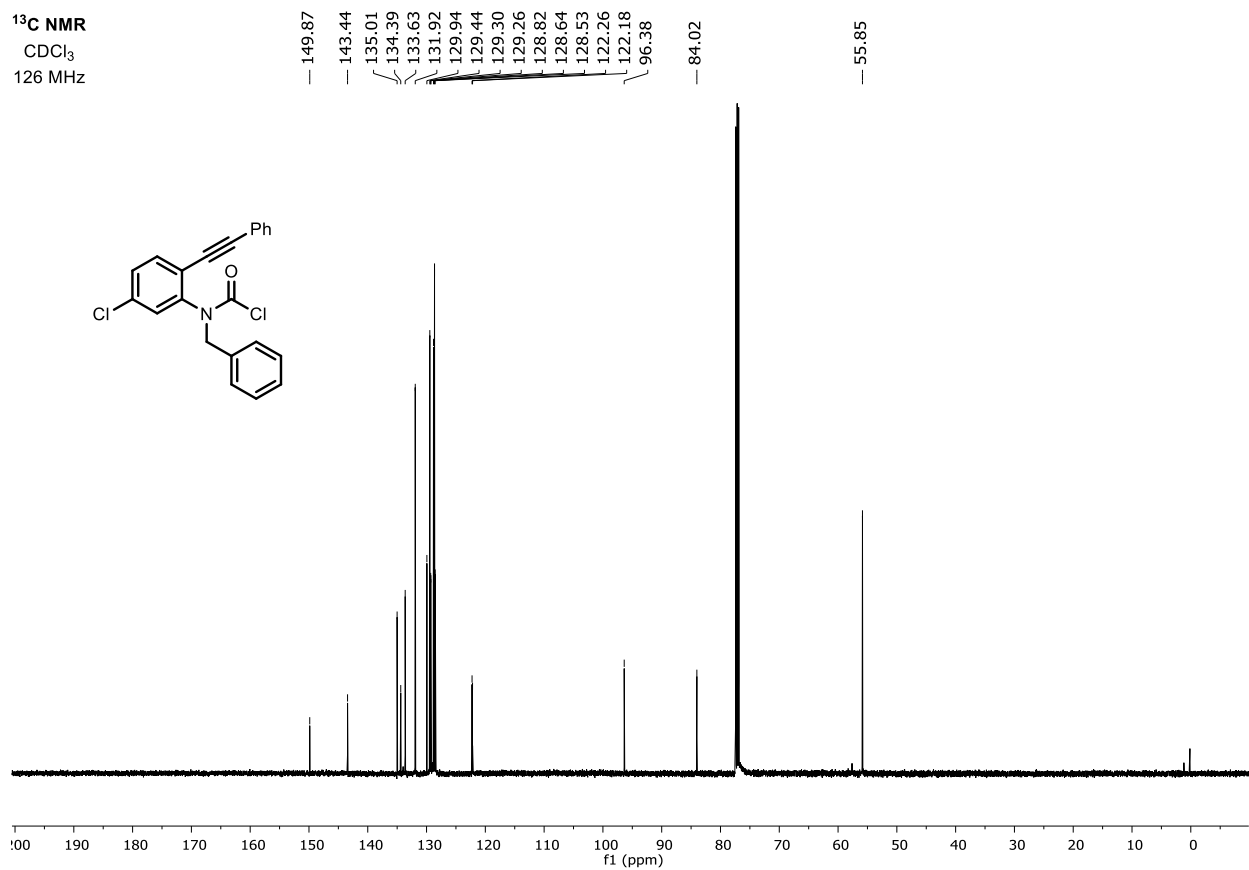


benzyl(5-chloro-2-(phenylethynyl)phenyl)carbamate (1p')

¹H NMR
CDCl₃
500 MHz

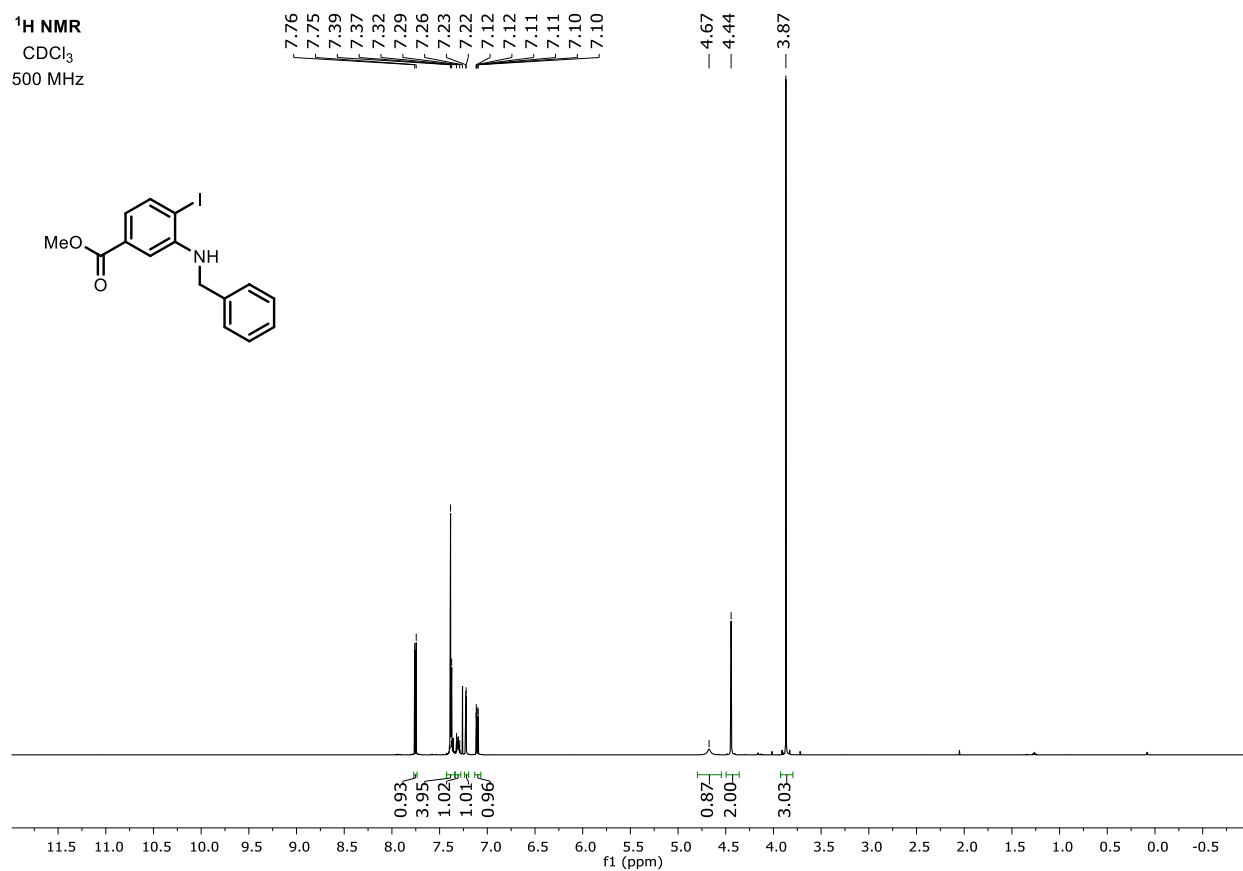


¹³C NMR
CDCl₃
126 MHz

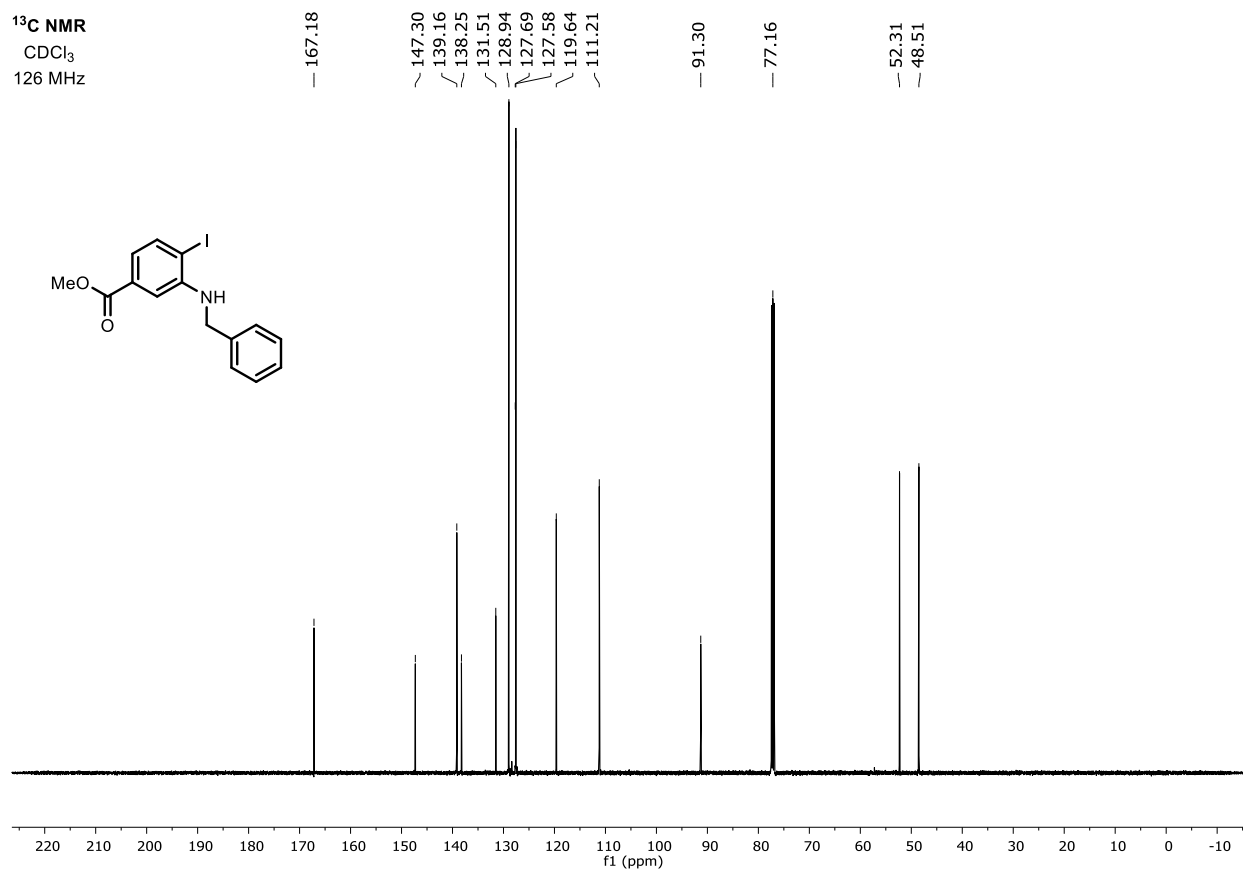


methyl 3-(benzylamino)-4-iodobenzoate (3q)

¹H NMR
CDCl₃
500 MHz

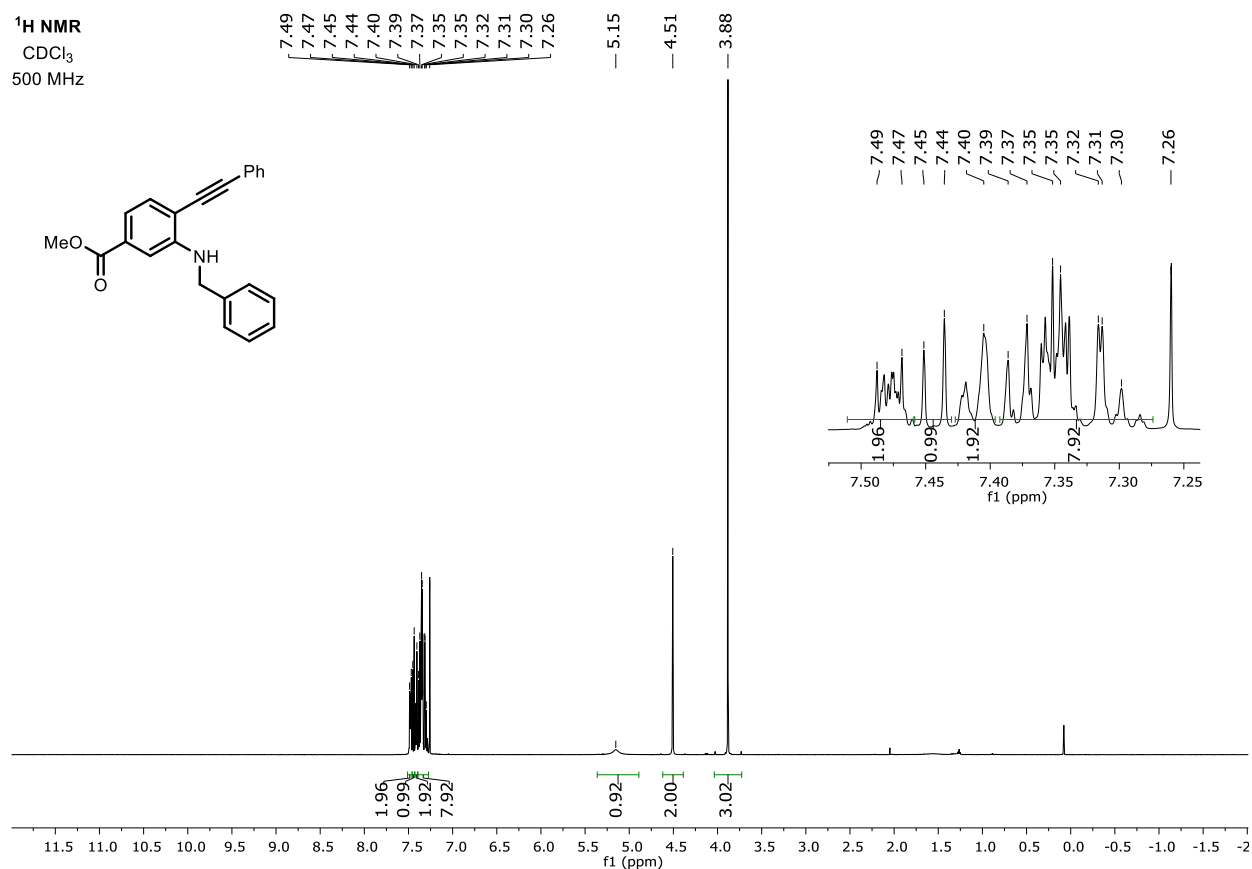


¹³C NMR
CDCl₃
126 MHz

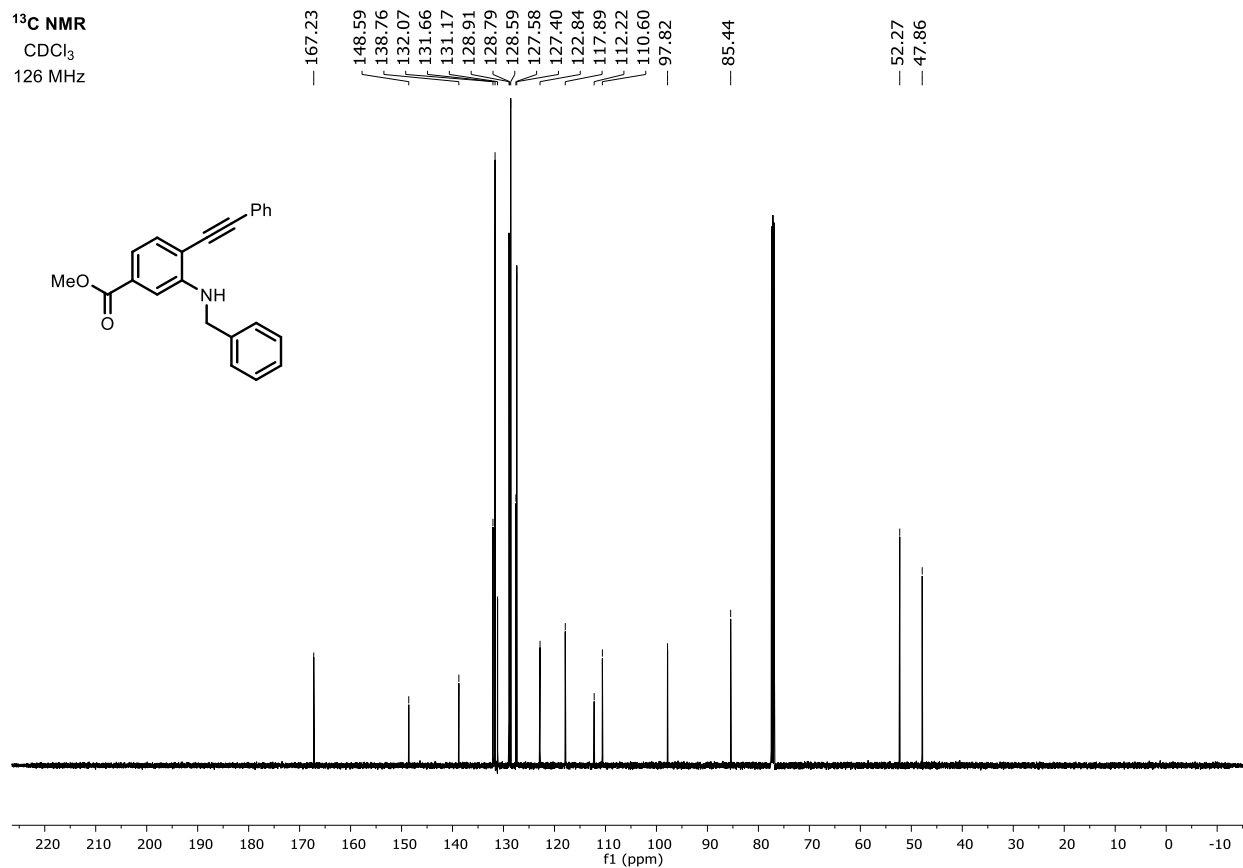


methyl 3-(benzylamino)-4-(phenylethynyl)benzoate (5q)

¹H NMR
CDCl₃
500 MHz

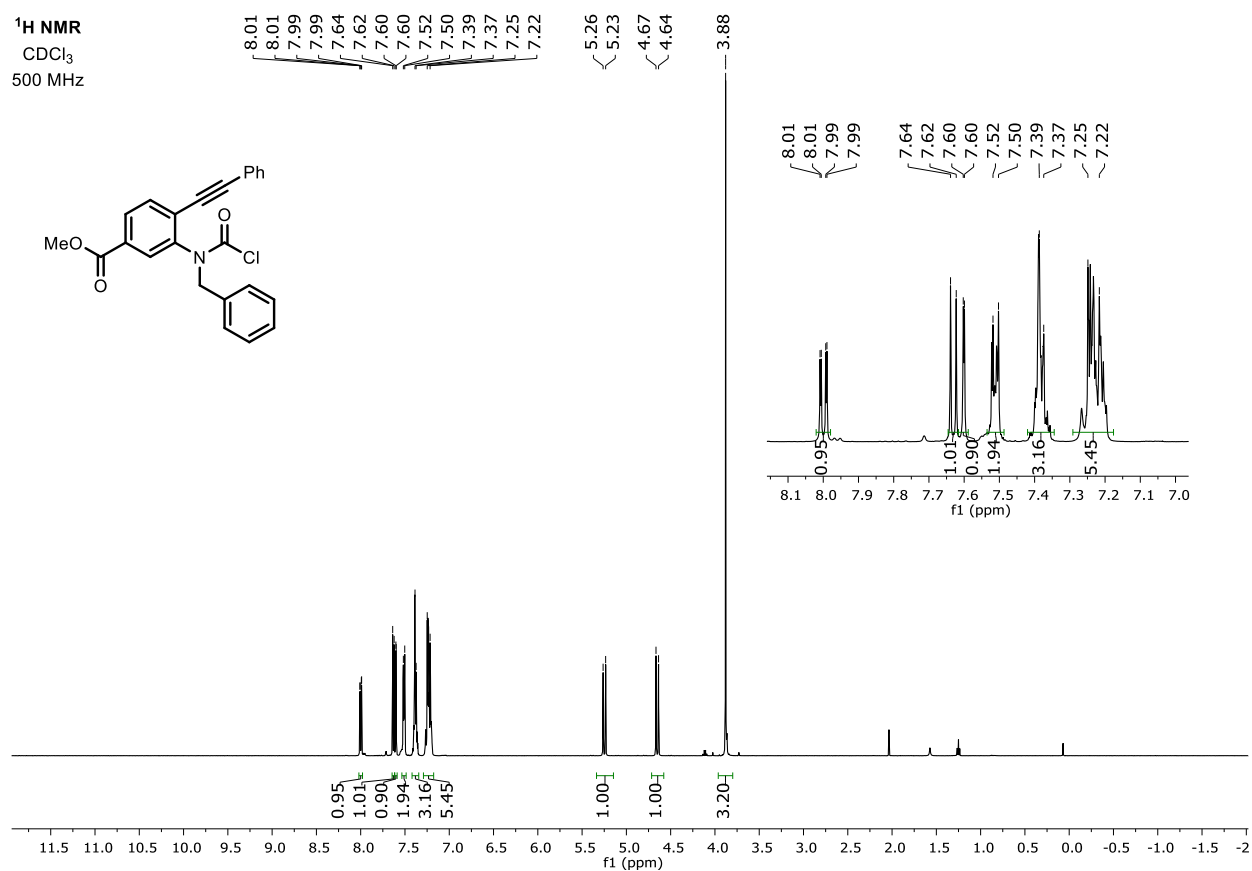
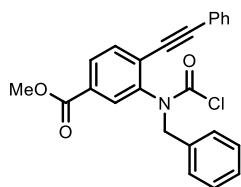


¹³C NMR
CDCl₃
126 MHz

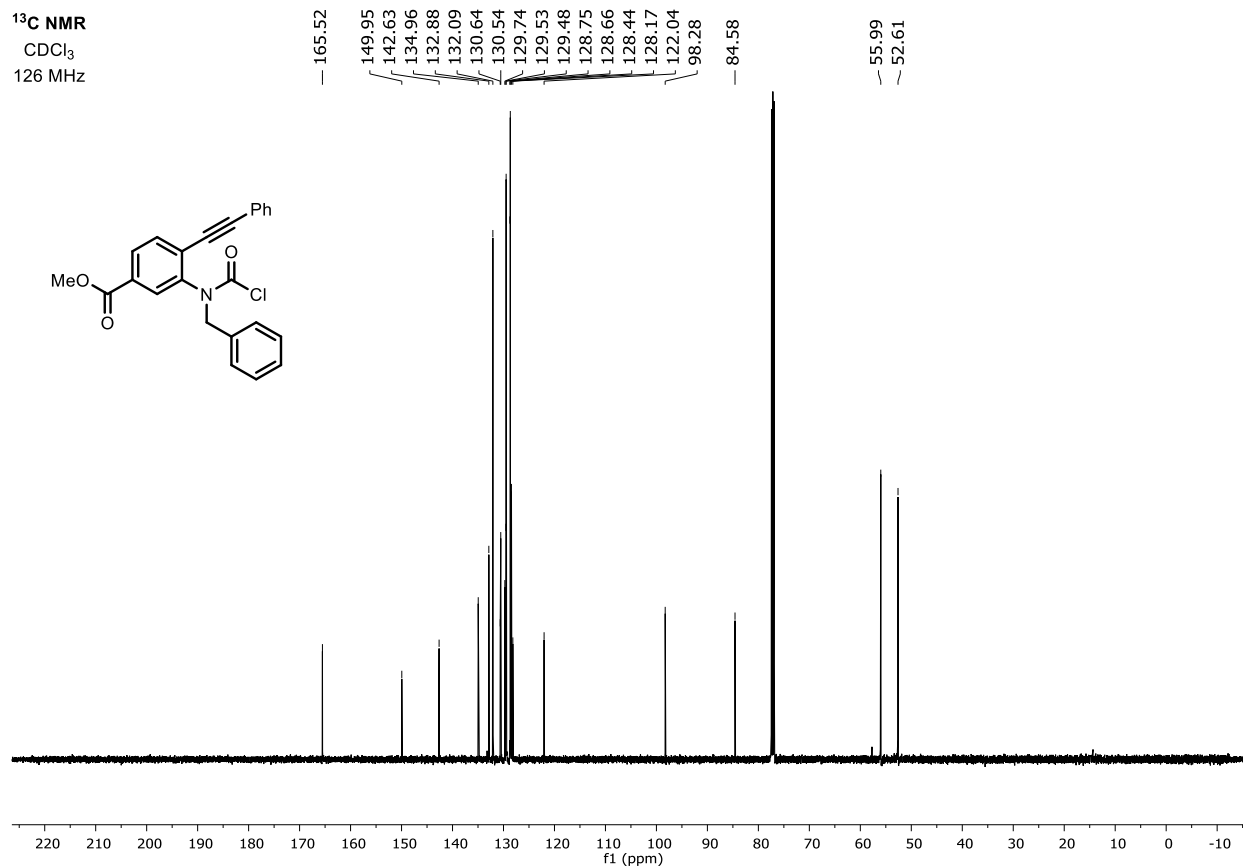
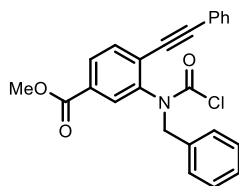


methyl 3-(benzyl(chlorocarbonyl)amino)-4-(phenylethynyl)benzoate (1q')

¹H NMR
CDCl₃
500 MHz



¹³C NMR
CDCl₃
126 MHz

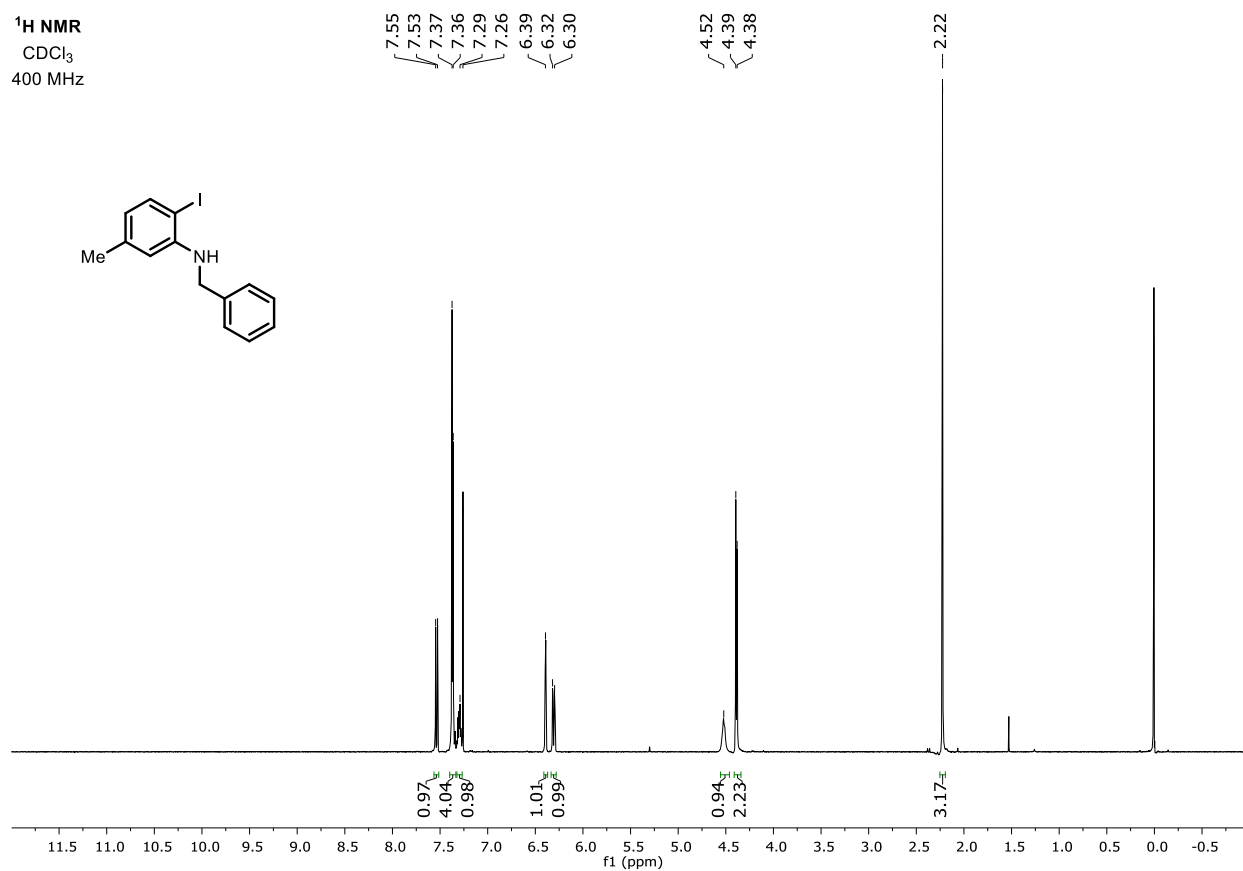


***N*-benzyl-2-iodo-5-methylaniline (3r)**

¹H NMR

CDCl₃

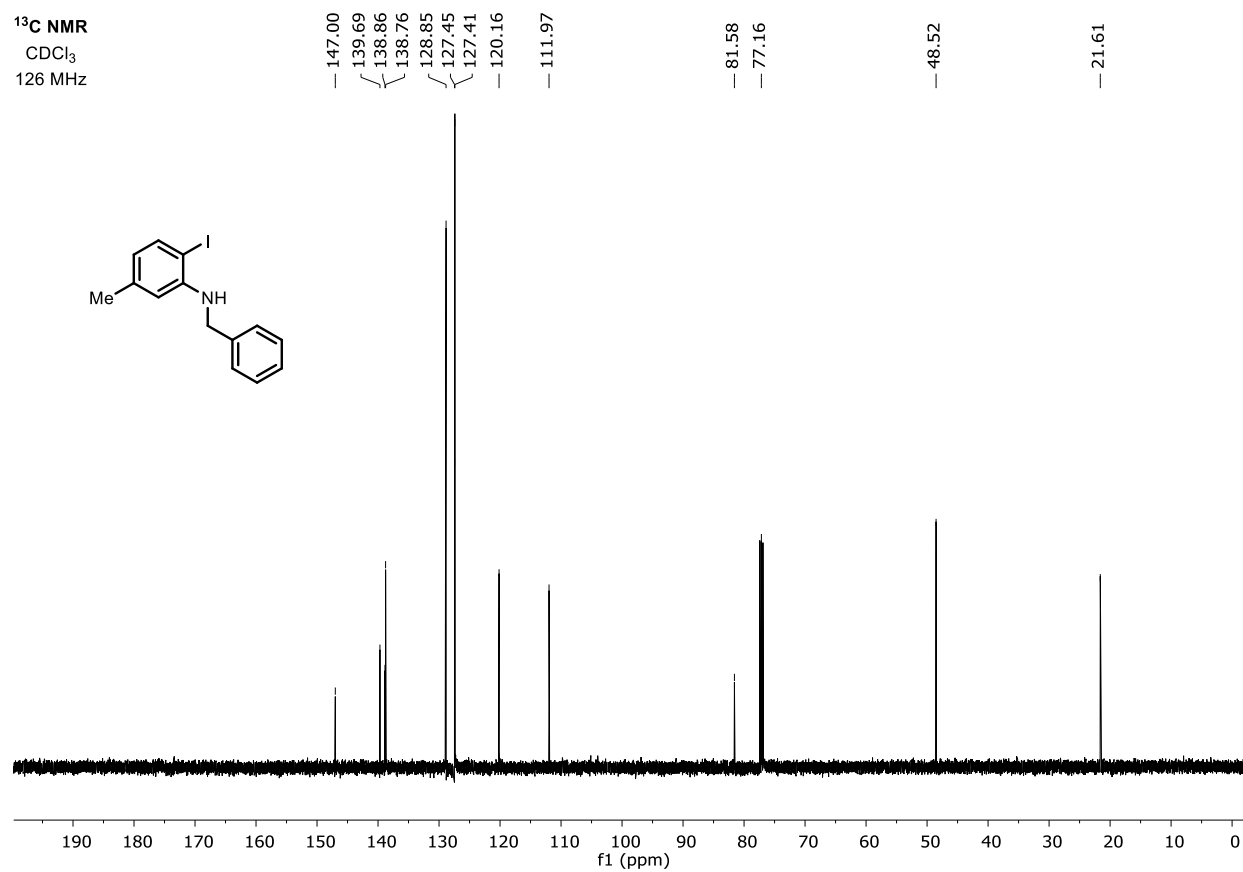
400 MHz



¹³C NMR

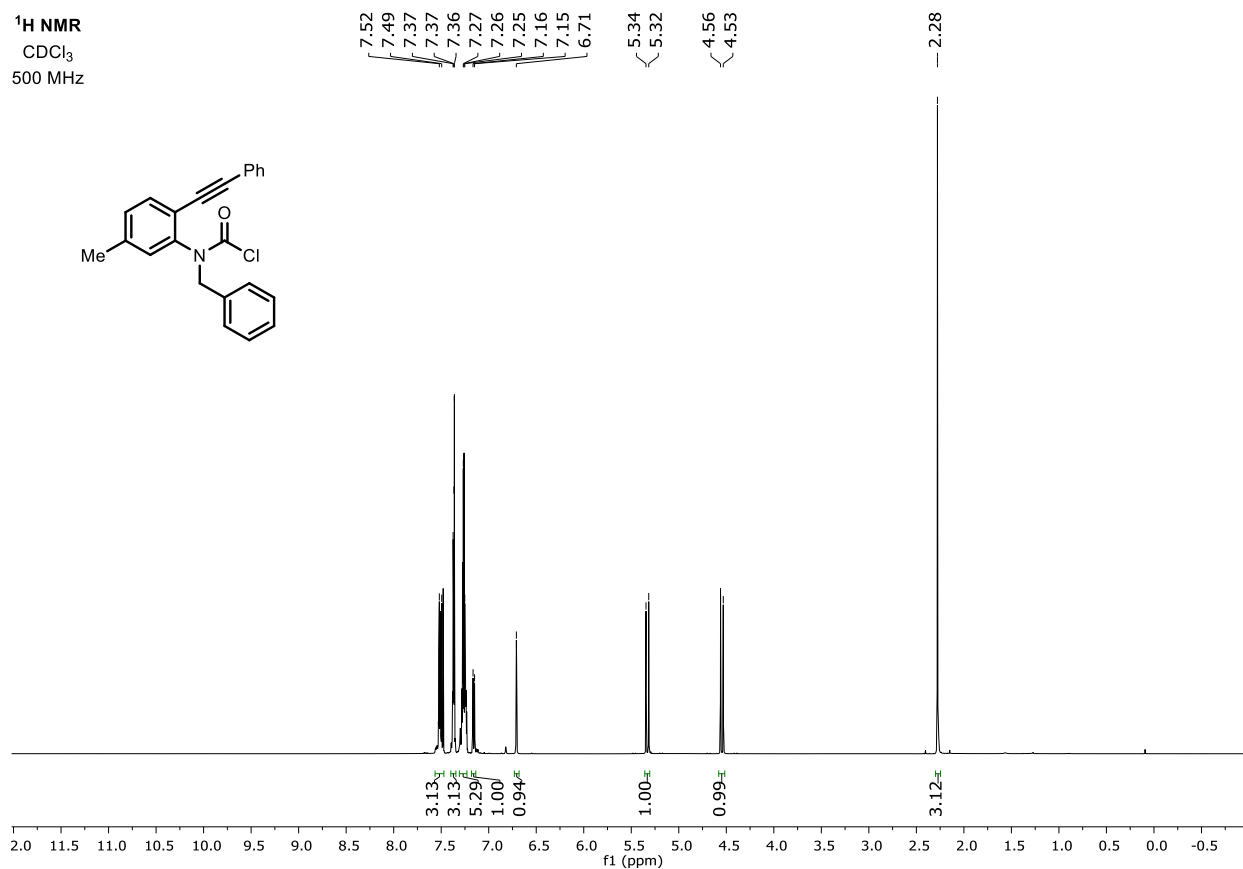
CDCl₃

126 MHz

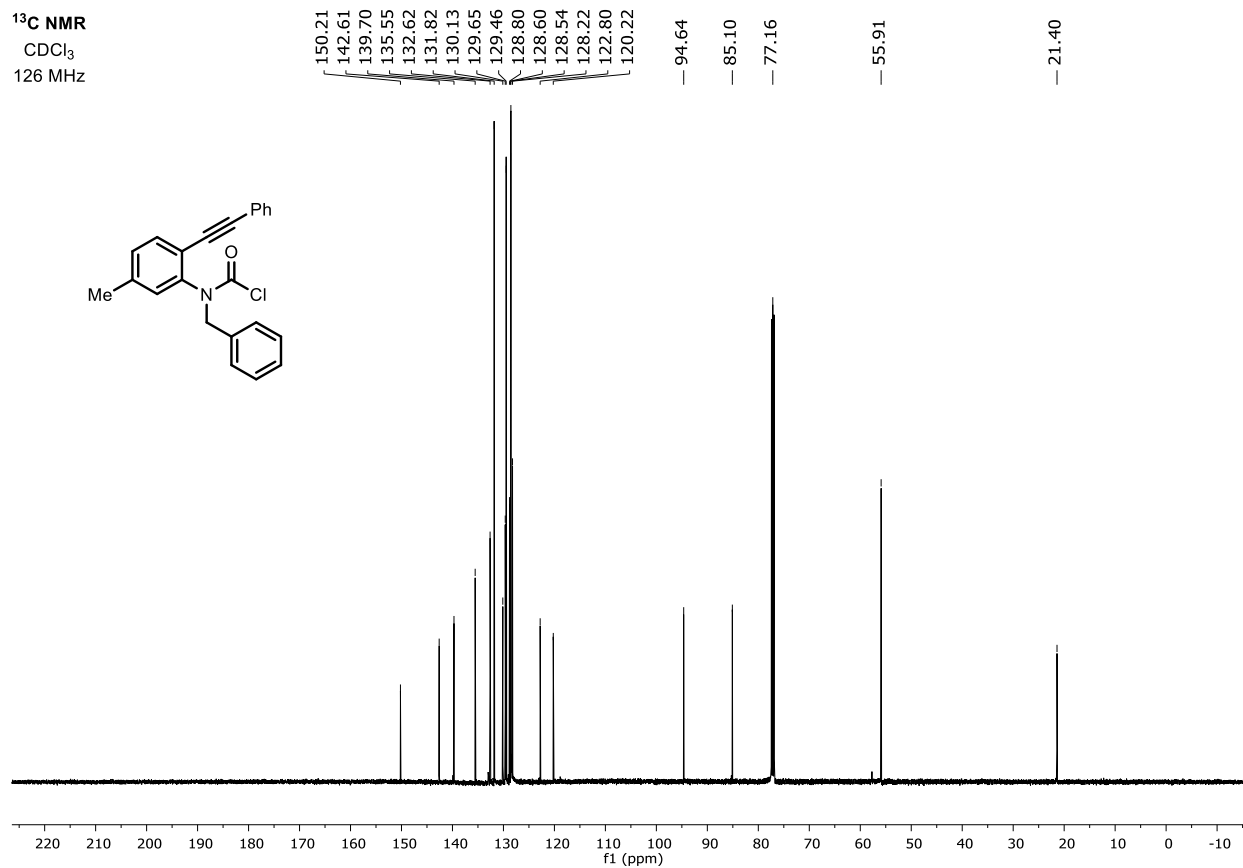


benzyl(5-methyl-2-(phenylethynyl)phenyl)carbamic chloride (1r')

¹H NMR
CDCl₃
500 MHz

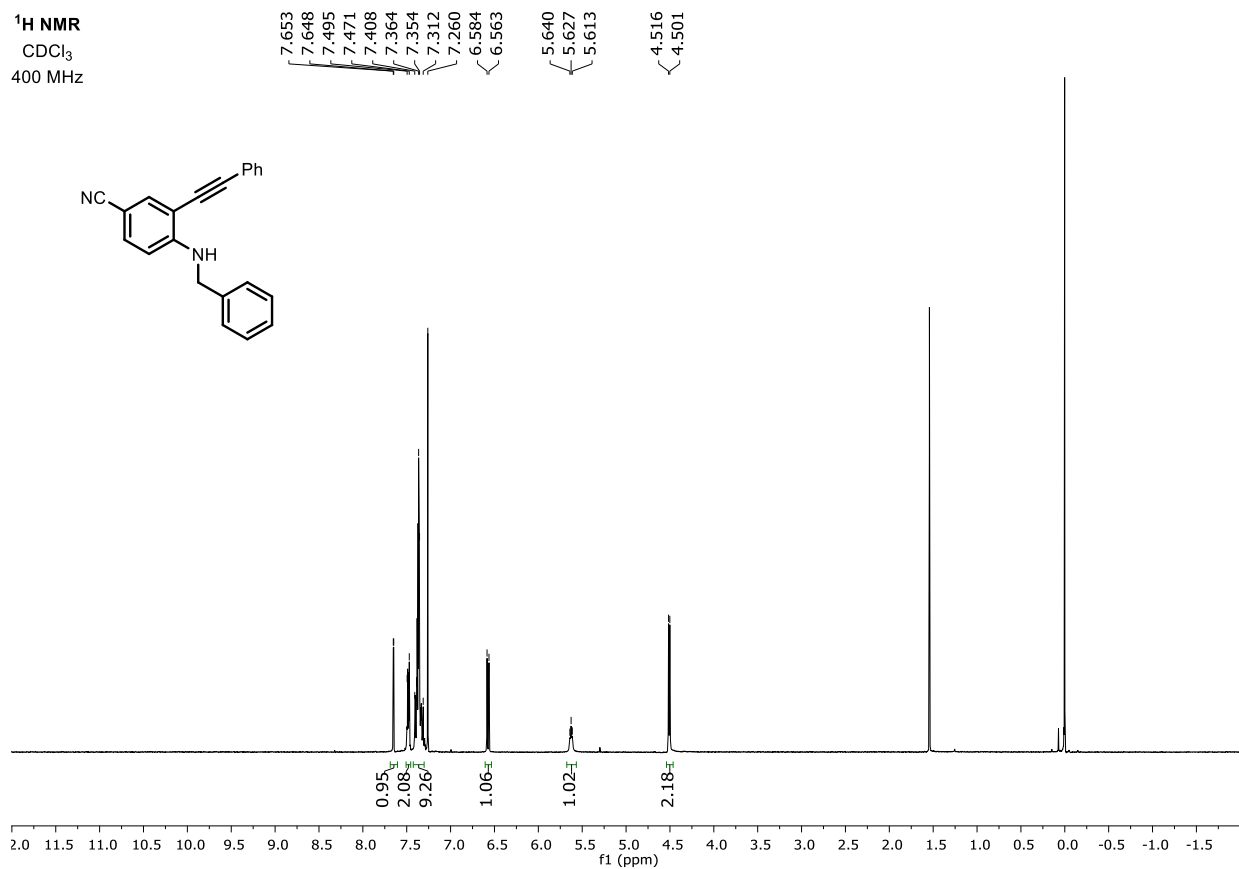


¹³C NMR
CDCl₃
126 MHz

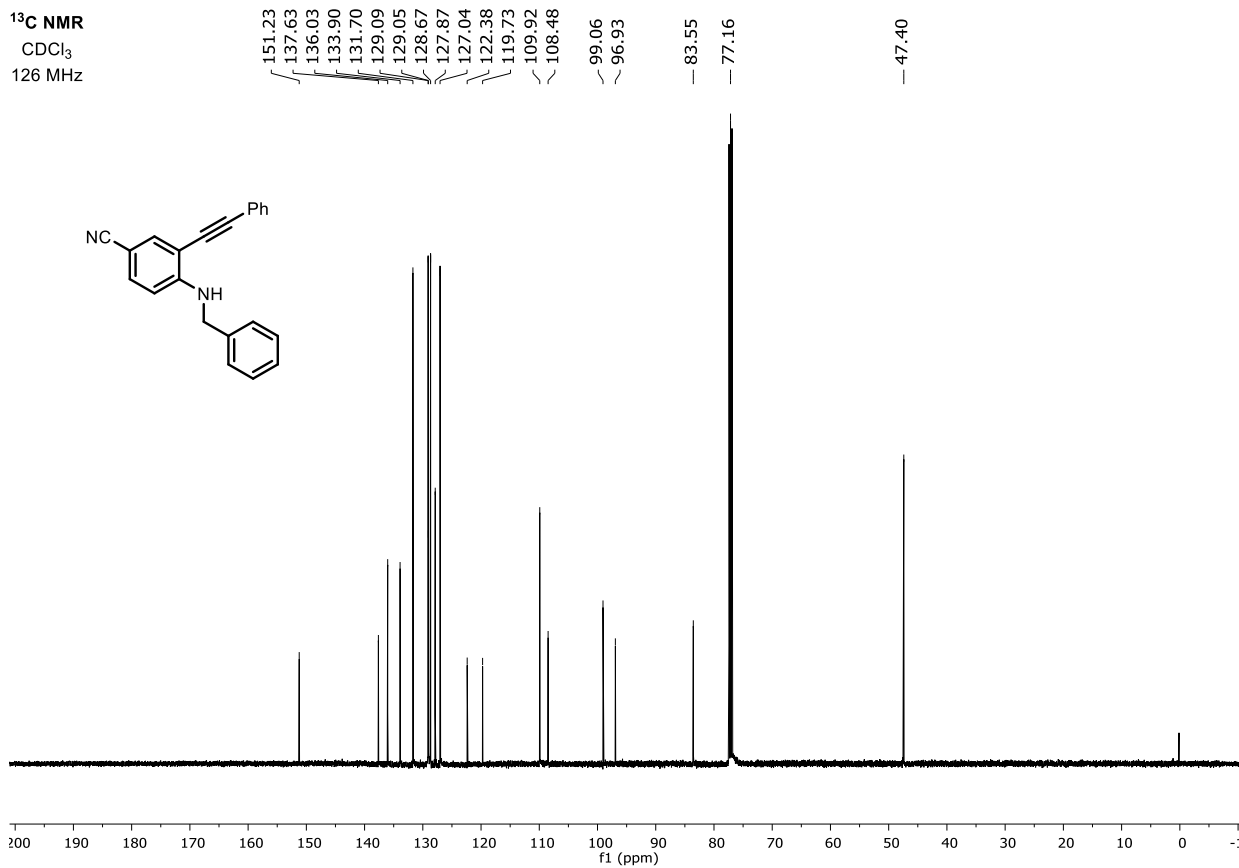


4-(benzylamino)-3-(phenylethynyl)benzonitrile (5s)

¹H NMR
CDCl₃
400 MHz

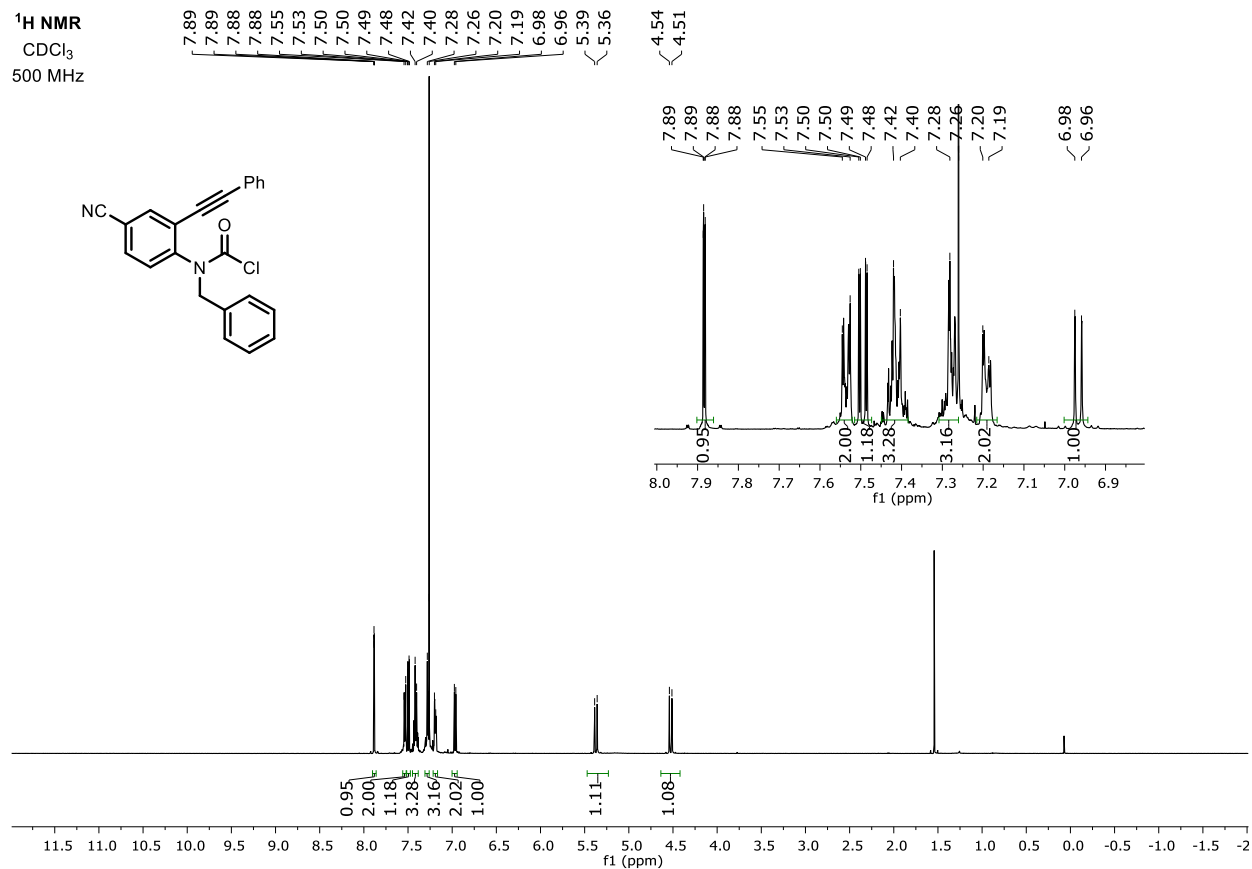
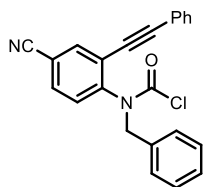


¹³C NMR
CDCl₃
126 MHz

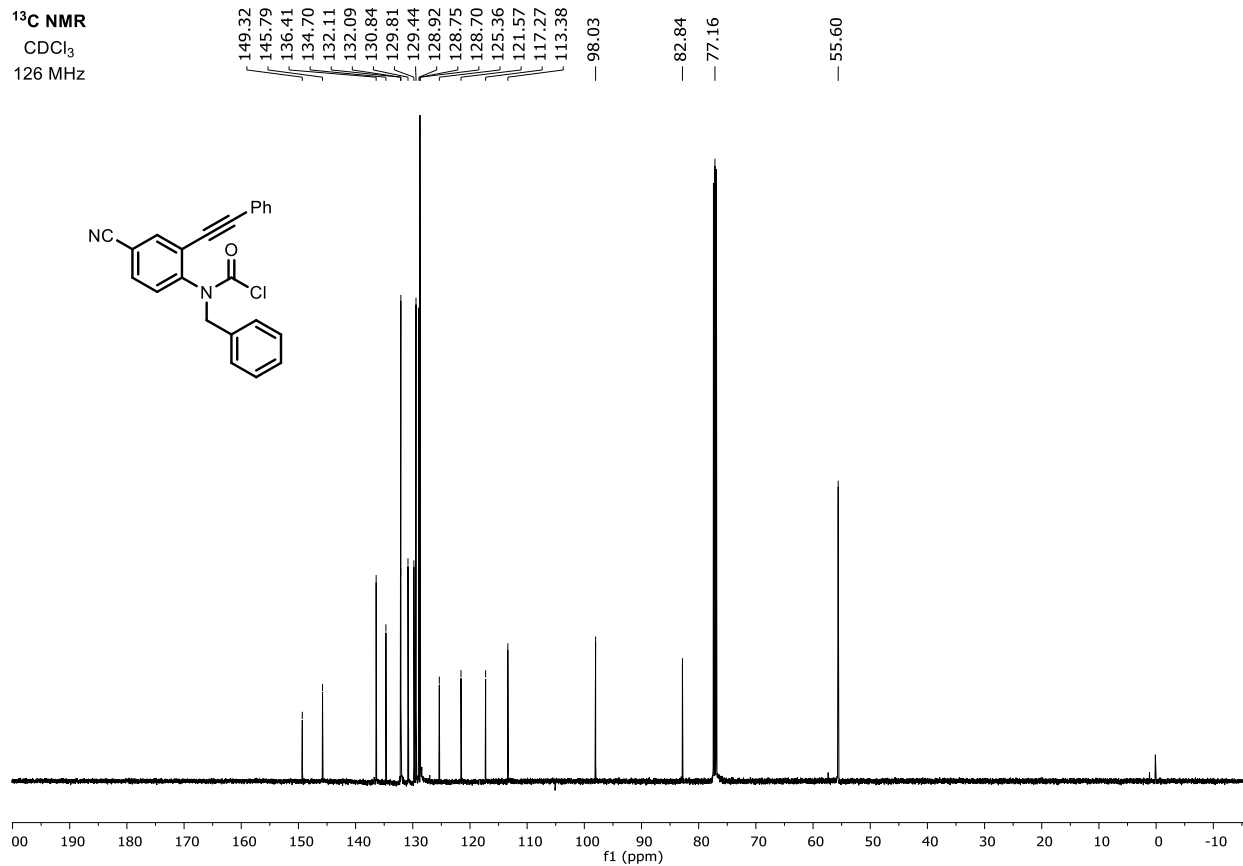
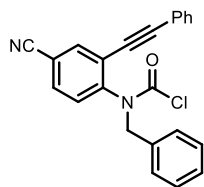


benzyl(4-cyano-2-(phenylethynyl)phenyl)carbamic chloride (1s')

¹H NMR
CDCl₃
500 MHz

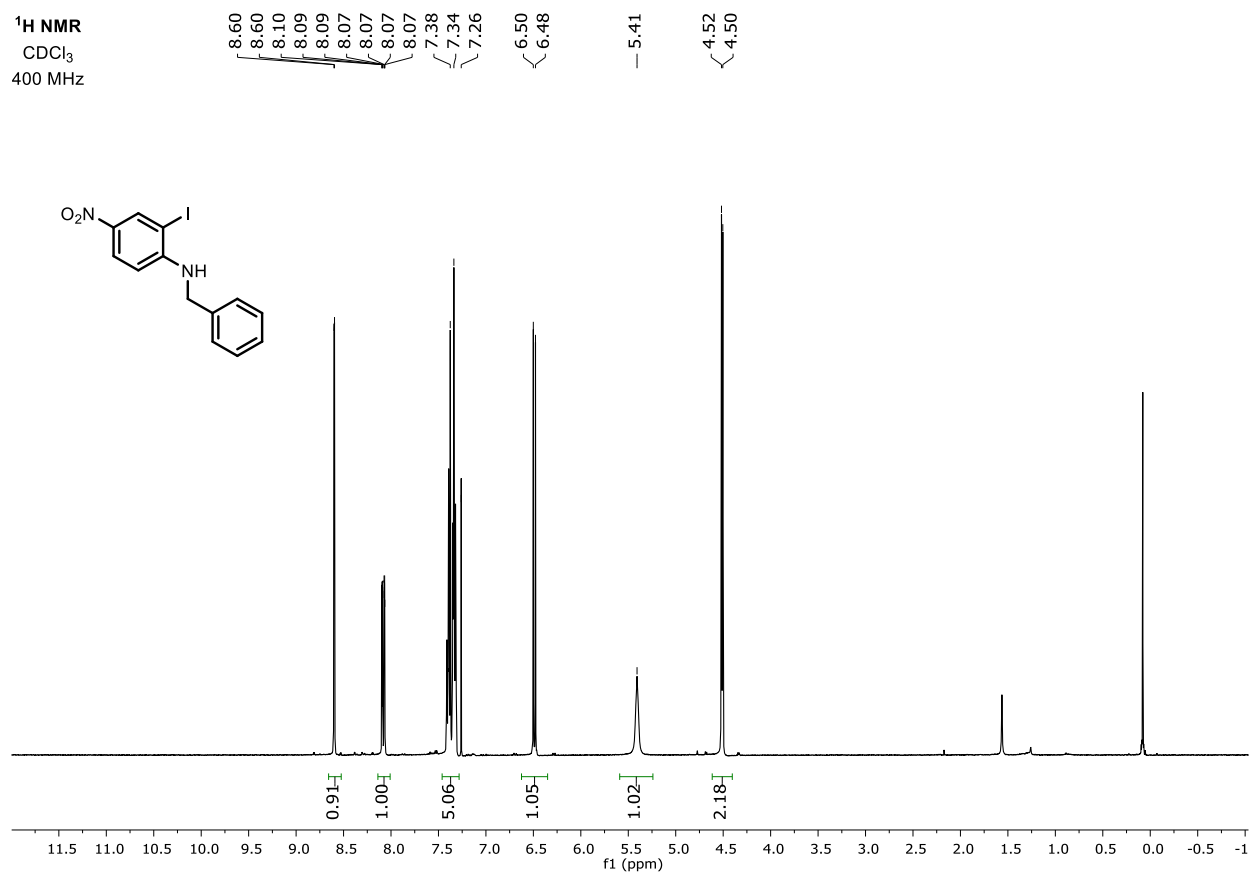


¹³C NMR
CDCl₃
126 MHz

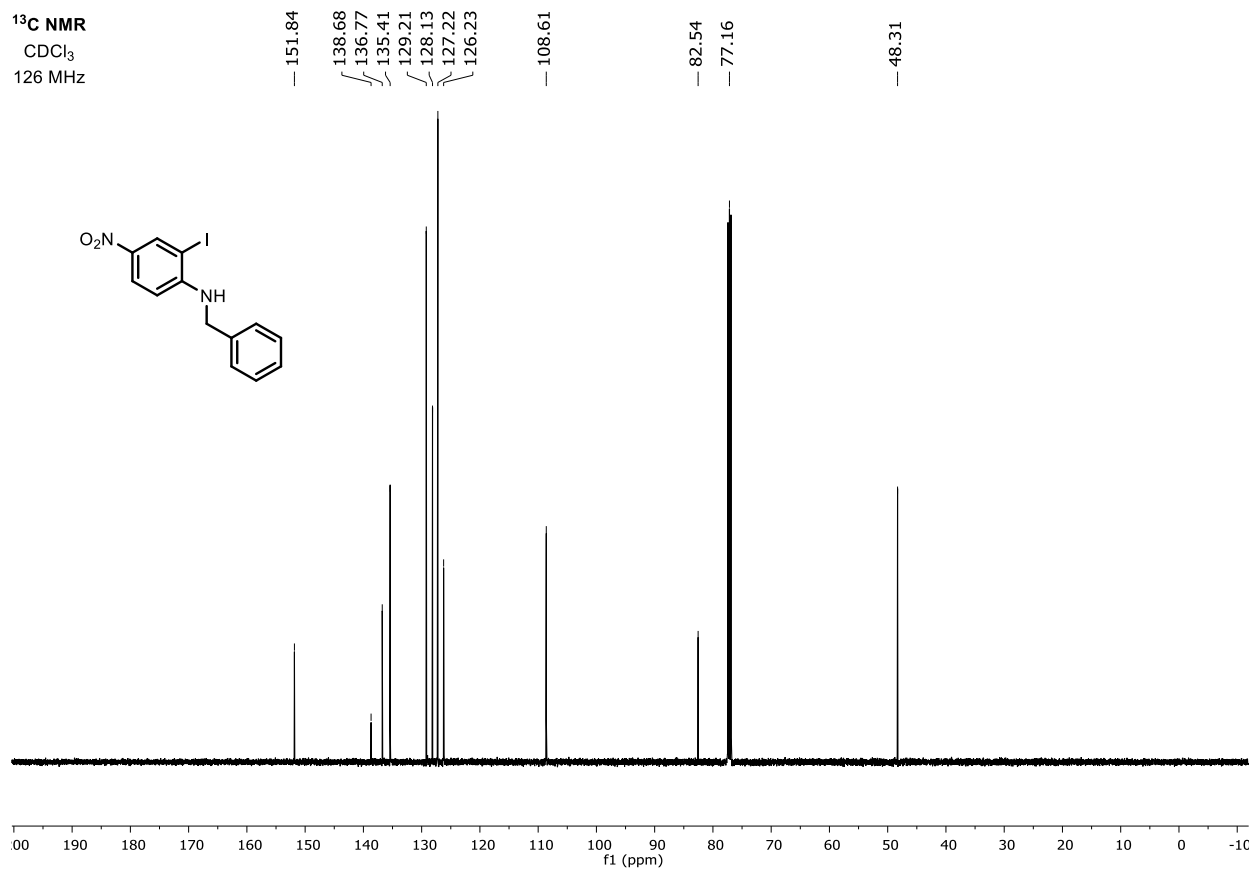


***N*-benzyl-2-iodo-4-nitroaniline (3t)**

¹H NMR
CDCl₃
400 MHz

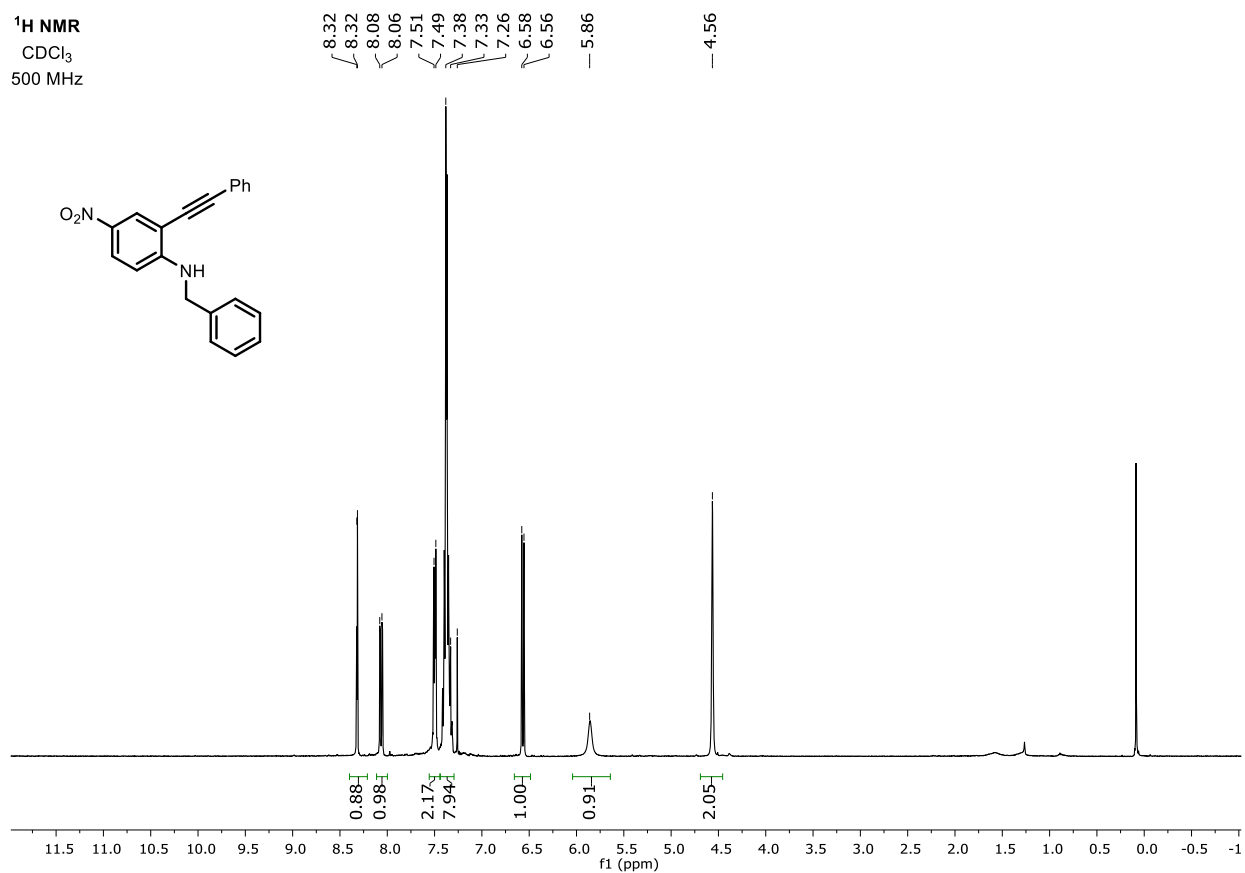


¹³C NMR
CDCl₃
126 MHz

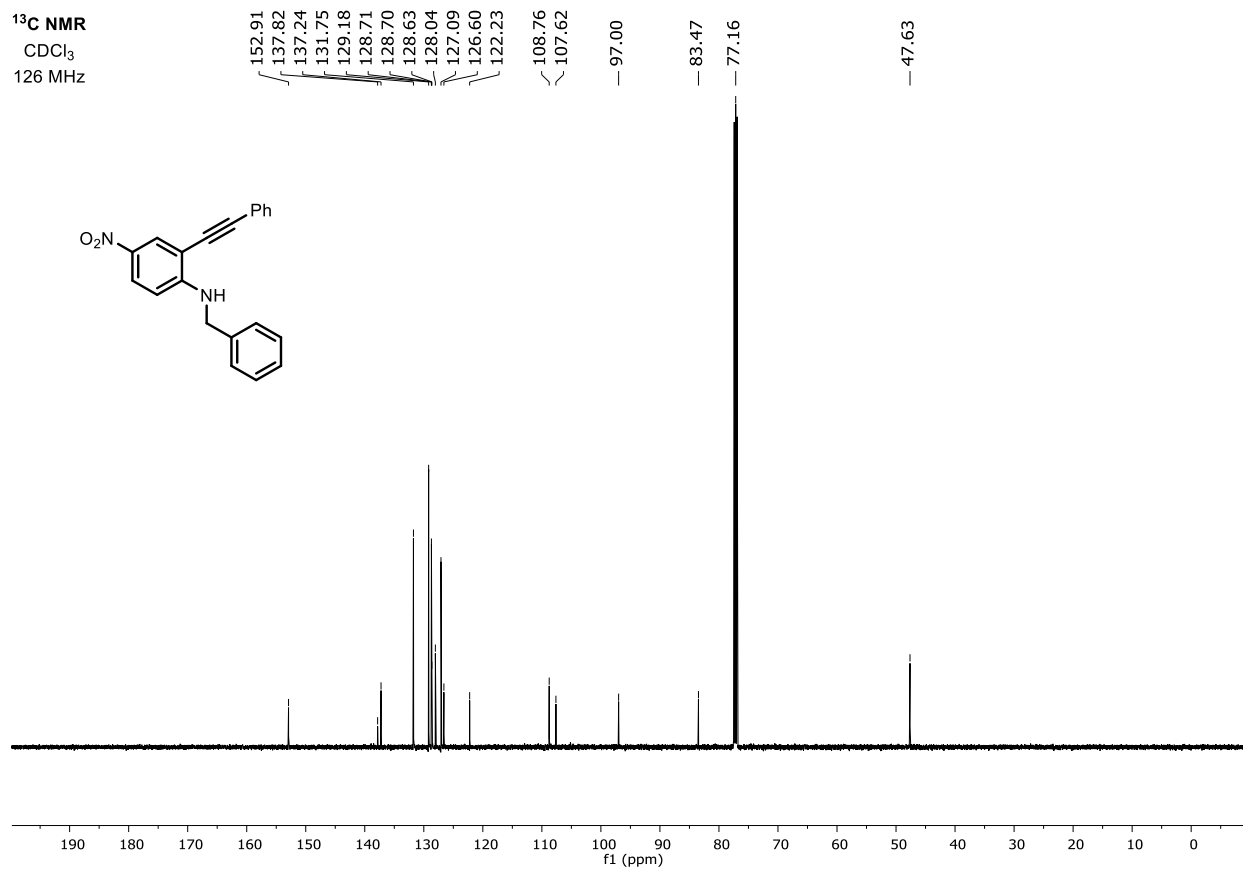


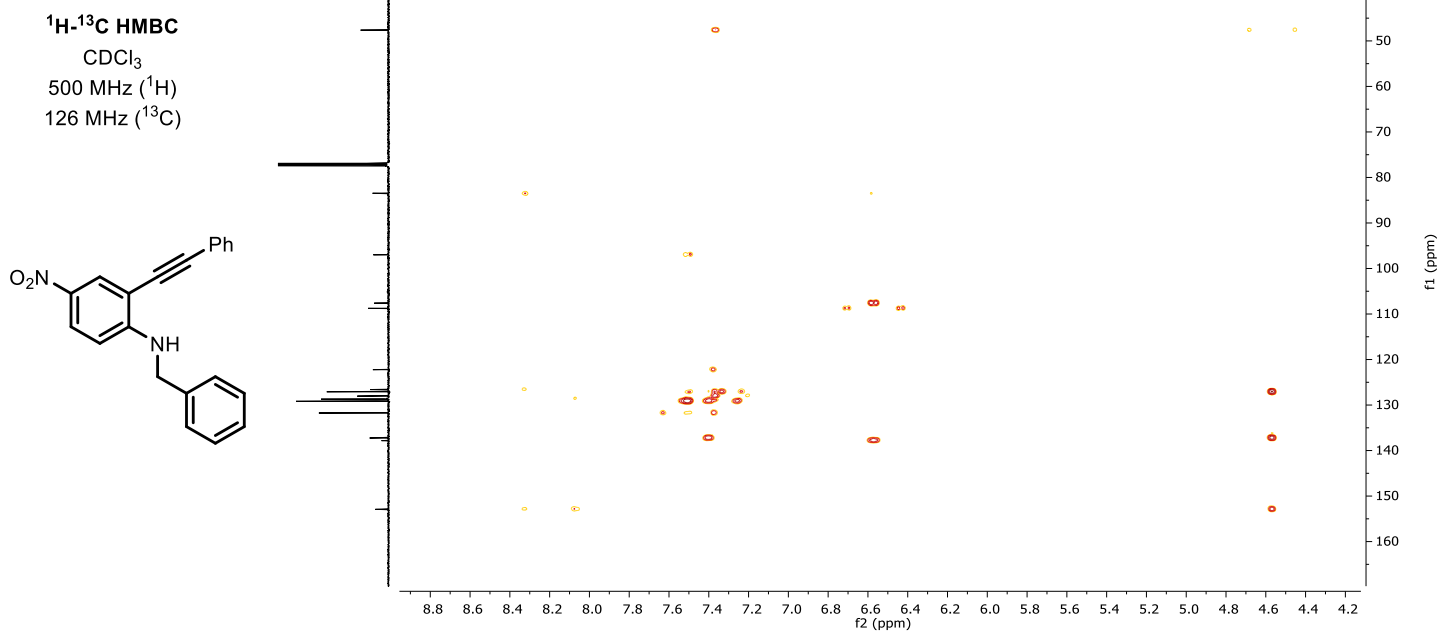
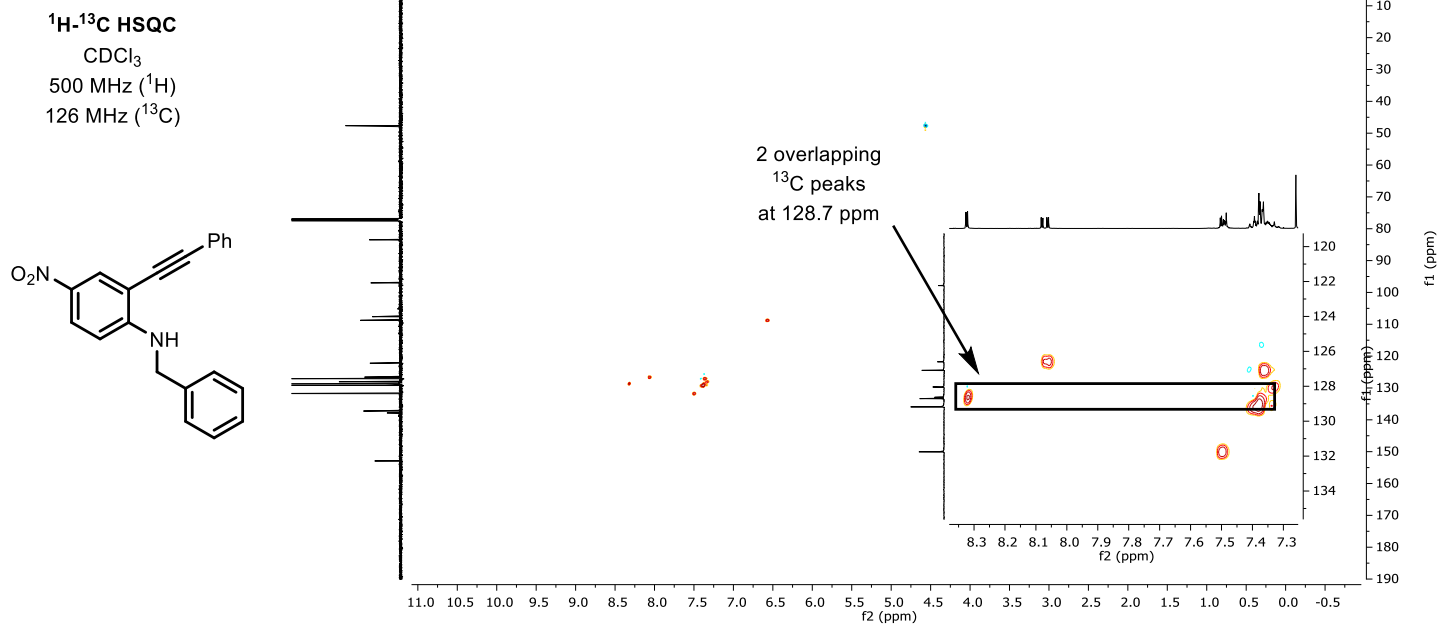
***N*-benzyl-4-nitro-2-(phenylethynyl)aniline (5t)**

¹H NMR
CDCl₃
500 MHz



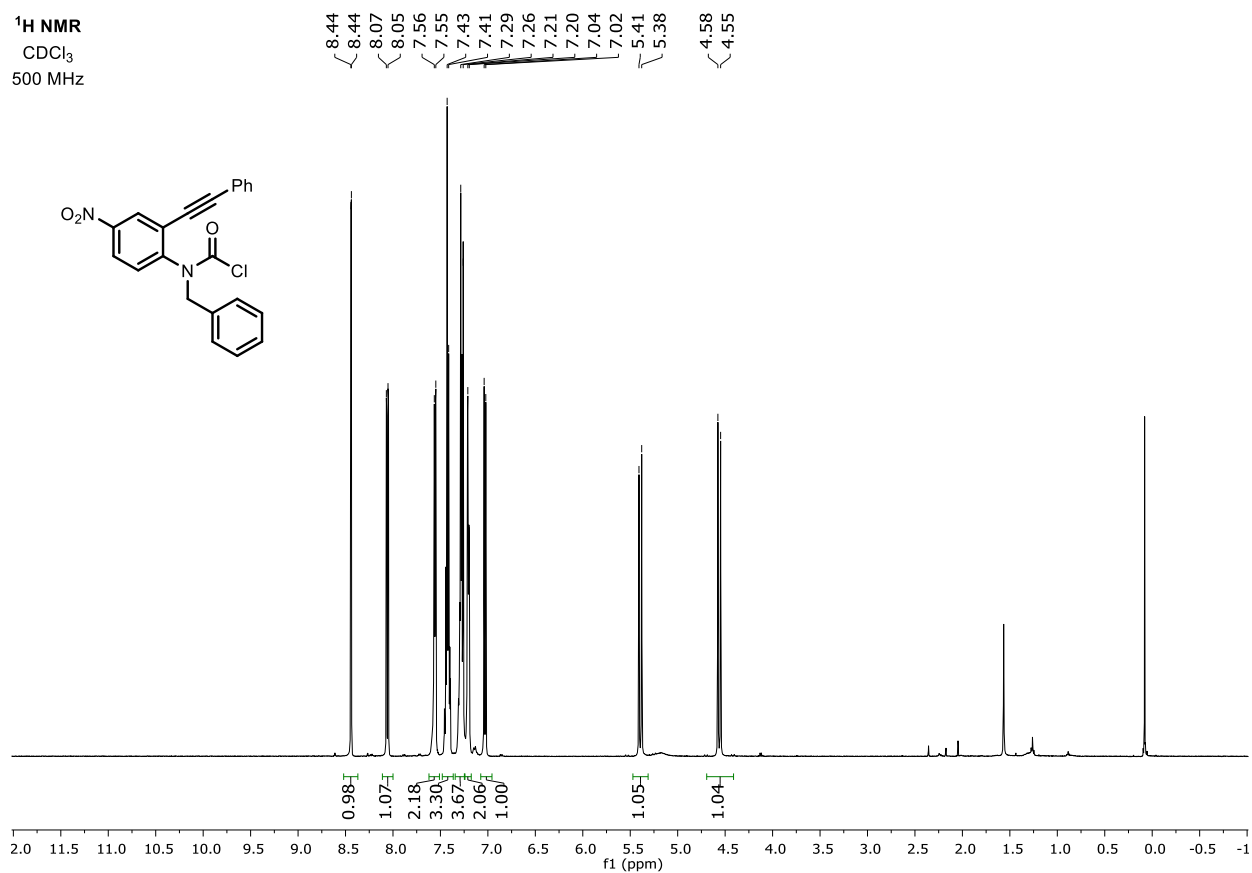
¹³C NMR
CDCl₃
126 MHz



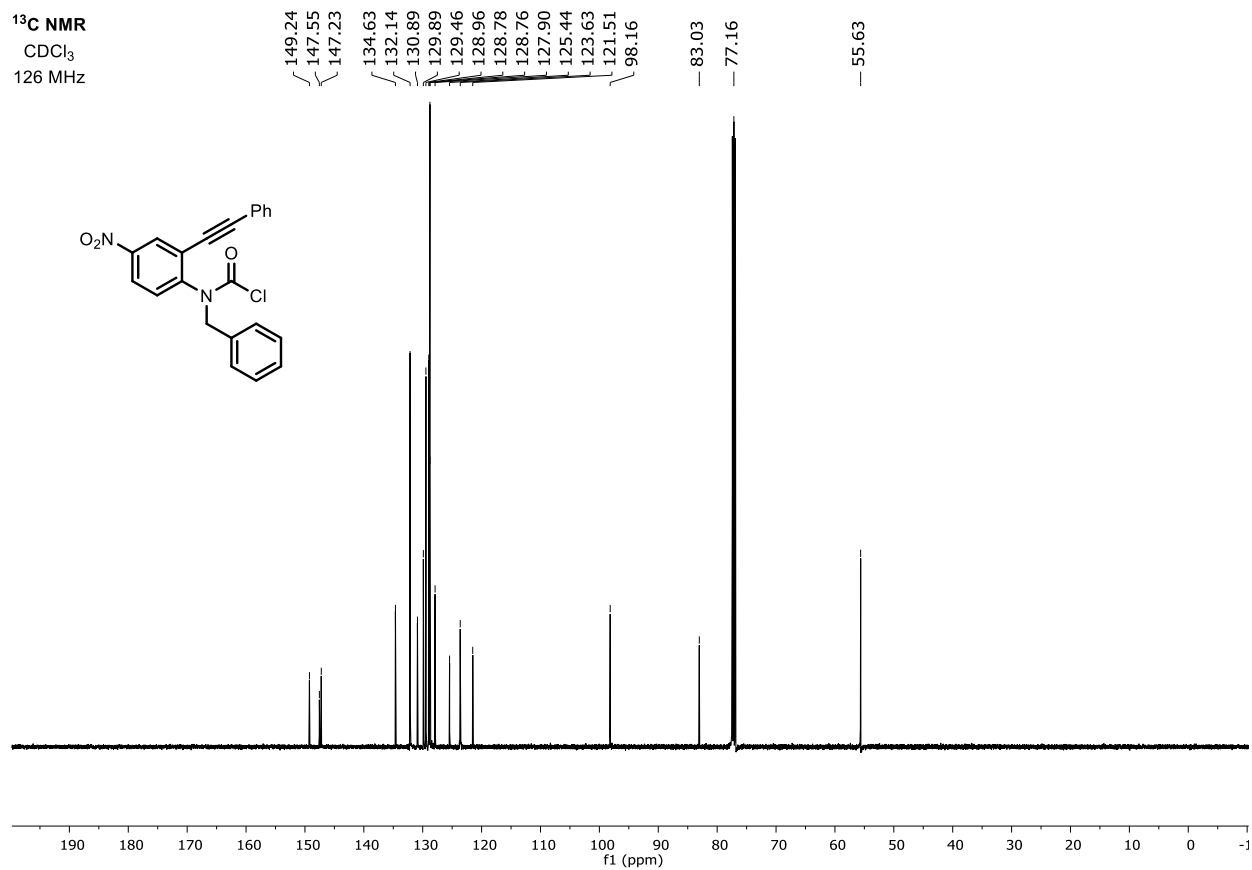


benzyl(4-nitro-2-(phenylethynyl)phenyl)carbamic chloride (1t')

¹H NMR
CDCl₃
500 MHz

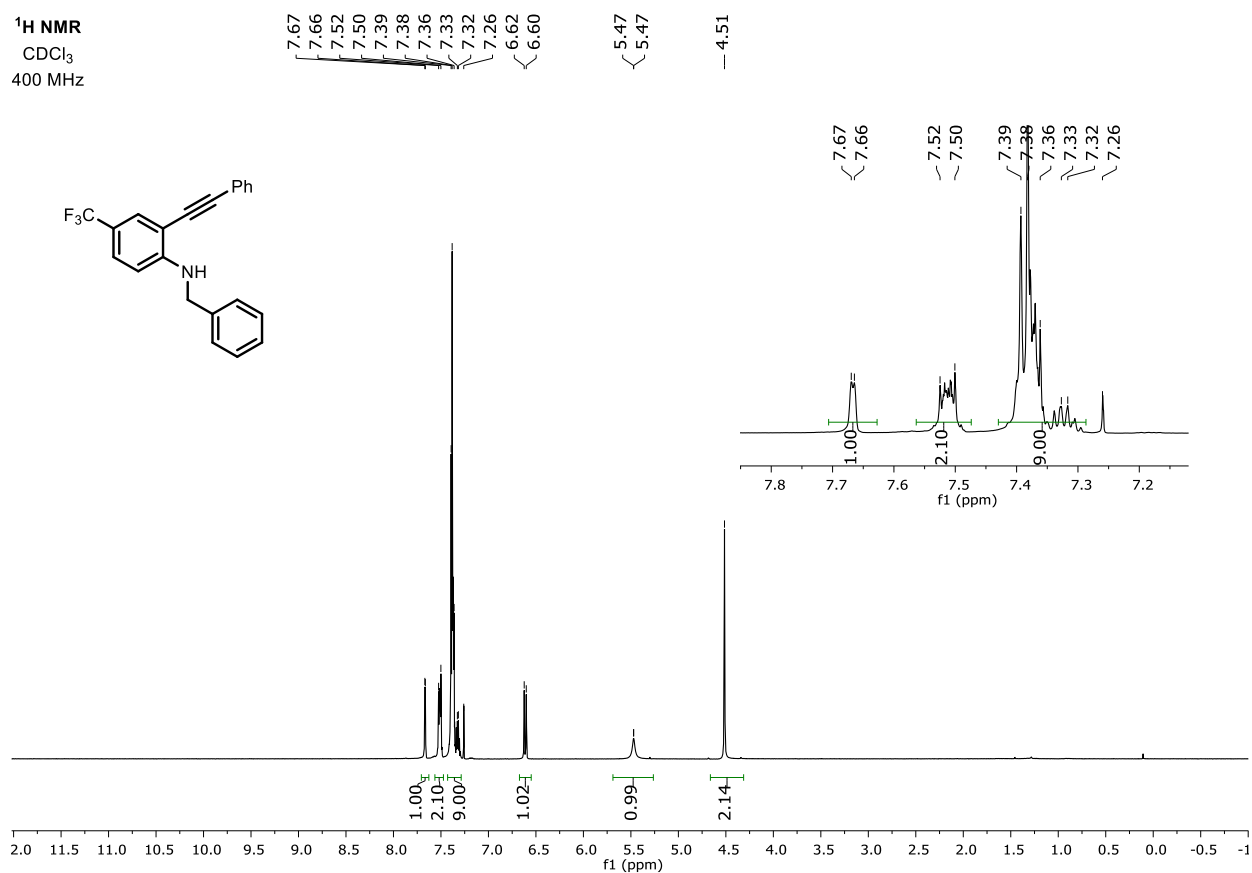


¹³C NMR
CDCl₃
126 MHz

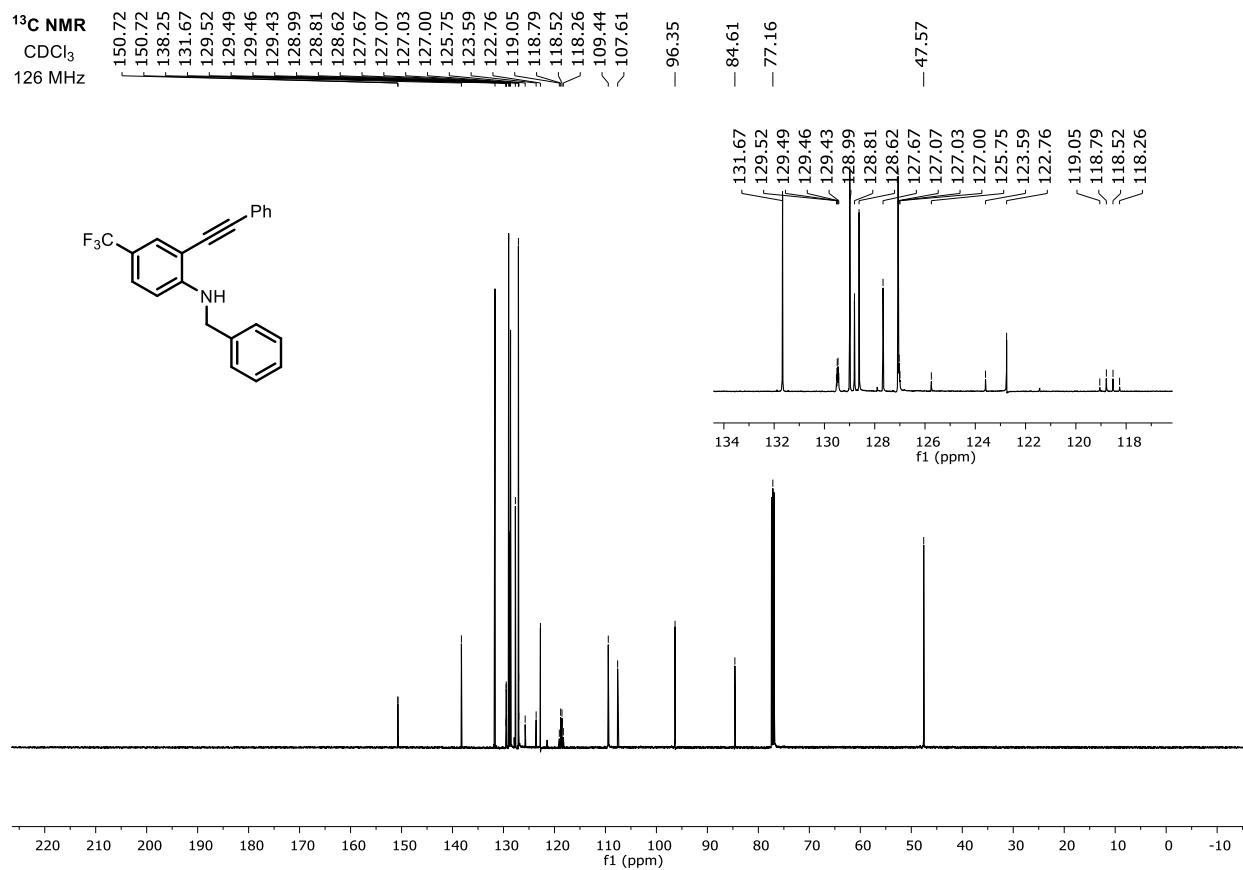


***N*-benzyl-2-(phenylethynyl)-4-(trifluoromethyl)aniline (5u)**

¹H NMR
CDCl₃
400 MHz

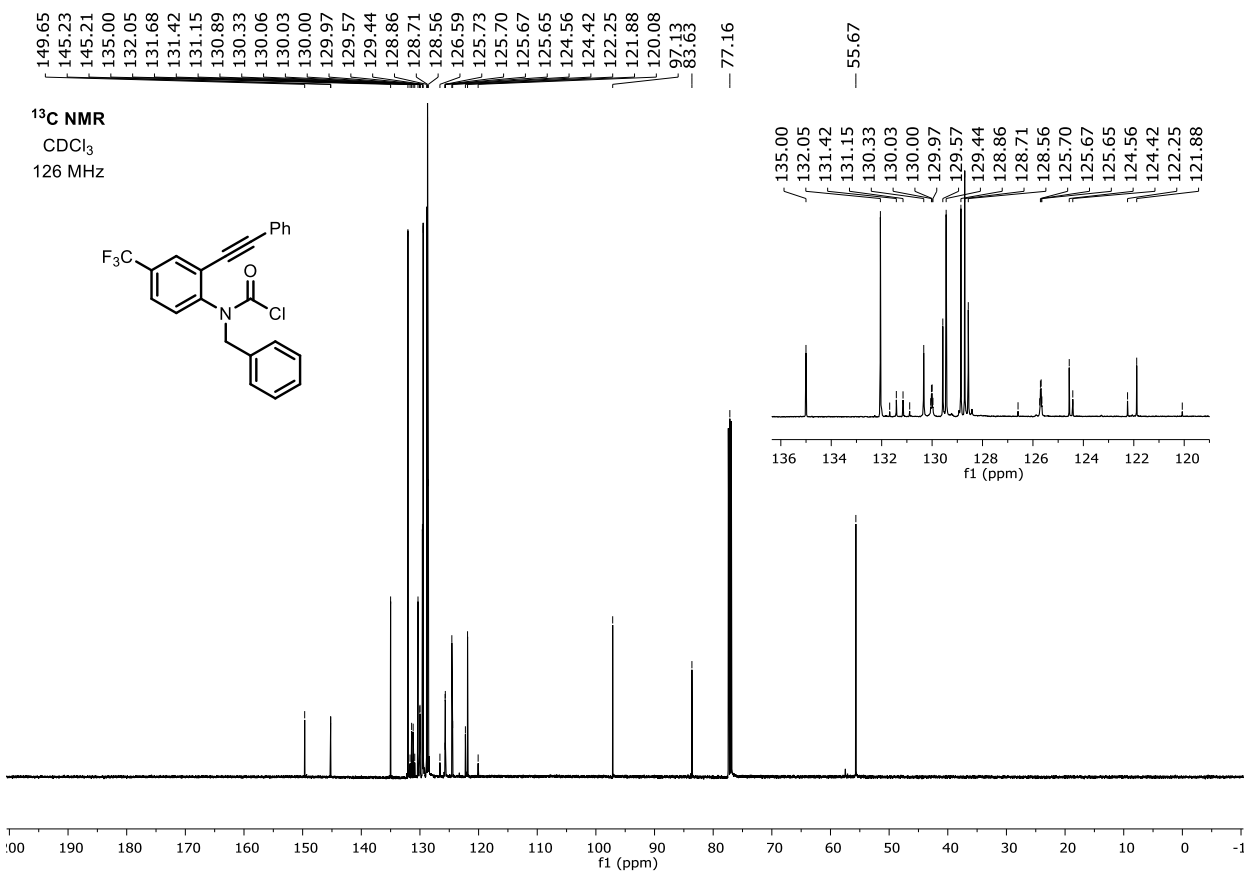
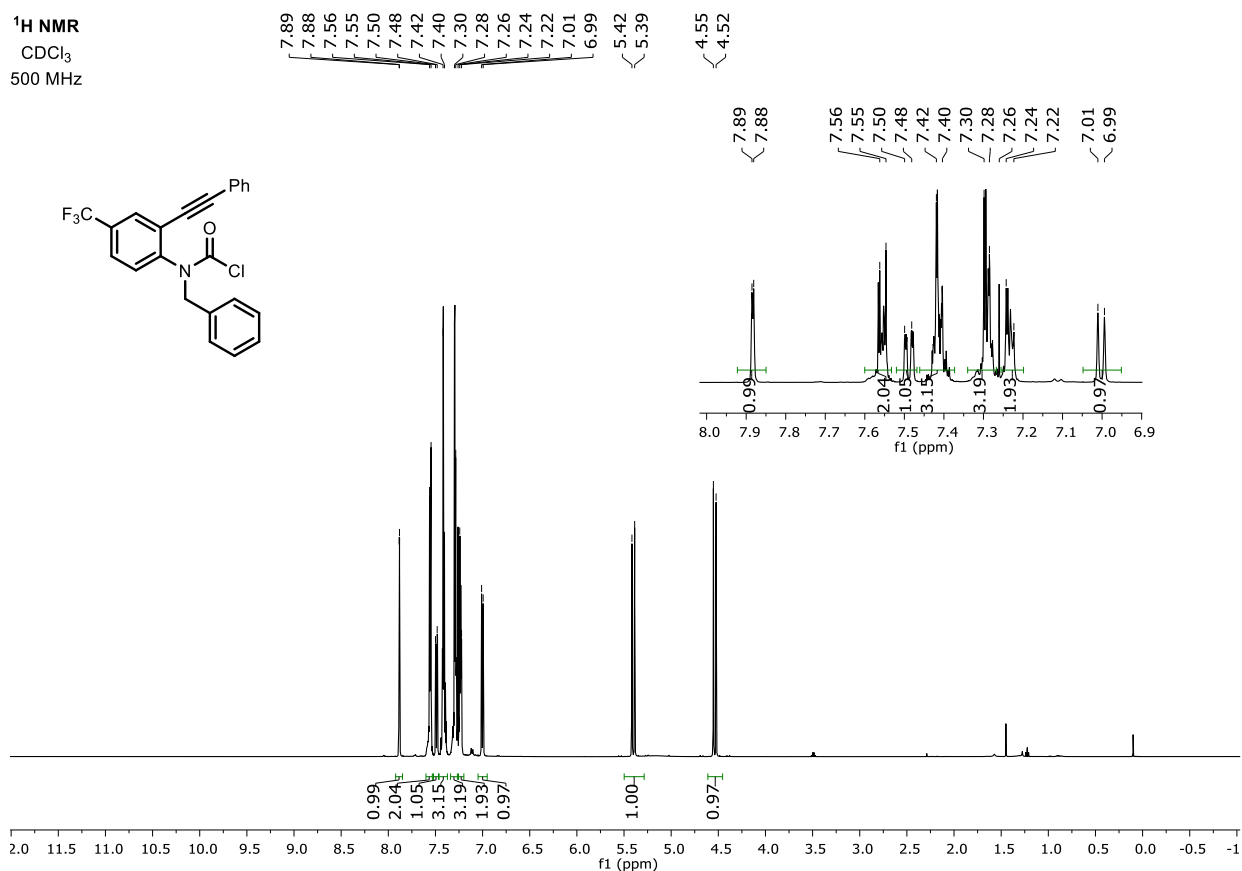


¹³C NMR
CDCl₃
126 MHz

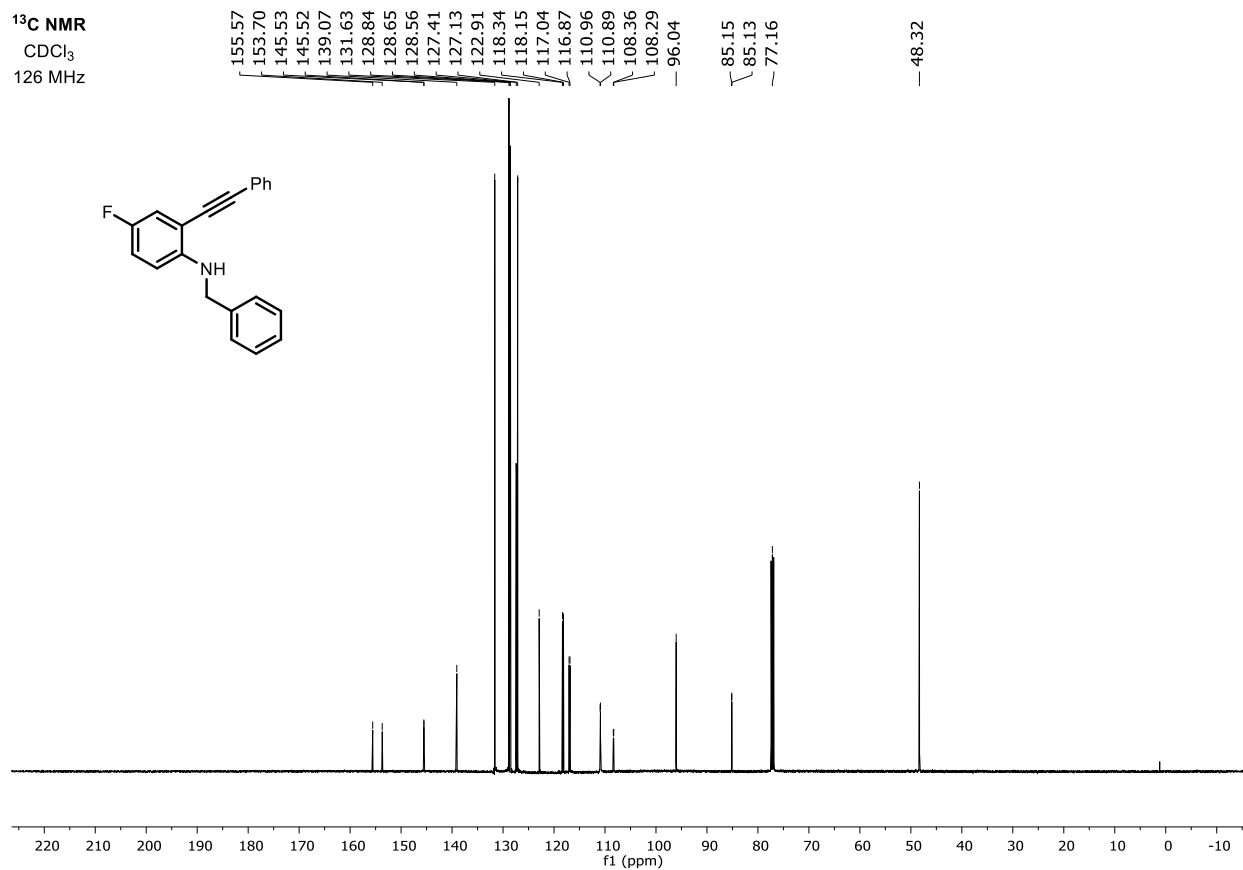
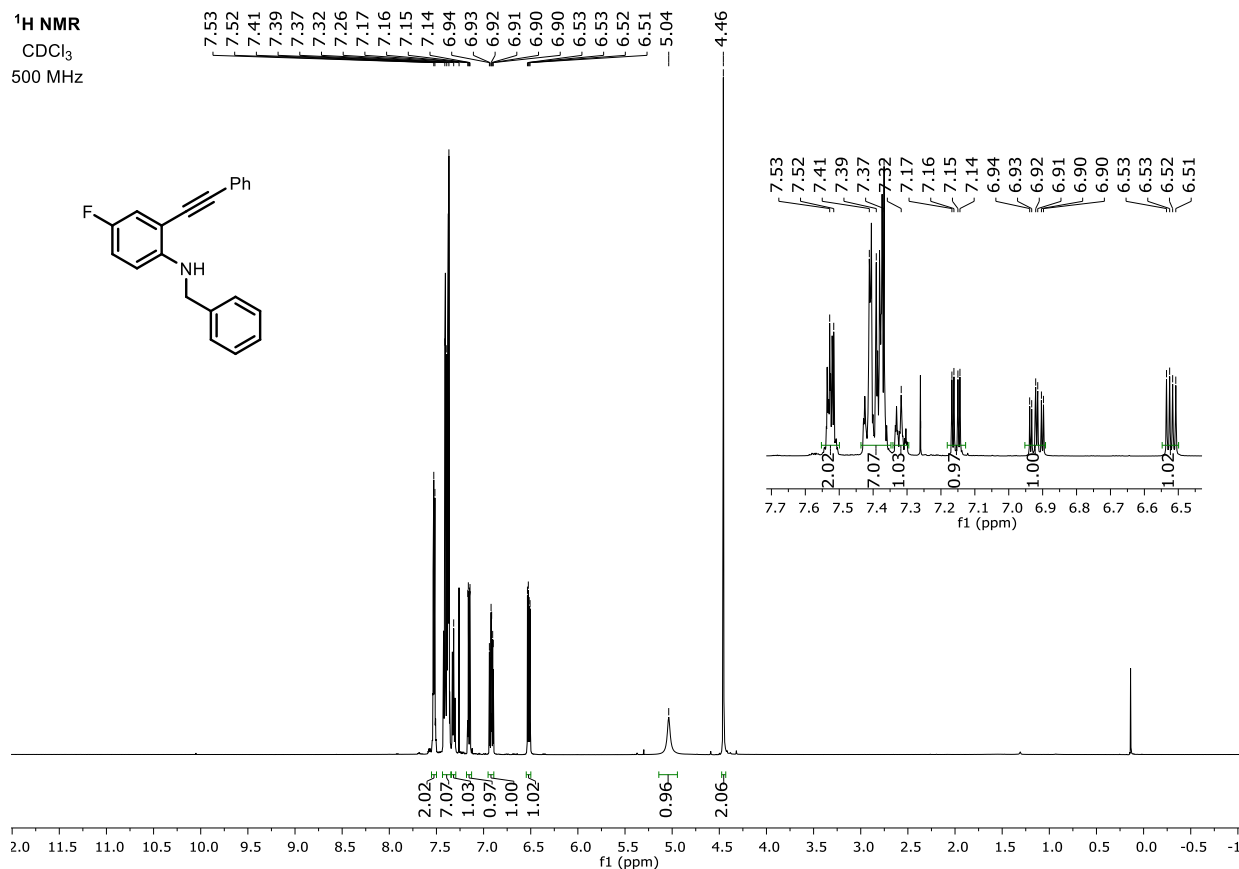


benzyl(2-(phenylethynyl)-4-(trifluoromethyl)phenyl)carbamate (1u')

¹H NMR
CDCl₃
500 MHz



***N*-benzyl-4-fluoro-2-(phenylethynyl)aniline (5v)**

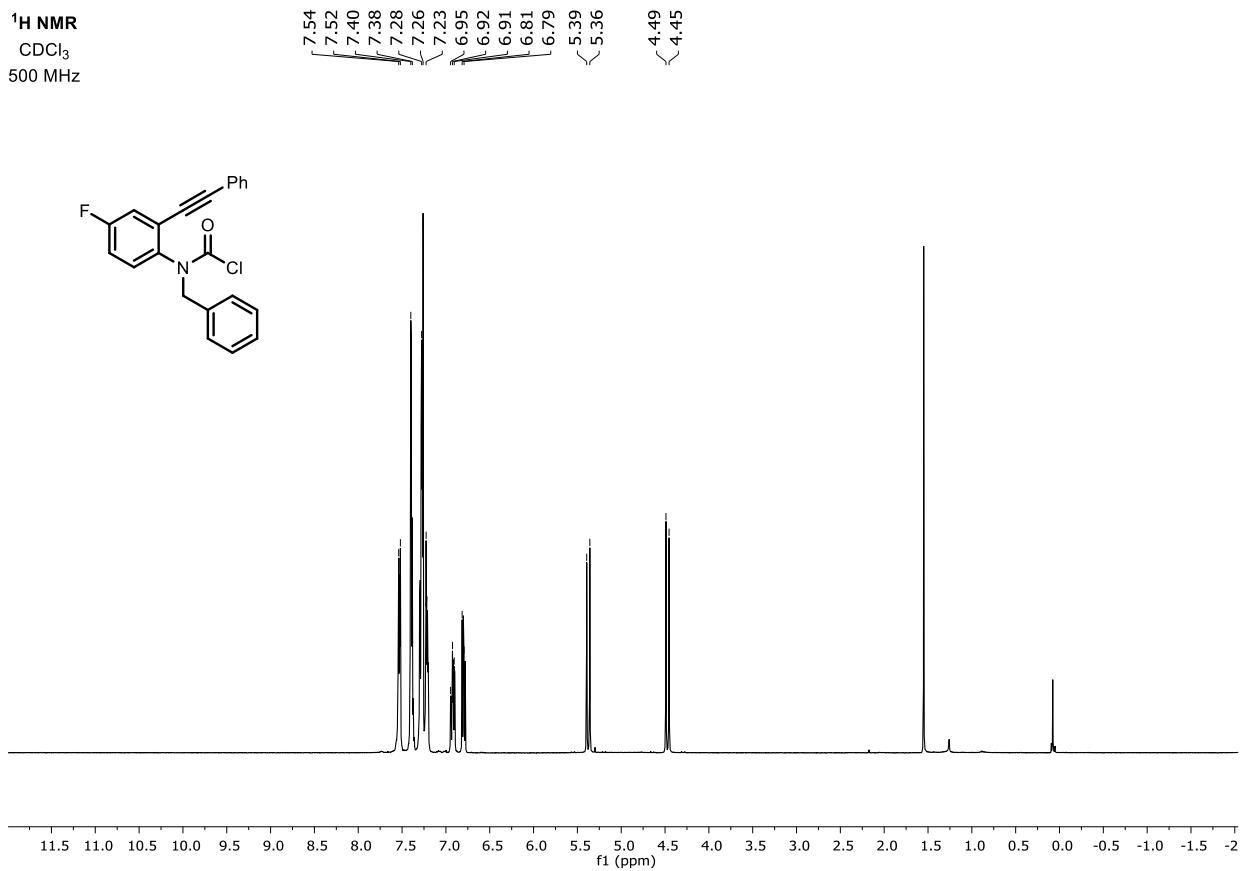
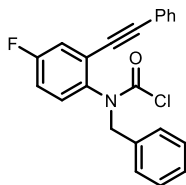


benzyl(4-fluoro-2-(phenylethynyl)phenyl)carbamic chloride (1v')

 CDCl_3

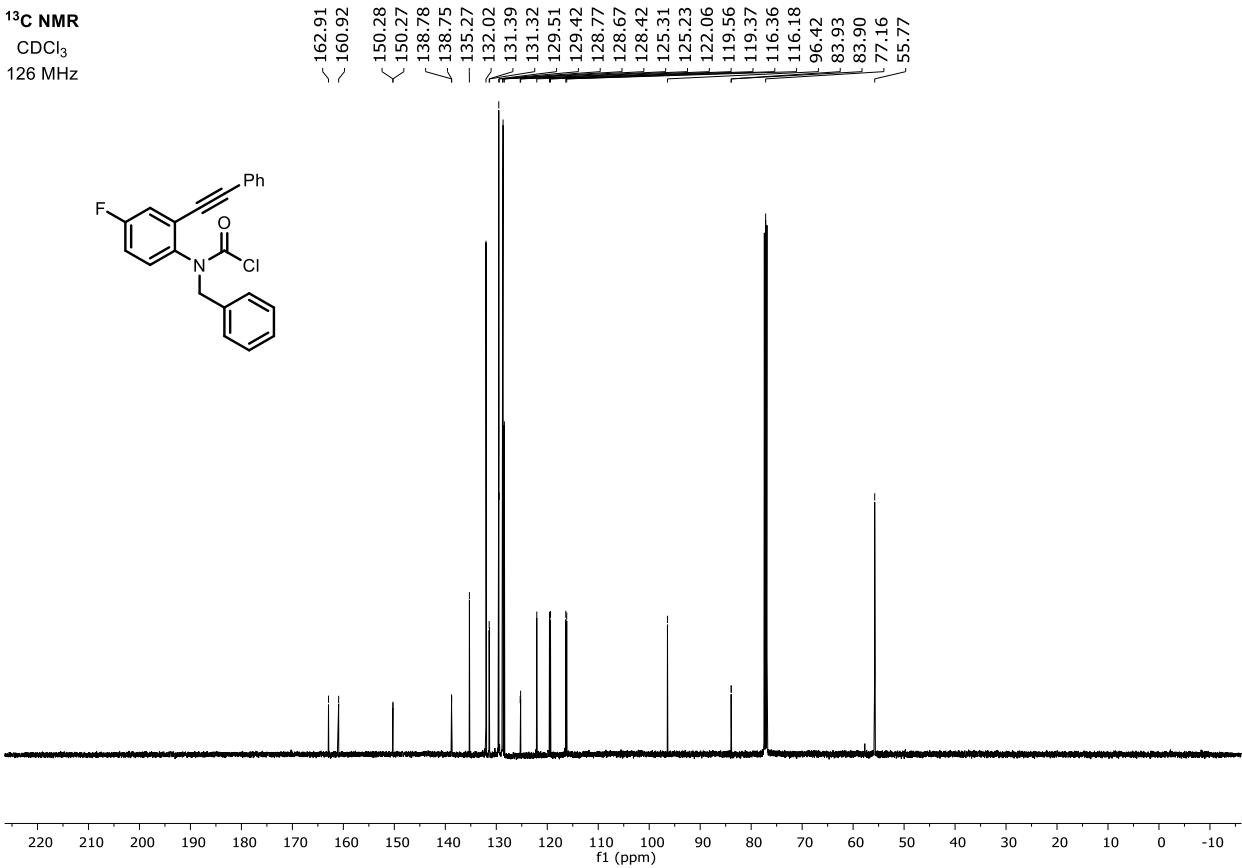
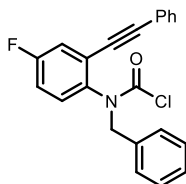
CDCl₃

500 MHz



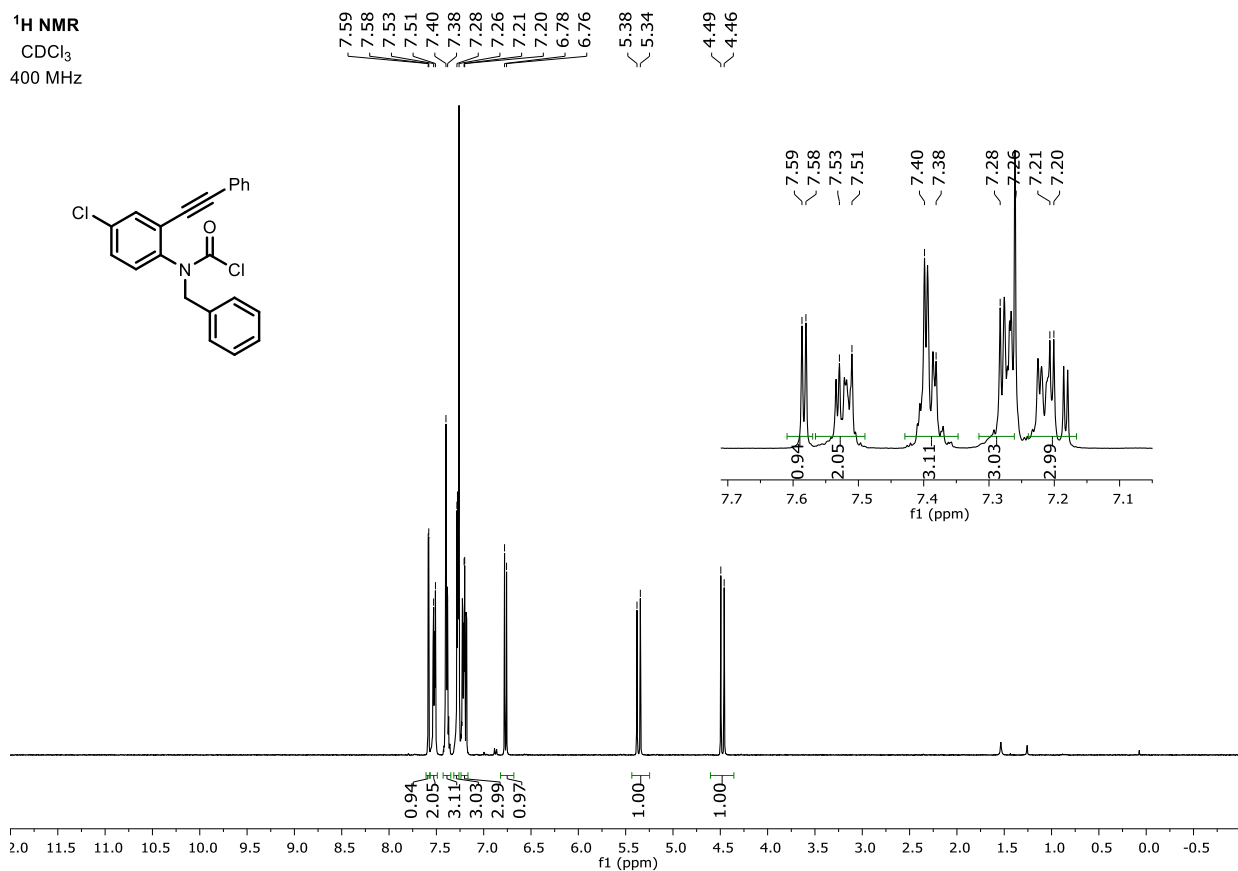
CDCl₃

126 MHz:

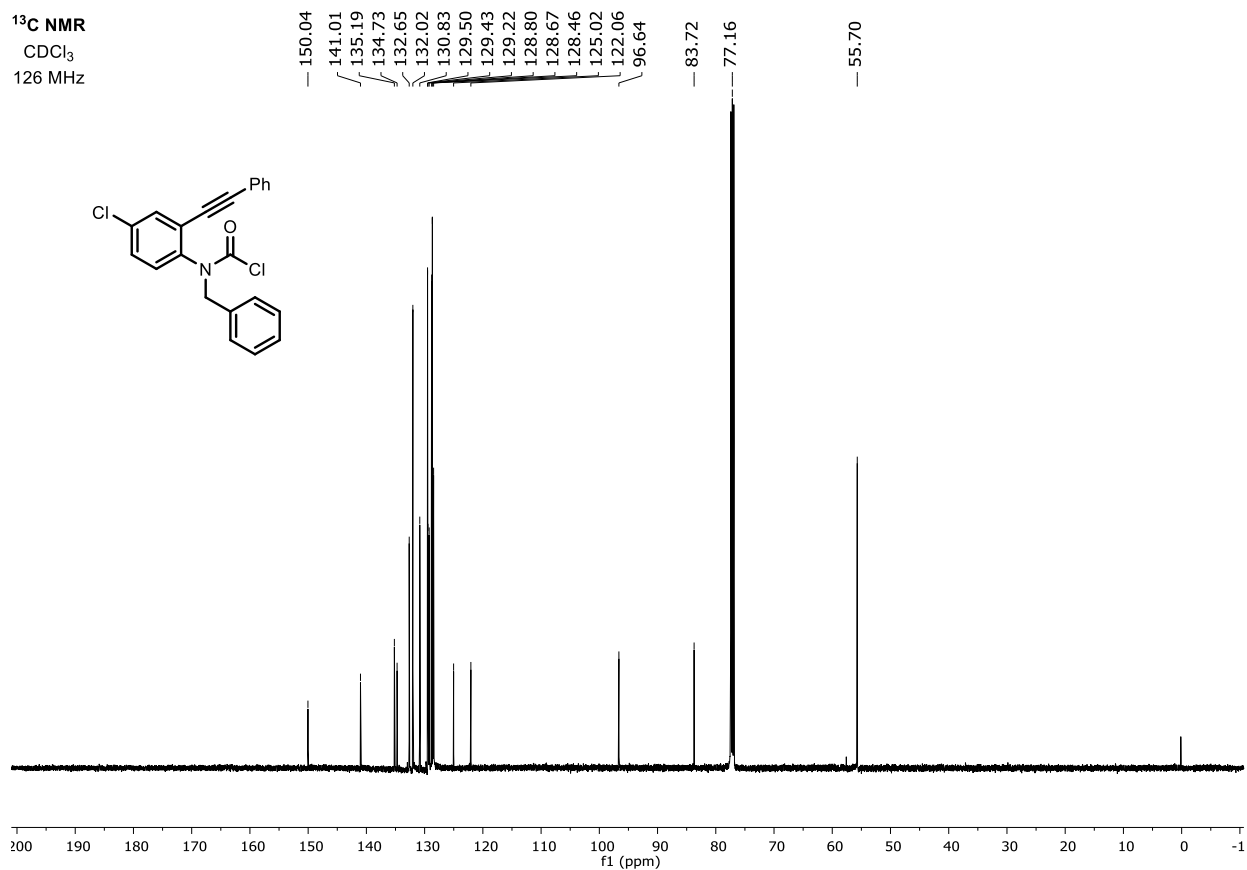


benzyl(4-chloro-2-(phenylethynyl)phenyl)carbamate (1w')

¹H NMR
CDCl₃
400 MHz

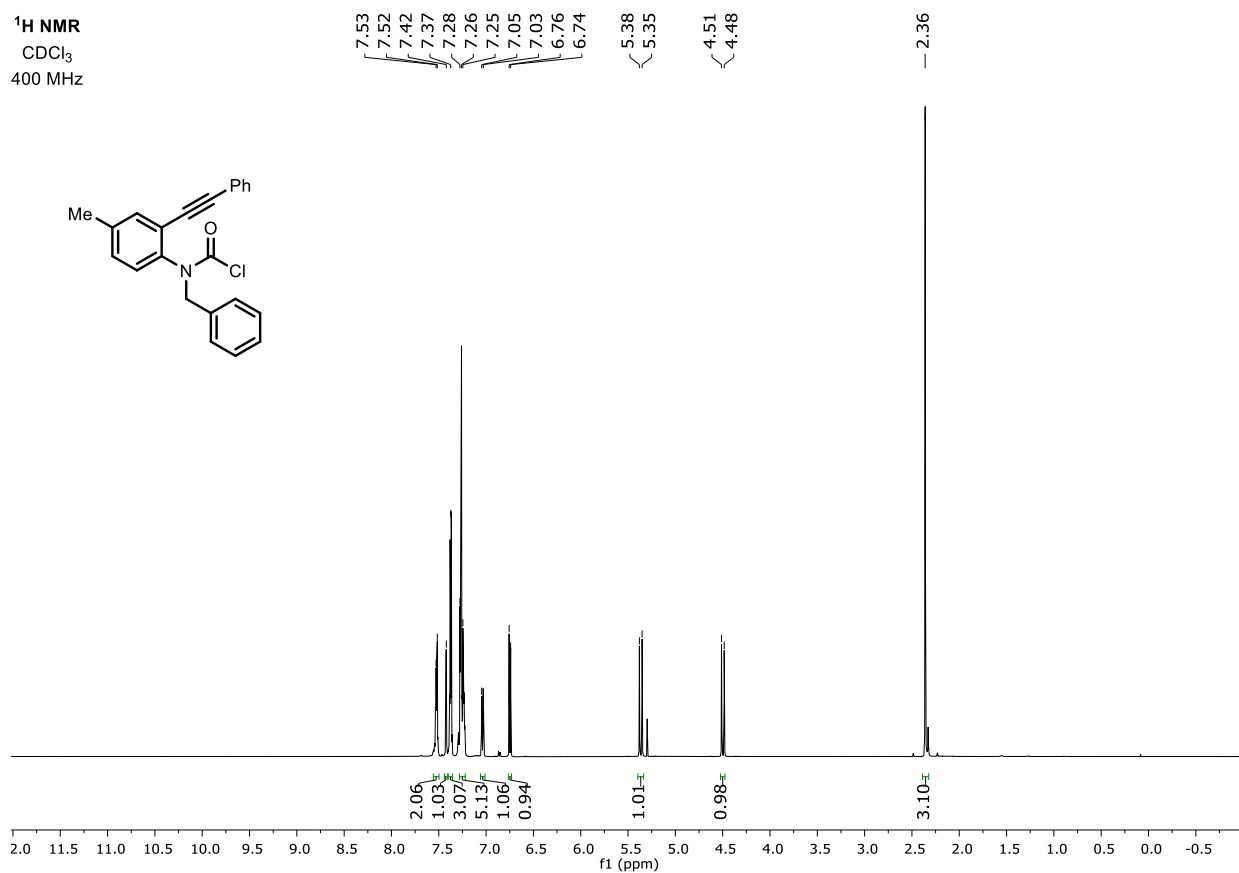


¹³C NMR
CDCl₃
126 MHz

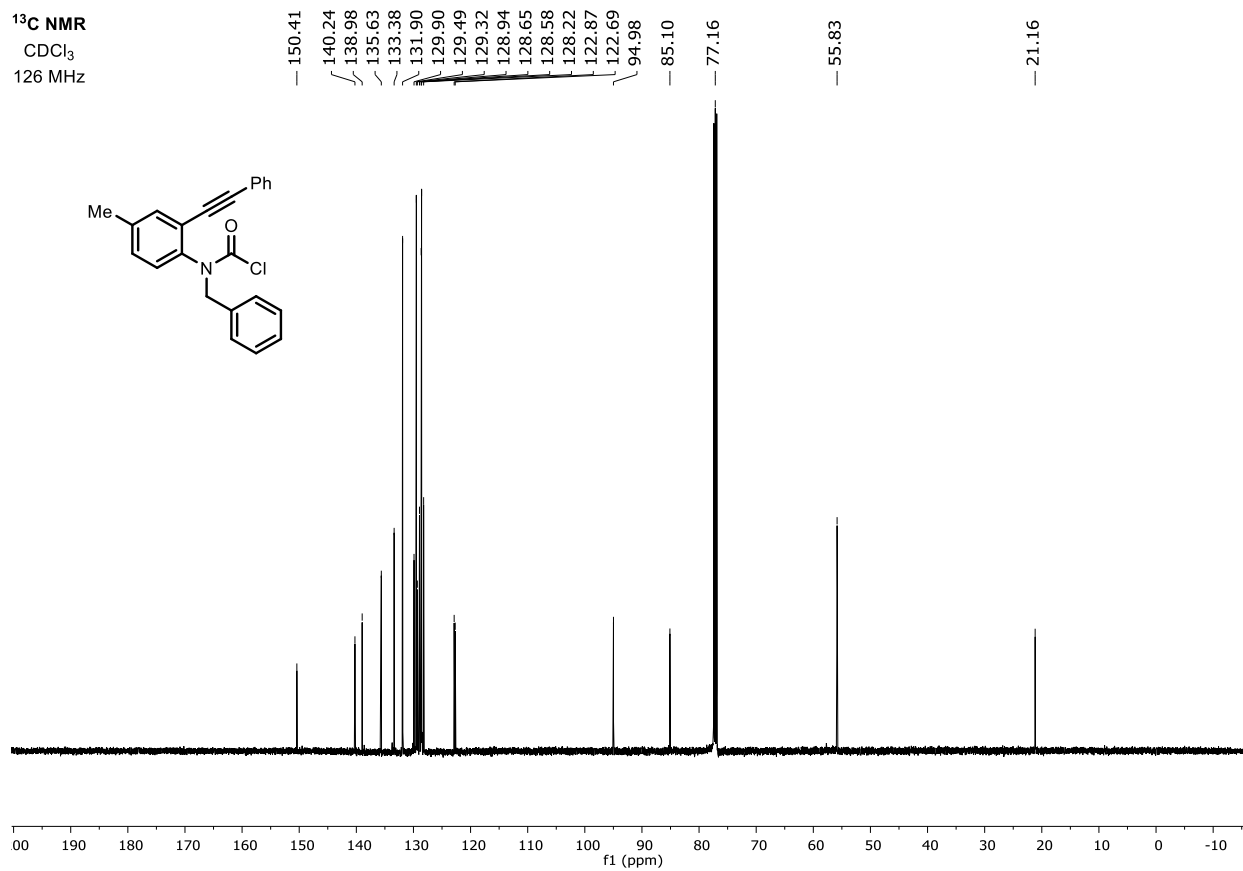


benzyl(4-methyl-2-(phenylethynyl)phenyl)carbamate (1x')

¹H NMR
CDCl₃
400 MHz

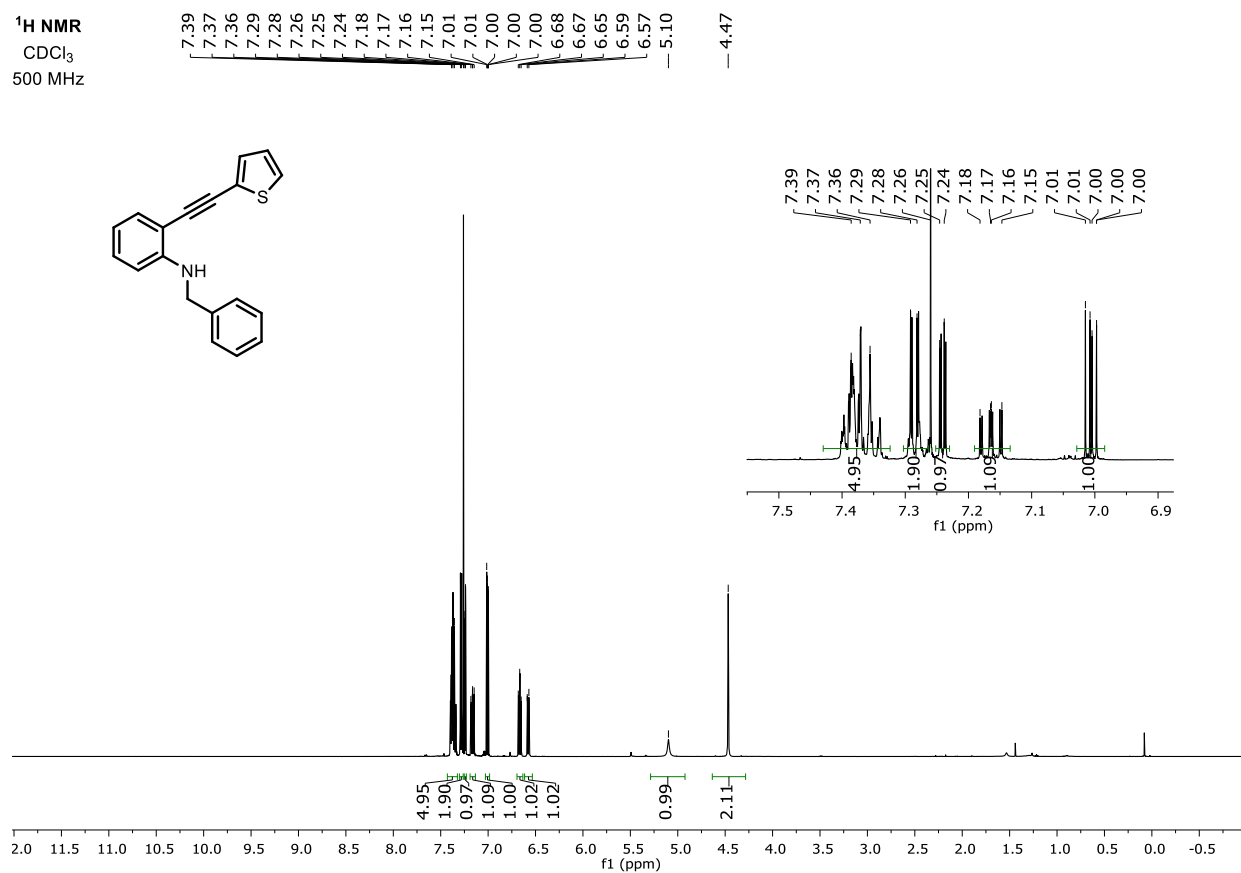


¹³C NMR
CDCl₃
126 MHz

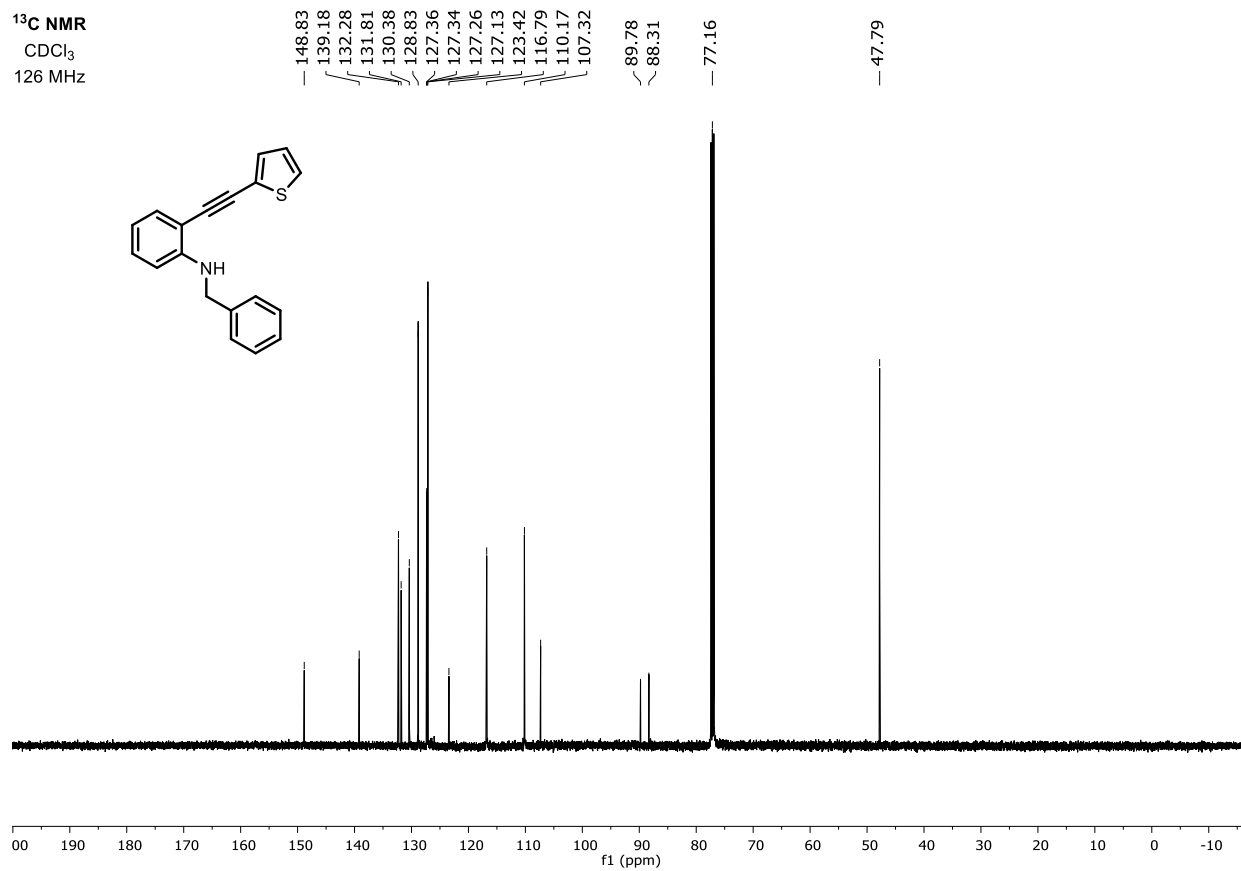


***N*-benzyl-2-(thiophen-2-ylethynyl)aniline (5y)**

¹H NMR
CDCl₃
500 MHz

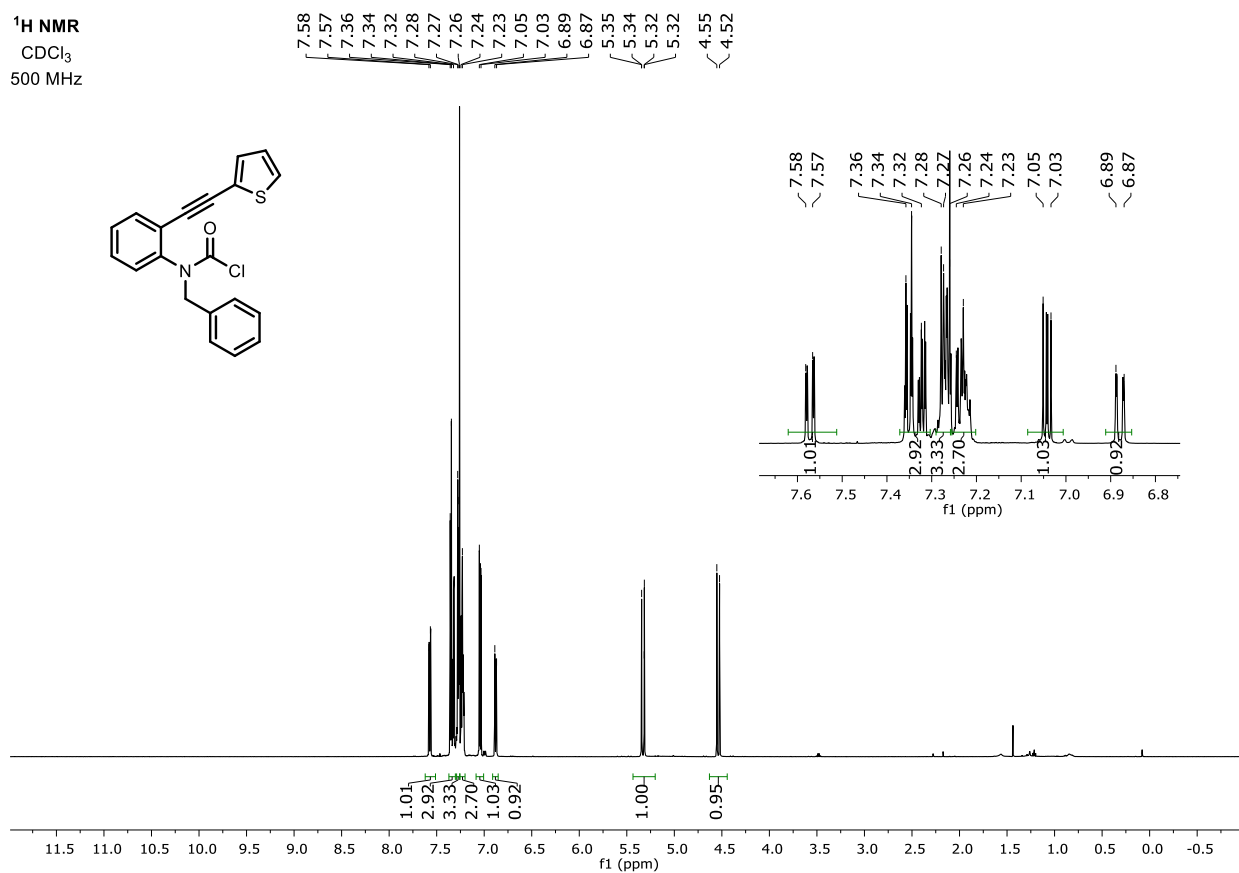


¹³C NMR
CDCl₃
126 MHz

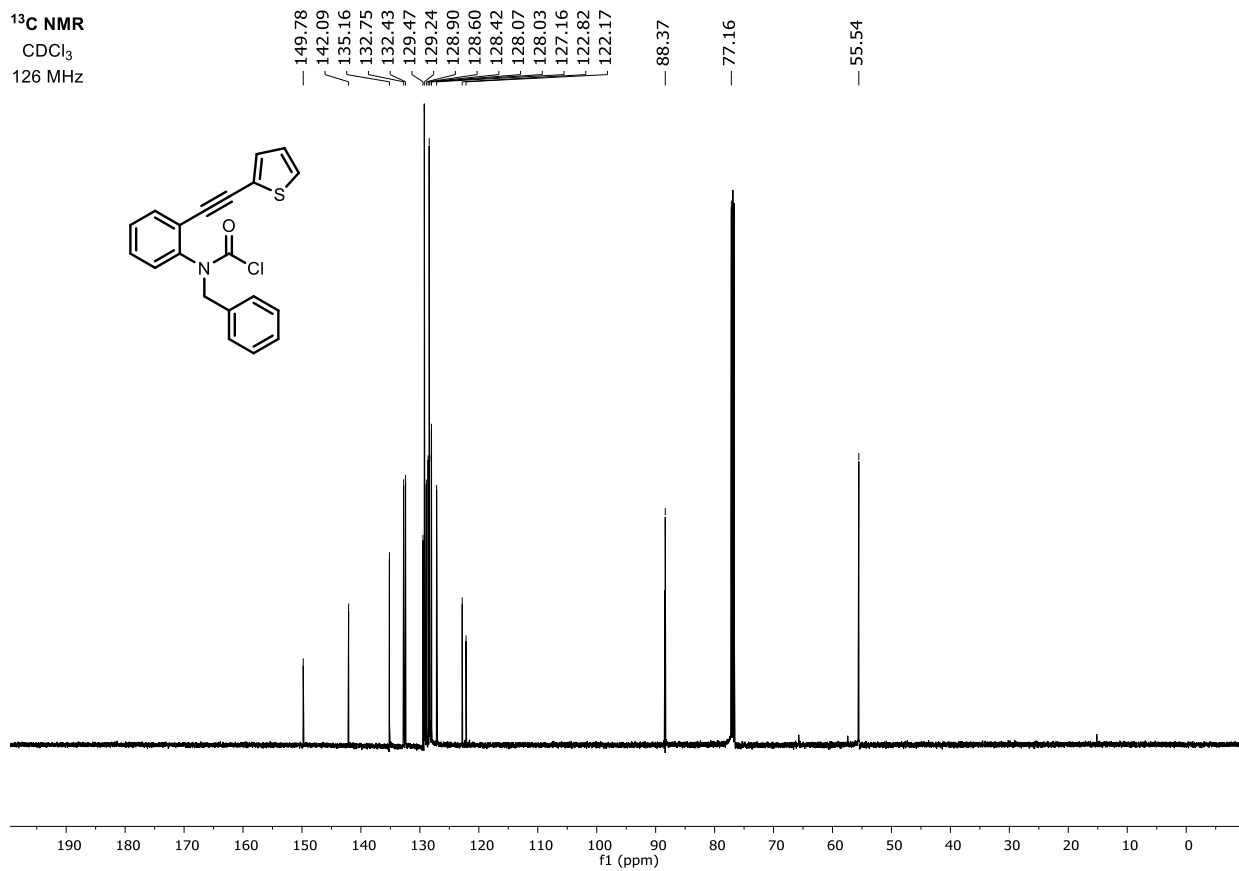


benzyl(2-(thiophen-2-ylethynyl)phenyl)carbamic chloride (1y')

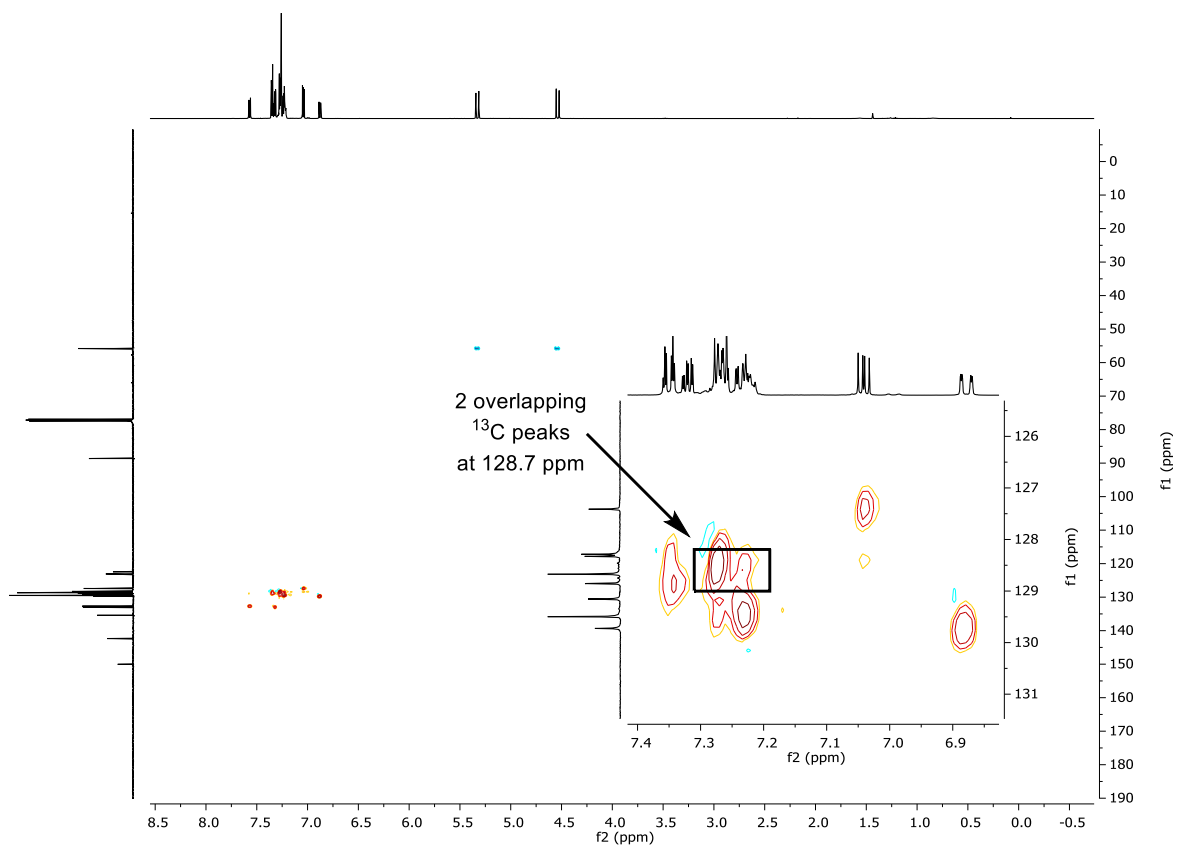
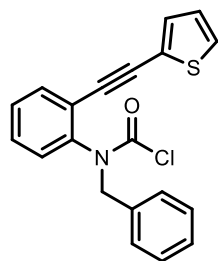
¹H NMR
CDCl₃
500 MHz



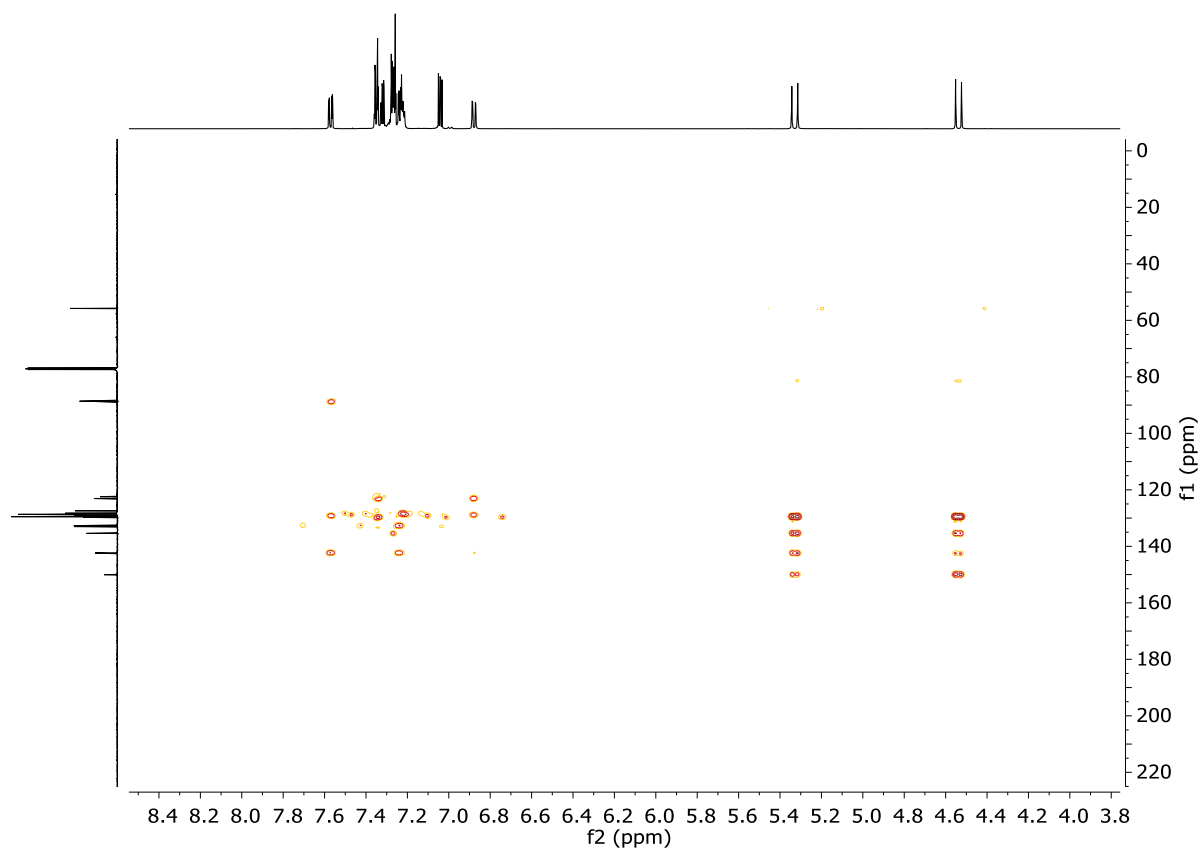
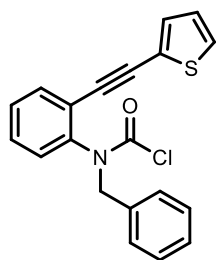
¹³C NMR
CDCl₃
126 MHz



^1H - ^{13}C HSQC
 CDCl_3
 500 MHz (^1H)
 126 MHz (^{13}C)

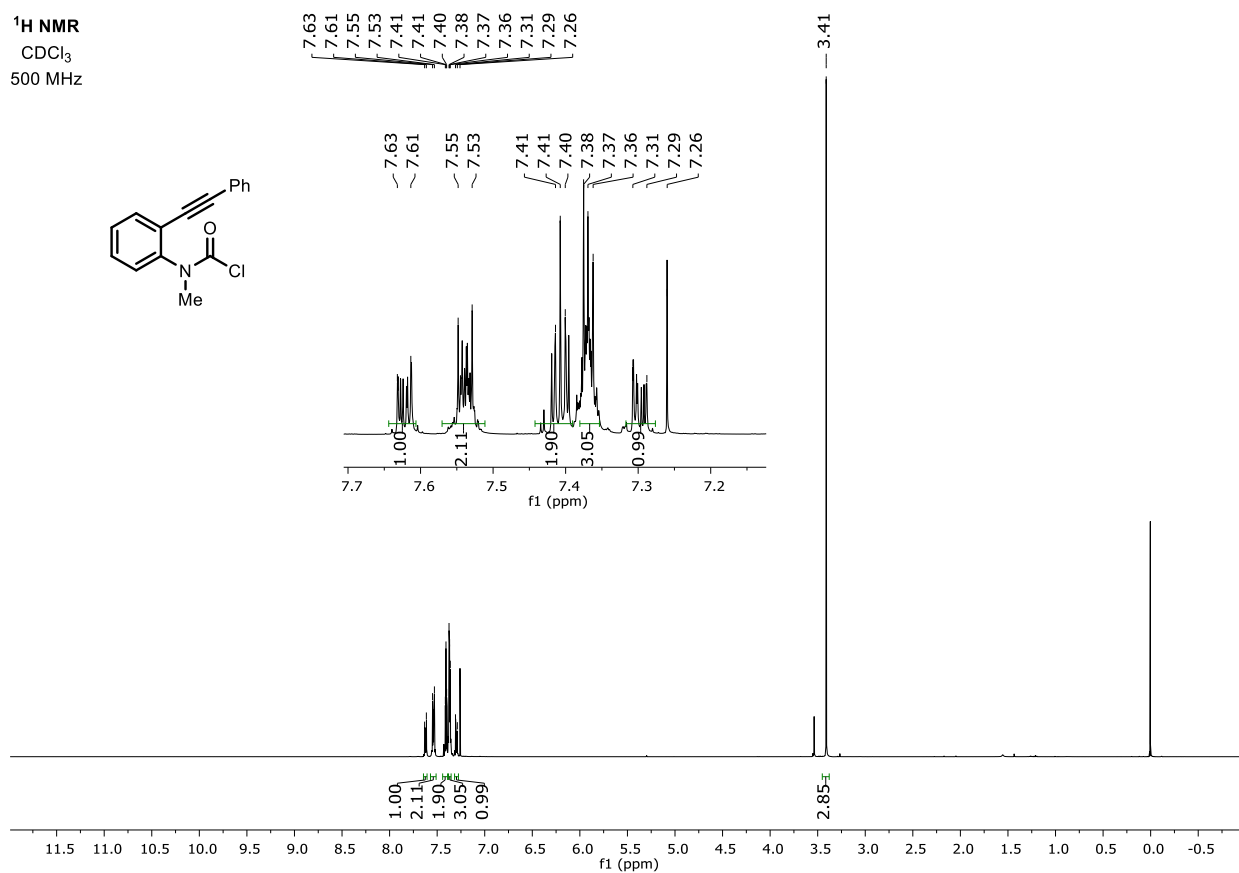


^1H - ^{13}C HMBC
 CDCl_3
 500 MHz (^1H)
 126 MHz (^{13}C)

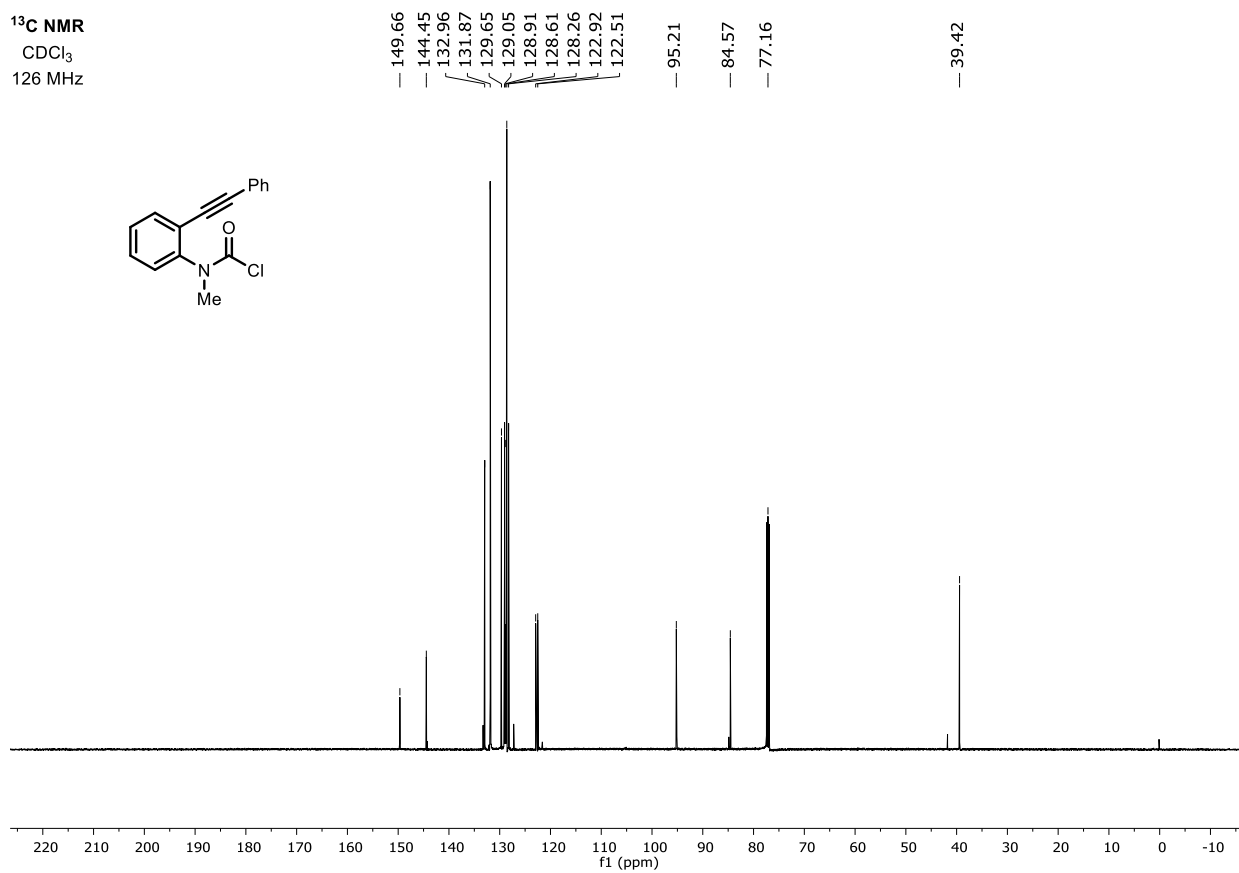


methyl(2-(phenylethynyl)phenyl)carbamate chloride (1z')

¹H NMR
CDCl₃
500 MHz

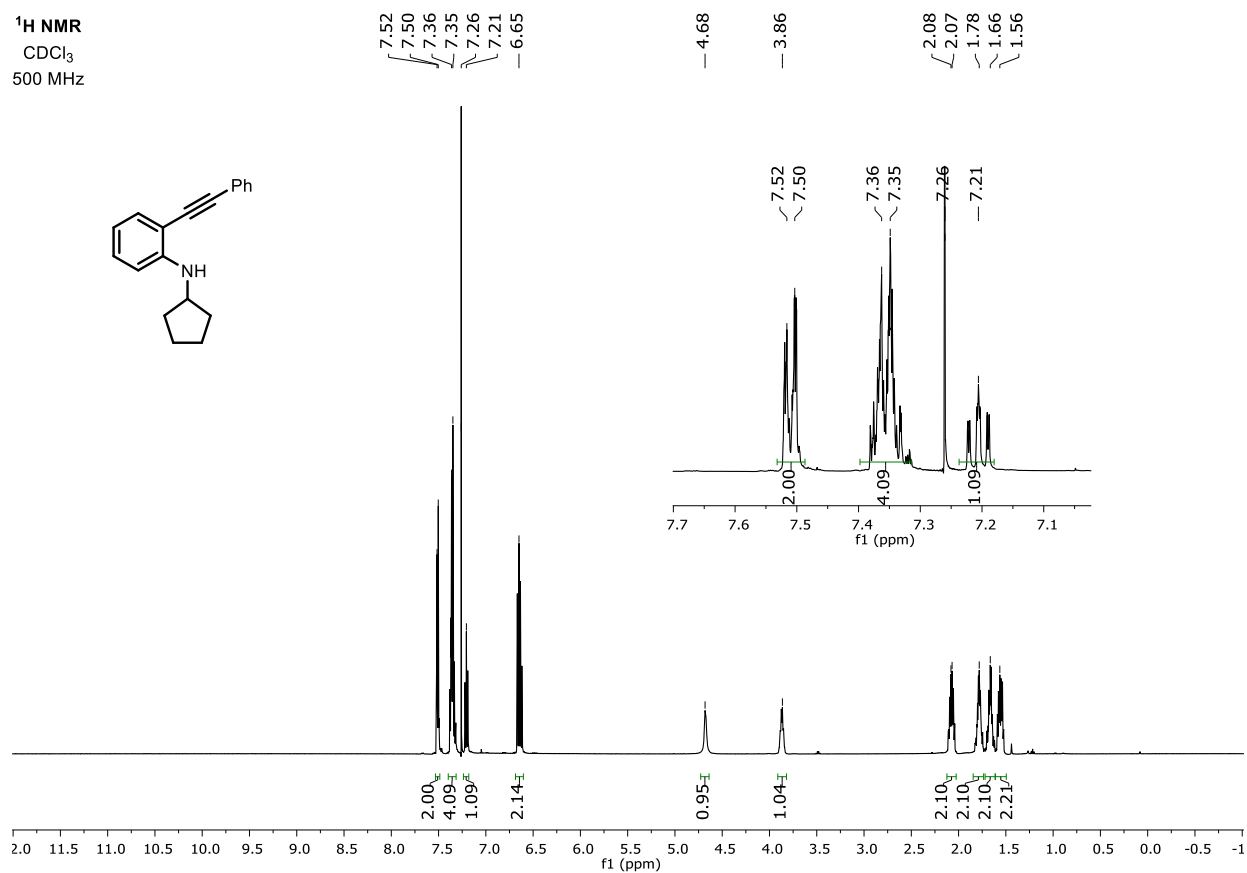


¹³C NMR
CDCl₃
126 MHz

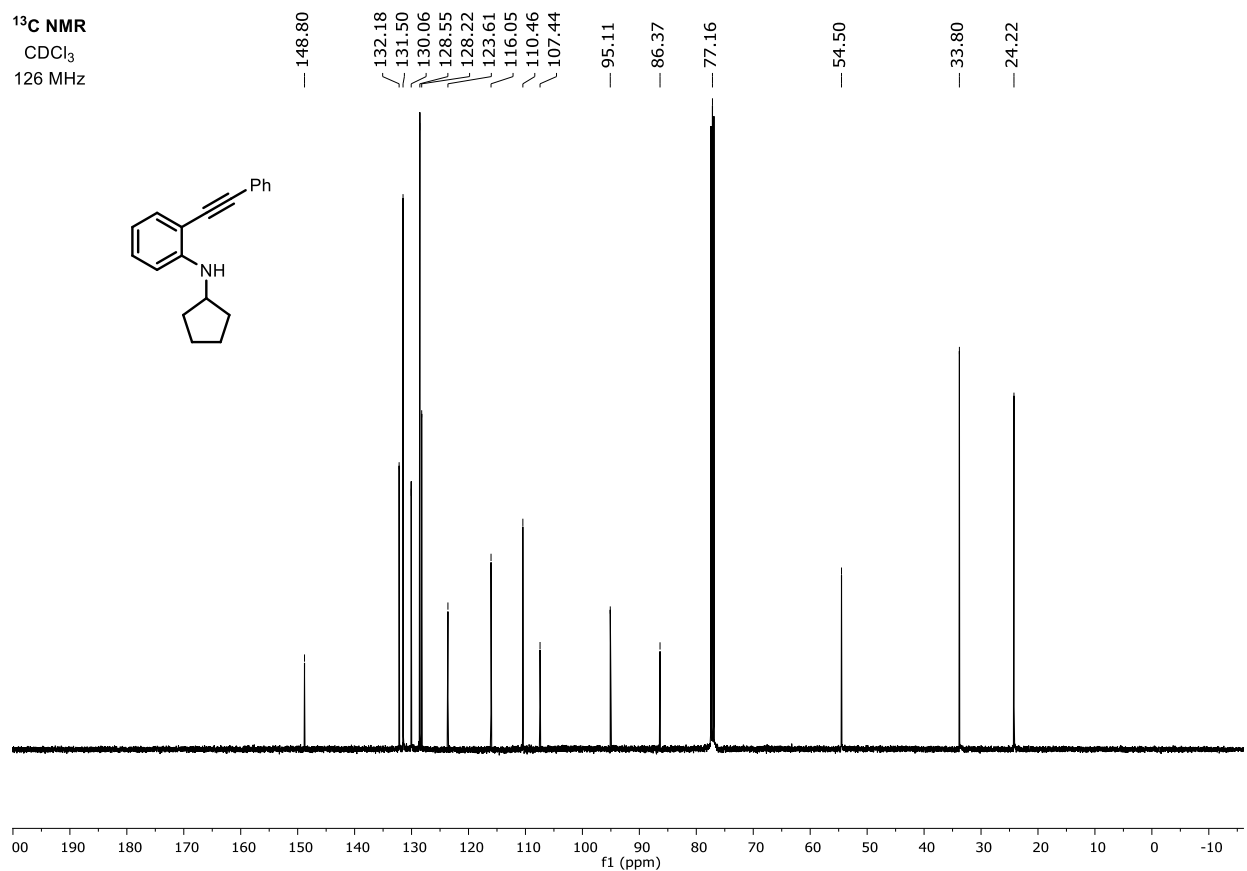


***N*-cyclopentyl-2-(phenylethynyl)aniline (5ab)**

¹H NMR
CDCl₃
500 MHz

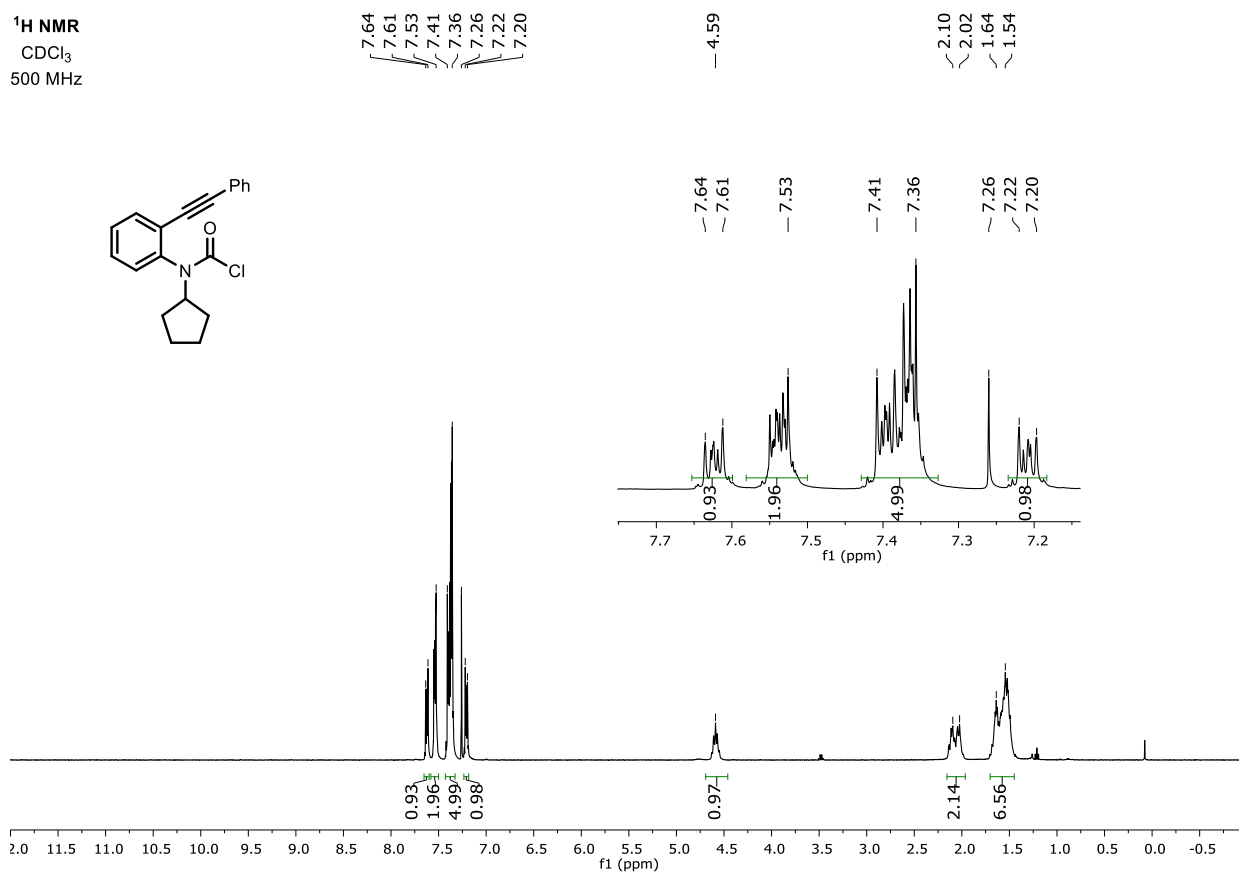


¹³C NMR
CDCl₃
126 MHz

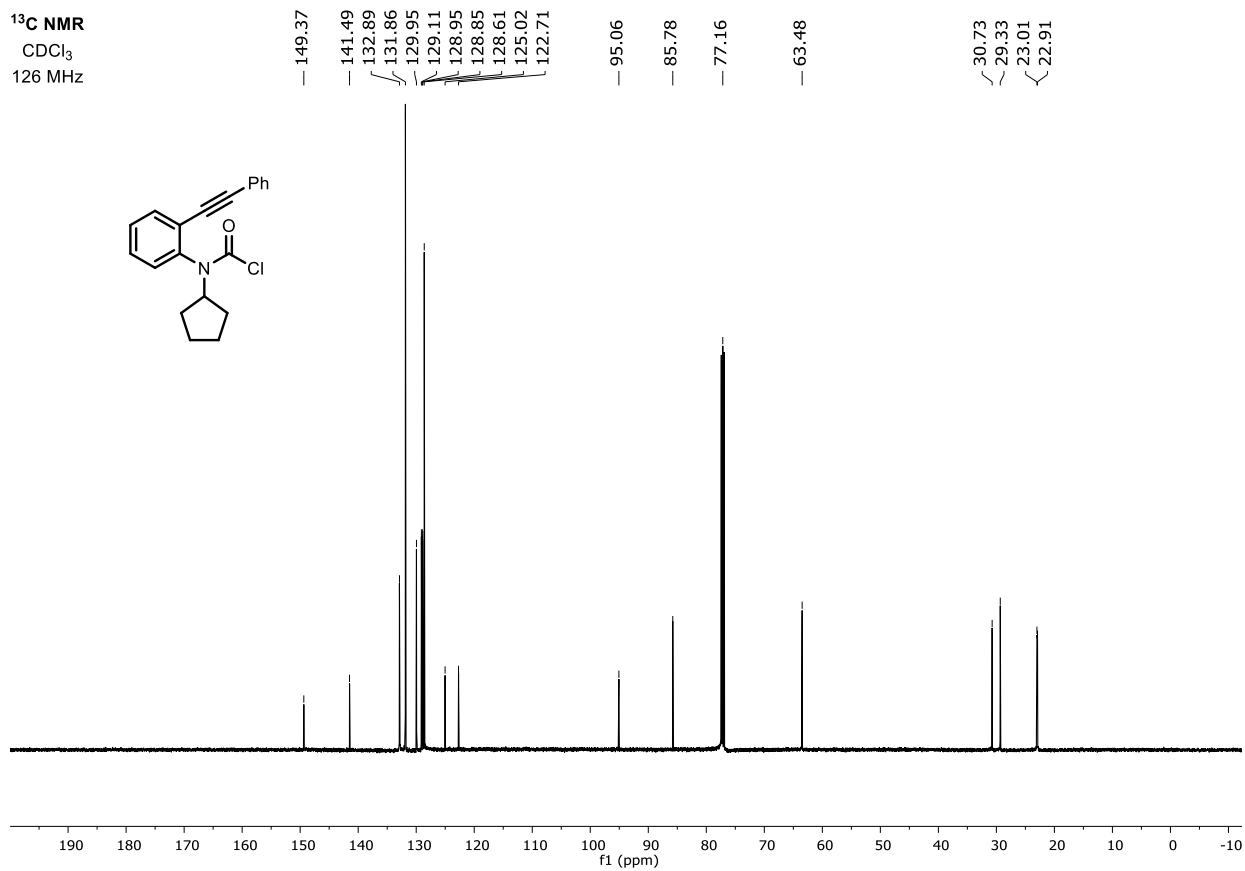


cyclopentyl(2-(phenylethynyl)phenyl)carbamic chloride (1ab')

¹H NMR
CDCl₃
500 MHz

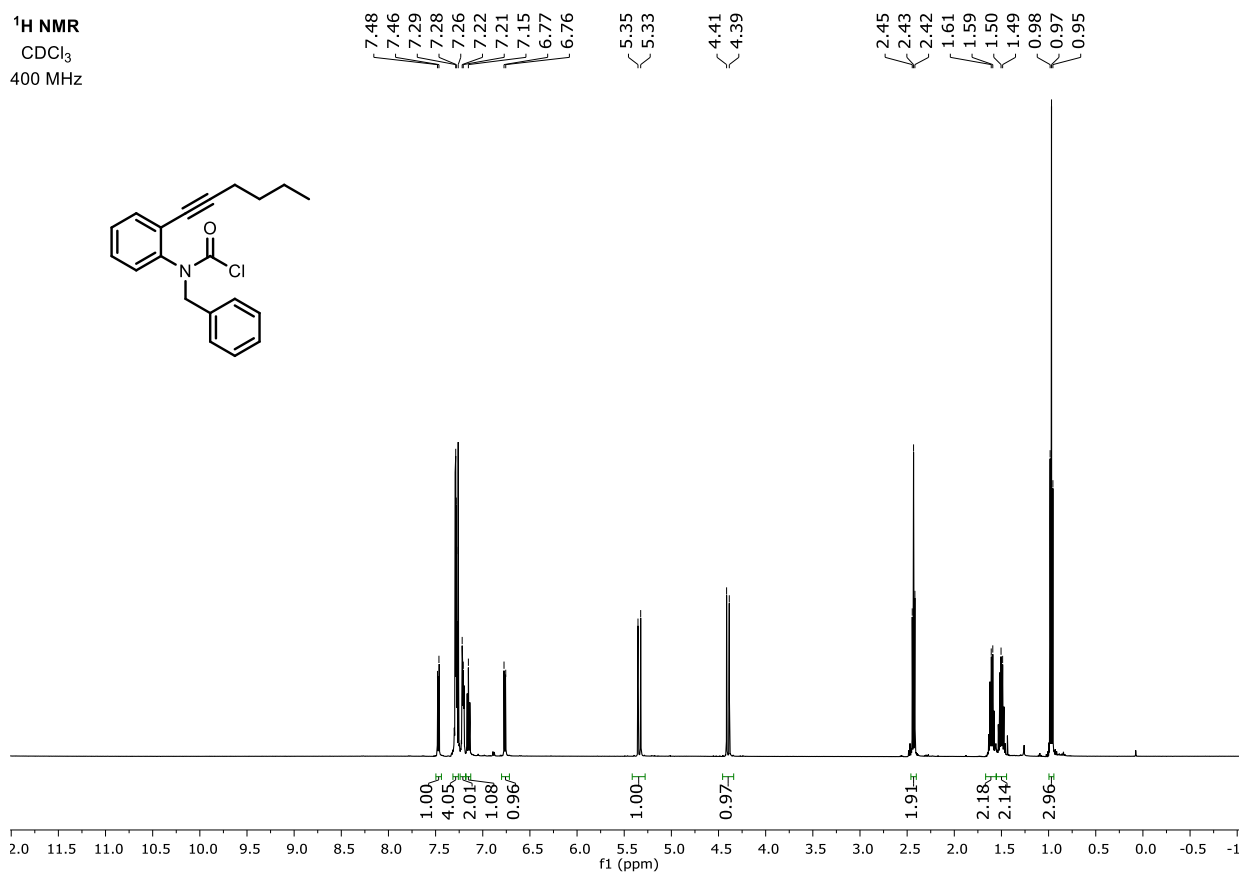


¹³C NMR
CDCl₃
126 MHz

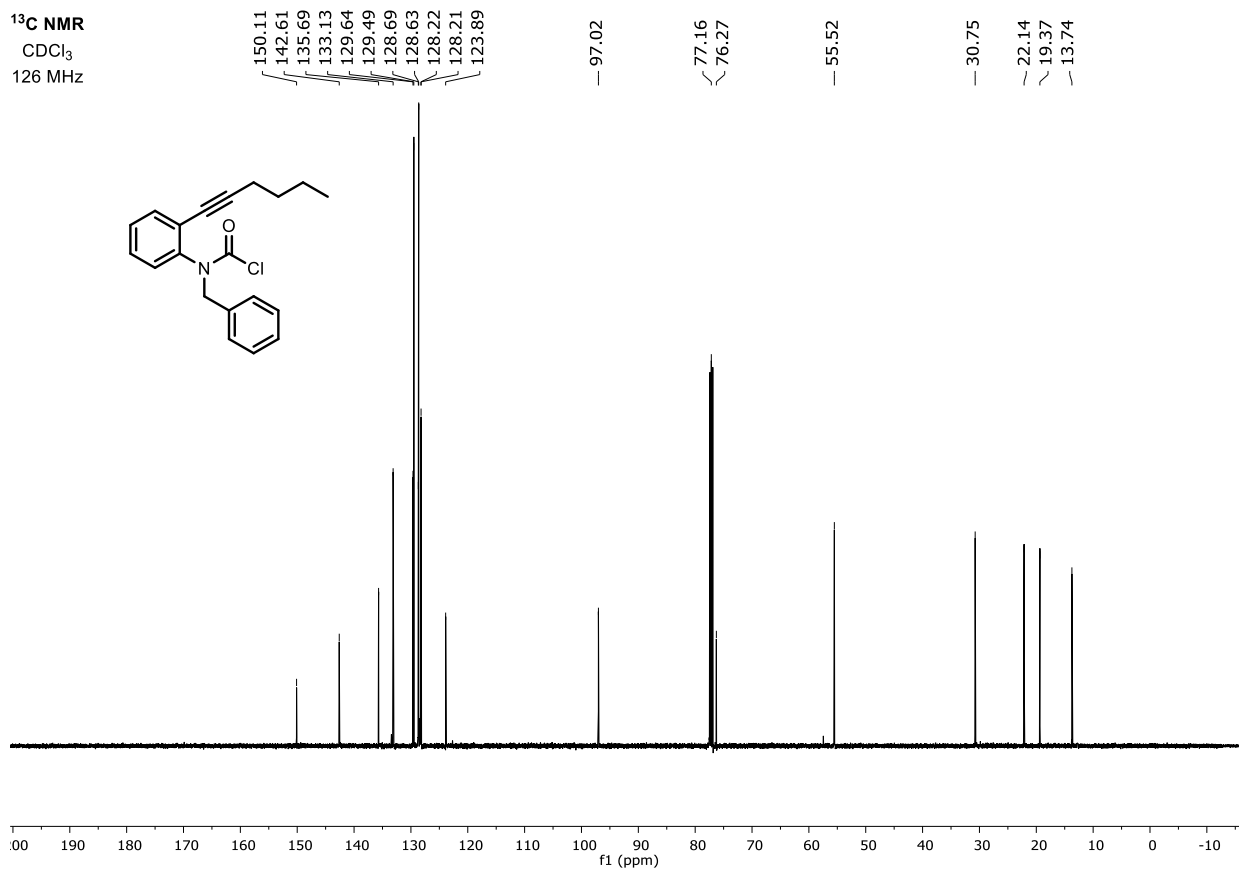


benzyl(2-(hex-1-yn-1-yl)phenyl)carbamic chloride (1ac')

¹H NMR
CDCl₃
400 MHz

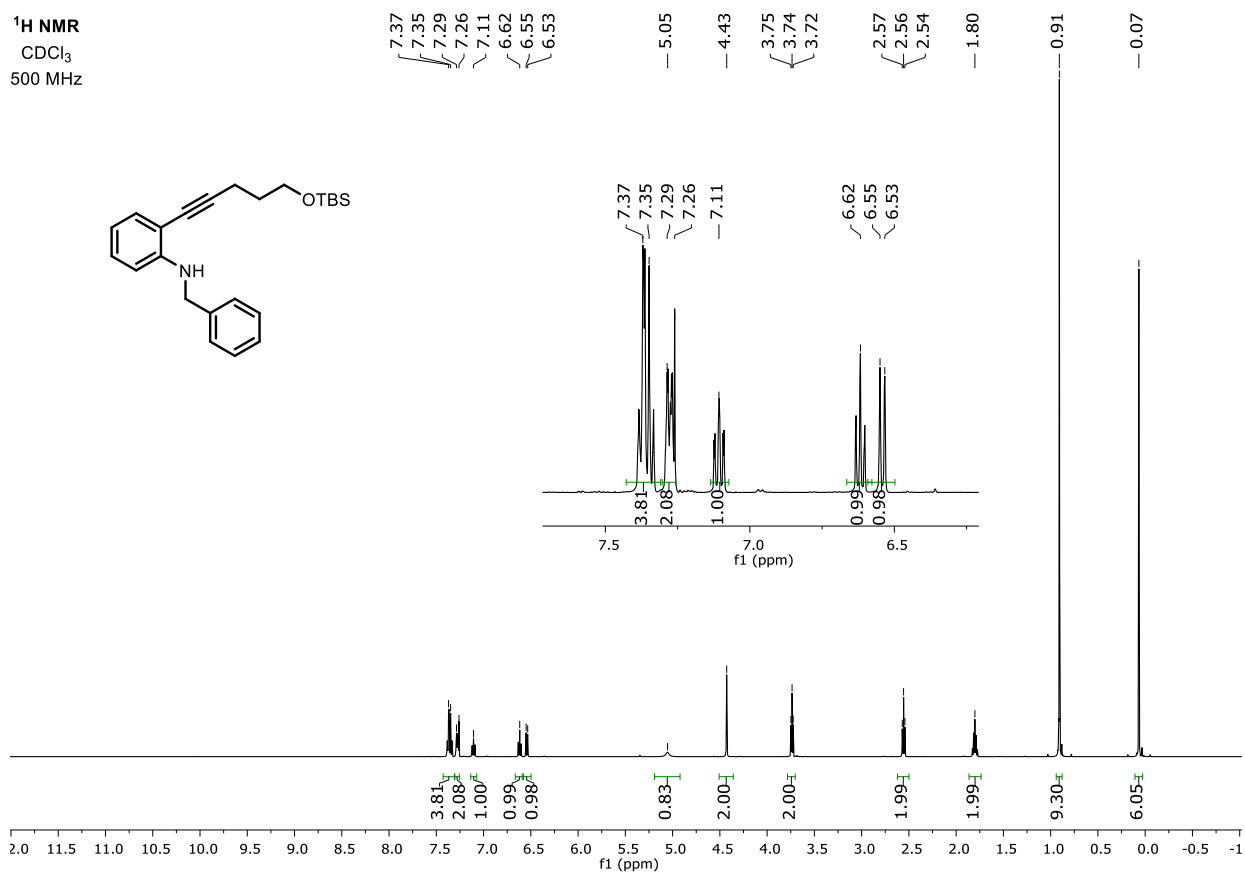


¹³C NMR
CDCl₃
126 MHz

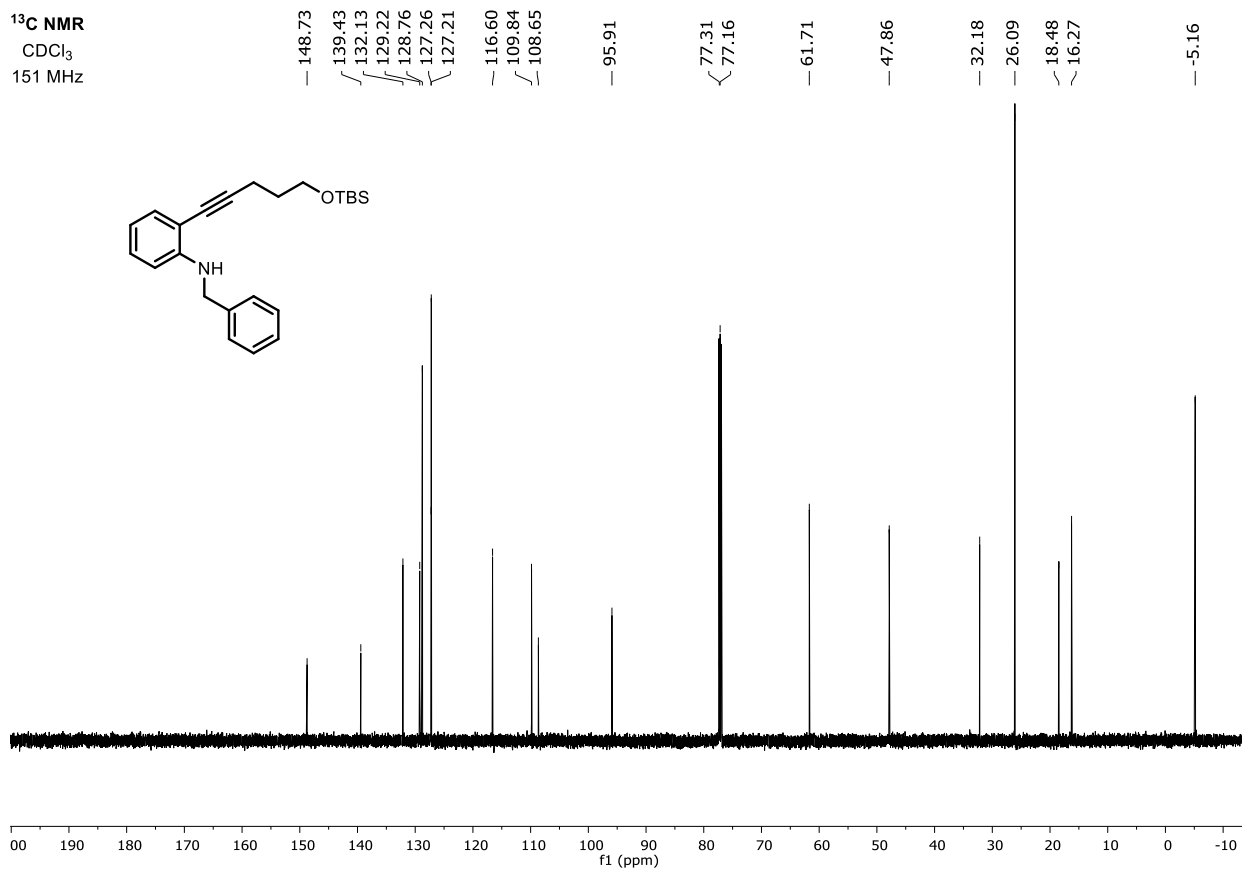


***N*-benzyl-2-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-yn-1-yl)aniline (5ad)**

¹H NMR
CDCl₃
500 MHz

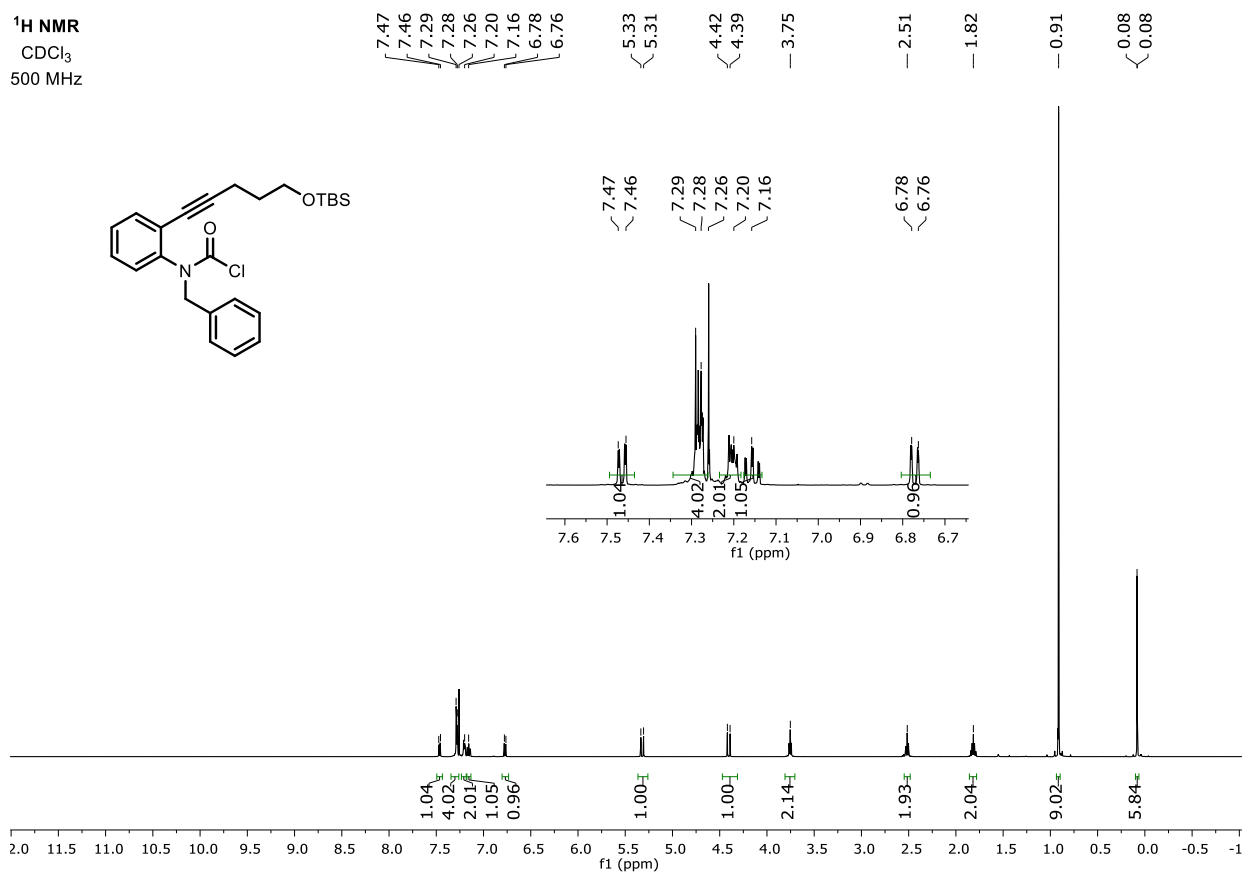


¹³C NMR
CDCl₃
151 MHz

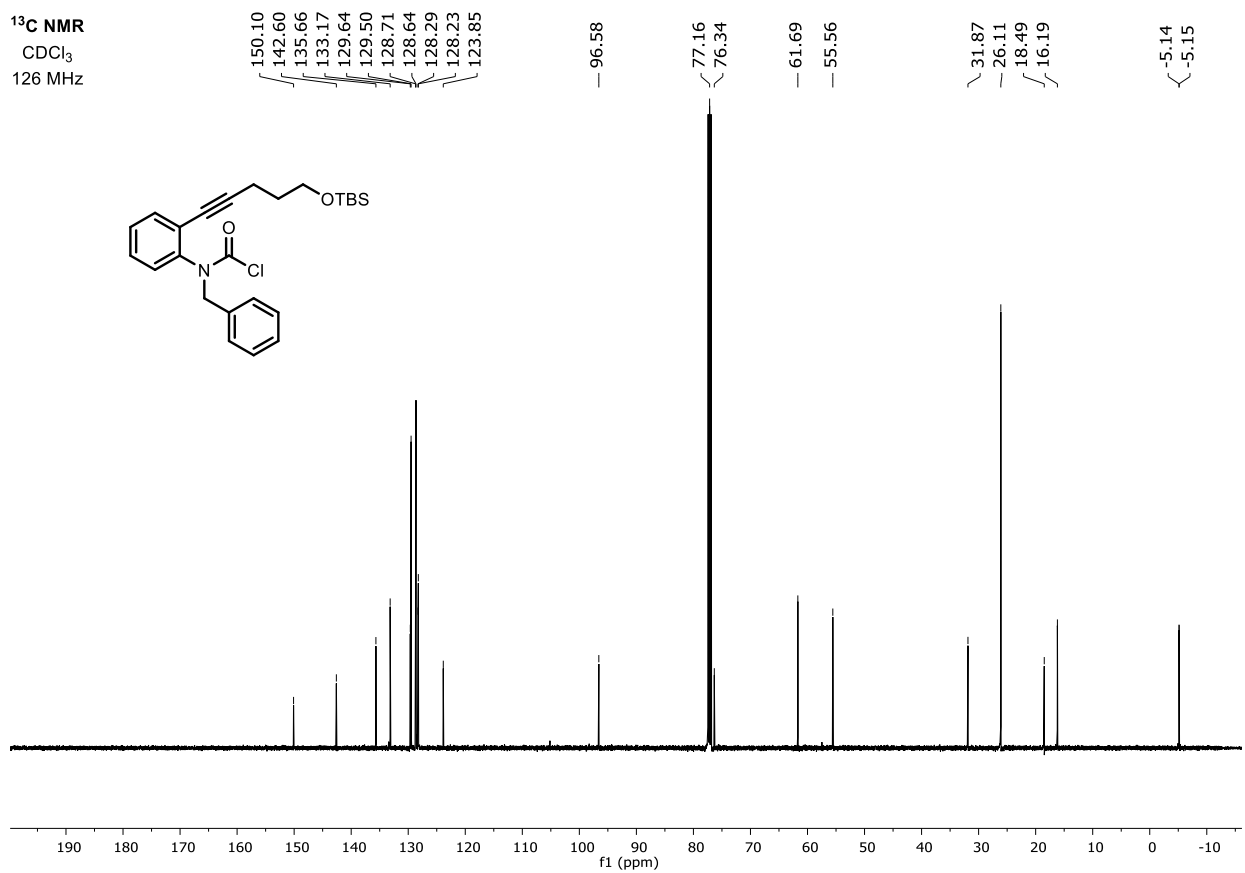


benzyl(2-(5-((tert-butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl)carbamic chloride (1ad)

¹H NMR
CDCl₃
500 MHz

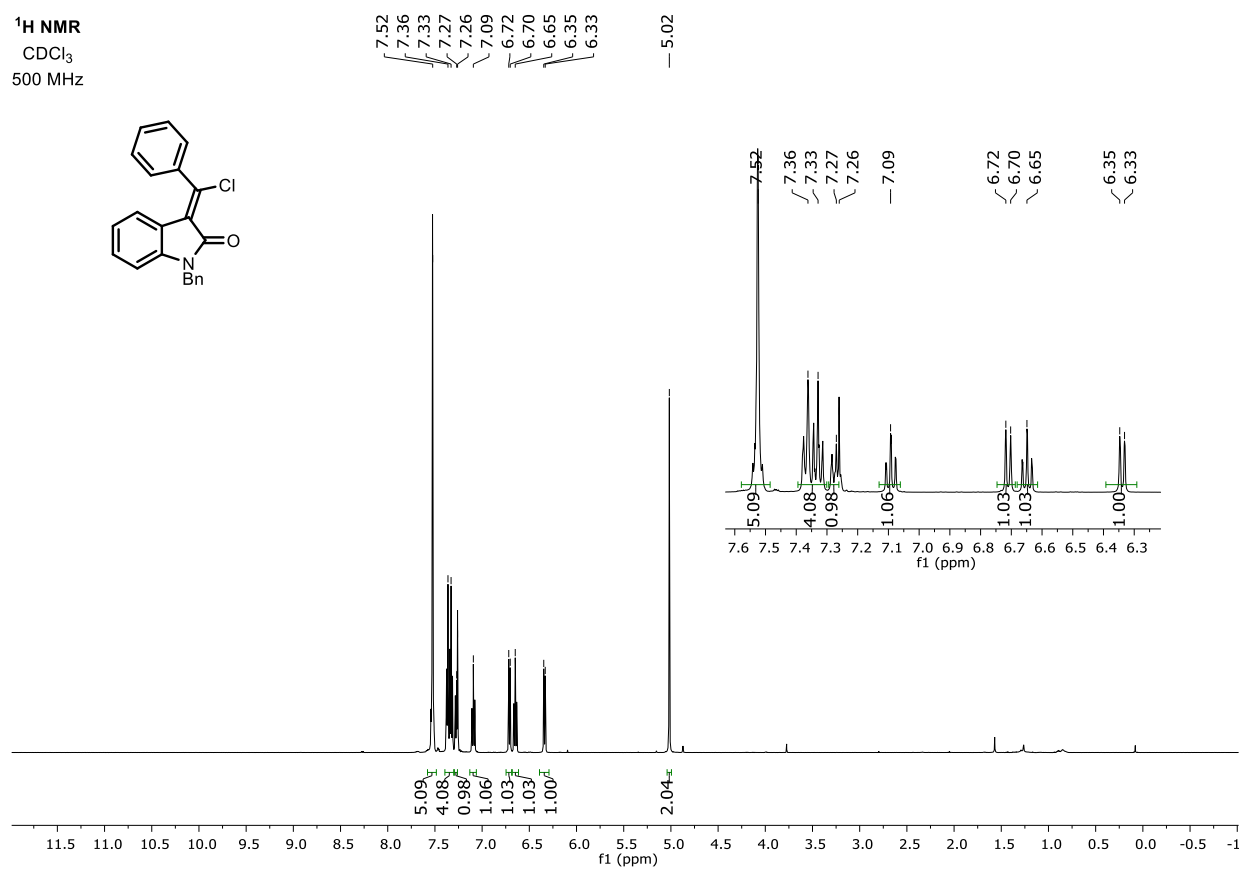


¹³C NMR
CDCl₃
126 MHz

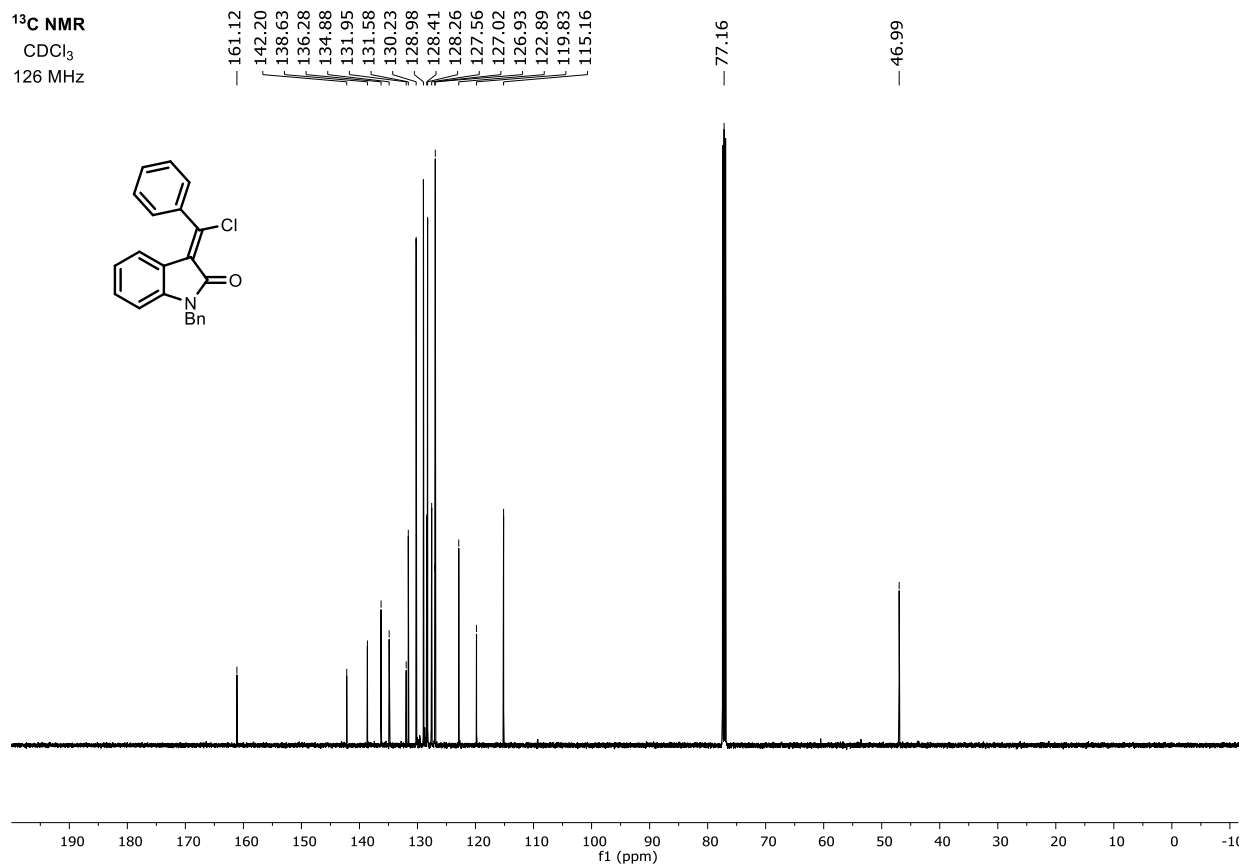


(Z)-1-benzyl-3-(chloro(phenyl)methylene)indolin-2-one (1b)

¹H NMR
CDCl₃
500 MHz

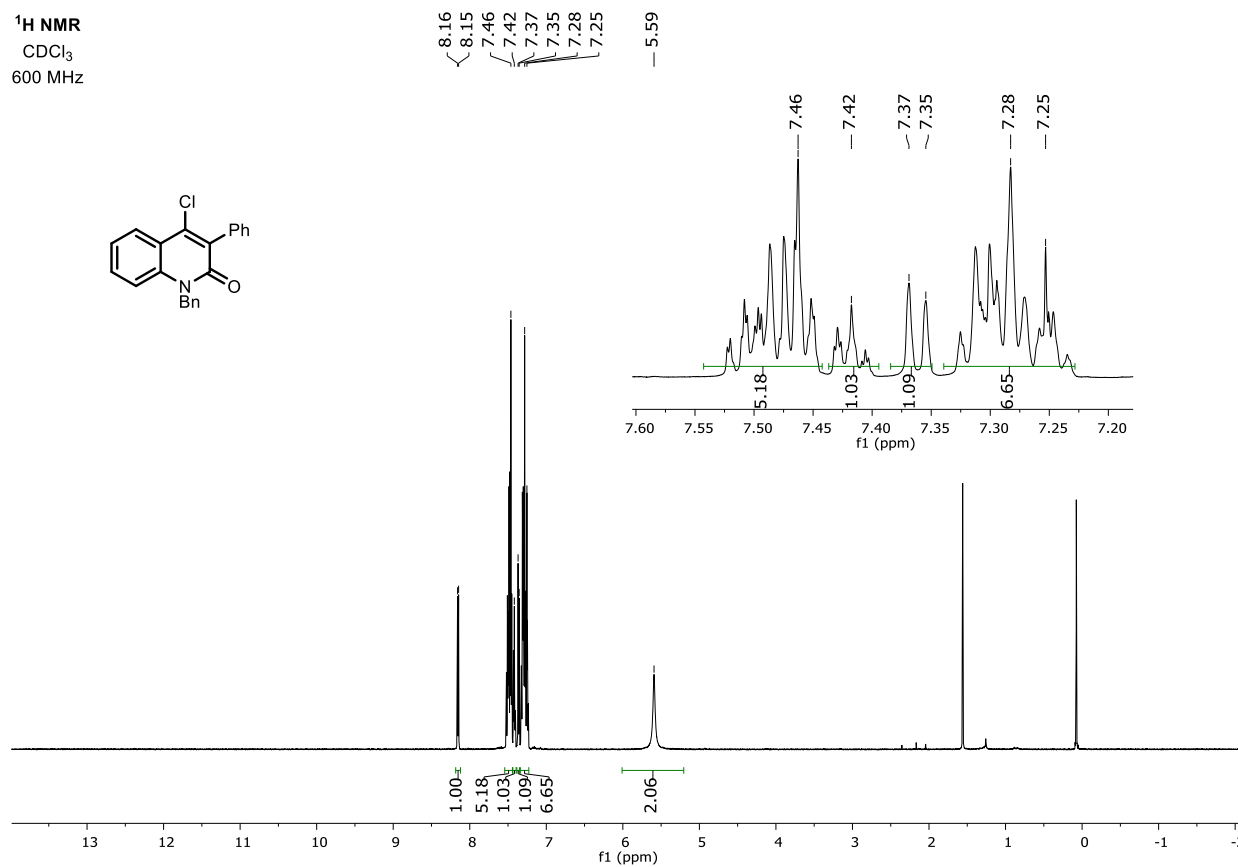


¹³C NMR
CDCl₃
126 MHz

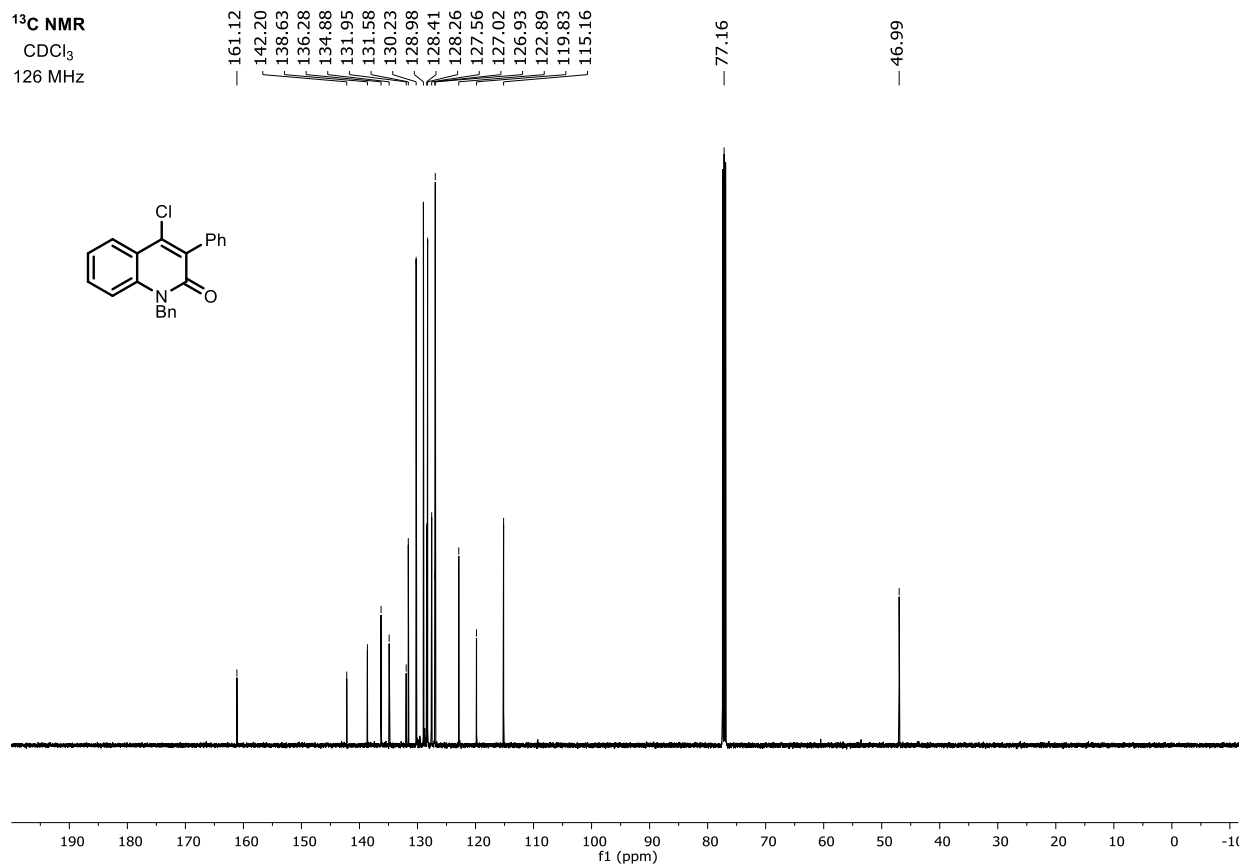


1-benzyl-4-chloro-3-phenylquinolin-2(1H)-one (2b)

¹H NMR
CDCl₃
600 MHz

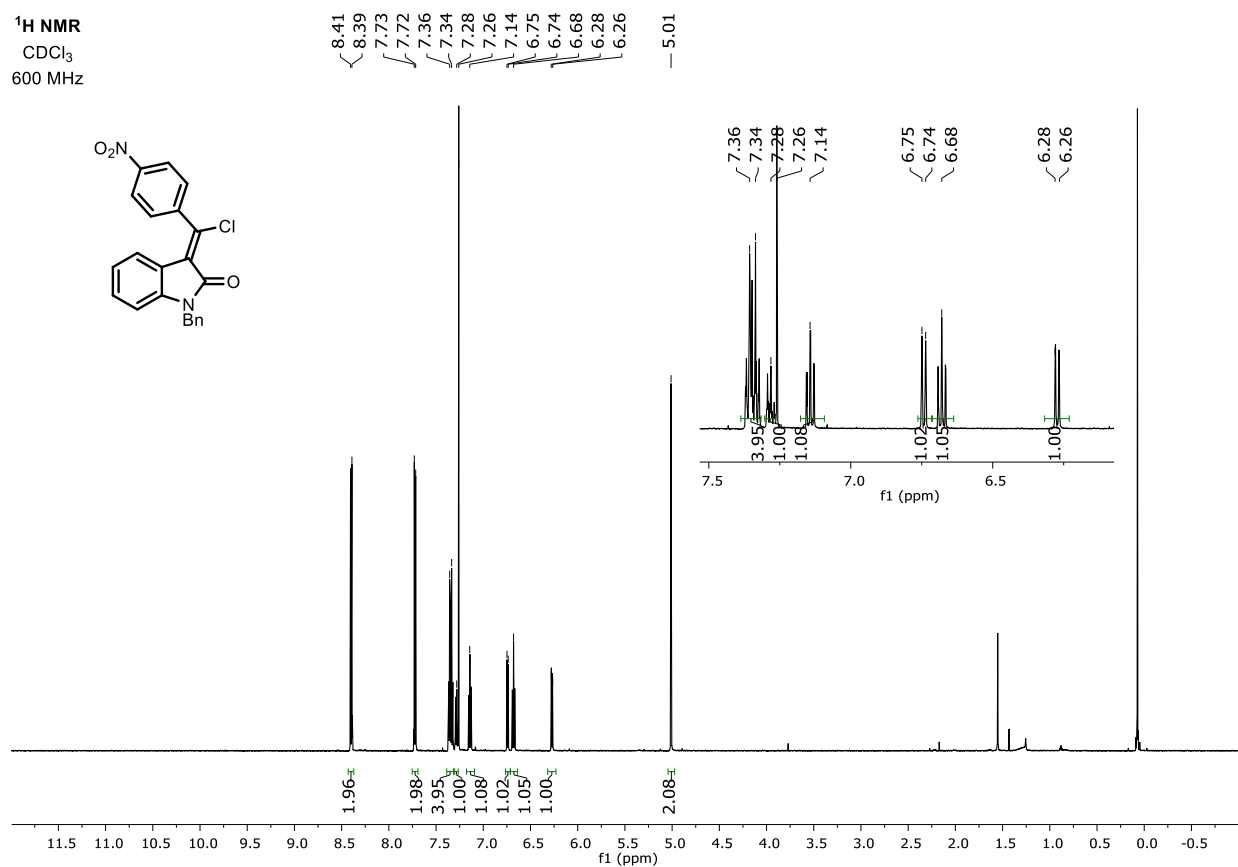


¹³C NMR
CDCl₃
126 MHz

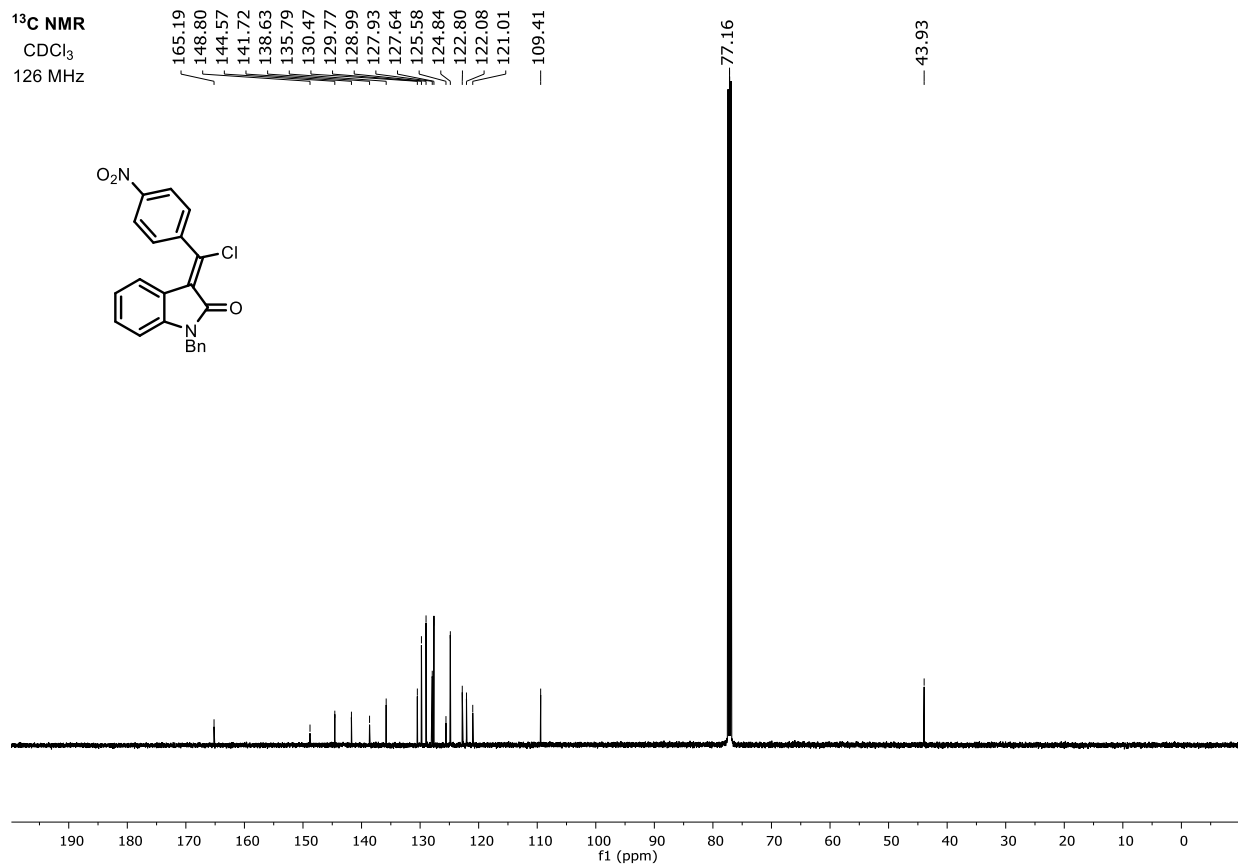


(Z)-1-benzyl-3-(chloro(4-nitrophenyl)methylene)indolin-2-one (1c)

¹H NMR
CDCl₃
600 MHz

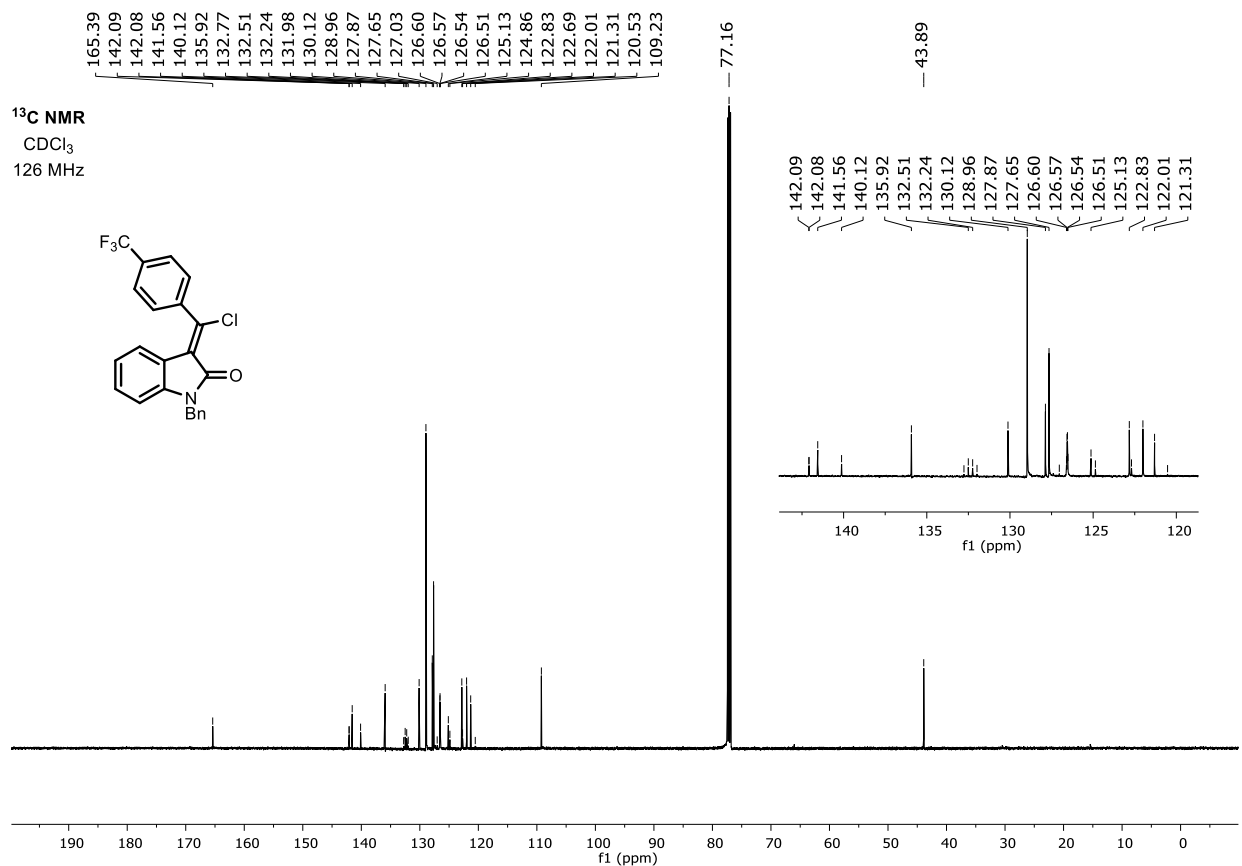
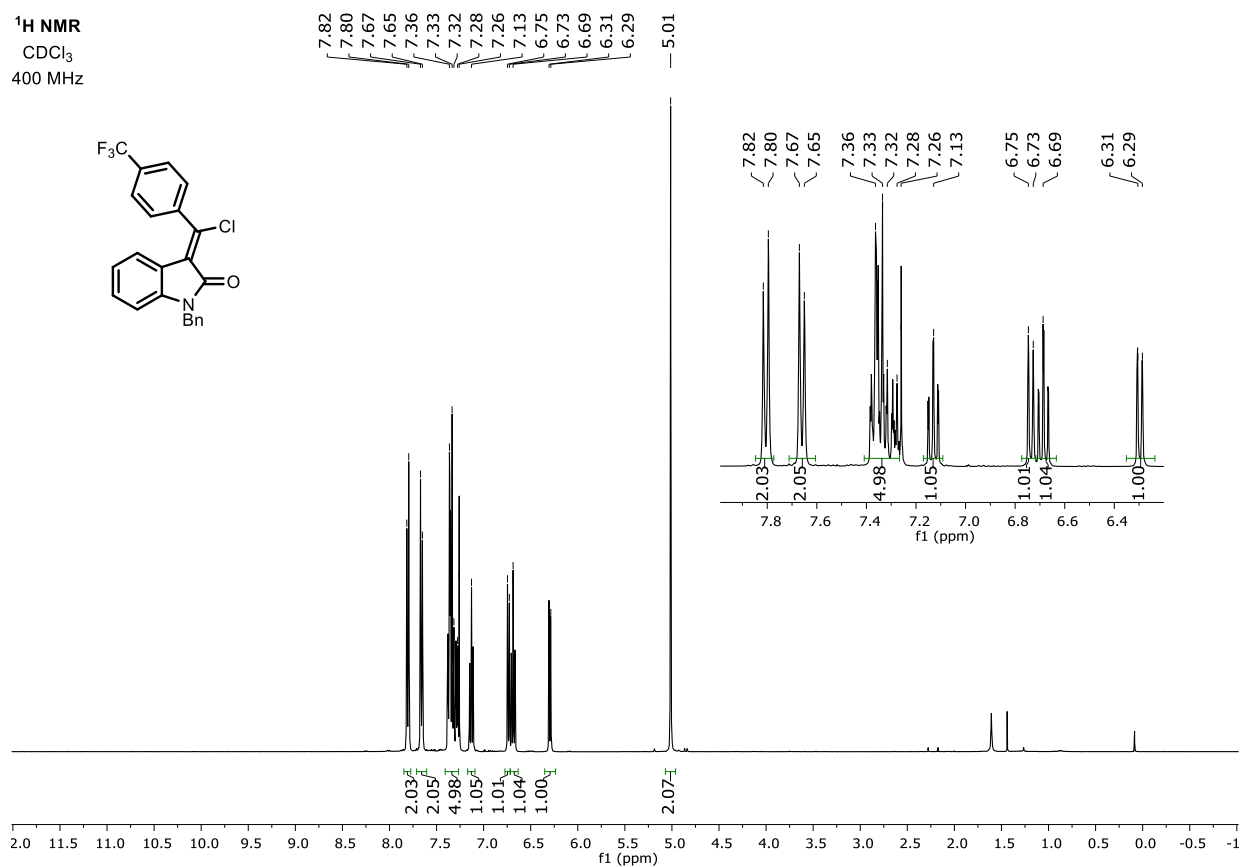


¹³C NMR
CDCl₃
126 MHz



(Z)-1-benzyl-3-(chloro(4-(trifluoromethyl)phenyl)methylene)indolin-2-one (1d)

¹H NMR
CDCl₃
400 MHz



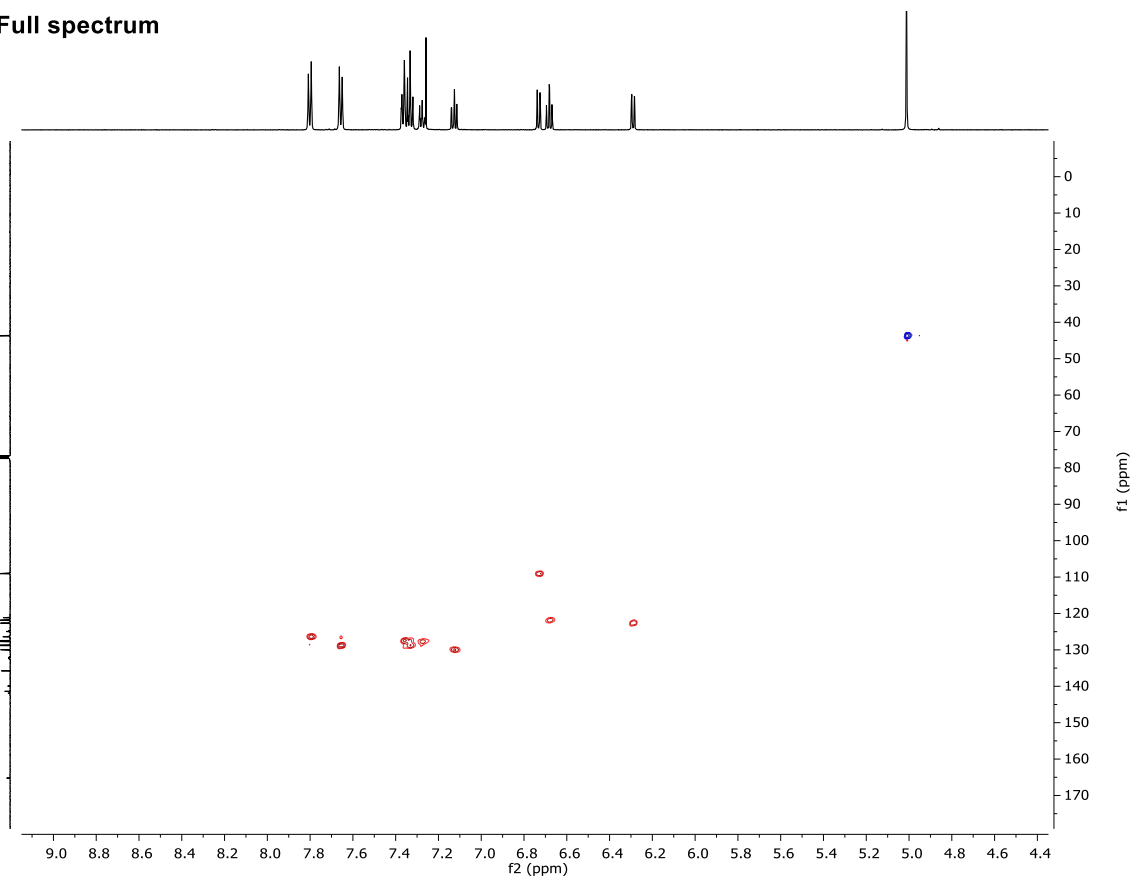
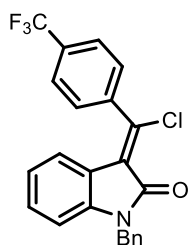
Full spectrum

^1H - ^{13}C HSQC

CDCl_3

500 MHz (^1H)

126 MHz (^{13}C)



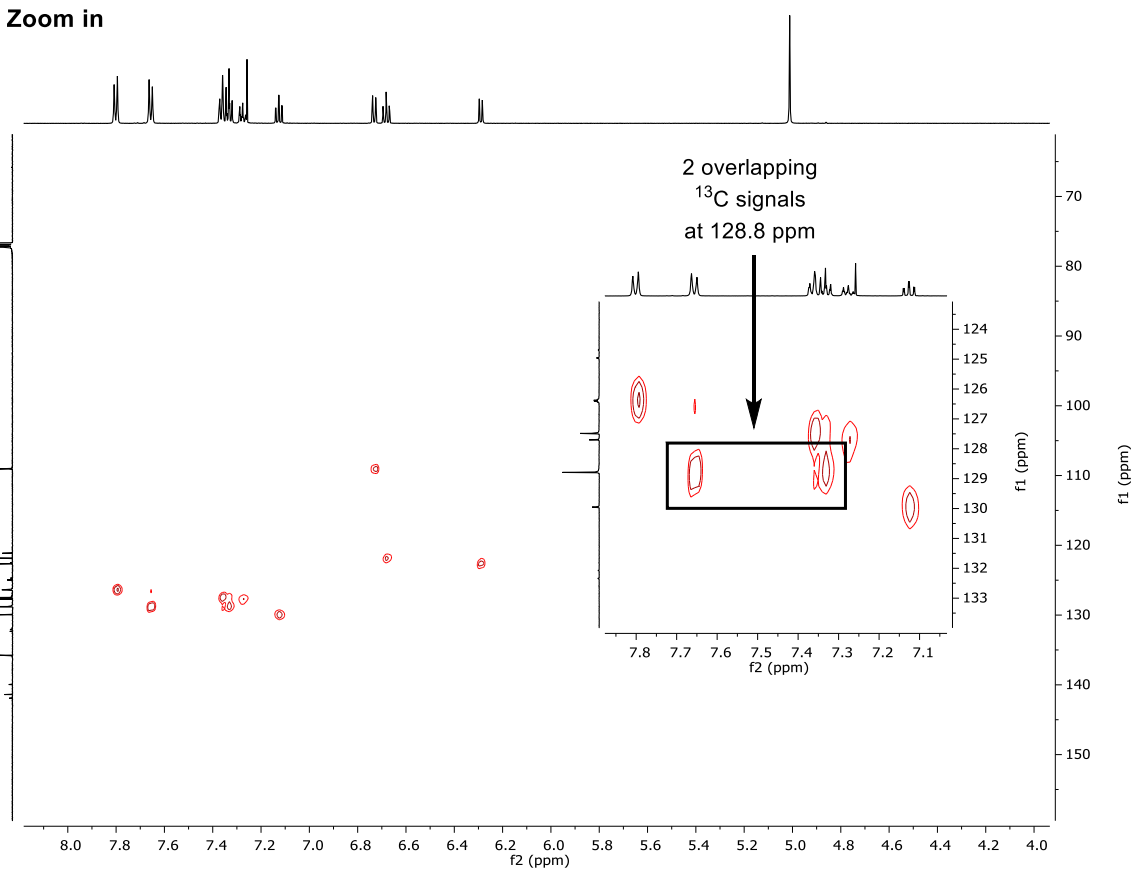
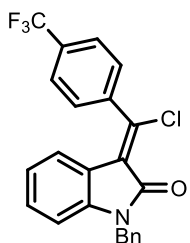
Zoom in

^1H - ^{13}C HSQC

CDCl_3

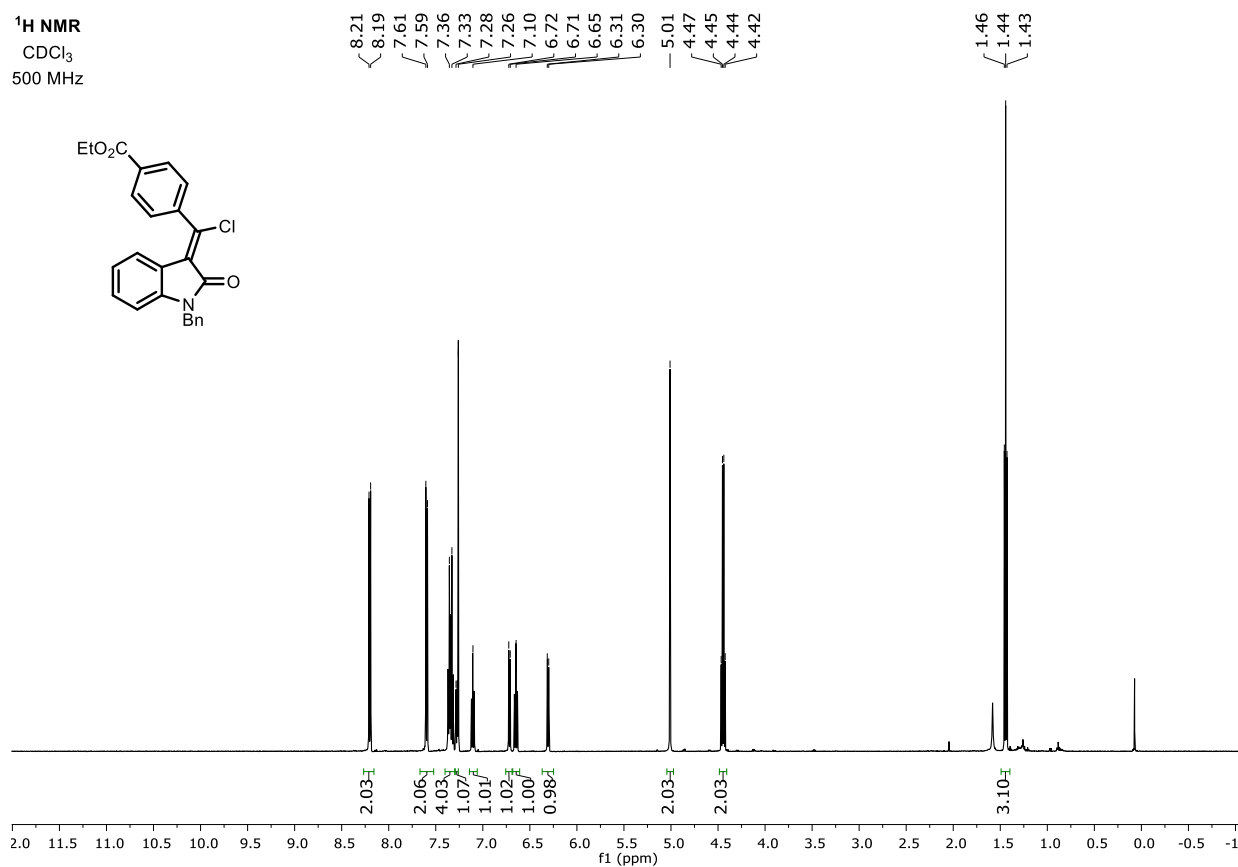
500 MHz (^1H)

126 MHz (^{13}C)

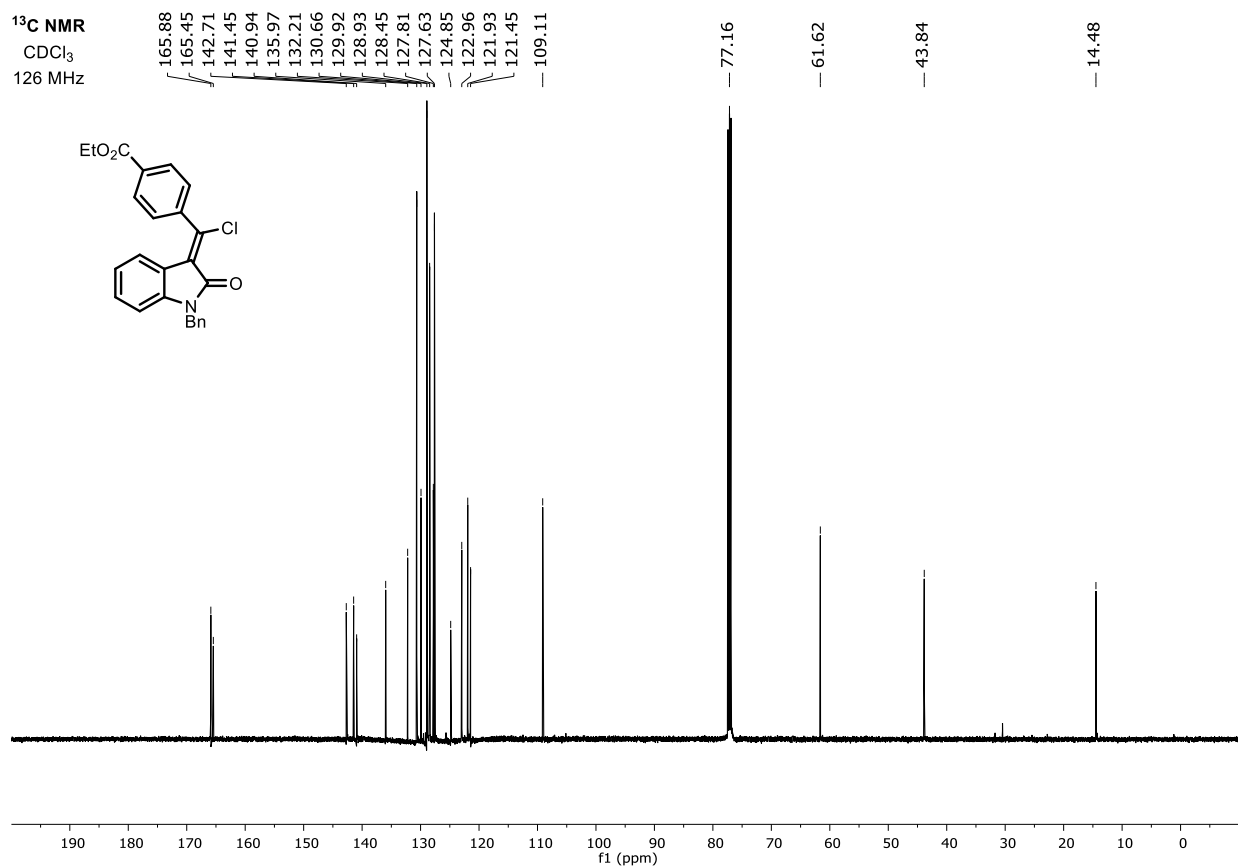


ethyl (Z)-4-((1-benzyl-2-oxoindolin-3-ylidene)chloromethyl)benzoate (1e)

¹H NMR
CDCl₃
500 MHz

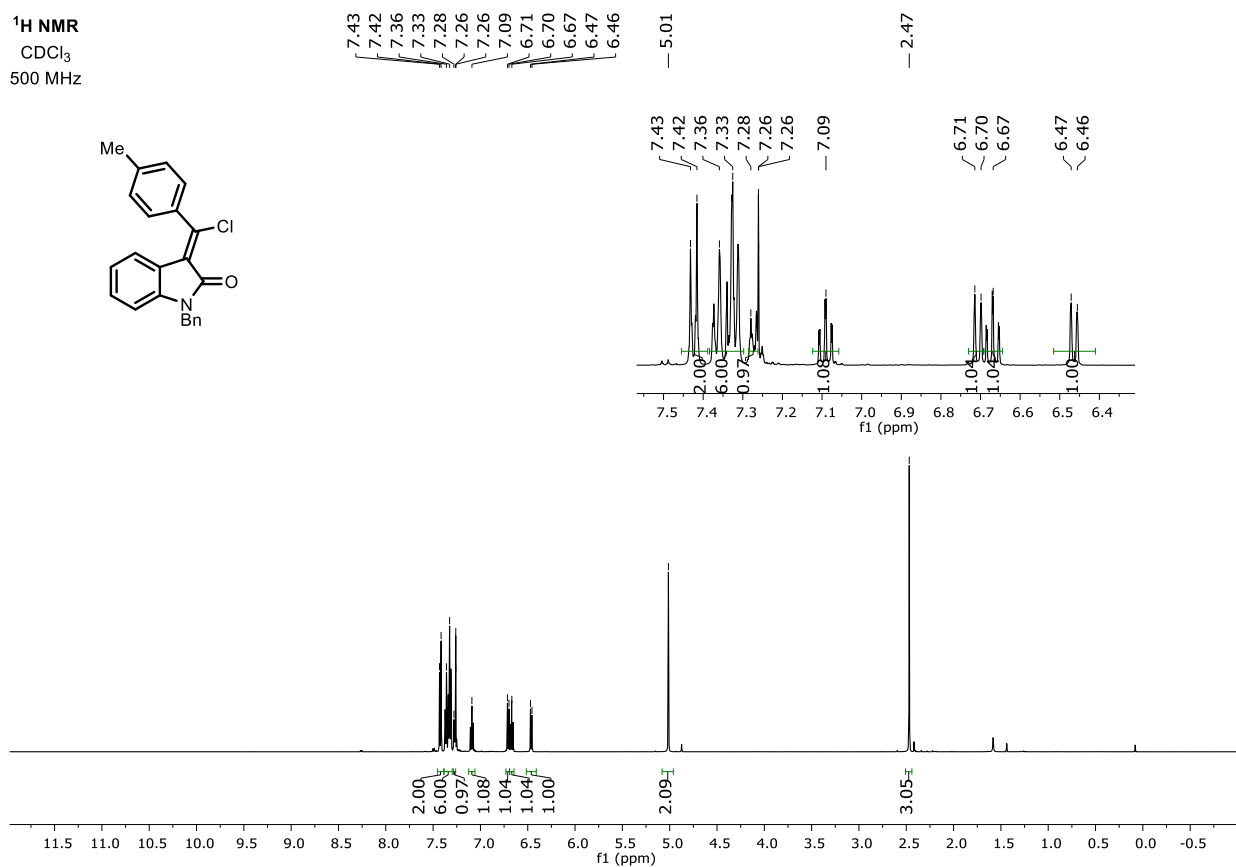
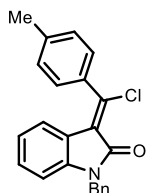


¹³C NMR
CDCl₃
126 MHz

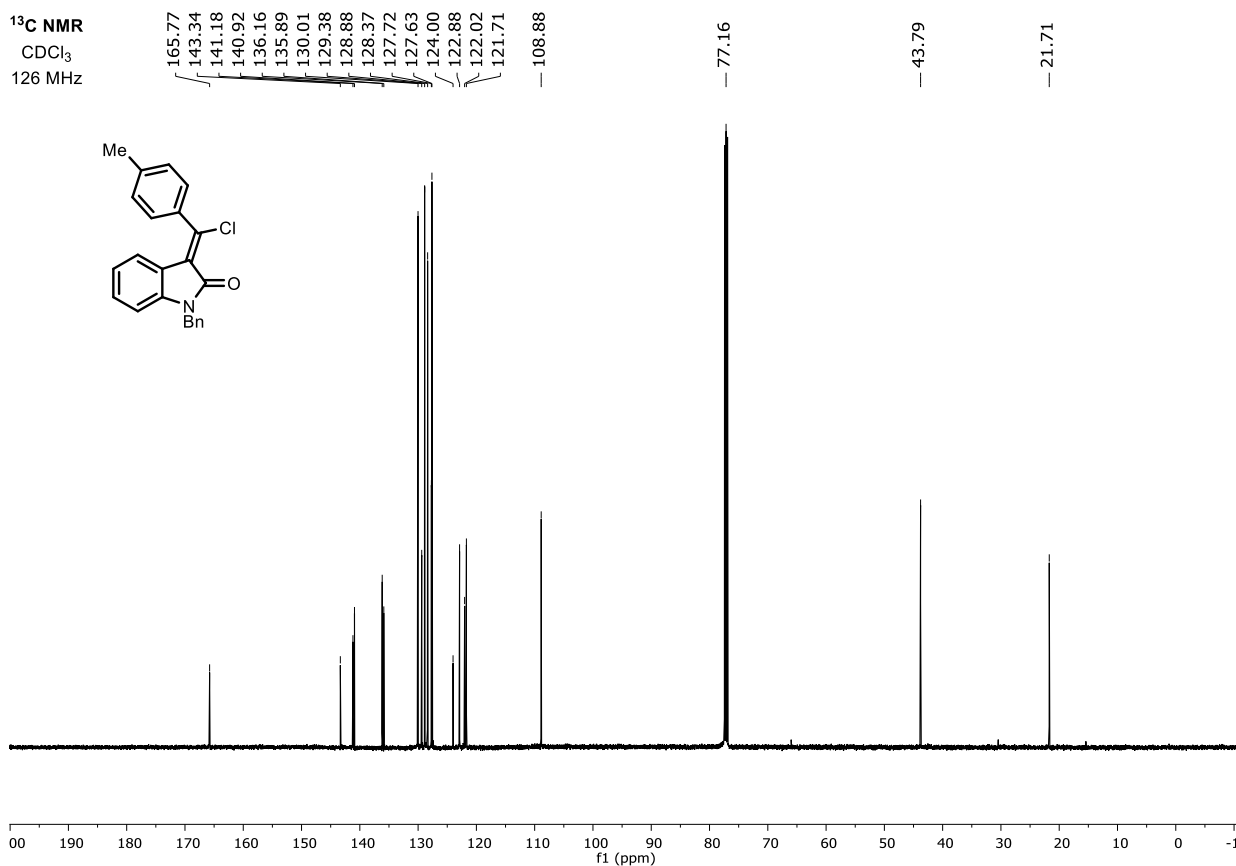
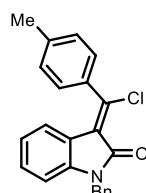


(Z)-1-benzyl-3-(chloro(*p*-tolyl)methylene)indolin-2-one (1f)

¹H NMR
CDCl₃
500 MHz

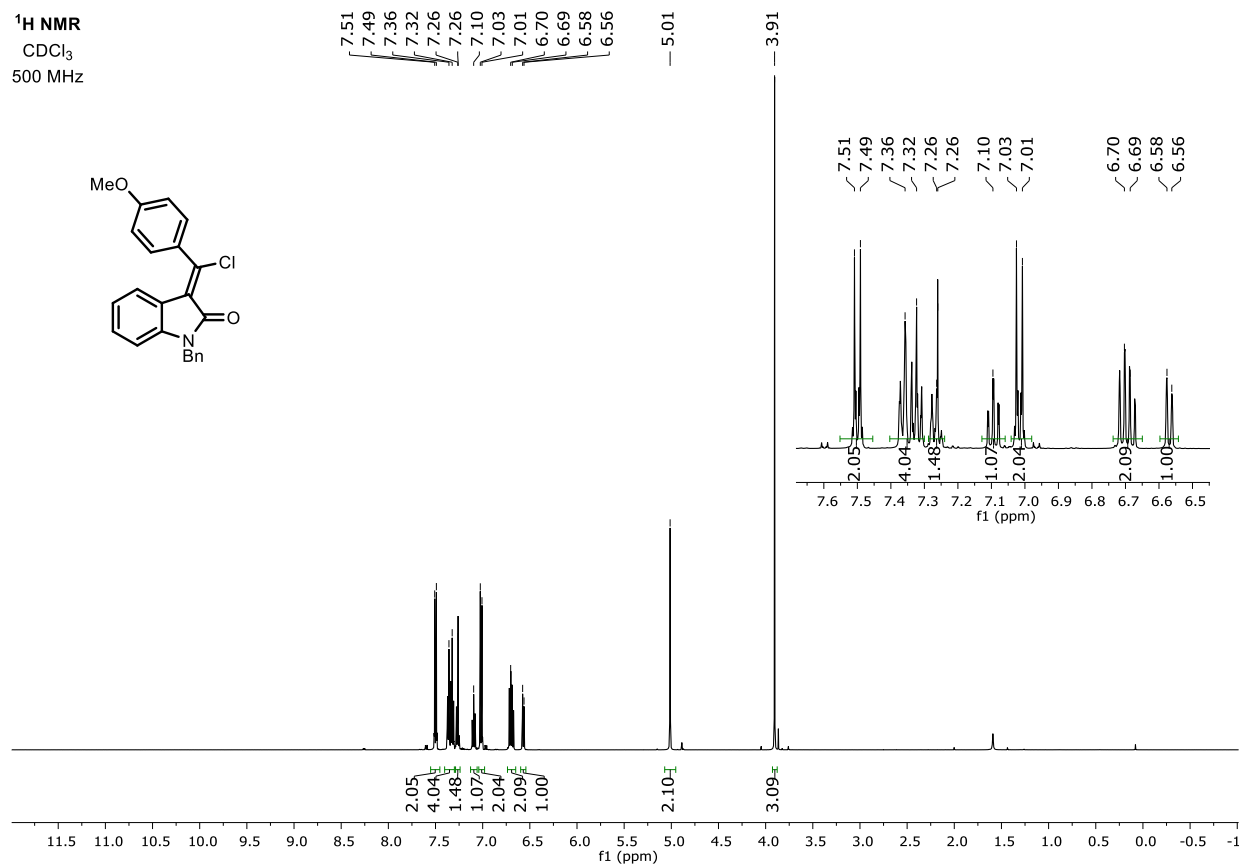
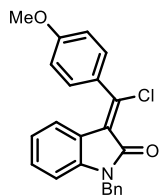


¹³C NMR
CDCl₃
126 MHz

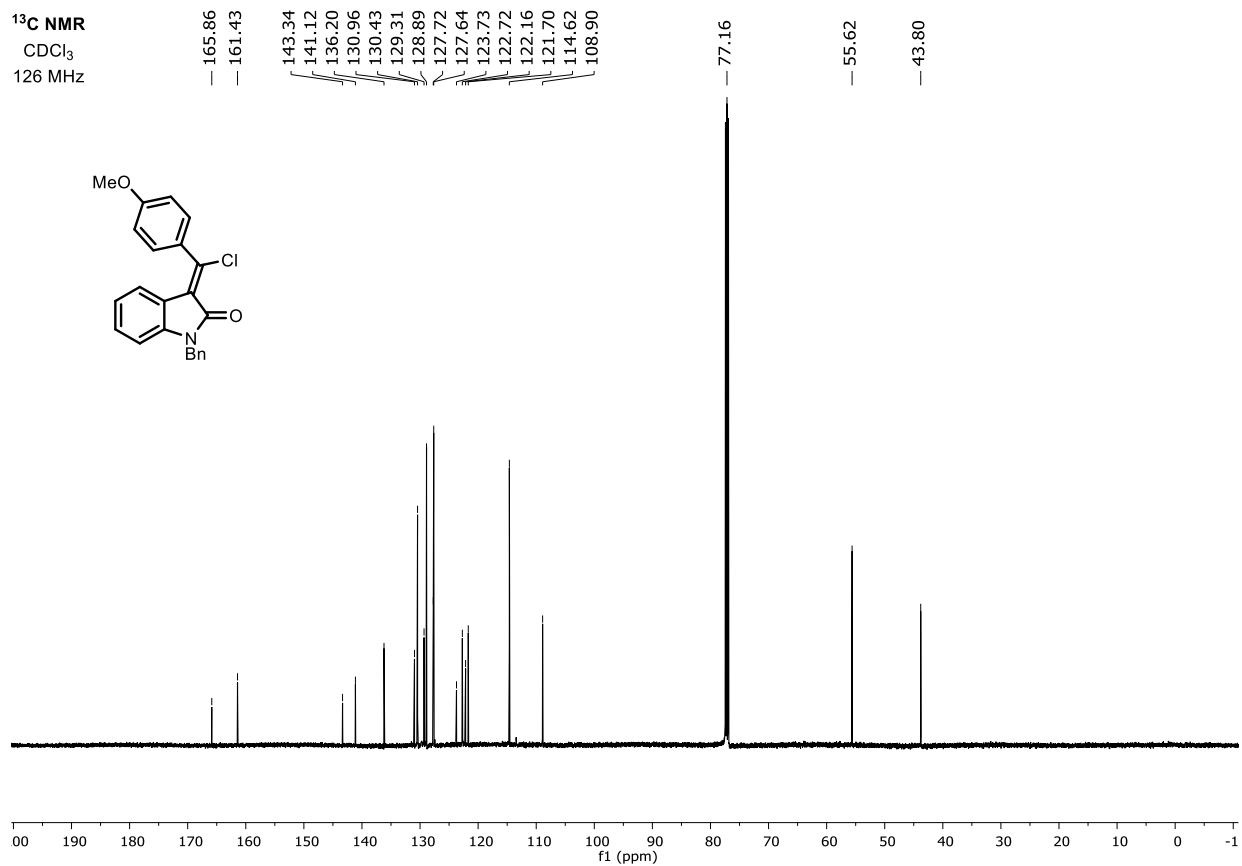
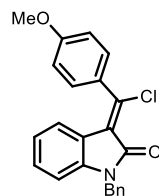


(Z)-1-benzyl-3-(chloro(4-methoxyphenyl)methylene)indolin-2-one (1g)

¹H NMR
CDCl₃
500 MHz

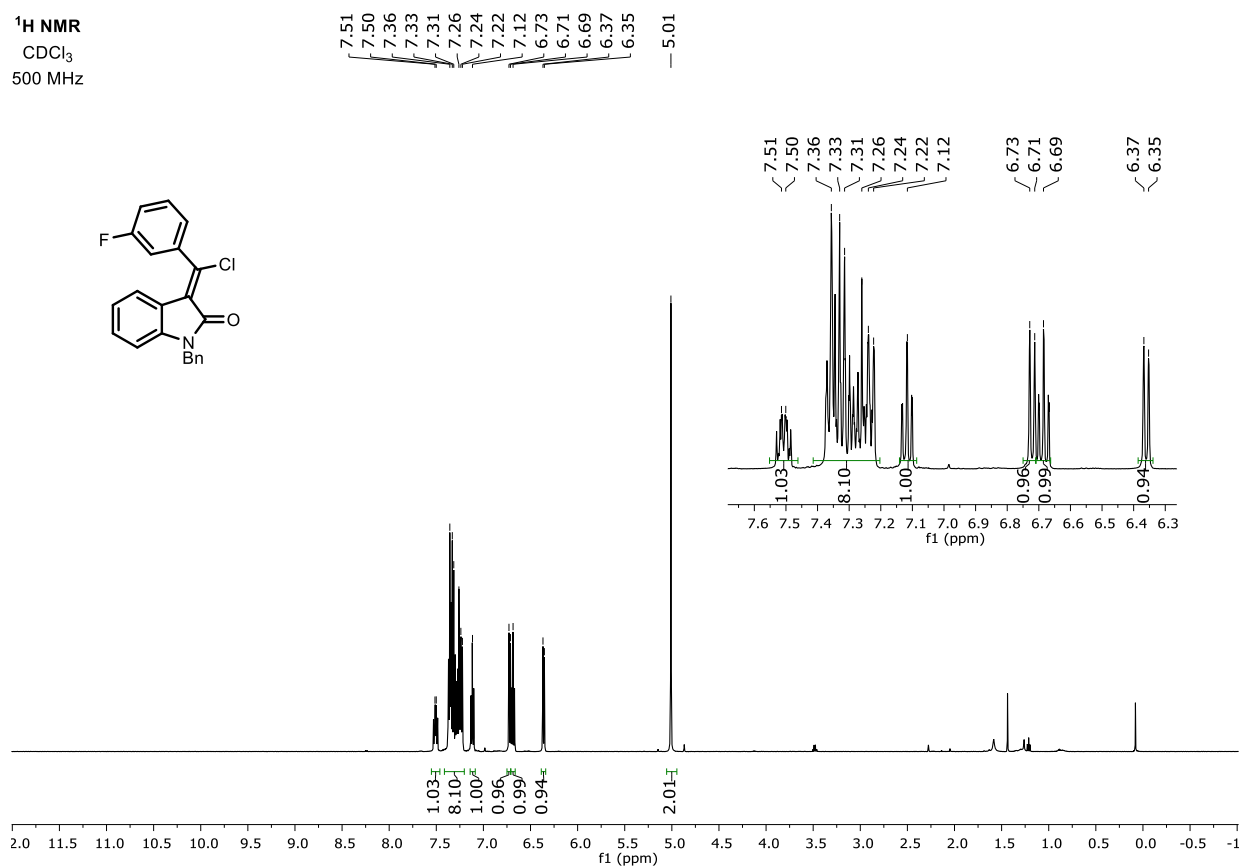


¹³C NMR
CDCl₃
126 MHz

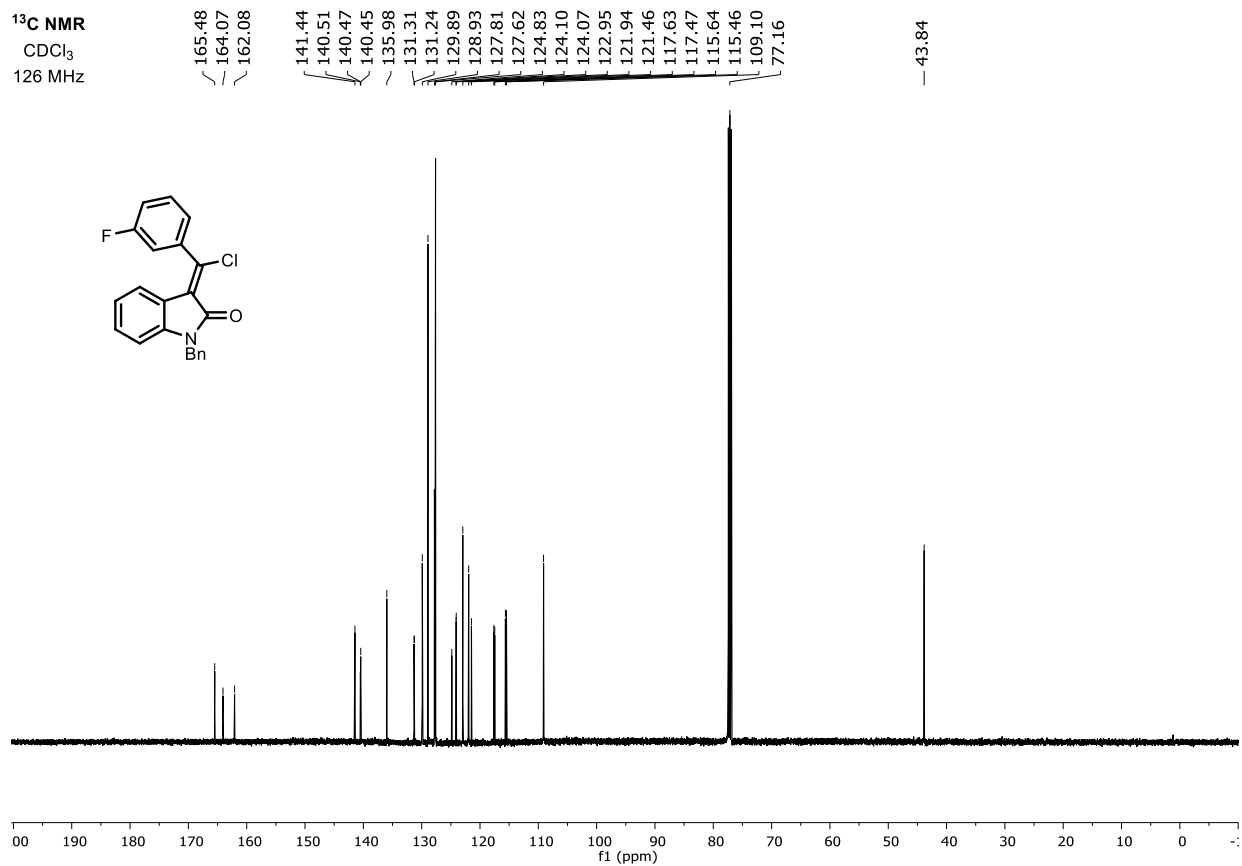


(Z)-1-benzyl-3-(chloro(3-fluorophenyl)methylene)indolin-2-one (1h)

¹H NMR
CDCl₃
500 MHz

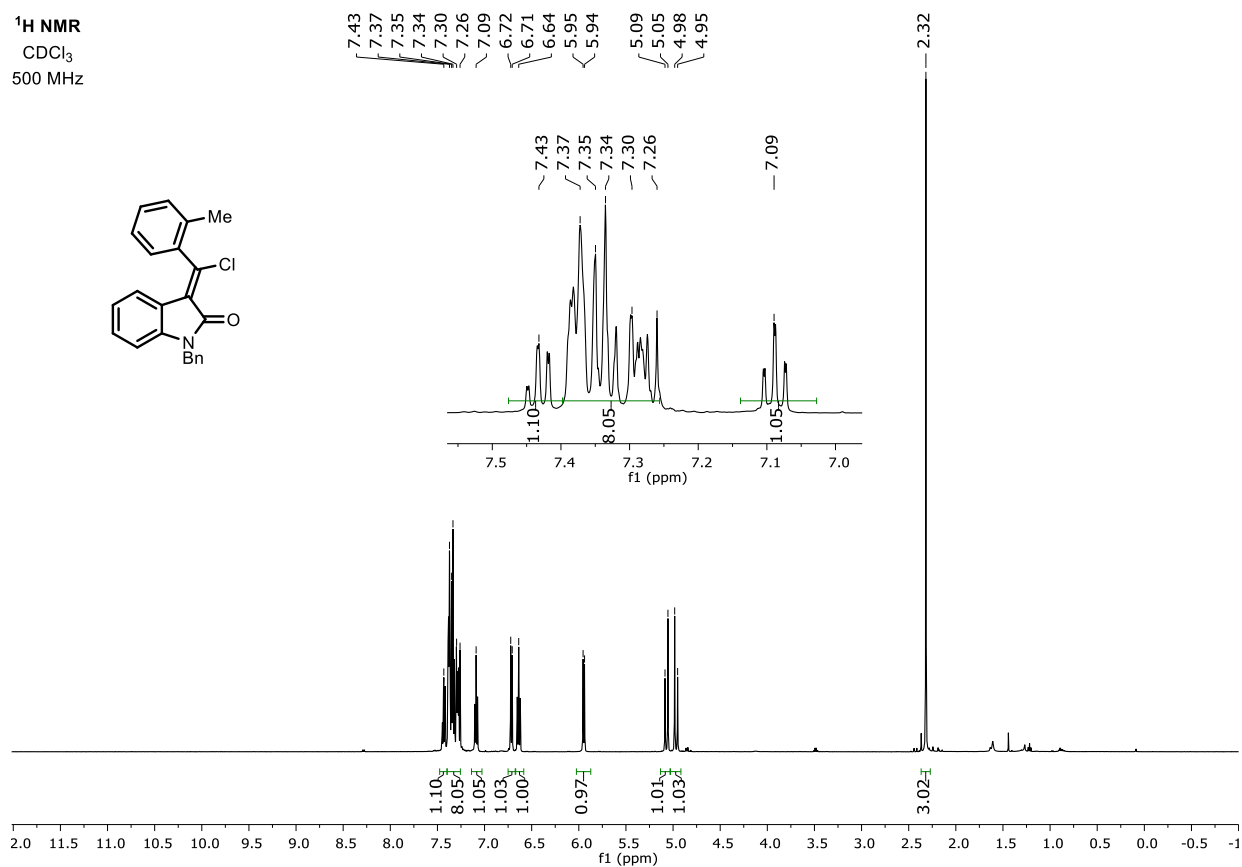


¹³C NMR
CDCl₃
126 MHz

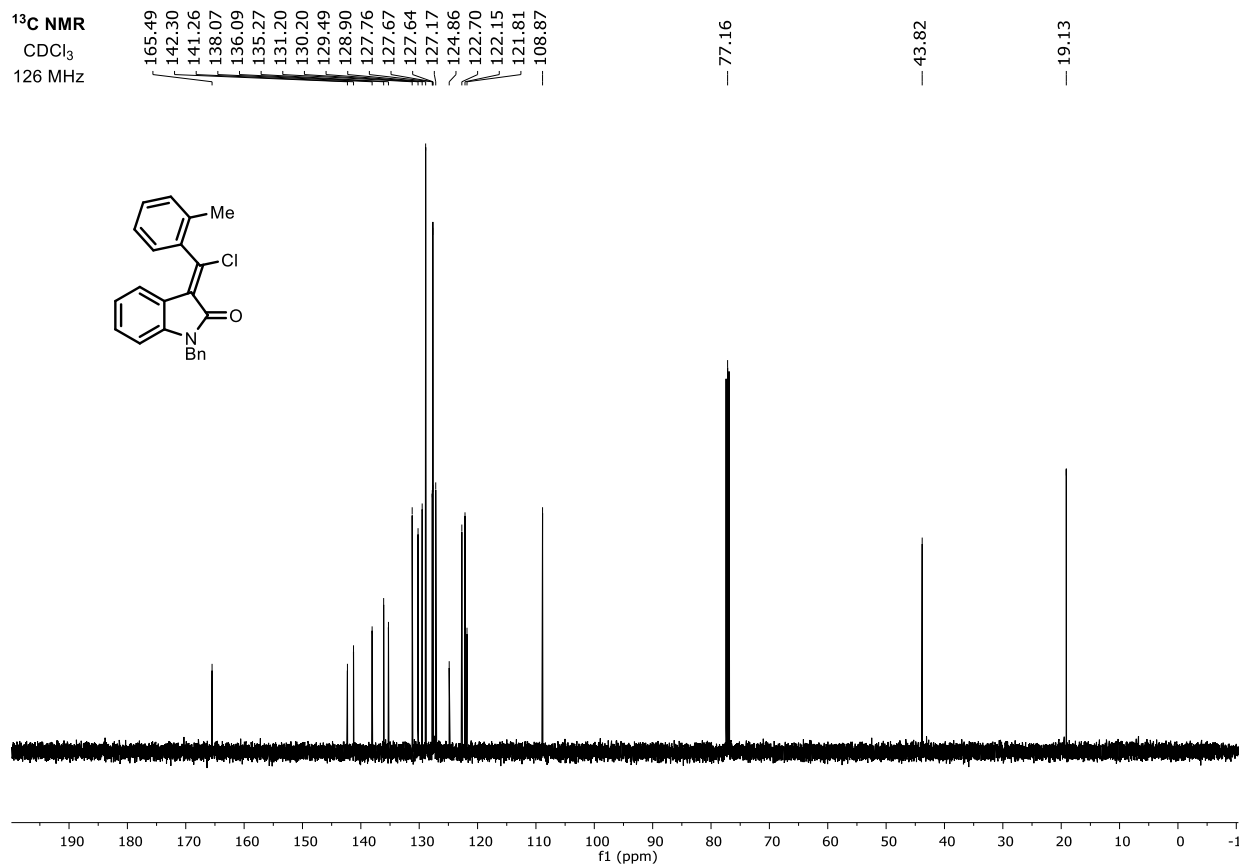


1-benzyl-3-(chloro(o-tolyl)methylene)indolin-2-one (1i)

¹H NMR
CDCl₃
500 MHz

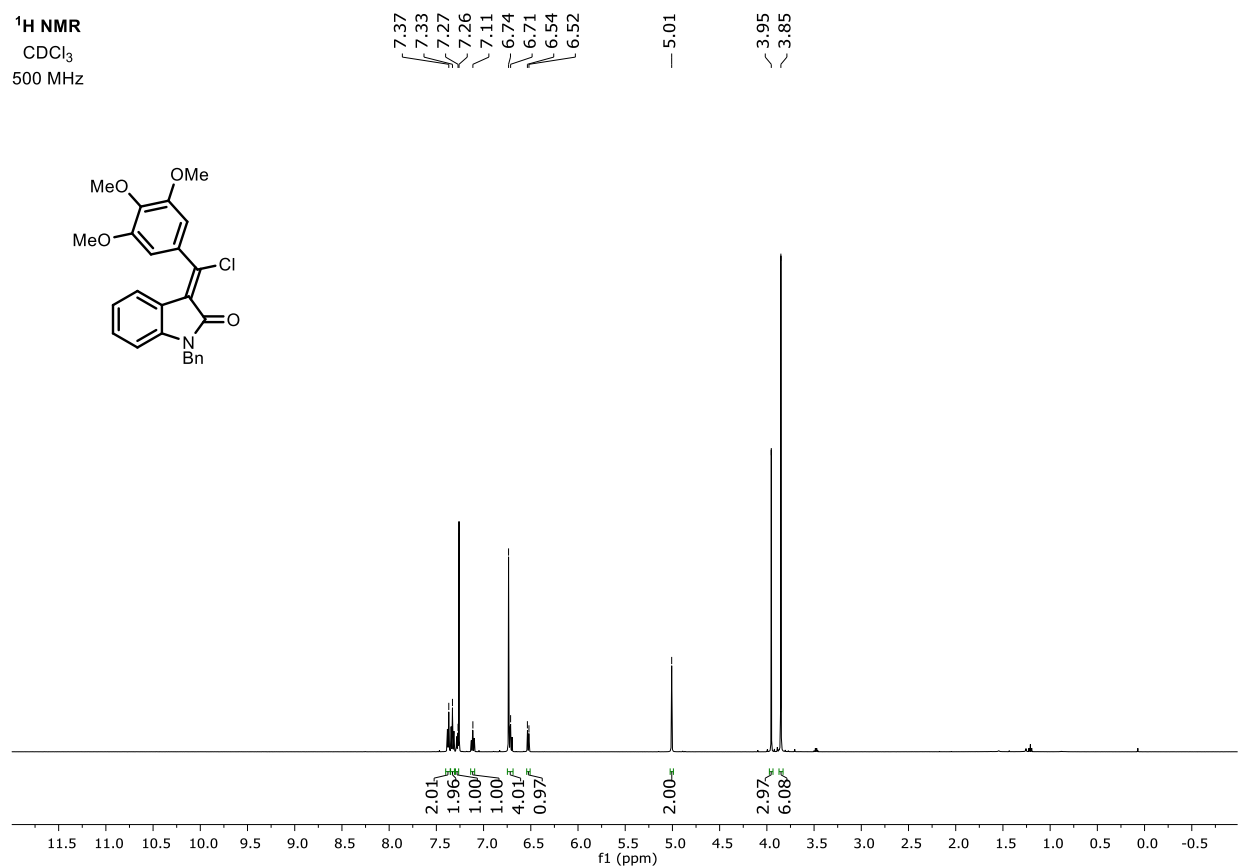


¹³C NMR
CDCl₃
126 MHz

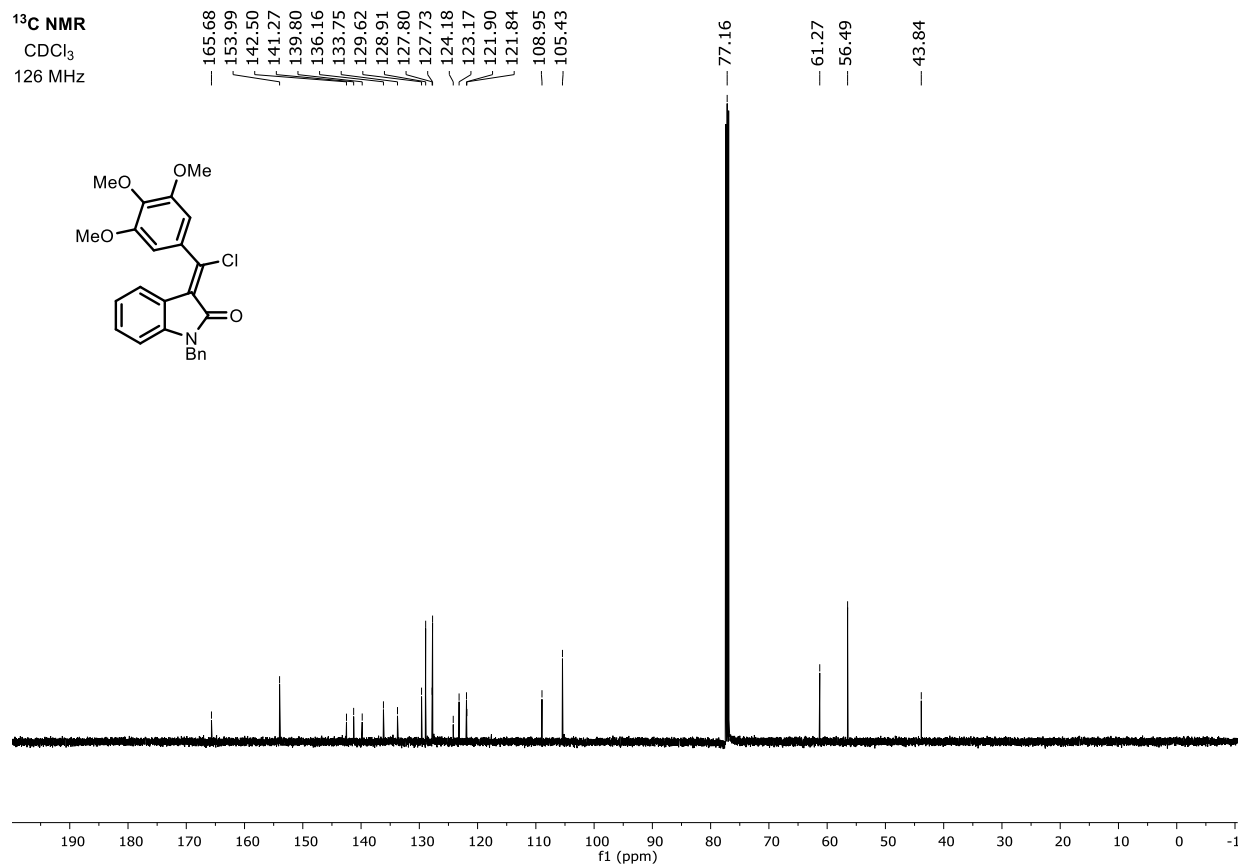


(Z)-1-benzyl-3-(chloro(3,4,5-trimethoxyphenyl)methylene)indolin-2-one (1j)

¹H NMR
CDCl₃
500 MHz

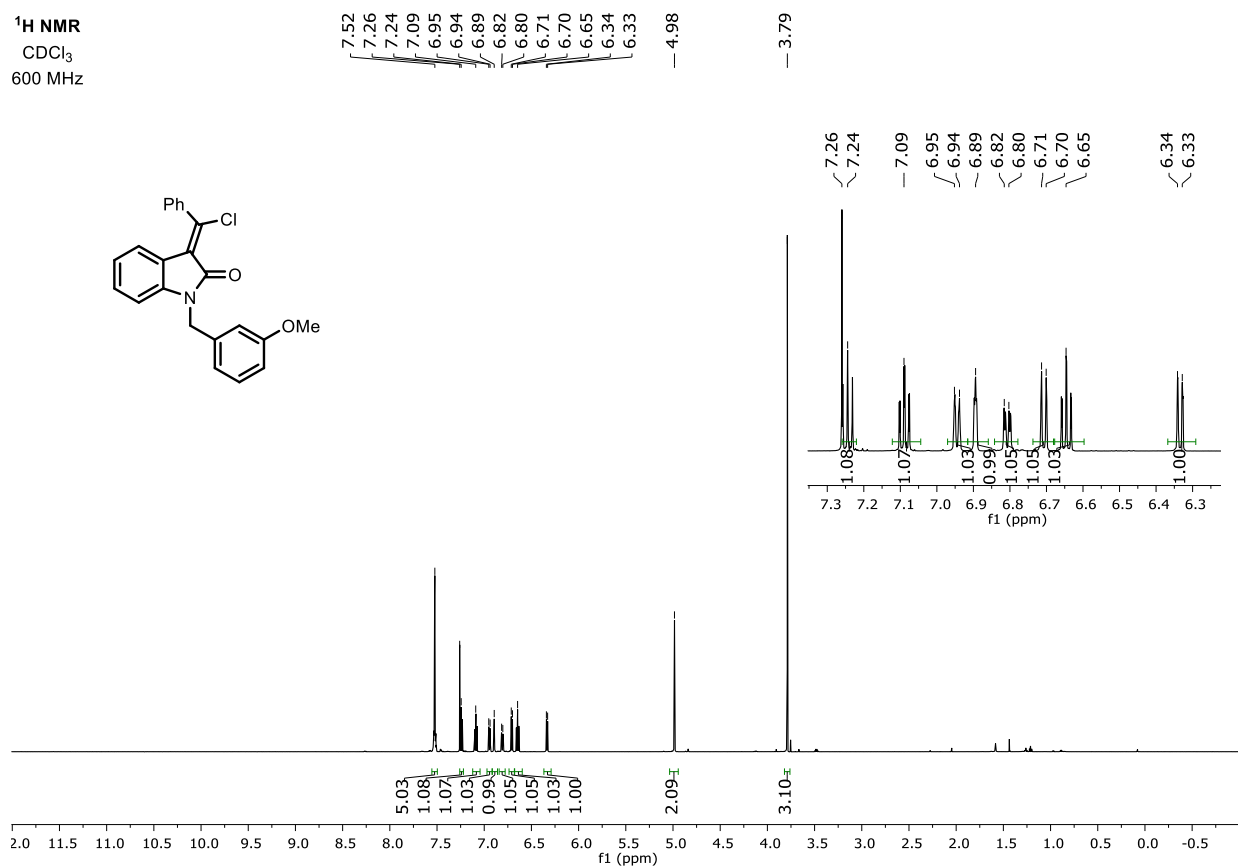


¹³C NMR
CDCl₃
126 MHz

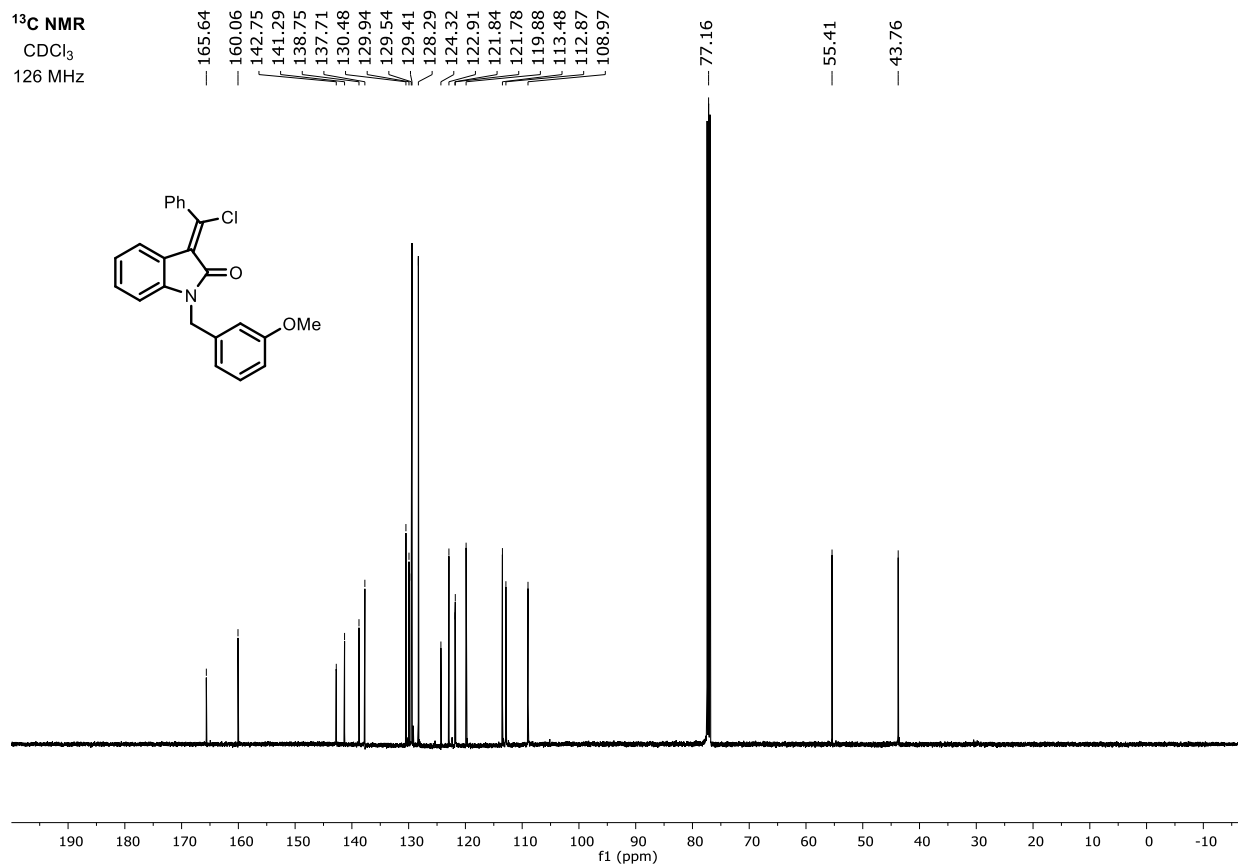


(Z)-3-(chloro(phenyl)methylene)-1-(3-methoxybenzyl)indolin-2-one (1k)

¹H NMR
CDCl₃
600 MHz

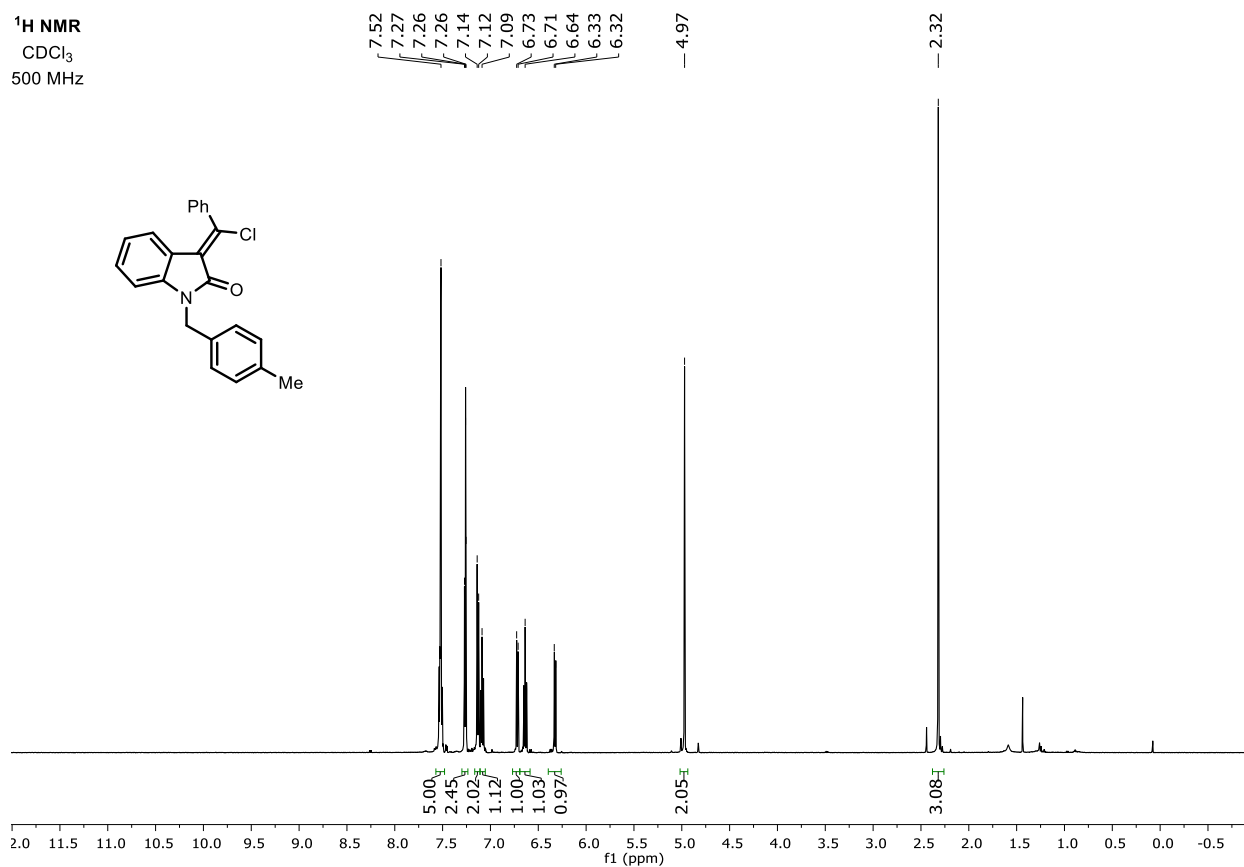


¹³C NMR
CDCl₃
126 MHz

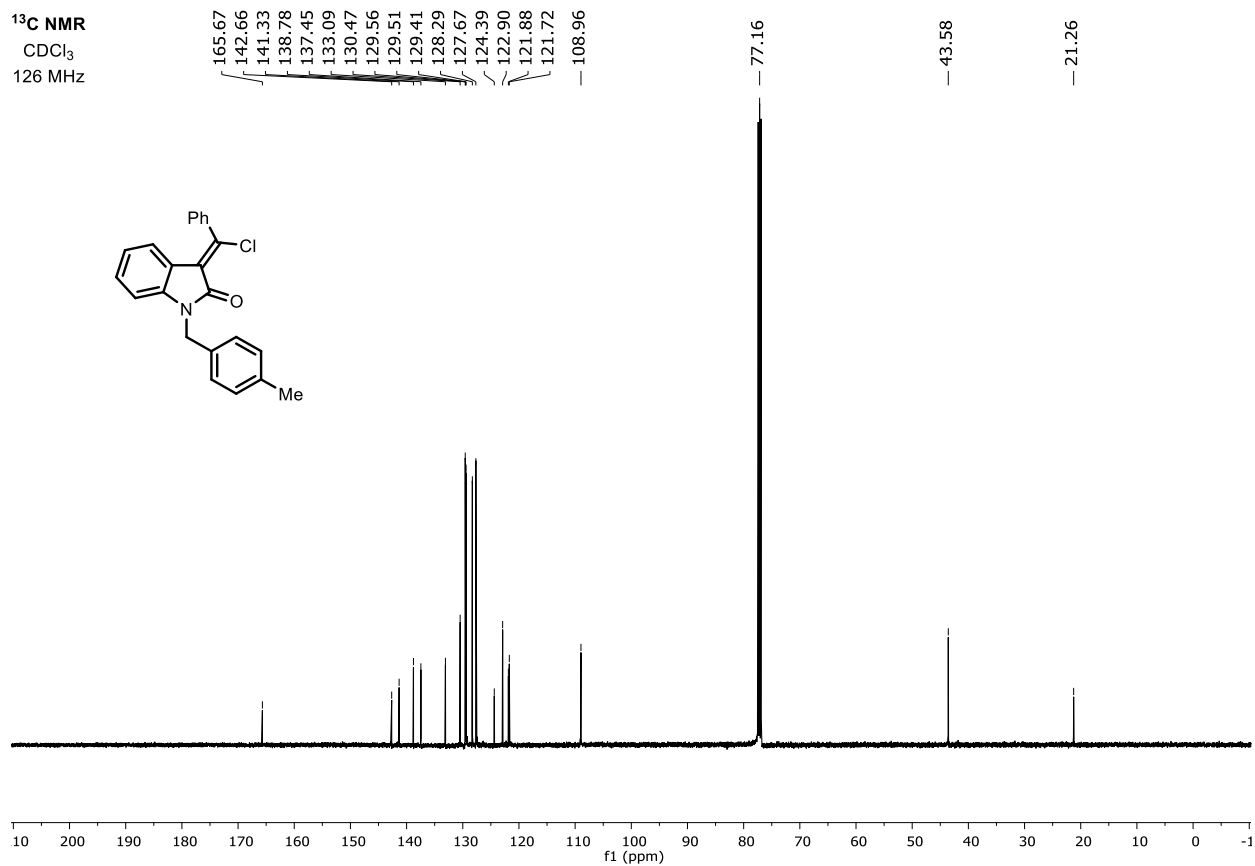


(Z)-3-(chloro(phenyl)methylene)-1-(4-methylbenzyl)indolin-2-one (1l)

¹H NMR
CDCl₃
500 MHz

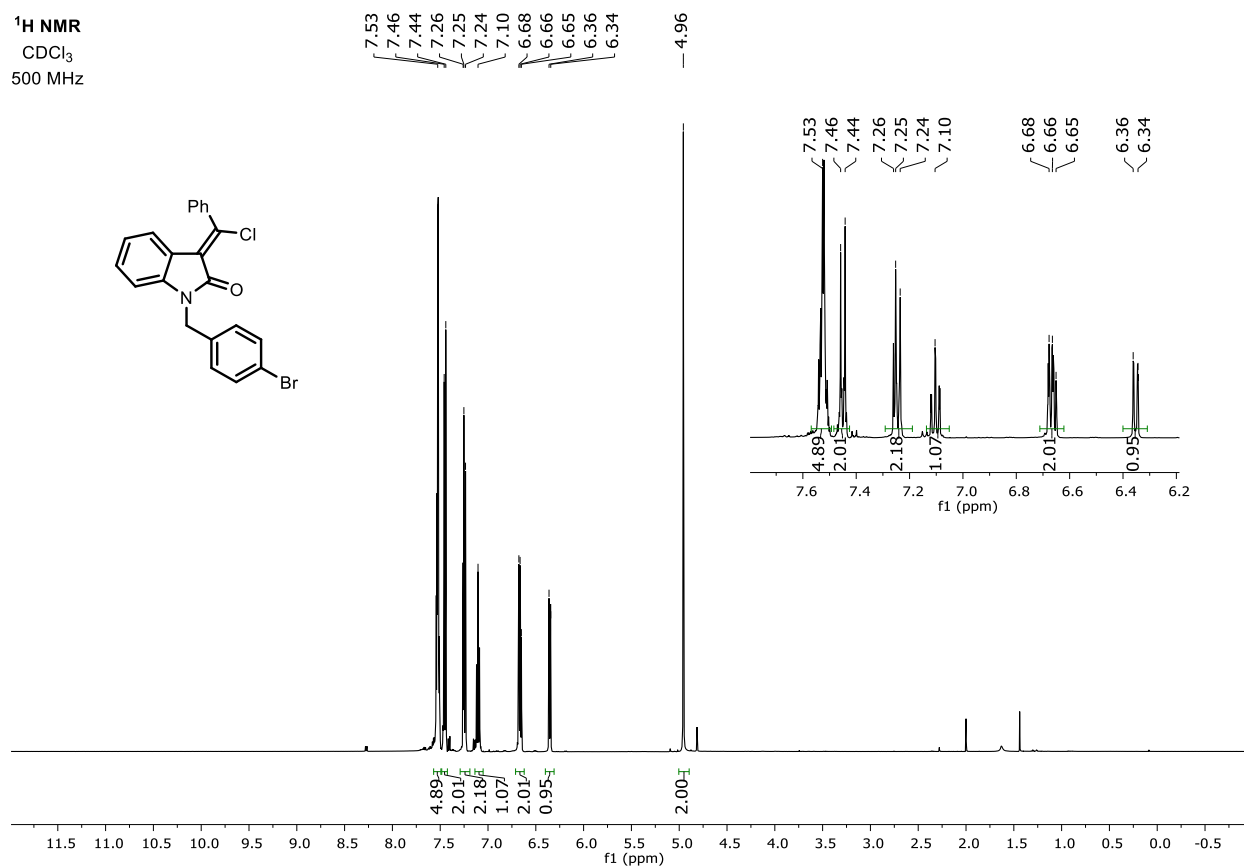


¹³C NMR
CDCl₃
126 MHz

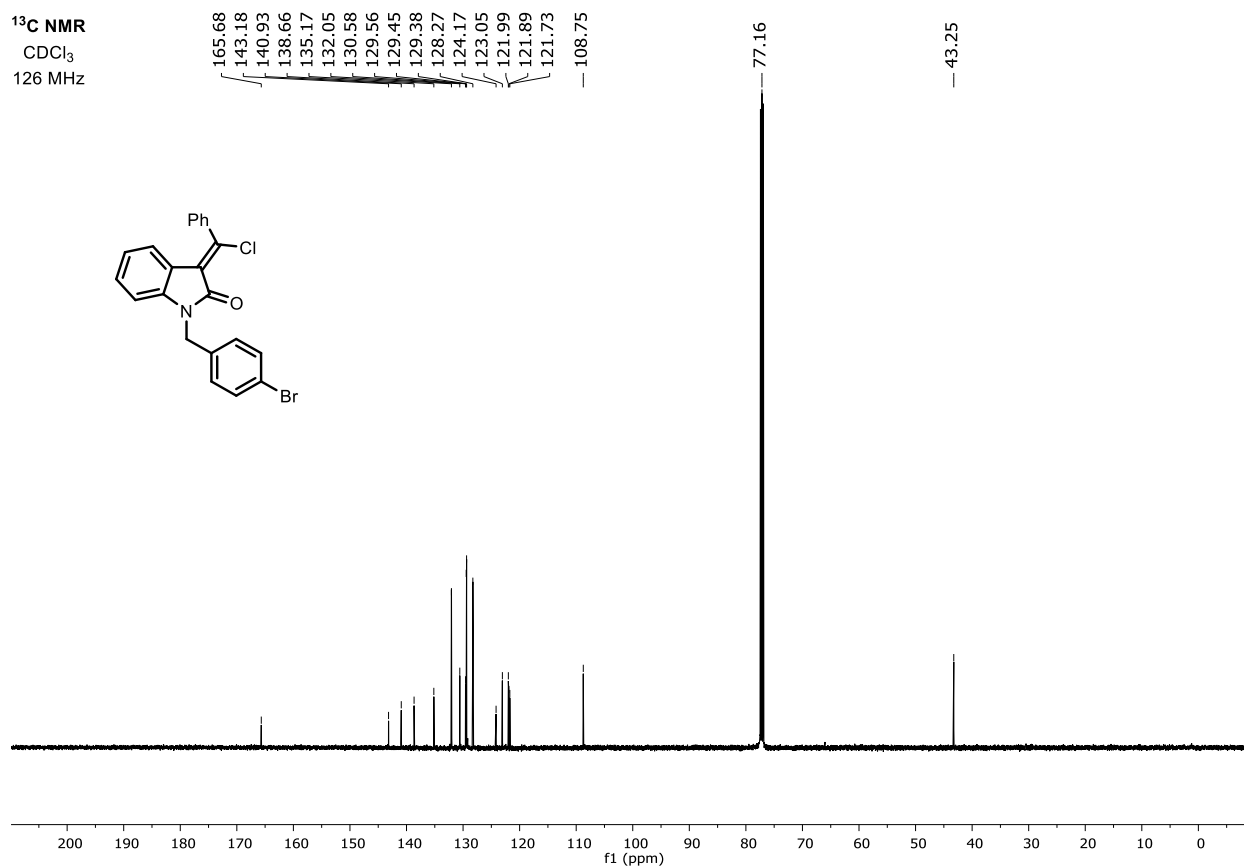


(Z)-1-(4-bromobenzyl)-3-(chloro(phenyl)methylene)indolin-2-one (1m)

¹H NMR
CDCl₃
500 MHz

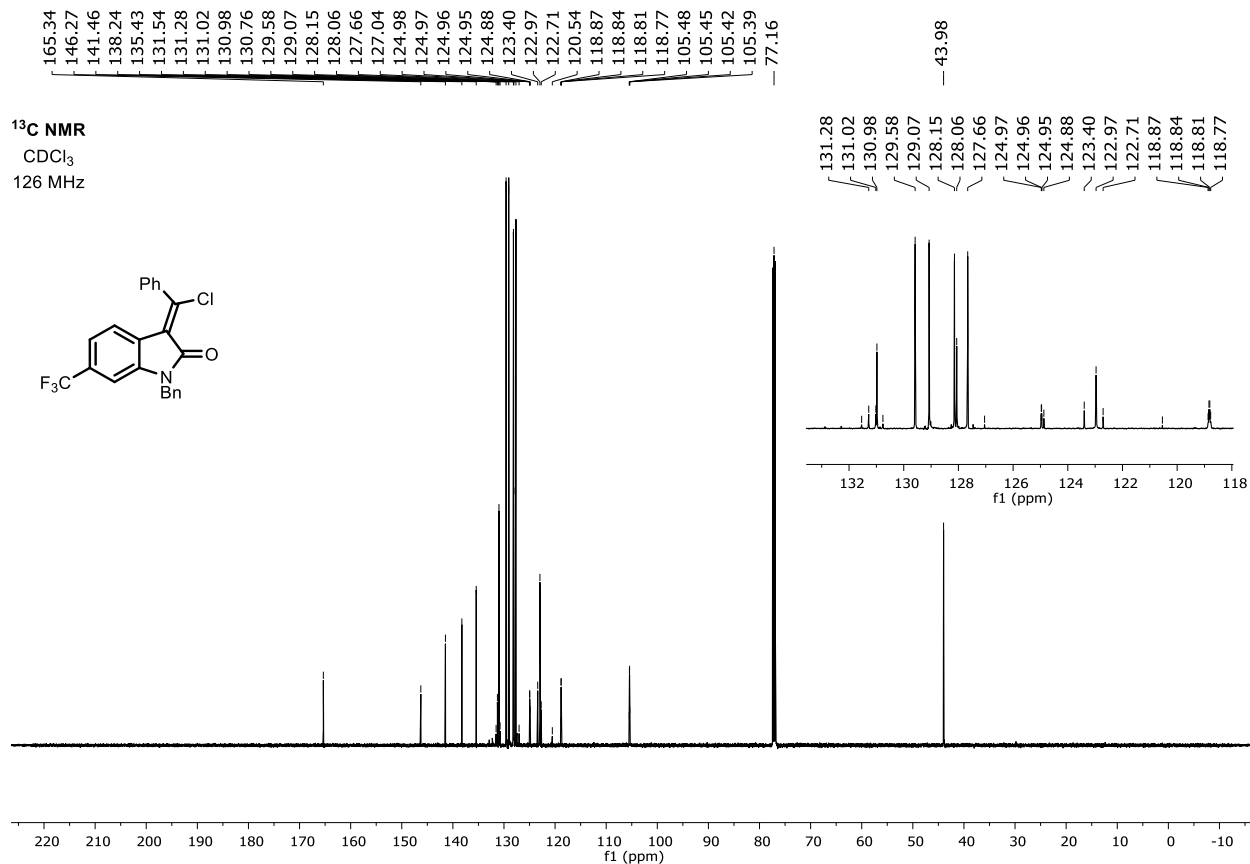
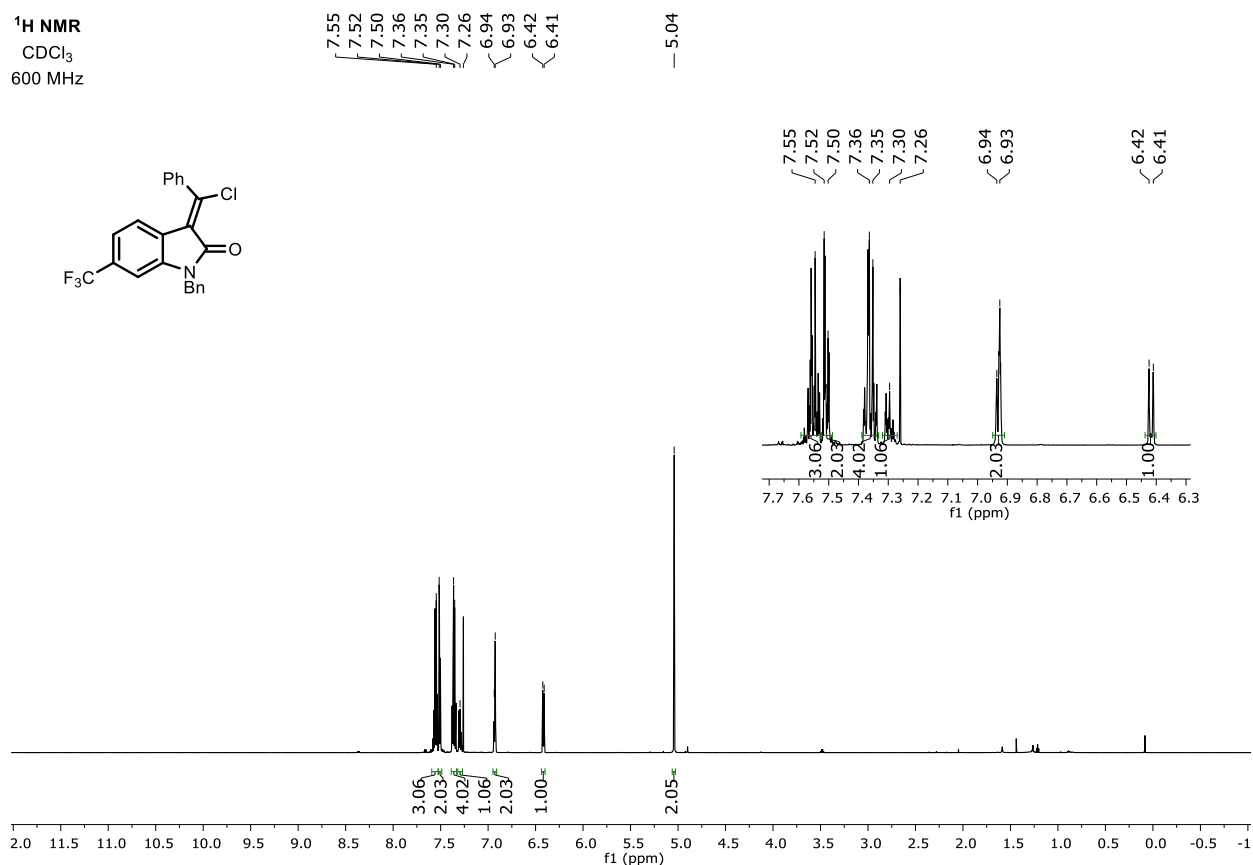


¹³C NMR
CDCl₃
126 MHz

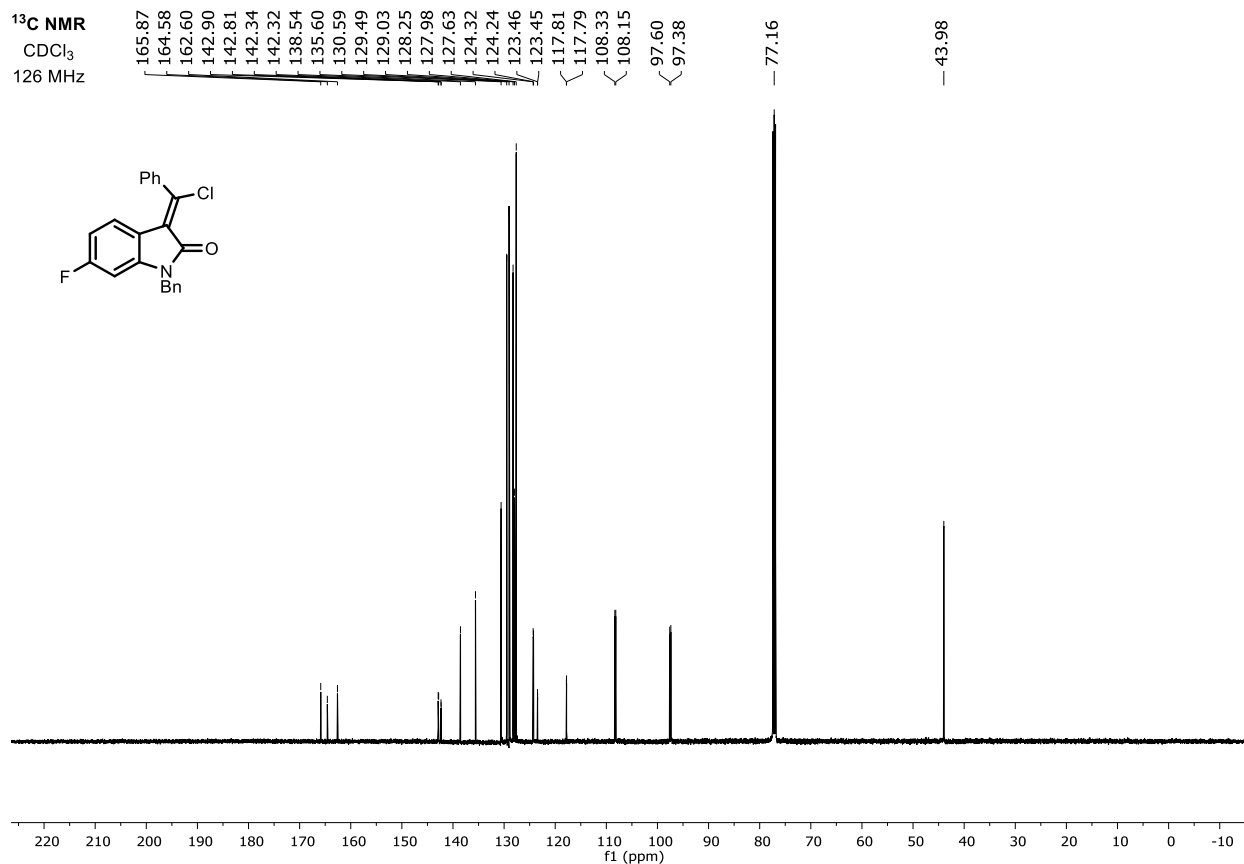
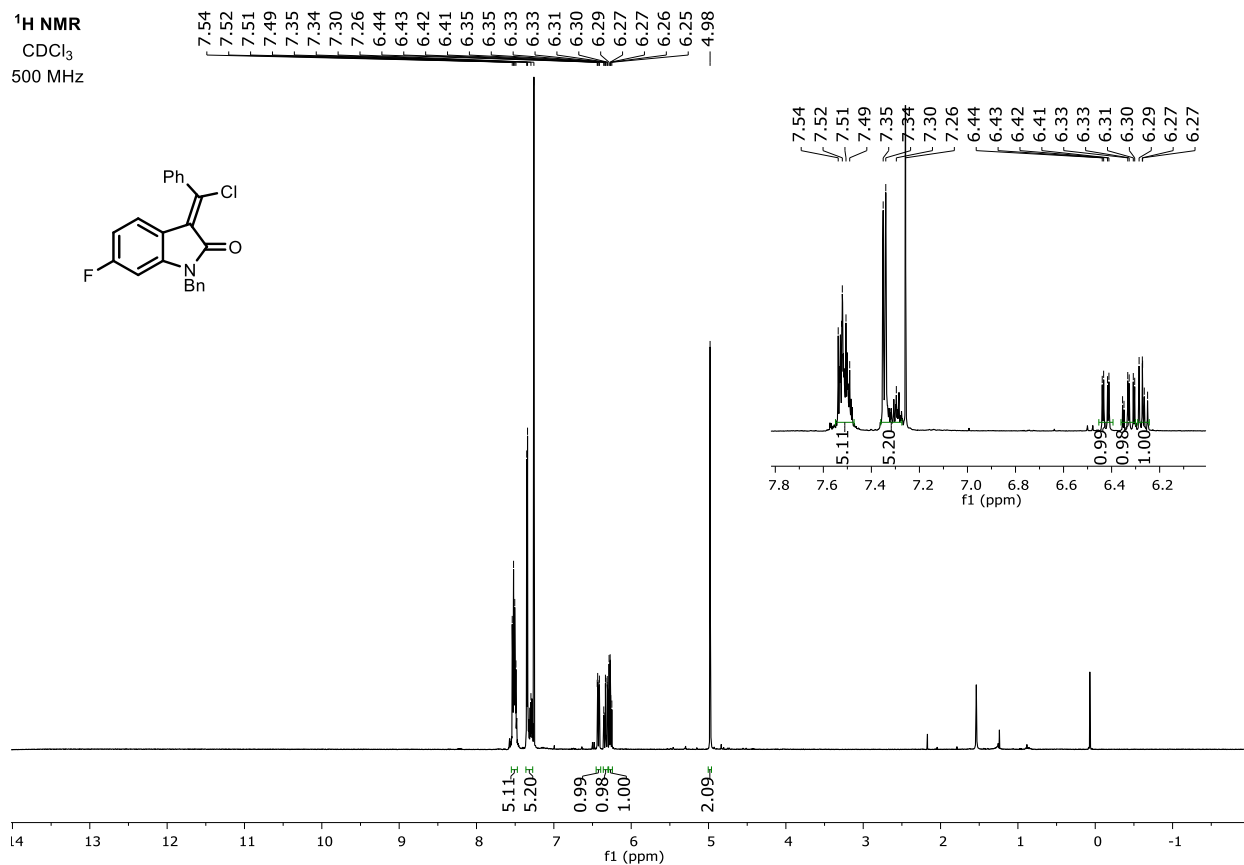


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-6-(trifluoromethyl)indolin-2-one (1n)

¹H NMR
CDCl₃
600 MHz

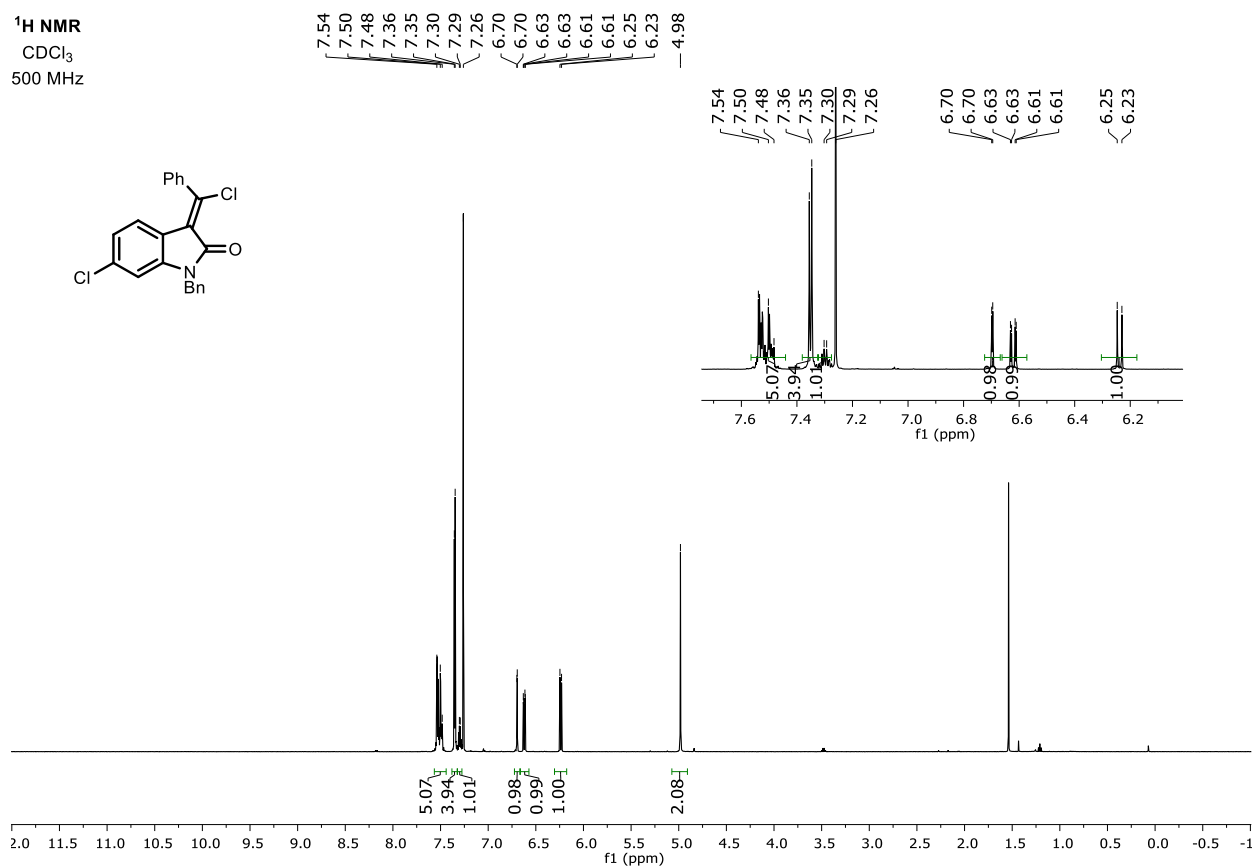


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-6-fluoroindolin-2-one (1o)

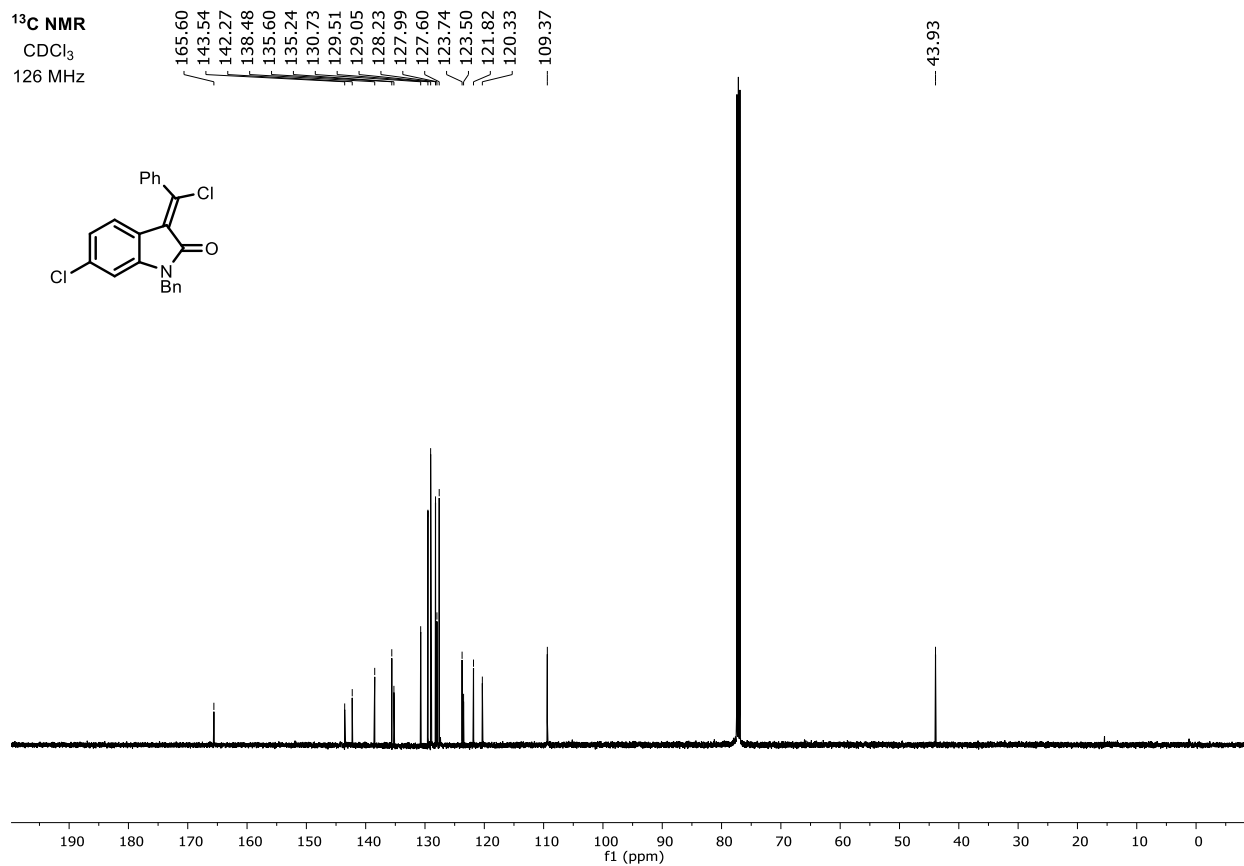


(Z)-1-benzyl-6-chloro-3-(chloro(phenyl)methylene)indolin-2-one (1p)

¹H NMR
CDCl₃
500 MHz

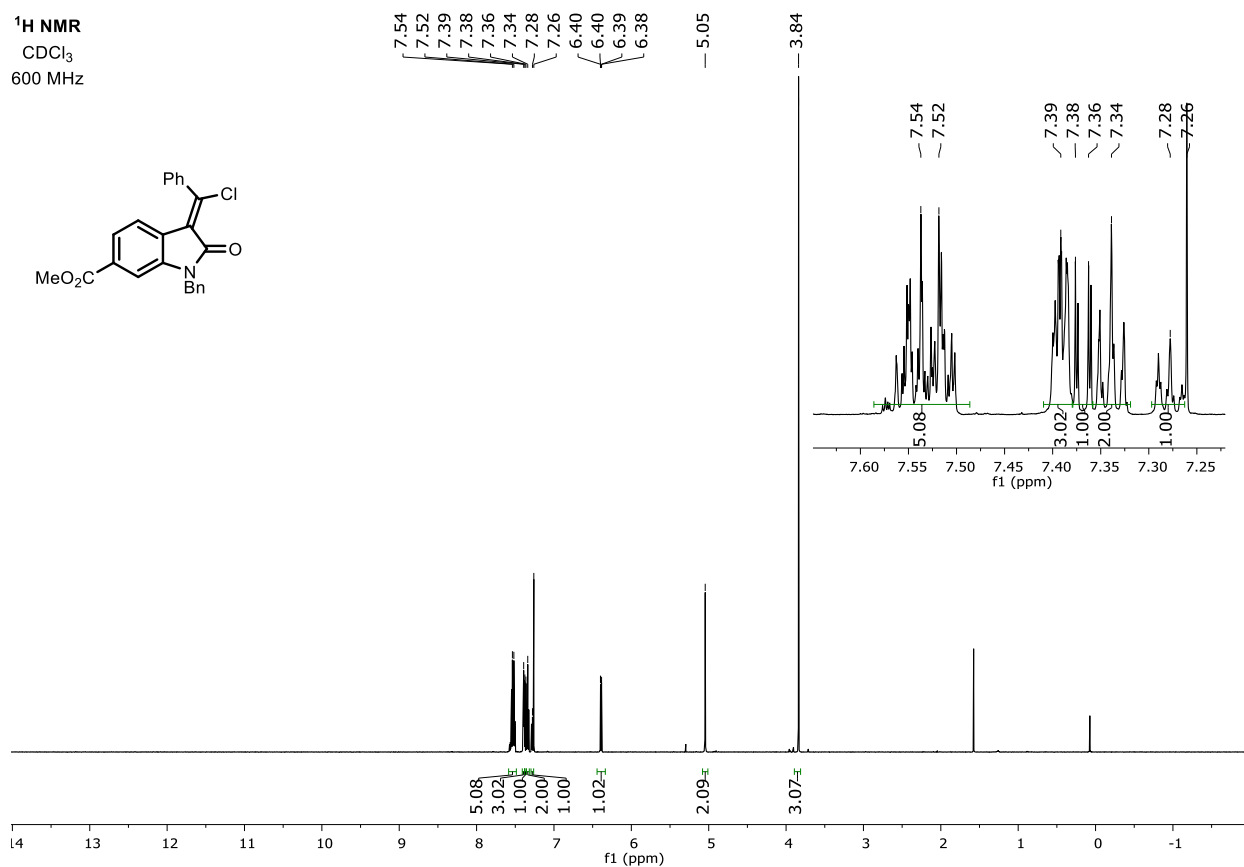


¹³C NMR
CDCl₃
126 MHz

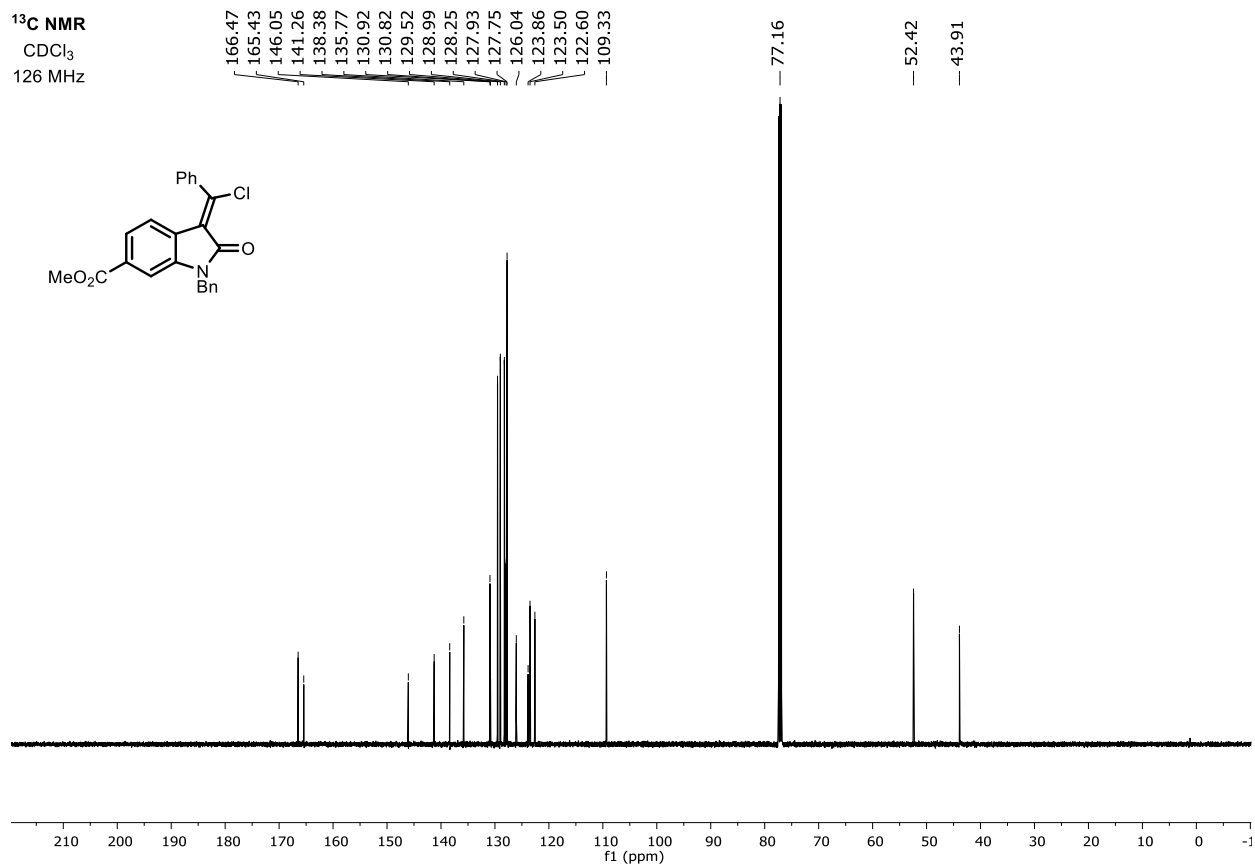


methyl (Z)-1-benzyl-3-(chloro(phenyl)methylene)-2-oxindoline-6-carboxylate (1q)

¹H NMR
CDCl₃
600 MHz

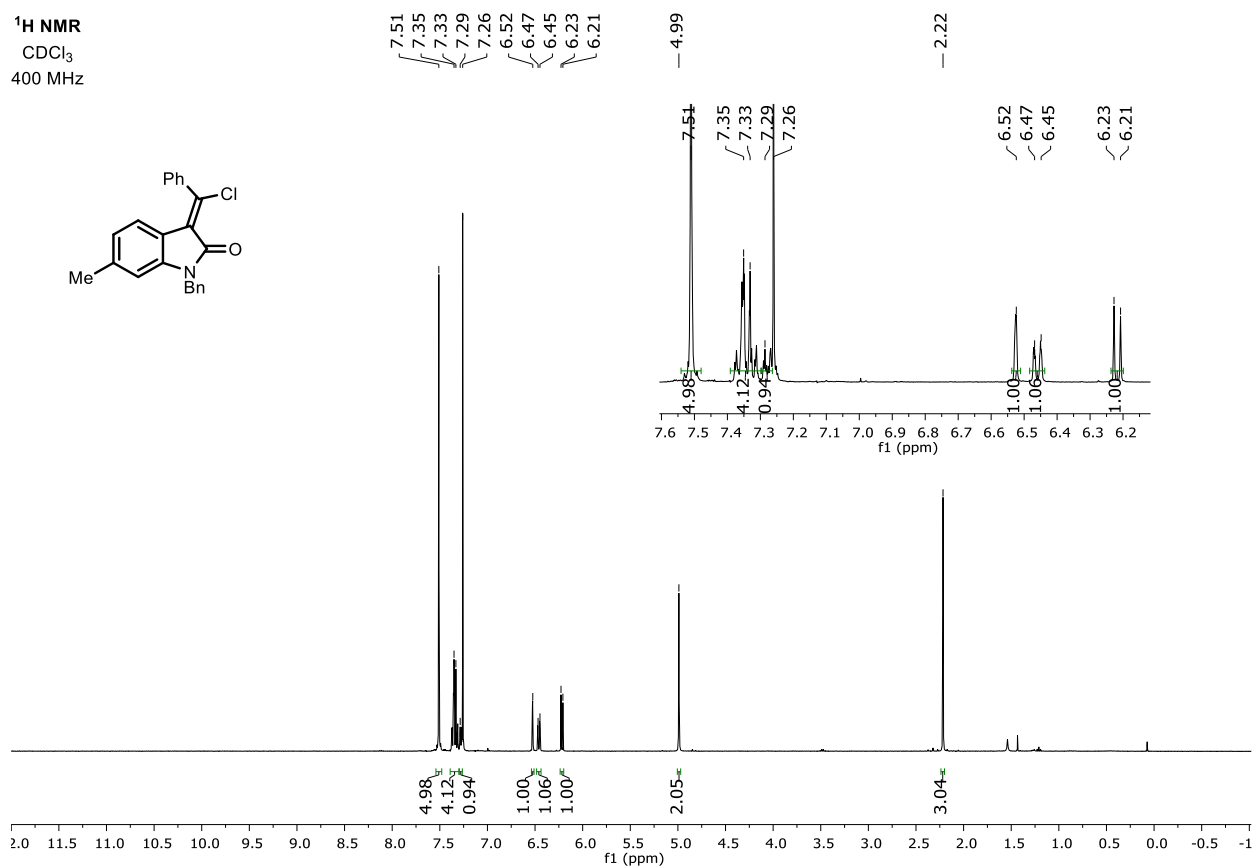


¹³C NMR
CDCl₃
126 MHz

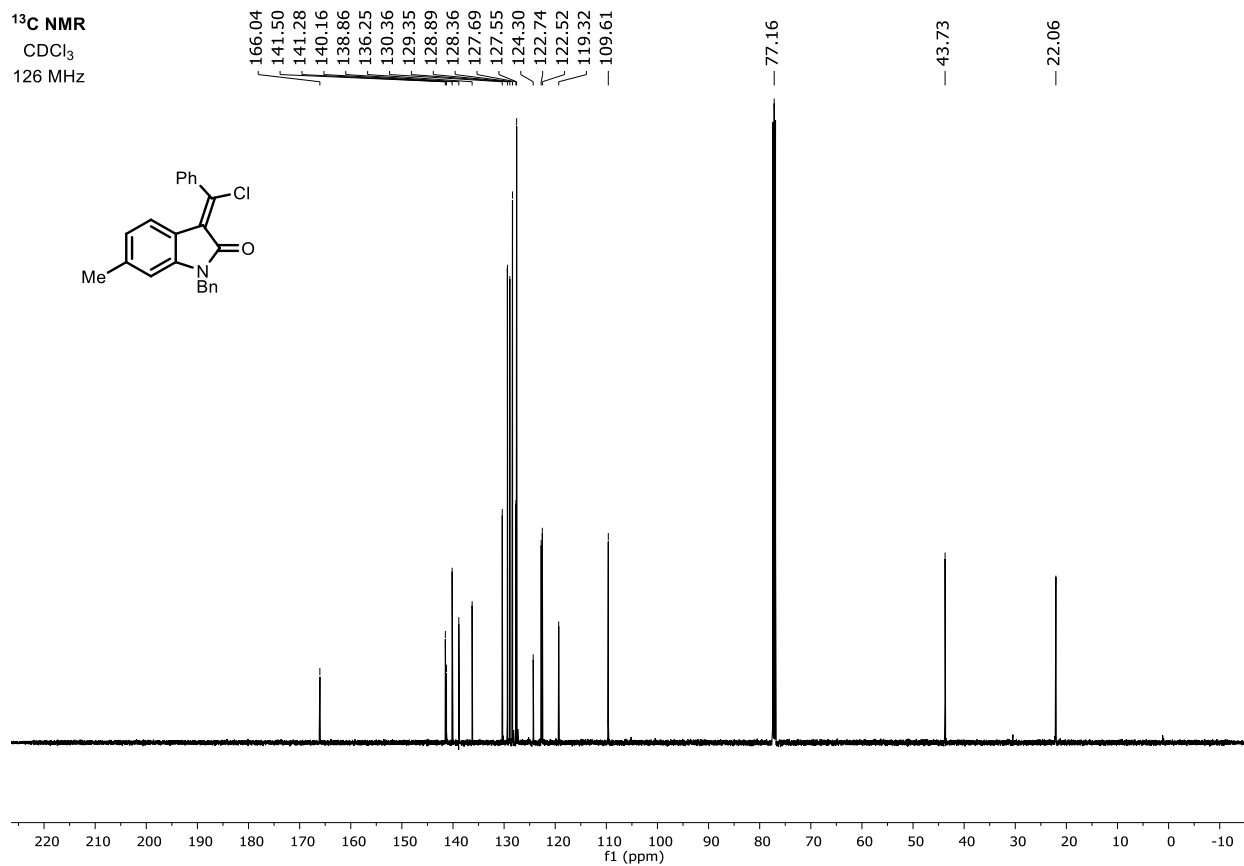


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-6-methylindolin-2-one (1r)

¹H NMR
CDCl₃
400 MHz

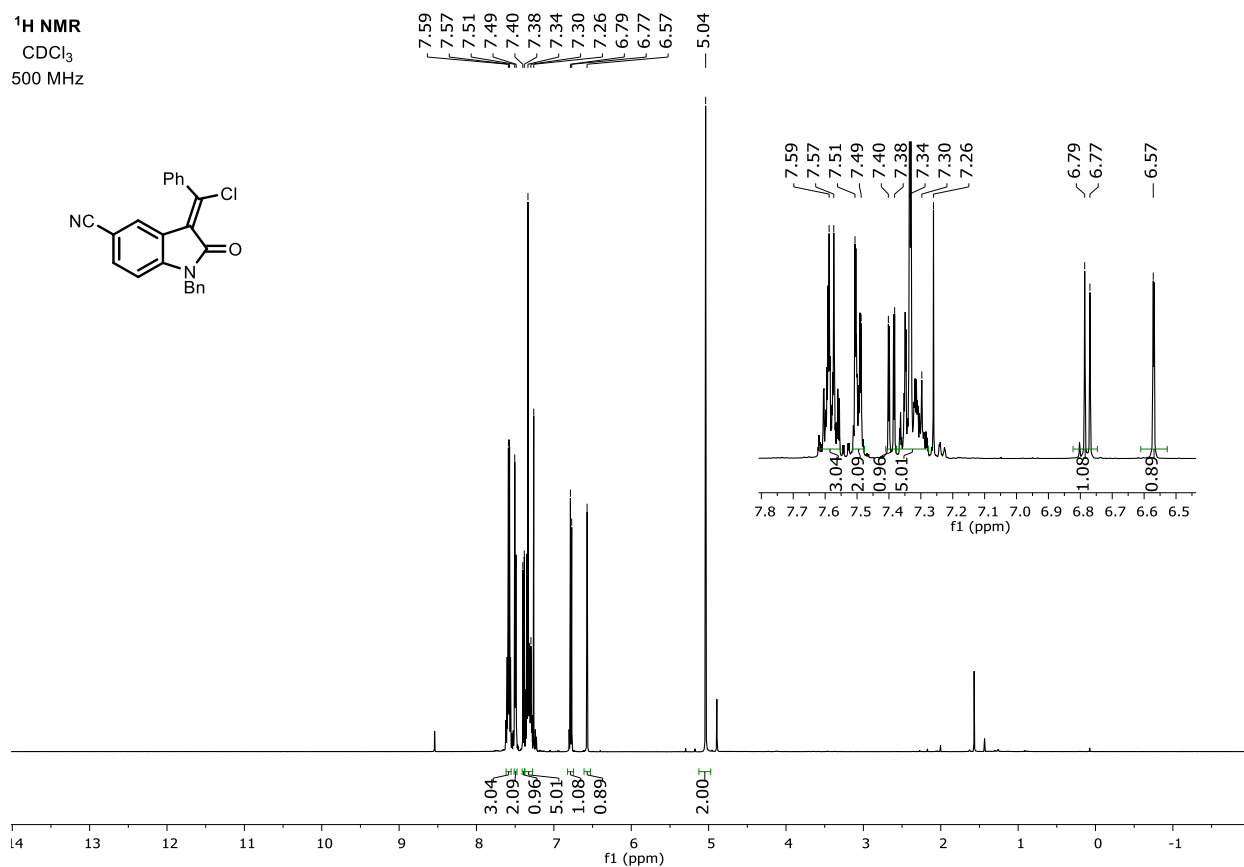


¹³C NMR
CDCl₃
126 MHz

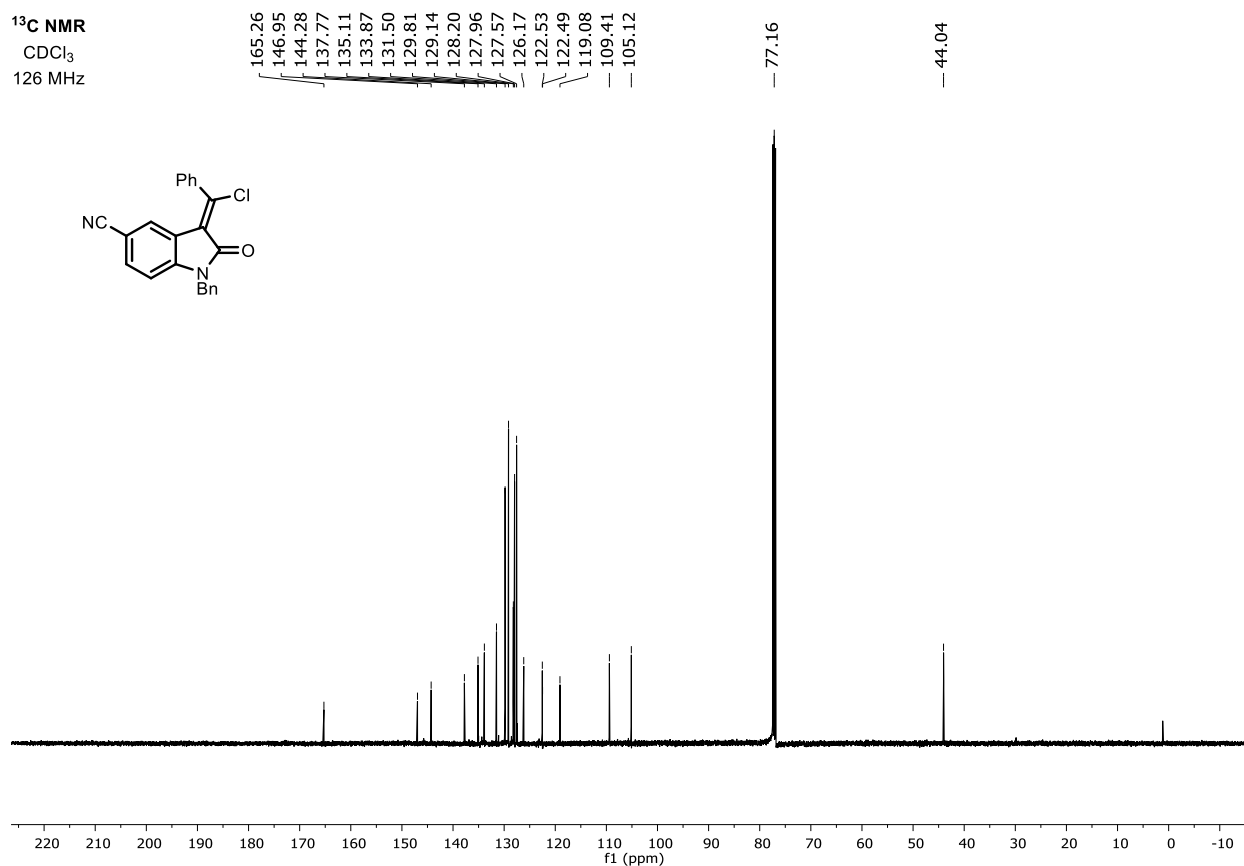


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-2-oxoindoline-5-carbonitrile (1s)

¹H NMR
CDCl₃
500 MHz

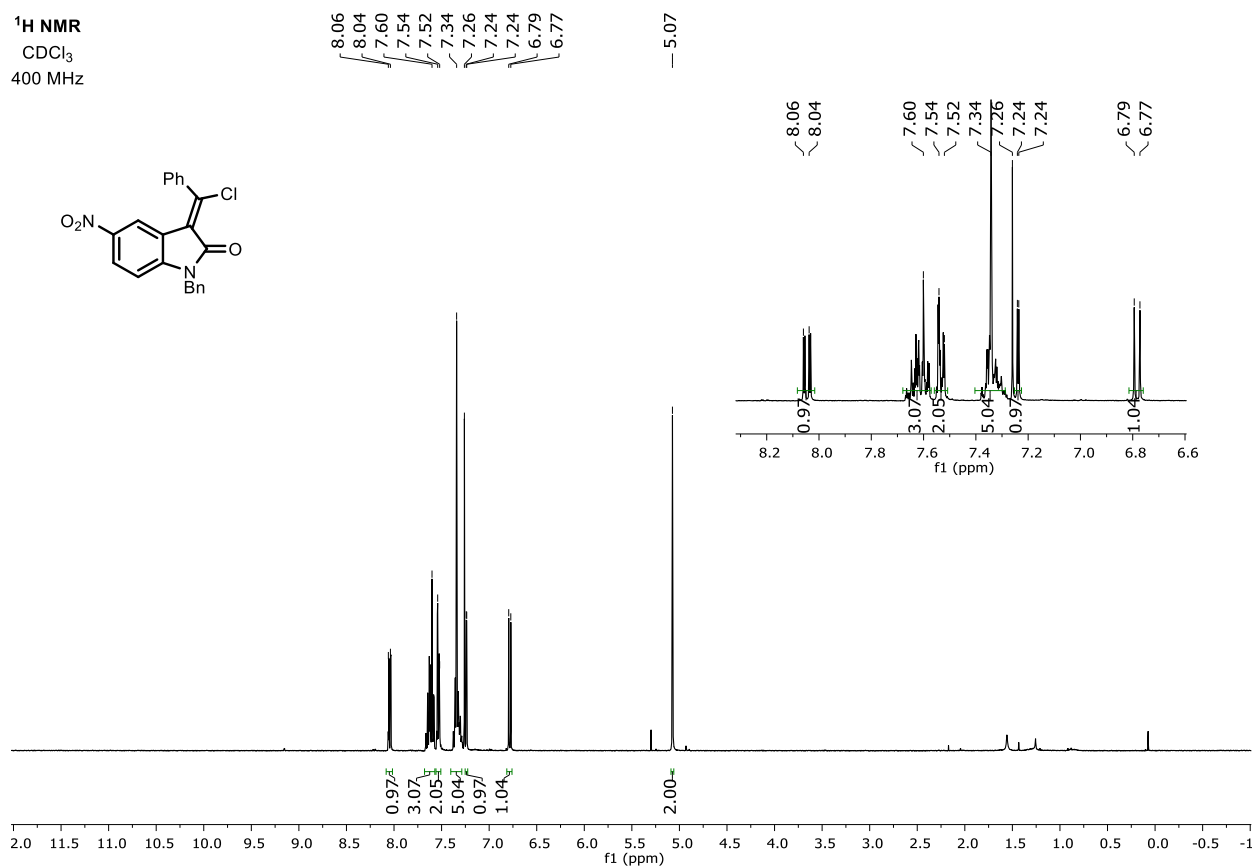


¹³C NMR
CDCl₃
126 MHz

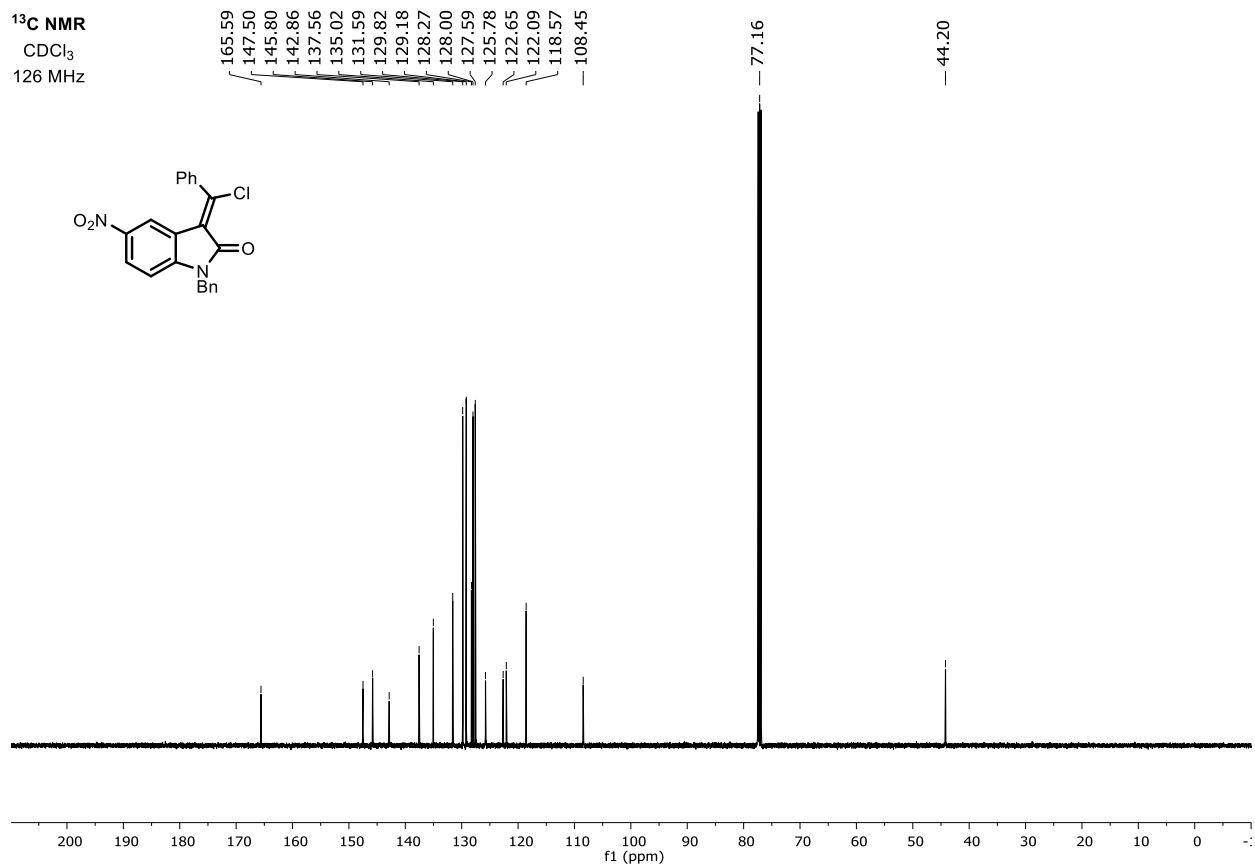


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-nitroindolin-2-one (1t)

¹H NMR
CDCl₃
400 MHz



¹³C NMR
CDCl₃
126 MHz

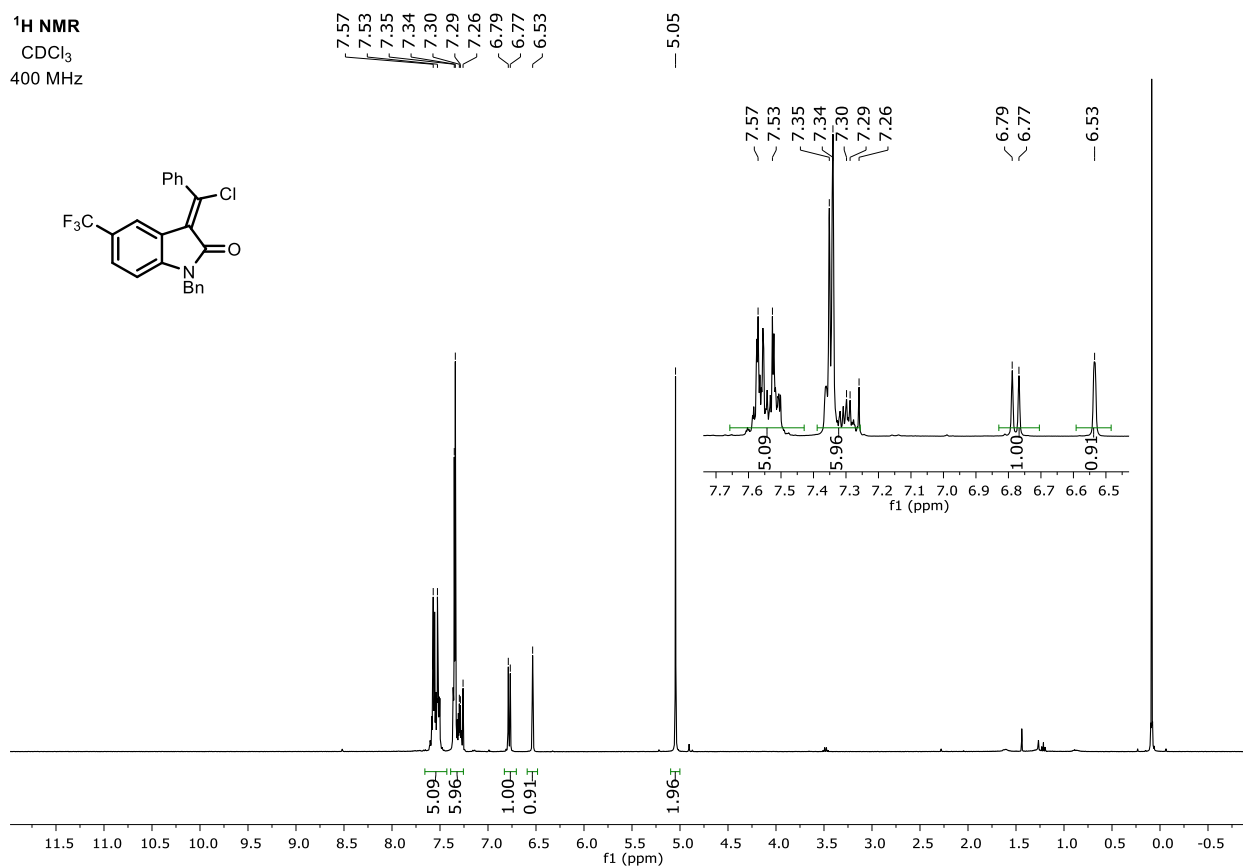
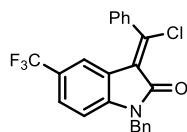


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-(trifluoromethyl)indolin-2-one (1u)

¹H NMR

CDCl₃

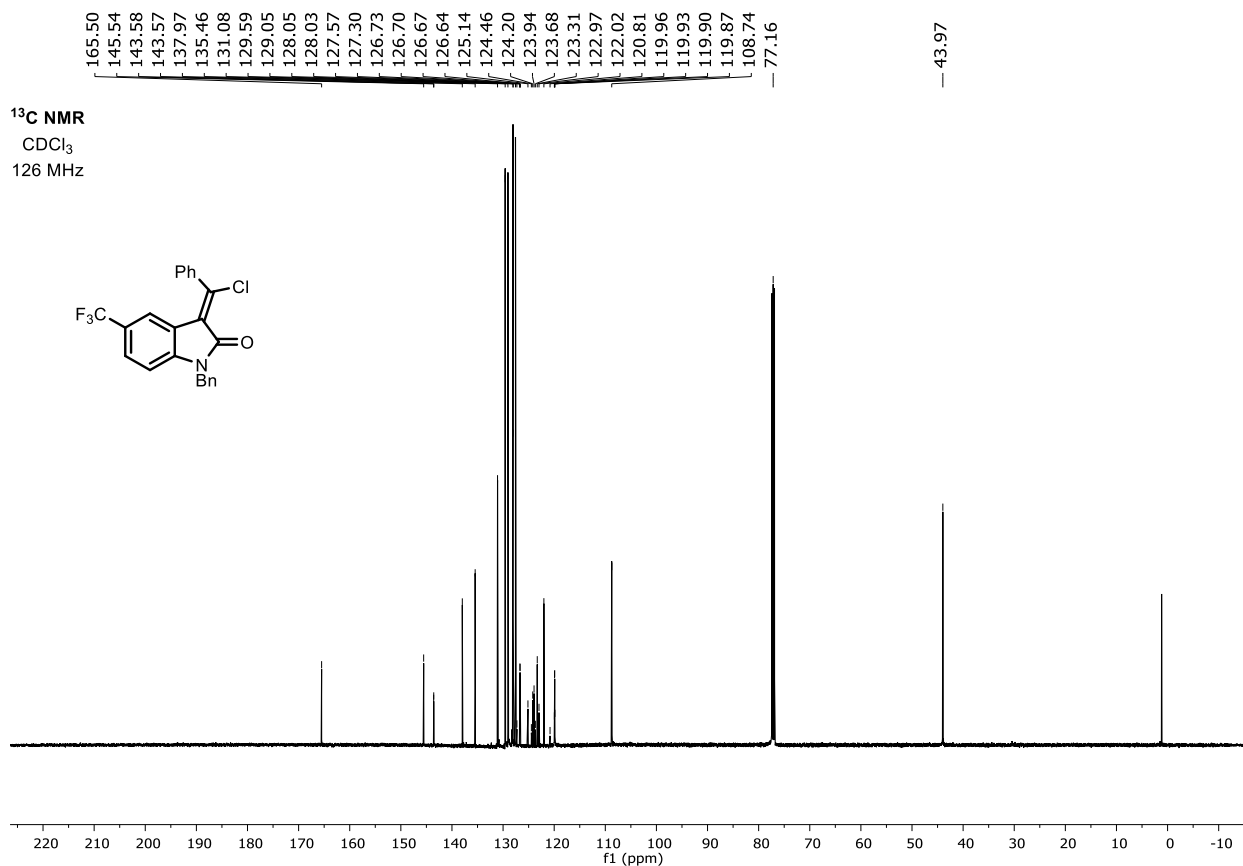
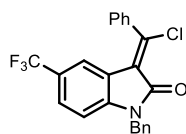
400 MHz



¹³C NMR

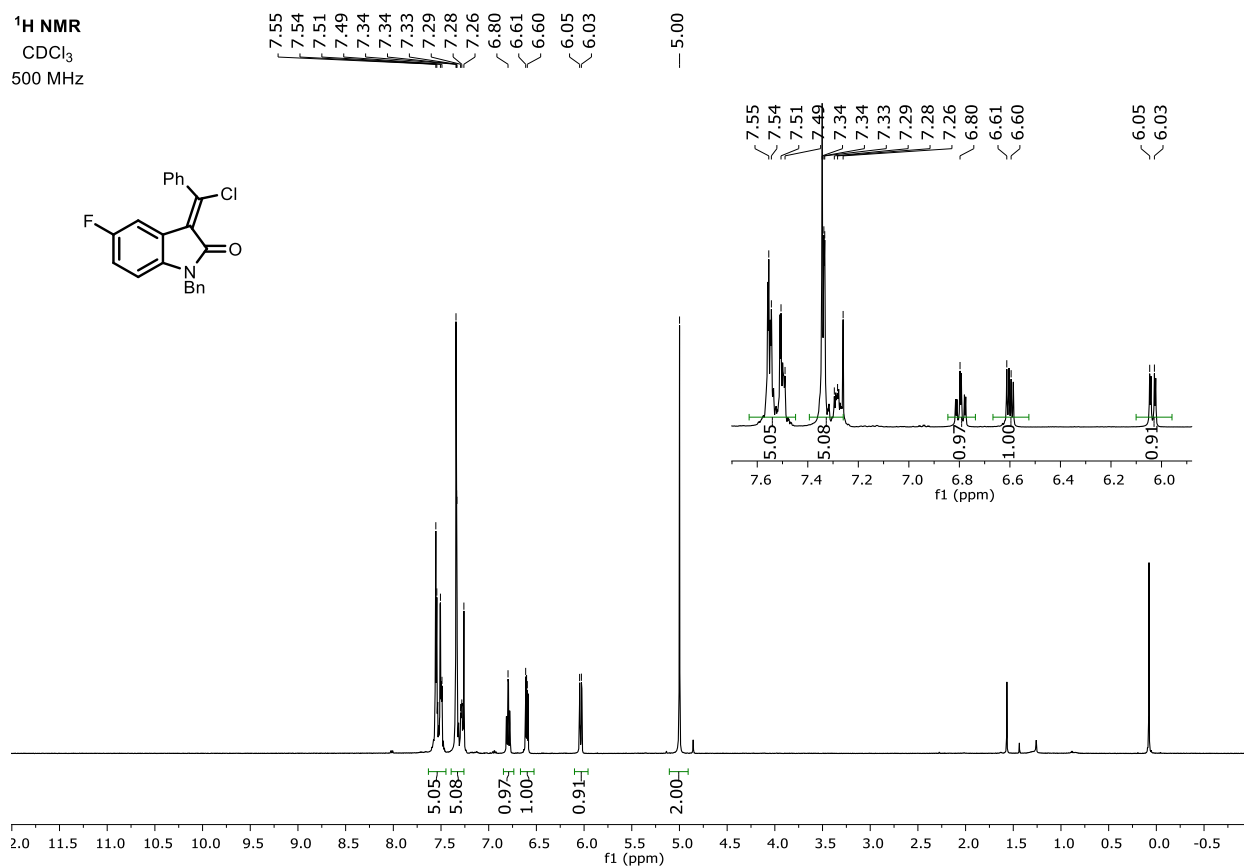
CDCl₃

126 MHz

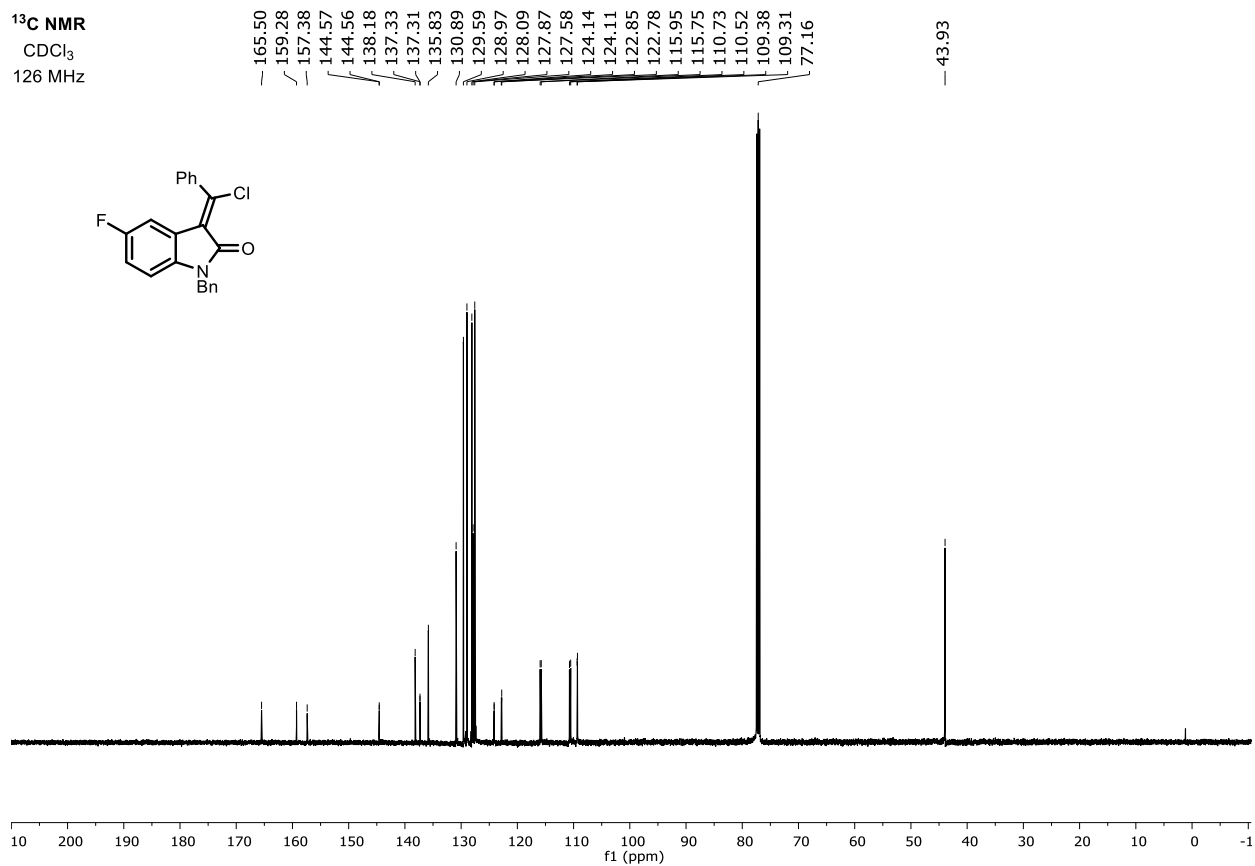


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-fluoroindolin-2-one (1v)

¹H NMR
CDCl₃
500 MHz

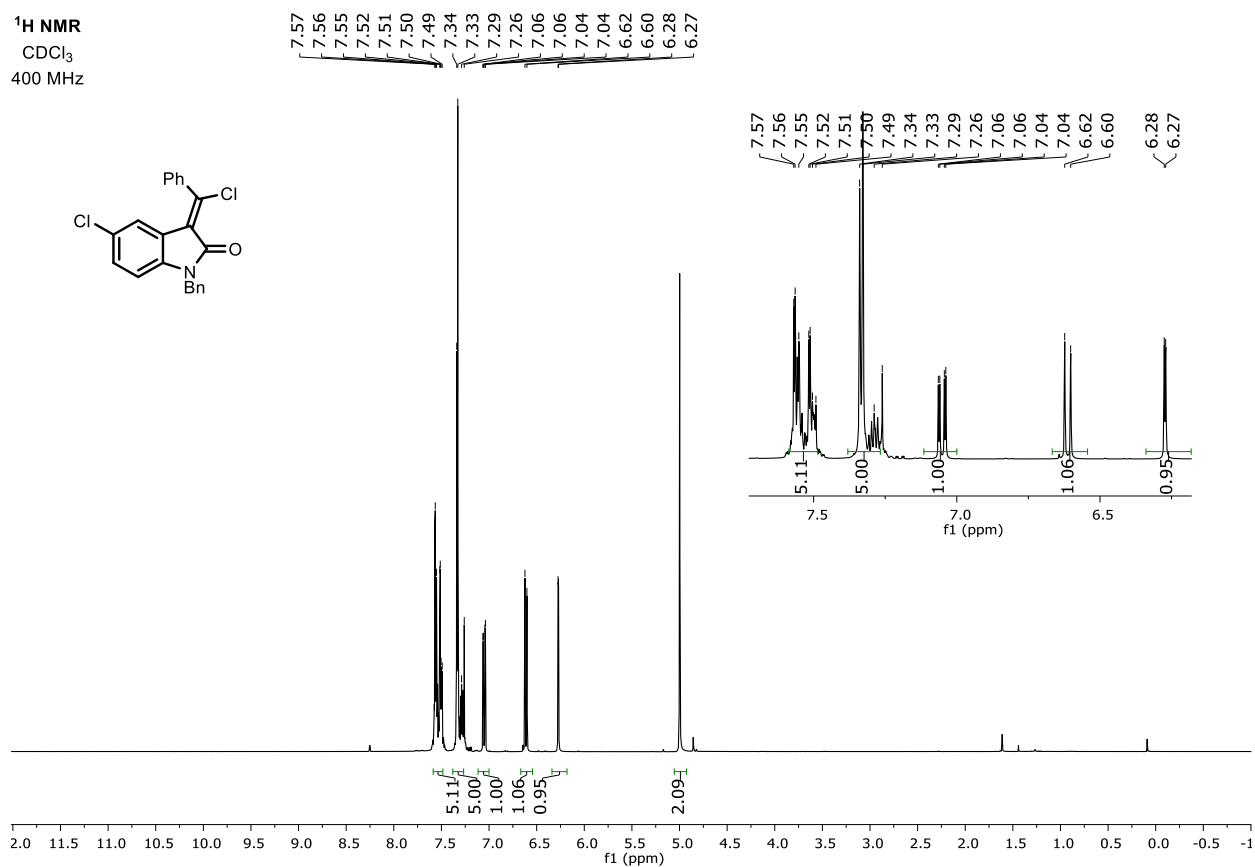


¹³C NMR
CDCl₃
126 MHz

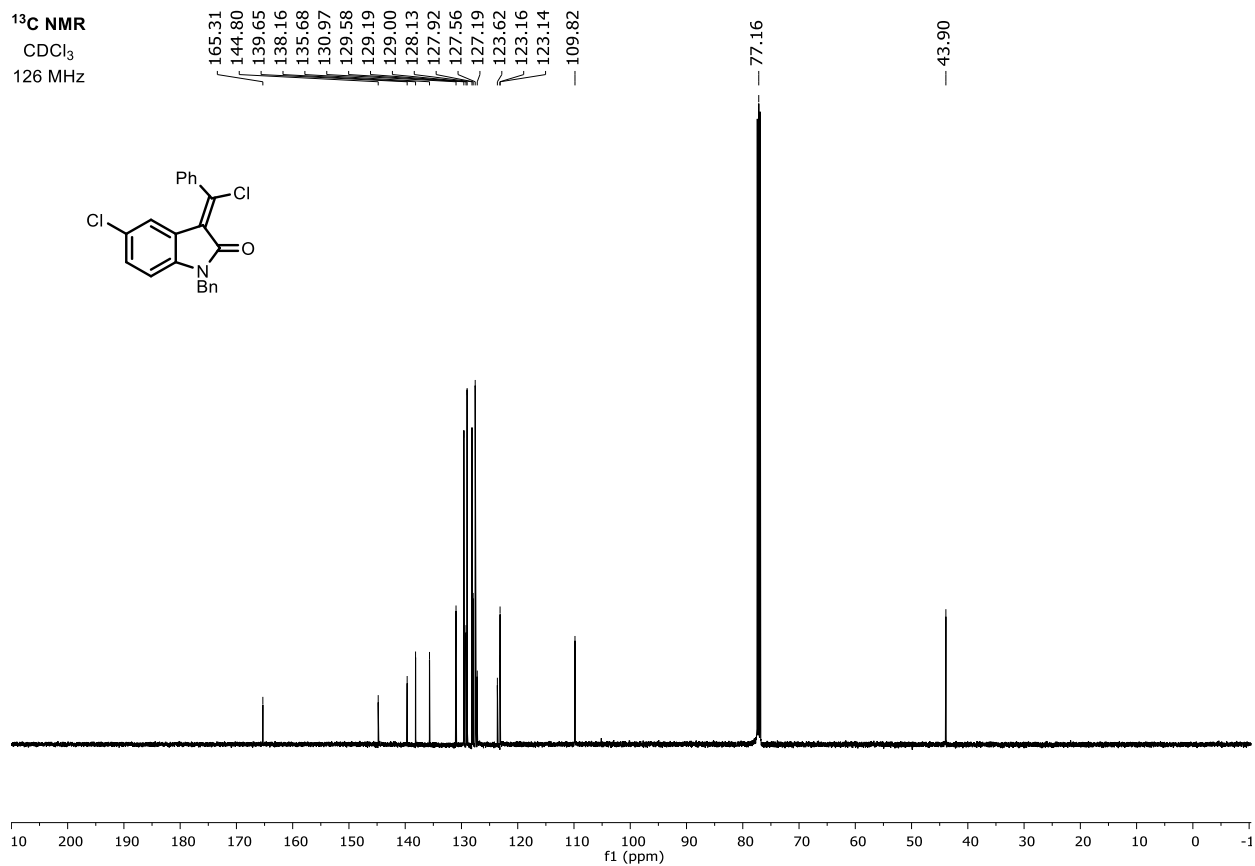


(Z)-1-benzyl-5-chloro-3-(chloro(phenyl)methylene)indolin-2-one (1w)

¹H NMR
CDCl₃
400 MHz

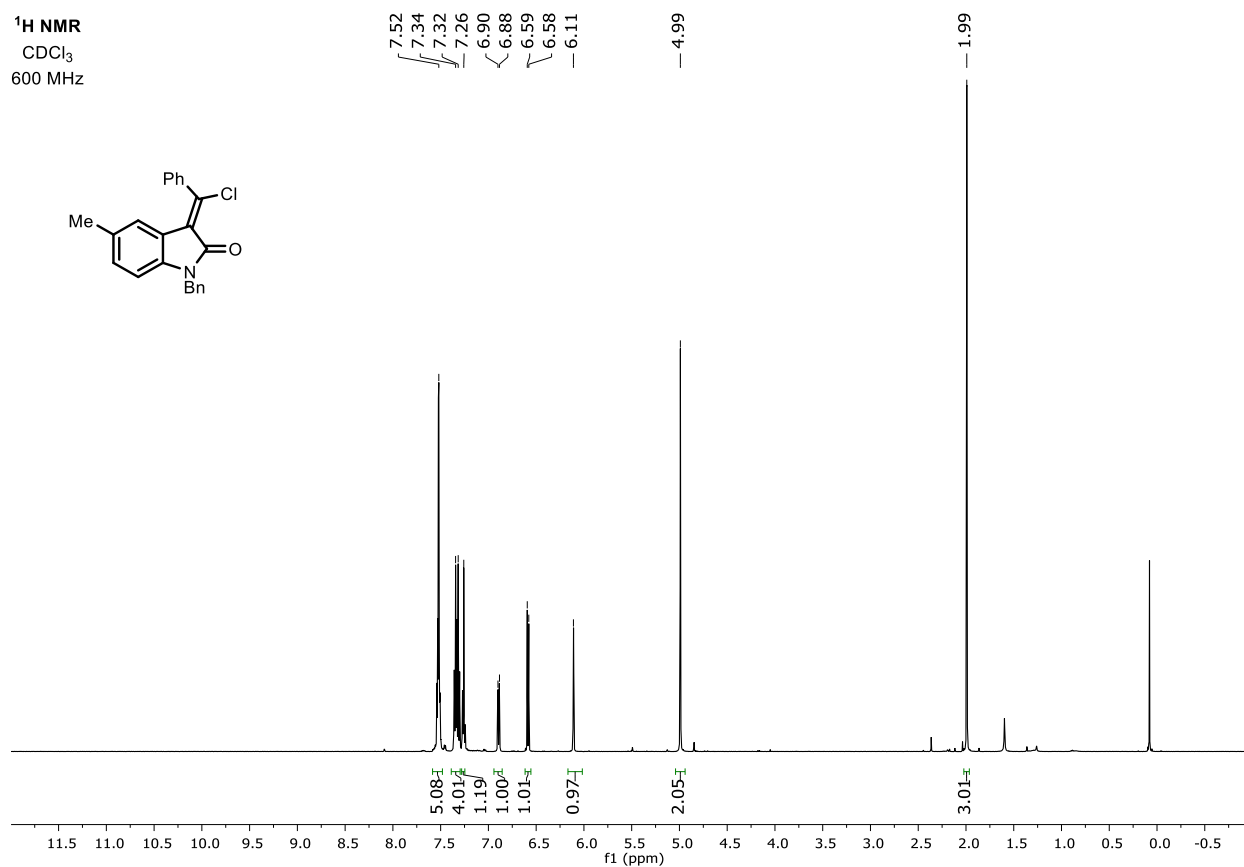


¹³C NMR
CDCl₃
126 MHz

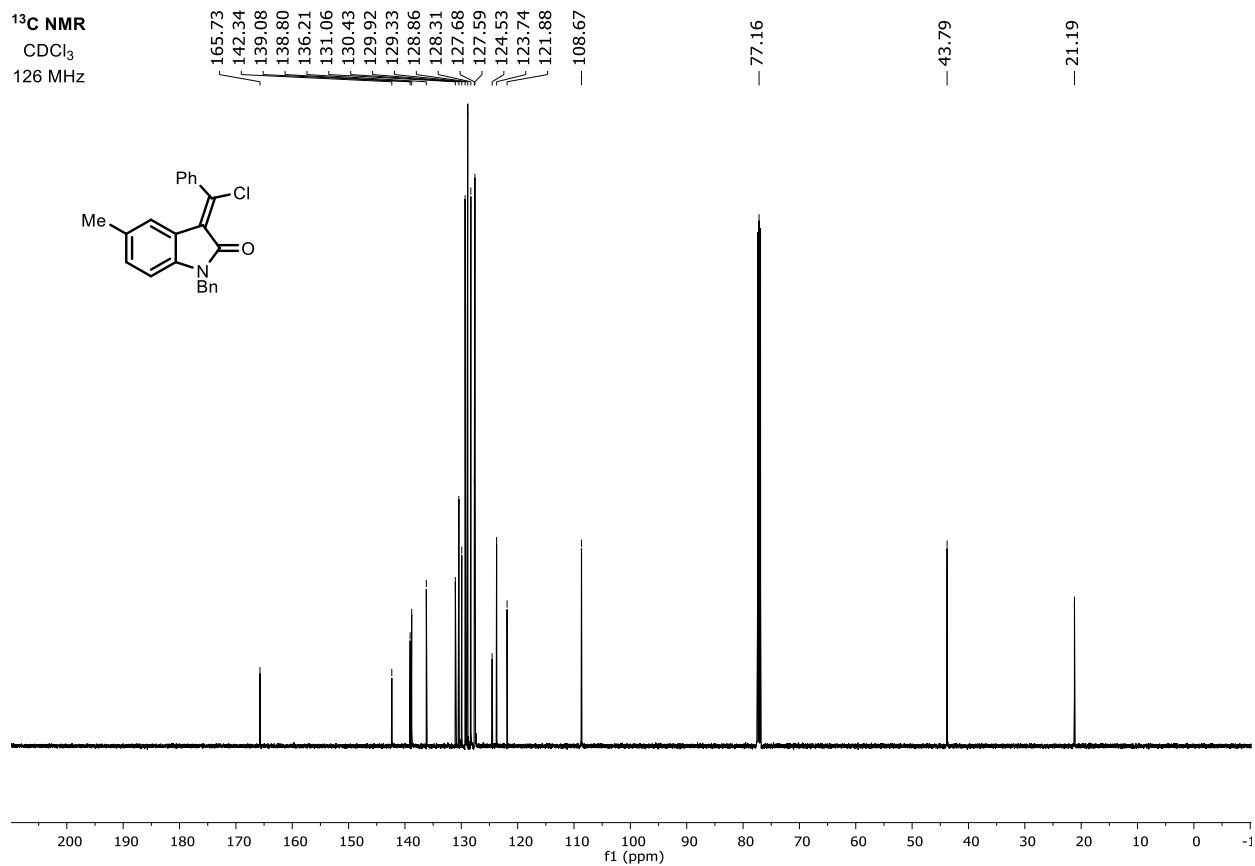


(Z)-1-benzyl-3-(chloro(phenyl)methylene)-5-methylindolin-2-one (1x)

¹H NMR
CDCl₃
600 MHz

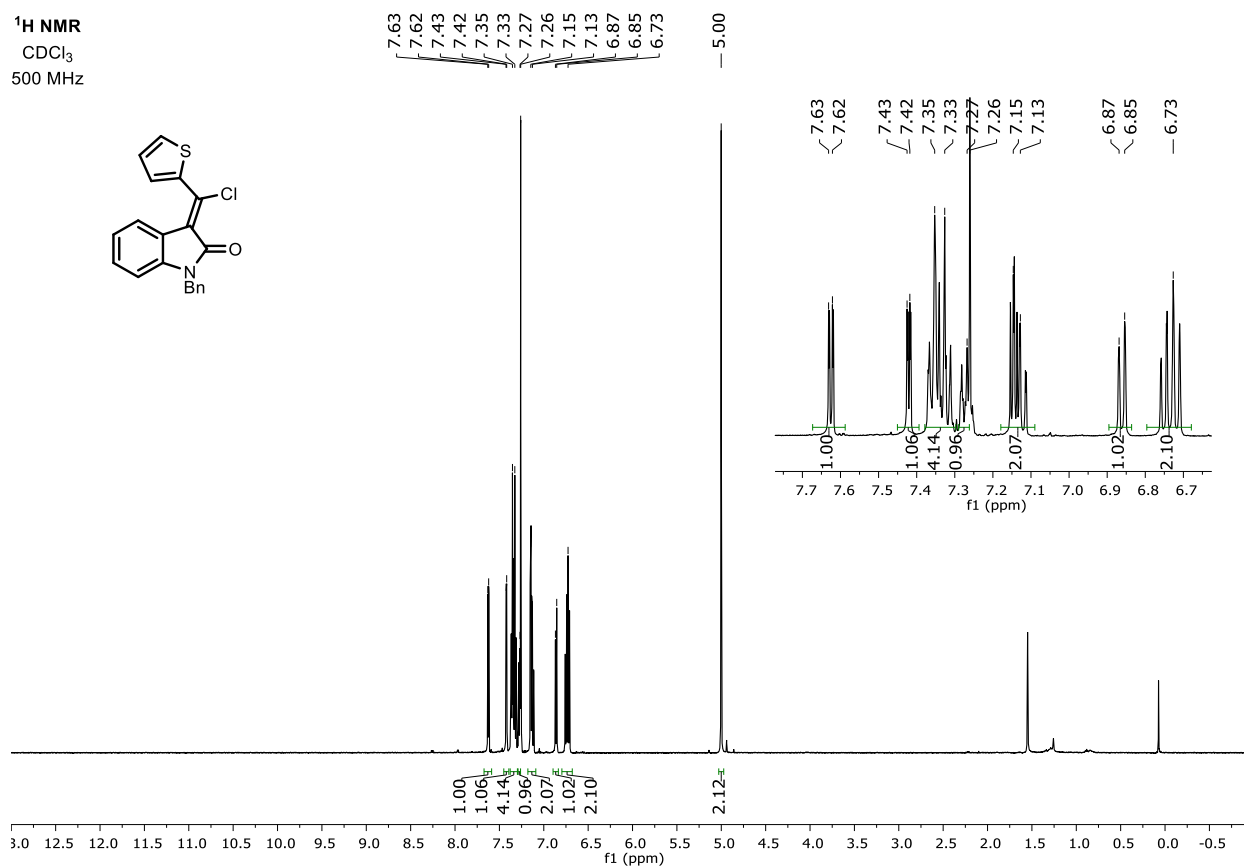


¹³C NMR
CDCl₃
126 MHz

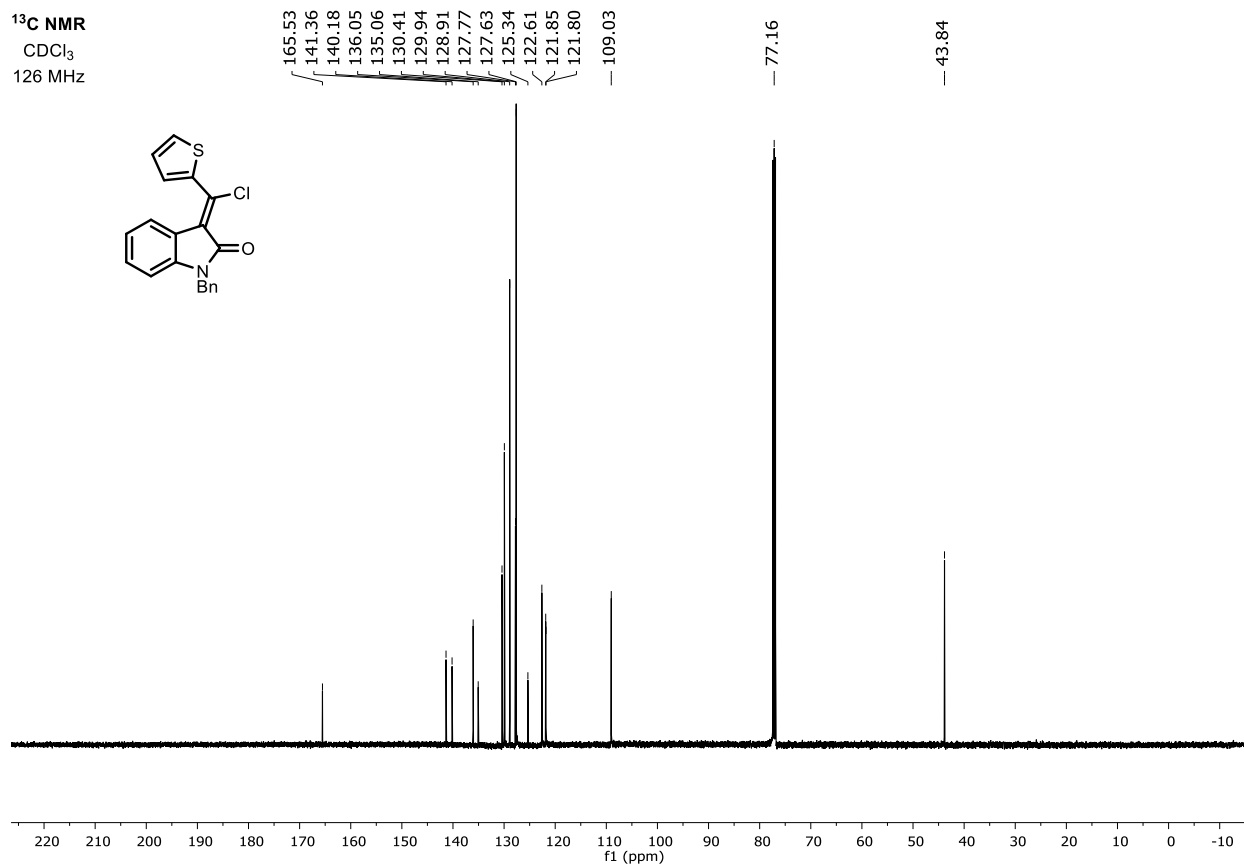


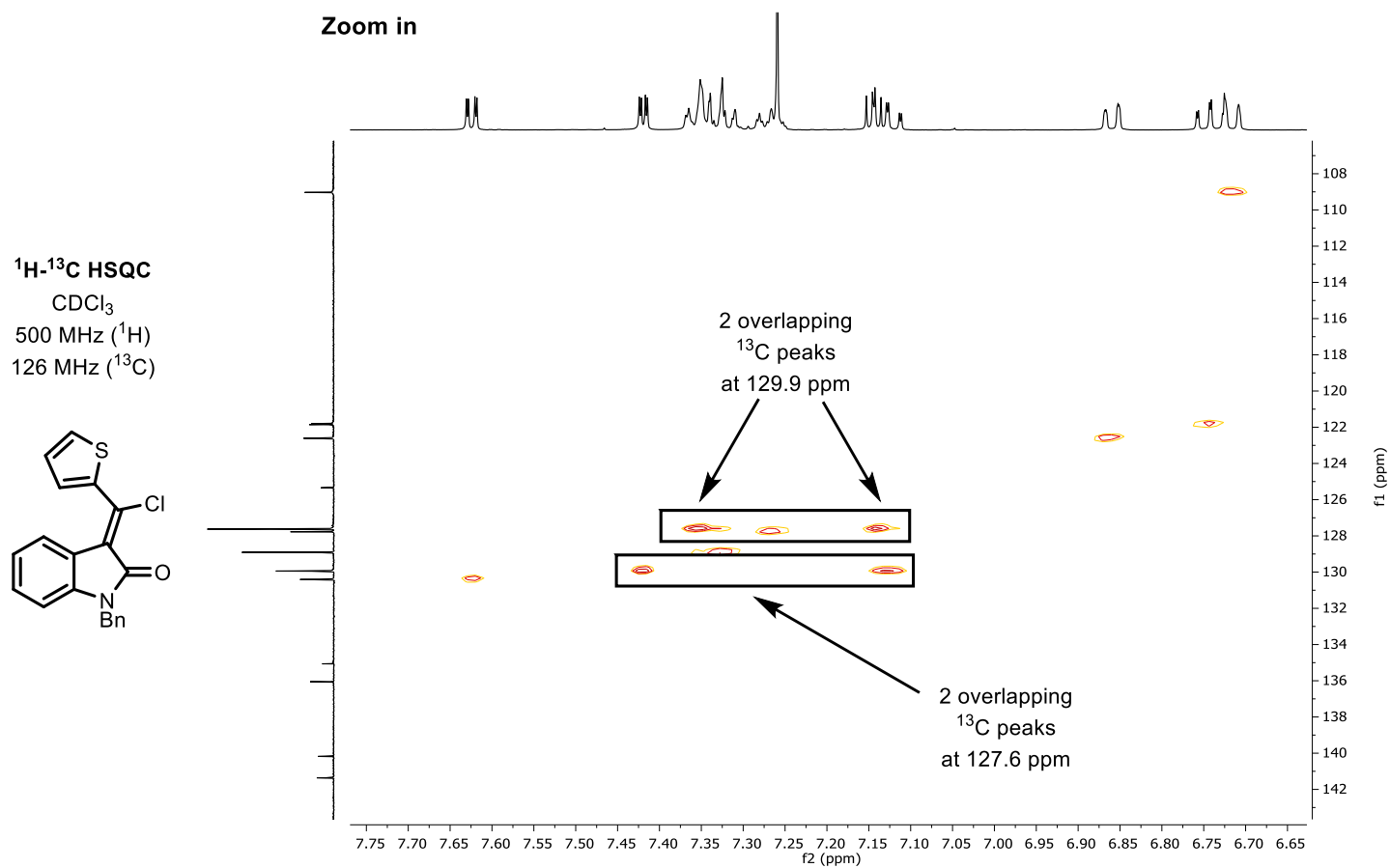
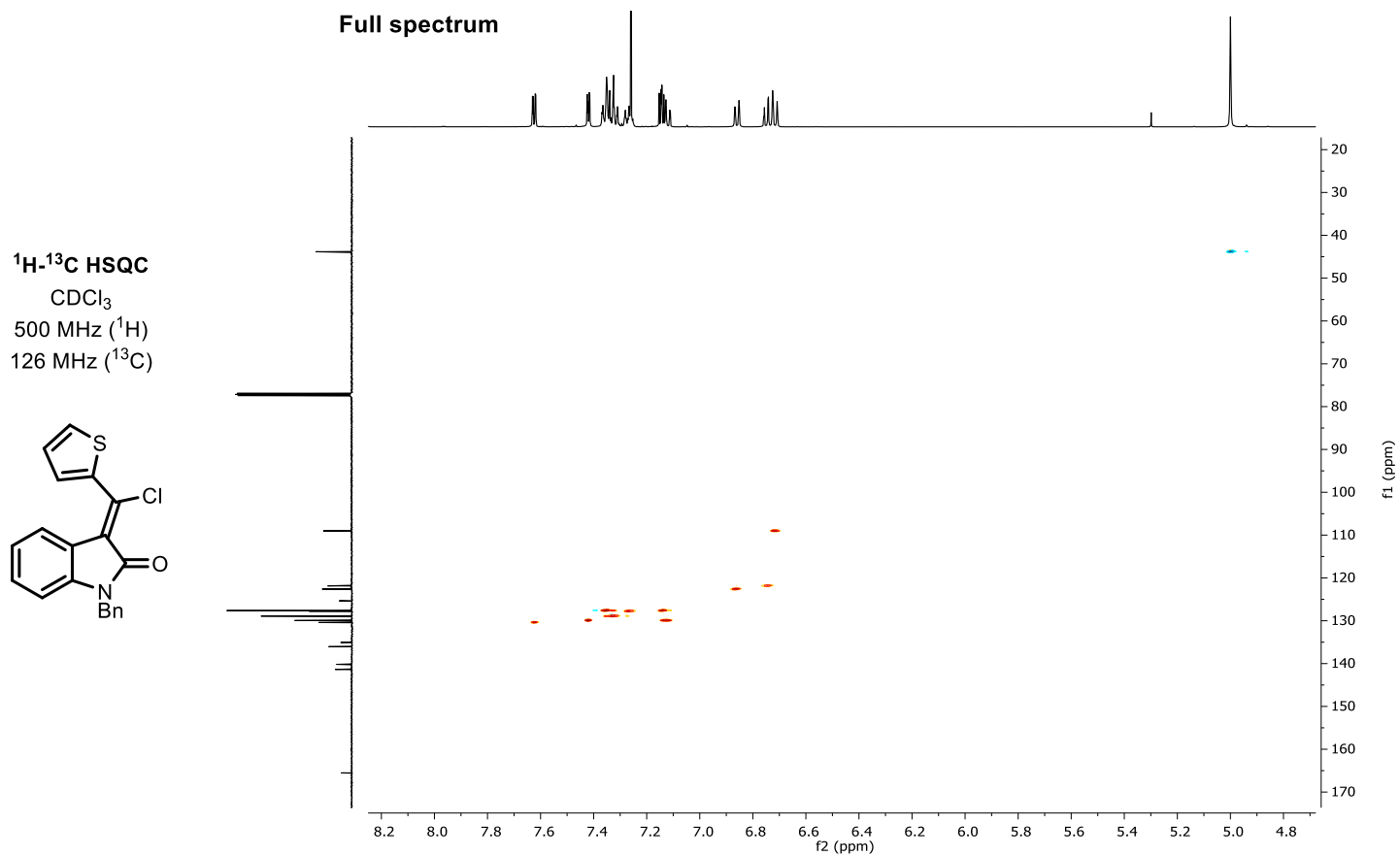
(Z)-1-benzyl-3-(chloro(thiophen-2-yl)methylene)indolin-2-one (1y)

¹H NMR
CDCl₃
500 MHz



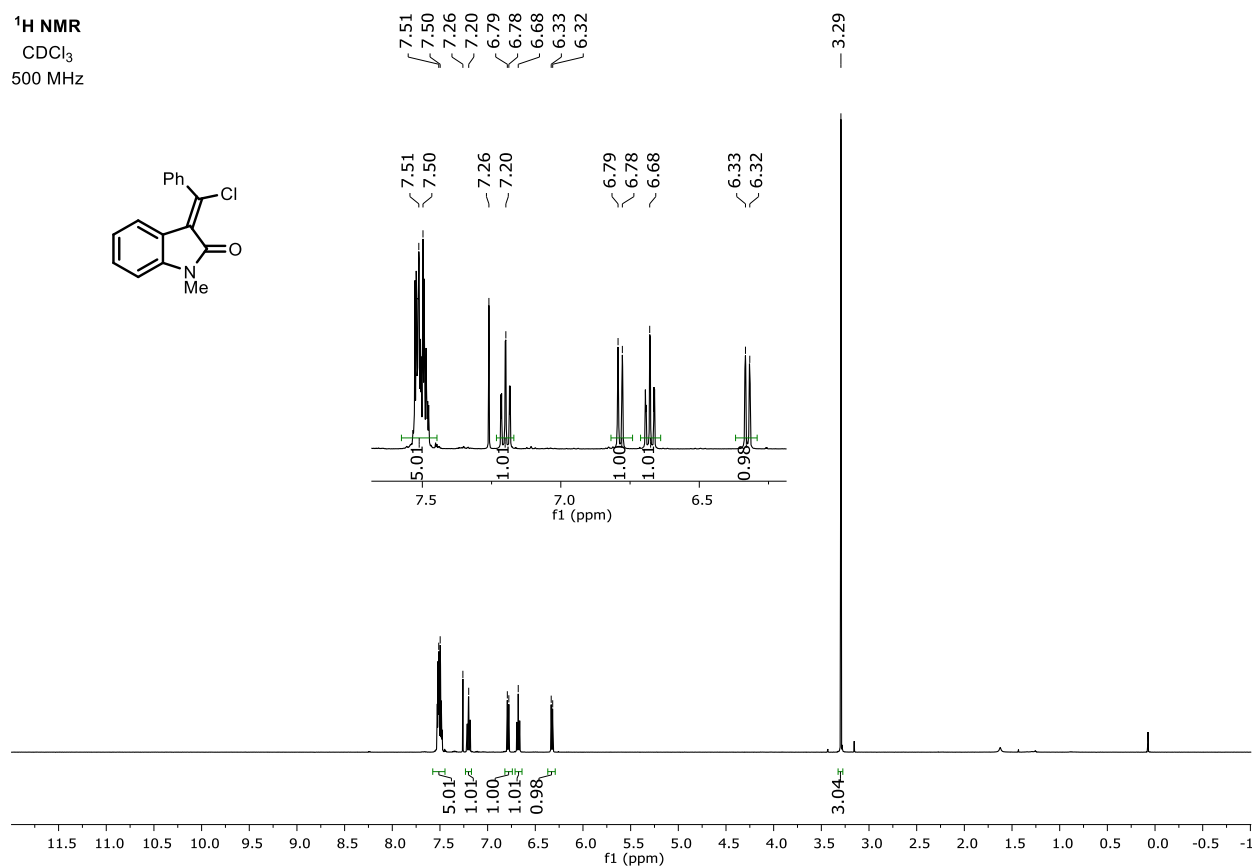
¹³C NMR
CDCl₃
126 MHz



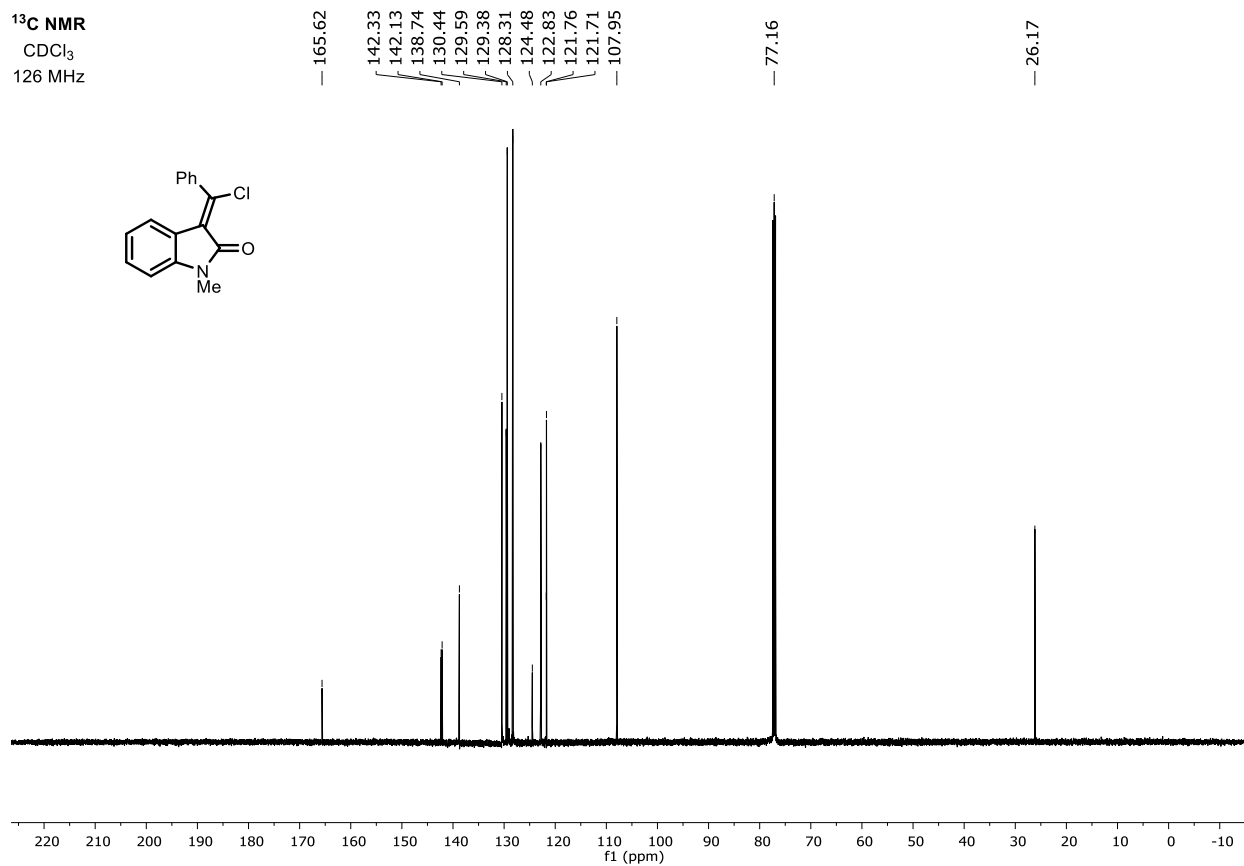


(Z)-3-(chloro(phenyl)methylene)-1-methylindolin-2-one (1z)

¹H NMR
CDCl₃
500 MHz

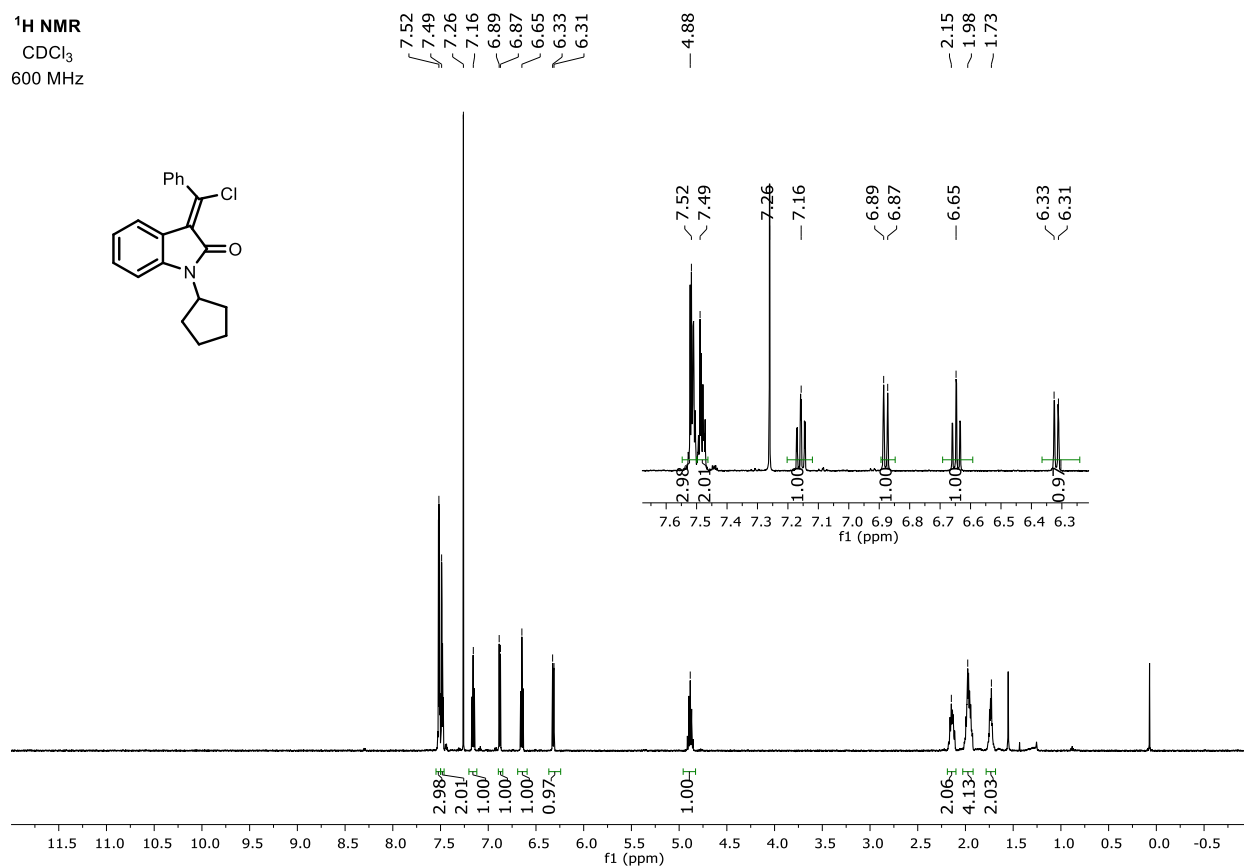


¹³C NMR
CDCl₃
126 MHz

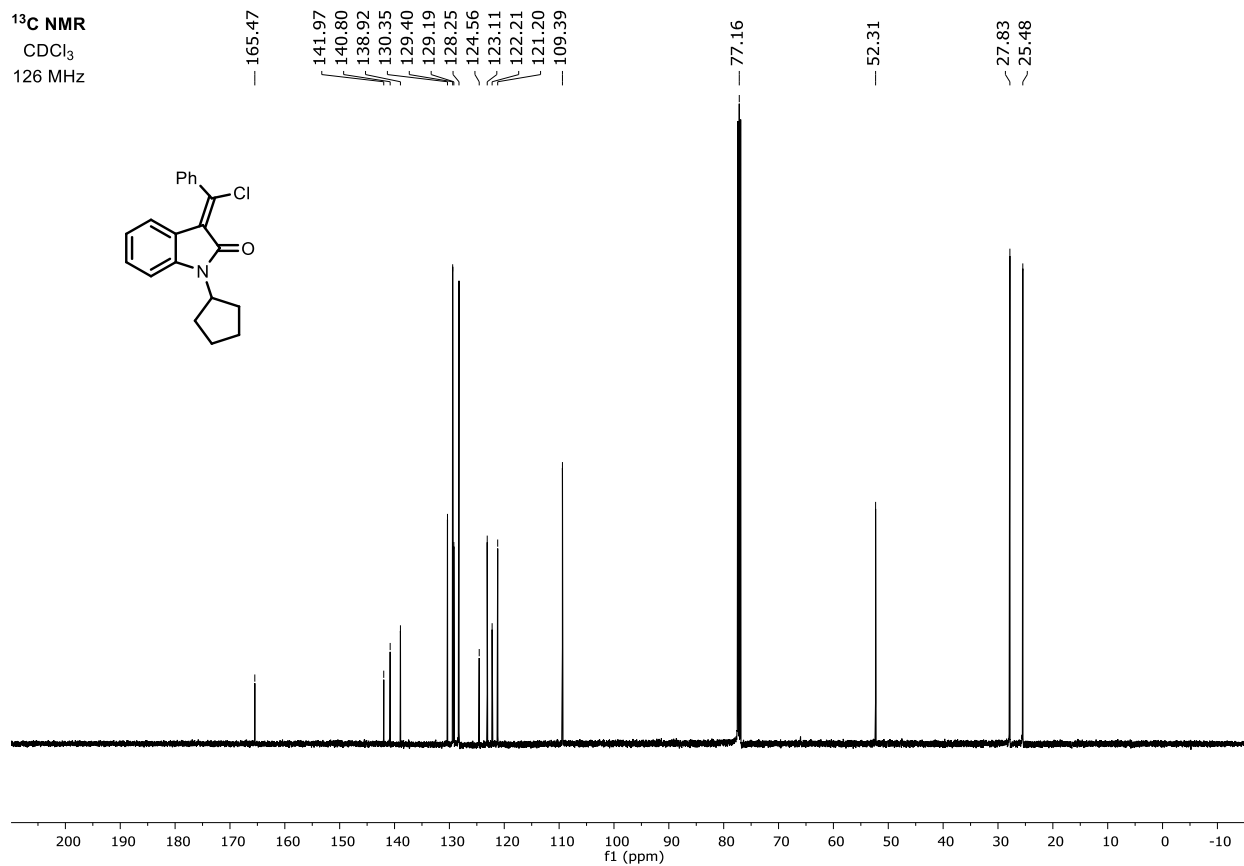


(Z)-3-(chloro(phenyl)methylene)-1-cyclopentylindolin-2-one (1ab)

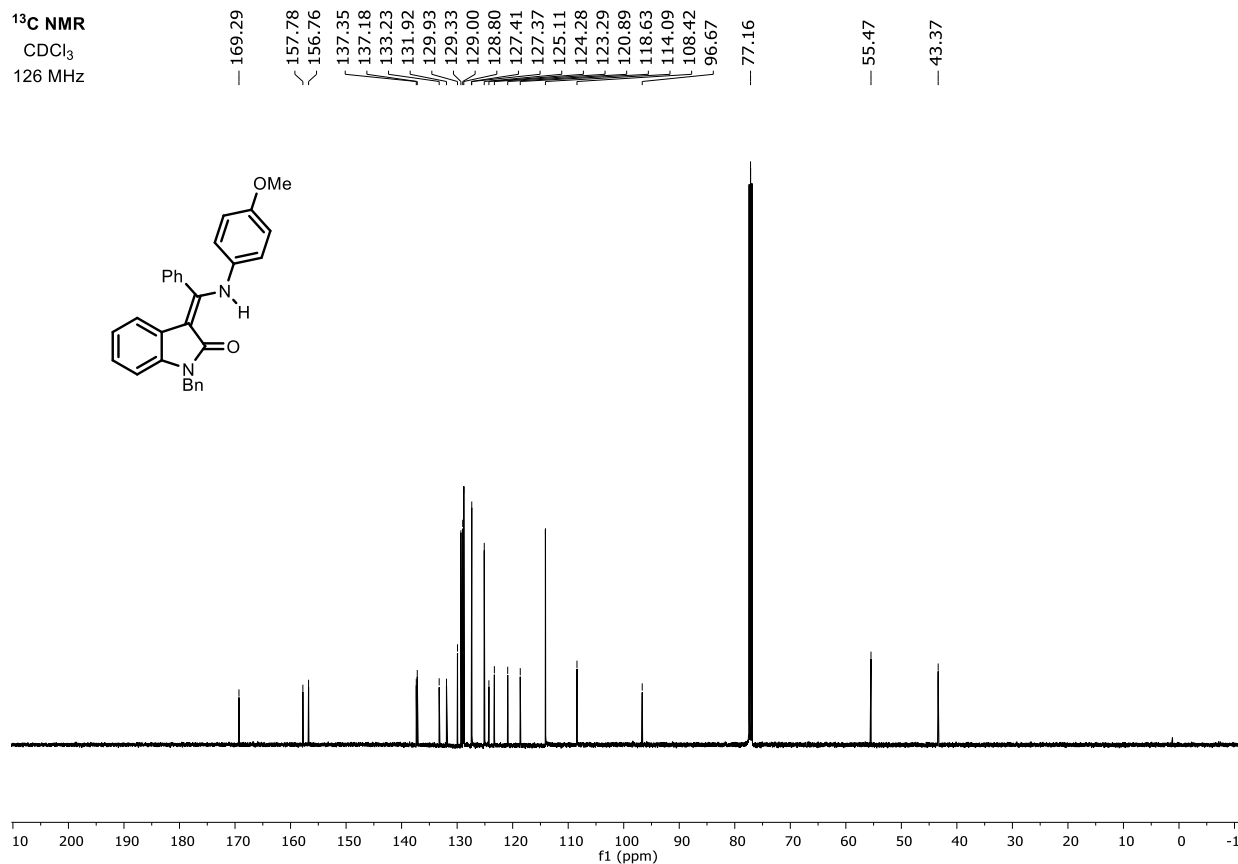
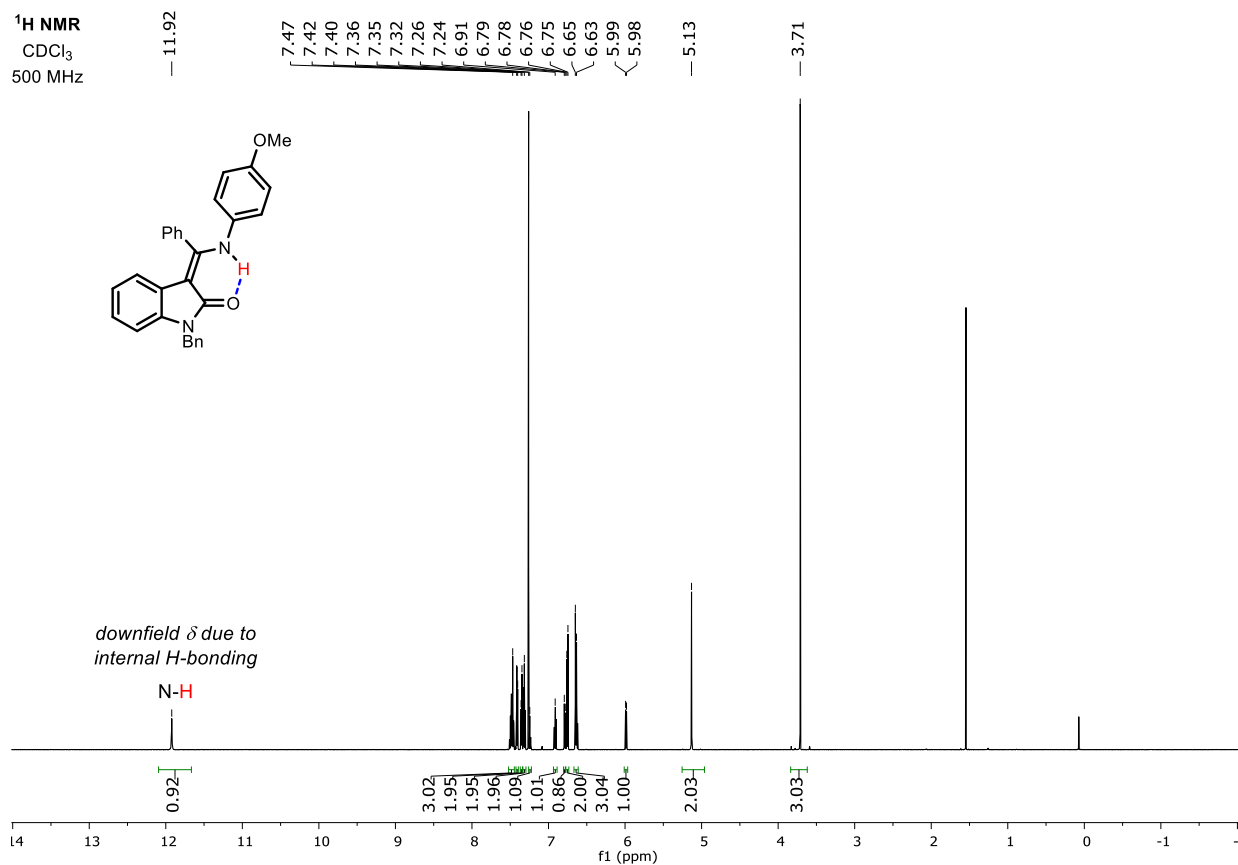
¹H NMR
CDCl₃
600 MHz



¹³C NMR
CDCl₃
126 MHz

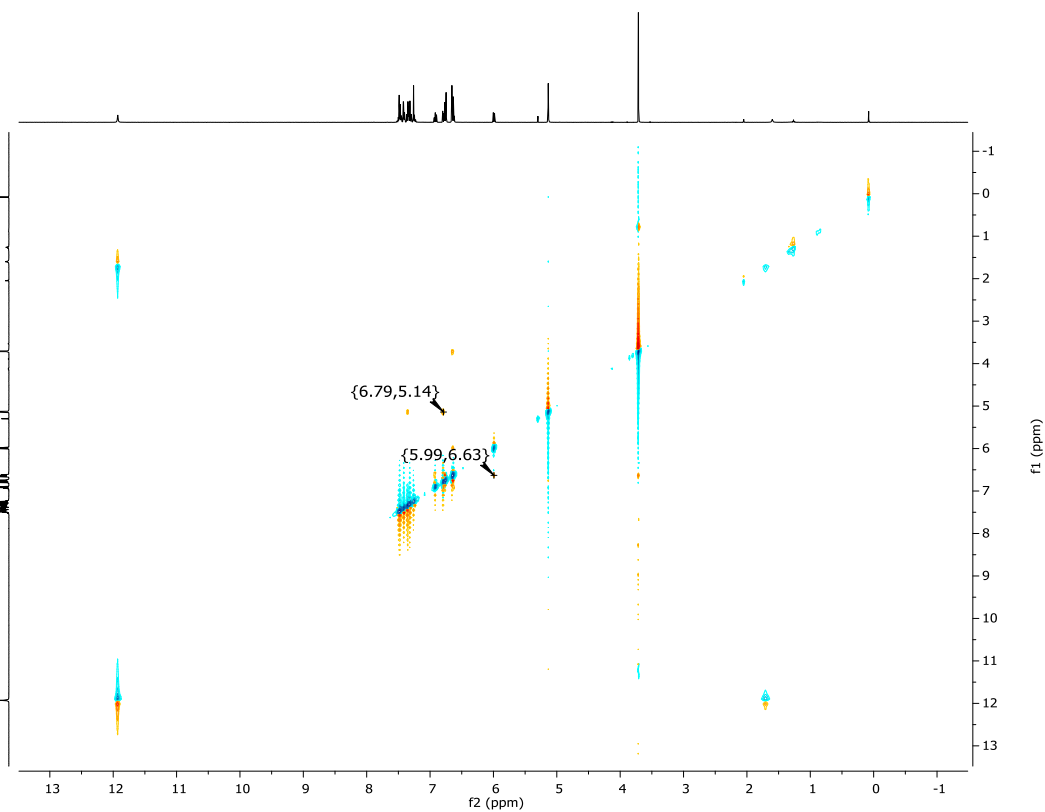
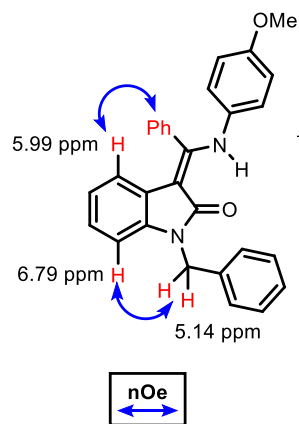


(Z)-1-benzyl-3-(((4-methoxyphenyl)amino)(phenyl)methylene)indolin-2-one (1ba)



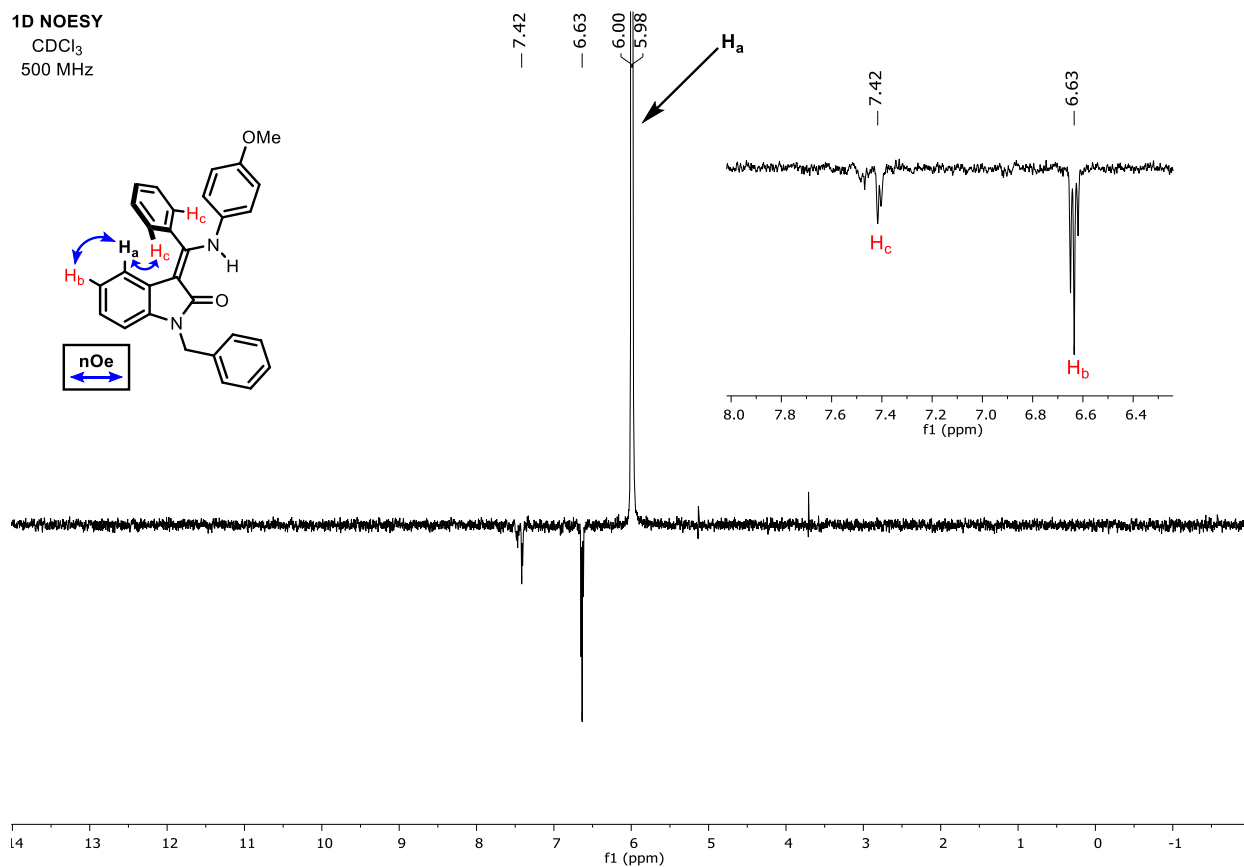
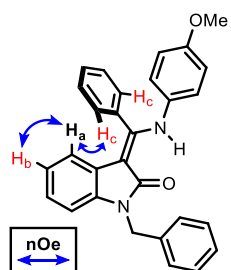
2D NOESY

CDCl₃
500 MHz



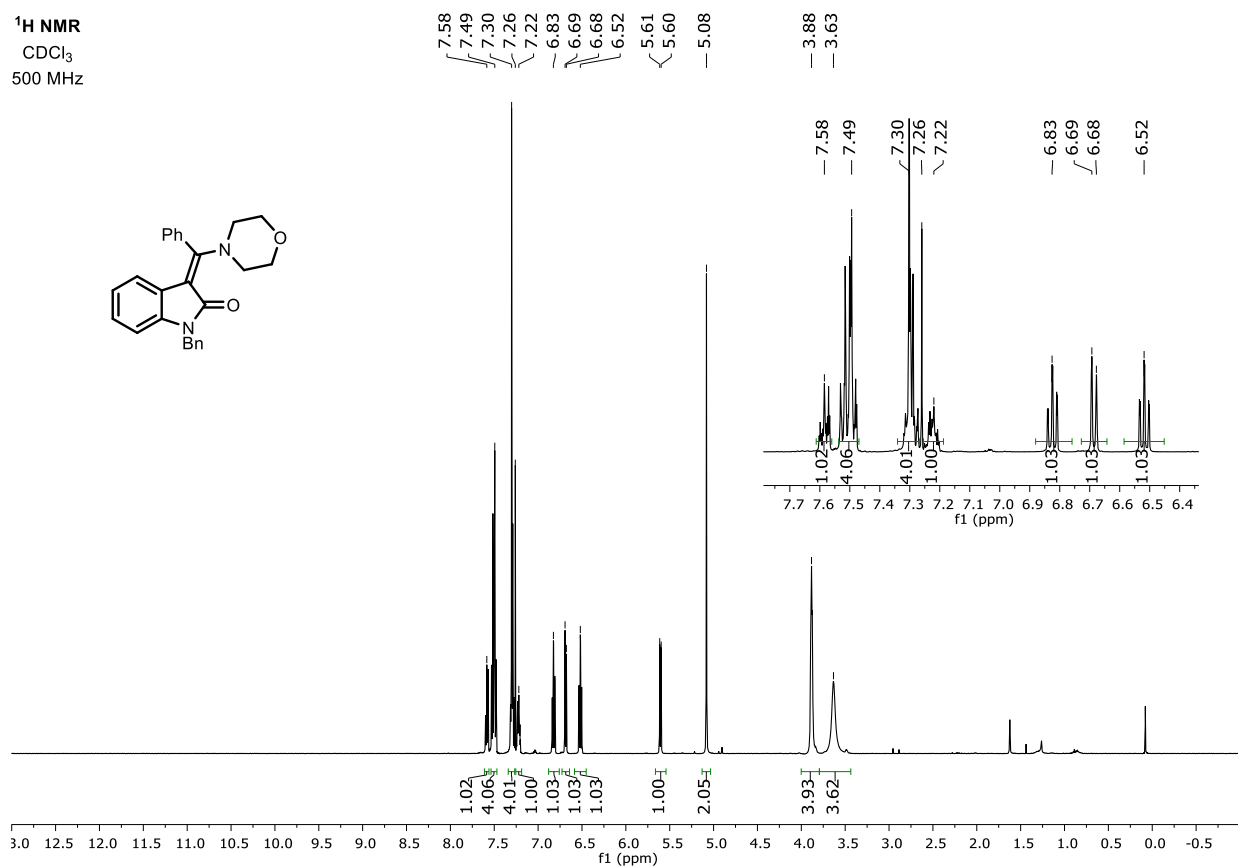
1D NOESY

CDCl₃
500 MHz

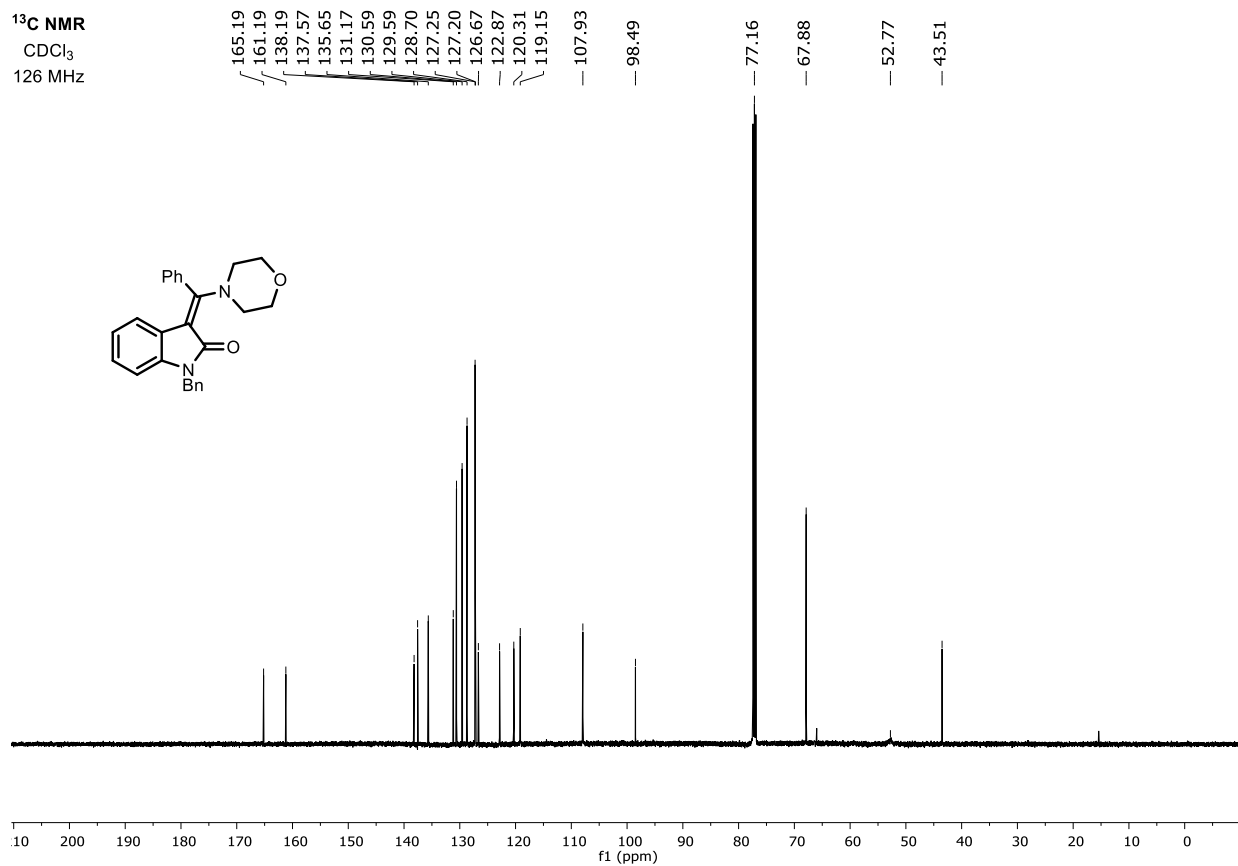


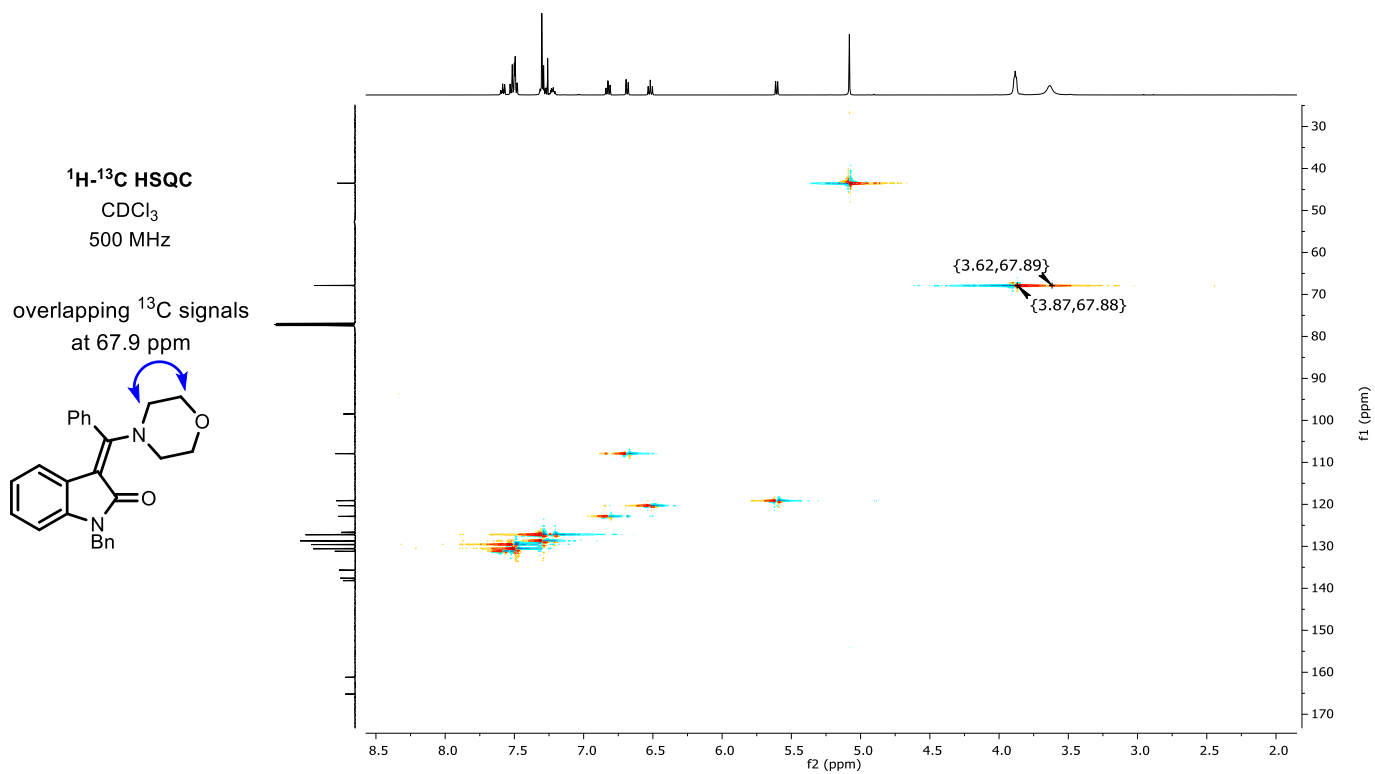
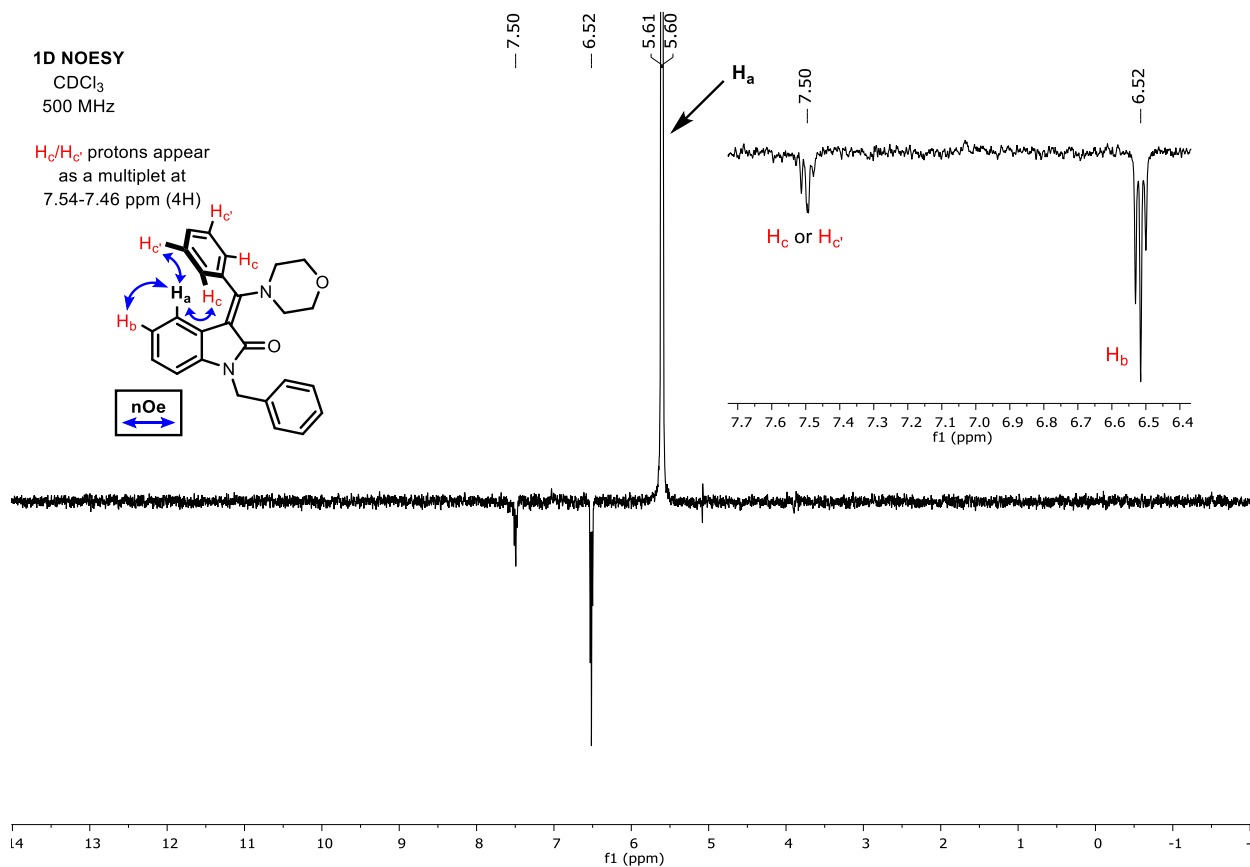
(Z)-1-benzyl-3-(morpholino(phenyl)methylene)indolin-2-one (1bb)

¹H NMR
CDCl₃
500 MHz



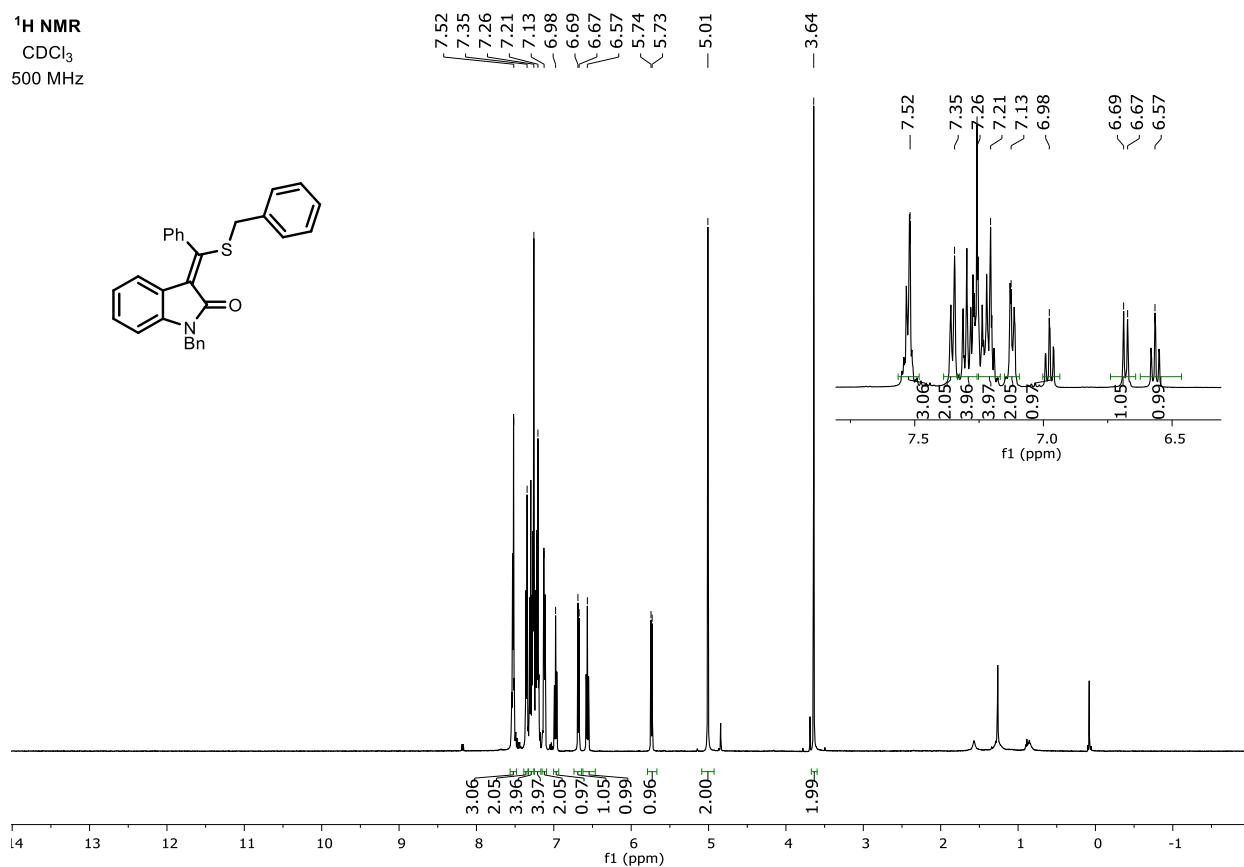
¹³C NMR
CDCl₃
126 MHz



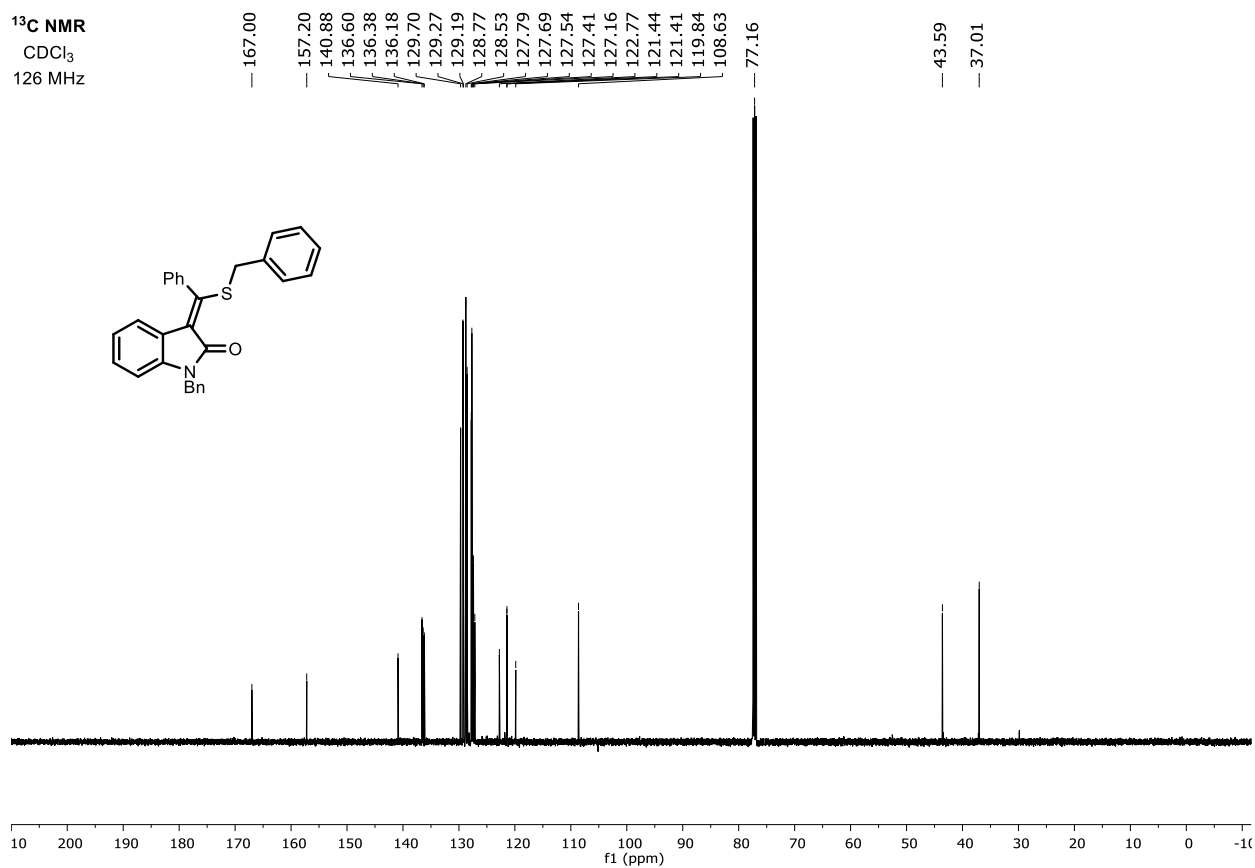


(Z)-1-benzyl-3-((benzylthio)(phenyl)methylene)indolin-2-one (1bd)

¹H NMR
CDCl₃
500 MHz



¹³C NMR
CDCl₃
126 MHz



CDCl₃
600 MHz

