

Supporting information

Lewis Base–Boryl Radicals Enabled the Desulfurizative Reduction and Annulation of Thioamides

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Table of Contents

1. General	S2
2. Synthesis of Thioamides	S2
3. Lewis base-boryl radicals enabled reduction of thioamides	S18
4. Mechanistic studies	S29
5. Lewis base-boryl radicals enabled annulation of thioamides	S30
5.1 Optimization of reaction conditions	S30
5.2 A proposed mechanism	S31
5.3 Radical annulation of thioamides	S32
6. References	S39
Appendix: ¹H and ¹³C NMR spectra for new compounds	S41

1. General

Unless otherwise noted, all reactions were performed under an nitrogen atmosphere using flame-dried glassware. Toluene was distilled over CaH₂. All new compounds were fully characterized. ¹H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in CDCl₃ [using CDCl₃ (for ¹H, δ = 7.26, DMSO-*d*₆ (for ¹H, δ = 2.50) as the internal standard]. ¹³C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in CDCl₃ [using CDCl₃ (for ¹³C, δ = 77.0), DMSO-*d*₆ (for ¹³C, δ = 39.5) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, m = multiplet, s br = single broad. High-resolution mass spectra were obtained with a Water XEVO G2 Q-Tof (Waters Corporation). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Commercially available reagents were purchased from Energy Chemical, J & K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc.

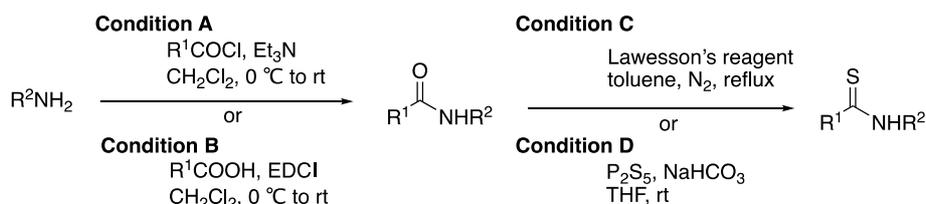
NHC-BH₃ (**2a**),¹ Pyridine-BH₃ (**2b**),² and DMAP-BH₃ (**2c**)³ were known compounds and prepared according to the literature procedures.

2. Synthesis of Thioamides

Thioamides **1a**,⁴ **1b**,⁴ **1u**,⁵ **1v**,⁶ **1x**,⁷ **1y**,⁸ **1z**,⁹ **1a'**,⁹ **1aa**,¹⁰ were known compounds and prepared according to the literature procedures.

Other thioamides used in this work were prepared by the following two methods:

Method 1



Condition A: To a solution of aniline and Et₃N (1.5 equiv) in CH₂Cl₂ was added acid chloride (1.1 equiv) at 0 °C. After addition, the mixture was stirred at

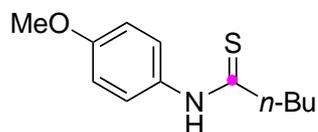
room temperature until TLC indicating aniline disappeared. The solvent was evaporated in *vacuo* and the crude material was submitted to the next step without further purification.

Condition B: Aniline and carboxylic acid (1.0 equiv) were dissolved in CH₂Cl₂, then 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.1 equiv) was added dropwise at 0 °C. The reaction was stirred at room temperature until TLC indicating reaction complete. The reaction mixture was poured into water and then extracted with CH₂Cl₂ (×2). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude material was used in the next step directly without further purification.

Condition C: A solution of amides and Lawesson's reagent (0.6 equiv) in toluene was refluxed under N₂ until TLC indicating amide disappeared. The reaction mixture was cooled to room temperature and evaporated. Purification of the crude product by flash column chromatography afforded desired thioamide product.

Condition D: To a mixture of amides and P₂S₅ (0.6 equiv) in THF was added sodium bicarbonate portionwise. The reaction was stirred at room temperature under N₂. After TLC indicating reaction complete, the suspension was poured into H₂O and extracted with ethyl acetate (x3). The organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated. The crude material was purified by flash column chromatography to give desired thioamide product.

***N*-(4-Methoxyphenyl)pentanethioamide (1c)**

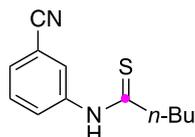


Following condition A and condition C, **1c** was obtained in 57% yield (1.31 g, 5.86 mmol) as rotamers (2.8:1) from the reaction of *p*-anisidine (1.27 g, 10.31 mmol) and valeryl chloride (1.4 mL, 11.80 mmol).

Yellow solid; mp: 63-65 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.82 (3Hx1, t, *J* = 7.2 Hz), 0.96 (3Hx2.8, t, *J* = 7.2 Hz), 1.26 (2Hx1, tq, *J* = 7.2, 7.2 Hz), 1.43 (2Hx2.8, tq, *J* = 7.2, 7.2 Hz), 1.72 (2Hx1, tt, *J* = 7.2, 7.8 Hz), 1.86 (2Hx2.8, tt, *J* = 7.2, 7.8 Hz), 2.56 (2Hx1,

t, $J = 7.8$ Hz), 2.80 (2Hx2.8, t, $J = 7.8$ Hz), 3.81 (3Hx2.8, s), 3.83 (3Hx1, s), 6.90-6.93 (2Hx2.8+2Hx1, m), 7.09 (2Hx1, d, $J = 8.8$ Hz), 7.50 (2Hx2.8, d, $J = 8.8$ Hz), 8.59 (1Hx2.8, s br), 9.26 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 13.7, 22.0, 22.1, 31.5, 31.7, 39.9, 47.8, 55.3, 55.4, 113.8, 114.5, 125.7, 126.9, 130.4, 131.5, 158.0, 159.0, 205.2, 209.8; ESIHRMS: Found: m/z 224.1111. Calcd for $\text{C}_{17}\text{H}_{18}\text{NOS}$: $(\text{M}+\text{H})^+$ 224.1109.

***N*-(3-Cyanophenyl)pentanethioamide (1d)**



Following condition A and condition D, **1d** was obtained in 19% yield (0.48 g, 2.20 mmol) as rotamers (>10:1) from the reaction of 3-aminobenzonitrile (1.37 g, 11.57 mmol) and valeryl chloride (1.5 mL, 12.64 mmol). ^1H and ^{13}C NMR were described for the major isomer.

Brown solid; mp: 72-73 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (3H, t, $J = 7.4$ Hz), 1.42 (2H, tq, $J = 7.6, 7.4$ Hz), 1.84 (2H, tt, $J = 7.6, 7.6$ Hz), 2.82 (2H, t, $J = 7.6$ Hz), 7.48-7.51 (2H, m), 7.95 (1H, d, $J = 7.2$ Hz), 8.14 (1H, s), 9.04 (1H, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 22.0, 31.7, 48.6, 112.5, 118.2, 126.9, 128.2, 129.8, 129.9, 139.4, 206.5; ESIHRMS: Found: m/z 219.0954. Calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{S}$: $(\text{M}+\text{H})^+$ 219.0956.

***N*-(2-Chlorophenyl)pentanethioamide (1e)**

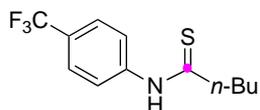


Following condition A and condition C, **1e** was obtained in 79% yield (1.80 g, 7.90 mmol) as rotamers (10:1) from the reaction of 2-chloroaniline (12.8 g, 10.0 mmol) and valeryl chloride (1.3 mL, 10.95 mmol). ^1H and ^{13}C NMR were described for the major isomer.

Yellow liquid; mp: 56-57 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.97 (3H, t, $J = 7.4$ Hz), 1.45 (2H, tq, $J = 7.2, 7.4$ Hz), 1.87 (2H, tt, $J = 7.6, 7.2$ Hz), 2.87 (2H, t, $J = 7.6$ Hz), 7.20 (1H, dd, $J = 7.6, 8.0$ Hz), 7.32 (1H, dd, $J = 7.6, 7.6$ Hz), 7.44 (1H, d, $J = 7.6$ Hz), 8.49 (1H, d, $J = 8.0$ Hz), 8.82 (1H, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 22.0,

31.6, 49.0, 125.7, 126.96, 127.03, 127.5, 129.4, 135.2, 205.7; ESIHRMS: Found: m/z 228.0617. Calcd for $C_{11}H_{15}ClNS$: $(M+H)^+$ 228.0614.

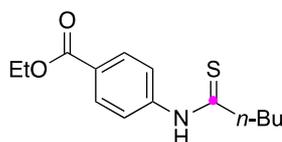
***N*-(4-(Trifluoromethyl)phenyl)pentanethioamide (1f)**



Following condition A and condition C, **1f** was obtained in 69% yield (1.80 g, 6.89 mmol) as rotamers (>10:1) from the reaction of 4-aminobenzotrifluoride (1.61 g, 9.98 mmol) and valeryl chloride (1.3 mL, 10.95 mmol). 1H and ^{13}C NMR were described for the major isomer.

Yellow solid; mp: 88-90 °C; 1H NMR (400 MHz, $CDCl_3$) δ 0.97 (3H, t, $J = 7.2$ Hz), 1.44 (2H, tq, $J = 7.2, 7.2$ Hz), 1.86 (2H, tt, $J = 7.6, 7.2$ Hz), 2.83 (2H, t, $J = 7.6$ Hz), 7.65 (2H, d, $J = 8.0$ Hz), 7.88 (2H, d, $J = 8.0$ Hz), 8.69 (1H, s br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 22.0, 31.7, 48.9, 123.5, 123.7 (q, $J = 270.4$ Hz), 126.0 (q, $J = 3.5$ Hz), 128.4 (q, $J = 32.6$ Hz), 141.4, 206.1; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.4 (3F, s); ESIHRMS: Found: m/z 262.0880. Calcd for $C_{12}H_{15}F_3NS$: $(M+H)^+$ 262.0877.

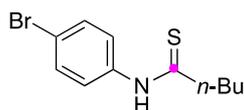
Ethyl 4-pentanethioamidobenzoate (1g)



Following condition A and condition C, **1g** was obtained in 89% yield (2.41 g, 9.11 mmol) as rotamers (>10:1) from the reaction of benzocaine (1.69 g, 10.24 mmol) and valeryl chloride (1.3 mL, 10.95 mmol). 1H and ^{13}C NMR were described for the major isomer.

Yellow solid; mp: 64-65 °C; 1H NMR (400 MHz, $CDCl_3$) δ 0.94 (3H, t, $J = 7.2$ Hz), 1.36-1.43 (5H, m), 1.83 (2H, tt, $J = 7.6, 7.8$ Hz), 2.81 (2H, t, $J = 7.8$ Hz), 4.35 (2H, q, $J = 7.1$ Hz), 7.85 (2H, d, $J = 8.4$ Hz), 8.03 (2H, d, $J = 8.4$ Hz), 9.08 (1H, s br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.2, 22.1, 31.8, 49.1, 61.1, 122.6, 128.0, 130.3, 142.5, 165.9, 205.7; ESIHRMS: Found: m/z 266.1223. Calcd for $C_{14}H_{20}NO_2S$: $(M+H)^+$ 266.1215.

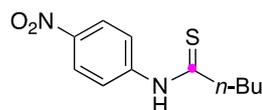
***N*-(4-Bromophenyl)pentanethioamide (1h)**



Following condition A and condition C, **1h** was obtained in 56% yield (1.51 g, 5.55 mmol) as rotamers (6.3:1) from the reaction of 4-bromoaniline (1.70 g, 9.91 mmol) and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow solid; mp: 114-115 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.84 (3Hx1, t, $J = 7.0$ Hz), 0.97 (3Hx6.3, t, $J = 7.4$ Hz), 1.28 (2Hx1, tq, $J = 7.6, 7.0$ Hz), 1.43 (2Hx6.3, tq, $J = 7.6, 7.4$ Hz), 1.74 (2Hx1, tt, $J = 7.6, 7.6$ Hz), 1.85 (2Hx6.3, tt, $J = 7.6, 7.8$ Hz), 2.59 (2Hx1, t, $J = 7.6$ Hz), 2.81 (2Hx6.3, t, $J = 7.8$ Hz), 7.05 (2Hx1, d, $J = 7.6$ Hz), 7.50-7.52 (2Hx6.3, m), 7.57-7.60 (2Hx6.3+2Hx1, m), 8.53 (1Hx6.3, s br), 9.16 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 13.8, 22.0, 22.1, 31.7, 40.1, 48.5, 119.9, 121.7, 125.5, 127.1, 131.9, 132.8, 136.5, 137.4, 205.7, 210.0; ESIHRMS: Found: m/z 272.0104. Calcd for $\text{C}_{11}\text{H}_{15}^{79}\text{BrNS}$: (M+H) $^+$ 272.0109.

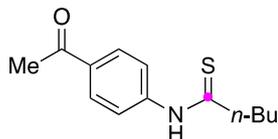
***N*-(4-Nitrophenyl)pentanethioamide (1i)**



Following condition A and condition C, **1i** was obtained in 98% yield (1.12 g, 4.70 mmol) from the reaction of 4-nitroaniline (0.67 g, 4.79 mmol) and valeryl chloride (0.6 mL, 5.05 mmol).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.96 (3H, t, $J = 7.4$ Hz), 1.43 (2H, tq, $J = 7.6, 7.4$ Hz), 1.85 (2H, tt, $J = 7.6, 7.8$ Hz), 2.84 (2H, t, $J = 7.8$ Hz), 8.05 (2H, d, $J = 8.8$ Hz), 8.26 (2H, d, $J = 8.8$ Hz), 8.92 (1H, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 21.9, 31.7, 49.1, 122.8, 124.4, 144.3, 144.4, 206.7; ESIHRMS: Found: m/z 239.0854; Calcd for $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2\text{S}$: (M+H) $^+$ 239.0854.

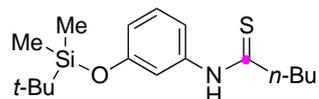
***N*-(4-Acetylphenyl)pentanethioamide (1j)**



Following condition A and condition C, **1j** was obtained in 40% yield (0.95 g, 4.04 mmol) from the reaction of 4-aminoacetophenone (1.36 g, 10.09 mmol) and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow solid; mp: 69-70 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.96 (3H, t, $J = 7.2$ Hz), 1.44 (2H, tq, $J = 7.6, 7.2$ Hz), 1.86 (2H, tt, $J = 7.6, 7.6$ Hz), 2.60 (3H, s), 2.84 (2H, t, $J = 7.6$ Hz), 7.91 (2H, d, $J = 8.4$ Hz), 7.99 (2H, d, $J = 8.4$ Hz), 8.85 (1H, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 22.0, 26.5, 31.8, 48.8, 122.7, 129.1, 134.3, 143.1, 197.5, 206.0; ESIHRMS: Found: m/z 236.1109. Calcd for $\text{C}_{13}\text{H}_{18}\text{NOS}$: $(\text{M}+\text{H})^+$ 236.1109.

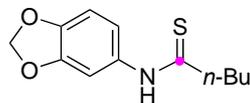
N-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)pentanethioamide (**1k**)



Following condition A and condition C, **1k** was obtained in 32% yield (1.05 g, 3.24 mmol) as rotamers (2.8:1) from the reaction of 3-((*tert*-butyldimethylsilyl)oxy)aniline (2.35 g, 10.14 mmol)¹¹ and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.21-0.22 (6Hx1+6Hx2.8, m), 0.83 (3Hx1, t, $J = 7.2$ Hz), 0.91-0.98 (9Hx1+9Hx2.8+3Hx2.8, m), 1.28 (2Hx1, tq, $J = 7.2, 7.2$ Hz), 1.42 (2Hx2.8, tq, $J = 7.2, 7.2$ Hz), 1.74 (2Hx1, tt, $J = 7.2, 7.8$ Hz), 1.84 (2Hx2.8, tt, $J = 7.2, 7.8$ Hz), 2.65 (2Hx1, t, $J = 7.8$ Hz), 2.79 (2Hx2.8, t, $J = 7.8$ Hz), 6.64 (1Hx1, s), 6.73-6.77 (1Hx1+1Hx2.8, m), 6.83 (1Hx1, d, $J = 8.0$ Hz), 7.15-7.17 (1Hx2.8, d, $J = 8.0$ Hz), 7.20 (1Hx1, s), 7.27 (1Hx2.8, dd, $J = 8.4, 8.8$ Hz), 7.45 (1Hx2.8, s), 8.69 (1Hx2.8, s br), 9.40 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ -4.5, 13.7, 13.8, 18.1, 18.2, 22.1, 22.2, 25.5, 25.6, 31.7, 31.8, 40.3, 49.0, 115.2, 116.2, 117.4, 118.4, 118.5, 119.9, 129.4, 130.3, 138.5, 139.6, 156.0, 156.6, 204.8, 209.8; ESIHRMS: Found: m/z 324.1821. Calcd for $\text{C}_{17}\text{H}_{30}\text{NOSSi}$: $(\text{M}+\text{H})^+$ 324.1817.

N-(Benzo[*d*][1,3]dioxol-5-yl)pentanethioamide (**1l**)

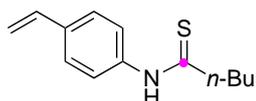


Following condition A and condition C, **1l** was obtained in 87% yield (2.10 g, 8.85 mmol) as rotamers (3.2:1) from the reaction of 3,4-(methylenedioxy)aniline (1.40 g, 10.17 mmol) and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow solid; mp: 91-92 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.84 (3Hx1, t, $J = 7.2$ Hz), 0.96 (3Hx3.2, t, $J = 7.4$ Hz), 1.28 (2Hx1, tq, $J = 7.6, 7.2$ Hz), 1.43 (2Hx3.2, tq, $J = 7.6, 7.4$ Hz), 1.73 (2Hx1, tt, $J = 7.6, 7.6$ Hz), 1.85 (2Hx3.2, tt, $J = 7.6, 7.6$ Hz), 2.57 (2Hx1, t, $J = 7.6$ Hz), 2.79 (2Hx3.2, t, $J = 7.6$ Hz), 6.0 (2Hx3.2, s), 6.1 (2Hx1, s), 6.63-6.64

(2Hx1, m), 6.79-6.83 (1Hx1+1Hx3.2, m), 6.89 (1Hx3.2, d, $J = 8.0$ Hz), 7.26 (1Hx3.2, s), 8.55 (1Hx3.2, s br), 9.19 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 13.8, 22.0, 22.1, 31.6, 31.7, 39.9, 47.9, 101.6, 101.9, 106.2, 106.9, 107.9, 108.4, 117.8, 119.4, 131.3, 132.5, 146.2, 147.4, 147.5, 148.2, 205.6, 210.2; ESIHRMS: Found: m/z 238.0908. Calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_2\text{S}$: $(\text{M}+\text{H})^+$ 238.0902.

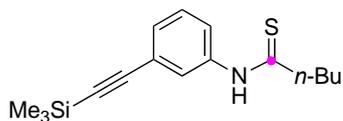
***N*-(4-Vinylphenyl)pentanethioamide(1n)**



Following condition A and condition C, **1n** was obtained in 37% yield (0.41 g, 1.87 mmol) as rotamers (4:1) from the reaction of 4-vinylaniline (0.60 g, 5.05 mmol) and valeryl chloride (0.7 mL, 5.90 mmol).

Yellow solid; mp: 69-70 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.83 (3Hx1, t, $J = 7.2$ Hz), 0.96 (3Hx4, t, $J = 7.4$ Hz), 1.28 (2Hx1, tq, $J = 7.6, 7.2$ Hz), 1.42 (2Hx4, tq, $J = 7.6, 7.4$ Hz), 1.74 (2Hx1, tt, $J = 7.6, 7.8$ Hz), 1.84 (2Hx4, tt, $J = 7.6, 7.6$ Hz), 2.62 (2H, t, $J = 7.8$ Hz), 2.79 (2Hx4, t, $J = 7.6$ Hz), 5.26 (1Hx4, d, $J = 10.8$ Hz), 5.33 (1Hx1, d, $J = 10.8$ Hz), 5.59 (1Hx4, d, $J = 17.6$ Hz), 5.71 (1Hx1, d, $J = 17.6$ Hz), 6.65-6.75 (1Hx1+1Hx4, m), 7.10 (2Hx1, d, $J = 8.0$ Hz), 7.40-7.46 (2Hx1+2Hx4, m), 7.63 (2Hx4, d, $J = 8.0$ Hz), 8.77 (1Hx4, s br), 9.45 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 13.8, 22.1, 22.2, 31.7, 40.1, 48.7, 114.4, 115.4, 123.8, 125.5, 126.6, 127.3, 135.4, 135.9, 136.1, 136.9, 137.3, 138.0, 205.1, 209.9; ESIHRMS: Found: m/z 220.1159. Calcd for $\text{C}_{13}\text{H}_{18}\text{NS}$: $(\text{M}+\text{H})^+$ 220.1160.

***N*-(3-((Trimethylsilyl)ethynyl)phenyl)pentanethioamide (1p)**

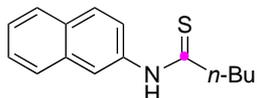


Following condition A and condition C, **1p** was obtained in 53% yield (1.54 g, 5.32 mmol) as rotamers (4.4:1) from the reaction of 3-((trimethylsilyl)ethynyl)aniline (1.90 g, 10.04 mmol)¹² and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.24-0.26 (9Hx1+9Hx4.4, m), 0.83 (3Hx1, t, $J = 7.4$ Hz), 0.96 (3Hx4.4, t, $J = 7.4$ Hz), 1.27 (2Hx1, tq, $J = 7.6, 7.4$ Hz), 1.42 (2Hx4.4, tq, $J = 7.6, 7.4$ Hz), 1.71 (2Hx1, tt, $J = 7.6, 7.8$ Hz), 1.84 (2Hx4.4, tt, $J = 7.6, 7.8$ Hz), 2.60 (2Hx1, t, $J = 7.8$ Hz), 2.78 (2Hx4.4, t, $J = 7.8$ Hz), 7.10 (1Hx1, d,

$J = 7.6$ Hz), 7.25-7.45 (2Hx1+2Hx4.4, m), 7.46 (1Hx1, d, $J = 7.6$ Hz), 7.66-7.68 (2Hx4.4, m), 8.74 (1Hx4.4, s br), 9.43 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 0.2, 13.8, 22.0, 31.7, 48.6, 95.3, 103.9, 123.9, 124.2, 127.2, 128.7, 130.3, 138.4, 205.7; ESIHRMS: Found: m/z 290.1399. Calcd for $\text{C}_{16}\text{H}_{24}\text{NSSi}$: $(\text{M}+\text{H})^+$ 290.1399.

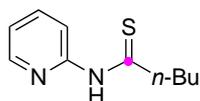
***N*-(Naphthalen-2-yl)pentanethioamide (1q)**



Following condition A and condition C, **1q** was obtained in 74% yield (1.85 g, 7.60 mmol) as rotamers (4:1) from the reaction of 2-aminonaphthalene (1.43 g, 10.00 mmol) and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow solid; mp: 77-78 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.80 (3Hx1, t, $J = 7.4$ Hz), 0.98 (3Hx4, t, $J = 7.4$ Hz), 1.26 (2Hx1, tq, $J = 7.4, 7.4$ Hz), 1.46 (2Hx4, tq, $J = 7.6, 7.4$ Hz), 1.78 (2Hx1, tt, $J = 7.6, 7.2$ Hz), 1.89 (2Hx4, tt, $J = 7.6, 7.8$ Hz), 2.68 (2Hx1, t, $J = 7.6$ Hz), 2.85 (2Hx4, t, $J = 7.8$ Hz), 7.23-7.25 (2Hx1, m), 7.46-7.49 (2Hx4, m), 7.54-7.56 (2Hx1, m), 7.59-7.62 (1Hx1+1Hx4, m), 7.80-7.90 (3Hx1+3Hx4, m), 8.29 (1Hx4, s), 8.84 (1Hx4, s br), 9.52 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 13.8, 22.0, 22.1, 31.7, 40.1, 48.3, 48.4, 53.4, 121.6, 122.9, 123.3, 123.6, 126.1, 126.4, 126.8, 127.1, 127.5, 127.7, 127.8, 128.4, 129.6, 131.8, 132.1, 133.1, 134.8, 135.9, 205.5, 209.8; ESIHRMS: Found: m/z 224.1158. Calcd for $\text{C}_{15}\text{H}_{18}\text{NS}$: $(\text{M}+\text{H})^+$ 224.1160.

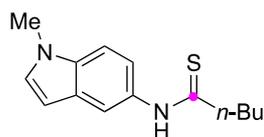
***N*-(Pyridin-2-yl)pentanethioamide (1r)**



Following condition A and condition C, **1r** was obtained in 50% yield (0.39 g, 2.01 mmol) from the reaction of 2-aminopyridine (0.38 g, 4.01 mmol) and valeryl chloride (1.3 mL, 10.95 mmol).

Yellow solid; mp: 52-53 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.93 (3H, t, $J = 7.2$ Hz), 1.40 (2H, tq, $J = 7.6, 7.2$ Hz), 1.84 (2H, tt, $J = 7.6, 7.8$ Hz), 2.84 (2H, t, $J = 7.8$ Hz), 7.17 (1H, ddd, $J = 7.6, 5.6, 0.8$ Hz), 7.78 (1H, ddd, $J = 8.4, 7.6, 1.6$ Hz), 8.37 (1H, dd, $J = 5.6, 1.6$ Hz), 9.11 (1H, dd, $J = 8.4, 0.8$ Hz), 9.96 (1H, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 22.0, 31.8, 49.9, 115.5, 121.4, 138.1, 147.9, 152.0, 205.0; ESIHRMS: Found: m/z 195.0958. Calcd for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{S}$: $(\text{M}+\text{H})^+$ 195.0956.

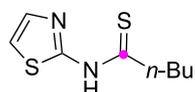
***N*-(1-Methyl-1*H*-indol-5-yl)pentanethioamide (1s)**



Following condition A and condition D, **1s** was obtained as rotamers (1.7:1) in 14% yield (0.23 g, 0.93 mmol) from the reaction of 1-methyl-1*H*-indol-5-amine (0.97 g, 6.67 mmol) and valeryl chloride (0.9 mL, 7.58 mmol).

Yellow solid; mp: 112-113 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.74 (3Hx1, t, *J* = 7.2 Hz), 0.97 (3Hx1.7, t, *J* = 7.2 Hz), 1.22 (2Hx1, tq, *J* = 7.6, 7.2 Hz), 1.44 (2Hx1.7, tq, *J* = 7.6, 7.2 Hz), 1.73 (2H, tt, *J* = 7.6, 7.6 Hz), 1.87 (2Hx1.7, tt, *J* = 7.6, 7.6 Hz), 2.58 (2H, t, *J* = 7.6 Hz), 2.81 (2Hx1.7, t, *J* = 7.6 Hz), 3.76 (3Hx1.7, s), 3.81 (3Hx1, s), 6.47-6.50 (1Hx1+1Hx1.7, m), 6.95 (1H, d, *J* = 8.0 Hz), 7.06 (1Hx1.7, s), 7.13 (1Hx1, s), 7.25-7.35 (2Hx1+2Hx1.7, m), 7.77 (1Hx1.7, s), 8.90 (1Hx1.7, s br), 9.54 (1Hx1, s br); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 13.9, 22.1, 22.2, 31.70, 31.73, 32.9, 33.0, 39.9, 48.0, 101.3, 101.4, 109.3, 109.9, 117.0, 118.1, 119.1, 119.4, 128.2, 128.5, 129.8, 129.9, 130.6, 130.8, 135.3, 135.7, 205.4, 210.0; ESIHRMS: Found: *m/z* 247.1269. Calcd for C₁₄H₁₉N₂S: (M+H)⁺ 247.1269.

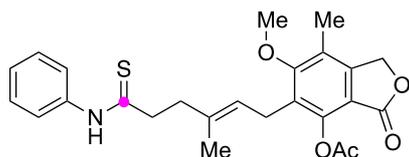
***N*-(Thiazol-2-yl)pentanethioamide (1t)**



Following condition A and condition C, **1t** was obtained in 41% yield (0.65 g, 3.25 mmol) from the reaction of 2-aminothiazole (0.79 g, 7.92 mmol) and valeryl chloride (1.0 mL, 8.42 mmol).

Yellow solid; mp: 128-130 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (3H, t, *J* = 7.2 Hz), 1.42 (2H, tq, *J* = 7.6, 7.2 Hz), 1.86 (2H, tt, *J* = 7.6, 7.8 Hz), 2.96 (2H, t, *J* = 7.8 Hz), 7.04 (1H, d, *J* = 3.6 Hz), 7.58 (1H, d, *J* = 3.6 Hz), 13.1 (1H, s br); ¹³C NMR (100 MHz, CDCl₃) δ 13.8, 22.1, 31.8, 46.7, 113.0, 136.2, 161.4, 202.5; ESIHRMS: Found: *m/z* 201.0520. Calcd for C₈H₁₃N₂S₂: (M+H)⁺ 201.0520.

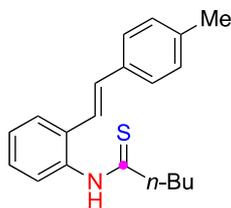
(*E*)-6-Methoxy-7-methyl-5-(3-methyl-6-(phenylamino)-6-thioxohex-2-en-1-yl)-3-oxo-1,3-dihydroisobenzofuran-4-yl acetate (1v)



Following condition B and condition D, **1v** was obtained in 28% yield (0.63 g, 1.39 mmol) as rotamers (10:1) from the reaction of (*E*)-6-(4-acetoxy-6-methoxy-3-oxo-1,3-dihydroisobenzofuran-5-yl)-4-methylhex-4-enoic acid (1.80 g, 4.96 mmol)¹³ and aniline (0.46 g, 4.94 mmol). ¹H and ¹³C NMR were described for the major isomer.

Yellow solid; mp: 107-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.82 (3H, s), 2.05 (3H, s), 2.42 (3H, s), 2.52 (2H, t, *J* = 5.8 Hz), 2.80 (2H, t, *J* = 5.8 Hz), 3.35 (2H, d, *J* = 7.2 Hz), 3.74 (3H, s), 3.94 (2H, s), 5.21 (1H, t, *J* = 7.2 Hz), 7.16 (1H, t, *J* = 7.2 Hz), 7.24 (2H, dd, *J* = 7.2, 7.6 Hz), 7.45 (2H, d, *J* = 7.6 Hz), 9.12 (1H, s br); ¹³C NMR (100 MHz, CDCl₃) δ 11.8, 16.9, 20.8, 23.4, 38.4, 47.2, 61.2, 68.3, 113.0, 123.0, 123.2, 123.5, 126.2, 128.2, 129.1, 134.5, 138.6, 145.3, 146.0, 162.3, 168.2, 170.2, 204.0; ESIHRMS: Found: *m/z* 454.1691. Calcd for C₂₅H₂₈NO₅S: (M+H)⁺ 454.1688.

(*E*)-*N*-(2-(4-Methylstyryl)phenyl)pentanethioamide (1ab**)**

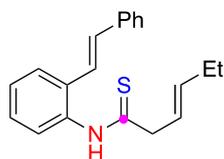


Following condition A and condition C, **1ab** was obtained in 87% yield (1.24 g, 4.01 mmol) as rotamers (2.4:1) from the reaction of (*E*)-2-(4-methylstyryl)aniline (0.96 g, 4.59 mmol)¹⁴ and valeryl chloride (0.6 mL, 5.05 mmol).

Yellow solid; mp: 98-99 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.70 (3Hx1, t, *J* = 7.4 Hz), 0.93 (3Hx2.4, t, *J* = 7.2 Hz), 1.15 (2Hx1, tq, *J* = 7.6, 7.4 Hz), 1.41 (2Hx2.4, tq, *J* = 7.2, 7.2 Hz), 1.63 (2Hx1, tt, *J* = 7.6, 7.6 Hz), 1.82 (2Hx2.4, tt, *J* = 7.2, 7.4 Hz), 2.33 (3Hx2.4+3Hx1, s), 2.11 (2Hx1, t, *J* = 7.6 Hz), 2.77 (2Hx2.4, t, *J* = 7.4 Hz), 6.94-6.97 (2Hx1+1Hx2.4, m), 7.02 (1Hx2.4, d, *J* = 14.8 Hz), 7.09-7.14 (2Hx1+2Hx2.4, m), 7.19-7.27 (2Hx1+2Hx2.4, m), 7.31-7.38 (3Hx1+3Hx2.4, m), 7.58 (1Hx2.4, d, *J* = 7.6 Hz), 7.69 (1Hx1, d, *J* = 7.6 Hz), 8.77 (1Hx2.4, s br), 9.34 (1Hx1, s br); ¹³C NMR (100 MHz, CDCl₃) δ 13.5, 13.8, 21.1, 21.2, 21.9, 22.1, 31.1, 31.8, 40.0, 47.1, 121.0, 122.0, 125.9, 126.1, 126.5, 126.6, 127.5, 127.7, 127.7, 127.9, 128.0, 128.8, 129.3, 129.4,

131.2, 132.1, 133.6, 133.7, 134.0, 134.4, 135.0, 136.0, 137.9, 138.3, 207.1, 210.7 ;
ESIHRMS: Found: m/z 310.1629. Calcd for $C_{20}H_{24}NS$: $(M+H)^+$ 310.1629.

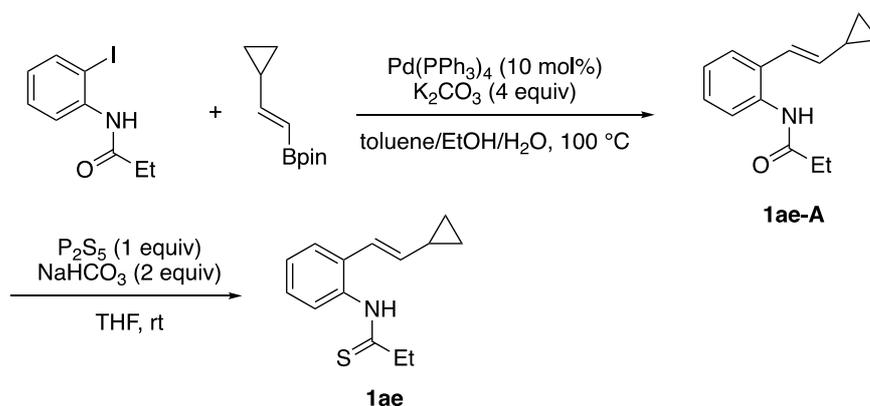
(*E*)-*N*-(2-((*E*)-styryl)phenyl)hex-3-enethioamide (1ac)



Following condition B and condition D, **1ac** was obtained in 76% yield (1.80 g, 5.85 mmol) as rotamers (5:1) from the reaction of (*E*)-2-styrylaniline (1.50 g, 7.68 mmol)¹⁴ and (*E*)-hex-3-enoic acid (0.88 g, 7.71 mmol).

Yellow solid; mp: 101-102 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.86 (3Hx1, t, J = 7.4 Hz), 0.94 (3Hx5, t, J = 7.4 Hz), 1.91 (2Hx1, dq, J = 7.4, 6.8 Hz), 1.37 (2Hx5, tq, J = 7.4, 7.2 Hz), 3.26 (2Hx1, d, J = 6.4 Hz), 3.67 (2Hx5, d, J = 6.8 Hz), 5.26 (1Hx1, dt, J = 14.8, 6.8 Hz), 5.50 (1Hx1, dt, J = 14.8, 6.4 Hz), 5.69 (1Hx5, dt, J = 14.0, 7.2 Hz), 5.85 (1Hx5, dt, J = 14.0, 6.8 Hz), 7.02 (2Hx5, s), 7.12 (2Hx1, s), 7.25-7.40 (5Hx1+5Hx5, m), 7.46 (2Hx5, d, J = 7.6 Hz), 7.50 (2Hx1, d, J = 7.6 Hz), 7.65-7.75 (2Hx1+2Hx5, m), 8.79 (1Hx5, s br), 9.14 (1Hx1, s br); ¹³C NMR (100 MHz, CDCl₃) δ 13.21, 13.24, 25.4, 25.6, 44.6, 51.4, 122.3, 122.5, 122.9, 123.2, 126.4, 126.5, 126.6, 126.8, 126.9, 127.9, 128.0, 128.16, 128.22, 128.4, 128.7, 128.8, 129.0, 132.4, 133.1, 134.5, 135.3, 135.8, 136.0, 136.5, 136.8, 140.0, 140.1, 202.9, 208.4; ESIHRMS: Found: m/z 308.1479. Calcd for $C_{20}H_{22}NS$: $(M+H)^+$ 308.1473.

(*E*)-*N*-(2-(2-cyclopropylvinyl)phenyl)propanethioamide (1ae)



To a solution of *N*-(2-iodophenyl)propanamide¹⁵ (5.00 g, 18.18 mmol), and (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane¹⁶ (3.52 g, 18.13 mmol), in toluene (20 mL), EtOH (8 mL) and H₂O (4 mL) was added Pd(PPh₃)₄ (2.36 g, 2.04 mmol) and K₂CO₃ (11.32 g, 81.90 mmol). The reaction mixture was stirred at 100 °C

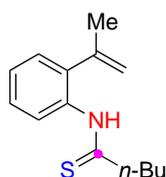
under N₂ for 12 h. The reaction was quenched with water and extracted three times with ethyl acetate. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and evaporated. The resulting crude material was purified by flash column chromatography to give (*E*)-*N*-(2-(2-cyclo propylvinyl)phenyl)propionamide (**1ae-A**) in 82% yield (3.21 g, 14.9 mmol).

White solid; mp: 106-107 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.49-0.54 (2H, m), 0.83-0.87 (2H, m), 1.27 (3H, t, *J* = 7.4 Hz), 1.55-1.64 (1H, m), 2.42 (2H, q, *J* = 7.4 Hz), 5.57 (1H, dd, *J* = 8.8, 15.6 Hz), 5.48 (1H, d, *J* = 15.6 Hz), 7.07 (1H, dd, *J* = 7.2, 8.0 Hz), 7.20 (1H, dd, *J* = 7.2, 7.6 Hz), 7.29 (1H, d, *J* = 7.6 Hz), 7.84 (1H, d, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 7.4, 9.8, 14.9, 30.6, 121.8, 123.3, 124.9, 126.7, 127.3, 130.0, 133.8, 139.3, 172.0; ESIHRMS: Found: *m/z* 216.1383. Calcd for C₂₀H₂₂NS: (M+H)⁺ 216.1388.

Following condition D, **1ae** was obtained in 80% yield (1.61 g, 7.54 mmol) as rotamers (1.3:1) from **1ae-A** (2.03 g, 9.43 mmol).

Yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.49-0.55 (2Hx1+2Hx1.2, m), 0.82-0.89 (2Hx1+2Hx1.3, m), 1.20 (3Hx1, t, *J* = 7.4 Hz), 1.44 (3Hx1.3, t, *J* = 7.6 Hz), 1.54-1.63 (1Hx1+1Hx1.3, m), 2.44 (2Hx1, q, *J* = 7.4 Hz), 2.88 (2Hx1.3, q, *J* = 7.6 Hz), 5.67 (1Hx1.3, dd, *J* = 9.2, 15.6 Hz), 5.72 (1Hx1, dd, *J* = 9.2, 15.6 Hz), 6.43 (1Hx1.3, d, *J* = 15.6 Hz), 6.50 (1Hx1, d, *J* = 15.6 Hz), 7.10 (1Hx1, d, *J* = 7.6 Hz), 7.20-7.32 (2Hx1+1Hx1.3, m), 7.31 (1Hx1.3, dd, *J* = 7.2, 7.6 Hz), 7.44-7.54 (1Hx1+1Hx1.3, m), 8.54 (1Hx1.3, s br), 9.17 (1Hx1, s br); ¹³C NMR (100 MHz, CDCl₃) δ 7.5, 7.7, 13.4, 13.8, 15.0, 15.1, 33.6, 40.7, 121.2, 121.6, 126.15, 126.20, 127.1, 127.2, 127.3, 127.4, 127.9, 128.8, 133.8, 134.1, 134.7, 135.0, 138.9, 139.8, 207.5, 211.9; ESIHRMS: Found: *m/z* 232.1156. Calcd for C₂₀H₂₂NS: (M+H)⁺ 232.1160.

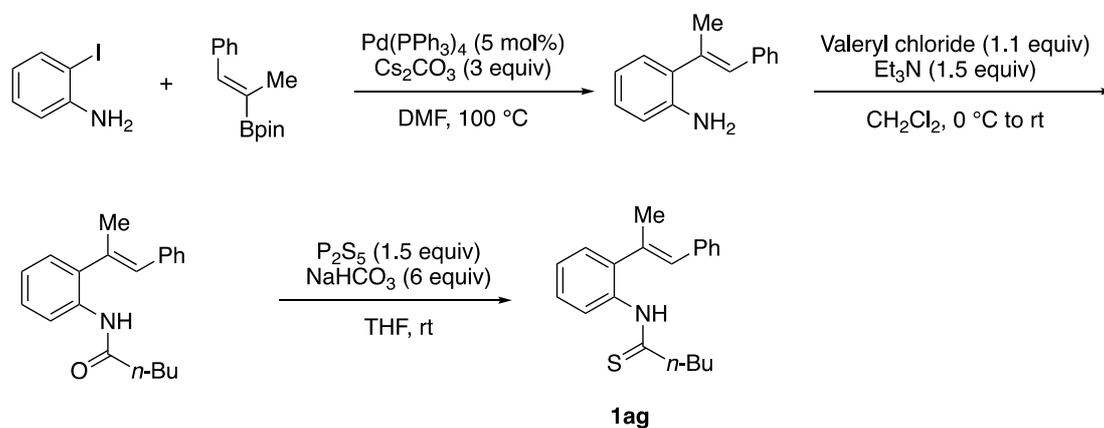
***N*-(2-(Prop-1-en-2-yl)phenyl)pentanethioamide (1af)**



Following condition A and condition D, **1af** was obtained in 66% yield (0.84 g, 3.60 mmol) as rotamers (4:1) from the reaction of 2-(prop-1-en-2-yl)aniline (0.72 g, 5.45 mmol)¹⁷ and valeryl chloride (0.7 mL, 5.90 mmol).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.82 (3Hx1, t, $J = 7.2$ Hz), 0.97 (3Hx4, t, $J = 7.4$ Hz), 1.27 (2Hx1, tq, $J = 7.6, 7.2$ Hz), 1.43 (2Hx4, tq, $J = 7.6, 7.4$ Hz) 1.74 (2Hx1, tt, $J = 7.6, 7.6$ Hz), 1.82 (2Hx4, tt, $J = 7.6, 7.6$ Hz), 2.05 (3Hx1+3Hx4, m), 2.55 (2Hx1, t, $J = 7.6$ Hz), 2.79 (2Hx4, t, $J = 7.6$ Hz), 4.99 (1Hx1, s), 5.01 (1Hx4, s), 5.30 (1Hx1, s), 5.33 (1Hx4, s), 7.14-7.15 (1Hx1, m), 7.23-7.32 (3Hx1+3Hx4, m), 8.22 (1Hx4, d, $J = 8.0$ Hz), 8.77 (1Hx4, s br), 9.19 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 13.8, 22.0, 22.2, 23.4, 24.0, 31.3, 31.6, 39.8, 48.6, 116.8, 117.9, 125.31, 125.32, 126.7, 126.8, 127.3, 128.1, 128.2, 129.4, 134.5, 134.9, 137.69, 137.70, 142.2, 142.6, 204.9, 209.7; ESIHRMS: Found: m/z 234.1319. Calcd for $\text{C}_{14}\text{H}_{20}\text{NS}$: $(\text{M}+\text{H})^+$ 234.1316.

(E)-N-(2-(1-Phenylprop-1-en-2-yl)phenyl)pentanethioamide (1ag)



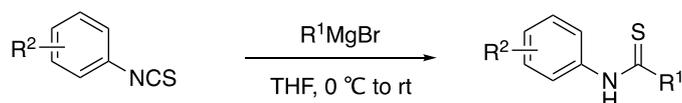
To a solution of 2-iodoaniline (2.17 g, 9.92 mmol) and (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (2.42 g, 9.93 mmol)¹⁸ in DMF (30 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (575.10 mg, 0.50 mmol) and CsCO_3 (9.74 g, 29.89 mmol). The reaction mixture was stirred at 100°C under N_2 until TLC indicating 2-iodoaniline disappeared. The reaction was quenched with water and extracted three times with ethyl acetate. The combined organic extracts were washed with H_2O , brine, and dried over Na_2SO_4 . The solvent was removed in *vacuo* and the resulting crude material was submitted to the next step without further purification.

Following condition A and condition D, **1ag** was obtained as rotamers (3.8:1) from the reaction of (*E*)-2-(1-phenylprop-1-en-2-yl)aniline and valeryl chloride (1.3 mL, 10.95 mmol). The overall yield of three step is 80% yield (2.45 g, 7.58 mmol).

Yellow solid; mp: $70\text{--}71^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.82 (3Hx1, t, $J = 7.4$ Hz), 0.87 (3Hx3.8, t, $J = 7.4$ Hz), 1.27 (2Hx1, tq, $J = 7.6, 7.4$ Hz), 1.37 (2Hx3.8, tq, $J = 7.6, 7.4$ Hz), 1.74-1.82 (2Hx1+2Hx3.8, m), 2.17 (3Hx1, s), 2.21 (3Hx3.8, s), 2.59 (2Hx1, t,

$J = 7.8$ Hz), 2.79 (2Hx3.8, t, $J = 7.8$ Hz), 6.51 (1Hx1+1Hx3.8, s), 7.19 (1Hx1, d, $J = 7.2$ Hz), 7.26-7.41 (8Hx1+8Hx3.8, m), 8.18 (1Hx3.8, d, $J = 8.0$ Hz), 8.69 (1Hx3.8, s br), 9.16 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 19.2, 19.7, 22.1, 22.3, 31.5, 31.7, 39.9, 48.6, 126.0, 126.8, 127.08, 127.09, 127.3, 128.0, 128.3, 128.37, 128.45, 128.8, 128.9, 129.01, 129.05, 129.7, 131.1, 132.2, 134.8, 135.2, 135.3, 136.9, 140.2, 142.1, 205.2, 209.8; ESIHRMS: Found: m/z 310.1625. Calcd for $\text{C}_{20}\text{H}_{24}\text{NS}$: $(\text{M}+\text{H})^+$ 310.1629.

Method 2



To a solution of isothiocyanate in THF was added Grignard reagent dropwise at 0 °C under N_2 atmosphere. After stirring for 10 minutes, the reaction mixture was warmed to room temperature. After isothiocyanate disappeared, the reaction mixture was quenched by saturated NH_4Cl (aq) and extracted three times with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The crude material was purified by flash column chromatography to give the desired thioamide.

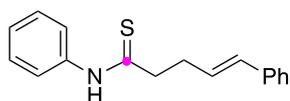
3-(1,3-Dioxan-2-yl)-*N*-phenylpropanethioamide (1m)



Thioamide **1m** was obtained in 78% yield (1.80 g, 7.16 mmol) as rotamers (10:1) from the reaction of (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide (10 mL, 1M in THF) and isothiocyanatobenzene (1.24 g, 9.17 mmol). ^1H and ^{13}C NMR were described for the major isomer.

Yellow solid; mp: 66-68 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.39-1.42 (1H, m), 2.08-2.17 (3H, m), 3.06 (2H, t, $J = 6.6$ Hz), 3.84 (2H, m), 4.16-4.20 (2H, m), 4.72 (1H, t, $J = 4.6$ Hz), 7.25 (1H, t, $J = 7.2$ Hz), 7.40 (2H, dd, $J = 7.2, 7.6$ Hz), 7.72 (2H, d, $J = 7.6$ Hz), 9.74 (1H, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 25.6, 33.28, 33.30, 42.8, 66.9, 100.7, 123.1, 126.5, 128.8, 139.0, 203.7; ESIHRMS: Found: m/z 252.1060. Calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{S}$: $(\text{M}+\text{H})^+$ 252.1058.

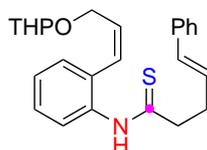
(E)-N,5-Diphenylpent-4-enethioamide (1o)



Thioamide **1o** was obtained in 74% yield (1.60 g, 5.98 mmol) as rotamers (3.8:1) from the reaction of (*E*)-(4-phenylbut-3-en-1-yl)magnesium bromide (10 mL, 1M in THF) and isothiocyanato benzene (1.09 g, 8.08 mmol).

Yellow solid, mp: 90-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.69-2.82 (2Hx2+2Hx3.8, m), 2.95 (2Hx3.8, t, *J* = 6.8 Hz), 6.09 (1Hx1, td, *J* = 6.8, 15.6 Hz), 6.27 (1Hx3.8, td, *J* = 6.8, 15.6 Hz), 6.34 (1Hx1, d, *J* = 15.6 Hz), 6.51(1Hx3.8, d, *J* = 15.6 Hz), 7.14 (2Hx1, d, *J* = 7.6 Hz), 7.20-7.43 (8Hx1+8Hx3.8, m), 7.61 (2Hx3.8, d, *J* = 8.0 Hz), 8.75 (1Hx3.8, s br), 9.44 (1Hx1, s br); ¹³C NMR (100 MHz, CDCl₃) δ 32.8, 32.9, 39.8, 48.3, 123.9, 125.7, 126.0, 126.1, 127.0, 127.1, 127.3, 127.9, 128.17, 128.22, 128.5, 128.6, 128.9, 129.7, 131.1, 131.9, 137.1, 137.2, 137.5, 138.5, 203.8, 208.6; ESIHRMS: Found: *m/z* 268.1160. Calcd for C₁₇H₁₈NS: (M+H)⁺ 268.1160.

(E)-5-Phenyl-N-(2-((Z)-3-((tetrahydro-2H-pyran-2-yl)oxy)prop-1-en-1-yl)phenyl)pent-4-enethioamide (1ad)

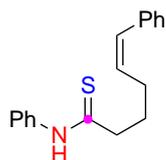


Thioamide **1ad** was obtained in 92% yield (1.71 g, 4.19 mmol) as rotamers (5.8:1) from the reaction of (*E*)-(4-phenylbut-3-en-1-yl)magnesium bromide (6 mL, 1M in THF) and (*Z*)-2-((3-(2-isothiocyanatophenyl)allyl)oxy)tetrahydro-2H-pyran (1.25 g, 4.56 mmol).¹⁹ ¹³C NMR was described for the major isomer.

Yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.50-1.57 (4Hx1+4Hx5.8, m), 1.66-1.82 (2Hx1+2Hx5.8, m), 2.80 (2Hx5.8, dt, *J* = 7.2, 7.2Hz), 2.89-2.97 (2Hx1+2Hx5.8, t, *J* = 7.2 Hz), 3.44-3.47 (1Hx1+1Hx5.8, m), 3.75-3.80 (1Hx1+1Hx5.8, m), 3.97 (1Hx5.8, dd, *J* = 7.2, 12.0Hz), 4.10 (1Hx1, dd, *J* = 7.2, 12.0Hz), 4.18 (1Hx5.8, dd, *J* = 6.8, 12.0 Hz), 4.33 (1Hx1, dd, *J* = 6.8, 12.0 Hz), 4.57 (1Hx5.8, s), 4.61 (1Hx1, s), 5.72 (1Hx1, td, *J* = 7.2, 10.8 Hz), 5.89 (1Hx5.8, td, *J* = 7.2, 10.8 Hz), 5.94-6.05 (1H, m), 6.27 (1Hx5.8, td, *J* = 7.2, 16.0 Hz), 6.48-6.53 (2Hx1+2Hx5.8, m), 7.14-7.36 (9Hx1+8Hx5.8, m), 7.76 (1Hx5.8, d, *J* = 8.0 Hz), 9.27 (1Hx5.8, s br), 9.34 (1Hx1, s

br); ^{13}C NMR (100 MHz, CDCl_3) δ 19.1, 19.4, 25.2, 28.5, 30.3, 30.5, 32.6, 32.8, 39.8, 47.0, 62.0, 62.5, 63.7, 63.9, 98.3, 98.4, 125.87, 125.94, 126.6, 126.8, 126.96, 127.10, 127.13, 127.8, 128.0, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 129.7, 130.0, 130.25, 130.29, 130.6, 130.9, 131.3, 131.8, 132.3, 135.8, 136.3, 137.0, 137.2, 204.7, 208.5; ESIHRMS: Found: m/z 430.1814. Calcd for $\text{C}_{25}\text{H}_{29}\text{NO}_2\text{SNa}$: $(\text{M}+\text{Na})^+$ 430.1817.

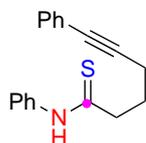
(Z)-N,6-diphenylhex-5-enethioamide (1ah)



Thioamide **1ah** was obtained in 33% yield (0.24 g, 0.85 mmol) as a mixture of isomers (rotamers, 3.9:1; $Z:E = 8:1$) from the reaction of (5-phenylpent-4-en-1-yl)magnesium bromide ($Z:E = 8:1$) (7 mL, 1M in THF) and isothiocyanatobenzene (3.49 g, 2.58 mmol). ^1H and ^{13}C NMR were described for the Z isomer.

Yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 1.93 (2Hx1, tt, $J = 7.2, 7.8$ Hz), 2.06 (2Hx3.9, tt, $J = 7.2, 7.4$ Hz), 2.28 (2Hx1, dt, $J = 7.2, 7.2$ Hz), 2.47 (2Hx3.9, dt, $J = 7.2, 7.2$ Hz), 2.61 (2Hx1, t, $J = 7.8$ Hz), 2.78 (2Hx3.9, t, $J = 7.4$ Hz), 5.51 (1Hx1, dt, $J = 7.2, 11.6$ Hz), 5.67 (1Hx3.9, dt, $J = 7.2, 11.6$ Hz), 6.37 (1Hx1, d, $J = 11.6$ Hz), 6.51 (1Hx3.9, d, $J = 11.6$ Hz), 7.11-7.47 (10Hx1+10Hx3.9, m), 8.52 (1Hx3.9, s br), 9.40 (1Hx1, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 27.2, 27.8, 29.56, 29.61, 39.7, 47.8, 123.8, 124.0, 125.6, 126.0, 126.5, 126.7, 126.9, 128.1, 128.2, 128.5, 128.6, 128.7, 128.8, 128.9, 129.6, 130.0, 131.5, 131.6, 137.2, 138.4, 204.8, 209.4; ESIHRMS: Found: m/z 304.1138. Calcd for $\text{C}_{18}\text{H}_{19}\text{NSNa}$: $(\text{M}+\text{Na})^+$ 304.1136.

N,6-Diphenylhex-5-ynethioamide(1ai)



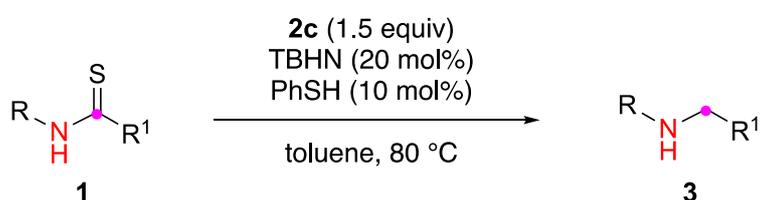
Thioamide **1ai** was obtained in 39% yield (1.11 g, 3.97 mmol) as rotamers (3.5:1) from the reaction of (5-phenylpent-4-yn-1-yl)magnesium bromide (15 mL, 1M in THF) and isothiocyanatobenzene (1.38 g, 10.19mmol).

Yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 2.10 (2Hx1, tt, $J = 7.6, 6.6$ Hz), 2.18 (2Hx3.5, tt, $J = 7.0, 6.4$ Hz), 2.44 (2Hx1, t, $J = 6.6$ Hz), 2.56 (2Hx3.5, t, $J = 6.4$ Hz), 2.79 (2Hx1, t, $J = 7.6$ Hz), 2.99 (2Hx3.5, t, $J = 7.0$ Hz), 7.17 (2Hx1, d, $J = 7.6$ Hz),

7.24-7.41 (8Hx1+8Hx3.5, m), 7.67 (2Hx3.5, d, $J = 7.6$ Hz), 8.93 (1Hx3.5, s br); ^{13}C NMR (100 MHz, CDCl_3) δ 18.2, 18.6, 27.9, 28.1, 38.7, 47.0, 81.5, 82.1, 88.8, 91.4, 123.4, 123.7, 123.7, 125.6, 126.9, 127.6, 127.9, 128.0, 128.1, 128.3, 128.9, 129.6, 131.45, 131.52, 137.4, 138.5, 203.9, 208.7; ESIHRMS: Found: m/z 280.1163. Calcd for $\text{C}_{18}\text{H}_{18}\text{NS}$: $(\text{M}+\text{H})^+$ 280.1160.

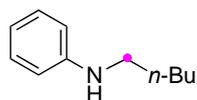
3. Lewis base-boryl radicals enabled reduction of thioamides

A general procedure:



To an N_2 flushed, over-dried glass tube with a magnetic stir bar, thioamides **1** (0.3 mmol), **2c** (0.45 mmol), TBHN (0.06 mmol), PhSH (0.03 mmol), and toluene (3 mL) were added. The tube was sealed and the reaction mixture was stirred at 80°C until the TLC analysis indicating the consumption of **1**. The resulting mixture was cooled down to room temperature and concentrated. The crude mixture was purified by flash column chromatography on silica gel to give pure amine **3**.

N-Entylaniline (**3a**)



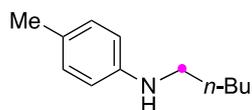
According to the general procedure, the reaction of *N*-phenylpentanethioamide **1a** (57.7 mg, 0.299 mmol), **2c** (60.1 mg, 1.5 equiv), TBHN (9.9 mg, 20 mol%), PhSH (3 μL , 10 mol%), and toluene (3 mL) under nitrogen at 80°C for 15 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 47.8 mg (98%) of **3a** as a colourless liquid.

1mmol scale reaction: according to the general procedure, the reaction of *N*-phenylpentanethioamide **1a** (193.5 mg, 1.001 mmol), **2c** (204.6 mg, 1.5 equiv), TBHN (35.5 mg, 20 mol %), PhSH (21 μL , 10 mol %), and toluene (5 mL) under

nitrogen at 80 °C for 15 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 153.6 mg (94%) of **3a**.

¹H NMR (400 MHz, CDCl₃) δ 0.94 (3H, t, *J* = 6.8 Hz), 1.35-1.41 (4H, m), 1.64 (2H, tt, *J* = 6.8, 7.0 Hz), 3.11 (2H, t, *J* = 7.0 Hz), 3.40 (1H, s br), 6.62 (2H, d, *J* = 8.0 Hz), 6.70 (1H, dd, *J* = 7.8, 8.0 Hz), 7.19 (2H, t, *J* = 7.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 29.27, 29.34, 44.0, 112.7, 117.1, 129.2, 148.5. The spectral data for this compound matches that reported in the literature.²⁰

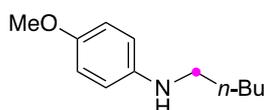
4-Methyl-*N*-pentylaniline (**3b**)



According to the general procedure, the reaction of *N*-(*p*-tolyl)hexanethioamide **1b** (104.2 mg, 0.503 mmol), **2c** (102.7 mg, 1.5 equiv), TBHN (17.8 mg, 20 mol%), PhSH (5 μL, 10 mol%), and toluene (5 mL) under nitrogen at 80 °C for 15 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 77.4 mg (87%) of **3b** as a colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (3H, t, *J* = 6.8 Hz), 1.32-1.38 (4H, m), 1.57 (2H, tt, *J* = 6.8, 7.2 Hz), 2.22 (3H, s), 3.06 (2H, t, *J* = 7.2 Hz), 3.38 (1H, s br), 6.51 (2H, d, *J* = 8.0 Hz), 6.97 (2H, d, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 20.3, 22.5, 29.27, 29.31, 44.3, 112.8, 126.2, 129.6, 146.3. The spectral data for this compound matches that reported in the literature.²¹

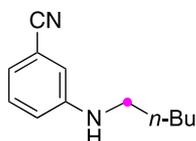
1mmol scale reaction: according to the general procedure, the reaction of *N*-(*p*-tolyl)hexanethioamide **1b** (207.0 mg, 0.9984 mmol), **2c** (203.8 mg, 1.5 equiv), TBHN (35.4 mg, 20 mol %), PhSH (21 μL, 10 mol %), and toluene (5 mL) under nitrogen at 80 °C for 15 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 139.5 mg (79%) of **3b**.

4-Methoxy-*N*-pentylaniline (**3c**)



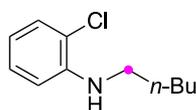
According to the general procedure, the reaction of *N*-(4-Methoxyphenyl)pentanethioamide **1c** (111.7 mg, 0.503 mmol), **2c** (101.6 mg, 1.5 equiv), TBHN (18.0 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 27 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 80.5 mg (83%) of **3c** as a colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.0$ Hz), 1.33-1.39 (4H, m), 1.61 (2H, tt, $J = 7.0, 7.2$ Hz), 3.06 (2H, t, $J = 7.0$ Hz), 3.75 (3H, s), 6.58 (2H, d, $J = 8.8$ Hz), 6.78 (2H, d, $J = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.5, 29.3(overlapped), 45.0, 55.8, 114.0, 114.8, 142.8, 151.9. The spectral data for this compound matches that reported in the literature.²²

3-(Pentylamino)benzonitrile (**3d**)



According to the general procedure, the reaction of *N*-(3-Cyanophenyl)pentanethioamide **1d** (65.5 mg, 0.300 mmol), **2c** (62.0 mg, 1.5 equiv), TBHN (10.3 mg, 20 mol%), PhSH (3 μ L, 10 mol%), and toluene (3 mL) under nitrogen at 80 $^{\circ}$ C for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) to afford 42.3 mg (75%) of **3d** as a yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (3H, t, $J = 6.4$ Hz), 1.35-1.39 (4H, m), 1.62 (2H, tt, $J = 7.0, 6.8$ Hz), 3.08 (2H, t, $J = 7.0$ Hz), 3.88 (1H, s br), 6.75-6.77 (2H, m), 6.92 (1H, d, $J = 7.6$ Hz), 7.20 (1H, t, $J = 7.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.4, 28.8, 29.1, 43.5, 112.8, 114.5, 117.0, 119.5, 120.2, 129.7, 148.6; ESIHRMS: Found: m/z 189.1396. Calcd for $\text{C}_{12}\text{H}_{17}\text{N}_2$: ($\text{M}+\text{H}$)⁺ 189.1392.

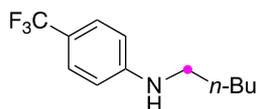
2-Chloro-*N*-pentylaniline (**3e**)



According to the general procedure, the reaction of *N*-(2-Chlorophenyl)pentanethioamide **1e** (114.1 mg, 0.501 mmol), **2c** (102.7 mg, 1.5 equiv), TBHN (17.7 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 1 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60 : 1) to afford 69.8 mg (70%) of **3e** as a colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.93 (3H, t, $J = 6.6$ Hz), 1.33-1.44 (4H, m), 1.67 (2H, tt, J

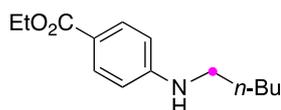
= 6.8, 7.2 Hz), 3.14 (2H, dt, $J = 4.8, 7.2$ Hz), 4.26 (1H, s br), 6.60 (1H, dd, $J = 7.6, 8.0$ Hz), 6.65 (1H, d, $J = 7.8$ Hz), 7.13 (1H, dd, $J = 7.6, 7.8$ Hz), 7.24 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.5, 29.0, 29.3, 43.6, 111.0, 116.7, 118.9, 127.7, 129.0, 144.2; ESIHRMS: Found: m/z 198.1055. Calcd for $\text{C}_{11}\text{H}_{17}\text{ClN}$: $(\text{M}+\text{H})^+$ 198.1050.

***N*-Pentyl-4-(trifluoromethyl)aniline (3f)**



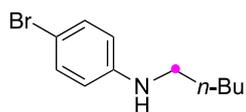
According to the general procedure, the reaction of *N*-(4-(Trifluoromethyl)phenyl)pentanethioamide **1f** (130.3 mg, 0.499 mmol), **2c** (101.9 mg, 1.5 equiv), TBHN (17.8 mg, 20 mol%), PhSH (5 μL , 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}\text{C}$ for 12 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 107.5 mg (94%) of **3f** as a colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.93 (3H, t, $J = 6.8$ Hz), 1.35-1.40 (4H, m), 1.63 (2H, tt, $J = 6.8, 7.6$ Hz), 3.13 (2H, t, $J = 6.8$ Hz), 3.95 (1H, s br), 6.58 (2 H, d, $J = 8.4$ Hz), 7.39 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.4, 29.0, 29.2, 43.4, 111.6, 118.3 (q, $J = 32.4$ Hz), 125.1 (q, $J = 268.5$ Hz), 126.5 (q, $J = 3.7$ Hz), 150.9; ^{19}F NMR(CDCl_3 , 376 MHz): δ -60.9 (3F, s); ESIHRMS: Found: m/z 232.1311. Calcd for $\text{C}_{12}\text{H}_{17}\text{F}_3\text{N}$: $(\text{M}+\text{H})^+$ 232.1313.

Ethyl 4-(pentylamino)benzoate (3g)



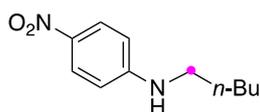
According to the general procedure, the reaction of Ethyl 4-pentanethioamidobenzoate **1g** (132.4 mg, 0.501 mmol), **2c** (101.6 mg, 1.5 equiv), TBHN (17.5 mg, 20 mol%), PhSH (5 μL , 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}\text{C}$ for 20 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) to afford 103.5 mg (88%) of **3g** as a white solid; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (3H, t, $J = 7.0$ Hz), 1.34-1.39 (7H, m), 1.63 (2H, tt, $J = 6.8, 7.2$ Hz), 3.13-3.17 (2H, m), 4.07 (1H, s br), 4.30 (2H, q, $J = 7.2$ Hz), 6.53 (2 H, d, $J = 8.4$ Hz), 7.86 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 14.3, 22.3, 28.9, 29.1, 43.2, 60.0, 111.1, 118.0, 131.4, 152.1, 166.8. The spectral data for this compound matches that reported in the literature.²³

4-Bromo-*N*-pentylaniline (3h)



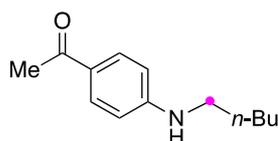
According to the general procedure, the reaction of *N*-(4-Bromophenyl)pentanethioamide **1h** (136.1 mg, 0.500 mmol), **2c** (101.9 mg, 1.5 equiv), TBHN (17.4 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 15 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100 : 1) to afford 84.8 mg (70%) of **3h** as a yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.91 (3H, t, J = 6.8 Hz), 1.33-1.35 (4H, m), 1.58 (2H, tt, J = 7.2, 7.2 Hz), 3.03 (2H, t, J = 7.2 Hz), 3.60 (1H, s), 6.44 (2H, d, J = 8.8 Hz), 7.21 (2H, d, J = 8.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.4, 29.0, 29.2, 43.9, 108.4, 114.1, 131.8, 147.4. The spectral data for this compound matches that reported in the literature.²²

4-Nitro-*N*-pentylaniline (**3i**)



According to the general procedure, the reaction of *N*-(4-Nitrophenyl)pentanethioamide **1i** (120.5 mg, 0.506 mmol), **2c** (103.4 mg, 1.5 equiv), TBHN (17.5 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 11 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford 34.3 mg (33%) of **3i** as a yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 0.92 (3H, t, J = 6.6 Hz), 1.35-1.40 (4H, m), 1.66 (2H, tt, J = 7.2, 6.4 Hz), 3.19 (2H, dt, J = 6.4, 6.4 Hz), 4.51 (1H, s), 6.51 (2H, d, J = 9.2 Hz), 8.07 (2H, d, J = 9.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.4, 28.8, 29.1, 43.4, 110.8, 126.4, 137.7, 153.4. The spectral data for this compound matches that reported in the literature.²¹

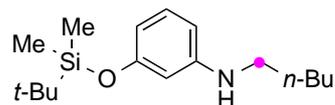
1-(4-(Pentylamino)phenyl)ethan-1-one (**3j**)



According to the general procedure, the reaction of *N*-(4-Acetylphenyl)pentanethioamide **1j** (118.0 mg, 0.501 mmol), **2c** (102.2 mg, 1.5 equiv), TBHN (17.5 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 3 h after flash column chromatography on silica gel (petroleum

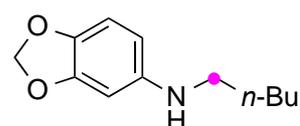
ether : ethyl acetate = 6 : 1) to afford 35.1 mg (34%) of **3j** as a white solid; mp: 91-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (3H, t, *J* = 6.6 Hz), 1.35-1.37 (4H, m), 1.63 (2H, tt, *J* = 6.4, 6.8 Hz), 2.49 (3H, s), 3.13-3.17 (2H, m), 4.25 (1H, s br), 6.53 (2H, d, *J* = 8.4 Hz), 7.81 (2H, d, *J* = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.4, 25.9, 28.9, 29.1, 43.2, 111.1, 126.3, 130.8, 152.3, 196.3; ESIHRMS: Found: *m/z* 206.1544. Calcd for C₁₃H₂₀NO: (M+H)⁺ 206.1545

3-((*tert*-Butyldimethylsilyloxy)-*N*-pentylaniline (**3k**))



According to the general procedure, the reaction of *N*-(3-((*tert*-Butyldimethylsilyloxy)phenyl)pentanethioamide **1k** (97.4 mg, 0.301 mmol), **2c** (61.4 mg, 1.5 equiv), TBHN (10.5 mg, 20 mol%), PhSH (3 μL, 10 mol%), and toluene (3 mL) under nitrogen at 80 °C for 9 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 73.0 mg (83%) of **3k** as a colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.19 (6H, s), 0.92 (3H, t, *J* = 6.8 Hz), 0.98 (9H, s), 1.36-1.40 (4H, m), 1.61 (2H, tt, *J* = 6.8, 7.2 Hz), 3.07 (2H, t, *J* = 7.2 Hz), 3.55 (1H, s br), 6.11 (1H, s), 6.19 (1H, d, *J* = 8.0 Hz), 6.22 (1H, d, *J* = 8.4 Hz), 7.00 (1H, dd, *J* = 8.0, 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ -4.4, 14.0, 18.2, 22.5, 25.7, 29.2, 29.3, 44.0, 104.4, 106.3, 108.9, 129.7, 149.9, 156.7; ESIHRMS: Found: *m/z* 294.2257. Calcd for C₁₇H₃₂NOSi: (M+H)⁺ 294.2253.

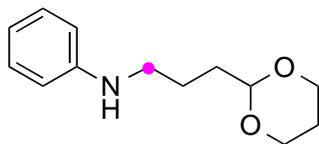
N-Pentylbenzo[*d*][1,3]dioxol-5-amine (**3l**)



According to the general procedure, the reaction of *N*-(Benzo[*d*][1,3]dioxol-5-yl)pentanethioamide **1l** (118.3 mg, 0.498 mmol), **2c** (101.9 mg, 1.5 equiv), TBHN (17.5 mg, 20 mol%), PhSH (5 μL, 10 mol%), and toluene (5 mL) under nitrogen at 80 °C for 11 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) to afford 90.4 mg (88%) of **3l** as a colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.93 (3H, t, *J* = 6.4 Hz), 1.36-1.41 (4H, m), 1.60 (2H, tt, *J* = 6.8, 7.2 Hz), 3.03 (2H, t, *J* = 7.2 Hz), 3.39 (1H, s br), 5.85 (2 H, s), 6.04 (1H, dd, *J* = 1.6, 8.4Hz), 6.25 (1H, d, *J* = 1.6 Hz), 6.66 (1H, d, *J* = 8.4 Hz); ¹³C NMR (100 MHz,

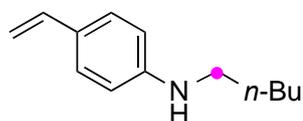
CDCl₃) δ 14.0, 22.4, 29.2, 29.3, 44.9, 95.7, 100.4, 104.1, 108.5, 139.3, 144.3, 148.2; ESIHRMS: Found: m/z 208.1339. Calcd for C₁₂H₁₈NO₂: (M+H)⁺ 208.1338.

N-(3-(1,3-Dioxan-2-yl)propyl)aniline (**3m**)



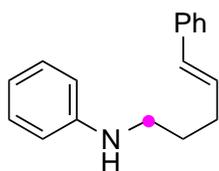
According to the general procedure, the reaction of 3-(1,3-Dioxan-2-yl)-*N*-phenylpropanethioamide **1m** (125.1 mg, 0.498 mmol), **2c** (101.5 mg, 1.5 equiv), TBHN (17.3 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 °C for 40 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) to afford 88.2 mg (80%) of **3m** as a colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.32-1.36 (1H, m), 1.70-1.75 (4H, m), 2.03-2.15 (1H, m), 3.14 (2H, t, J = 6.6 Hz), 3.71 (1H, s br), 3.74-3.80 (2H, m), 4.10-4.14 (2H, m), 4.58 (1H, t, J = 4.4 Hz), 6.59 (2 H, d, J = 8.0 Hz), 6.68 (1H, t, J = 7.4 Hz), 7.17 (2H, dd, J = 7.4, 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 23.7, 25.6, 32.5, 43.5, 66.7, 101.8, 112.5, 116.9, 129.1, 148.3; ESIHRMS: Found: m/z 222.1493. Calcd for C₁₃H₂₀NO₂: (M+H)⁺ 222.1494.

N-Pentyl-4-vinylaniline (**3n**)



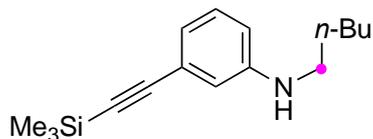
To a solution of thioamide **1n** (65.7 mg, 0.300 mol) in toluene (3 mL) was added **2c** (61.6 mg, 0.453 mmol), BEt₃ (0.15 mL, 1.0 M in hexane) and PhSH (3 μ L, 0.029 mmol). The reaction was stirred at 40 °C under air for 4 h. The solvent was removed in *vacuo* and the resulting crude material was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 80 : 1) to afford 29.7 mg (52%) of **3n** as a yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (3H, t, J = 6.6 Hz), 1.35-1.37 (4H, m), 1.61 (2H, tt, J = 6.8, 7.2 Hz), 3.10 (2H, t, J = 7.2 Hz), 3.65 (1H, s br), 4.99 (1H, d, J = 10.8 Hz), 5.51 (1H, d, J = 17.6 Hz), 6.54 (2H, d, J = 8.4 Hz), 6.61 (1H, dd, J = 10.8, 17.6 Hz), 7.24 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 29.2, 29.3, 43.9, 109.1, 112.5, 126.8, 127.3, 136.7, 148.3; ESIHRMS: Found: m/z 190.1599. Calcd for C₁₃H₂₀N: (M+H)⁺ 190.1596.

(*E*)-*N*-(5-Phenylpent-4-en-1-yl)aniline (**3o**)



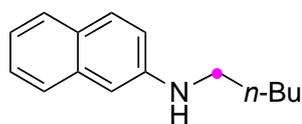
According to the general procedure, the reaction of (*E*)-*N*,5-Diphenylpent-4-enethioamide **1o** (133.6 mg, 0.500 mmol), **2c** (102.7 mg, 1.5 equiv), TBHN (17.5 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 36 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100 : 1) to afford 81.2 mg (68%) of **3o** as a brown liquid; ^1H NMR (400 MHz, CDCl_3) δ 1.75 (2H, tt, $J = 7.2, 7.2$ Hz), 2.29 (2H, dt, $J = 6.8, 7.2$ Hz), 3.13 (2H, t, $J = 7.2$ Hz), 3.57 (1H, s br), 6.21 (1H, td, $J = 6.8, 15.6$ Hz), 6.40 (1H, d, $J = 15.6$ Hz), 6.57 (2H, d, $J = 8.0$ Hz), 6.68 (1H, t, $J = 7.2$ Hz), 7.14-7.20 (3H, m), 7.26-7.33 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 29.0, 30.5, 43.3, 112.6, 117.1, 125.9, 126.9, 128.4, 129.2, 129.8, 130.4, 137.5, 148.3. The spectral data for this compound matches that reported in the literature.²⁴

N-Pentyl-3-((trimethylsilyl)ethynyl)aniline (**3p**)



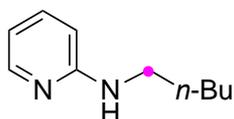
According to the general procedure, the reaction of *N*-(3-((Trimethylsilyl)ethynyl)phenyl)pentanethioamide **1p** (87.9 mg, 0.304 mmol), **2c** (62.0 mg, 1.5 equiv), TBHN (10.1 mg, 20 mol%), PhSH (3 μ L, 10 mol%), and toluene (3 mL) under nitrogen at 80 $^{\circ}$ C for 22 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 62.3 mg (79%) of **3p** as a yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.24 (9H, s), 0.92 (3H, t, $J = 6.4$ Hz), 1.35-1.37 (4H, m), 1.61 (2H, tt, $J = 6.4, 7.2$ Hz), 3.08 (2H, t, $J = 7.2$ Hz), 3.60 (1H, s br), 6.55 (1H, d, $J = 8.0$ Hz), 6.69 (1H, s), 6.80 (1H, d, $J = 7.6$ Hz), 7.08 (1H, dd, $J = 7.6, 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 0.0, 14.0, 22.4, 29.1, 29.3, 43.8, 92.9, 105.9, 113.5, 115.4, 120.9, 123.6, 128.9, 148.2. ESIHRMS: Found: m/z 260.1839. Calcd for $\text{C}_{16}\text{H}_{26}\text{NSi}$: ($\text{M}+\text{H}$) $^+$ 260.1835.

N-Pentyl-naphthalen-2-amine (**3q**)



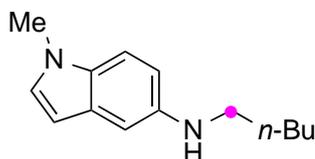
According to the general procedure, the reaction of *N*-(Naphthalen-2-yl)pentanethioamide (**1q**) (121.8 mg, 0.500 mmol), **2c** (101.9 mg, 1.5 equiv), TBHN (18.0 mg, 20 mol%), PhSH (5 μ L, 10 mol%), and toluene (5 mL) under nitrogen at 80 $^{\circ}$ C for 14 min after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60 : 1) to afford 87.1 mg (82%) of **3q** as a yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 0.96 (3H, t, $J = 7.0$ Hz), 1.36-1.48 (4H, m), 1.70 (2H, tt, $J = 7.2, 7.2$ Hz), 3.22 (2H, t, $J = 7.2$ Hz), 3.80 (1H, s br), 6.81 (1H, d, $J = 1.6$ Hz), 6.88 (1H, dd, $J = 1.6, 8.4$ Hz), 7.20 (1H, dd, $J = 7.4, 8.4$ Hz), 7.37 (1H, dd, $J = 7.4, 8.4$ Hz), 7.62-7.64 (2H, m), 7.67 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.5, 29.0, 29.3, 43.9, 104.0, 117.9, 121.7, 125.8, 126.2, 127.3, 127.6, 128.8, 135.3, 146.1. ESIHRMS: Found: m/z 214.1594. Calcd for $\text{C}_{15}\text{H}_{20}\text{N}$: (M+H) $^+$ 214.1596.

N-Pentylpyridin-2-amine (**3r**)



According to the general procedure, the reaction of *N*-(Pyridin-2-yl)pentanethioamide (**1r**) (50.8 mg, 0.298 mmol), **2c** (60.9 mg, 1.5 equiv), TBHN (9.9 mg, 20 mol%), PhSH (3 μ L, 10 mol%), and toluene (3 mL) under nitrogen at 80 $^{\circ}$ C for 3 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1 + 5% NEt_3) to afford 21.0 mg (43%) of **3r** as a yellow colorless; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (3H, t, $J = 6.8$ Hz), 1.32-1.37 (4H, m), 1.62 (2H, tt, $J = 7.2, 7.2$ Hz), 3.23 (2H, dt, $J = 6.8, 7.2$ Hz), 4.51 (1H, s br), 6.36 (1H, d, $J = 8.4$ Hz), 6.54 (1H, dd, $J = 6.0, 7.6$ Hz), 7.40 (1H, dd, $J = 7.6, 8.4$ Hz), 8.06 (1H, d, $J = 6.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.4, 29.2, 30.9, 42.2, 106.2, 112.5, 137.5, 148.0, 158.9. The spectral data for this compound matches that reported in the literature.²⁵

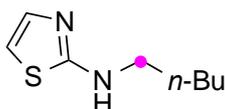
1-Methyl-*N*-pentyl-1*H*-indol-6-amine (**3s**)



According to the general procedure, the reaction of *N*-(1-Methyl-1*H*-indol-5-yl)pentanethioamide (**1s**) (74.3 mg, 0.302 mmol), **2c** (61.6 mg, 1.5 equiv), TBHN (10.4 mg, 20 mol%), PhSH (3 μ L, 10 mol%), and toluene (3 mL) under nitrogen at 80 $^{\circ}$ C for 3 h, after flash column chromatography on silica gel (petroleum ether : ethyl

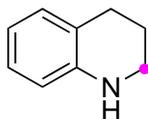
acetate = 40 : 1 + 10% NEt₃) to afford 39.2 mg (60%) of **3s** as a yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (3H, t, *J* = 6.8 Hz), 1.41-1.46 (4H, m), 1.69 (2H, tt, *J* = 7.2, 7.2 Hz), 3.18 (2H, t, *J* = 7.2 Hz), 3.26 (1H, s br), 3.74 (3H, s), 6.35 (1H, d, *J* = 2.8 Hz), 6.69 (1H, d, *J* = 8.8 Hz), 6.88 (1H, s), 6.97 (1H, d, *J* = 2.8 Hz), 7.17 (1H, d, *J* = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 29.40, 29.43, 32.8, 45.5, 99.6, 102.5, 109.7, 111.8, 128.7, 129.3, 131.2, 142.3; ESIHRMS: Found: *m/z* 217.1705. Calcd for C₁₄H₂₁N₂: (M+H)⁺ 217.1705.

***N*-Pentylthiazol-2-amine (3t)**



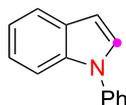
According to the general procedure, the reaction of *N*-(Thiazol-2-yl)pentanethioamide (**1t**) (100.0 mg, 0.500 mmol), **2c** (101.8 mg, 1.5 equiv), TBHN (17.9 mg, 20 mol%), PhSH (5 μL, 10 mol%), and toluene (5 mL) under nitrogen at 80 °C for 11 h, after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1 + 10% NEt₃) to afford 45.8 mg (54%) of **3t** as a white solid; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (3H, t, *J* = 6.4 Hz), 1.33-1.41 (4H, m), 1.66 (2H, tt, *J* = 6.8, 7.0 Hz), 3.24 (2H, t, *J* = 7.0 Hz), 5.62 (1H, s br), 6.47 (1H, d, *J* = 3.6 Hz), 7.10 (1H, d, *J* = 3.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 22.3, 29.0, 29.0, 46.2, 106.0, 139.0, 170.8; ESIHRMS: Found: *m/z* 171.0957. Calcd for C₈H₁₅N₂S: (M+H)⁺ 171.0956.

1,2,3,4-Tetrahydroquinoline (3u)



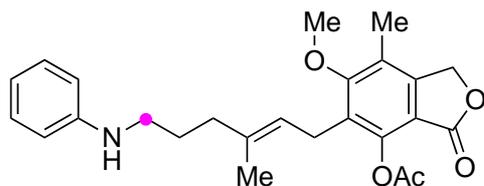
According to the general procedure, the reaction of 3,4-dihydroquinoline-2(1*H*)-thione (**1u**) (81.9 mg, 0.502 mmol), **2c** (102.5 mg, 1.5 equiv), TBHN (18.6 mg, 20 mol%), PhSH (5 μL, 10 mol%), and toluene (5 mL) under nitrogen at 80 °C for 14 min, after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 54.6 mg (82%) of **3u** as a yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 1.98 (2H, tt, *J* = 5.6, 6.4 Hz), 2.81 (2H, t, *J* = 6.4 Hz), 3.33 (2H, t, *J* = 5.6 Hz), 3.82 (1H, s br), 6.50 (1H, d, *J* = 8.0 Hz), 6.65 (1H, dd, *J* = 7.2, 7.2 Hz), 6.99-7.03 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 22.1, 26.9, 41.9, 114.1, 116.8, 121.3, 126.6, 129.4, 144.7. The spectral data for this compound matches that reported in the literature.²⁶

1-phenyl-1*H*-indole (3v)



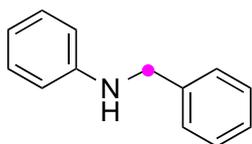
According to the general procedure, the reaction of 1-phenylindoline-2-thione (**1v**) (68.0 mg, 0.302 mmol), **2c** (62.2 mg, 1.5 equiv), TBHN (11.4 mg, 20 mol%), PhSH (3 μ L, 10 mol%), and toluene (3 mL) under nitrogen at 80 $^{\circ}$ C for 5 h, after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30 : 1) to afford 34.9 mg (60%) of **3v** as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.67 (1H, d, $J = 1.6$ Hz), 7.14-7.23 (2H, m), 7.32-7.34 (2H, m), 7.48-7.49 (4H, m), 7.56 (1H, d, $J = 8.0$ Hz), 7.68 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 103.5, 110.4, 120.3, 121.1, 122.3, 124.3, 126.4, 127.9, 129.3, 129.5, 135.8, 139.8. The spectral data for this compound matches that reported in the literature.²⁷

(*E*)-6-Methoxy-7-methyl-5-(3-methyl-6-(phenylamino)hex-2-en-1-yl)-3-oxo-1,3-dihydroisobenzofuran-4-yl acetate (3w)



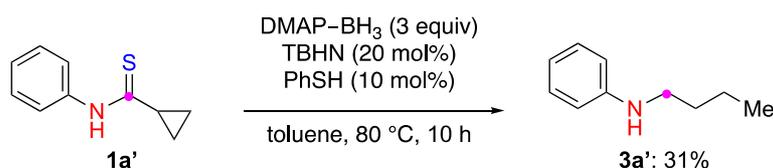
According to the general procedure, the reaction of (*E*)-6-Methoxy-7-methyl-5-(3-methyl-6-(phenylamino)-6-thioxohex-2-en-1-yl)-3-oxo-1,3-dihydroisobenzofuran-4-yl acetate (**1w**) (90.2 mg, 0.199 mmol), **2c** (40.5 mg, 1.5 equiv), TBHN (7.3 mg, 20 mol%), PhSH (2 μ L, 10 mol%), and toluene (2 mL) under nitrogen at 80 $^{\circ}$ C for 16 min, after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford 66.6 mg (79%) of **3w** as a white solid; mp: 98-99 $^{\circ}$ C; ^1H NMR (400 MHz, CDCl_3) δ 1.70 (2H, tt, $J = 6.8, 7.2$ Hz), 1.80 (3H, s), 2.08 (2H, t, $J = 7.2$ Hz), 2.21 (3H, s), 2.39 (3H, s), 3.05 (2H, t, $J = 6.8$ Hz), 3.37 (2H, d, $J = 6.0$ Hz), 3.79 (3H, s), 5.14 (3H, m), 6.55 (2H, d, $J = 8.0$ Hz), 6.66 (1H, t, $J = 7.0$ Hz), 7.14 (2H, dd, $J = 7.0, 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 11.7, 16.1, 20.5, 23.5, 27.3, 36.9, 43.3, 61.1, 68.3, 112.6, 113.4, 117.0, 121.9, 122.9, 129.1, 129.3, 135.5, 145.8, 146.1, 148.3, 162.6, 168.3, 169.0; ESIHRMS: Found: m/z 424.2126. Calcd for $\text{C}_{25}\text{H}_{30}\text{NO}_5$: ($\text{M}+\text{H}$)⁺ 424,2124.

N-benzylaniline (3x)



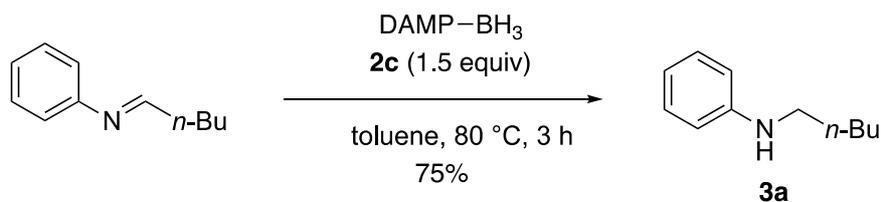
According to the general procedure, the reaction of *N*-phenylbenzothioamide (**1x**) (63.8 mg, 0.299 mmol), **2c** (61.1 mg, 1.5 equiv), TBHN (11.0 mg, 20 mol%), PhSH (3 μ L, 10 mol%), and toluene (3 mL) under nitrogen at 80 $^{\circ}$ C for 3 h, after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 40 : 1) to afford 19.8 mg (79%) of **3x** as colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 4.02 (1H, s br), 4.32 (2H, s), 6.63 (2H, d, $J = 8.0$ Hz), 6.71 (1H, t, $J = 7.0$ Hz), 7.17 (2H, dd, $J = 7.0, 8.0$ Hz), 7.27-7.38 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 48.3, 112.8, 117.5, 127.2, 127.5, 128.6, 129.2, 139.4, 148.1. The spectral data for this compound matches that reported in the literature.²⁸

4. Mechanistic studies



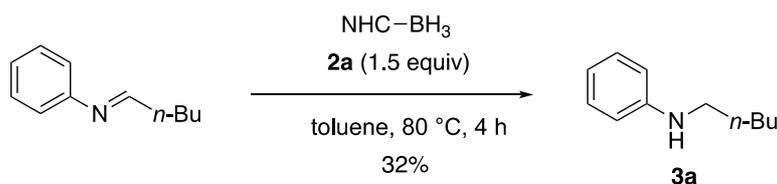
A solution of thioamide **1a'** (88.4 mg, 0.499 mmol), DMAP- BH_3 (203.2 mg, 1.493 mmol), TBHN (34.7 mg, 0.199 mmol) and PhSH (10 μ L, 0.098 mmol) in toluene (5 mL) was stirred at 80 $^{\circ}$ C for 10 h under nitrogen atmosphere. The reaction mixture was concentrated. Purification by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 50 : 1) gave **3a'** (23.1 mg, 0.155 mmol) in 31% yield as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 0.97 (3H, t, $J = 7.2$ Hz), 1.44 (2H, tq, $J = 7.2, 7.6$ Hz), 1.62 (1H, tt, $J = 7.2, 7.6$ Hz), 3.12 (2H, t, $J = 7.2$ Hz), 3.59 (1H, s br), 6.61 (2H, d, $J = 8.0$ Hz), 6.70 (1H, t, $J = 7.4$ Hz), 7.18 (2H, dd, $J = 7.2, 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 20.3, 31.6, 43.6, 112.6, 117.0, 129.2, 148.5. The spectral data for this compound matches that reported in the literature.²⁹

Reduction of an imine by DMAP- BH_3 (**2c**)



A solution of (*E*)-*N*-phenylpentan-1-imine (81.7 mg, 0.507 mmol) (prepared by the condensation of aniline and pentanal in the presence of 4 Å molecular sieves and used after filtration and evaporation) and DMAP-BH₃ (103.9 mg, 0.763 mmol) in toluene (5 mL) was stirred at 80 °C for 3 h under nitrogen atmosphere. The reaction mixture was concentrated. Purification by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 50 : 1) gave *N*-benzylaniline **3a** (62.2 mg, 0.381 mmol) in 75% yield.

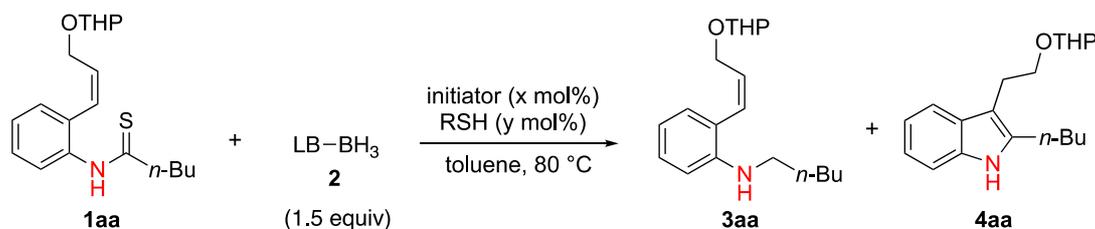
Reduction of an imine by NHC-BH₃ (**2a**)



A solution of (*E*)-*N*-phenylpentan-1-imine (79.4 mg, 0.494 mmol) (prepared by the condensation of aniline and pentanal in the presence of 4 Å molecular sieves and used after filtration and evaporation) and NHC-BH₃ (79.5 mg, 0.742 mmol) in toluene (5 mL) was stirred at 80 °C for 4 h under nitrogen atmosphere. The reaction mixture was concentrated. Purification by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 50 : 1) gave **3a** (25.8 mg, 0.158 mmol) in 32% yield.

5. Radical cyclization of thioamides

5.1 Optimization of reaction conditions^a

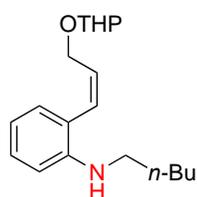


Entry	LB-BH ₃ (2)	Initiaor (x mol%)	RSH (y mol%)	3aa yield [%] ^b	4aa yield [%] ^b
1	2c	TBHN (20)	PhSH (10)	19	27

2	2c	TBHN (20)	PhSH (100)	43	11
3	2a	AIBN (50)	PhSH (20)	20	13
4	2a	AIBN (50)	PhSH (100)	77	trace
5	2a	AIBN (50)	C ₉ H ₁₉ C(CH ₃) ₂ SH (20)	trace	70 (60) ^c
6	2a	AIBN (50)	Ph ₃ CSH (20)	trace	73 (64) ^c
7	2a	AIBN (20)	Ph ₃ CSH (20)	7	30
8	2c	AIBN (50)	Ph ₃ CSH (20)	trace	24

^a Reaction conditions: **1aa** (0.3-0.5 mmol), LB-BH₃ (**2**, 1.5 equiv), initiator (x mol%), RSH (y mol%), toluene (0.1 M), 80 °C under nitrogen. ^b Yield based on ¹H NMR analysis of the crude product using tetrachloroethane as an internal standard. ^c Isolated yield.

(*E*)-*N*-Pentyl-2-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-en-1-yl)aniline (**3aa**)



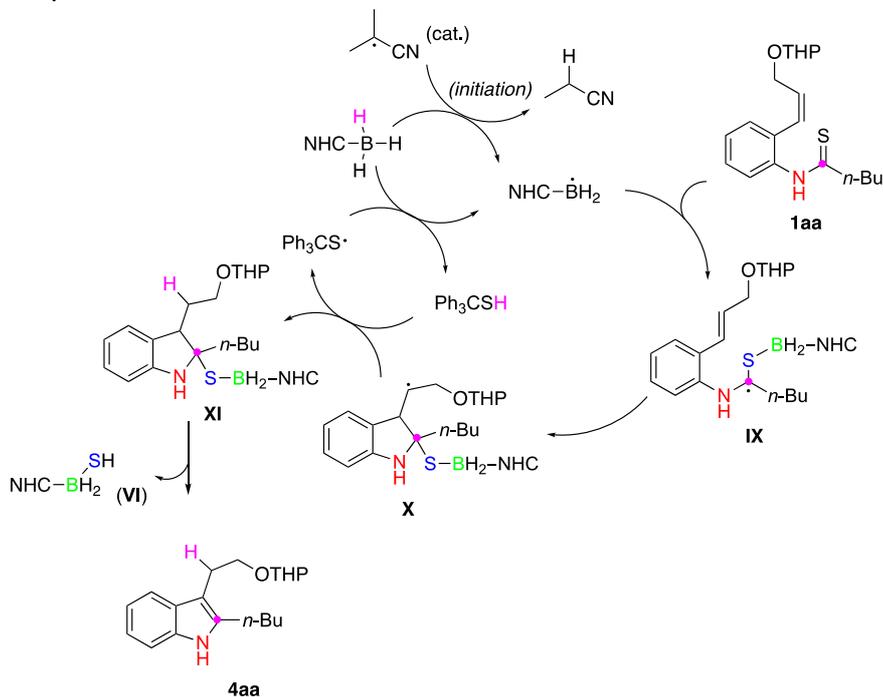
Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 0.92 (3H, t, *J* = 7.0 Hz), 1.36-1.40 (4H, m), 1.50-1.65 (7H, m), 1.80-1.85 (1H, m), 3.11 (2H, t, *J* = 7.2 Hz), 3.43-3.49 (1H, m), 3.66 (1H, s br), 3.82-3.87 (1H, m), 4.12 (1H, ddd, *J* = 1.6, 7.2, 12.4 Hz), 4.38 (1H, ddd, *J* = 1.6, 6.0, 12.4 Hz), 4.59 (1H, dd, *J* = 3.2, 4.0 Hz), 5.96 (1H, ddd, *J* = 6.0, 7.2, 11.2 Hz), 6.44 (1H, d, *J* = 11.2 Hz), 6.61 (1H, d, *J* = 8.0 Hz), 6.66 (1H, ddd, *J* = 0.8, 7.6, 7.6 Hz), 6.96 (1H, d, *J* = 8.0 Hz), 7.17 (2H, ddd, *J* = 1.2, 7.6, 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 19.5, 22.5, 25.4, 29.2, 29.4, 30.7, 30.9, 43.9, 62.3, 64.5, 98.7, 110.0, 116.1, 121.8, 127.7, 128.7, 129.6, 130.5, 145.7; ESIHRMS: Found: *m/z* 304.2278. Calcd for C₁₉H₃₁NO₂: (M+H)⁺ 304.2277.

5.2 A proposed mechanism for the annulation reaction

A possible reaction mechanism for the formation of indole **4aa** was outlined in the Scheme below. The NHC-boryl radical, which was first generated by hydrogen atom abstraction from NHC-BH₃ in the initiation step, adds to the C=S bond of **1aa** to generate intermediate **IX**. An intramolecular cyclization takes place to construct the indoline ring framework **X**. Hydrogen atom transfer from Ph₃CSH to the resulting

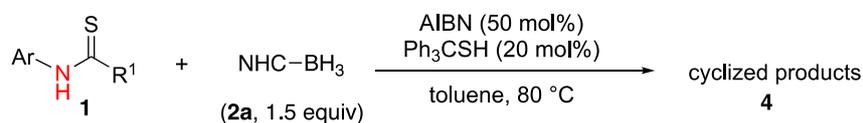
carbon radical forms intermediate **XI**. The subsequent elimination of **VI** affords product **4aa**.

A possible reaction mechanism for the formation of **4aa**:



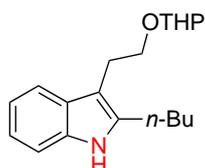
5.3 Lewis base-boryl radicals enabled annulation of thioamides

A general procedure:



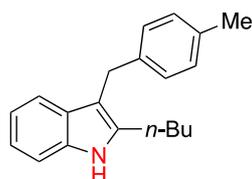
To an N_2 flushed, over-dried glass tube with a magnetic stir bar, unsaturated thioamides **1** (0.3 mmol), **2a** (0.45 mmol), AIBN (0.15 mmol), Ph_3CSH (0.06 mmol), and toluene (3 mL) were added. The tube was sealed and the reaction mixture was stirred at 80°C until the TLC analysis indicating the consumption of **1**. The resulting mixture was cooled down to room temperature and concentrated. The crude mixture was purified by flash column chromatography on silica gel to give pure cyclic products **4**.

2-Butyl-3-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethyl)-1H-indole (**4aa**)



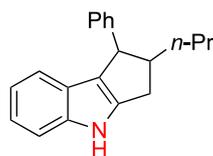
According to the general procedure, the reaction of **1aa** (100.0 mg, 0.300 mmol), **2a** (48.6 mg, 1.5 equiv), AIBN (24.4 mg, 50 mol%), Ph₃CSH (16.4 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 4 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 15 : 1) to afford 57.9 mg (64%) of **4aa** as a colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (3H, t, *J* = 7.4 Hz), 1.38 (2H, tq, *J* = 7.2, 7.4 Hz), 1.48-1.66 (7H, m), 1.80-1.88 (1H, m), 2.74 (2H, t, *J* = 7.8 Hz), 3.02 (2H, t, *J* = 7.6 Hz), 3.47 (1H, td, *J* = 4.4, 11.2 Hz), 3.59 (1H, dd, *J* = 8.0, 16.8 Hz), 3.81-3.86 (1H, m), 3.92 (1H, dd, *J* = 8.0, 16.8 Hz), 4.60 (1H, m), 7.04-7.12 (2H, m), 7.26 (1H, d, *J* = 7.2 Hz), 7.54 (1H, d, *J* = 7.6 Hz), 7.79 (1H, s br); ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 19.6, 22.5, 25.0, 25.4, 25.9, 30.7, 32.1, 62.3, 67.9, 98.9, 108.0, 110.2, 118.2, 119.0, 120.9, 128.8, 135.2, 136.4. The spectral data for this compound matches that reported in the literature.¹⁰

2-Butyl-3-(4-methylbenzyl)-1*H*-indole (**4ab**)



According to the general procedure, the reaction of **1ab** (93.4 mg, 0.302 mmol), **2a** (48.2 mg, 1.5 equiv), AIBN (24.5 mg, 50 mol%), Ph₃CSH (16.8 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 4.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50 : 1) to afford 70.9 mg (85%) of **4ab** as a yellow liquid; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (3H, t, *J* = 7.2 Hz), 1.33 (2H, tq, *J* = 7.2, 7.6 Hz), 1.58 (2H, tt, *J* = 7.6, 7.8 Hz), 2.27 (3H, s), 2.70 (2H, t, *J* = 7.8 Hz), 4.03 (2H, s), 6.98-7.10 (6H, m), 7.24 (1H, d, *J* = 8.0 Hz), 7.36 (1H, d, *J* = 8.0 Hz), 7.71 (1H, s br); ¹³C NMR (100 MHz, CDCl₃) δ 13.8, 20.9, 22.4, 25.9, 29.6, 31.9, 110.1, 118.5, 119.1, 120.9, 128.1, 128.2, 128.8, 128.9, 134.9, 135.2, 136.2, 138.6; ESIHRMS: Found: *m/z* 278.1906. Calcd for C₂₀H₂₄N: (M+H)⁺ 278.1909.

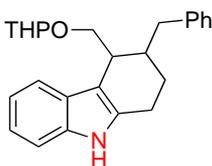
1-Phenyl-2-propyl-1,2,3,4-tetrahydrocyclopenta[*b*]indole (**4ac**)



According to the general procedure, the reaction of **1ac** (92.7 mg, 0.302 mmol), **2a** (48.7 mg, 1.5 equiv), AIBN (24.8 mg, 50 mol%), Ph₃CSH (16.9 mg, 20 mol%), and

toluene (3 mL) under nitrogen at 80 °C for 12 h after flash column chromatography on silica gel (petroleum ether : dichloromethane = 3 : 1) to afford 44.9 mg (54%) of **4ac** as a colorless liquid; A mixture of diastereomers (dr = 1:1) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 0.80 (3Hx1, t, *J* = 7.2 Hz), 0.90 (3Hx1, t, *J* = 7.2 Hz), 0.93-1.01 (1Hx1, m), 1.12-1.20 (1Hx1, m), 1.28-1.36 (2Hx1+1Hx1, m), 1.39-1.48 (1Hx1, m), 1.61-1.65 (1Hx1, m), 1.76-1.84 (1Hx1, m), 2.60-2.76 (2Hx1+1Hx1, m), 2.99 (1Hx1, dd, *J* = 7.6, 15.2 Hz), 3.14 (1Hx1, dd, *J* = 7.6, 14.8 Hz), 3.20-3.26 (1Hx1, m), 4.00 (1Hx1, d, *J* = 6.4 Hz), 4.41 (1Hx1, d, *J* = 8.0 Hz), 6.92-7.02 (3Hx1+2Hx1, m), 7.07 (2Hx1, dd, *J* = 7.2, 7.2 Hz), 7.13-7.23 (3Hx1+2Hx1, m), 7.25-7.33 (3Hx1+3Hx1, m), 7.88-7.91 (1Hx1+1Hx1, m br); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 14.3, 21.2, 21.6, 31.6, 32.2, 34.6, 37.4, 47.8, 49.5, 51.7, 55.8, 111.2, 111.3, 118.5, 118.7, 119.48, 119.54, 120.6, 120.7, 121.1, 122.4, 124.4, 124.5, 126.0, 126.1, 127.78, 127.81, 128.2, 128.8, 140.6, 140.7, 142.3, 142.6, 143.1, 145.4; ESIHRMS: Found: *m/z* 276.1749. Calcd for C₂₀H₂₂N: (M+H)⁺ 276.1752.

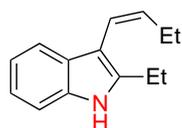
3-Benzyl-4-(((tetrahydro-2H-pyran-2-yl)oxy)methyl)-2,3,4,9-tetrahydro-1H-carbazole (4ad)



According to the general procedure, the reaction of **1ad** (126.3 mg, 0.310 mmol), **2a** (49.5 mg, 1.5 equiv), AIBN (25.8 mg, 50 mol%), Ph₃CSH (16.8 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 12.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 15 : 1) to afford 52.7 mg (45%) of **4ad** as a colorless liquid; A mixture of diastereomers (dr = 1:1:1) was obtained. ¹H NMR (400 MHz, CDCl₃) δ 1.45-1.84 (14H, m), 1.99-2.02 (1H, m), 2.25-2.27 (1H, m), 2.56-2.79 (8H, m), 3.06 (1H, td, *J* = 5.2, 13.2Hz), 3.15-3.18 (1H, m), 3.33-3.48 (4H, m), 3.58-3.85 (4H, m), 4.06-4.19 (2H, m), 4.50-4.60 (2H, m), 7.01-7.12 (4H, m), 7.21-7.32 (12H, m), 7.54-7.61 (2H, m), 7.71 (1H, brs), 7.78-7.79 (1H, brs); ¹³C NMR (100 MHz, CDCl₃) δ 19.18, 19.23, 19.26, 19.39, 19.54, 22.14, 22.27, 22.99, 23.13, 23.72, 23.79, 25.43, 25.46, 25.49, 30.63, 30.65, 30.66, 35.02, 35.19, 35.94, 36.14, 36.46, 37.42, 38.25, 38.34, 39.39, 39.61, 39.93, 40.01, 61.83, 61.84, 61.92, 62.20, 68.66, 68.76, 69.89, 71.03, 97.83, 98.93, 99.22, 99.36, 108.70, 108.80, 110.23, 110.24,

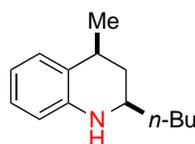
110.38, 110.41, 112.07, 112.61, 118.32, 118.35, 118.65, 118.88, 118.97, 119.03, 120.84, 121.96, 125.69, 125.72, 126.00, 127.43, 127.58, 127.88, 127.92, 128.16, 128.22, 129.08, 129.10, 129.14, 133.79, 133.81, 134.30, 134.55, 135.86, 135.88, 135.95, 136.00, 141.26, 141.30, 141.58, 141.68; ESIHRMS: Found: m/z 376.2273; Calcd for $C_{25}H_{31}NO_2$: $(M+H)^+$ 376.2277.

(Z)-3-(But-1-en-1-yl)-2-ethyl-1H-indole (4ae)



According to the general procedure, the reaction of **1ae** (68.9 mg, 0.298 mmol), **2a** (47.8 mg, 1.5 equiv), AIBN (24.6 mg, 50 mol%), Ph_3CSH (16.6 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 11 h after flash column chromatography on basic alumina (petroleum ether : ethyl acetate = 100 : 1) to afford *Z* isomer of **4ae** as a colorless liquid; 1H NMR analysis of the crude reaction mixture using tetrachloroethane as an internal standard showed that a mixture of *E/Z* isomers (*E:Z* = 2:1) was formed in 58% yield, however, only the *Z* isomer was isolated after purification by flash column chromatography and the *E* isomer was probably decomposed during such process. The characterization data were described for the *Z* isomer. Colorless liquid; 1H NMR (400 MHz, $DMSO-d_6$) δ 0.93 (3H, t, $J = 7.6$ Hz), 1.22 (3H, t, $J = 7.6$ Hz), 2.05 (2H, dq, $J = 7.2, 7.6$ Hz), 2.65 (2H, q, $J = 7.6$ Hz), 5.61 (1H, dt, $J = 7.2, 10.8$ Hz), 6.35 (1H, d, $J = 10.8$ Hz), 6.93-7.02 (2H, m), 7.24-7.28 (2H, m), 11.0 (1H, s br); ^{13}C NMR (100 MHz, $DMSO-d_6$) δ 13.7, 14.2, 19.6, 22.6, 107.5, 110.6, 118.4, 118.5, 120.2, 120.3, 127.4, 133.4, 135.3, 138.4; ESIHRMS: Found: m/z 200.1433. Calcd for $C_{14}H_{17}N$: $(M+H)^+$ 200.1439.

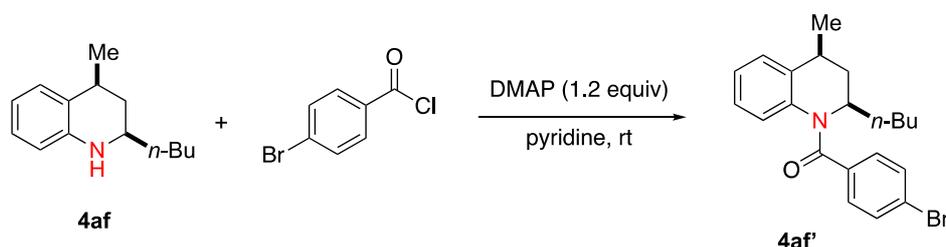
(2*R,4*S**)-2-Butyl-4-methyl-1,2,3,4-tetrahydroquinoline (4af)**



According to the general procedure, the reaction of **1af** (69.0 mg, 0.296 mmol), **2a** (47.6 mg, 1.5 equiv), AIBN (25.5 mg, 50 mol%), Ph_3CSH (16.8 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 12.5 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100 : 1) to afford 43.7 mg (73%) of **4af** as a colorless liquid; A mixture of diastereomers (*dr* = 5.8:1) was obtained; 1H NMR

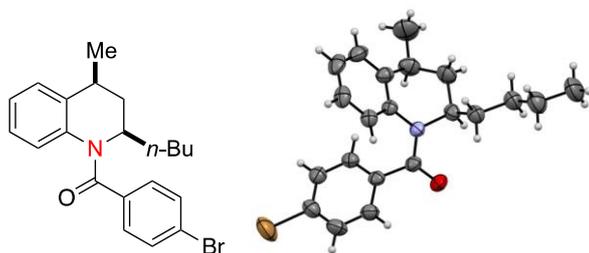
(400 MHz, CDCl₃) δ 0.93-0.96 (3Hx1+3Hx5.8, m), 1.28-1.49 (10Hx1+9Hx5.8, m), 1.87-1.91 (1Hx5.8, m), 2.90-2.98 (1Hx1+1Hx5.8, m), 3.23-3.33 (1Hx1+1Hx5.8, m), 3.75 (1Hx5.8, s br), 6.48 (1Hx5.8, d, *J* = 8.0 Hz), 6.50 (1Hx1, d, *J* = 8.0 Hz), 6.64 (1Hx1, dd, *J* = 7.6, 8.0 Hz), 6.66 (1Hx5.8, dd, *J* = 7.6, 8.0 Hz), 6.98 (1Hx1+1Hx5.8, dd, *J* = 7.6, 7.6 Hz), 7.04 (1Hx1, d, *J* = 7.6 Hz), 7.14 (1H x5.8, d, *J* = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 20.3, 22.8, 24.5, 27.7, 29.9, 30.8, 35.2, 36.5, 36.7, 38.6, 46.9, 51.8, 113.9, 114.1, 116.8, 117.1, 126.5, 126.7, 126.7, 126.8, 129.0, 144.1, 144.7; ESIHRMS: Found: *m/z* 204.1753. Calcd for C₁₄H₂₂N: (M+H)⁺ 204.1752.

Determination of the relative stereochemistry of the major isomer:



To a solution of **4af** (85,1 mg, 0.42 mol, dr = 5.8:1) in pyridine (5 mL) were added *p*-bromobenzoyl chloride (122.0 mg, 0.556 mmol) and DMAP (12.0 mg, 0.098 mmol) at room temperature. After 16 h, water was added and the mixture was extracted with CH₂Cl₂. The organic layer was washed with 1N HCl, dried over Na₂SO₄, filtered, concentrated and purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 30 : 1) to afforded **4af'** (65.9 mg, 0.171 mmol, dr = 5.8:1) in 40% yield as white solid. Recrystallization of the diastereomers from petroleum ether/ethyl acetate provided colorless crystals.

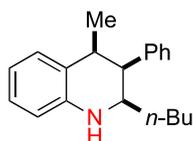
(4-Bromophenyl)((2*R*,4*S*)-2-butyl-4-methyl-3,4-dihydroquinolin-1(2*H*)-yl)methanone (**4af'**)



Colorless crystal (CCDC 1574325); mp: 147-149 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (3H, t, *J* = 7.0 Hz), 1.11-1.16 (1H, m), 1.23-1.34 (5H, m), 1.41 (3H, d, *J* = 6.4 Hz), 1.72-1.77 (1H, m), 2.50 (1H, ddd, *J* = 4.4, 8.8, 17.2 Hz), 2.74-2.79 (1H, m), 4.72-4.78 (1H, m), 6.46 (1H, d, *J* = 7.6 Hz), 6.90 (1H, dd, *J* = 7.6, 7.6 Hz), 7.02 (2H,

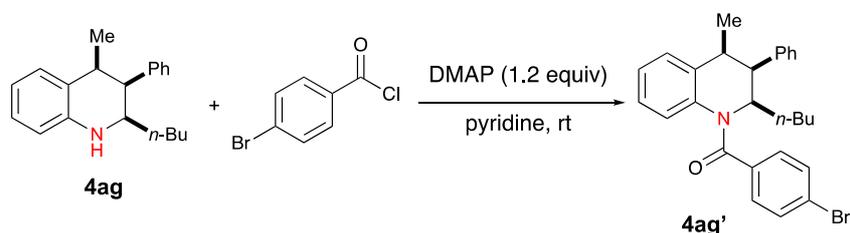
d, $J = 8.8$ Hz), 7.12 (1H, dd, $J = 7.6, 7.6$ Hz), 7.23 (1H, d, $J = 7.6$ Hz), 7.28 (1H, d, $J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 16.8, 22.6, 27.6, 30.0, 35.7, 40.6, 53.3, 123.3, 124.0, 125.7, 126.1, 126.7, 130.2, 130.9, 135.2, 138.3, 139.5, 168.2; ESIHRMS: Found: m/z 386.1120. Calcd for $\text{C}_{21}\text{H}_{24}^{79}\text{BrNO}$: $(\text{M}+\text{H})^+$ 386.1120.

(2*R,3*S**,4*S**)-2-butyl-4-methyl-3-phenyl-1,2,3,4-tetrahydroquinoline (4ag)**



According to the general procedure, the reaction of **1ag** (93.0 mg, 0.301 mmol), **2a** (47.9 mg, 1.5 equiv), AIBN (25.2 mg, 50 mol%), Ph_3CSH (17.0 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 4 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60 : 1) to afford 74.1 mg (88%) of **4ag** as a colorless liquid; A mixture of diastereomers (dr = 9:1) was obtained; ^1H and ^{13}C NMR were described for the major isomer; ^1H NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, $J = 7.2$ Hz), 1.11 (3H, d, $J = 6.8$ Hz), 1.28-1.39 (6H, m), 3.00 (1H, dd, $J = 2.4, 4.4$ Hz), 3.44 (1H, dq, $J = 4.4, 6.8$ Hz), 3.69 (1H, dt, $J = 2.4, 6.4$ Hz), 3.83 (1H, s br), 6.55 (1H, d, $J = 7.6$ Hz), 6.71 (1H, t, $J = 7.4$ Hz), 7.04-7.07 (3H, m), 7.13 (1H, d, $J = 7.6$ Hz), 7.18-7.19 (3H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 17.2, 22.6, 28.1, 33.7, 35.2, 48.5, 55.3, 113.3, 117.6, 125.4, 126.2, 126.8, 127.0, 127.7, 130.3, 138.5, 144.7; ESIHRMS: Found: m/z 280.2070. Calcd for $\text{C}_{20}\text{H}_{26}\text{N}$: $(\text{M}+\text{H})^+$ 280.2065.

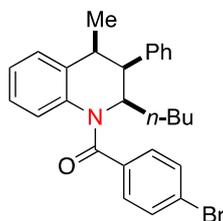
Determination of the relative stereochemistry of the major isomer:



To a solution of **4ag** (197 mg, 0.705 mmol, dr = 9 : 1) in pyridine (5 mL) were added *p*-bromobenzoyl chloride (199.9 mg, 0.911 mmol) and DMAP (18.5 mg, 0.151 mmol) at room temperature. After 12 h, water was added and the mixture was extracted with CH_2Cl_2 . The organic layer was washed with 1N HCl, dried over Na_2SO_4 , filtered, concentrated and purified by flash column chromatography (silica

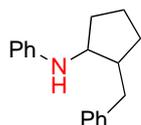
gel; petroleum ether : ethyl acetate = 40 : 1) to afford **4ag'** (177 mg, 0.383 mmol, dr = 9 : 1) in 54% yield as white solid. Recrystallization of the diastereomers from petroleum ether/ethyl acetate provided colorless crystals.

(4-Bromophenyl)((2*R,3*S**,4*S**)-2-butyl-4-methyl-3-phenyl-3,4-dihydroquinolin-1(2*H*)-yl)methanone (**4ag'**)**



Colorless crystal (CCDC 1574329); mp: 171-173 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.61 (3H, t, *J* = 7.0 Hz), 0.90-1.01 (2H, m), 1.03-1.30 (6H, m), 1.66-1.72 (1H, m), 3.31 (1H, dq, *J* = 5.2, 6.4 Hz), 3.82 (1H, dd, *J* = 5.2, 9.2 Hz), 5.12 (1H, dt, *J* = 6.0, 9.2 Hz), 6.36 (2H, d, *J* = 7.6 Hz), 6.57 (1H, d, *J* = 8.0 Hz), 6.98-7.05 (6H, m), 7.10-7.14 (2H, m), 7.31 (2H, d, *J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 14.9, 22.3, 28.3, 31.8, 34.9, 52.7, 58.8, 123.9, 125.8, 125.9, 126.50, 126.53, 127.3, 130.0, 130.3, 131.0, 135.4, 137.3, 137.5, 139.5, 168.3; ESIHRMS: Found: *m/z* 462.1432. Calcd for C₂₇H₂₉⁷⁹BrNO: (M+H)⁺ 462.1433.

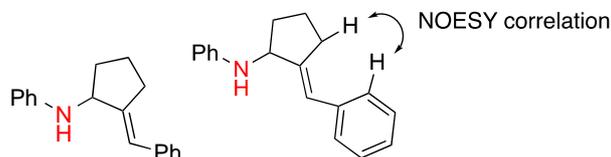
***N*-(2-Benzylcyclopentyl)aniline (**4ah**)**



According to the general procedure, the reaction of **1ah** (84.9 mg, 0.302 mmol), **2a** (48.1 mg, 1.5 equiv), AIBN (24.6 mg, 50 mol%), Ph₃CSH (16.4 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 2 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60 : 1) to afford 59.4 mg (78%) of **4ah** as a colorless liquid; a mixture of diastereomers (dr = 1 : 1) was obtained; ¹H NMR (400 MHz, CDCl₃) δ 1.29-1.51 (1Hx1+2Hx1, m), 1.57-1.84 (4Hx1+3Hx1, m), 1.91-2.03 (1Hx1+1Hx1, m), 2.12-2.21 (1Hx1, m), 2.36-2.43 (1Hx1+1Hx1, m), 2.56 (1Hx1, dd, *J* = 8.8, 13.2 Hz), 2.81-2.91 (1Hx1+1Hx1, m), 3.41-3.46 (1Hx1, m), 3.60 (1Hx1+1Hx1, s br), 3.78-3.81 (1Hx1, m), 6.48 (2Hx1, d, *J* = 8.0 Hz), 6.62 (2Hx1, d, *J* = 8.0 Hz), 6.68 (2Hx1, dd, *J* = 8.0, 8.0 Hz), 6.68 (2H, dd, *J* = 7.6, 8.0 Hz), 7.11-7.28 (6Hx1+8Hx1, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.9, 22.3, 29.0, 30.1, 31.8, 32.7,

35.2, 40.1, 44.4, 48.7, 56.6, 59.6, 113.0, 113.1, 116.82, 116.83, 125.6, 125.9, 128.2, 128.3, 128.8, 128.9, 129.1, 129.2, 141.0, 141.6, 147.9, 148.1. ESIHRMS: Found: m/z 252.1756. Calcd for $C_{18}H_{22}N$: $(M+H)^+$ 252.1752.

(E)-N-(2-Benzylidenecyclopentyl)aniline (4ai)



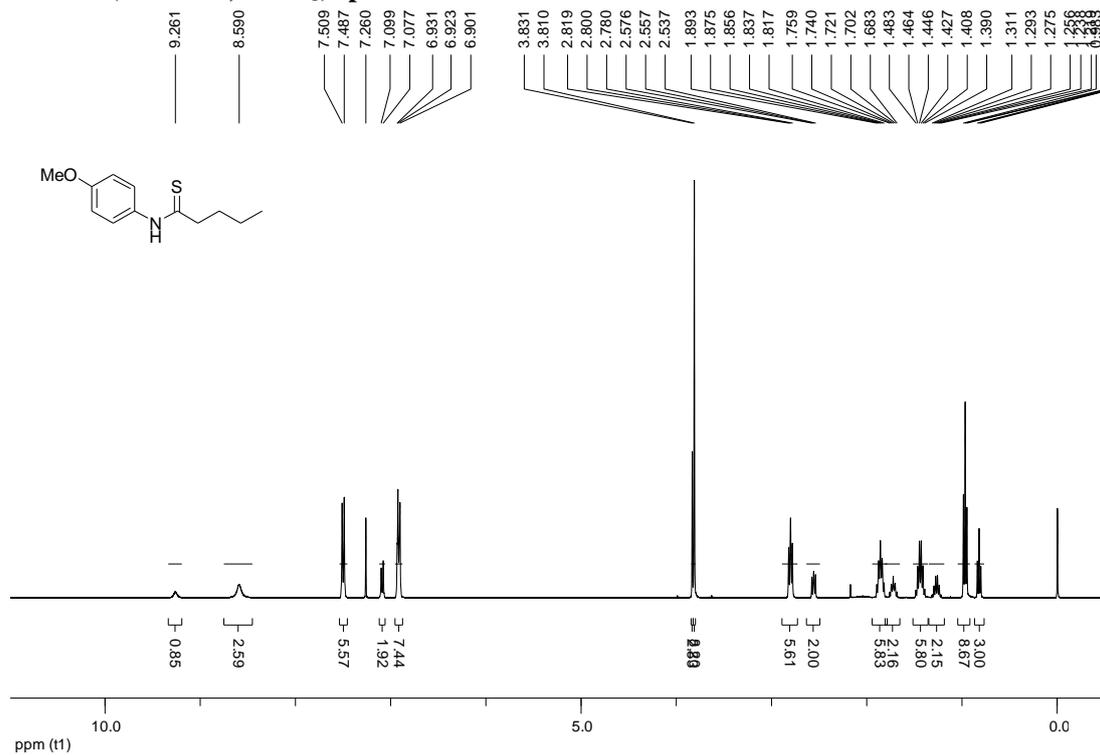
According to the general procedure, the reaction of **1ai** (83.6 mg, 0.299 mmol), **2a** (48.1 mg, 1.5 equiv), AIBN (24.1 mg, 50 mol%), Ph_3CSH (16.0 mg, 20 mol%), and toluene (3 mL) under nitrogen at 80 °C for 12 h after flash column chromatography on silica gel (petroleum ether : ethyl acetate = 60 : 1) to afford 26.6 mg (36%) of **4ai** as a colorless liquid; the stereochemistry was assigned based on NOESY interaction. 1H NMR (400 MHz, $CDCl_3$) δ 1.49-1.58 (1H, m), 1.70-1.79 (1H, m), 1.88-1.95 (1H, m), 2.16-2.24 (1H, m), 2.72 (2H, t, $J = 7.8$ Hz), 4.35 (1H, dd, $J = 6.4, 6.8$ Hz), 6.56 (1H, s), 6.70-6.74 (3H, m), 7.18-7.22 (3H, m), 7.32-7.35 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 30.3, 33.1, 59.6, 113.0, 117.2, 122.8, 126.4, 128.2, 128.30, 128.33, 129.3, 137.9, 146.8, 147.9. ESIHRMS: Found: m/z 250.1593. Calcd for $C_{18}H_{20}N$: $(M+H)^+$ 250.1596.

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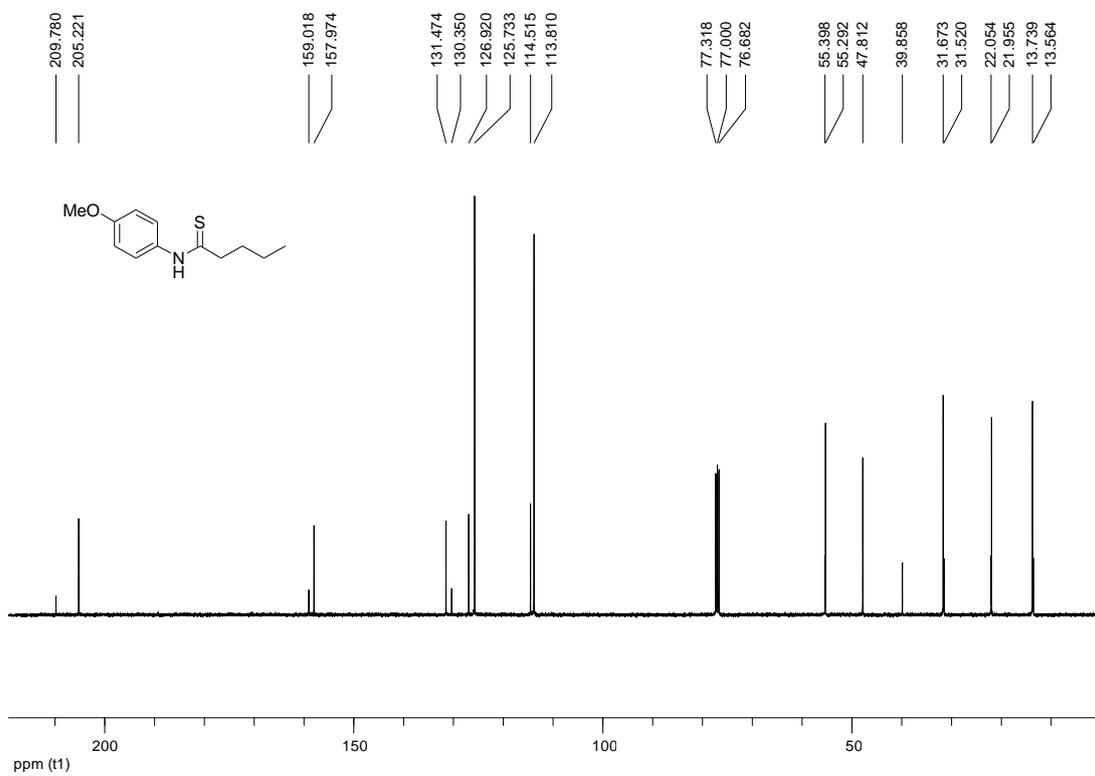
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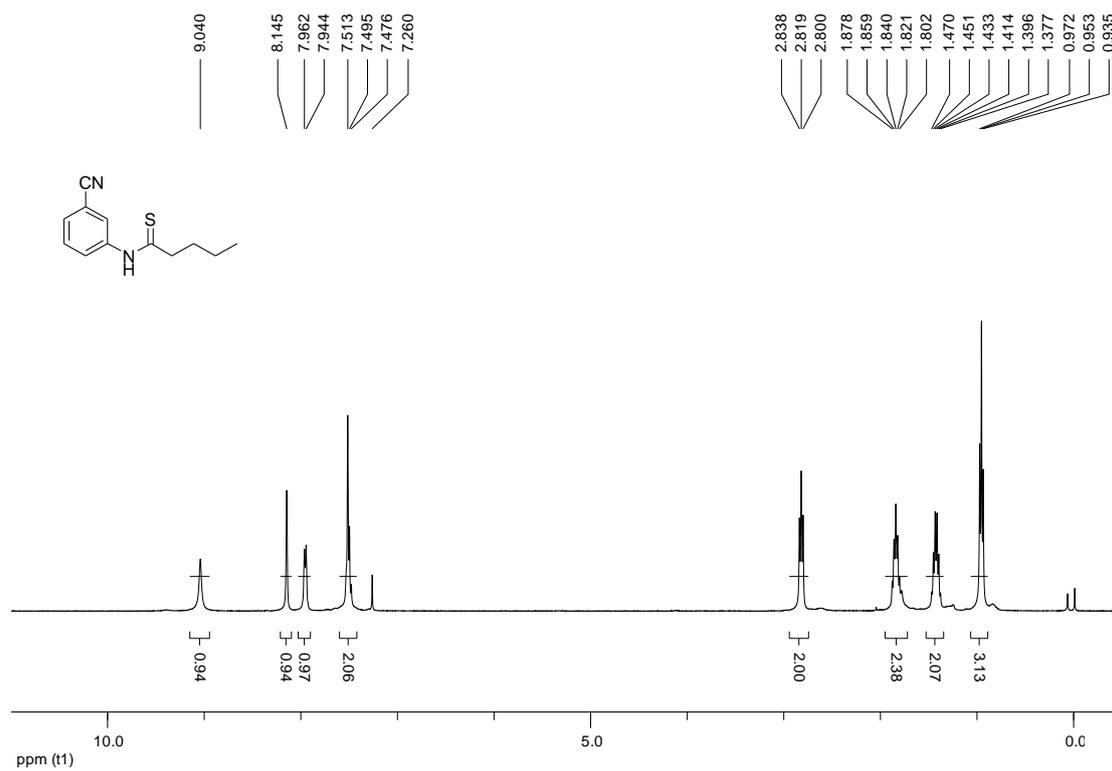
¹H NMR (400 MHz, CDCl₃) spectrum of 1c



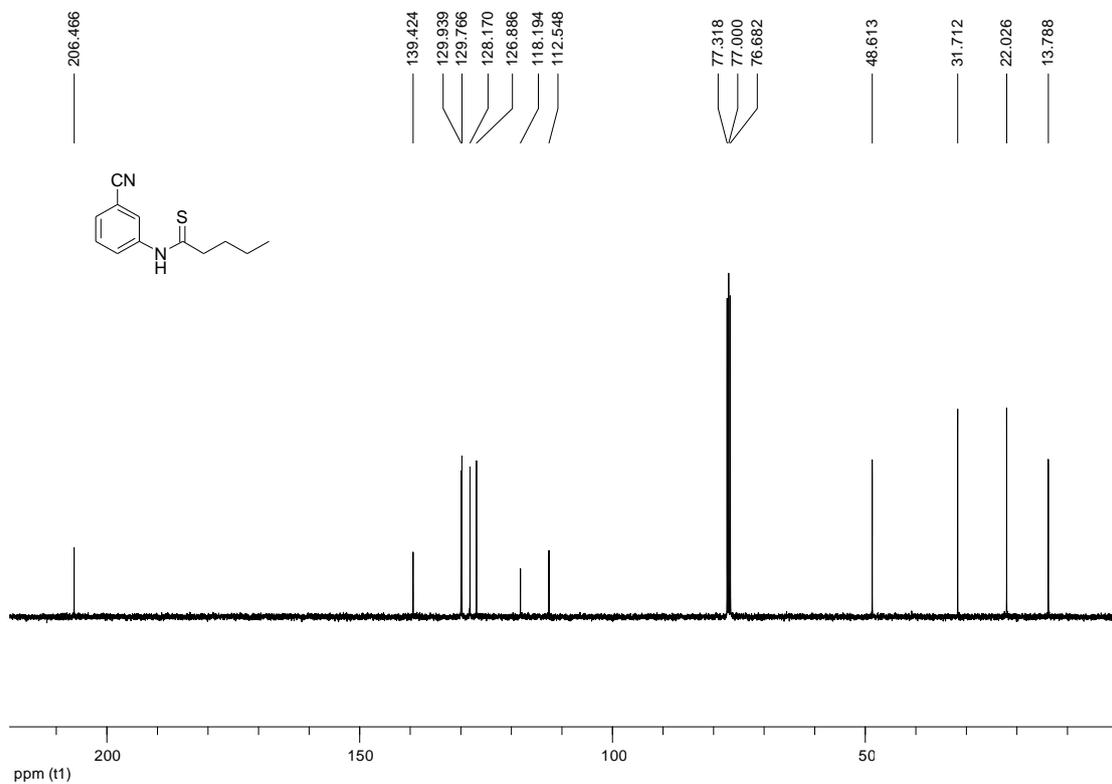
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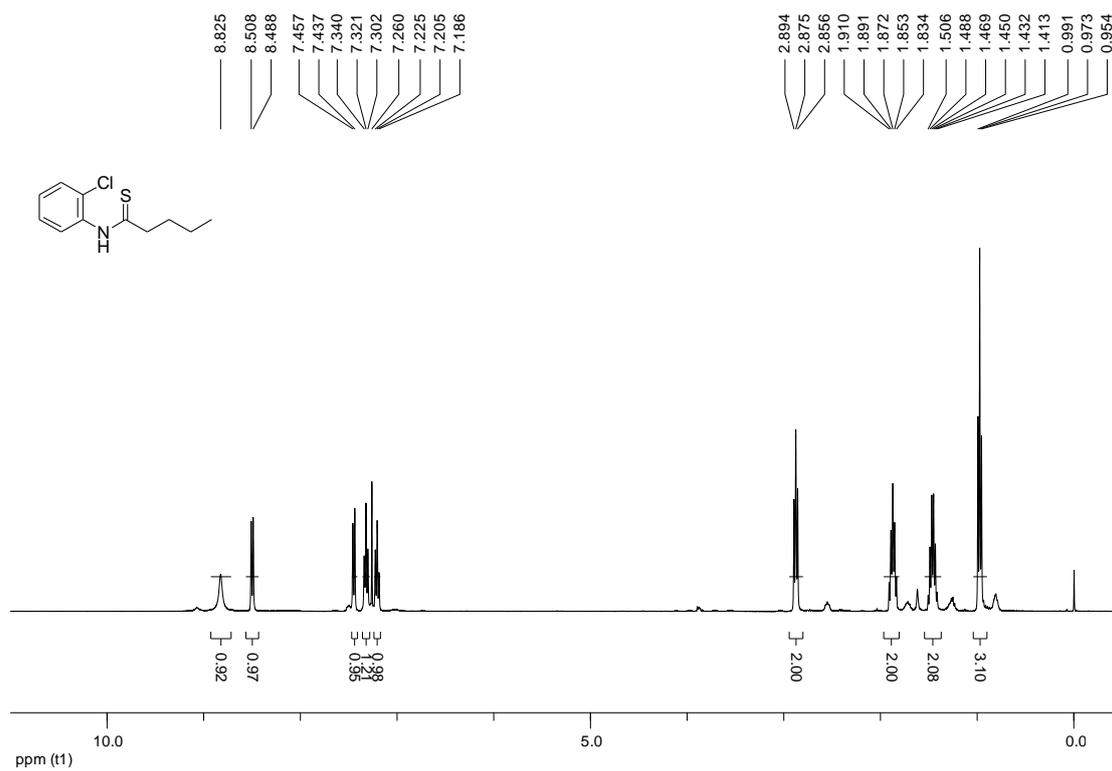
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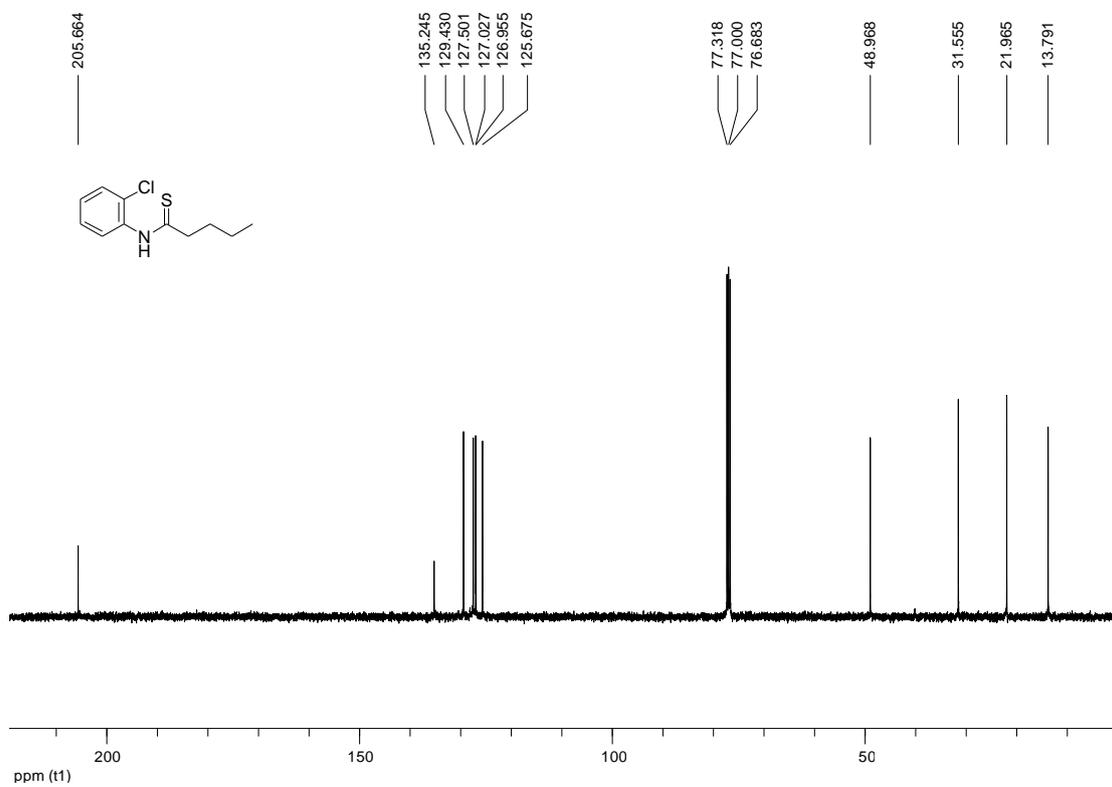
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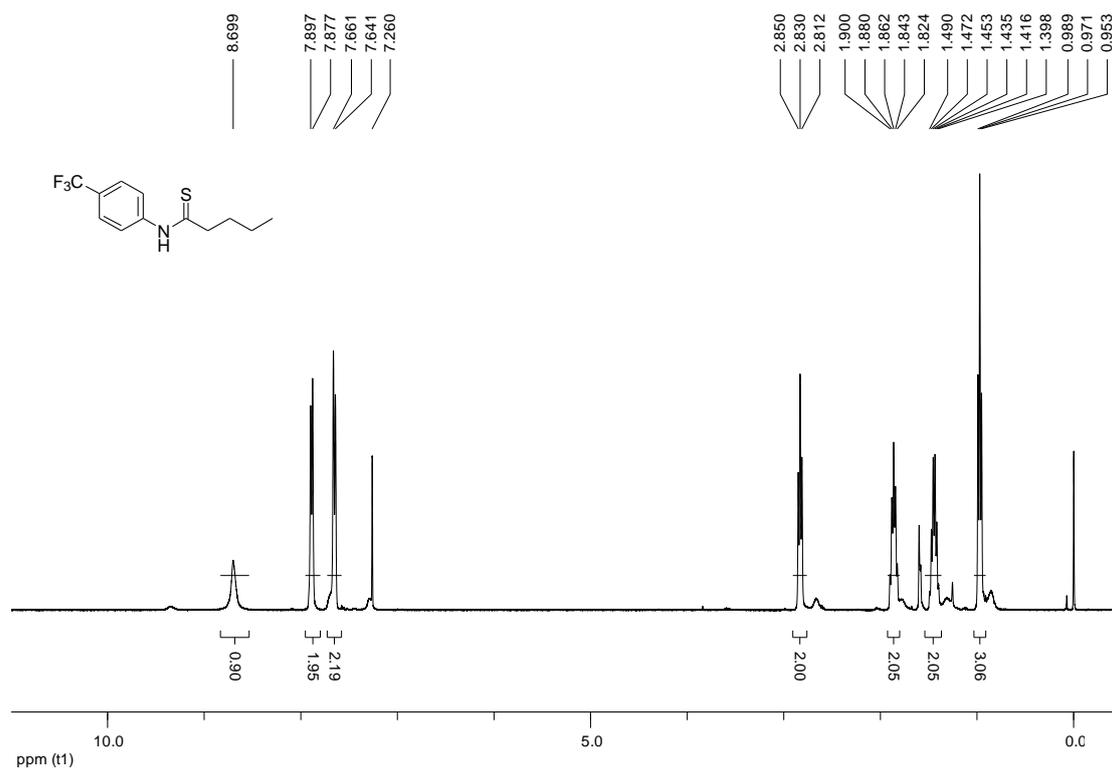
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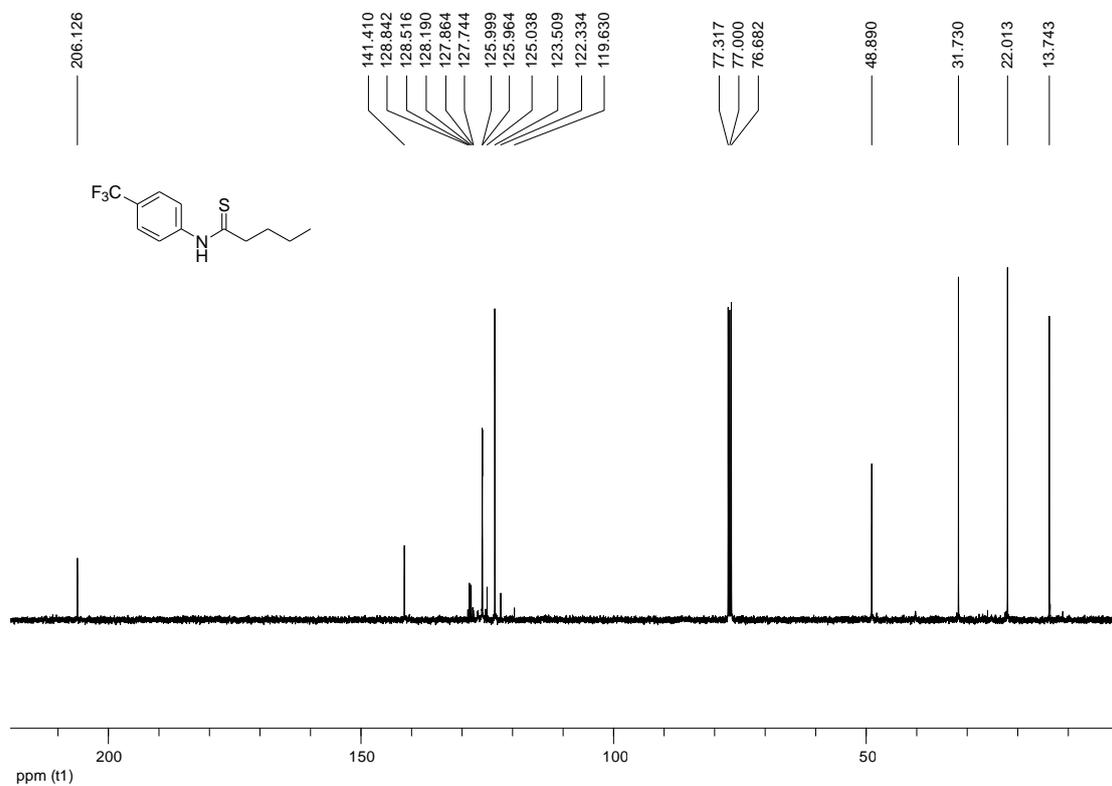
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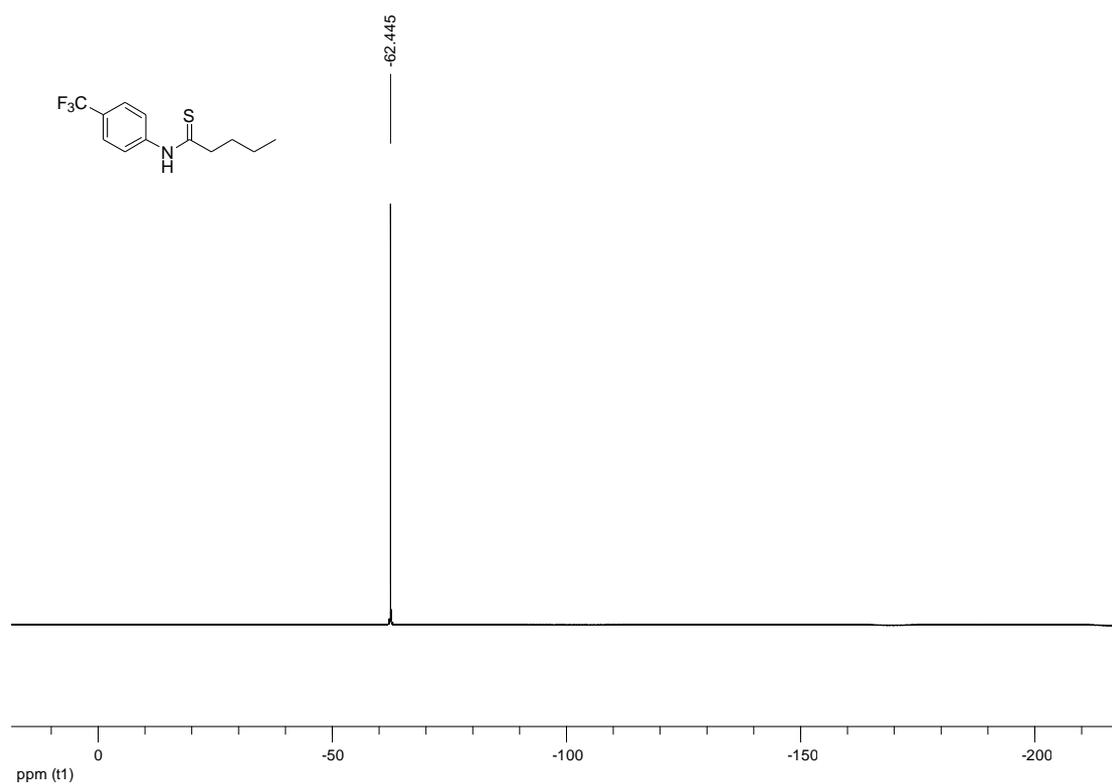
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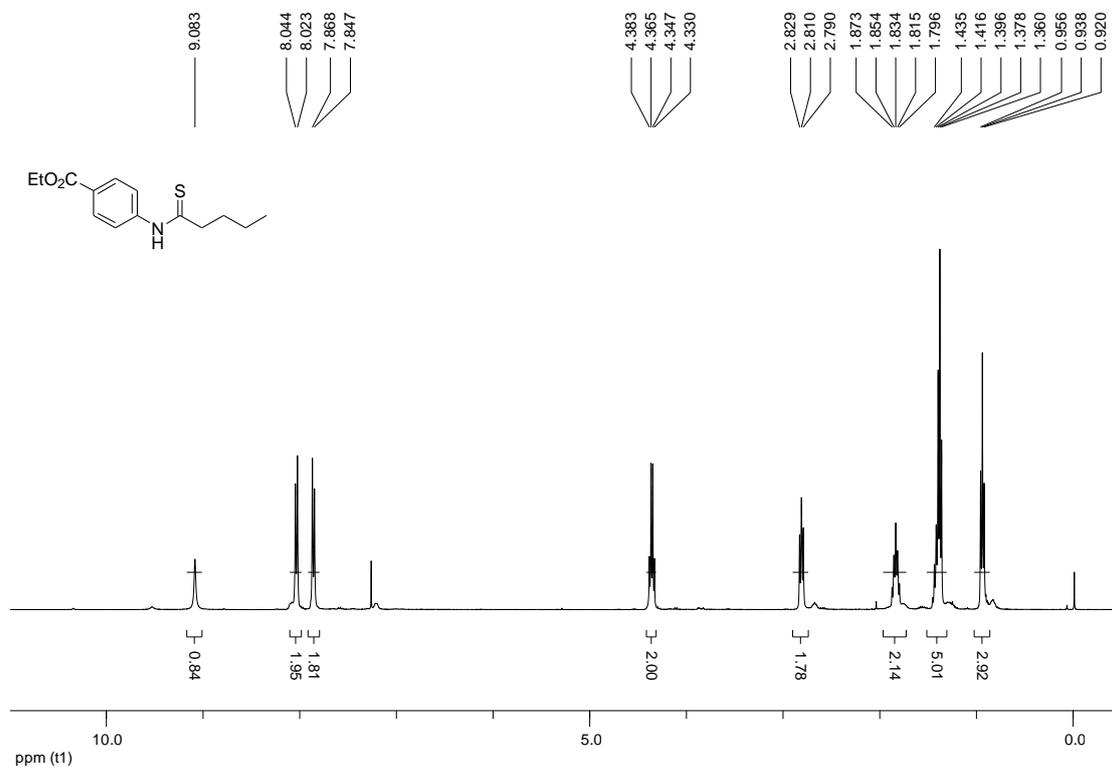
¹³C NMR (100MHz, CDCl₃) spectrum of 1f



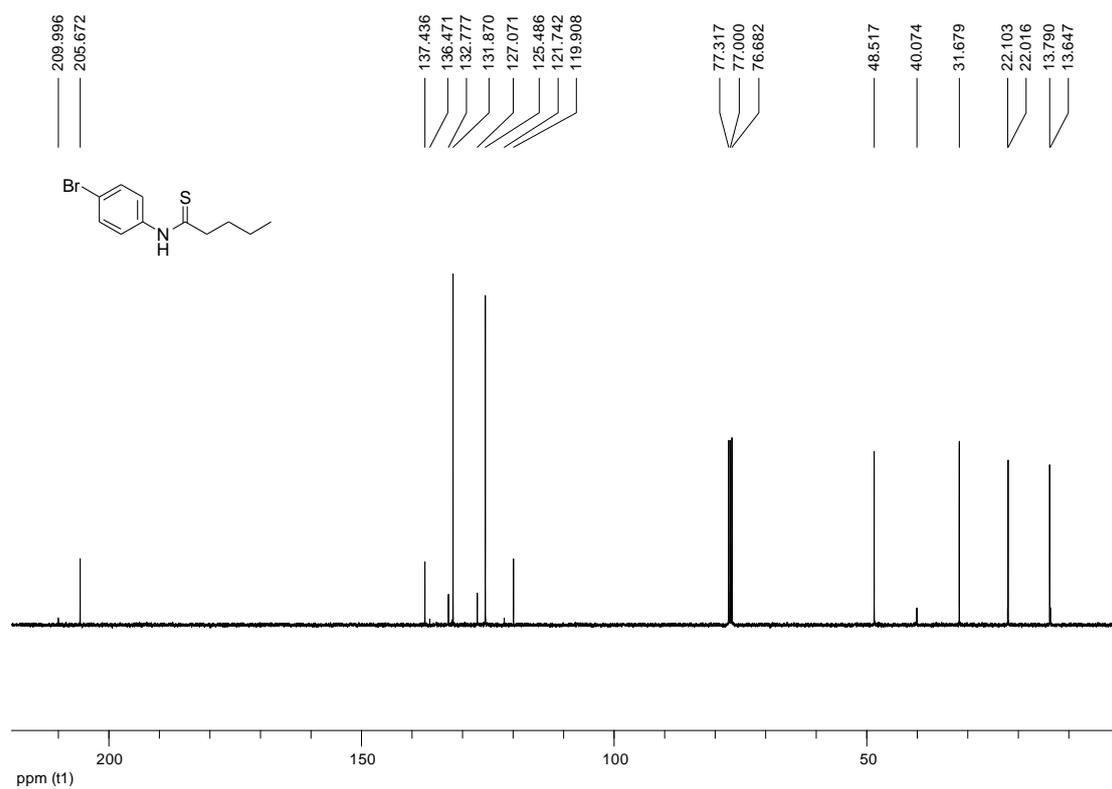
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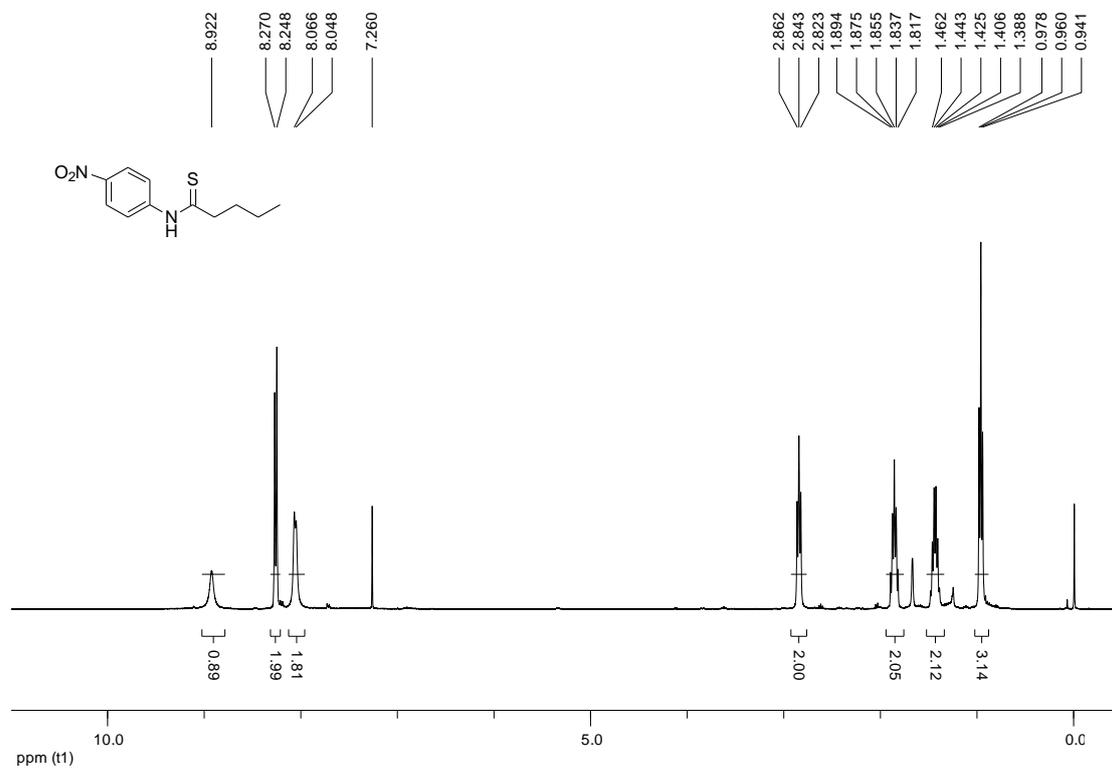
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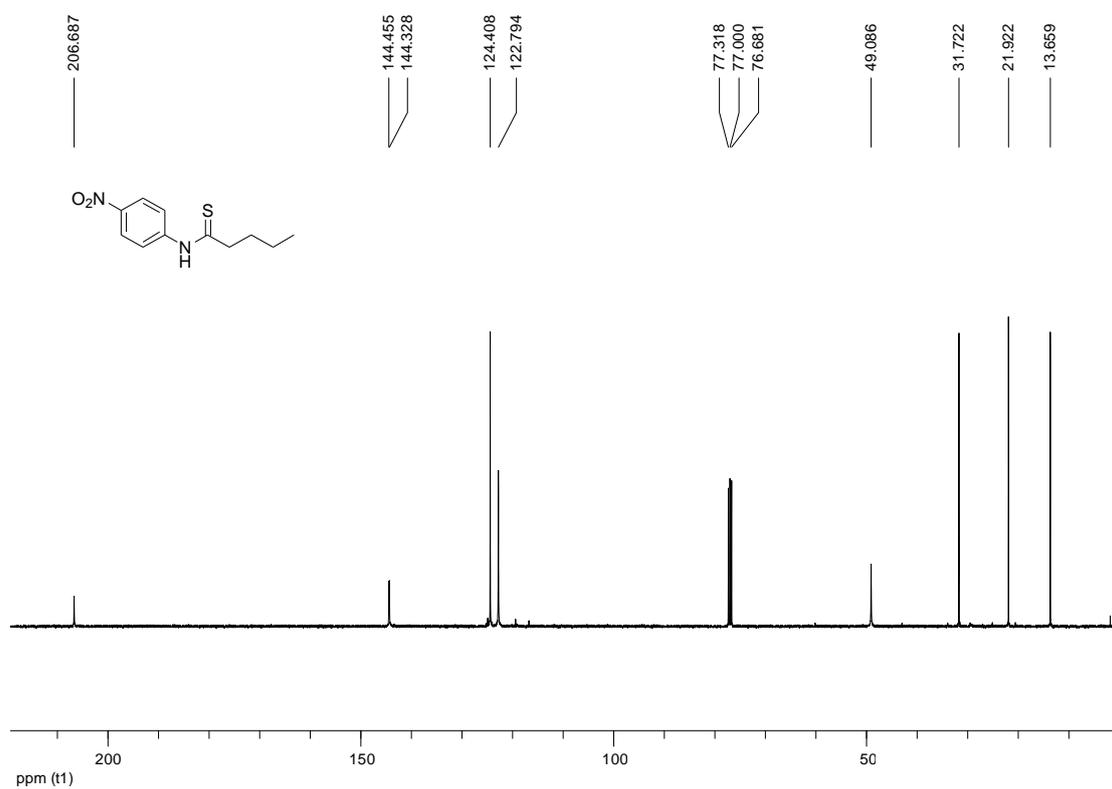
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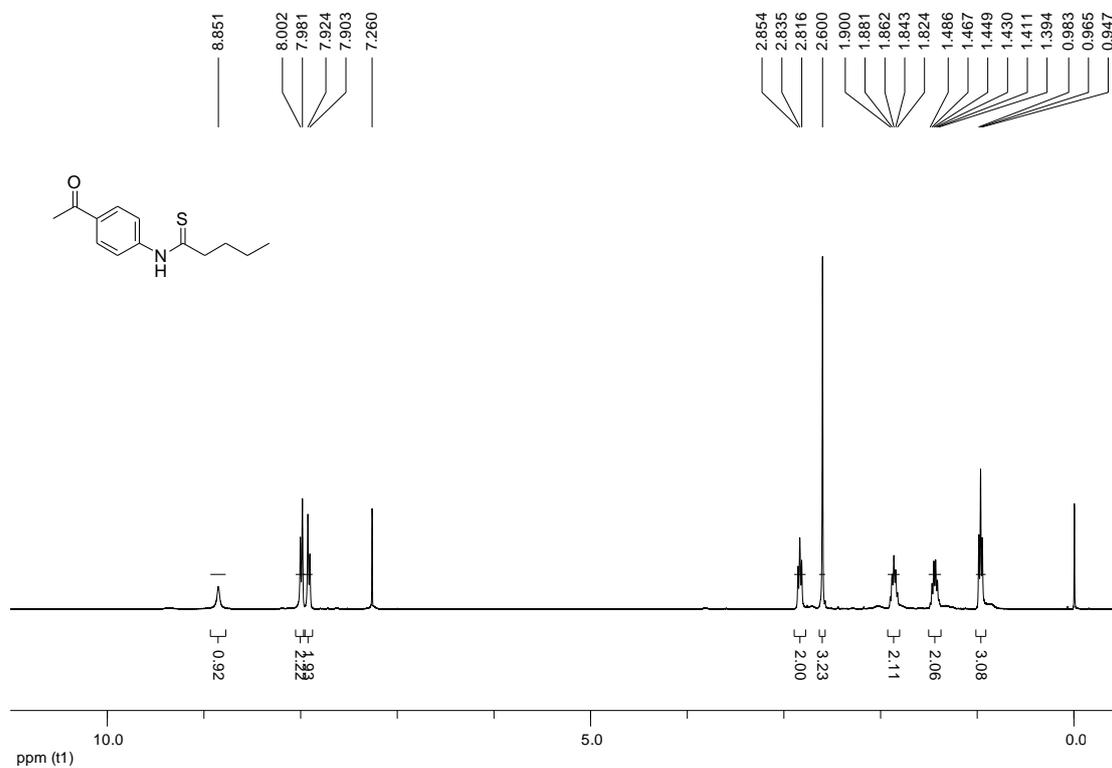
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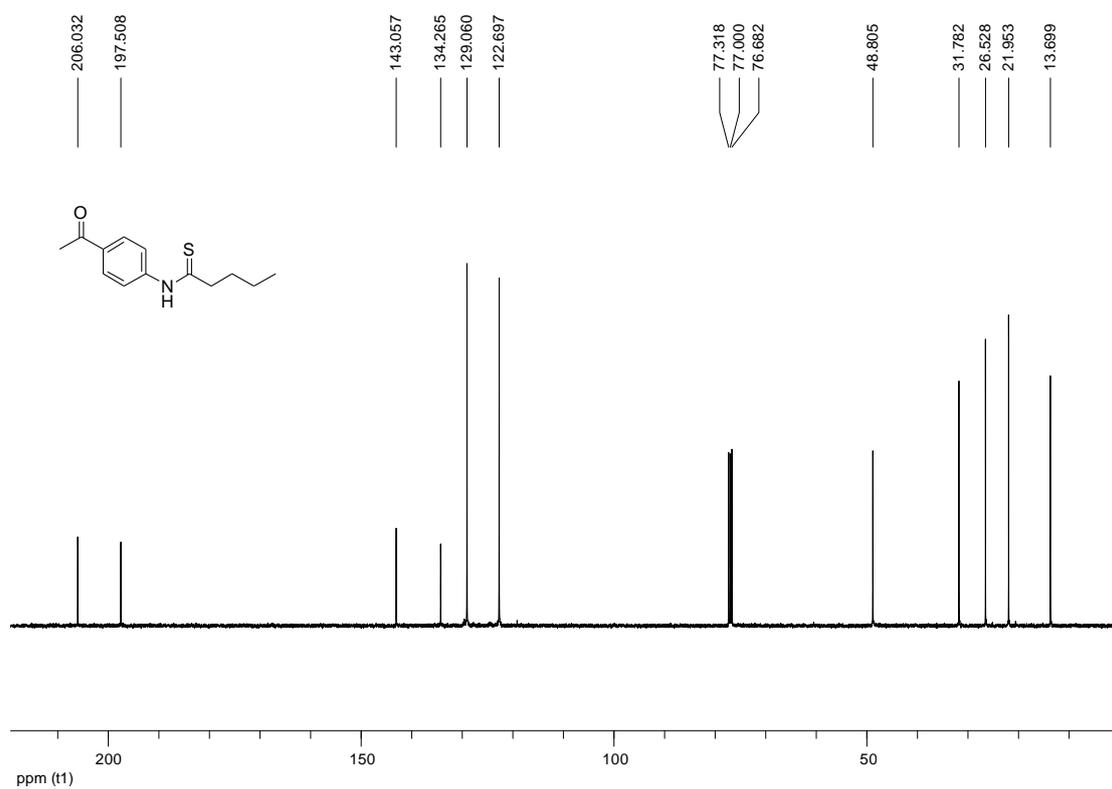
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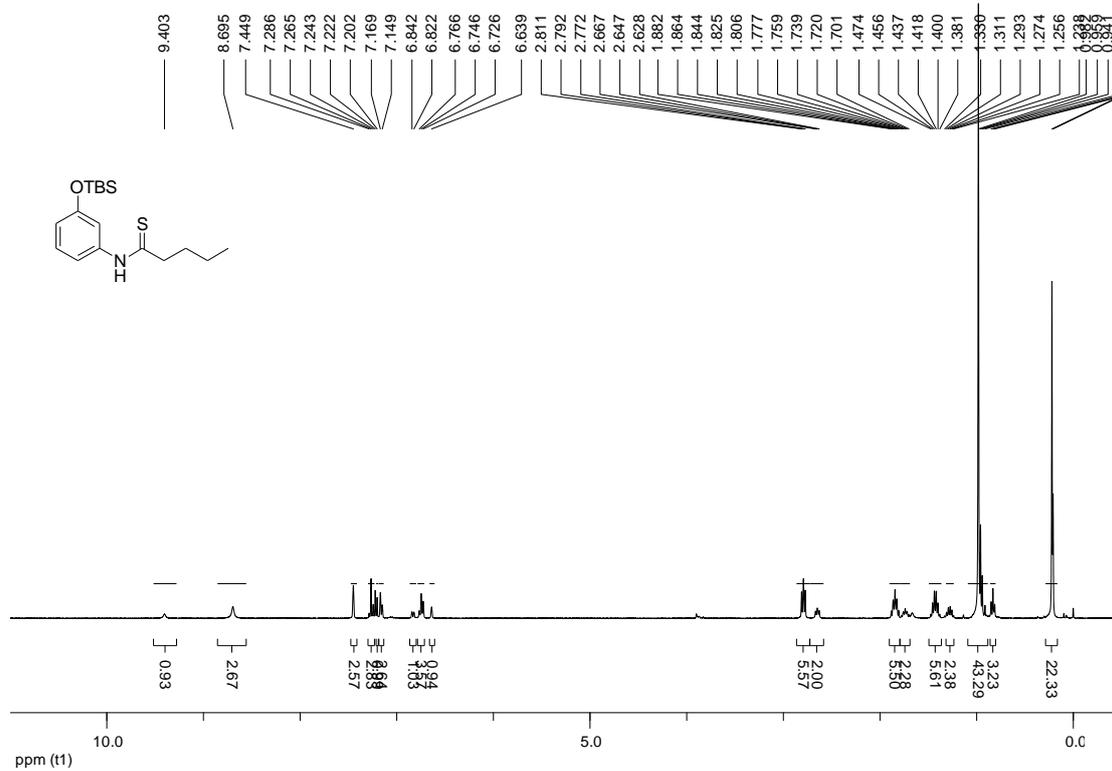
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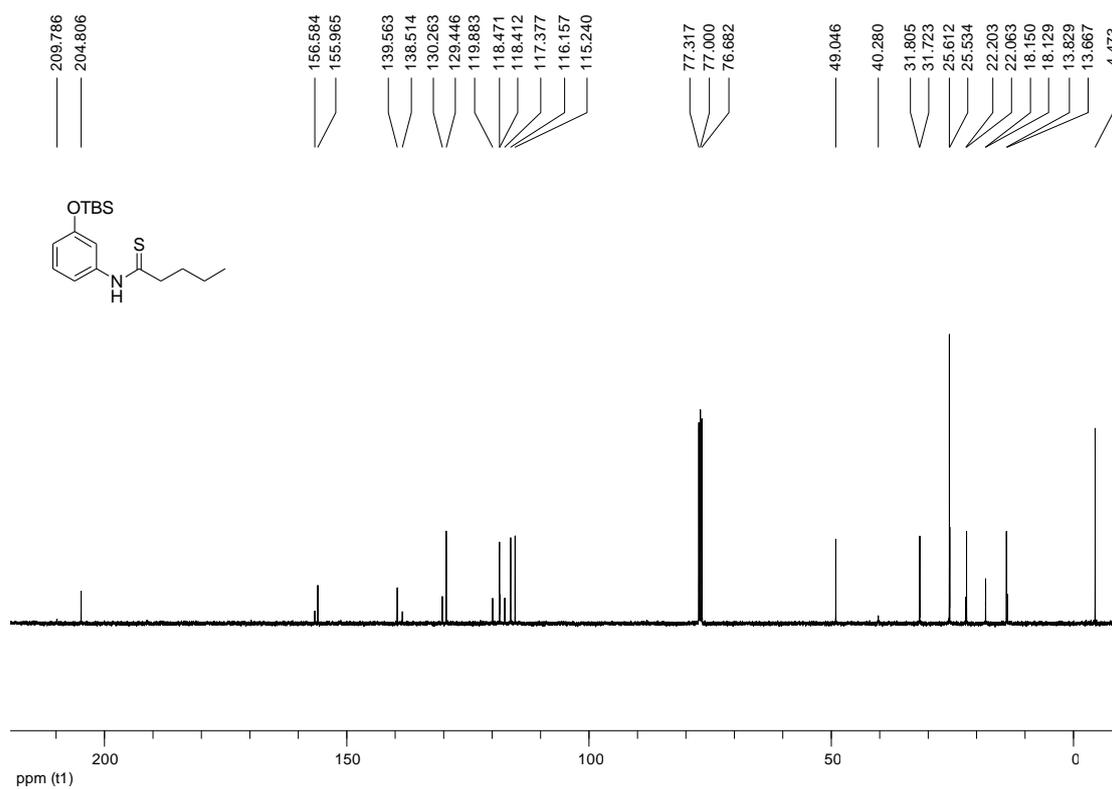
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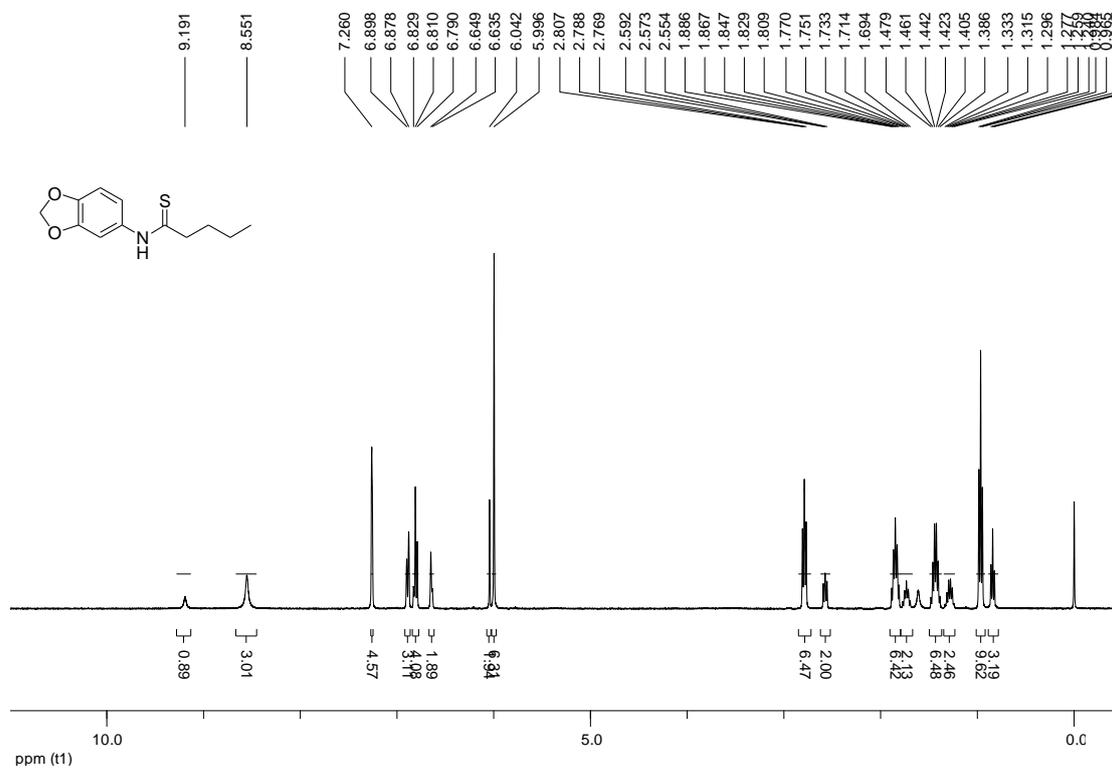
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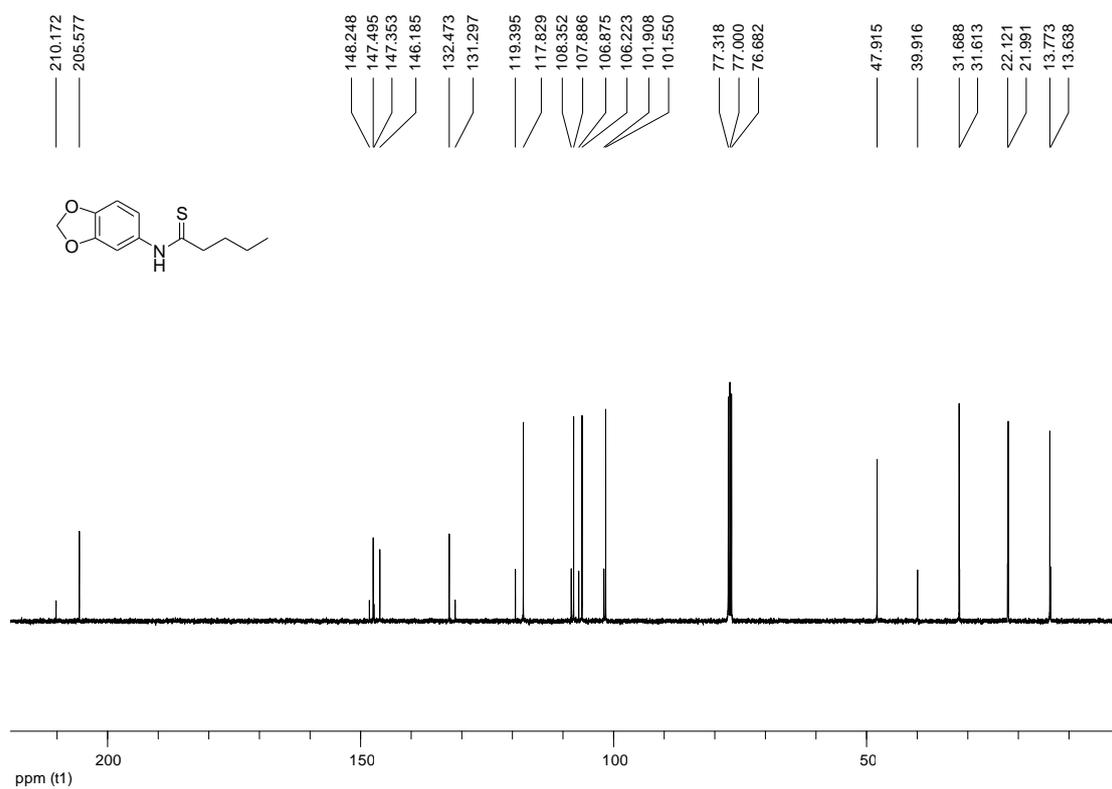
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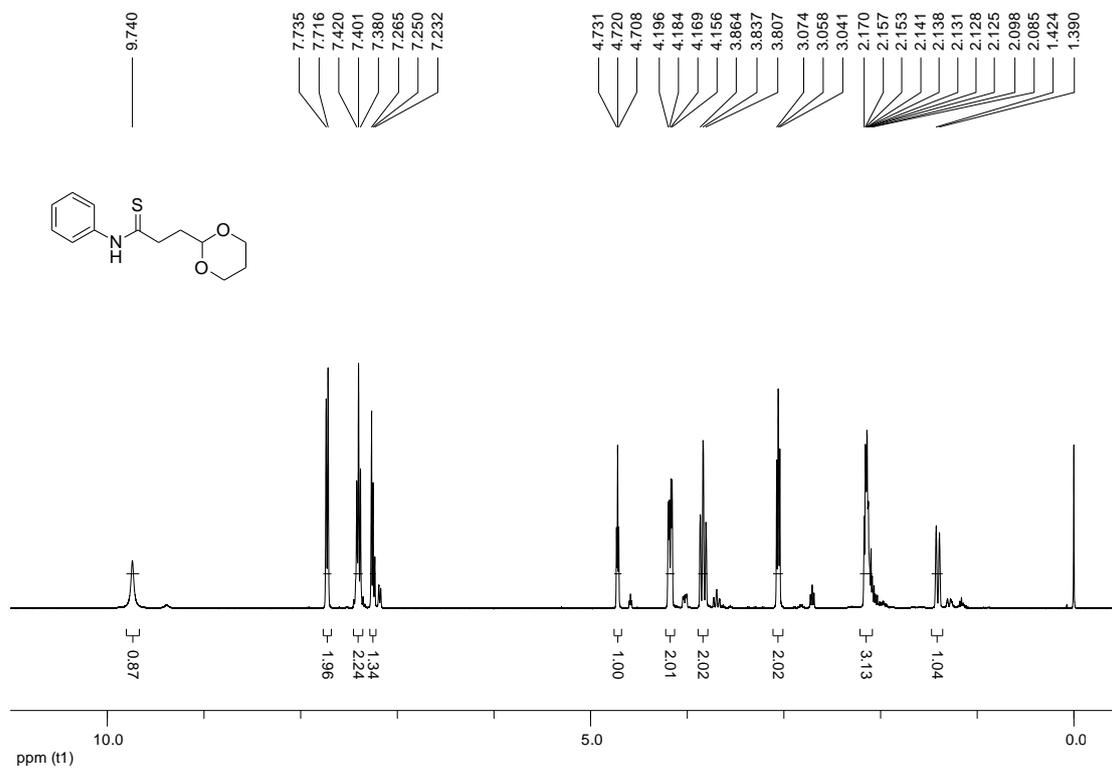
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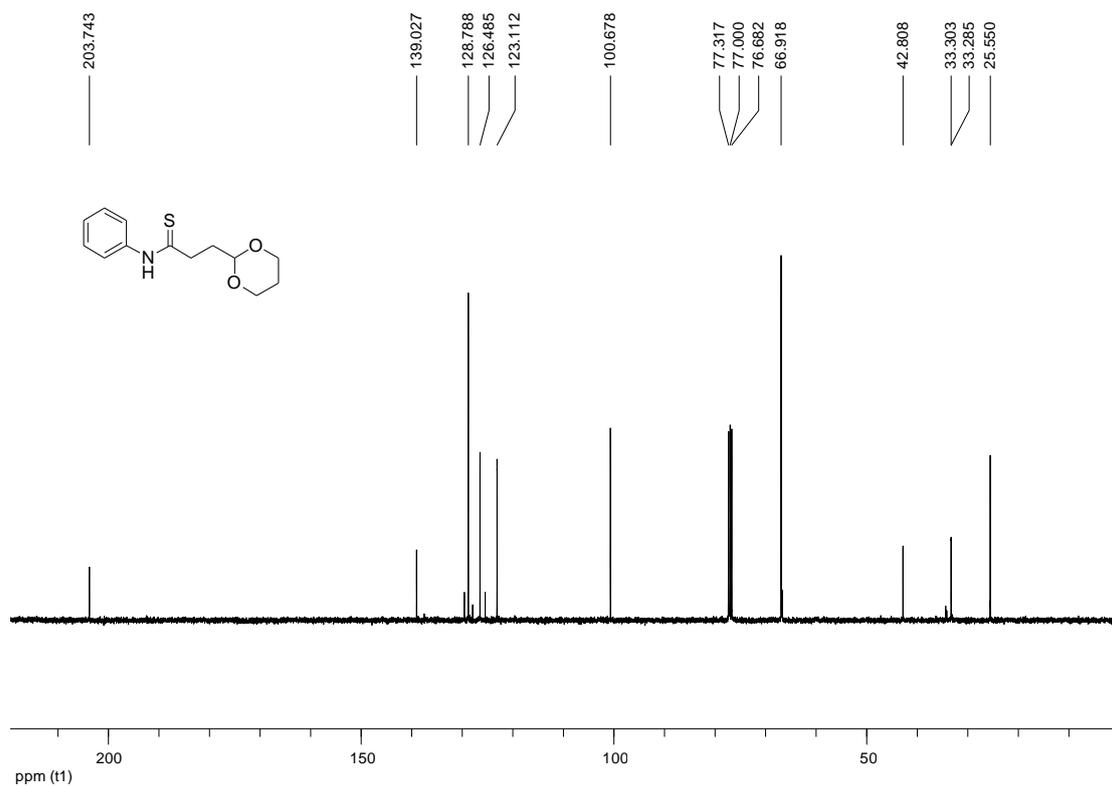
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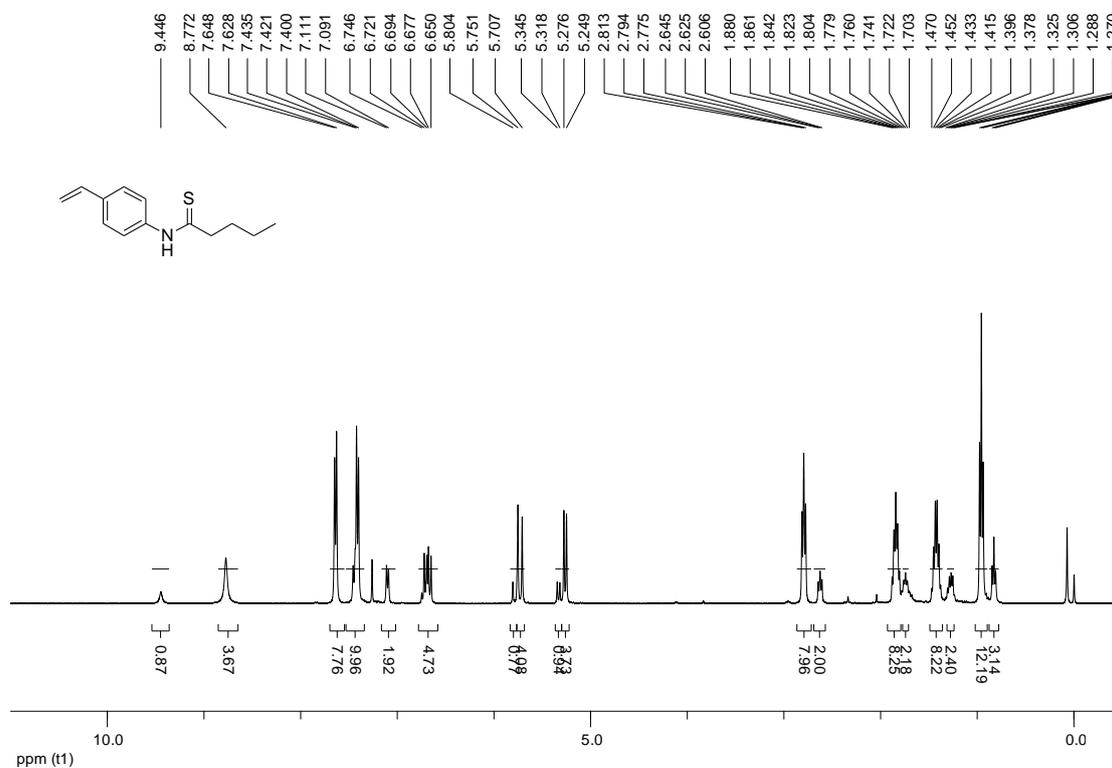
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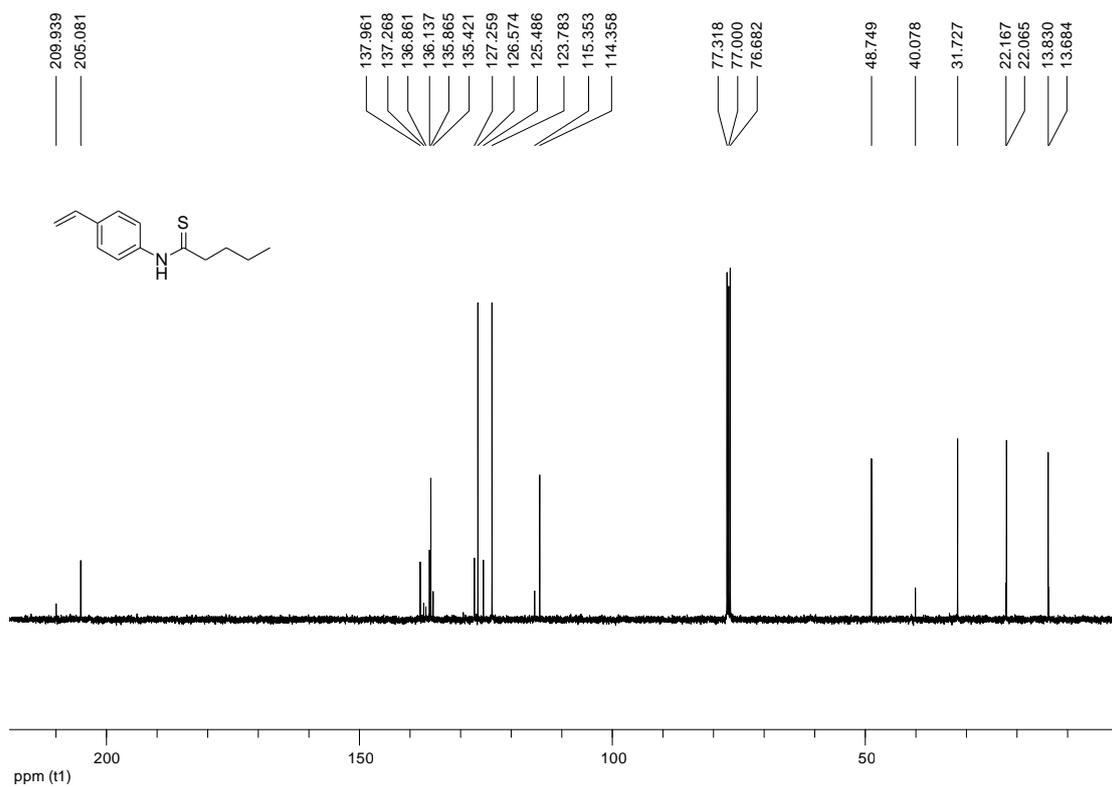
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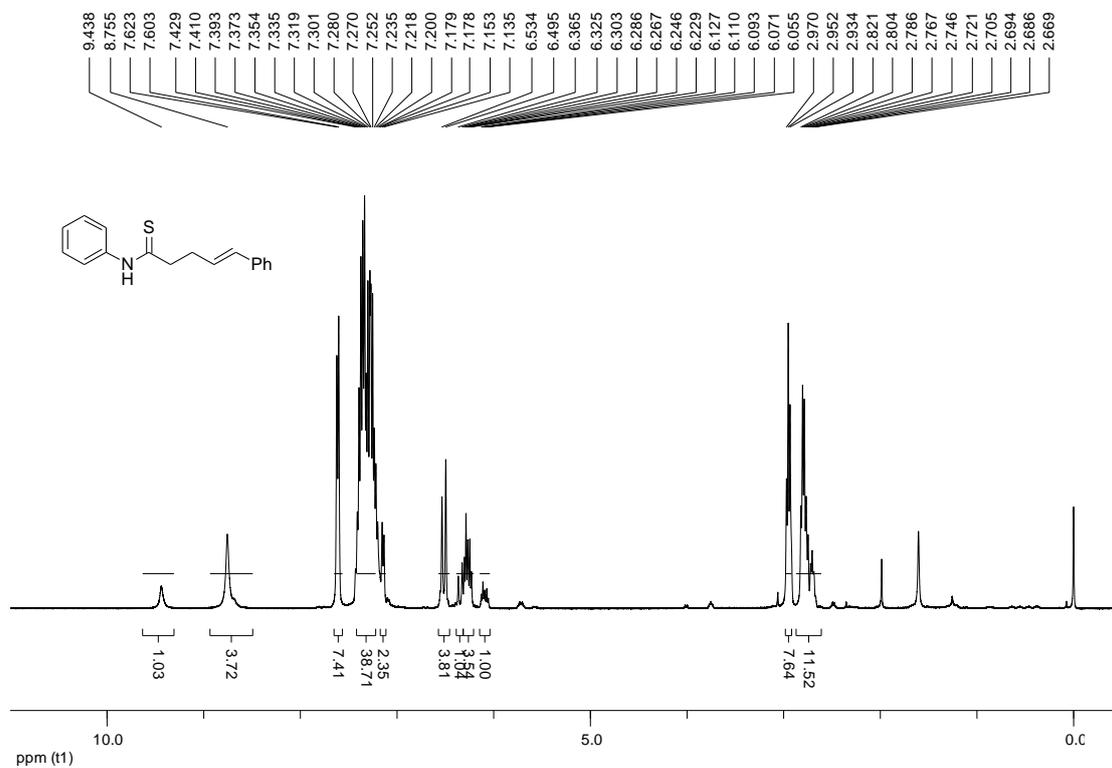
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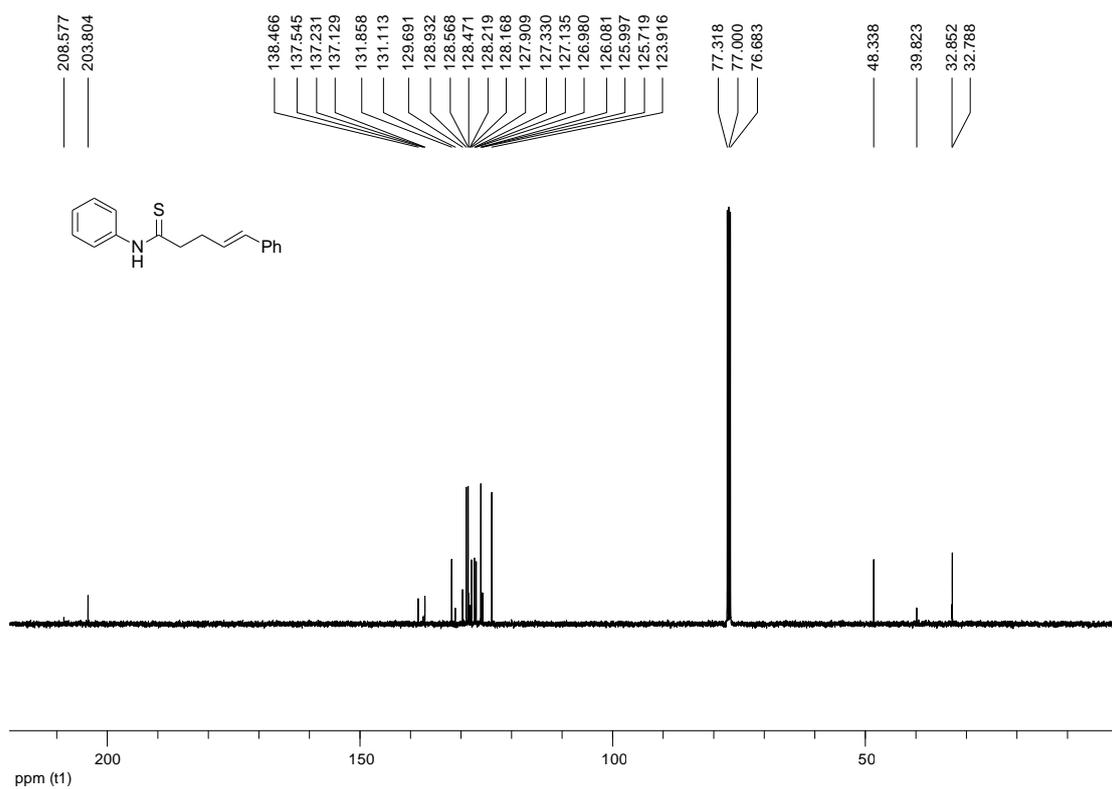
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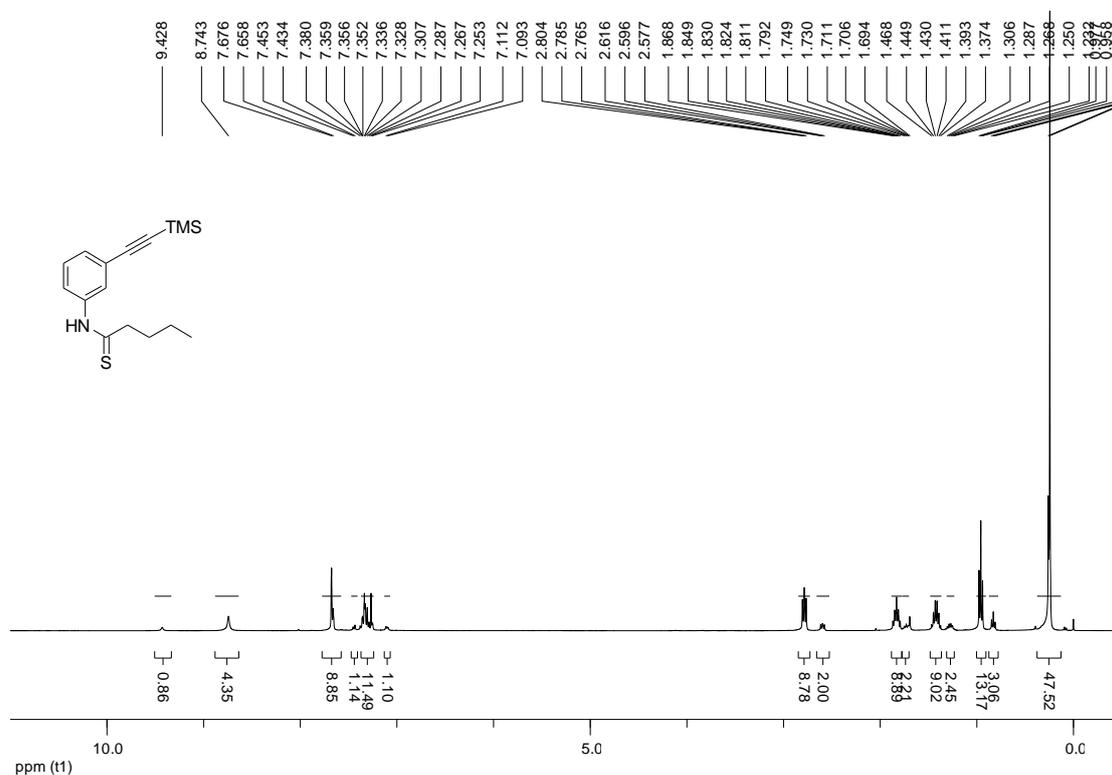
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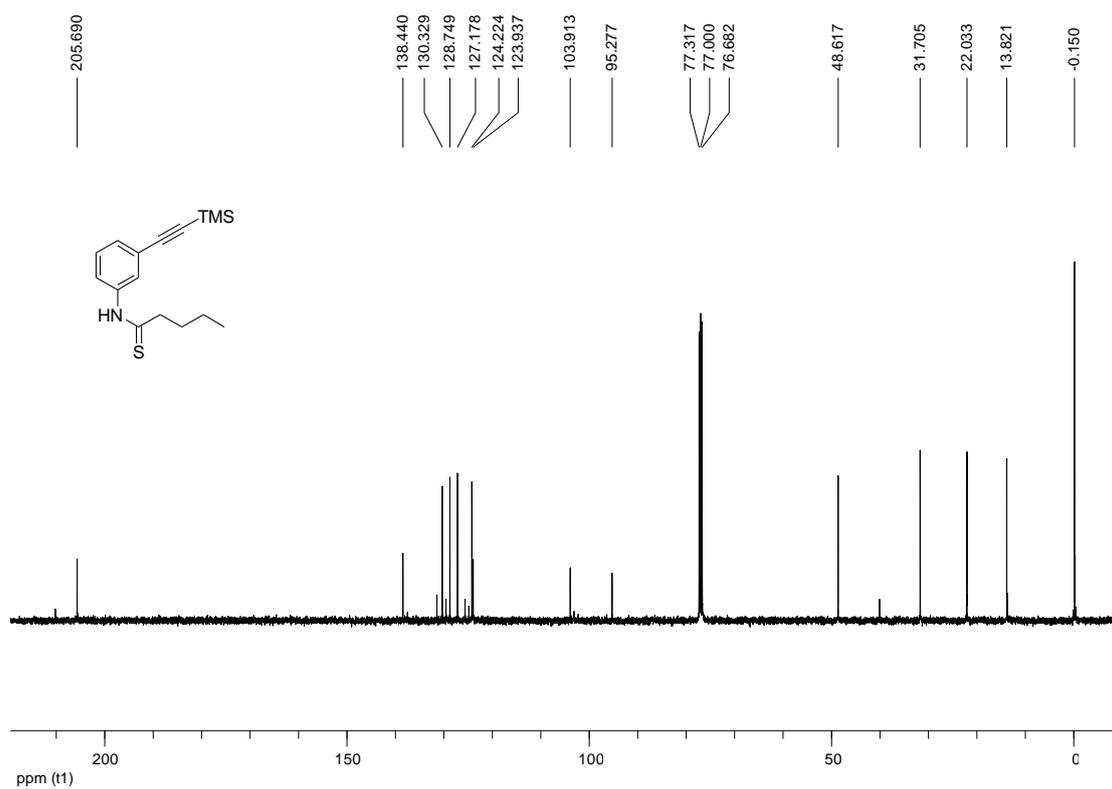
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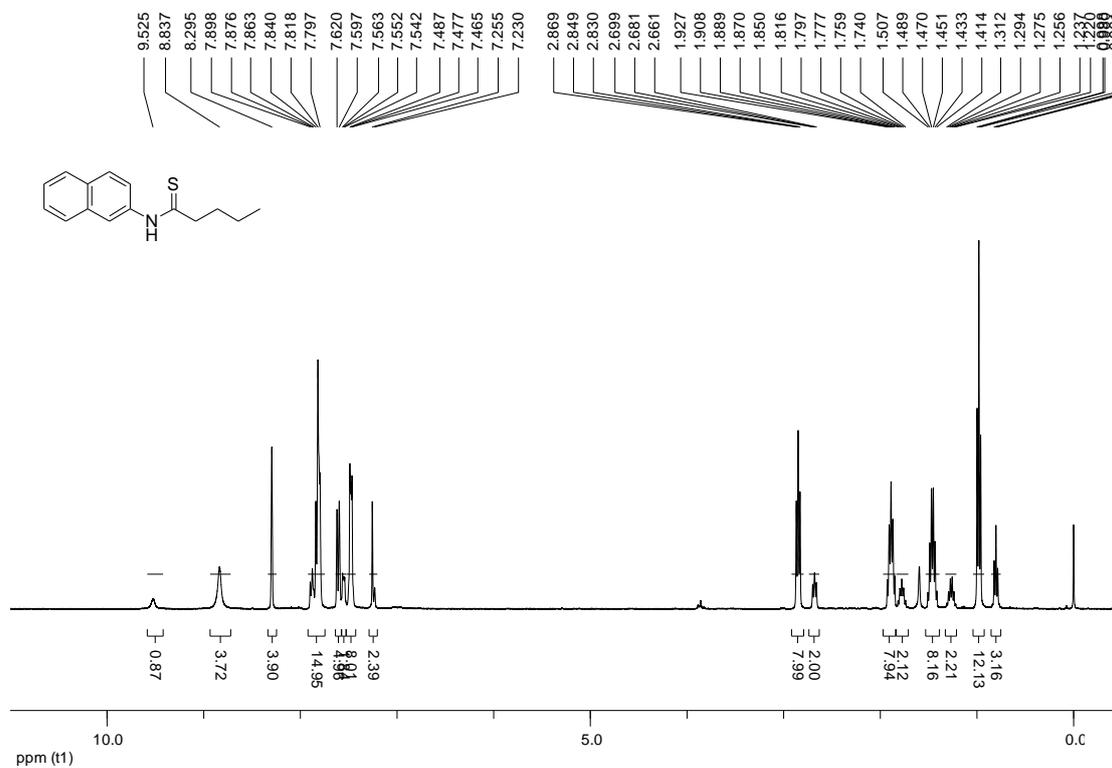
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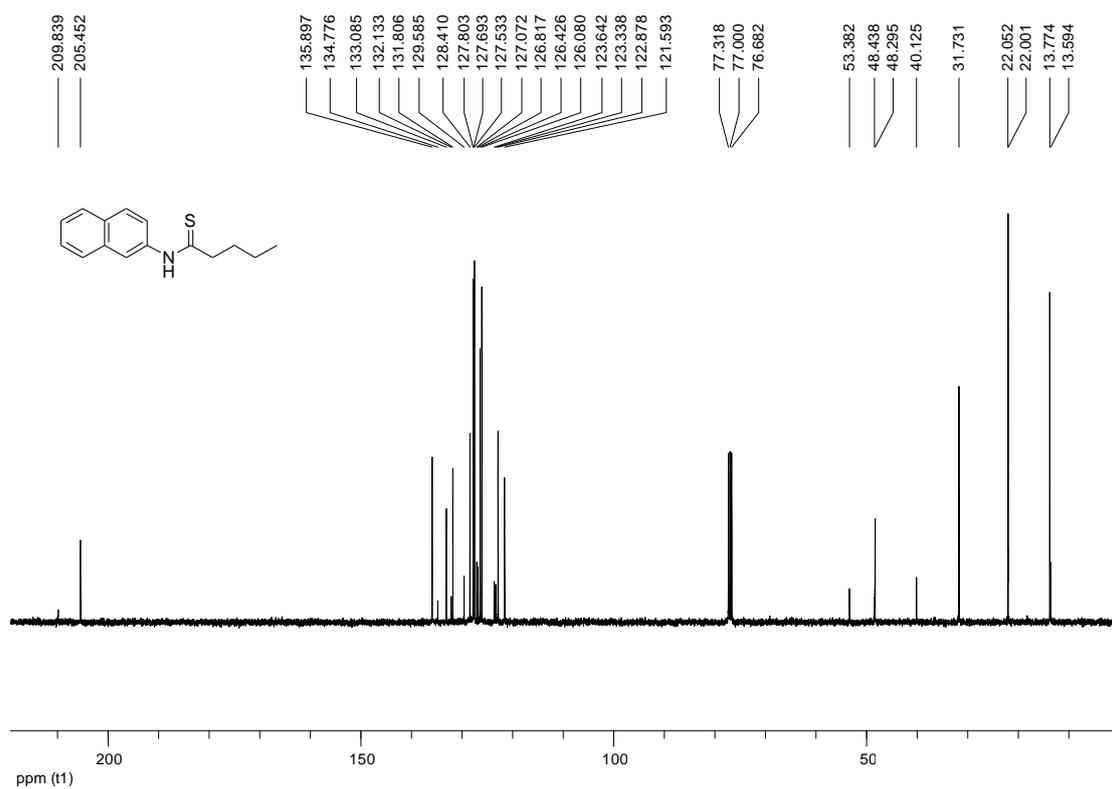
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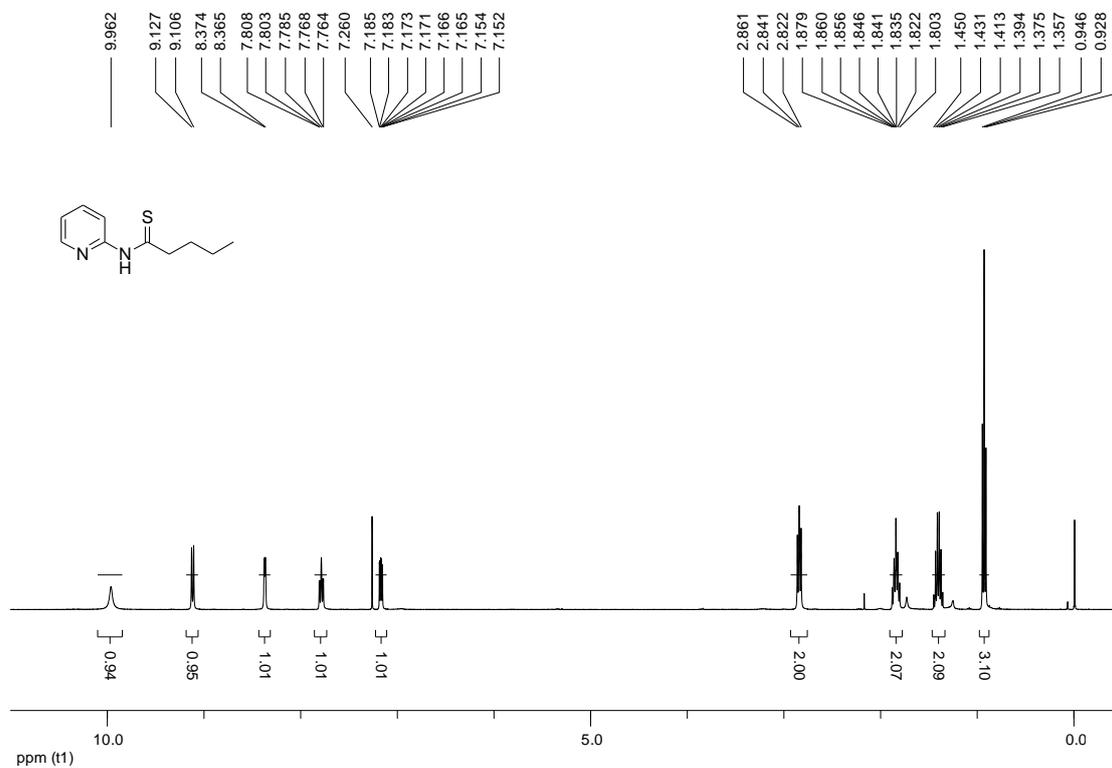
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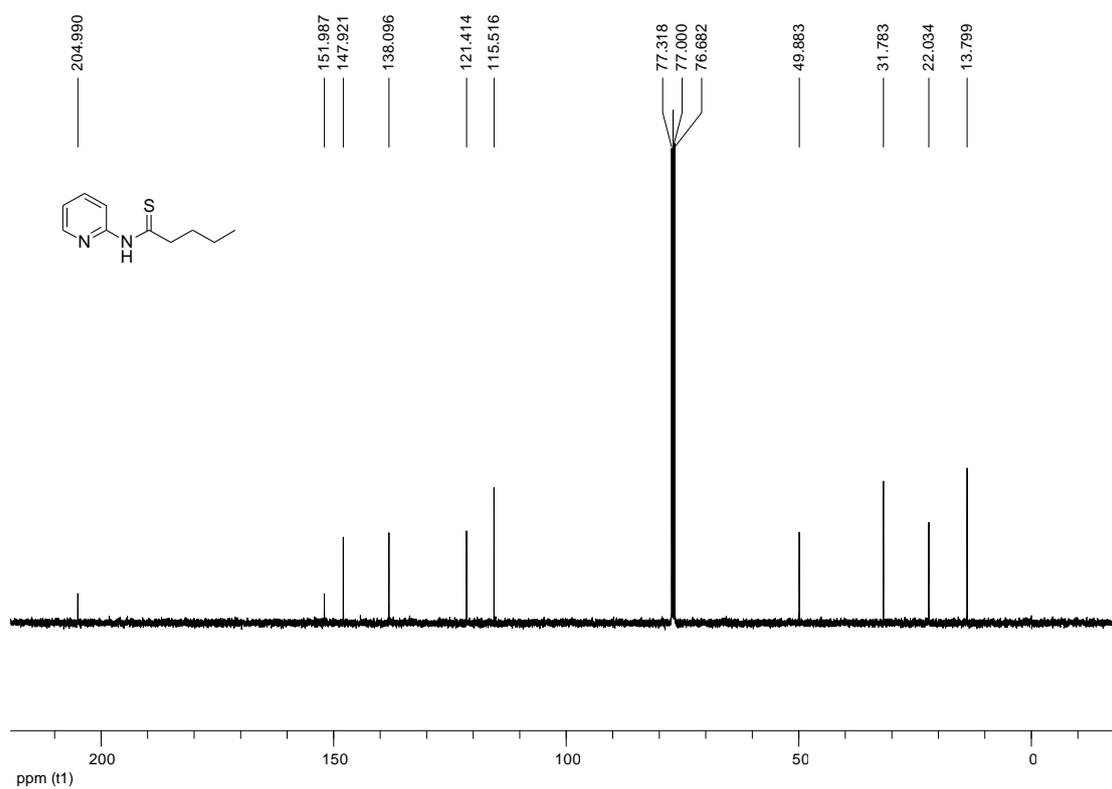
¹³C NMR (100MHz, CDCl₃) spectrum of 1q



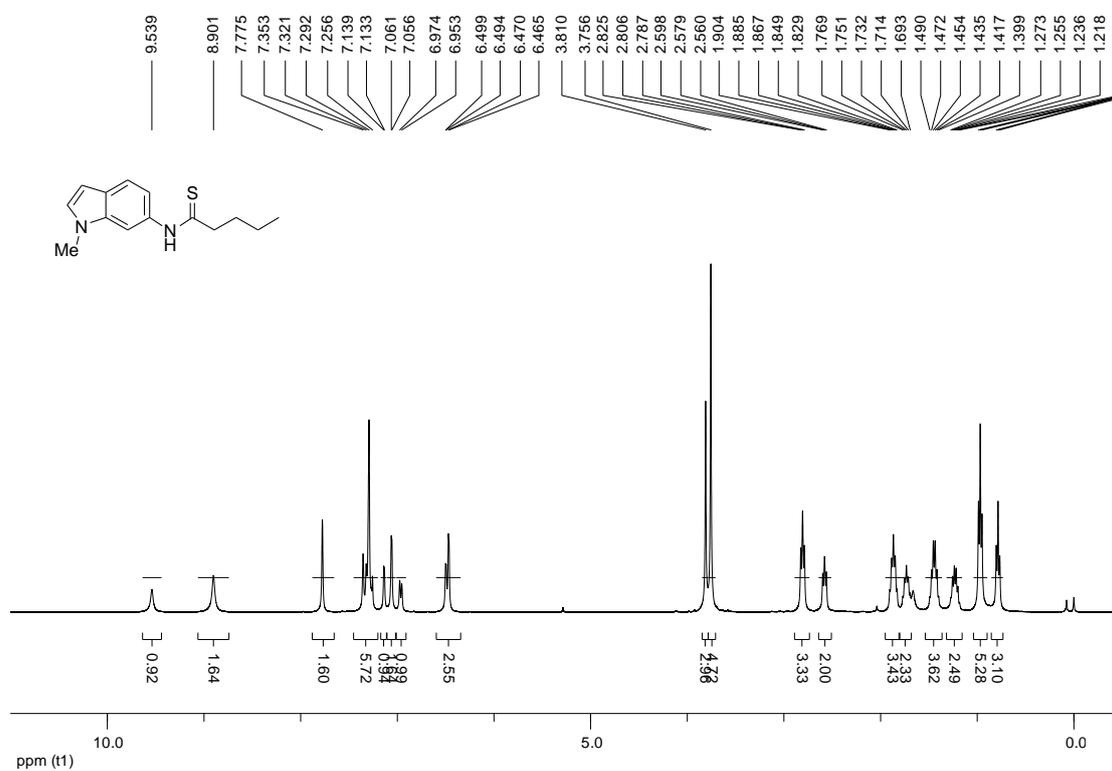
¹H NMR (400 MHz, CDCl₃) spectrum of 1r



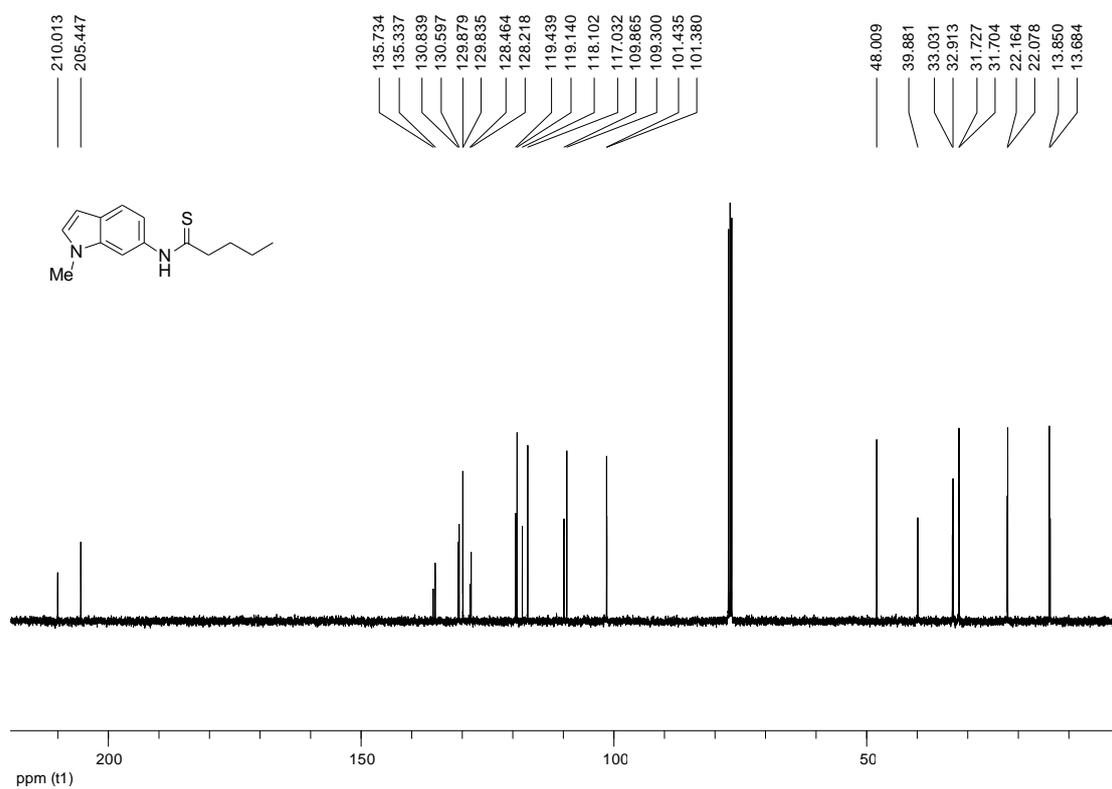
¹³C NMR (100MHz, CDCl₃) spectrum of 1r



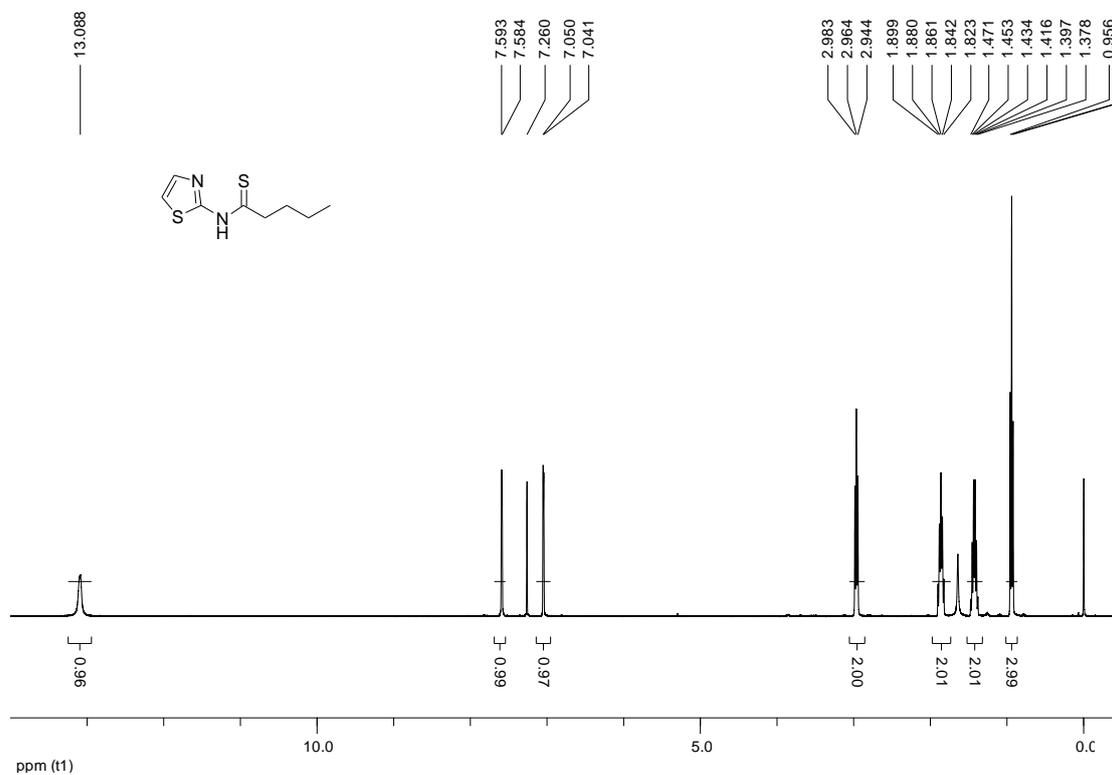
¹H NMR (400 MHz, CDCl₃) spectrum of 1s



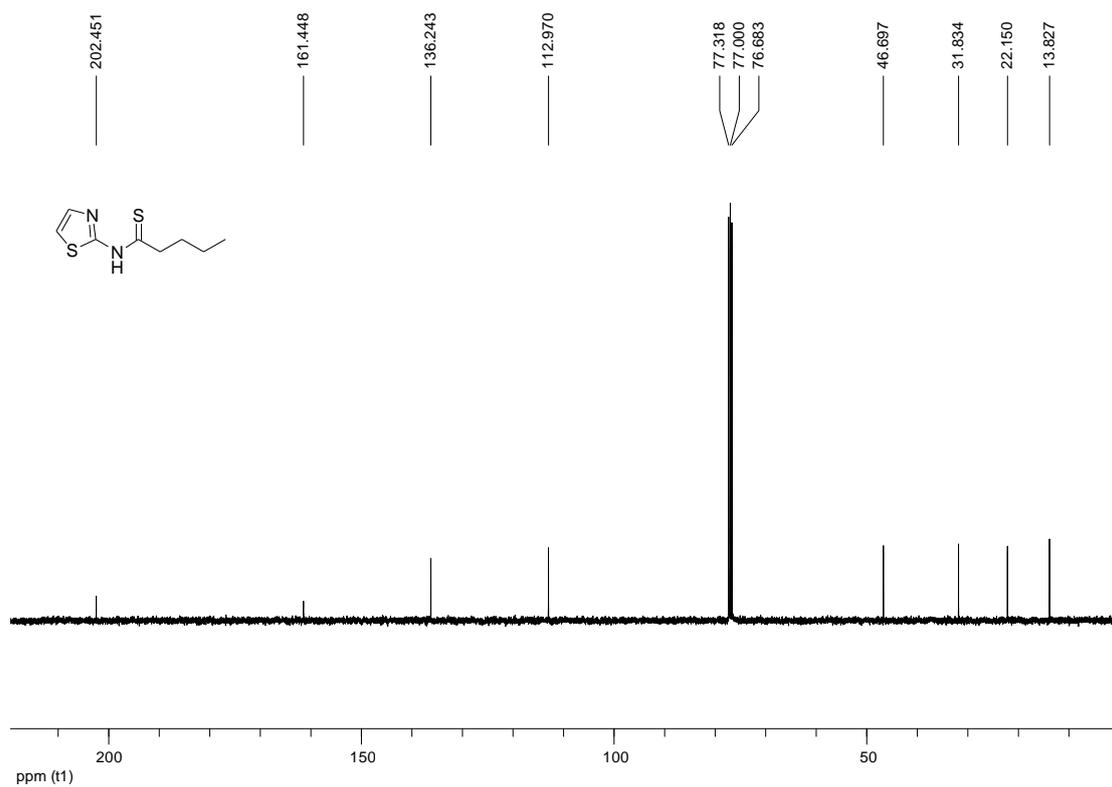
¹³C NMR (100MHz, CDCl₃) spectrum of 1s



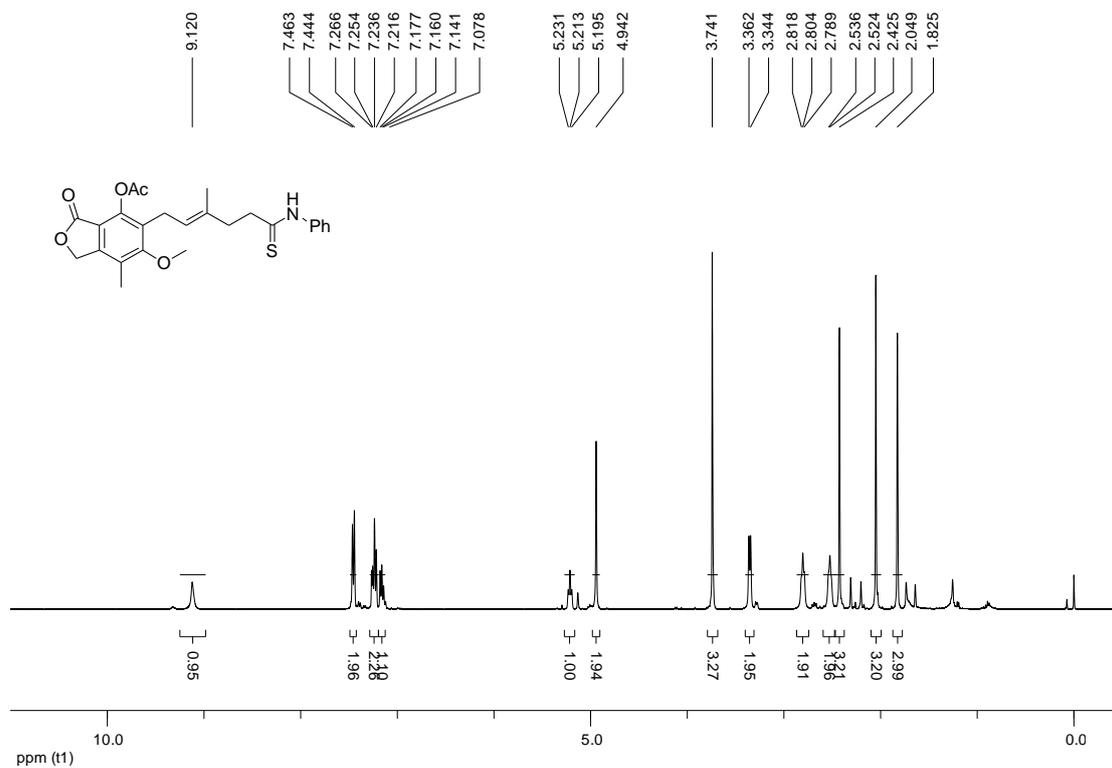
¹H NMR (400 MHz, CDCl₃) spectrum of 1t



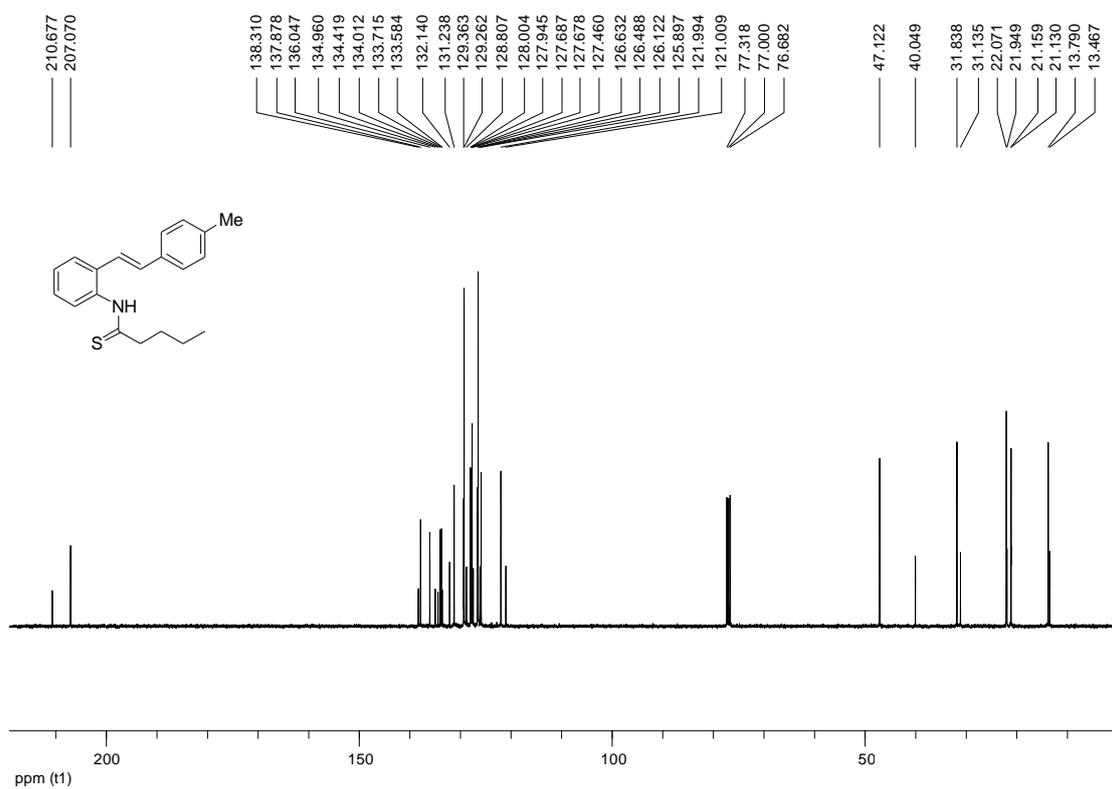
¹³C NMR (100MHz, CDCl₃) spectrum of 1t



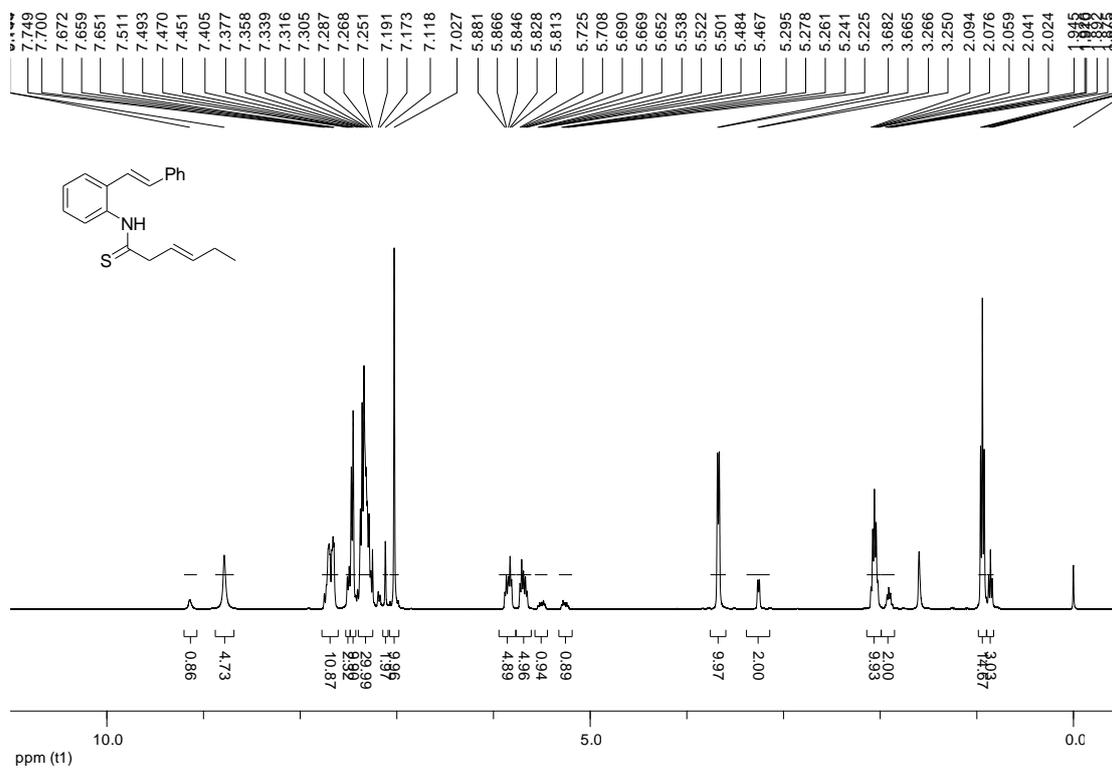
¹H NMR (400 MHz, CDCl₃) spectrum of 1w



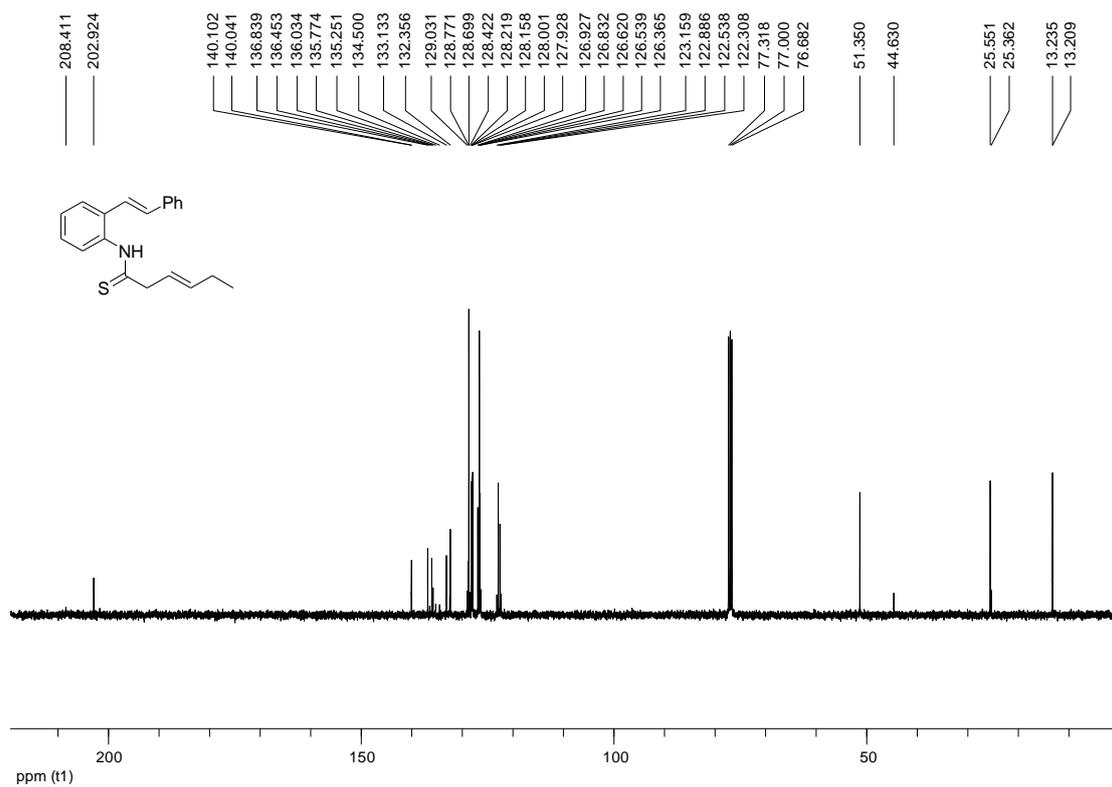
¹³C NMR (100MHz, CDCl₃) spectrum of 1ab



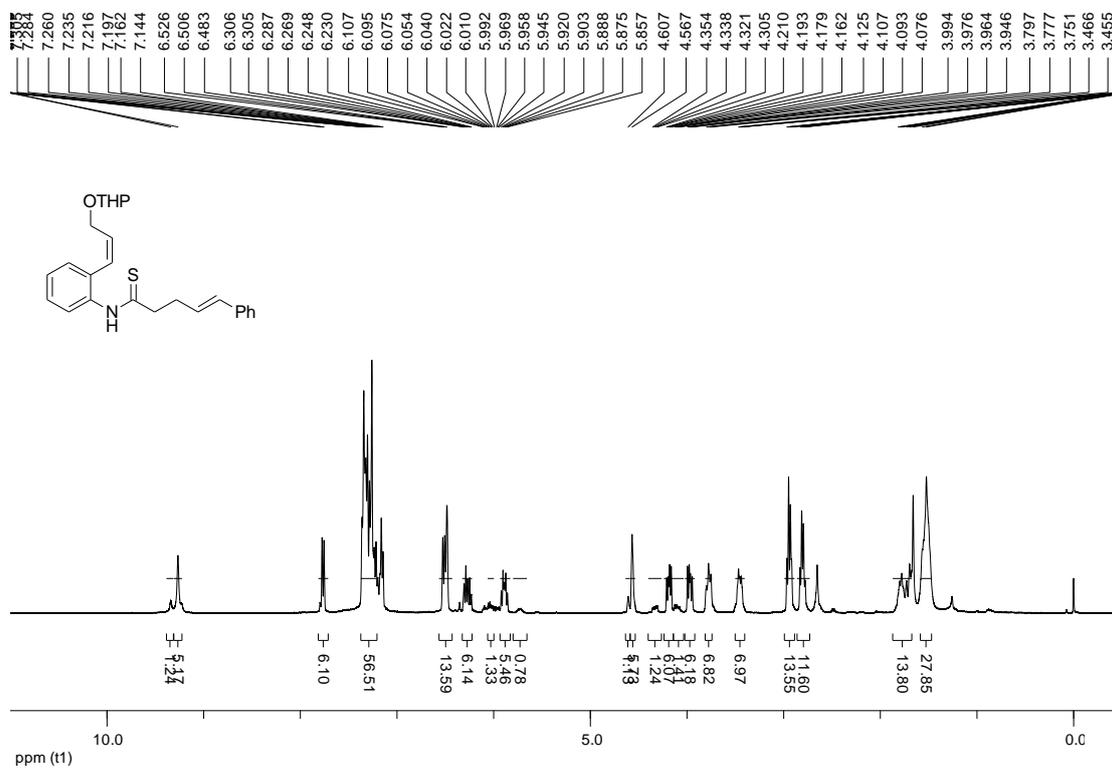
¹H NMR (400 MHz, CDCl₃) spectrum of 1ac



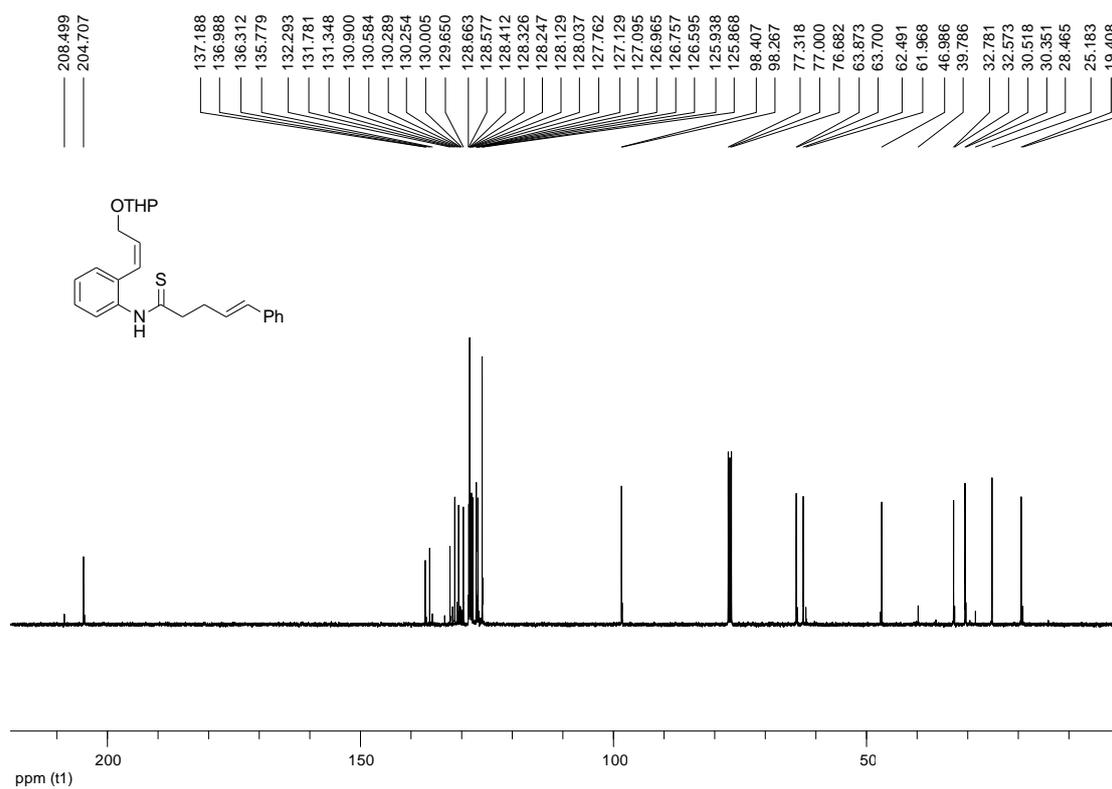
¹³C NMR (100MHz, CDCl₃) spectrum of 1ac



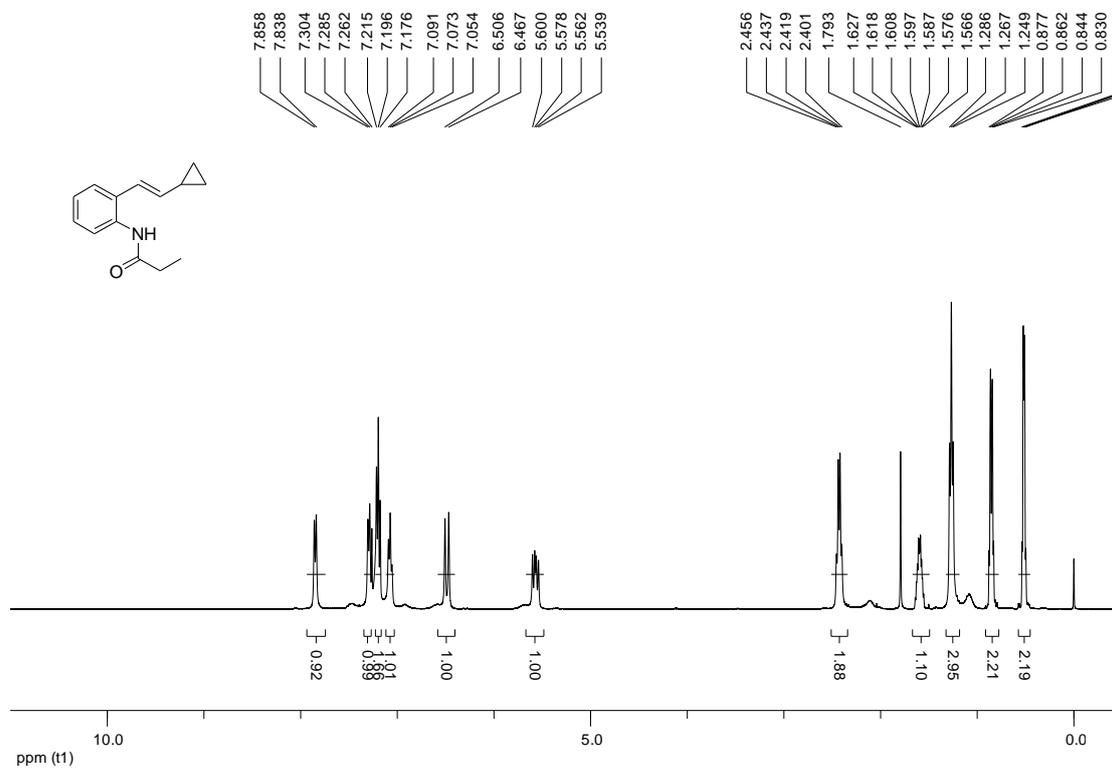
¹H NMR (400 MHz, CDCl₃) spectrum of 1ad



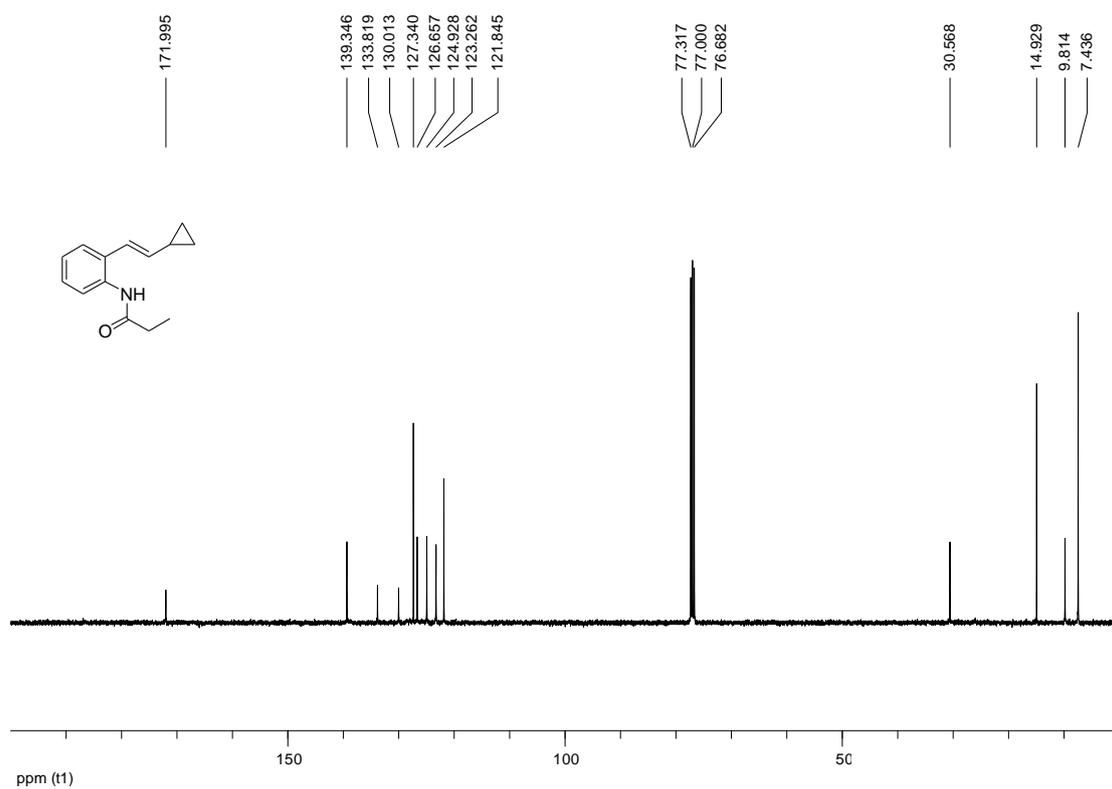
¹³C NMR (100MHz, CDCl₃) spectrum of 1ad



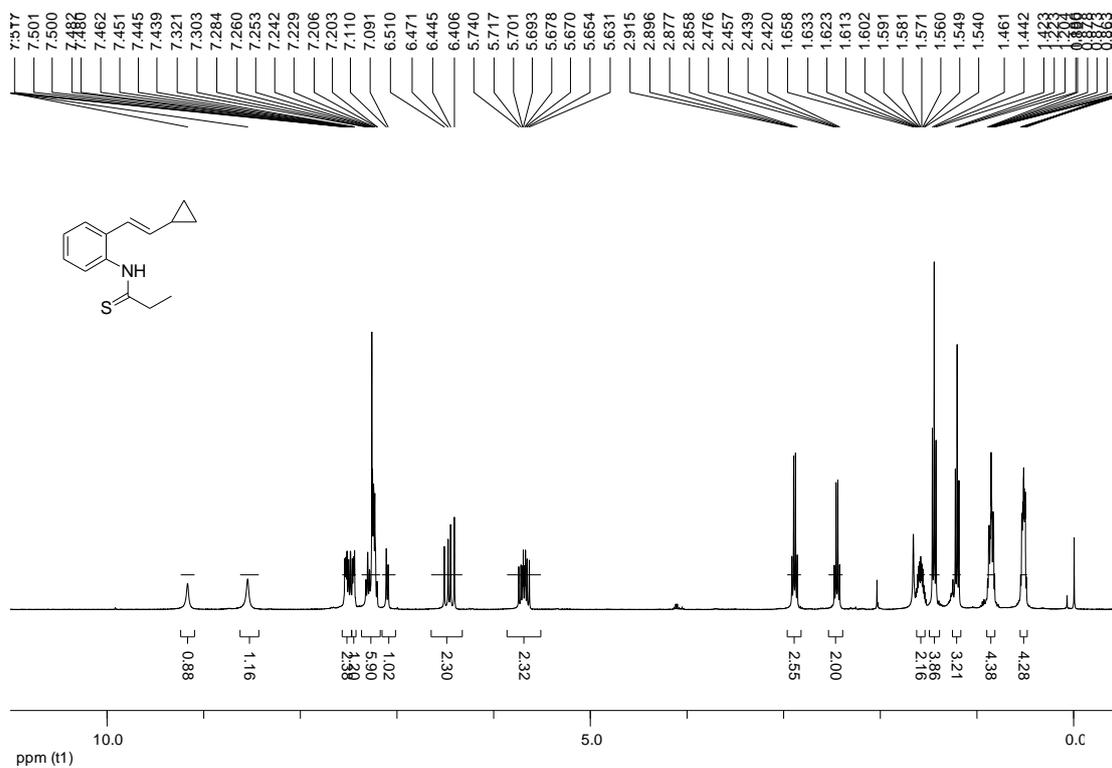
¹H NMR (400 MHz, CDCl₃) spectrum of 1ae-A



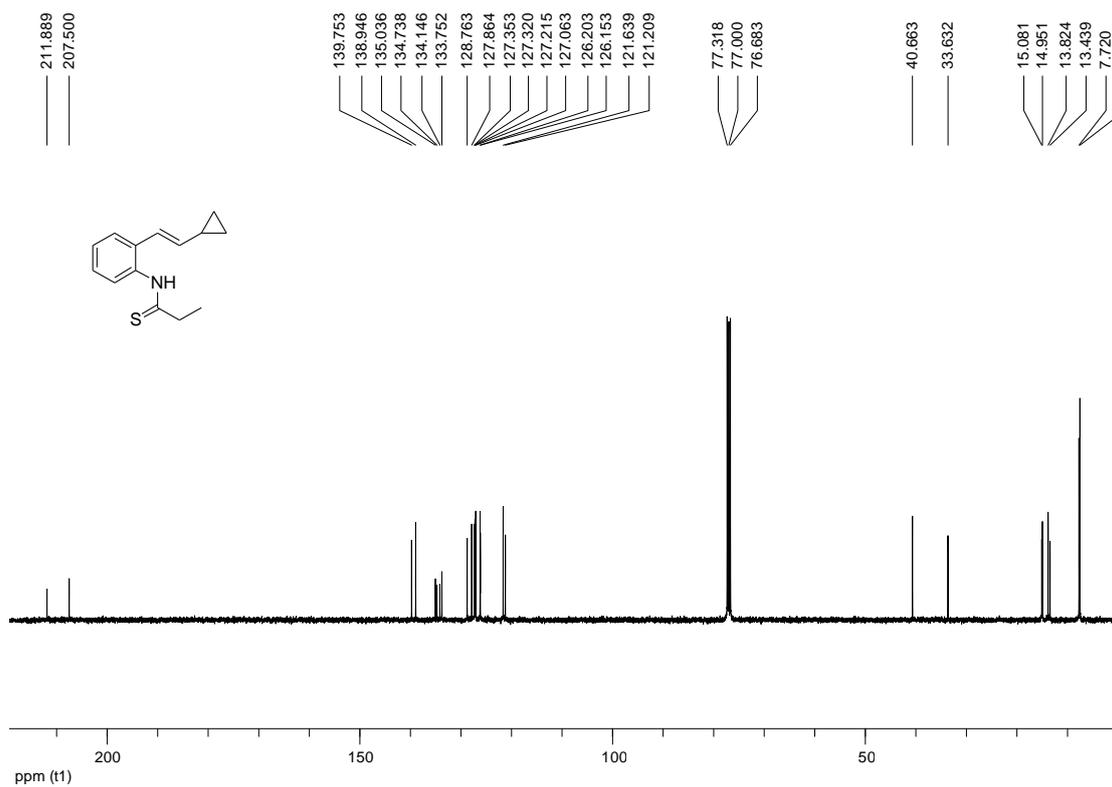
¹³C NMR (100MHz, CDCl₃) spectrum of 1ae-A



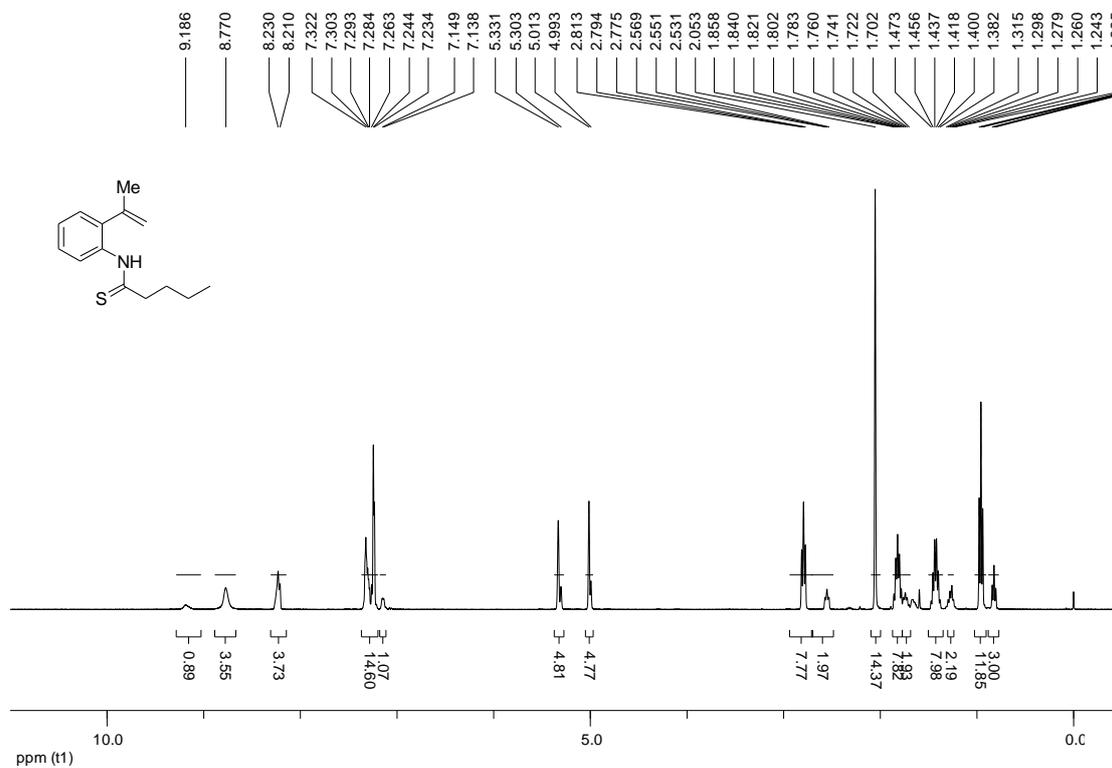
¹H NMR (400 MHz, CDCl₃) spectrum of 1ae



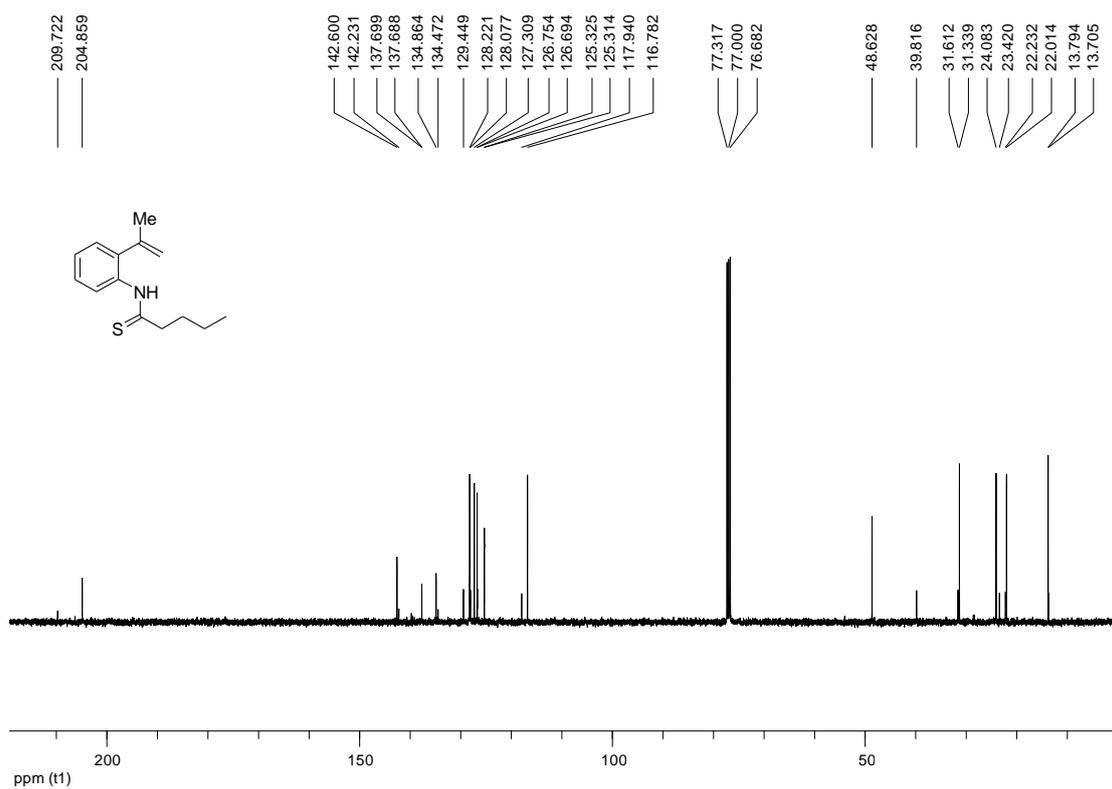
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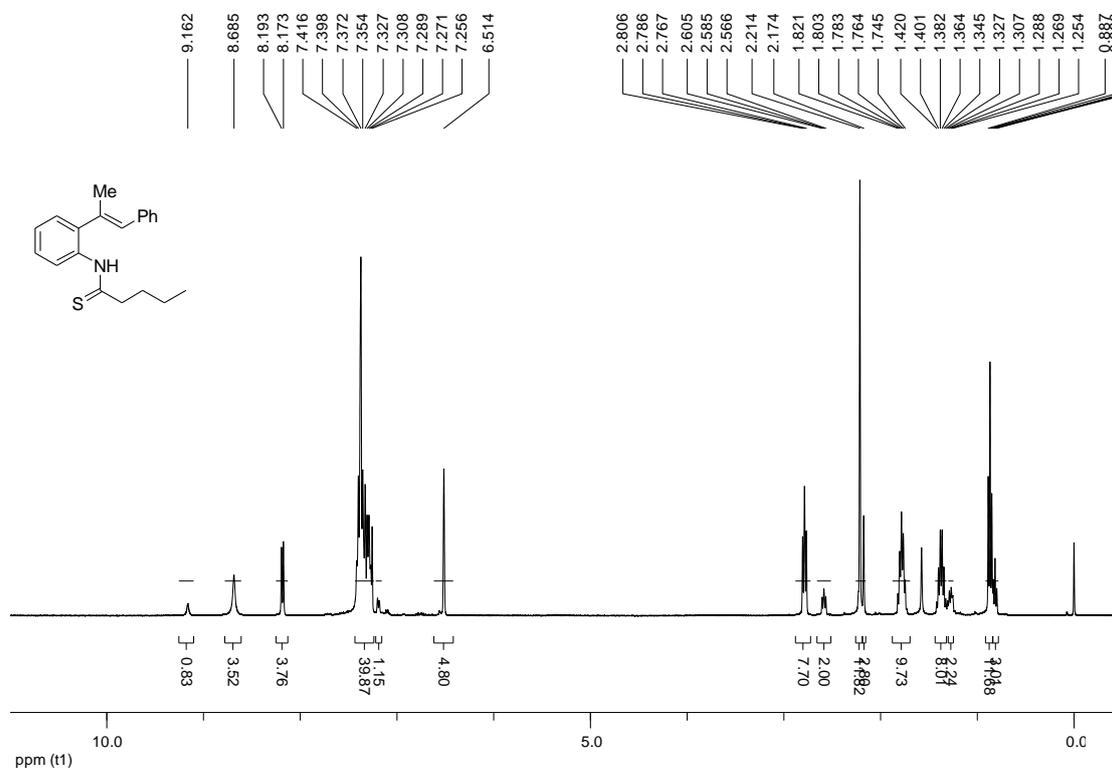
¹H NMR (400 MHz, CDCl₃) spectrum of 1af



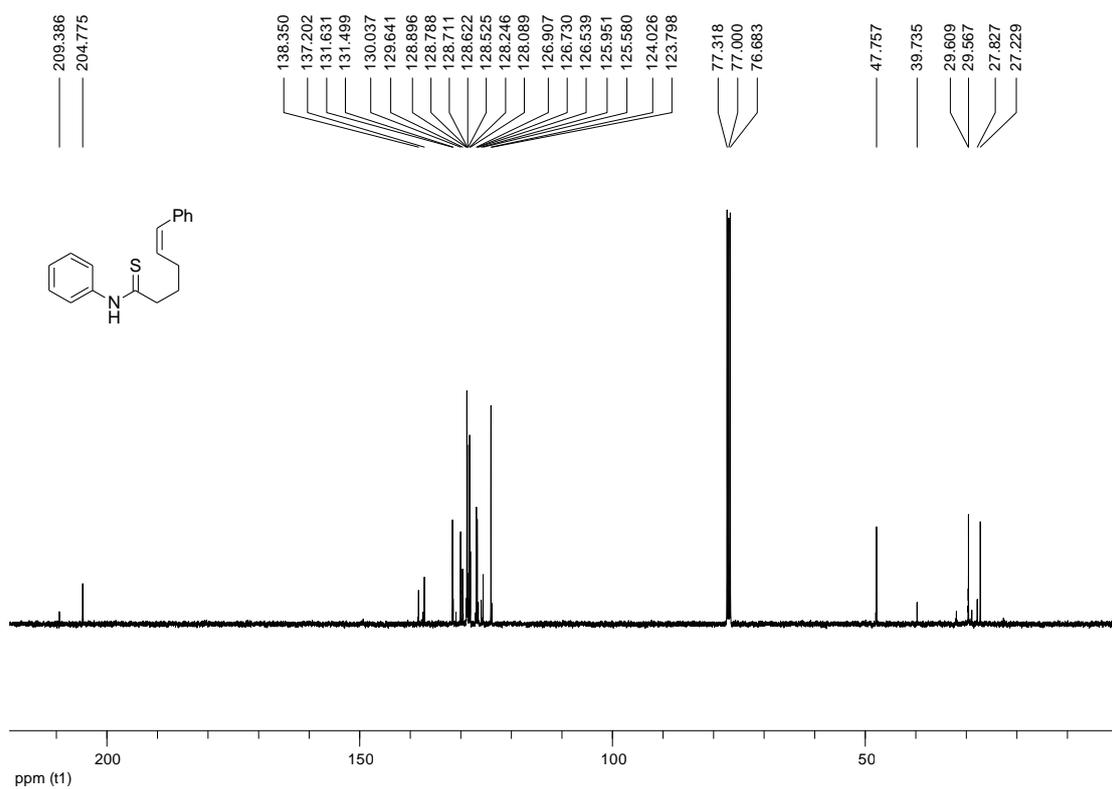
¹³C NMR (100MHz, CDCl₃) spectrum of 1af



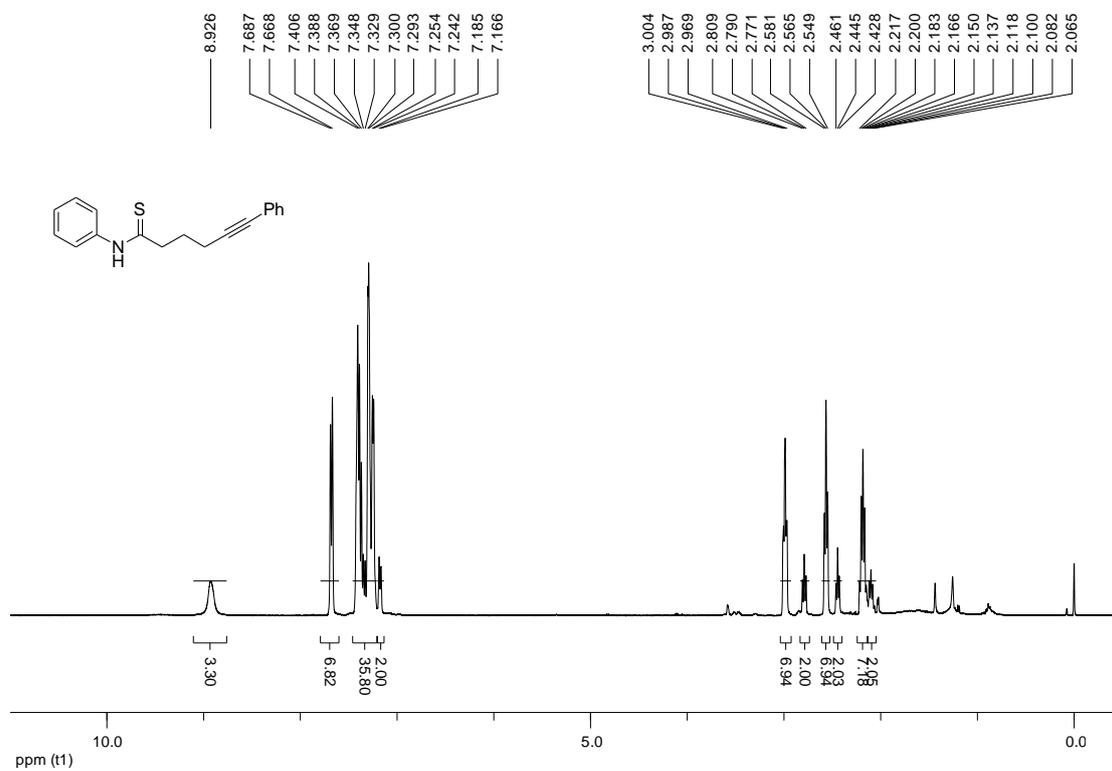
¹H NMR (400 MHz, CDCl₃) spectrum of 1ag



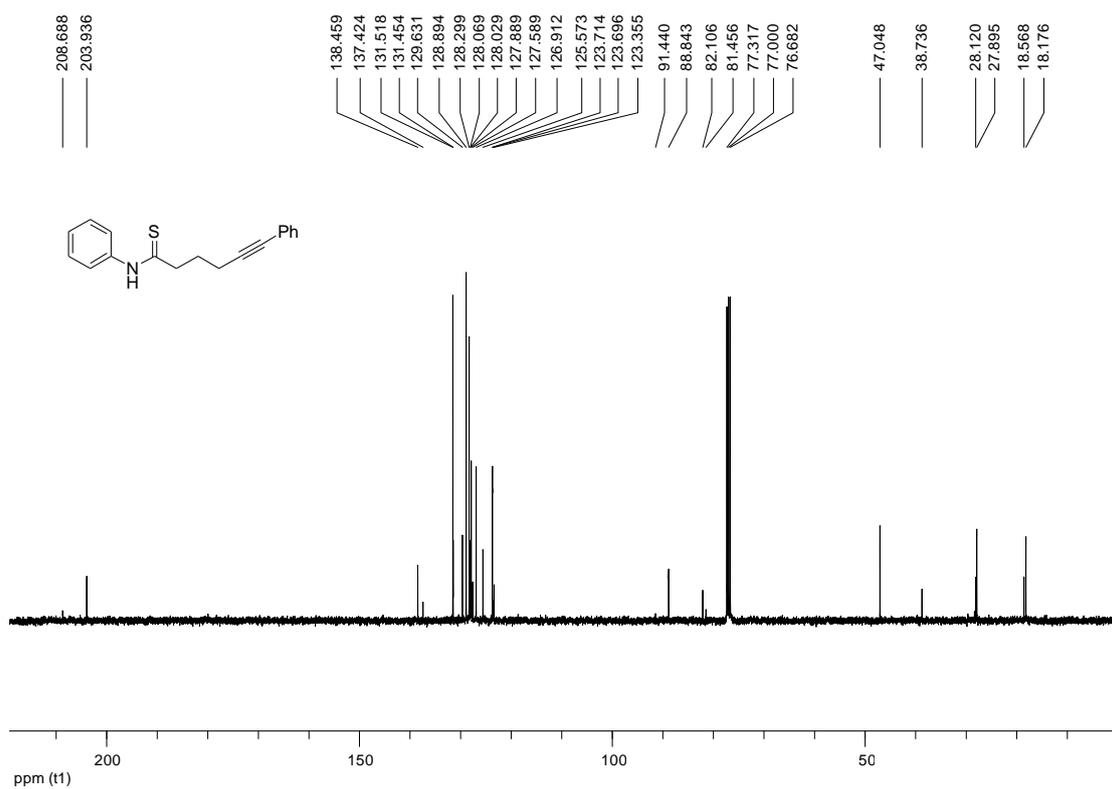
¹³C NMR (100MHz, CDCl₃) spectrum of 1ah



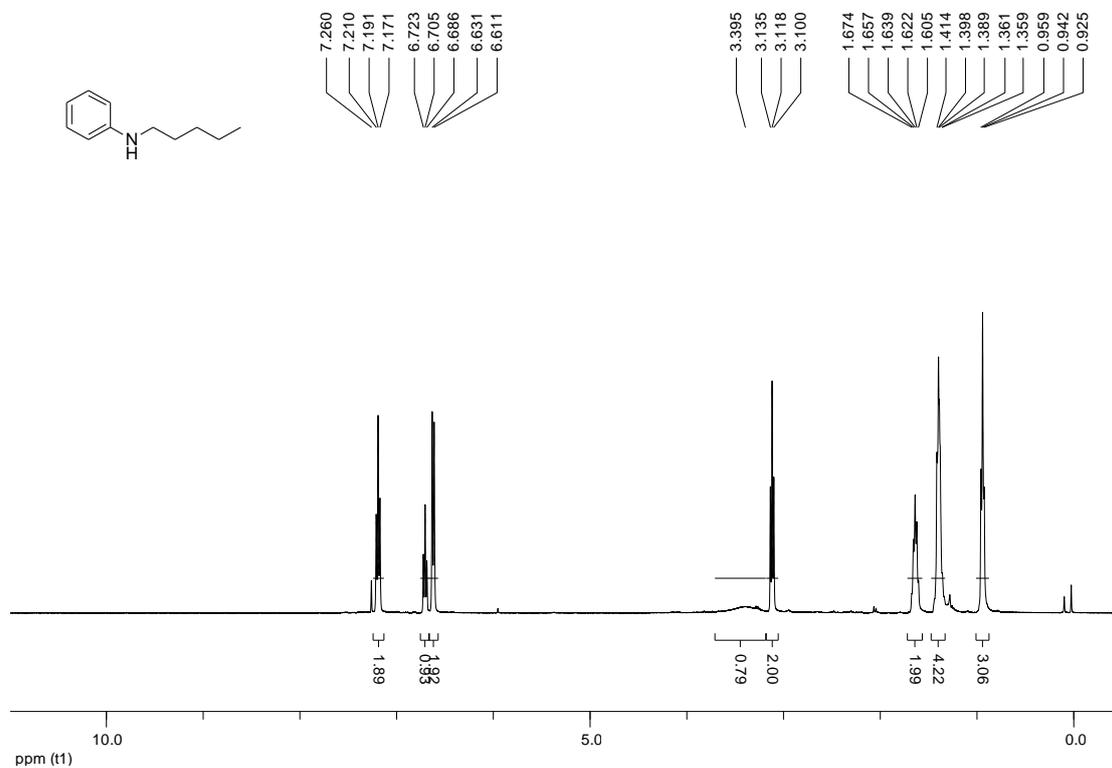
¹H NMR (400 MHz, CDCl₃) spectrum of 1ai



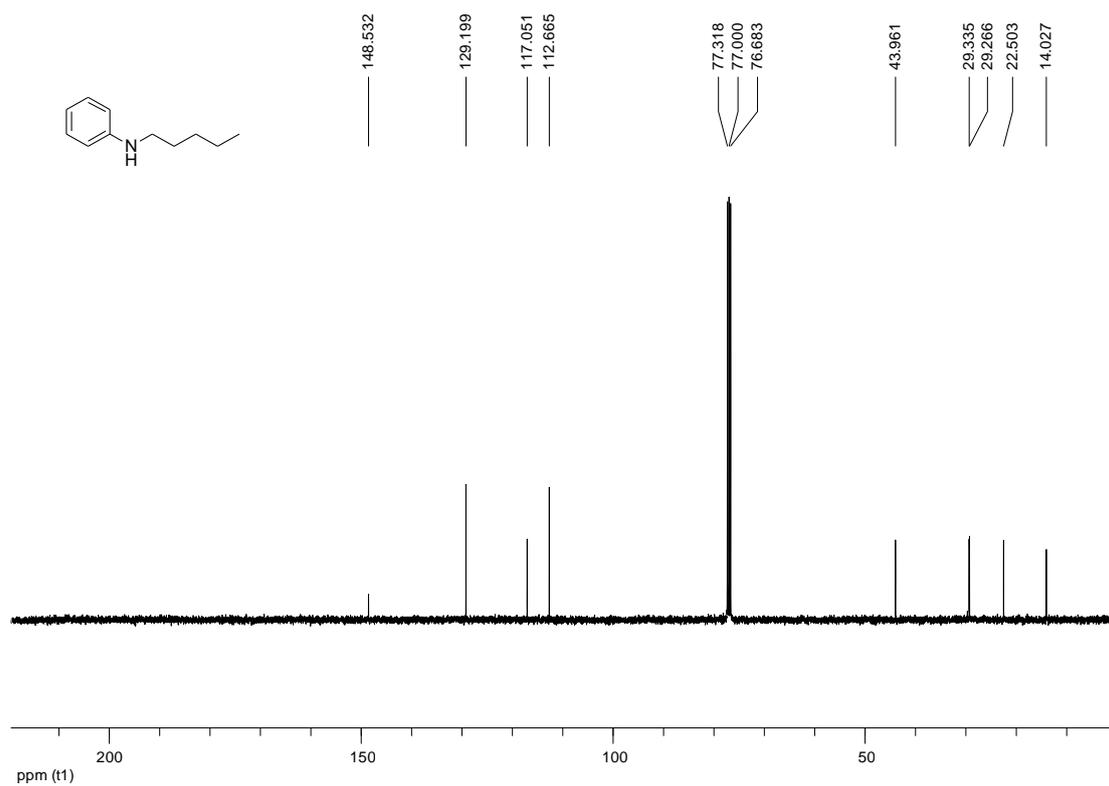
¹³C NMR (100MHz, CDCl₃) spectrum of 1ai



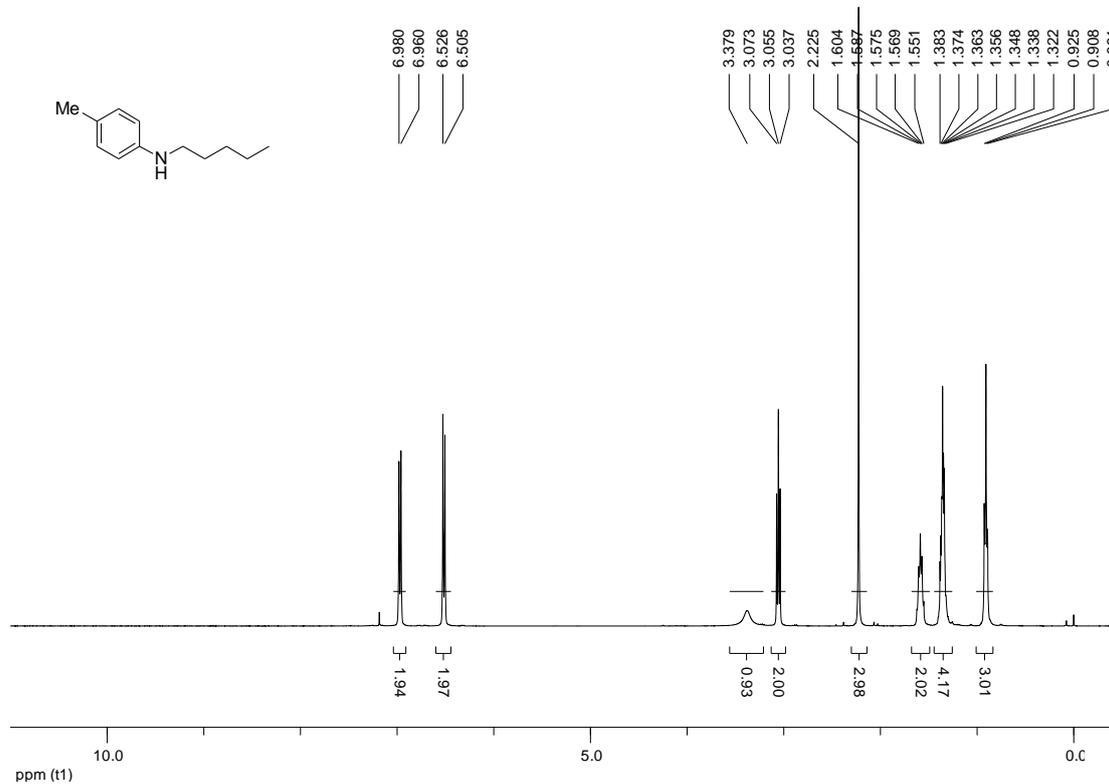
¹H NMR (400 MHz, CDCl₃) spectrum of 3a



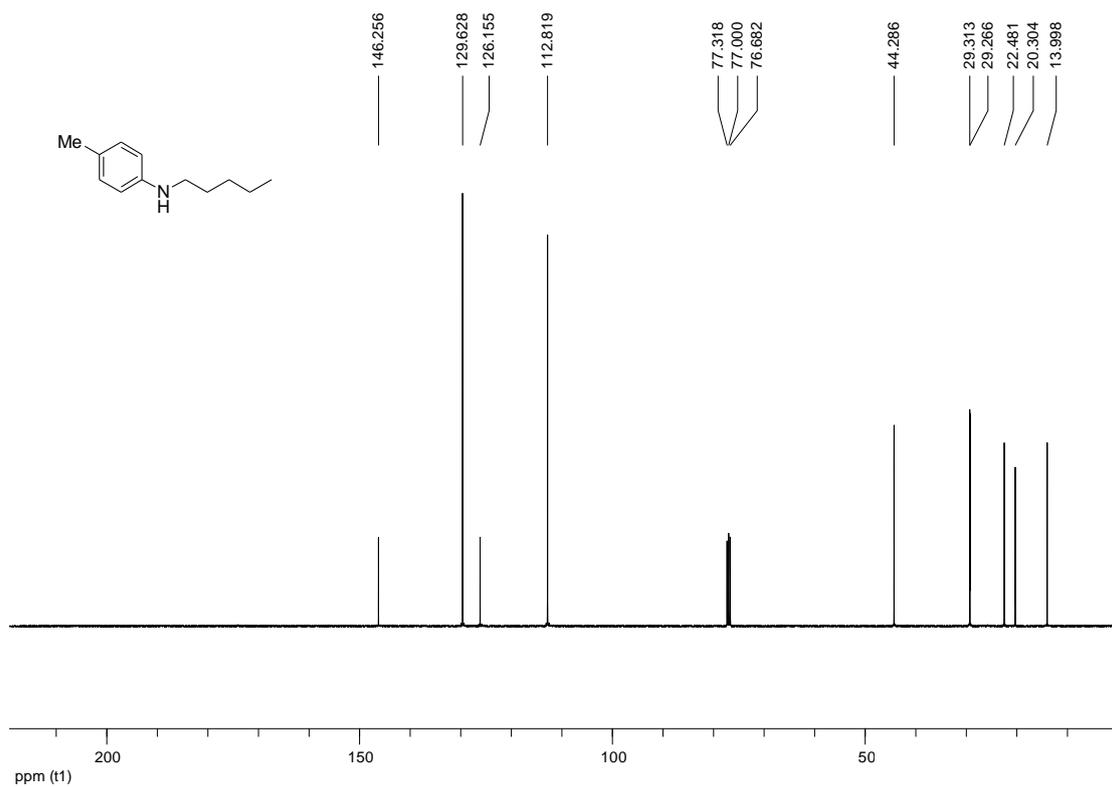
¹³C NMR (100MHz, CDCl₃) spectrum of 3a



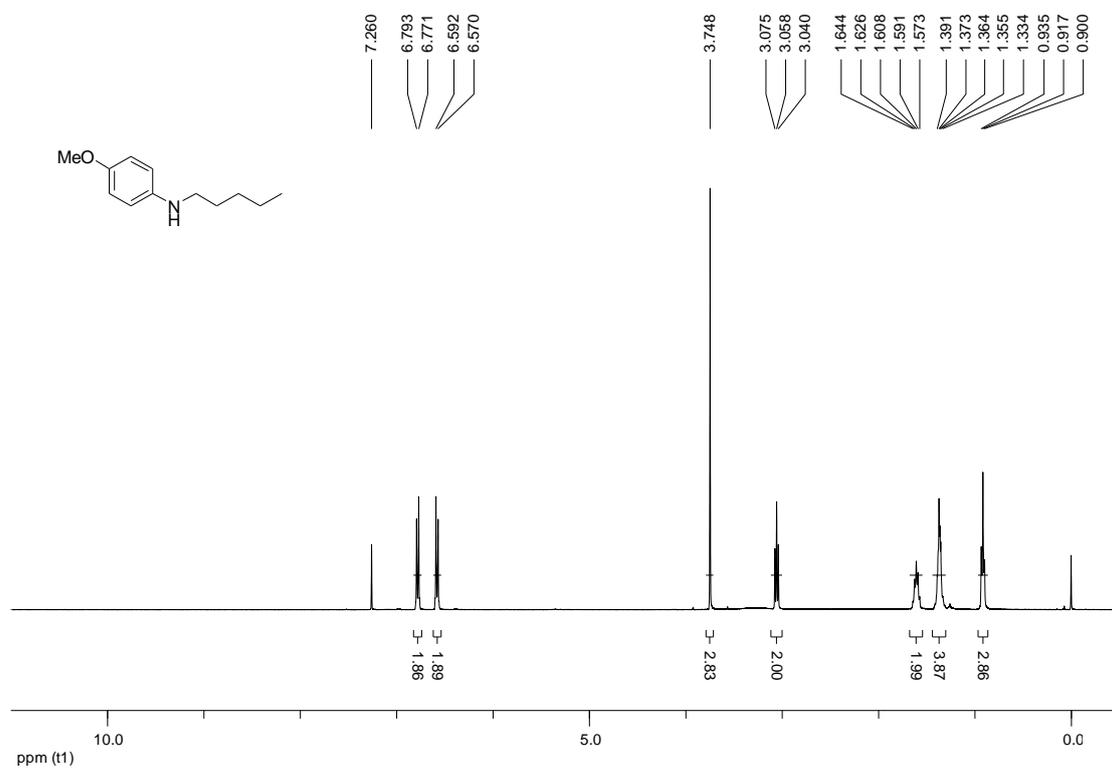
¹H NMR (400 MHz, CDCl₃) spectrum of 3b



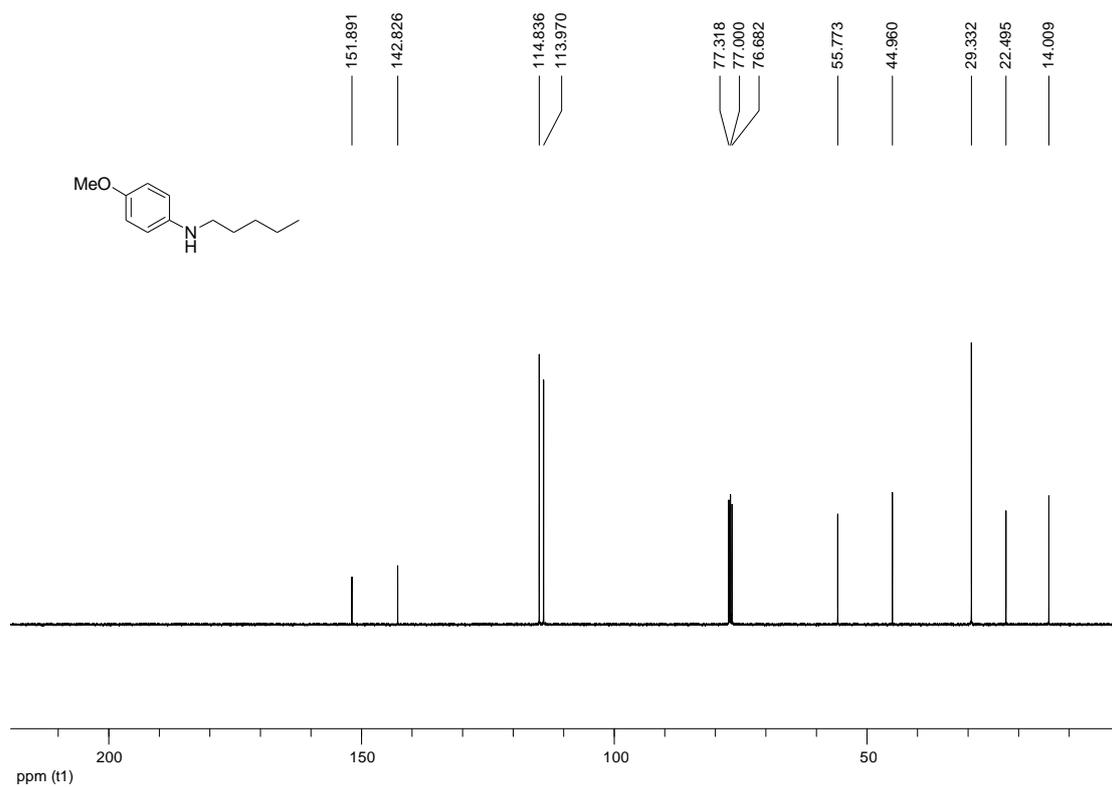
¹³C NMR (100MHz, CDCl₃) spectrum of 3b



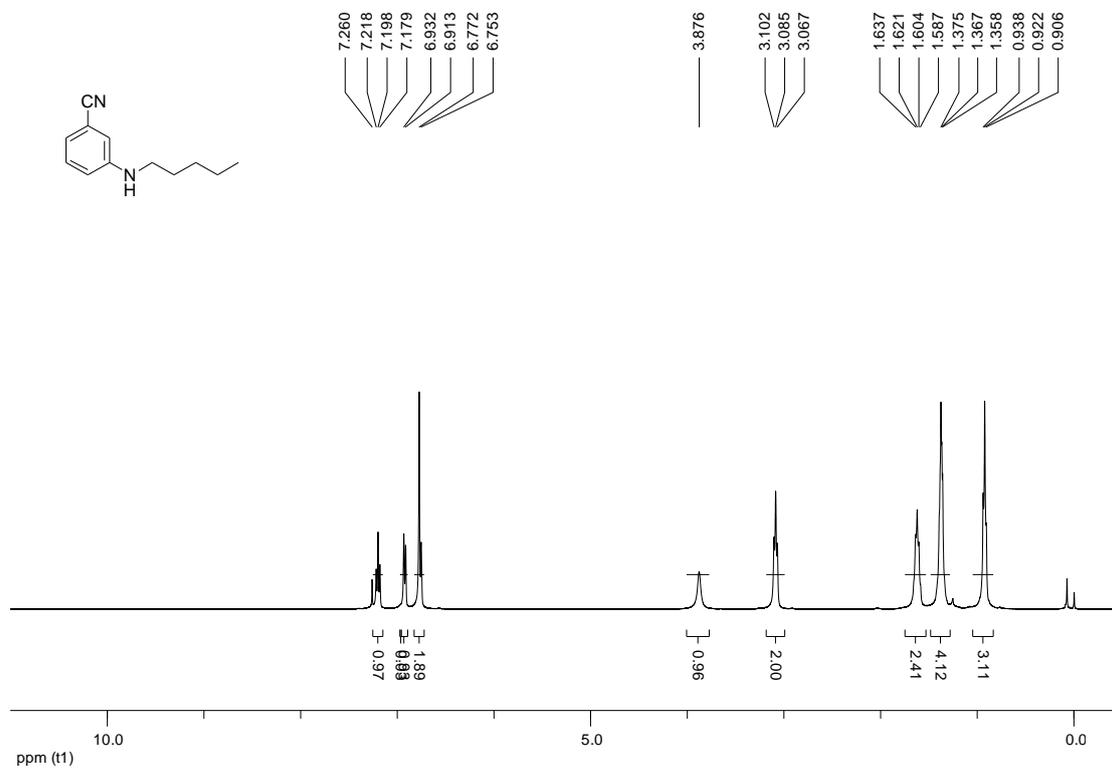
¹H NMR (400 MHz, CDCl₃) spectrum of 3c



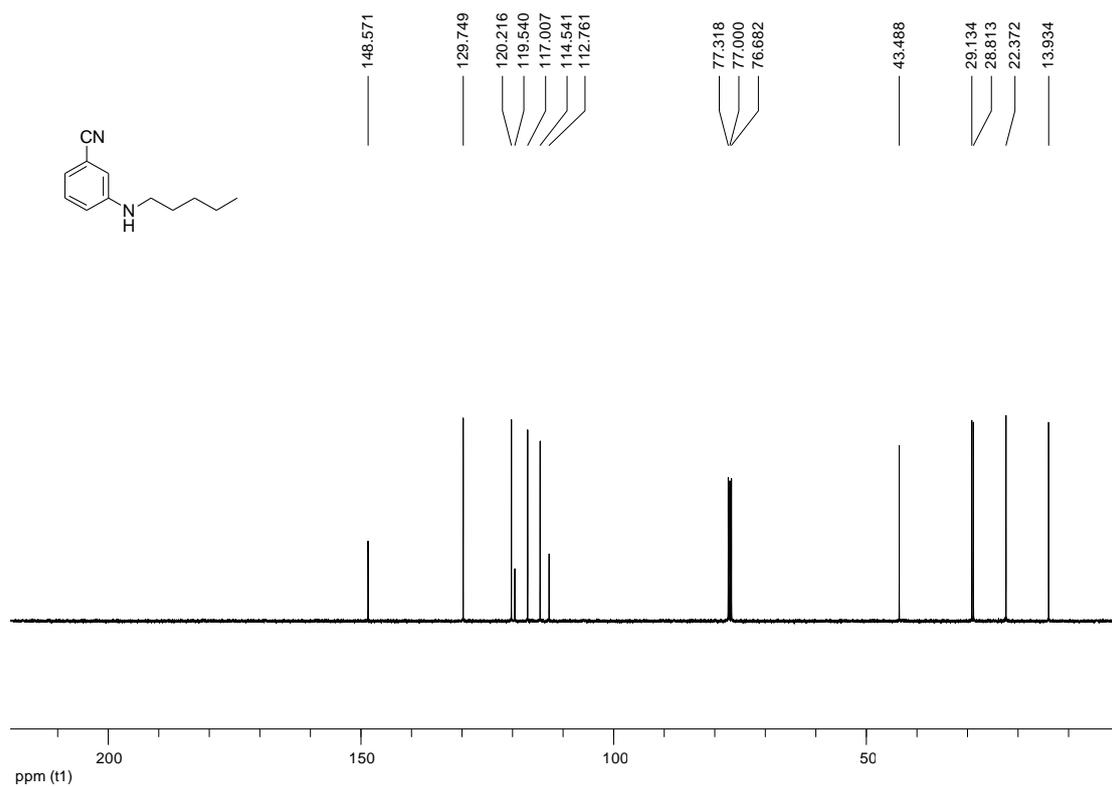
¹³C NMR (100MHz, CDCl₃) spectrum of 3c



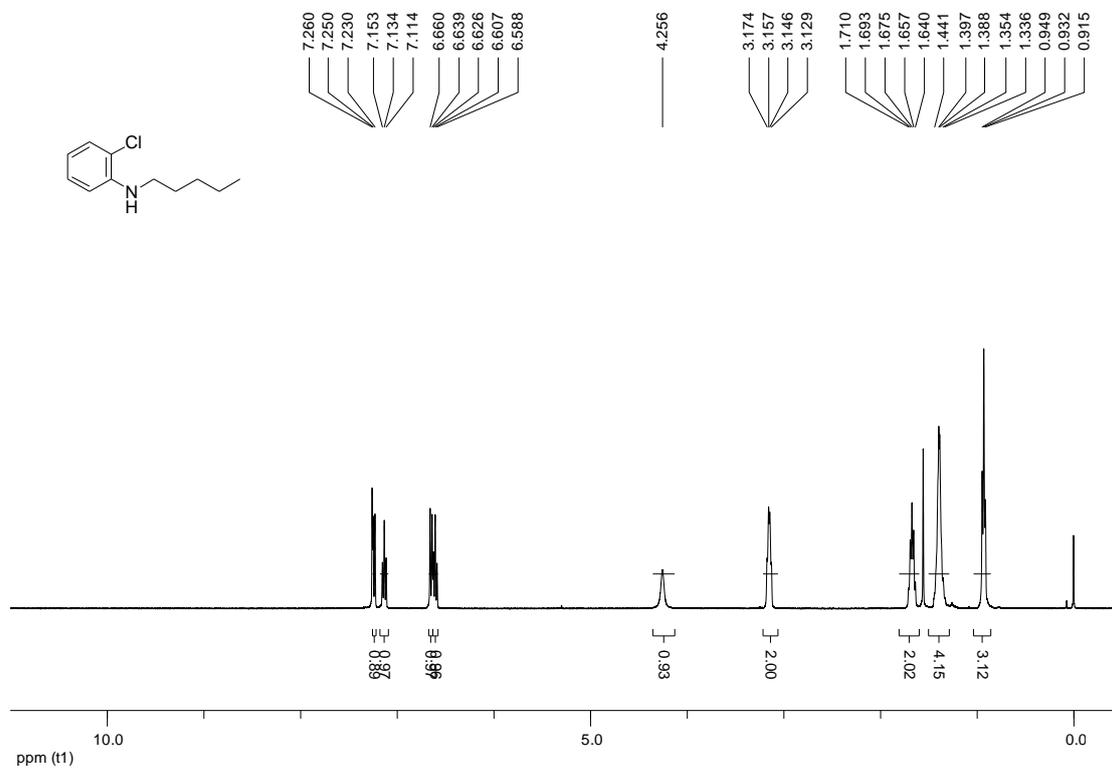
¹H NMR (400 MHz, CDCl₃) spectrum of 3d



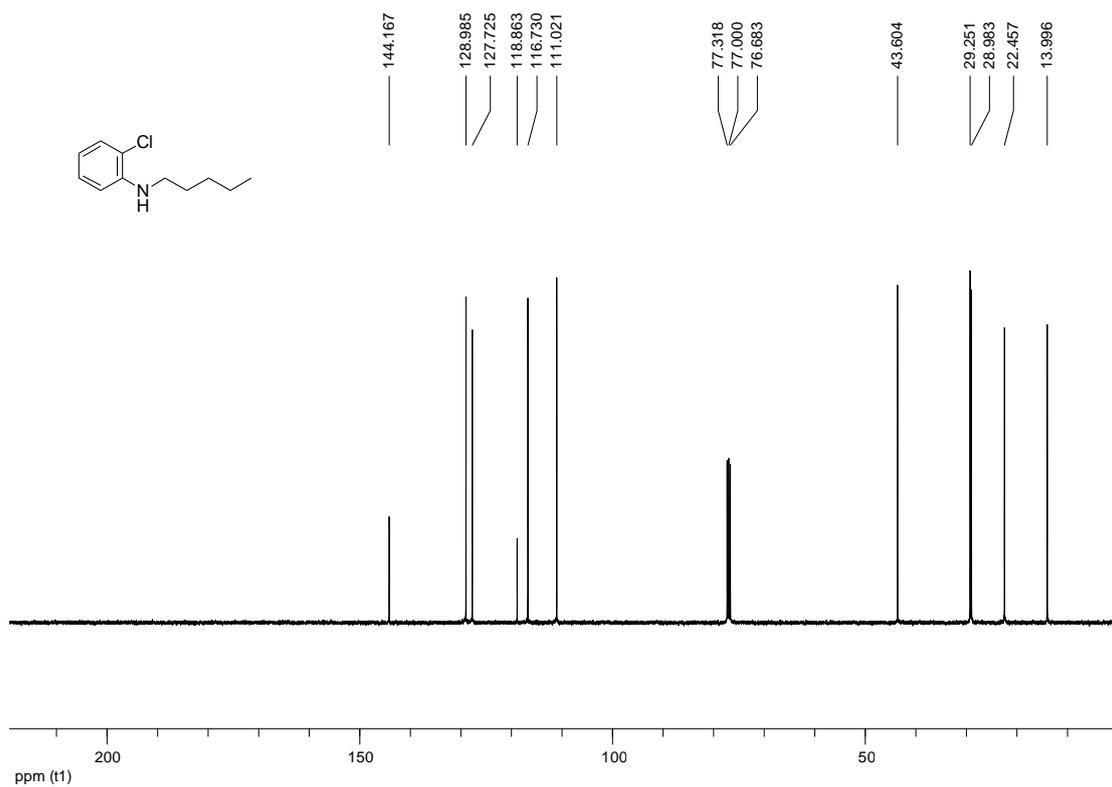
¹³C NMR (100MHz, CDCl₃) spectrum of 3d



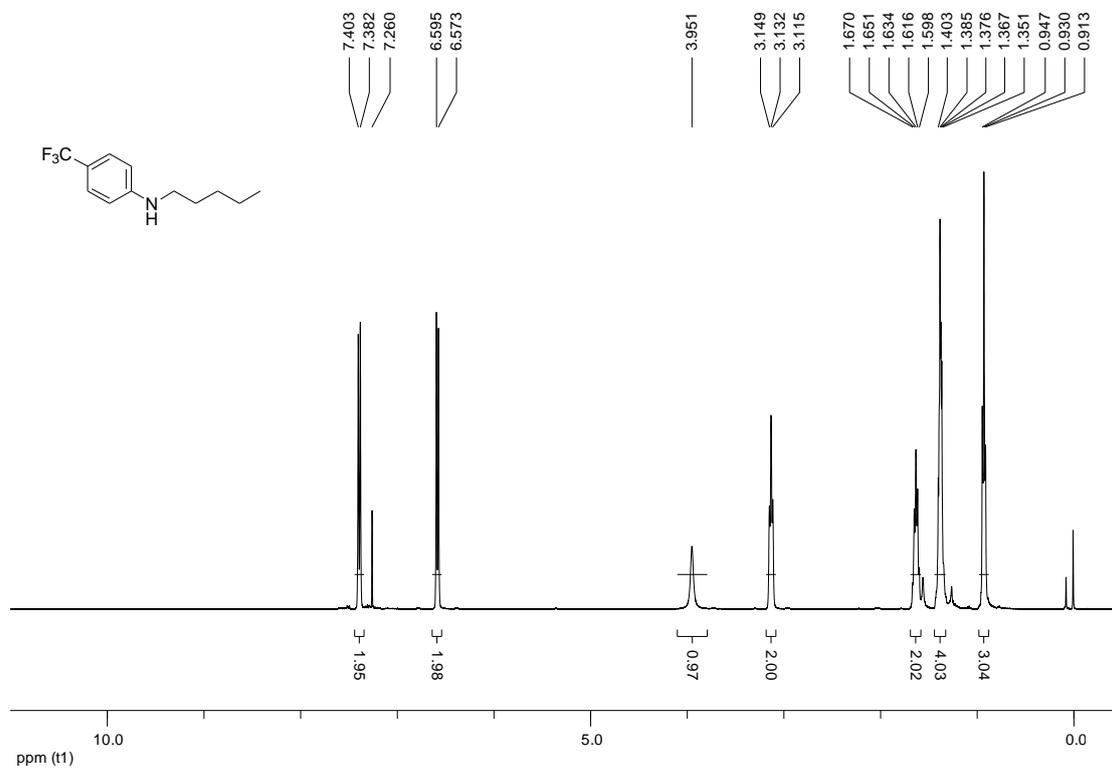
¹H NMR (400 MHz, CDCl₃) spectrum of 3e



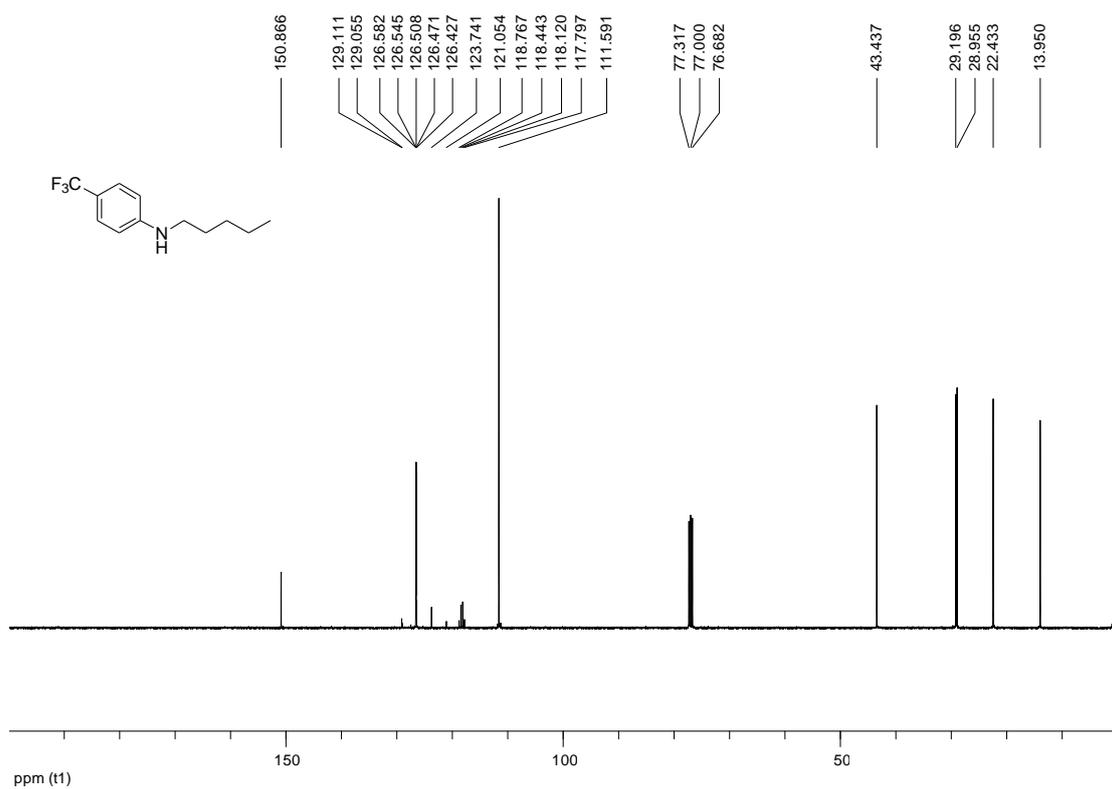
¹³C NMR (100MHz, CDCl₃) spectrum of 3e



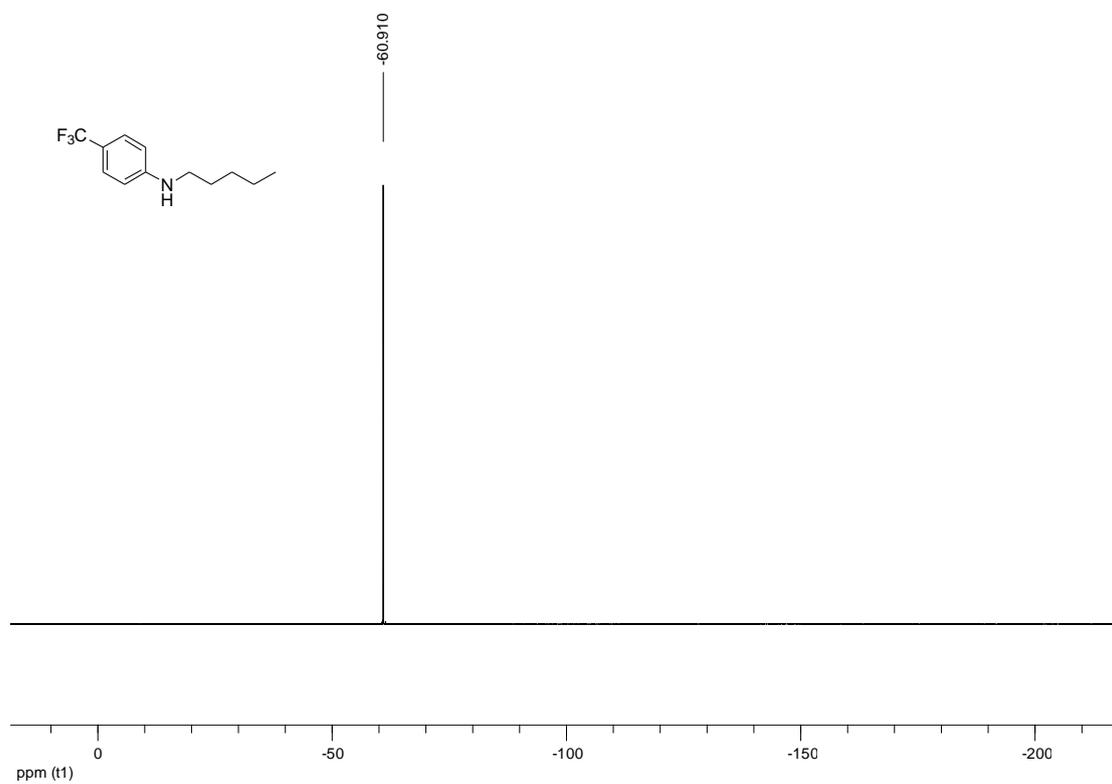
¹H NMR (400 MHz, CDCl₃) spectrum of 3f



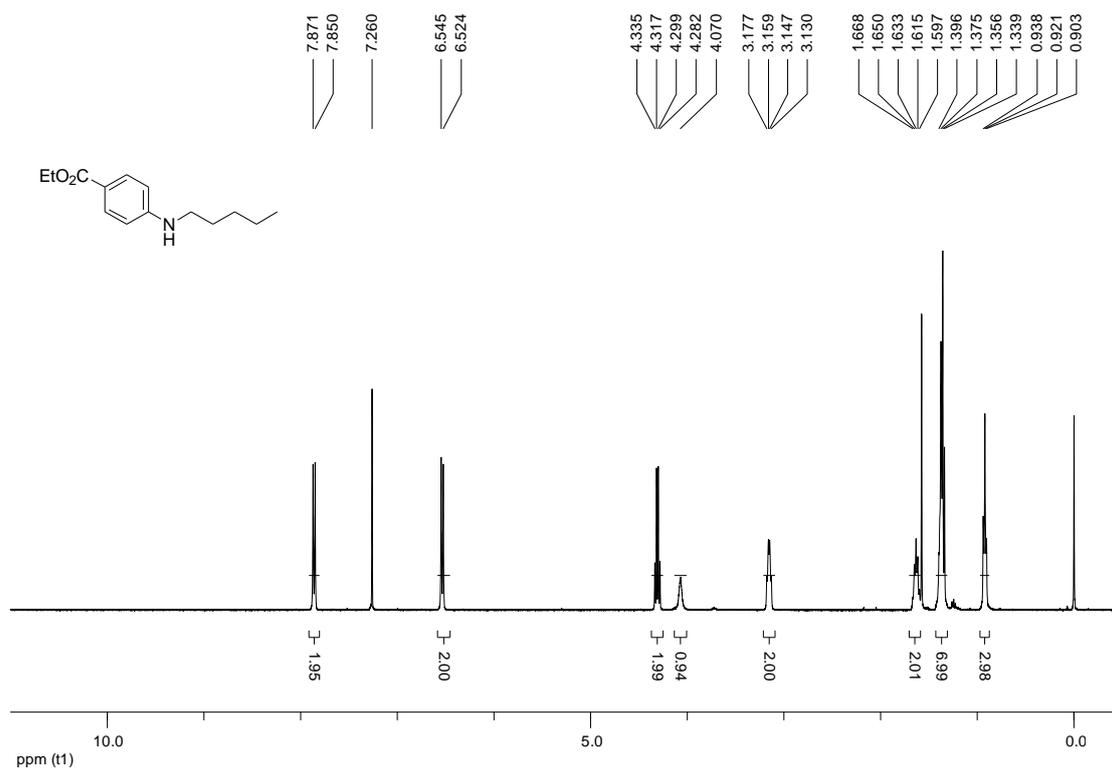
¹³C NMR (100MHz, CDCl₃) spectrum of 3f



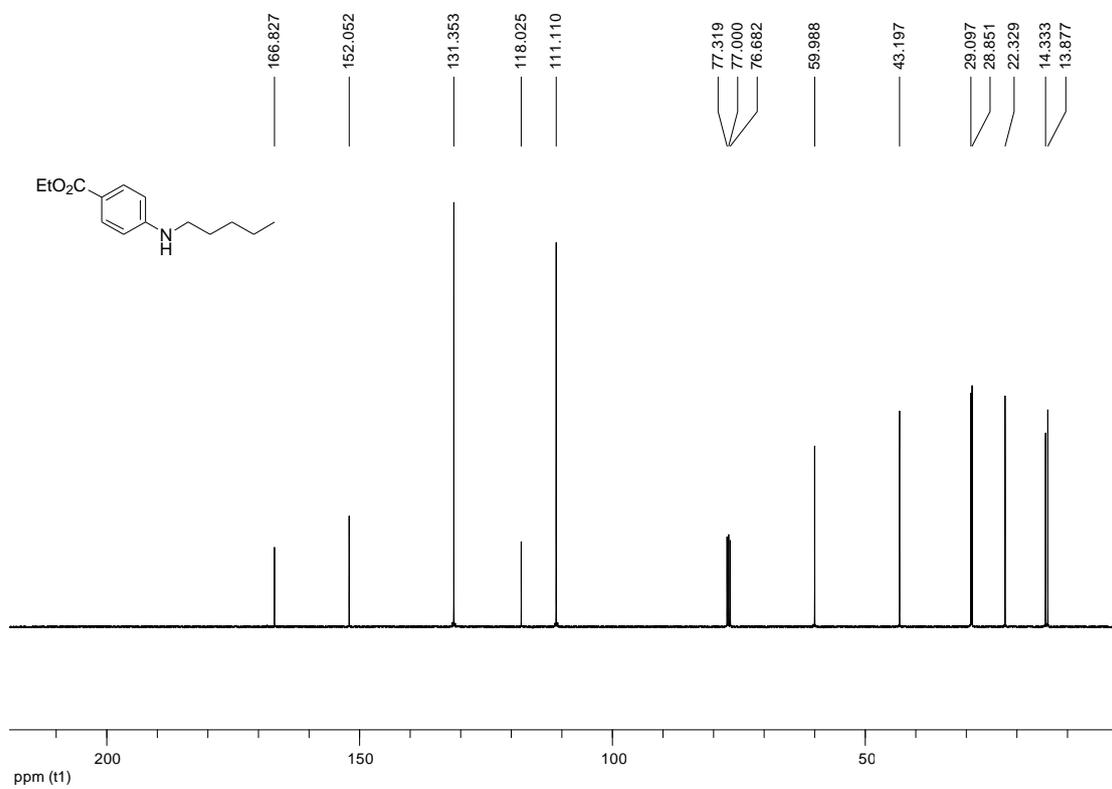
¹⁹F NMR (376 MHz, CDCl₃) spectrum of 3f



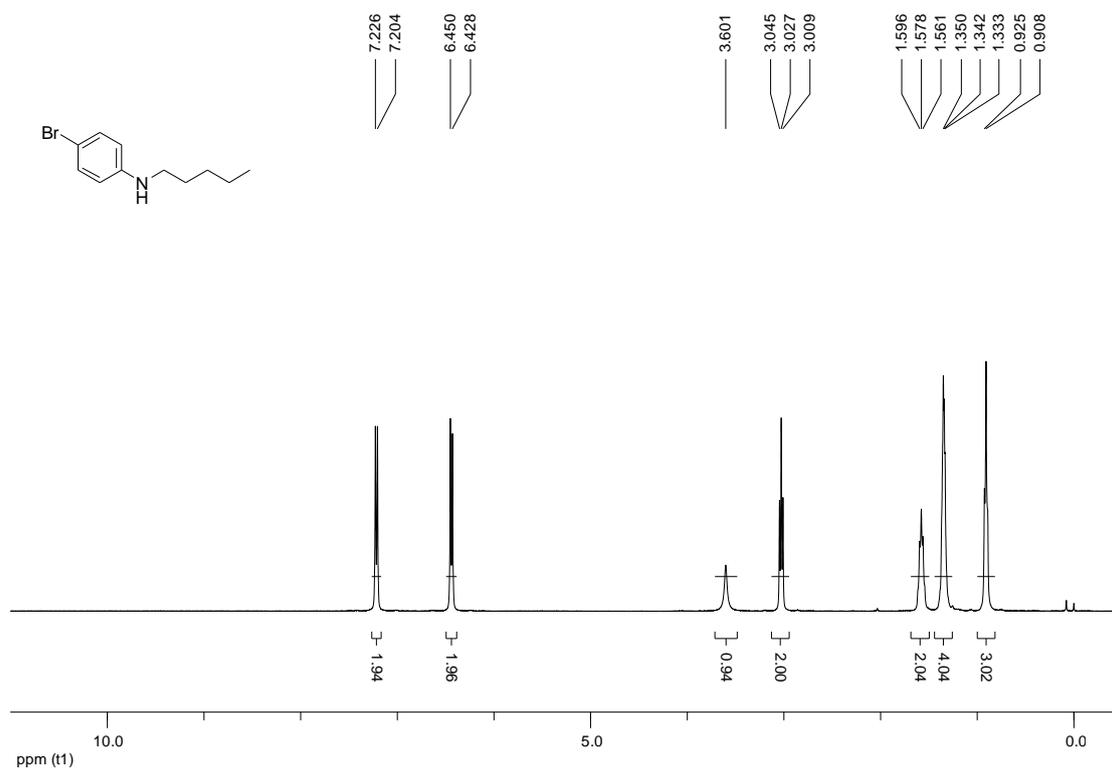
¹H NMR (400 MHz, CDCl₃) spectrum of 3g



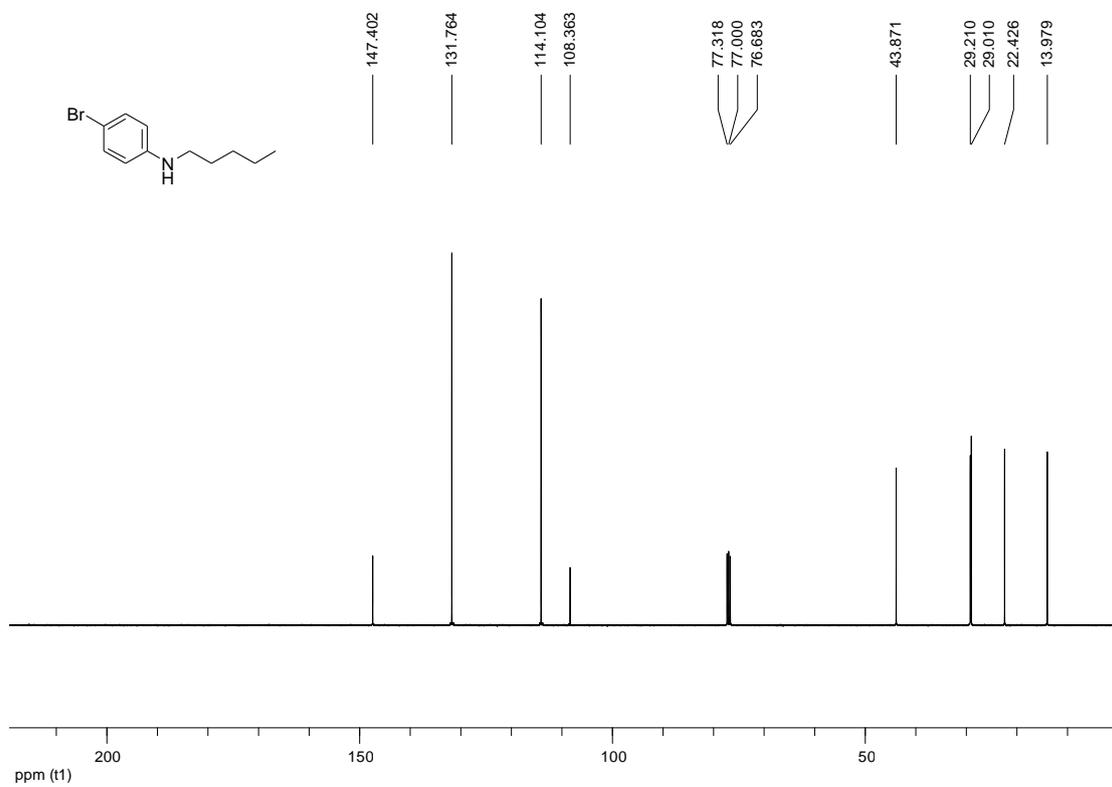
¹³C NMR (100MHz, CDCl₃) spectrum of 3g



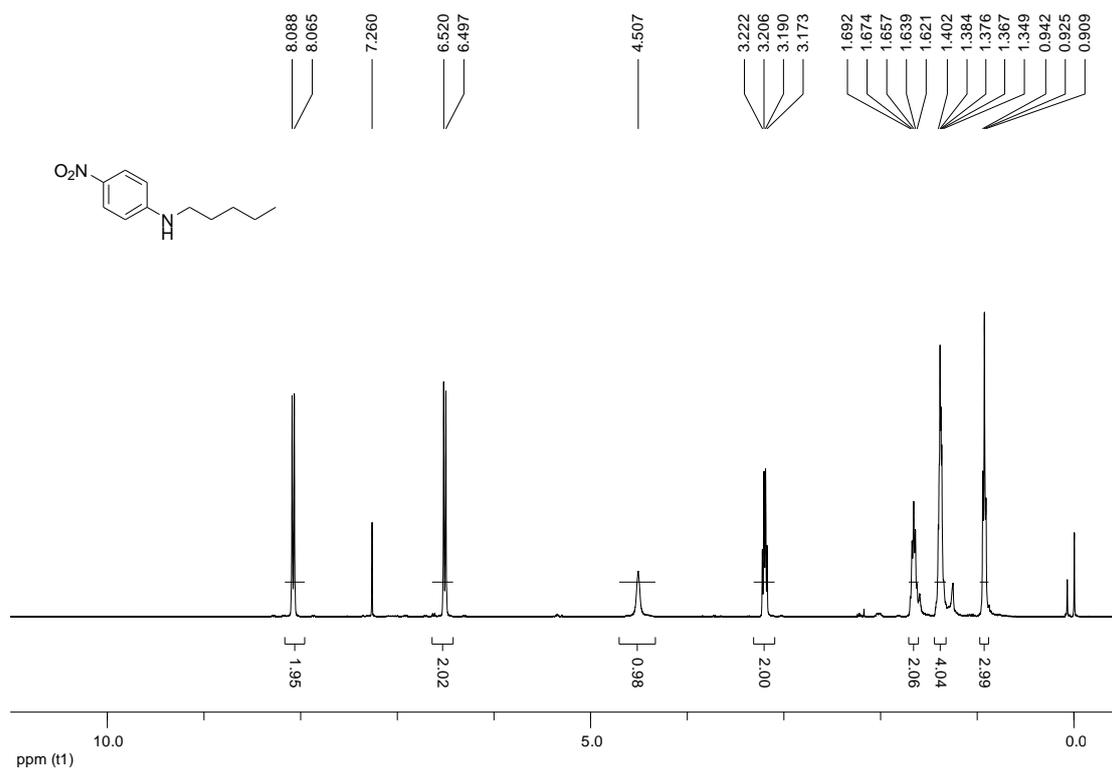
¹H NMR (400 MHz, CDCl₃) spectrum of 3h



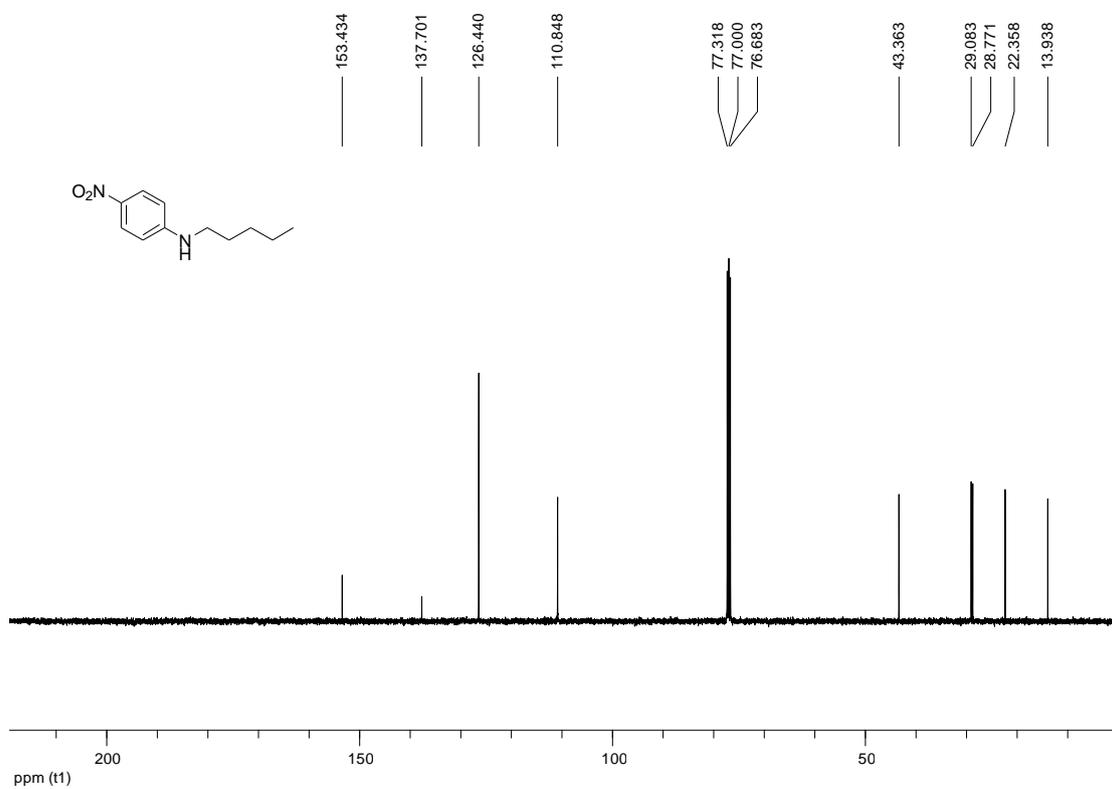
¹³C NMR (100MHz, CDCl₃) spectrum of 3h



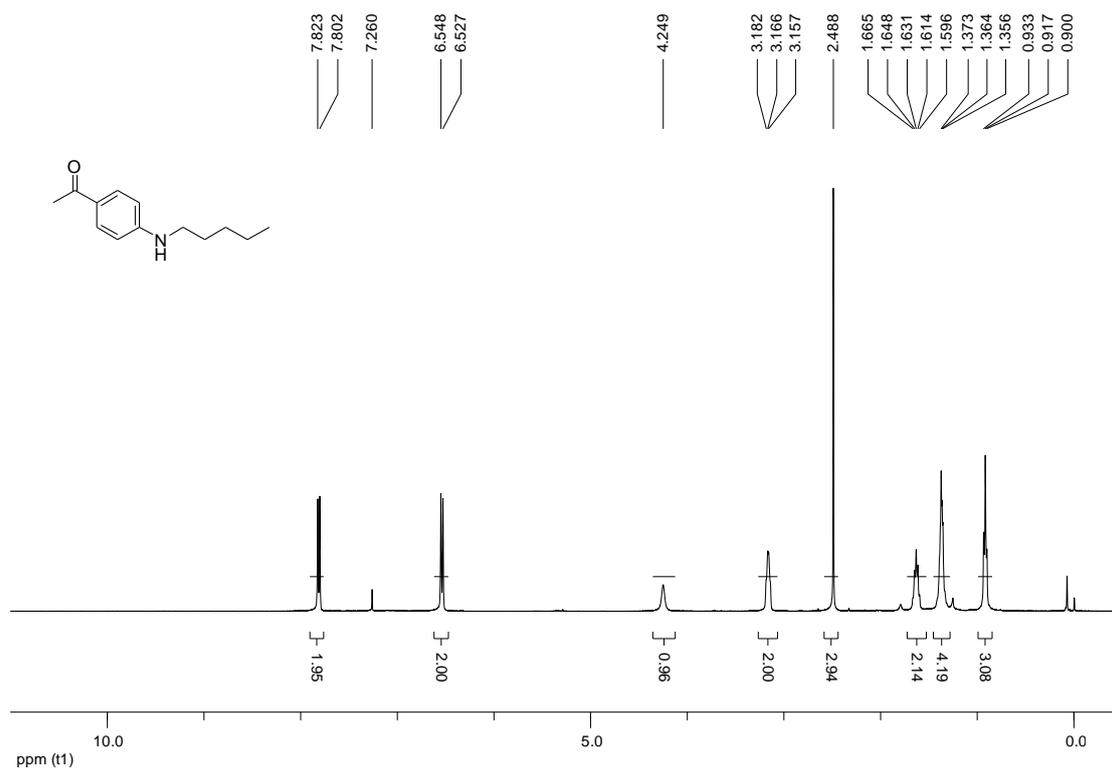
¹H NMR (400 MHz, CDCl₃) spectrum of 3i



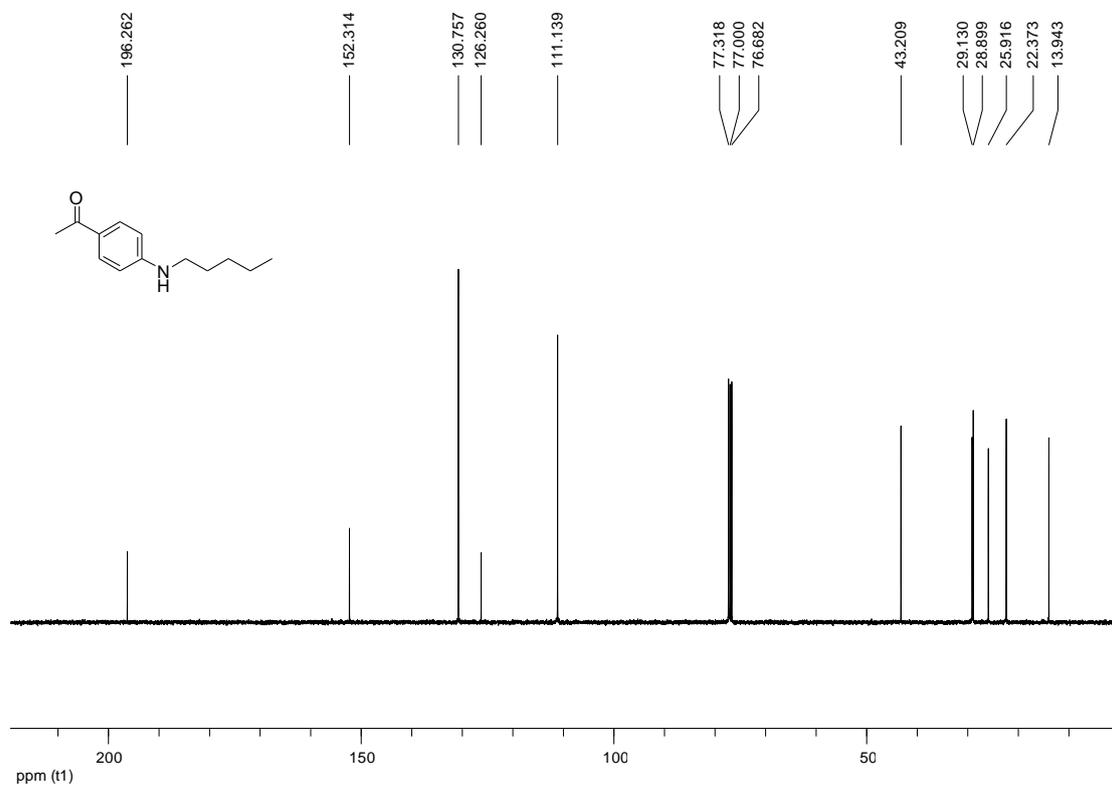
¹³C NMR (100MHz, CDCl₃) spectrum of 3i



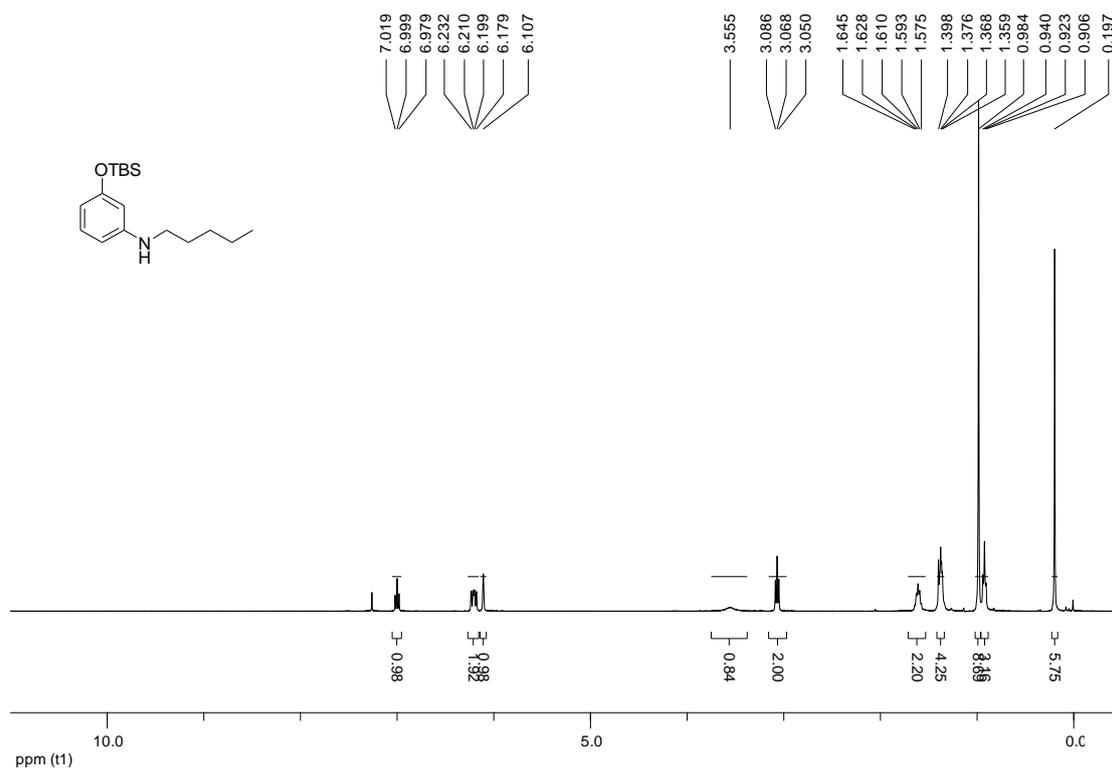
¹H NMR (400 MHz, CDCl₃) spectrum of 3j



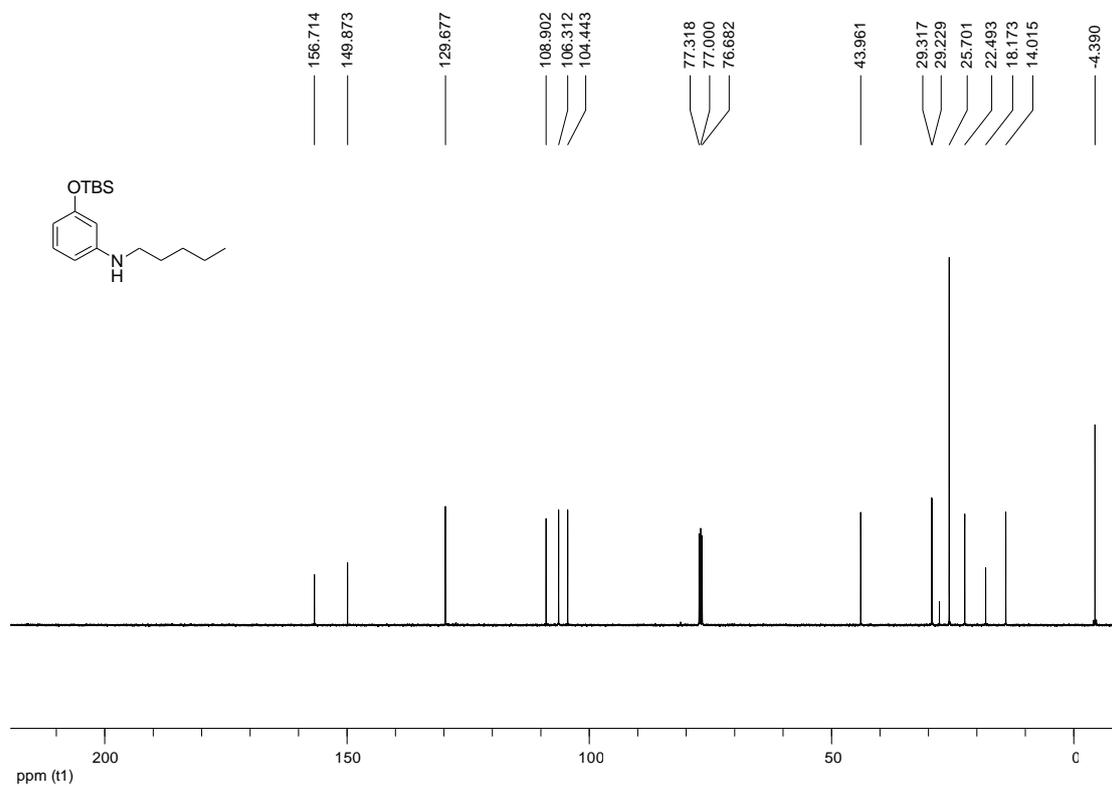
¹³C NMR (100MHz, CDCl₃) spectrum of 3j



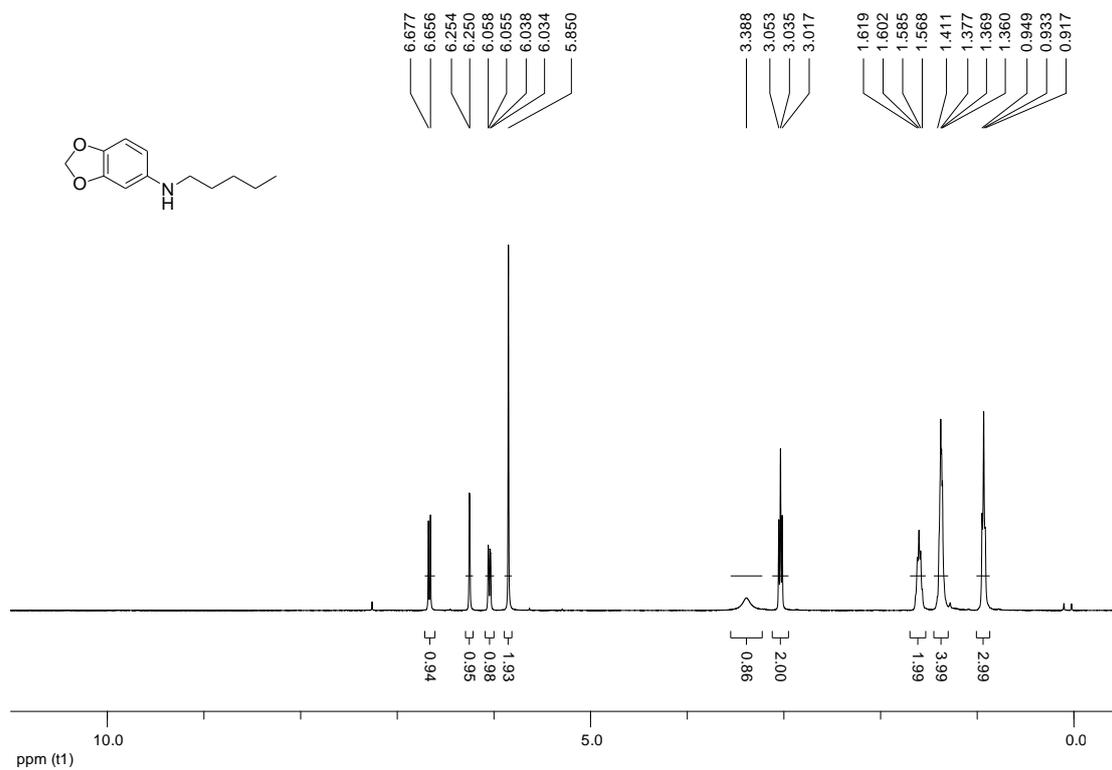
¹H NMR (400 MHz, CDCl₃) spectrum of 3k



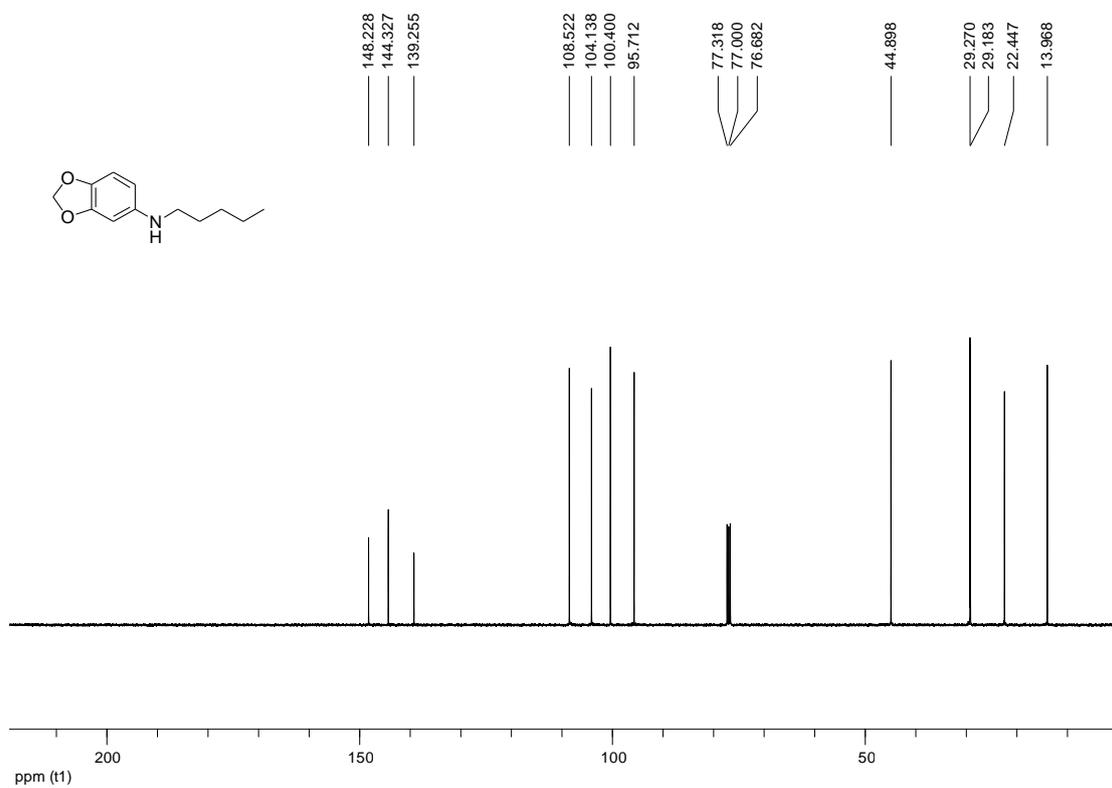
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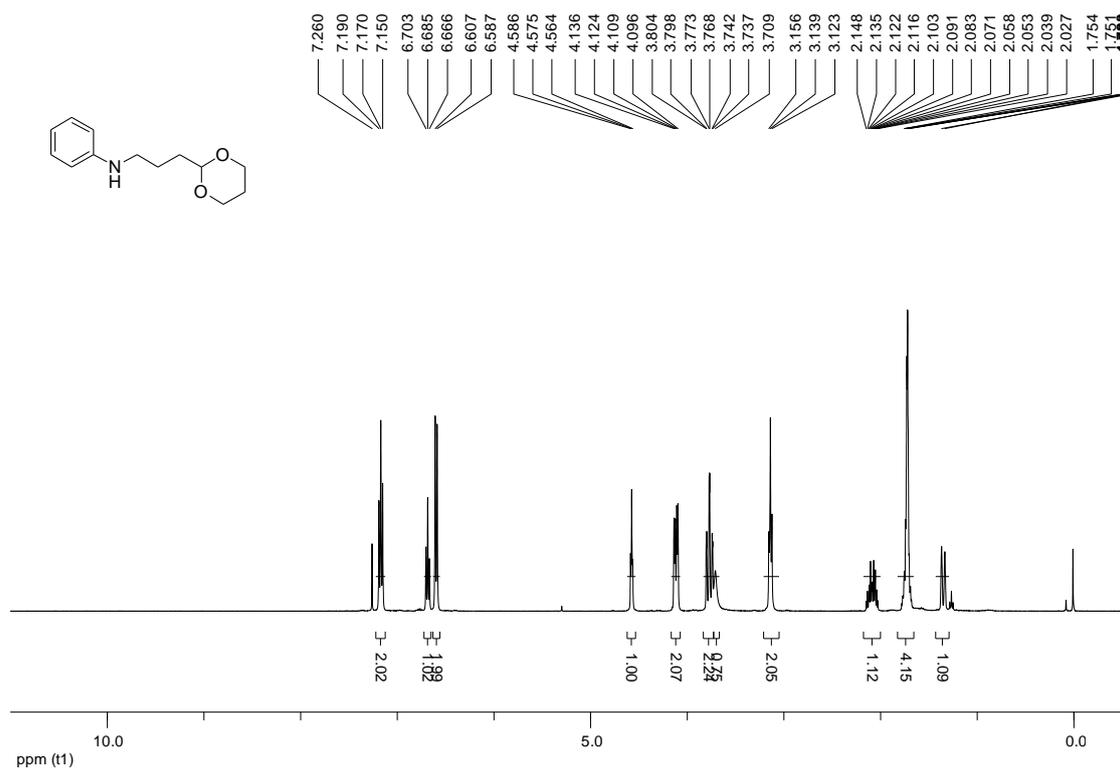
¹H NMR (400 MHz, CDCl₃) spectrum of 31



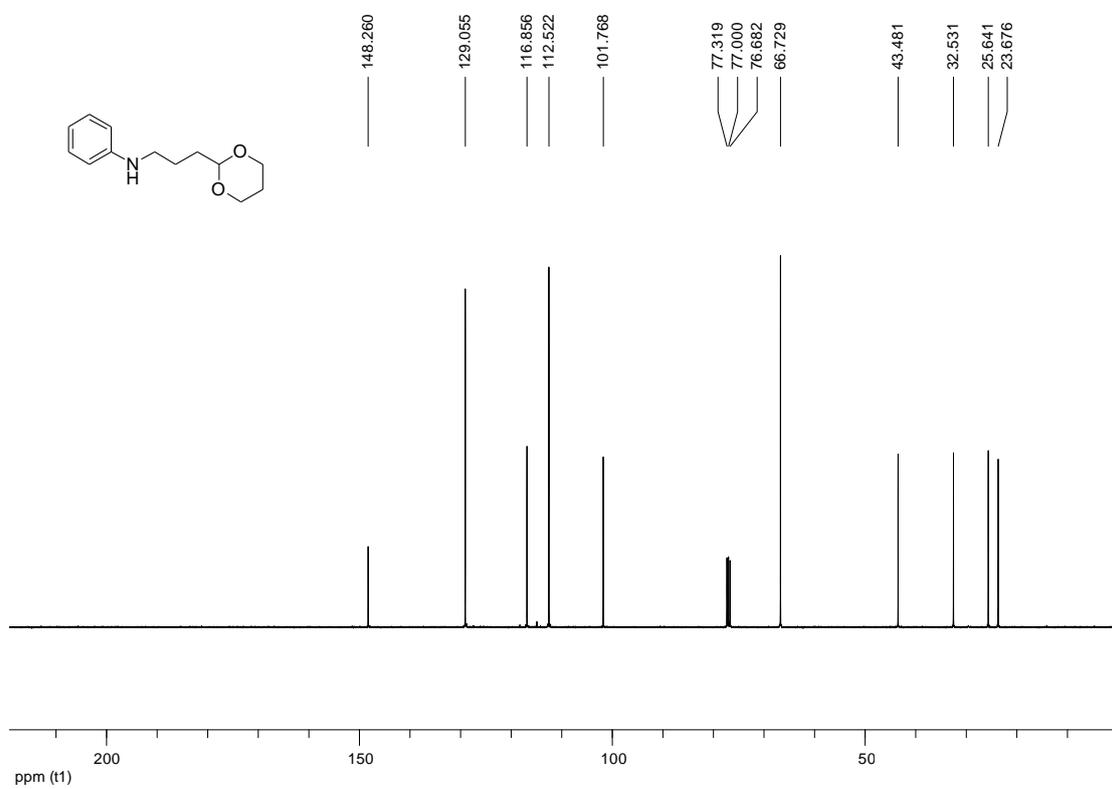
¹³C NMR (100MHz, CDCl₃) spectrum of 31



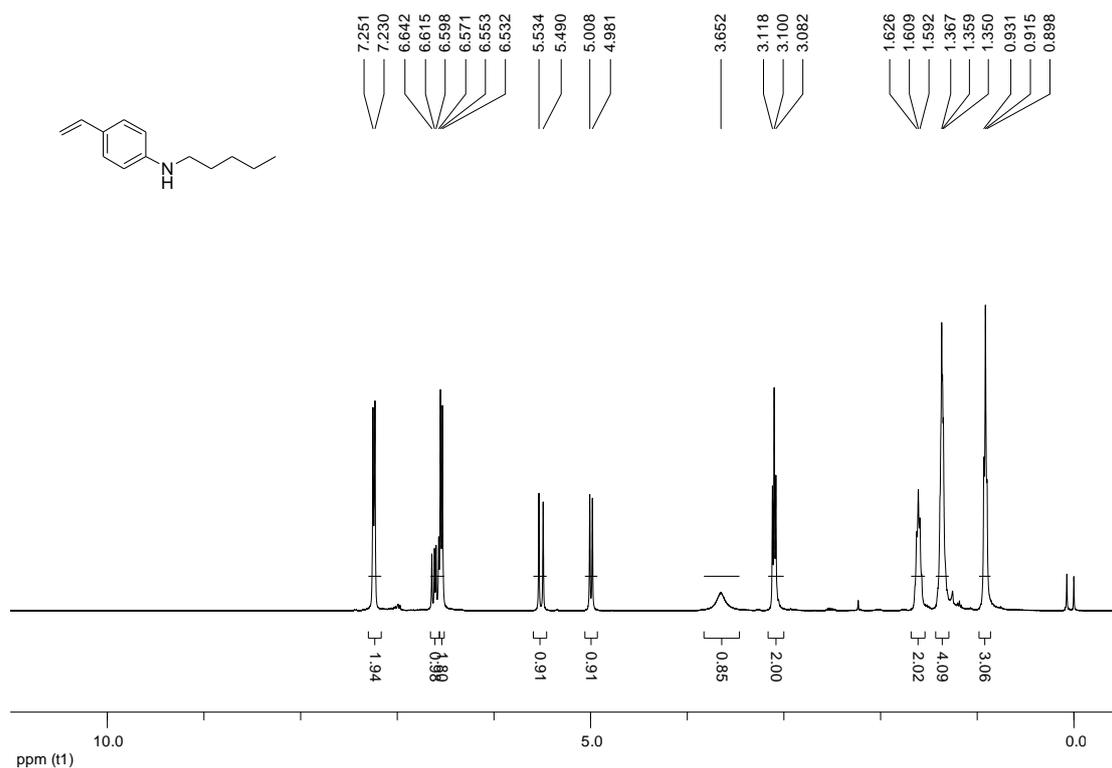
¹H NMR (400 MHz, CDCl₃) spectrum of 3m



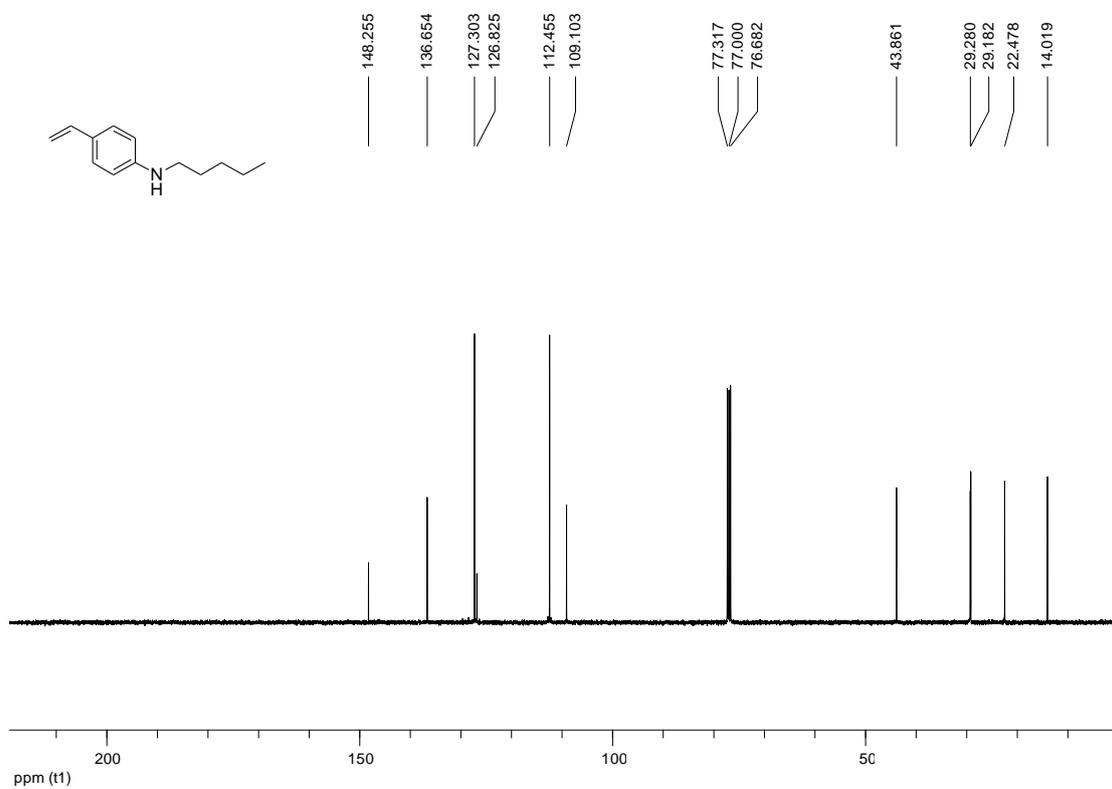
¹³C NMR (100MHz, CDCl₃) spectrum of 3m



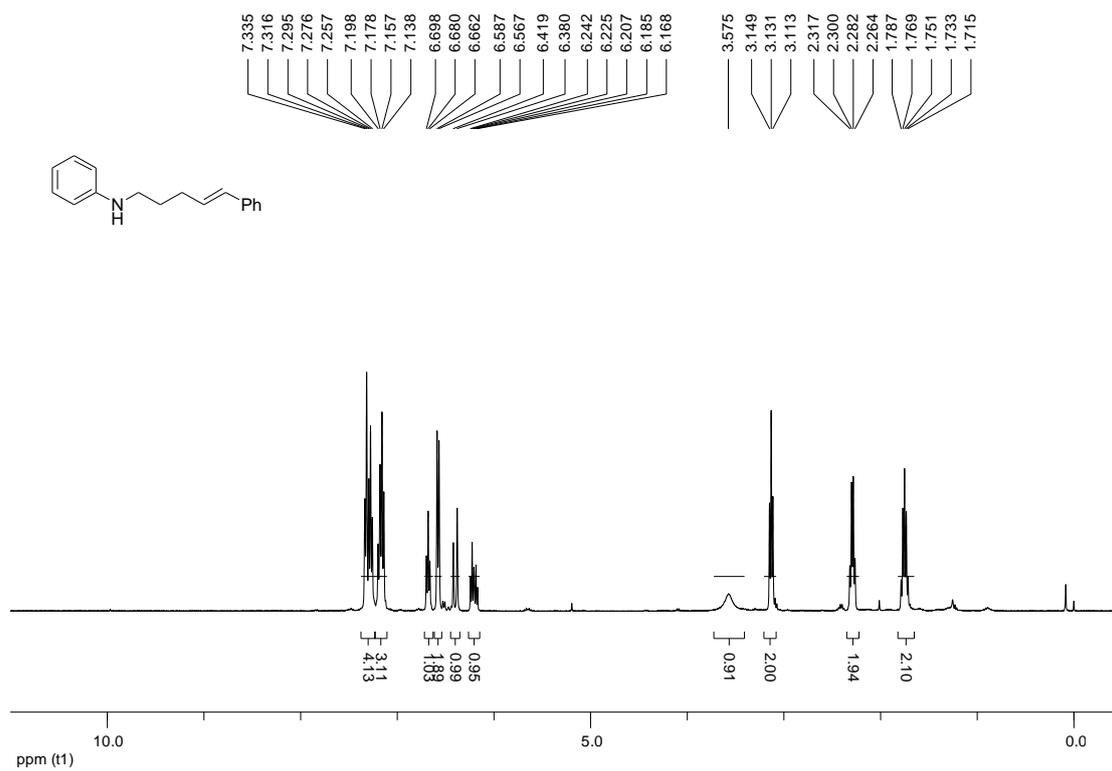
¹H NMR (400 MHz, CDCl₃) spectrum of 3n



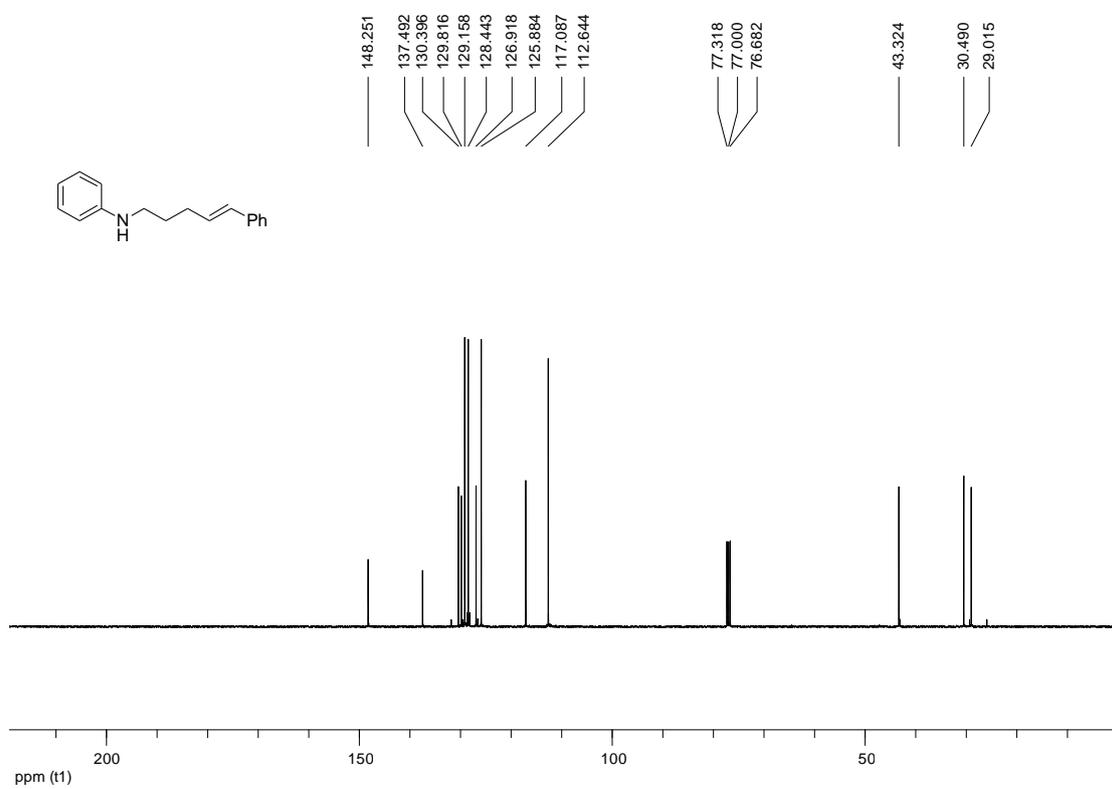
¹³C NMR (100MHz, CDCl₃) spectrum of 3n



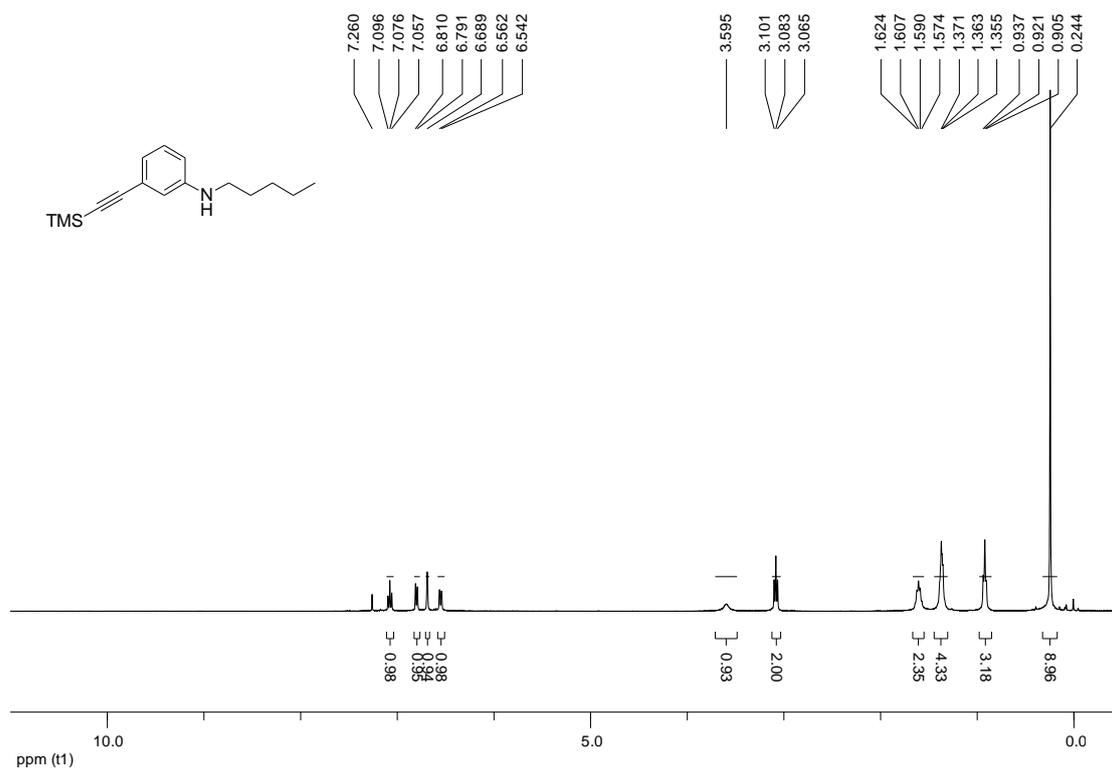
¹H NMR (400 MHz, CDCl₃) spectrum of 3o



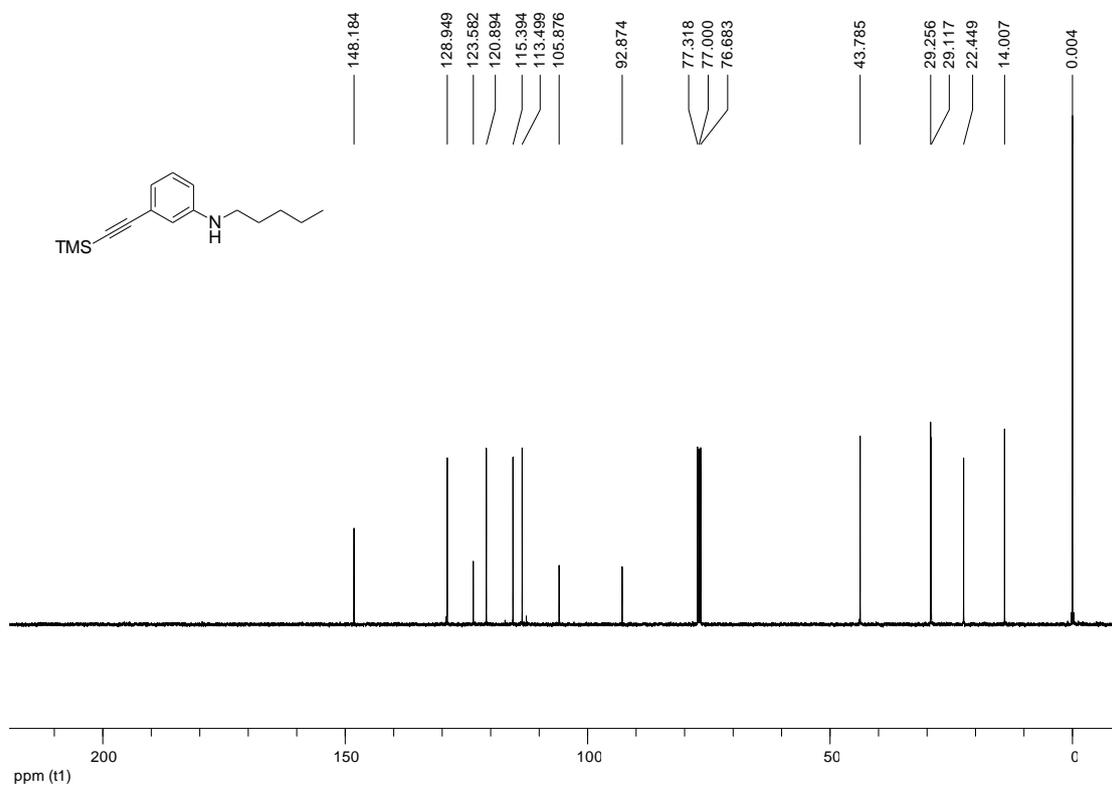
¹³C NMR (100MHz, CDCl₃) spectrum of 3o



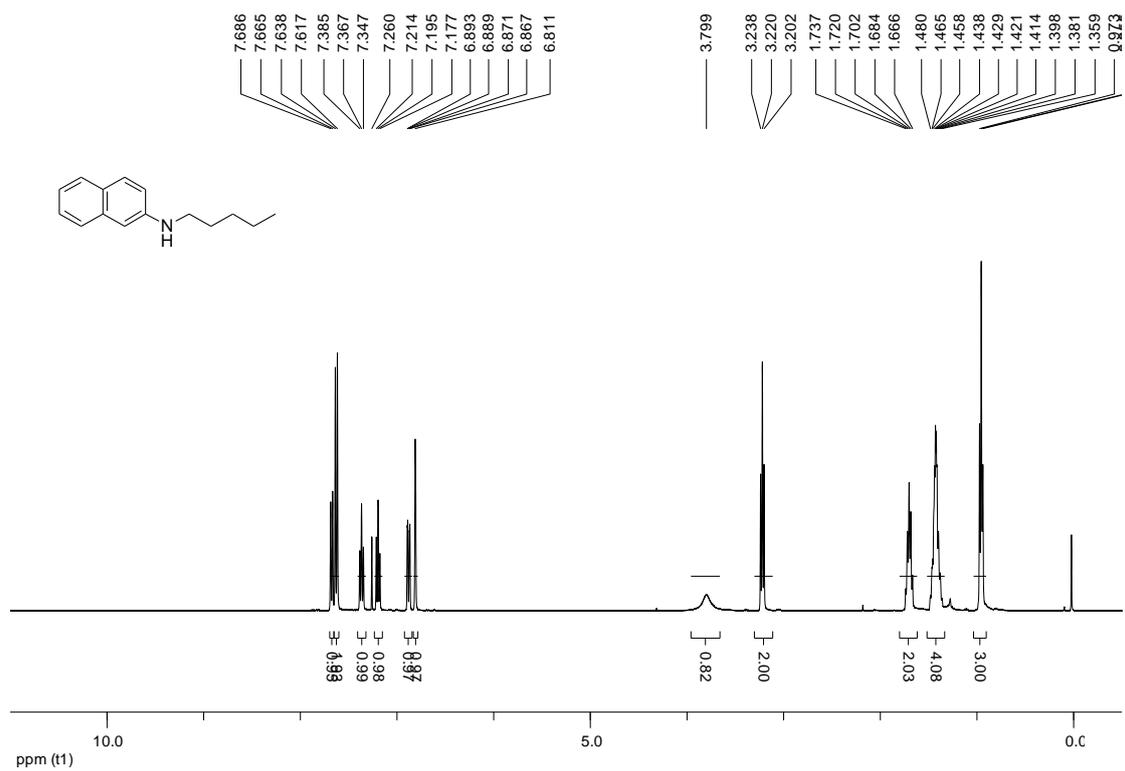
¹H NMR (400 MHz, CDCl₃) spectrum of 3p



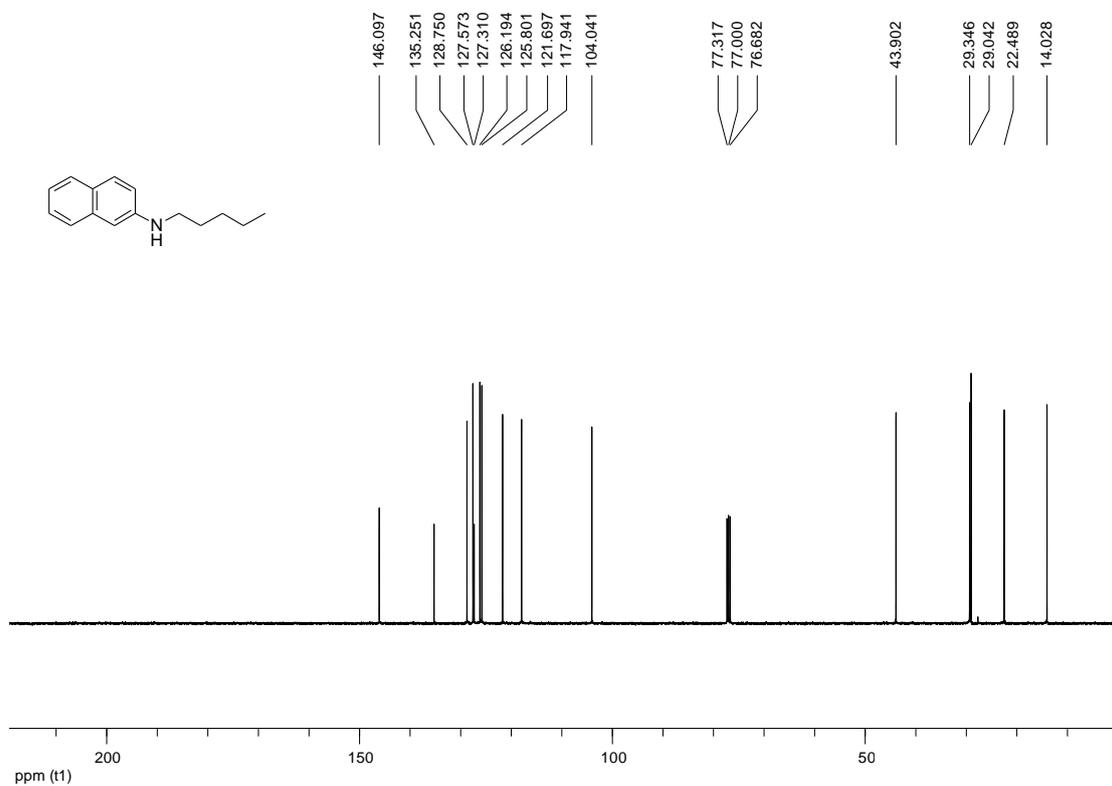
¹³C NMR (100MHz, CDCl₃) spectrum of 3p



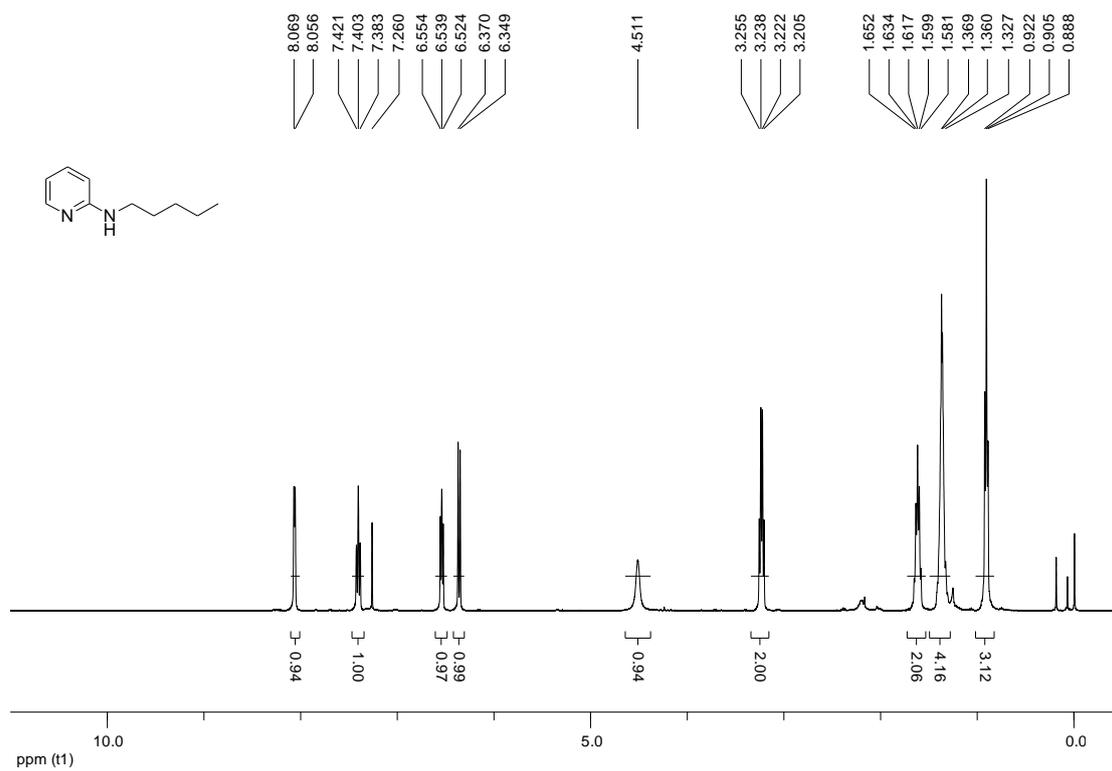
¹H NMR (400 MHz, CDCl₃) spectrum of 3q



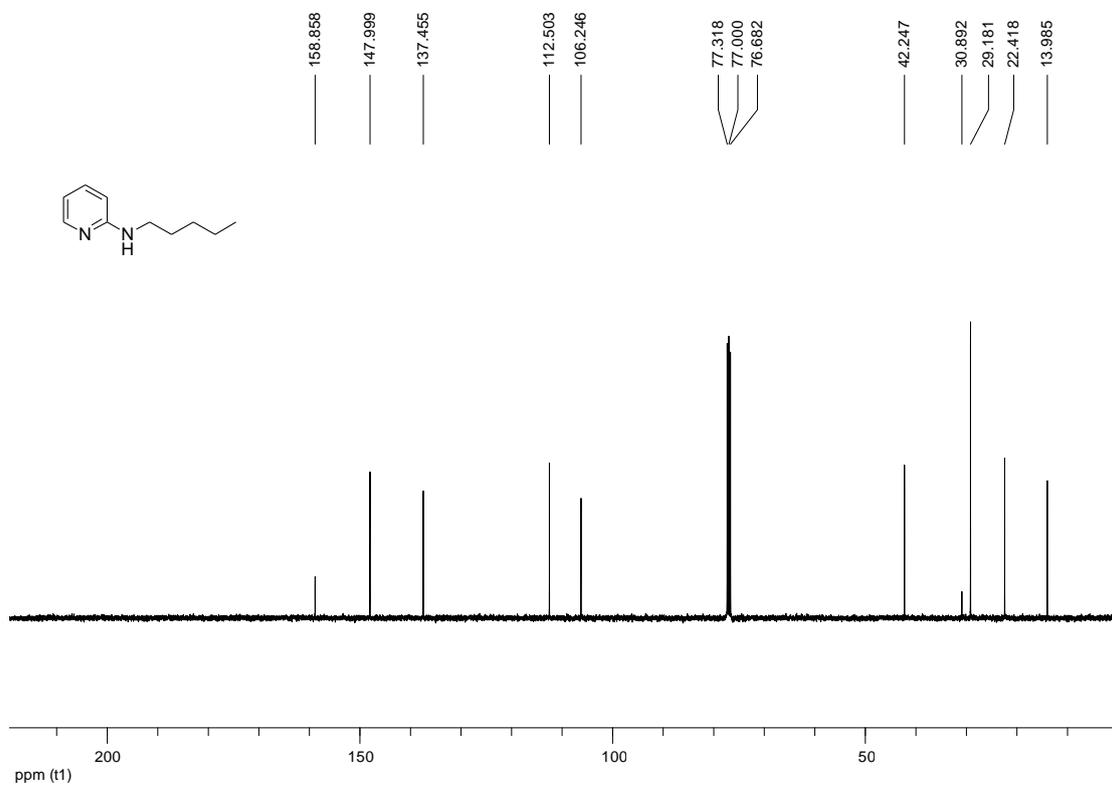
¹³C NMR (100MHz, CDCl₃) spectrum of 3q



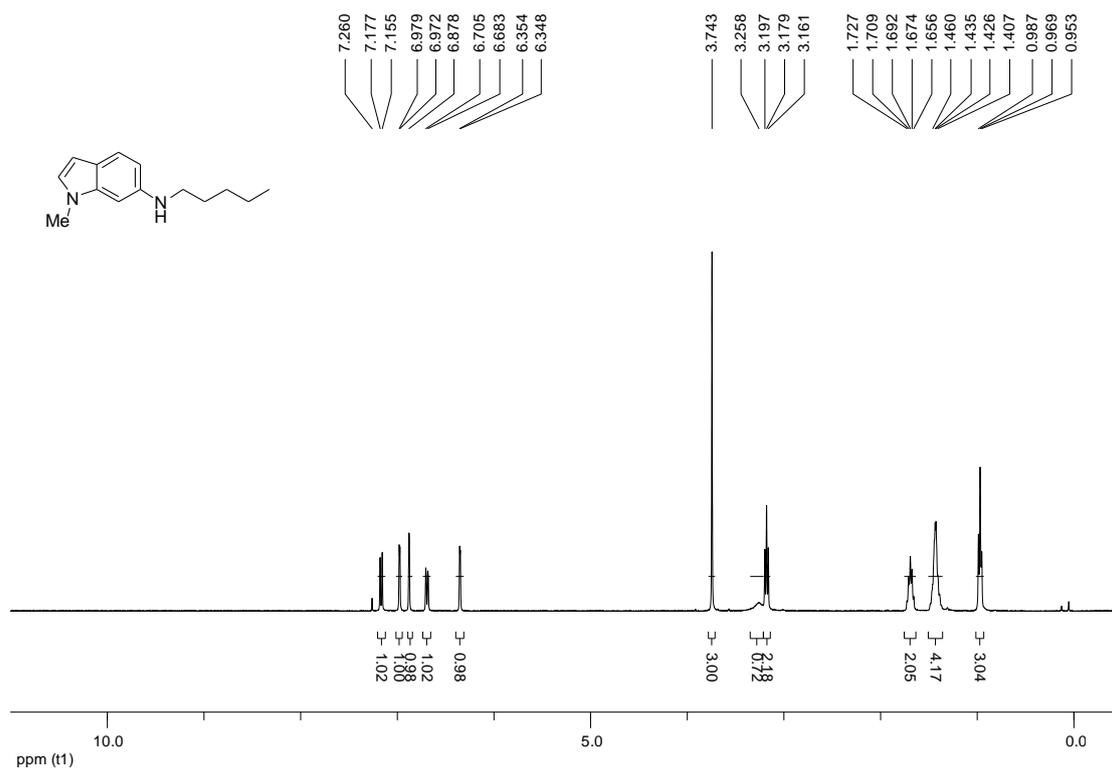
¹H NMR (400 MHz, CDCl₃) spectrum of 3r



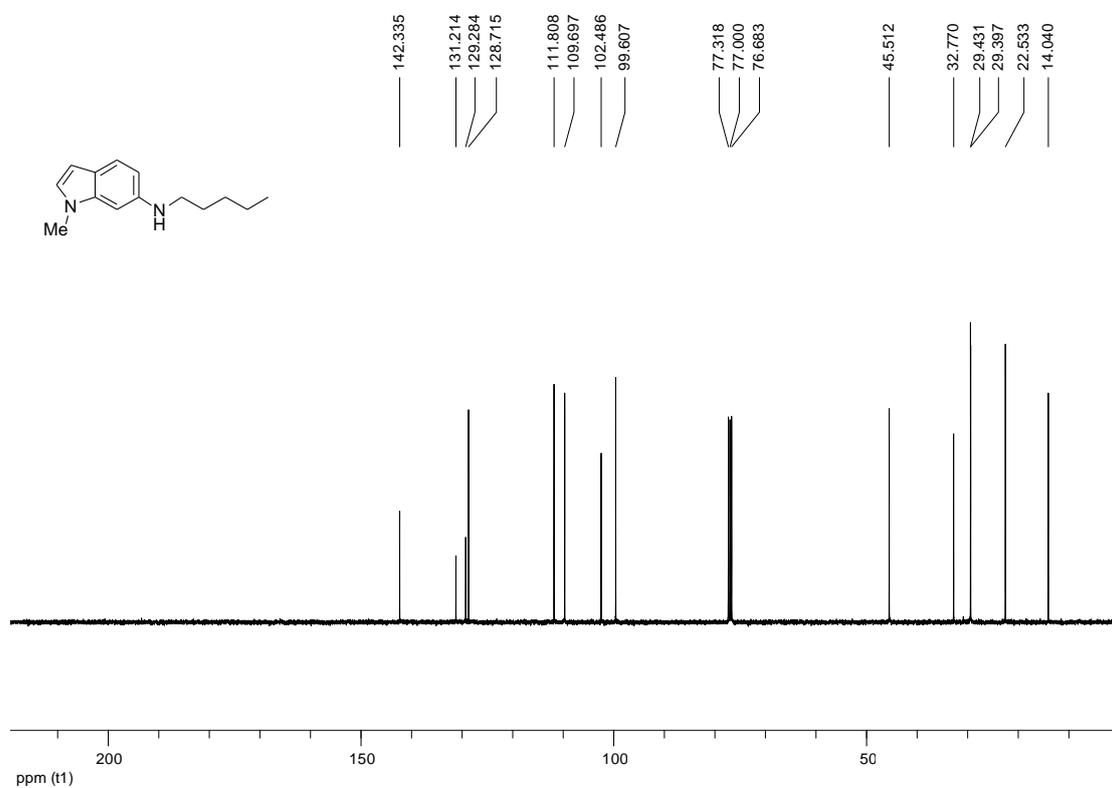
¹³C NMR (100MHz, CDCl₃) spectrum of 3r



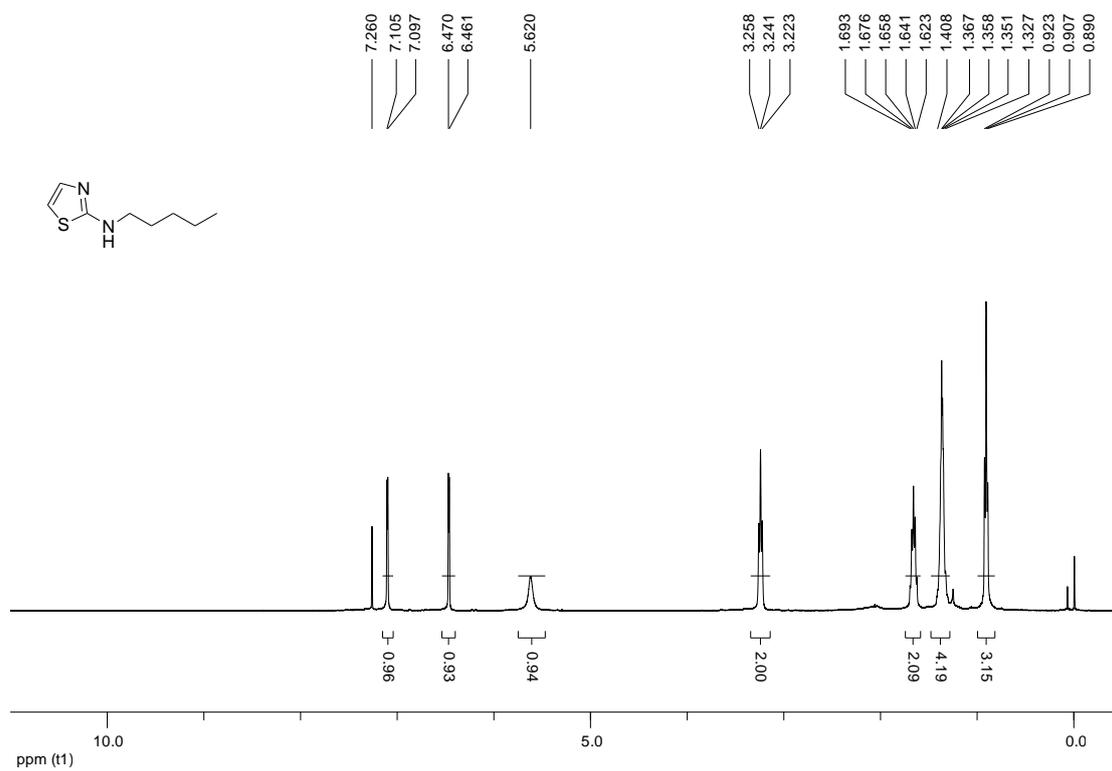
¹H NMR (400 MHz, CDCl₃) spectrum of 3s



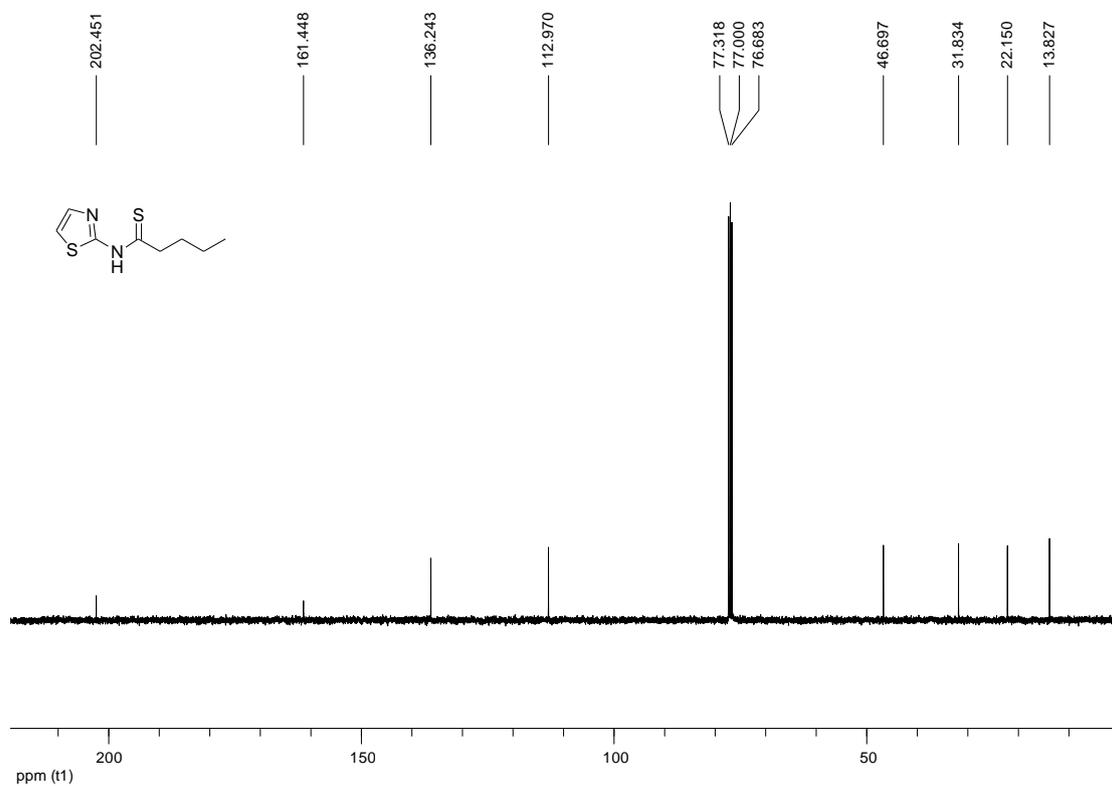
¹³C NMR (100MHz, CDCl₃) spectrum of 3s



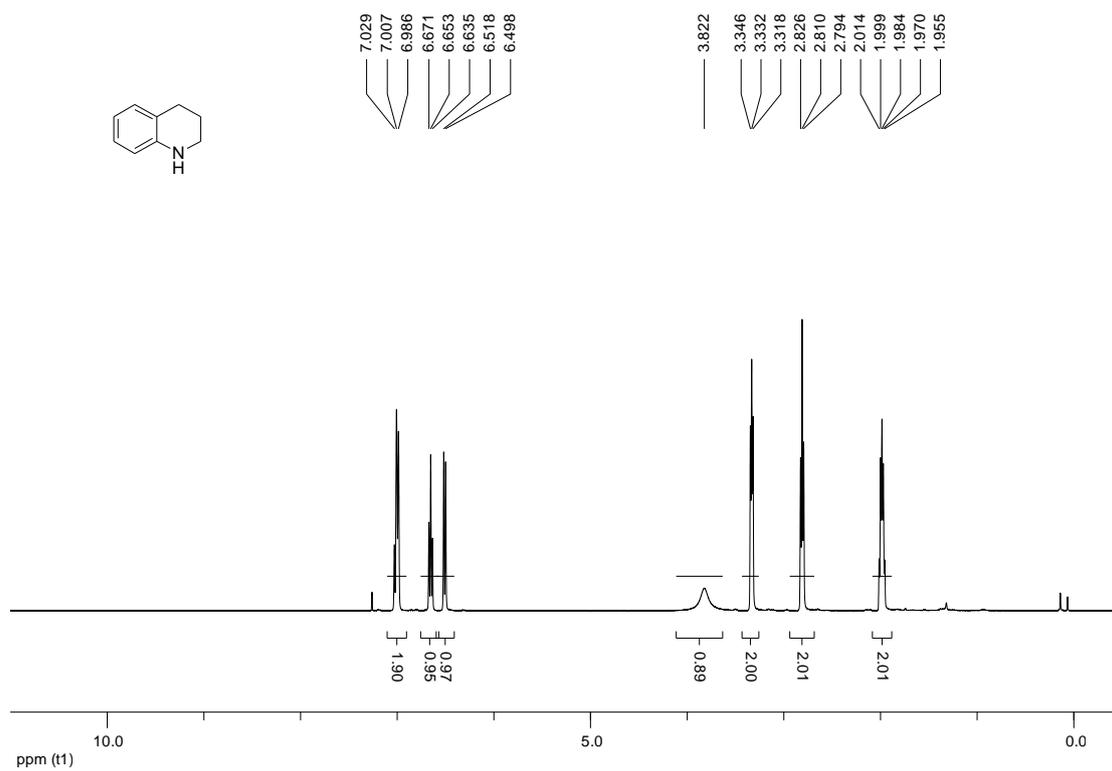
¹H NMR (400 MHz, CDCl₃) spectrum of 3t



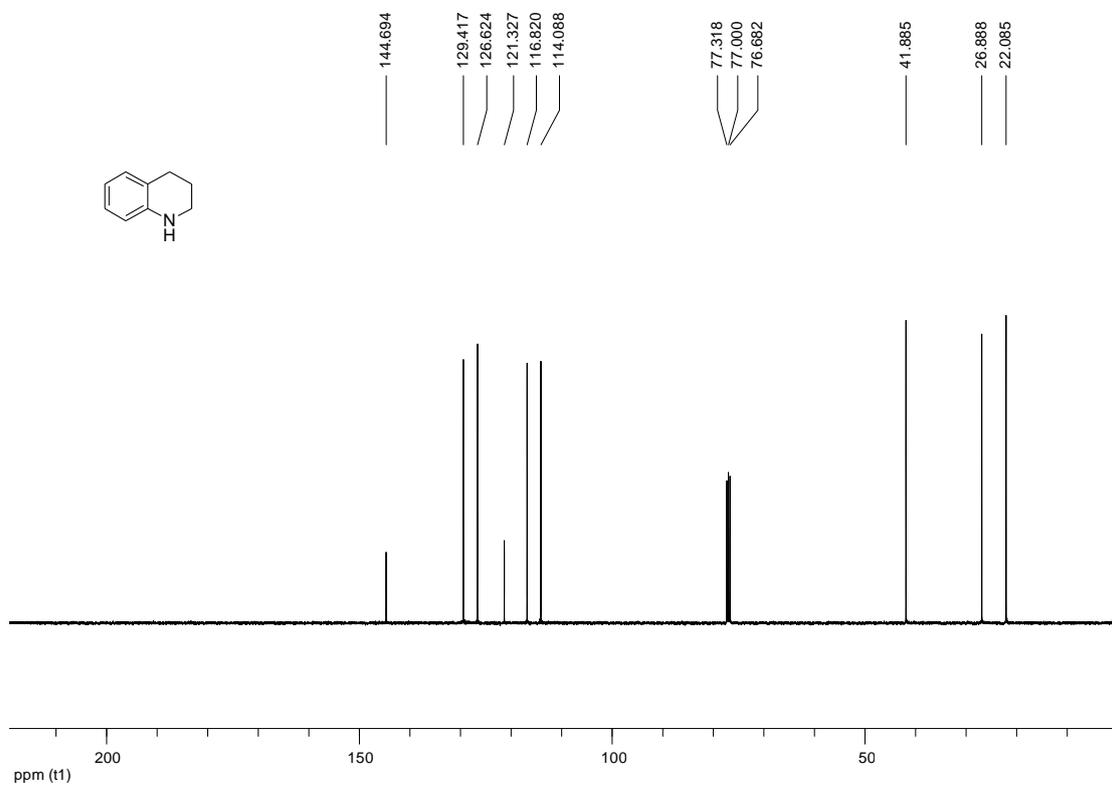
¹³C NMR (100MHz, CDCl₃) spectrum of 3t



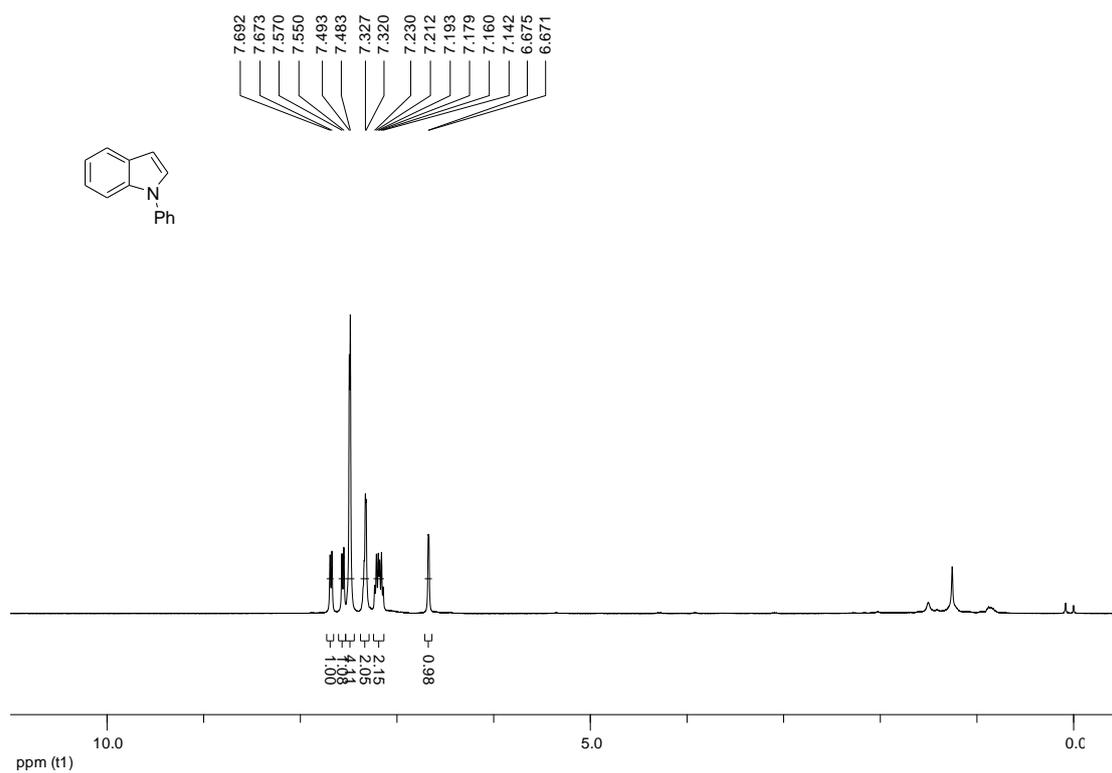
¹H NMR (400 MHz, CDCl₃) spectrum of 3u



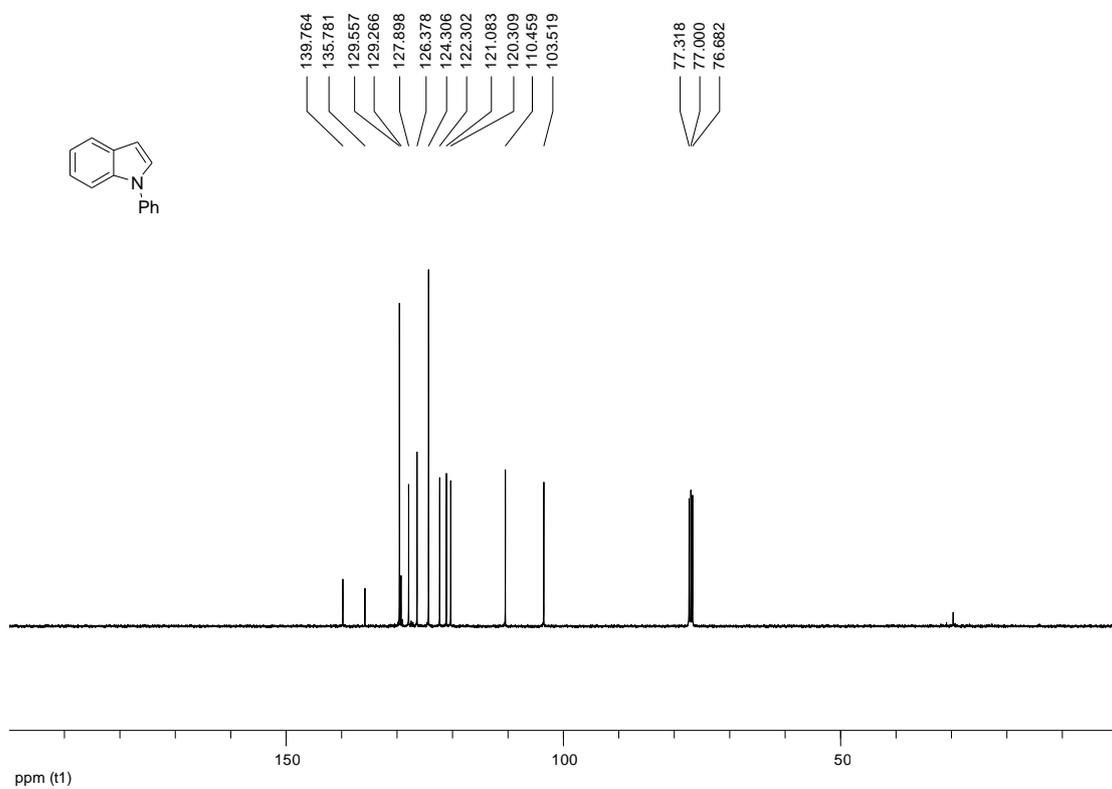
¹³C NMR (100MHz, CDCl₃) spectrum of 3u



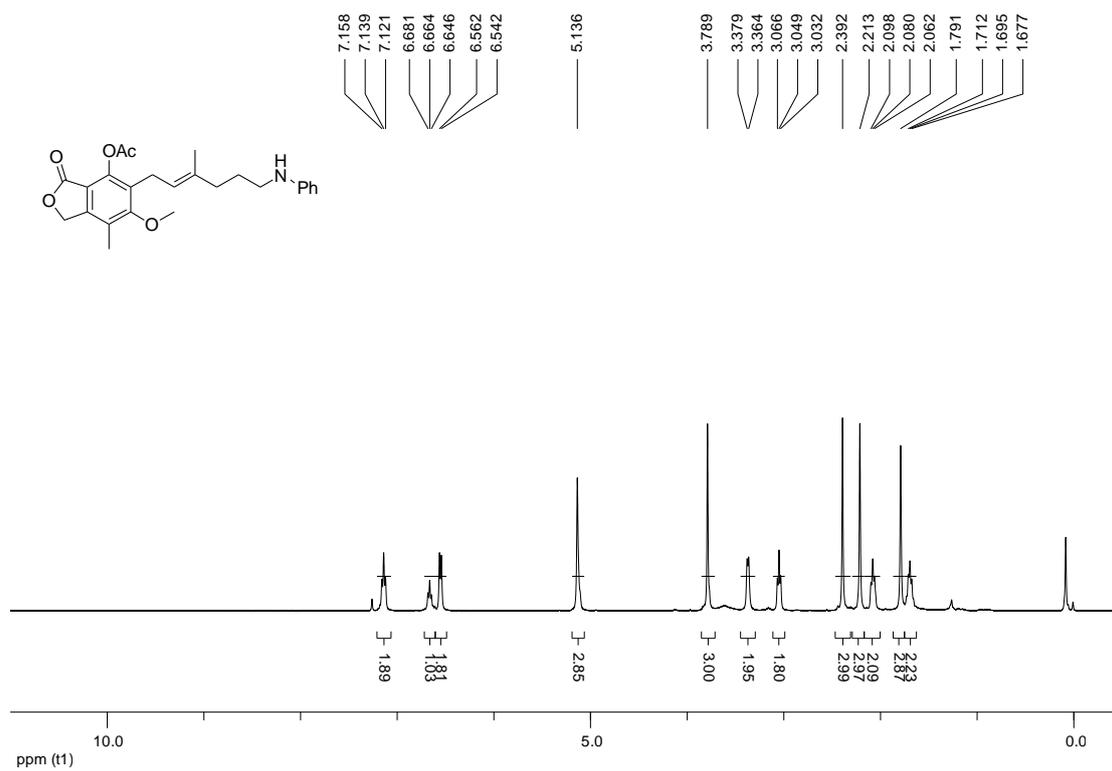
¹H NMR (400 MHz, CDCl₃) spectrum of 3v



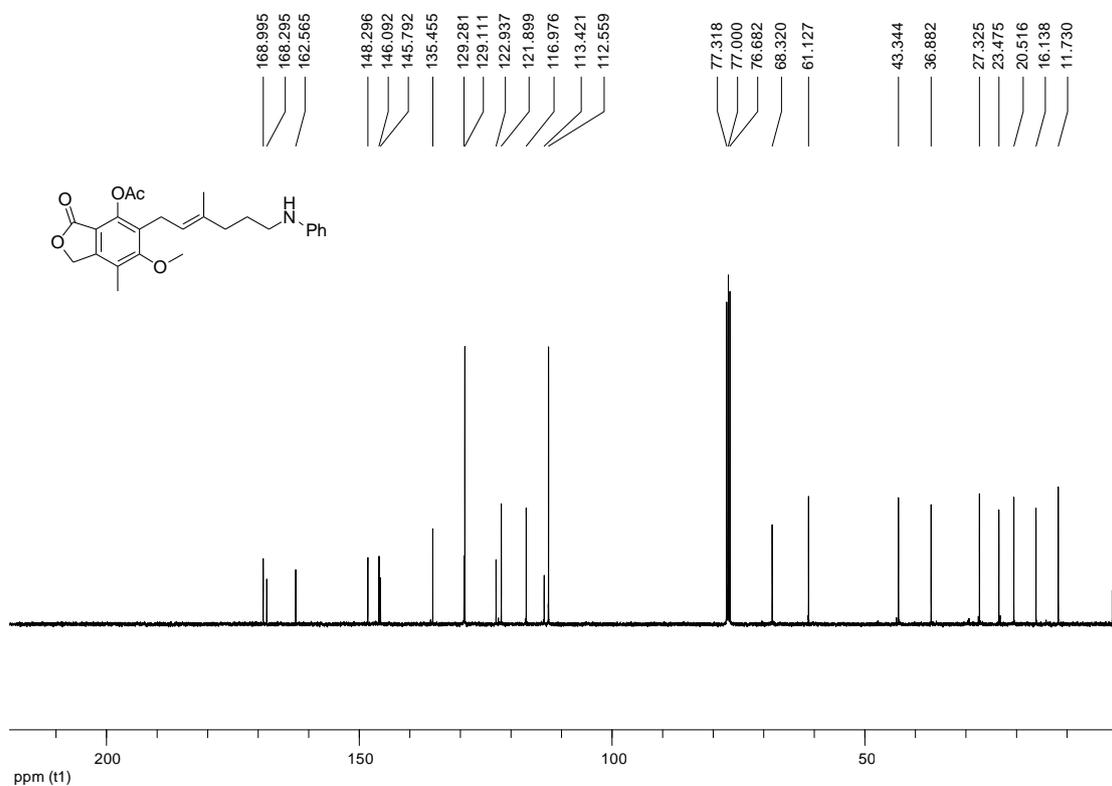
¹³C NMR (100MHz, CDCl₃) spectrum of 3v



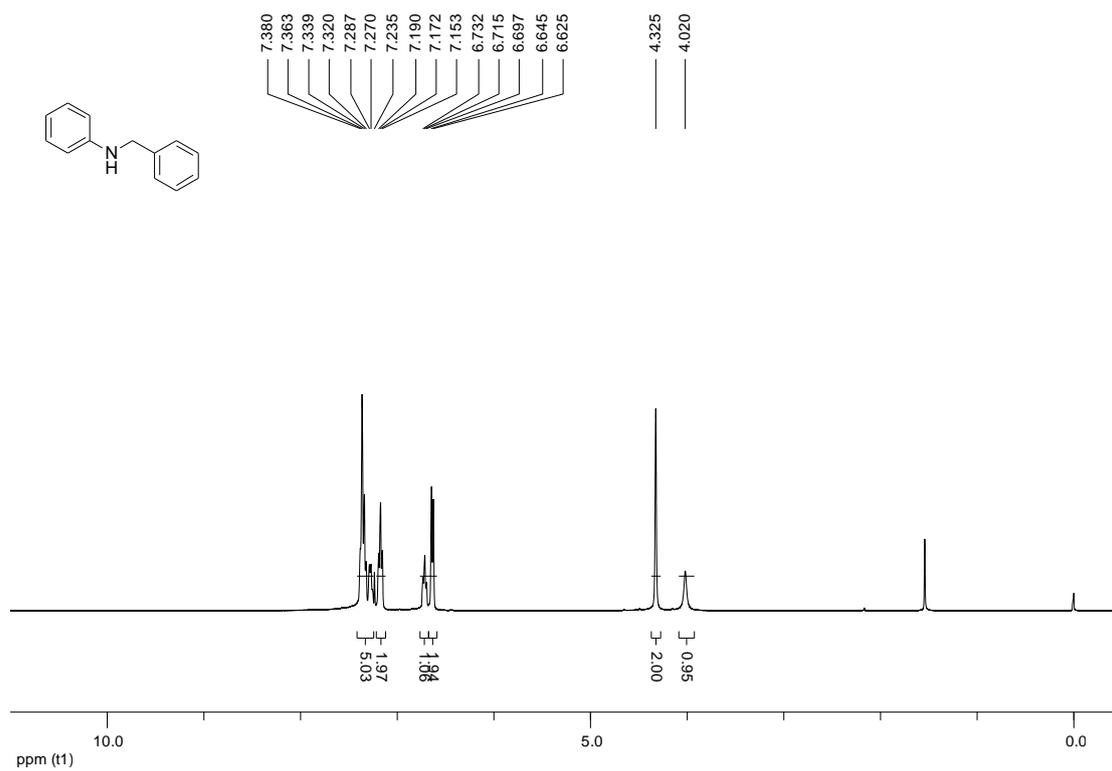
¹H NMR (400 MHz, CDCl₃) spectrum of 3w



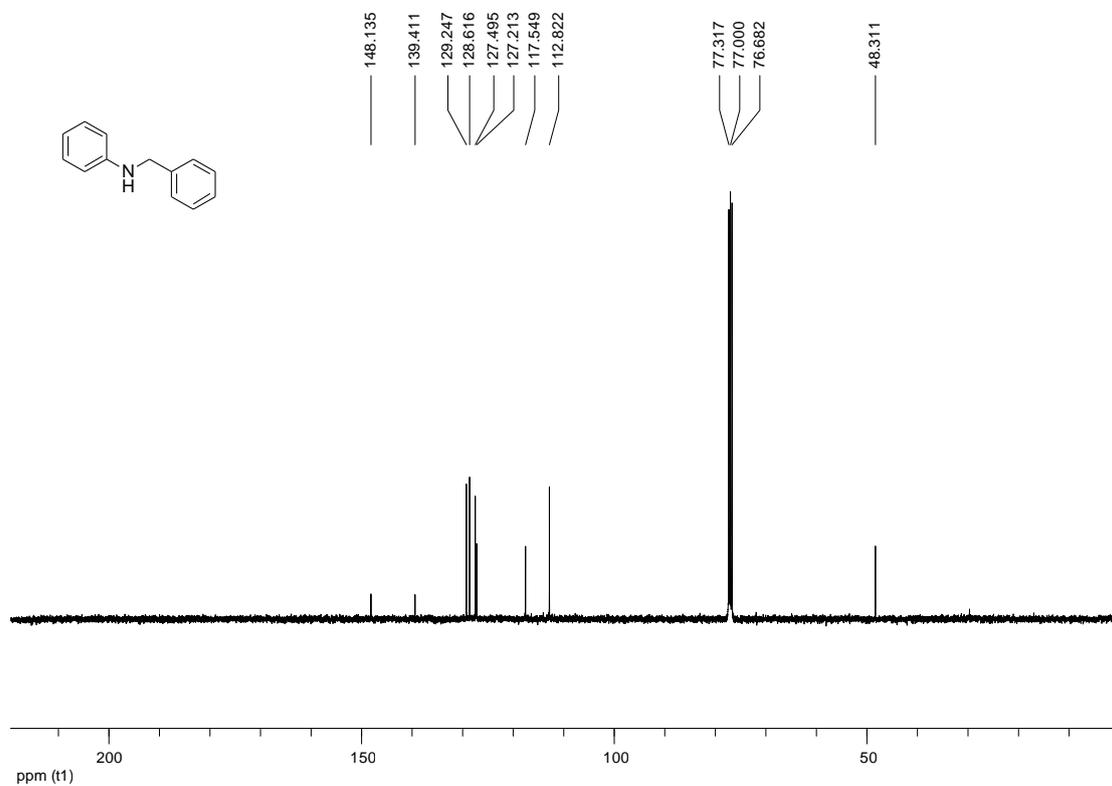
¹³C NMR (100MHz, CDCl₃) spectrum of 3w



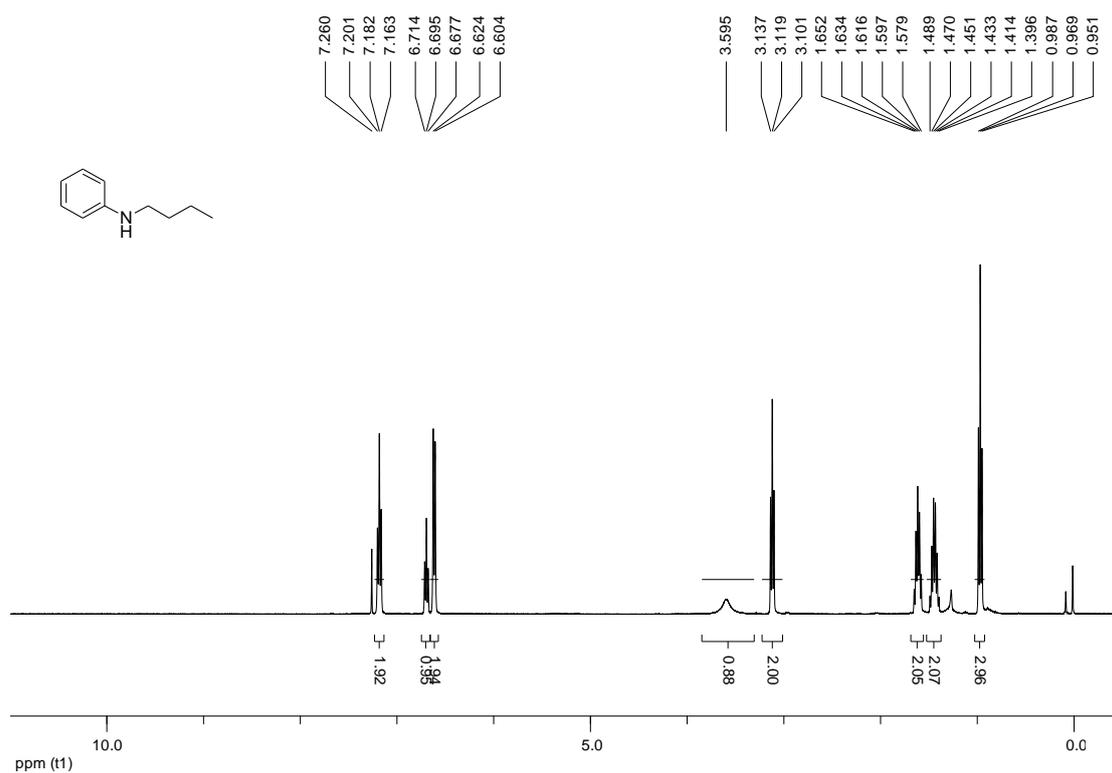
¹H NMR (400 MHz, CDCl₃) spectrum of 3x



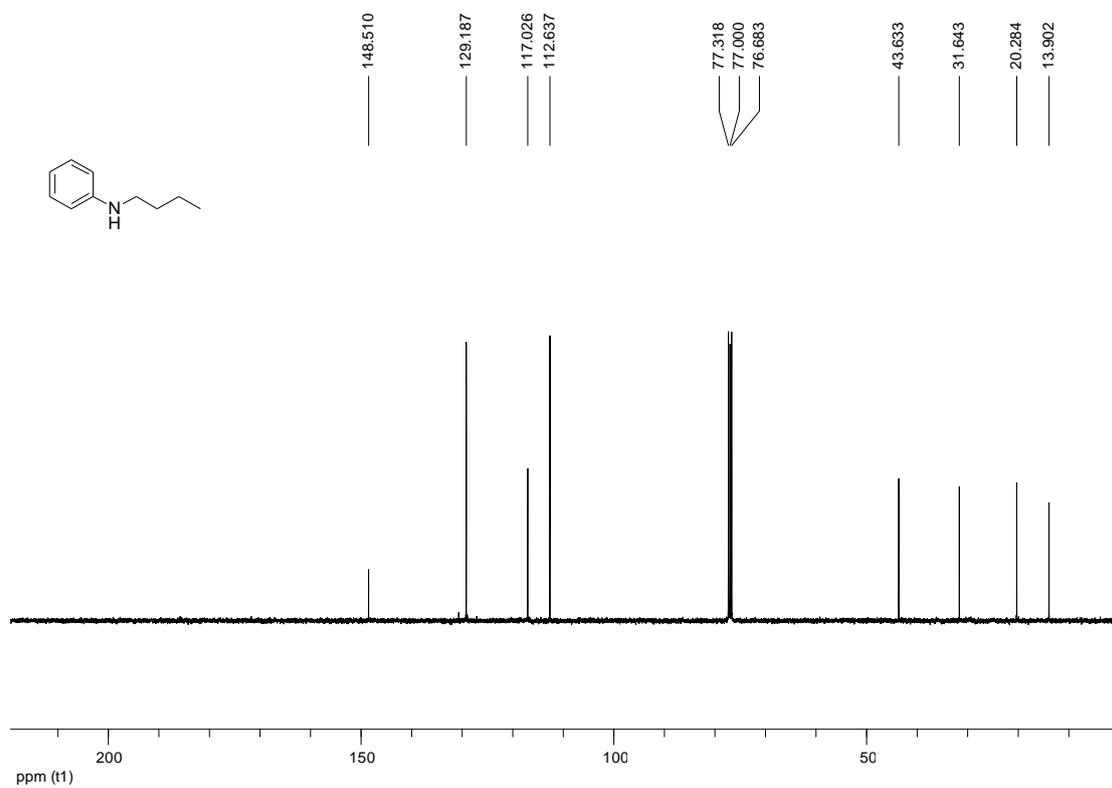
¹³C NMR (100MHz, CDCl₃) spectrum of 3x



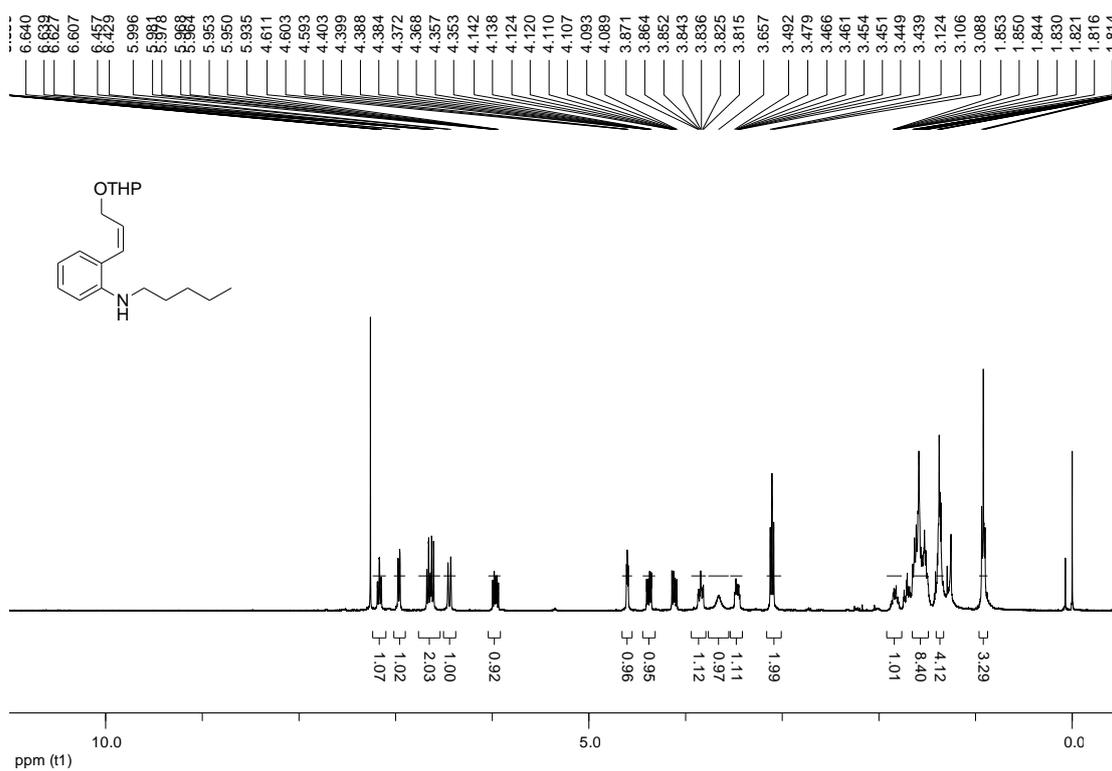
¹H NMR (400 MHz, CDCl₃) spectrum of 3a'



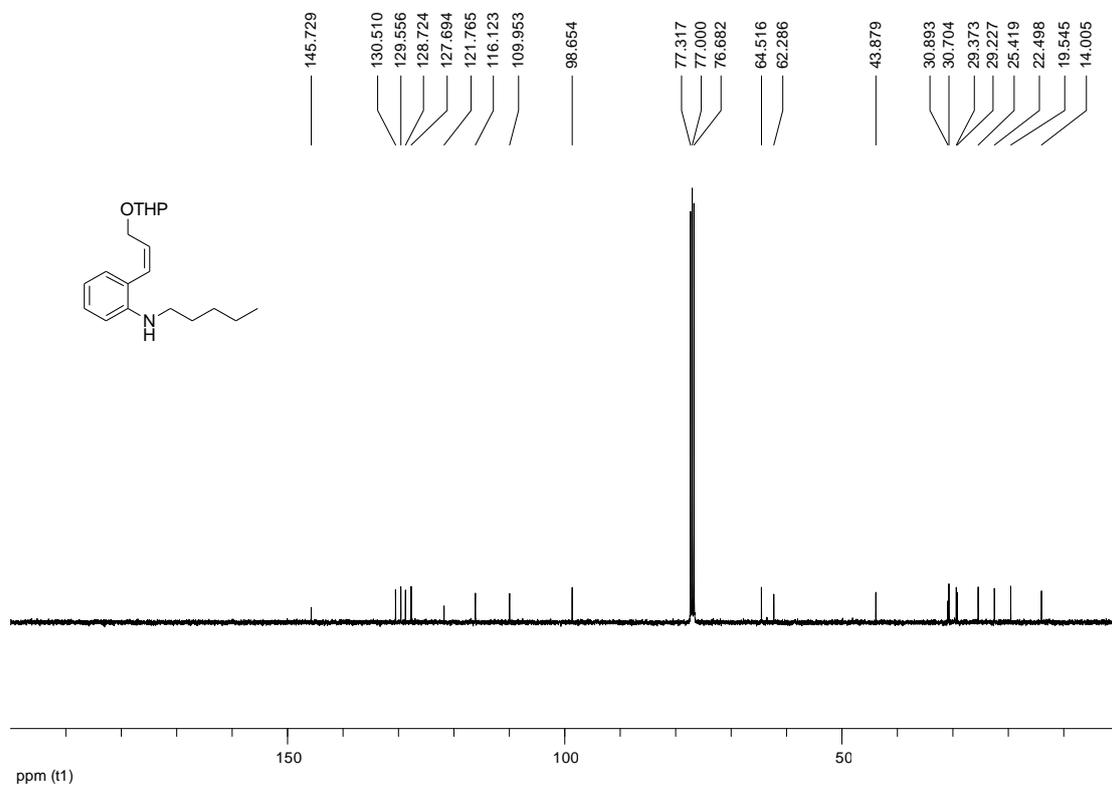
¹³C NMR (100MHz, CDCl₃) spectrum of 3a'



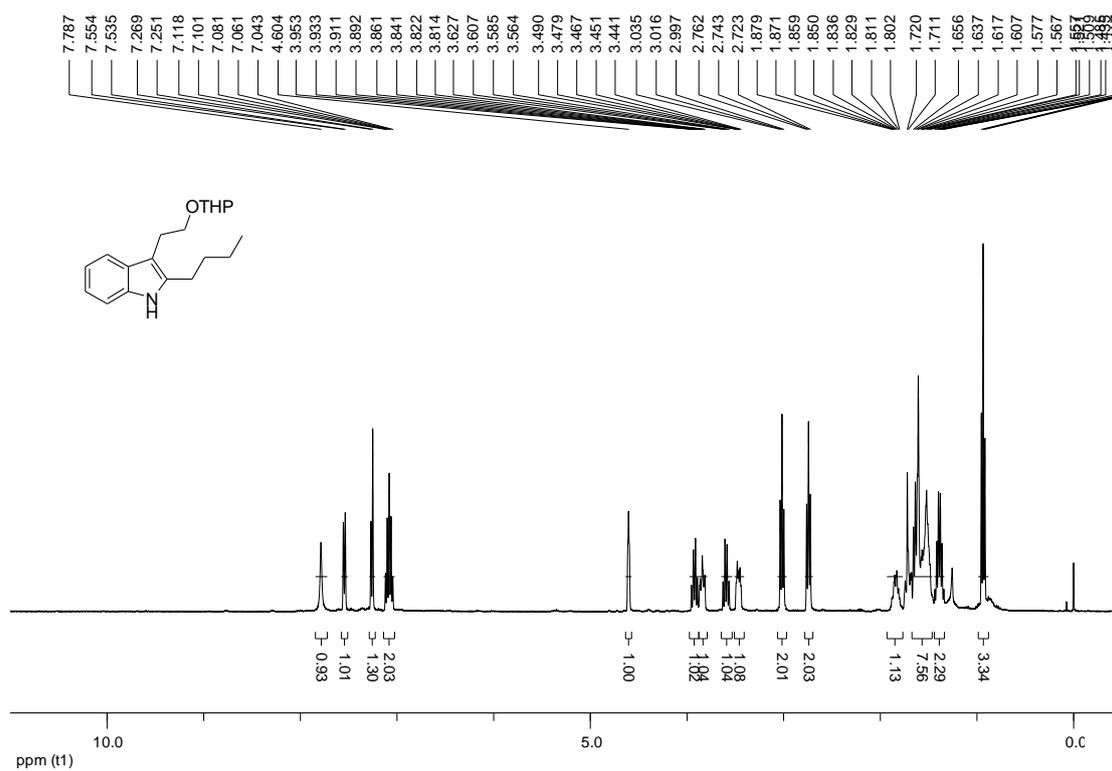
¹H NMR (400 MHz, CDCl₃) spectrum of 3aa



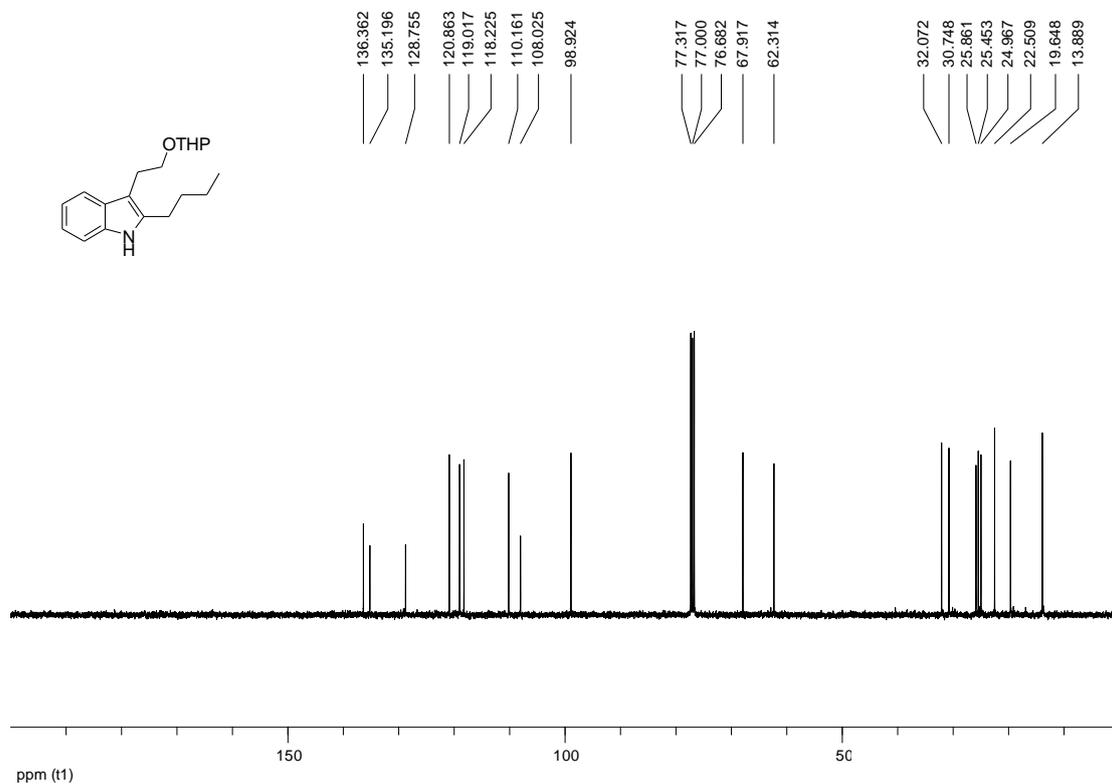
¹³C NMR (100MHz, CDCl₃) spectrum of 3aa



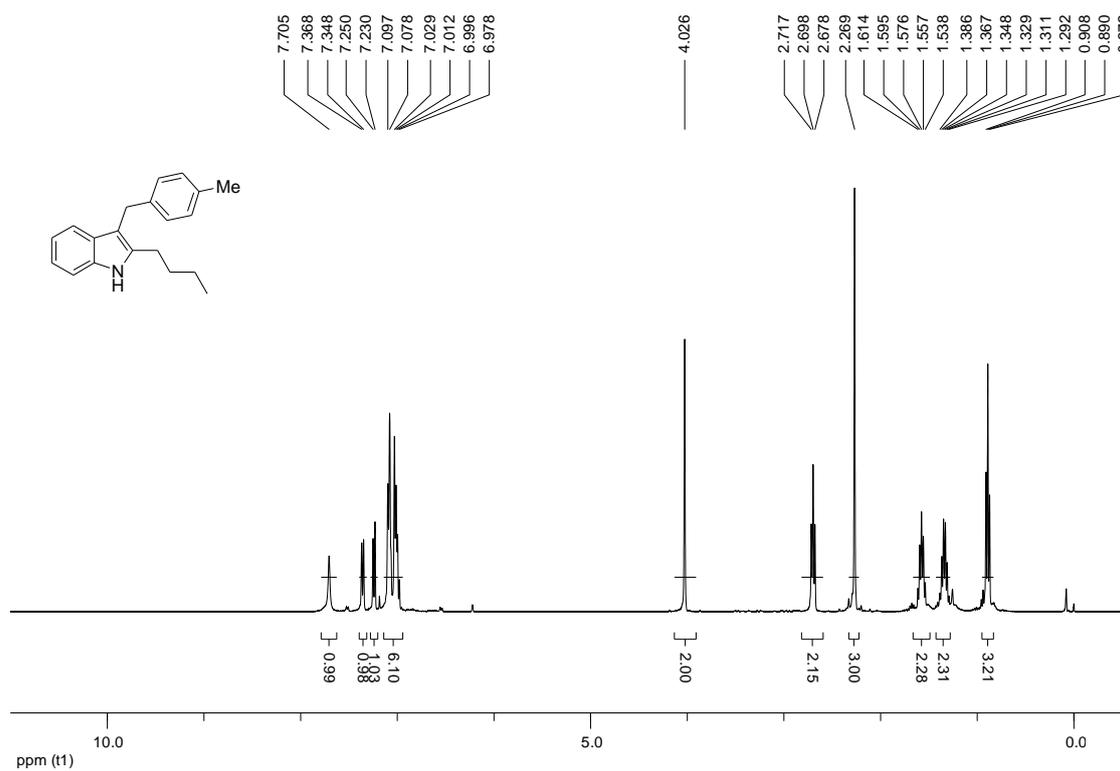
¹H NMR (400 MHz, CDCl₃) spectrum of 4aa



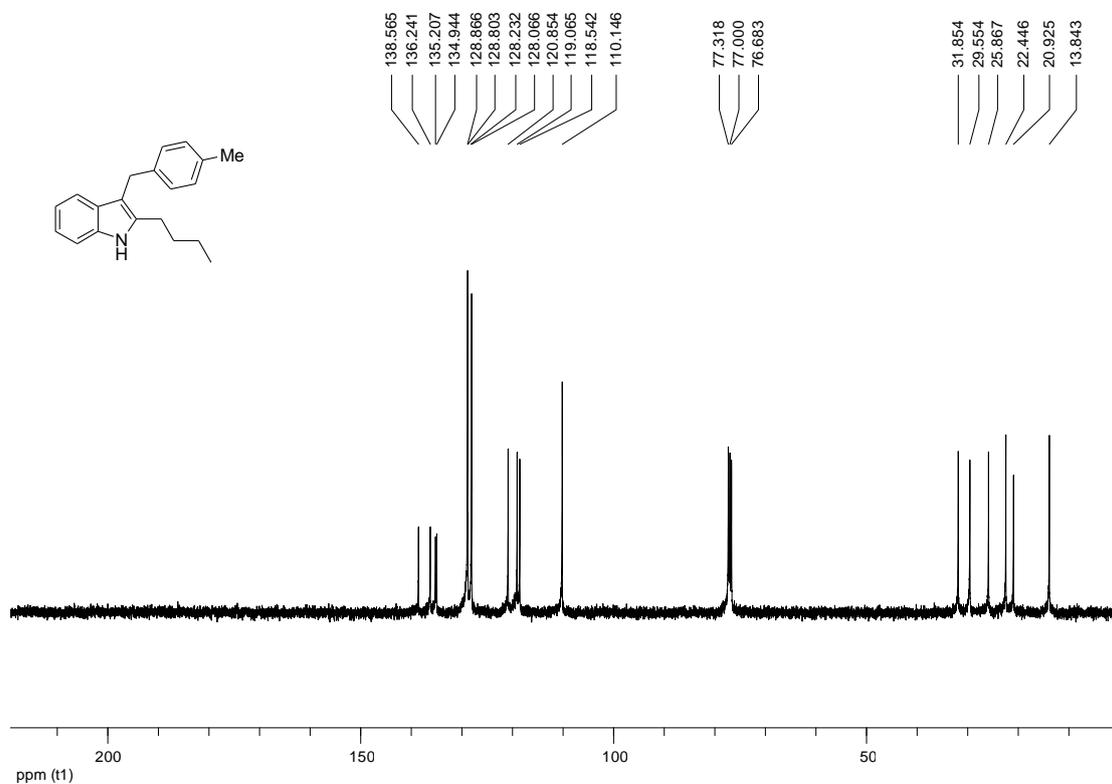
¹³C NMR (100MHz, CDCl₃) spectrum of 4aa



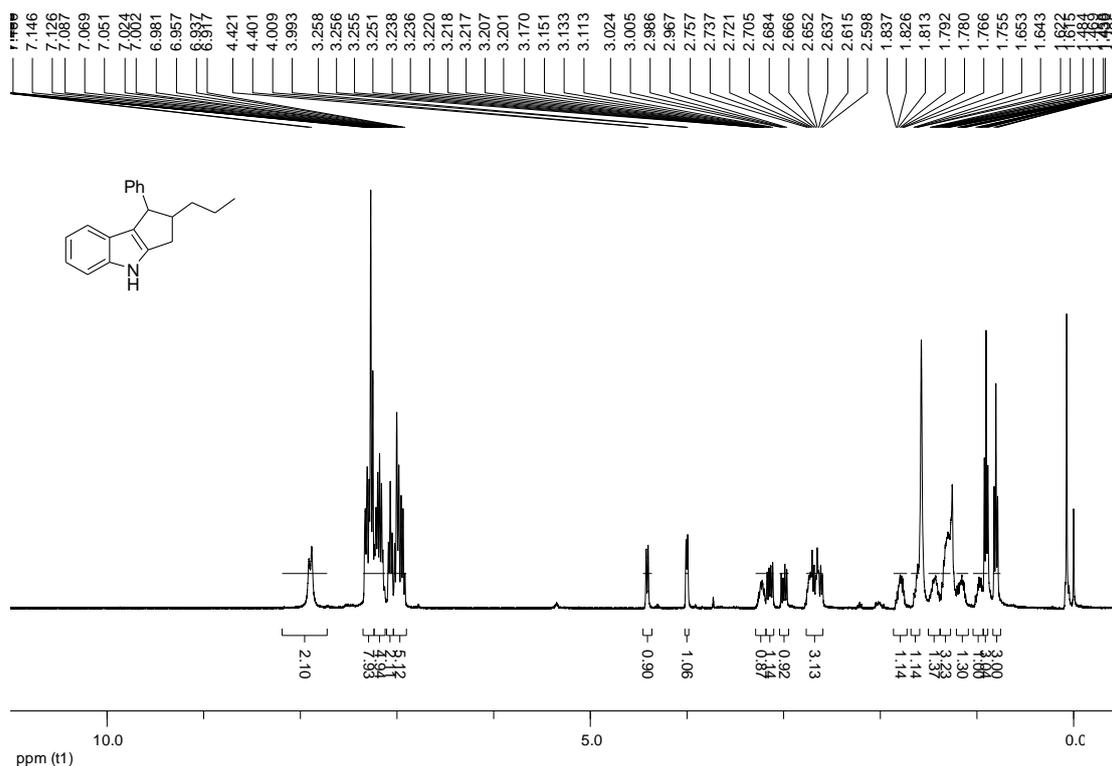
¹H NMR (400 MHz, CDCl₃) spectrum of 4ab



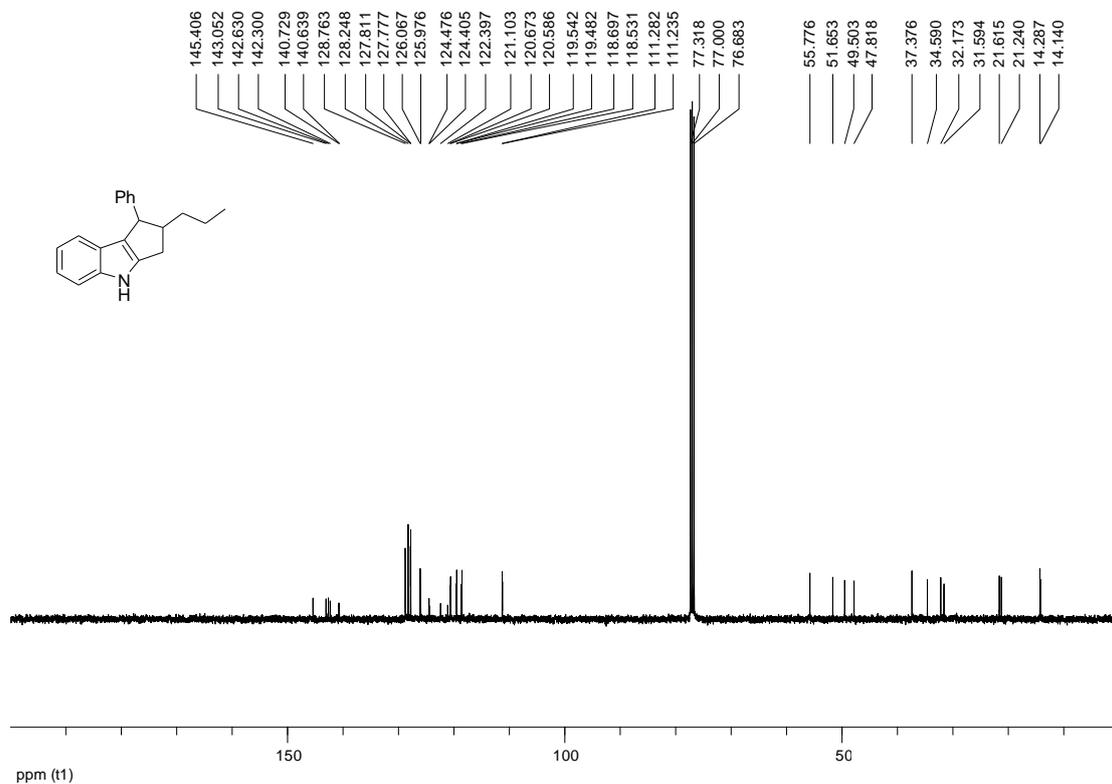
¹³C NMR (100MHz, CDCl₃) spectrum of 4ab



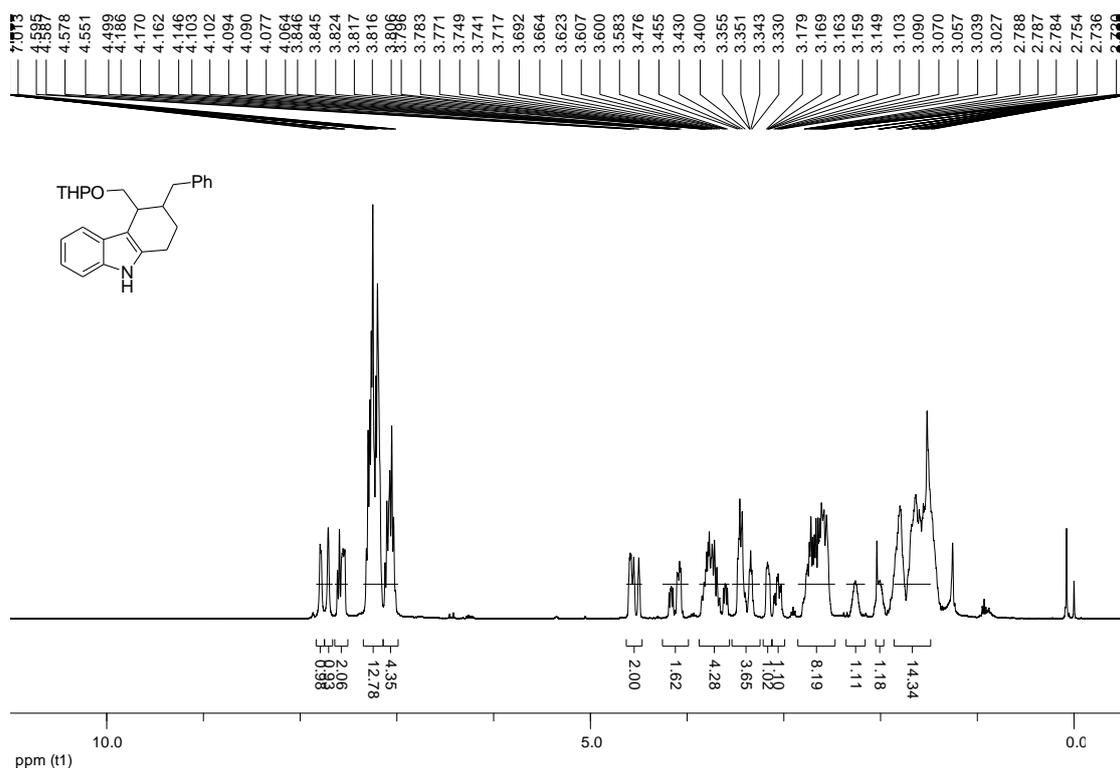
¹H NMR (400 MHz, CDCl₃) spectrum of 4ac



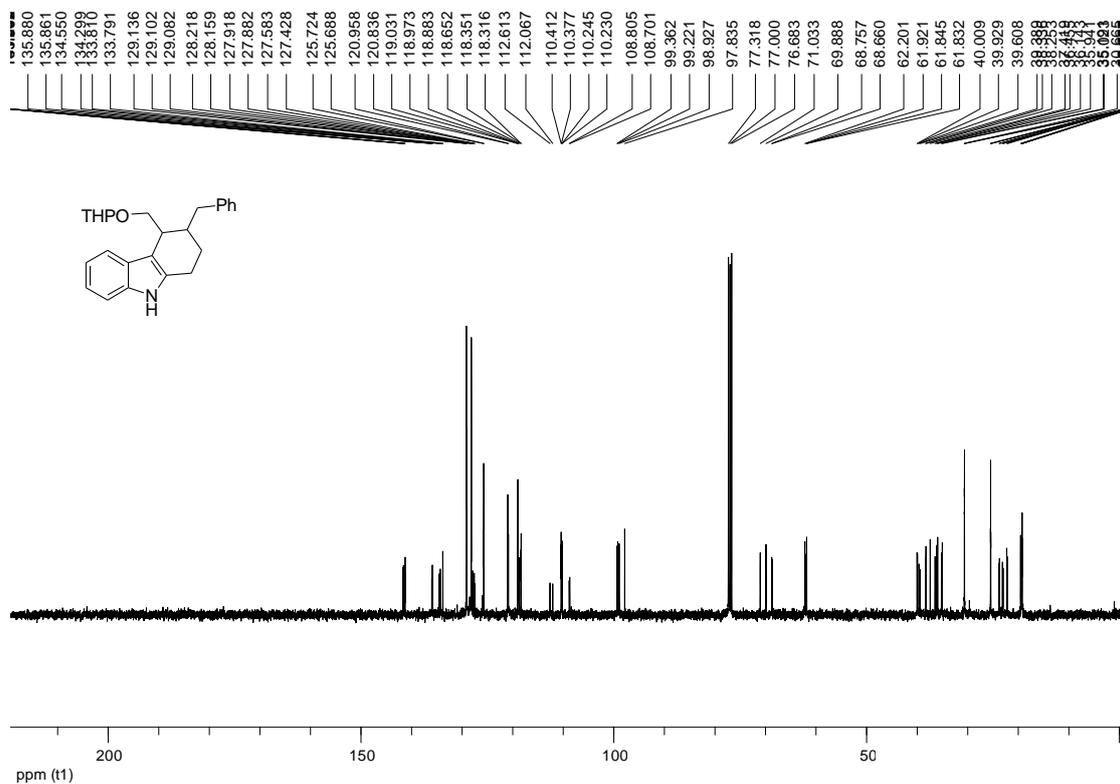
¹³C NMR (100MHz, CDCl₃) spectrum of 4ac



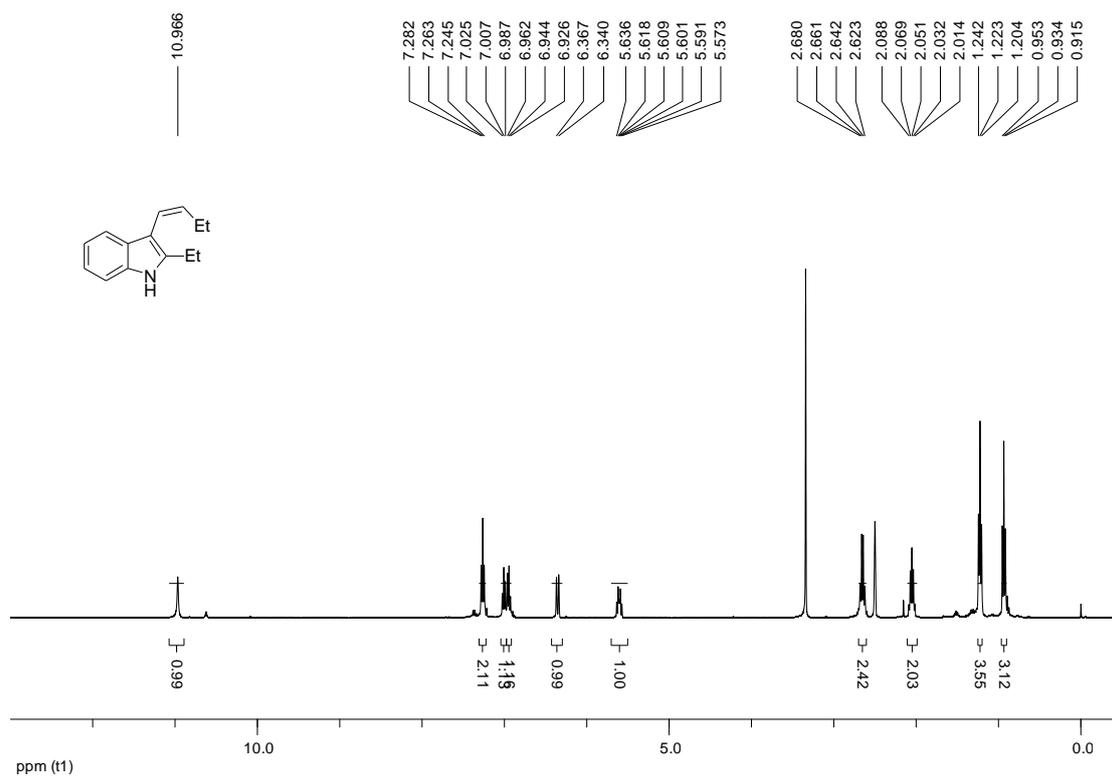
¹H NMR (400 MHz, CDCl₃) spectrum of 4ad



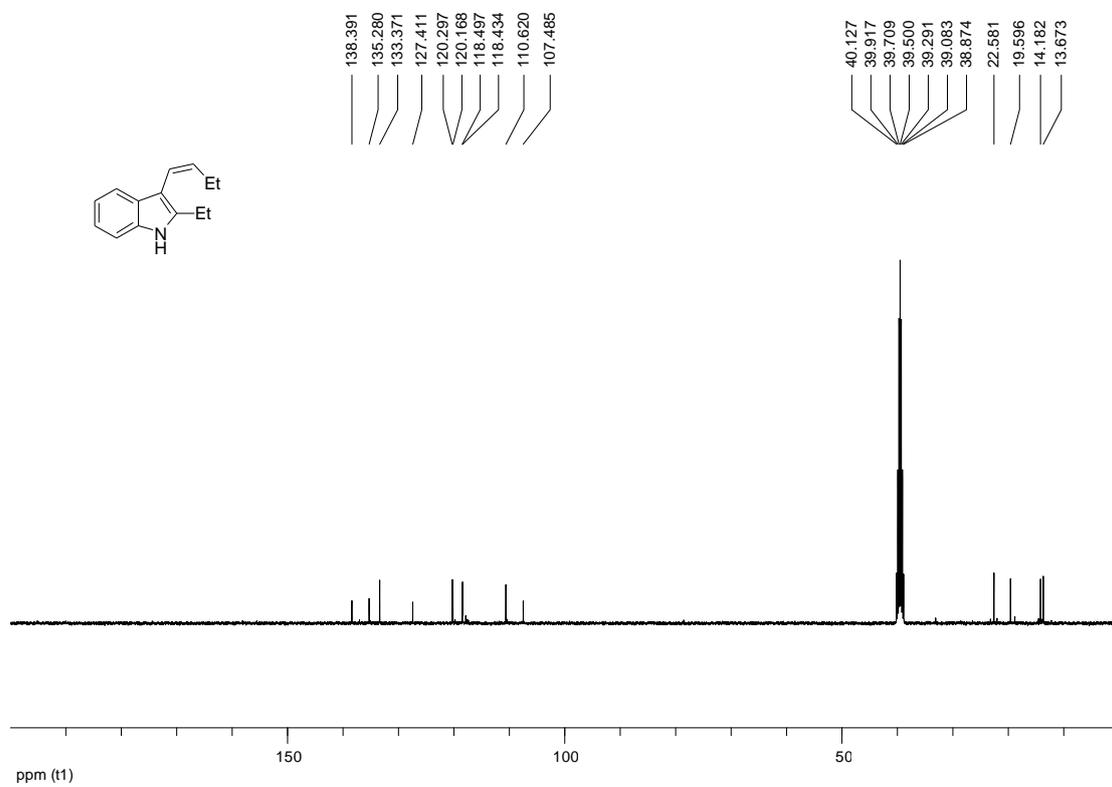
¹³C NMR (100MHz, CDCl₃) spectrum of 4ad



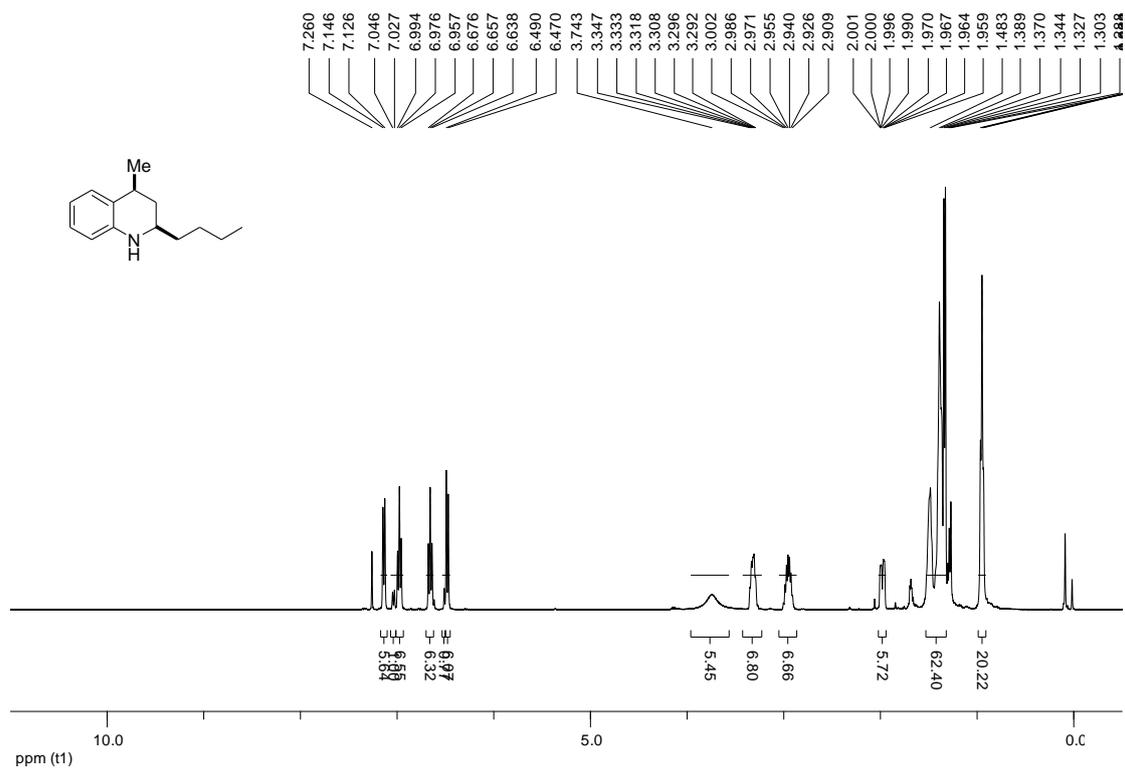
¹H NMR (400 MHz, DMSO-*d*₆) spectrum of 4ae



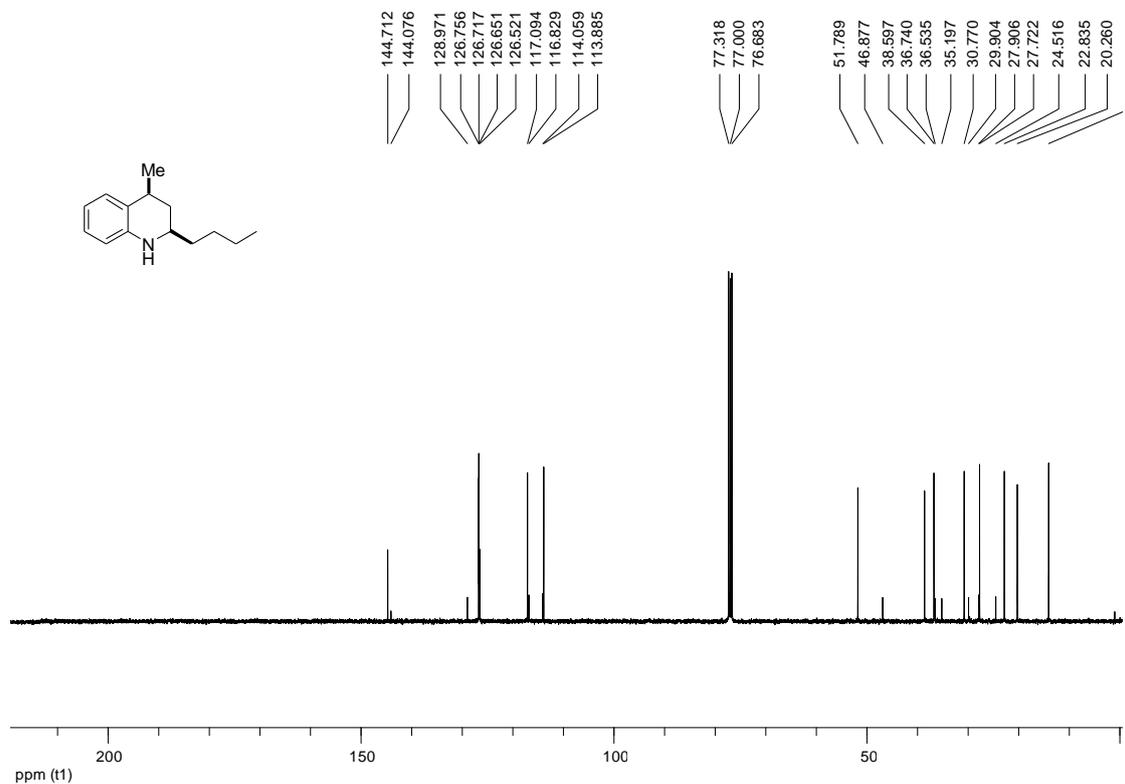
¹³C NMR (100MHz, DMSO-*d*₆) spectrum of 4ae



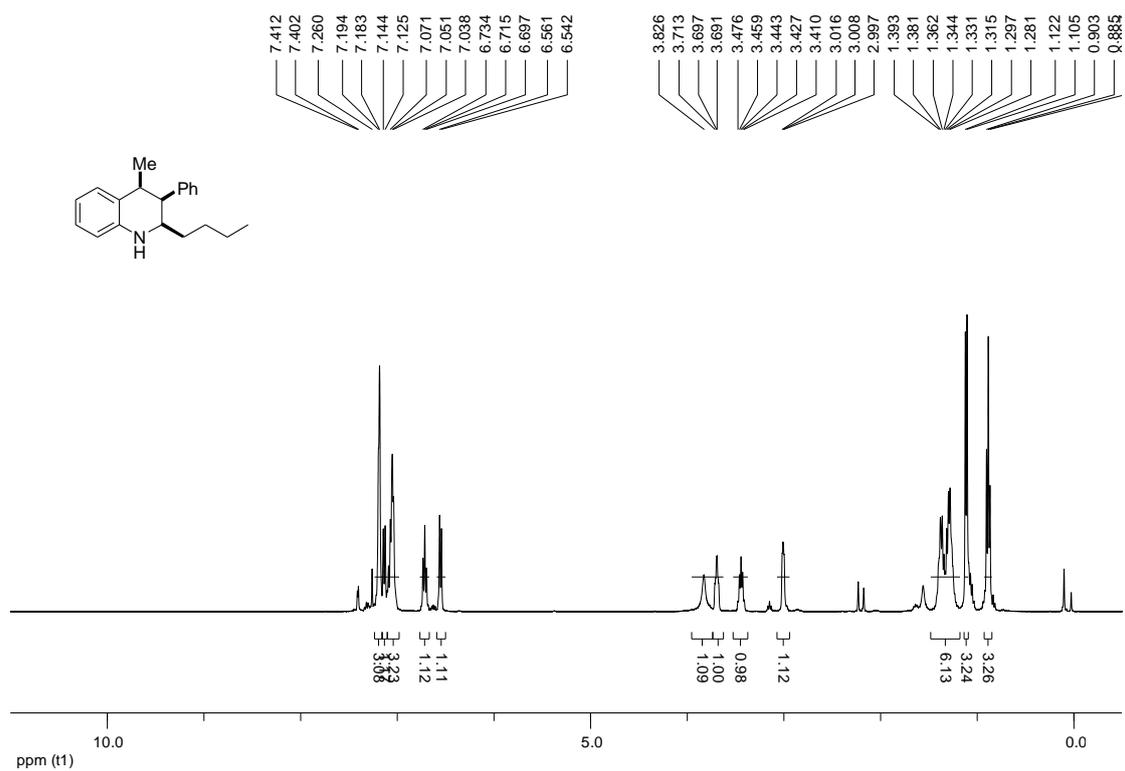
¹H NMR (400 MHz, CDCl₃) spectrum of 4af



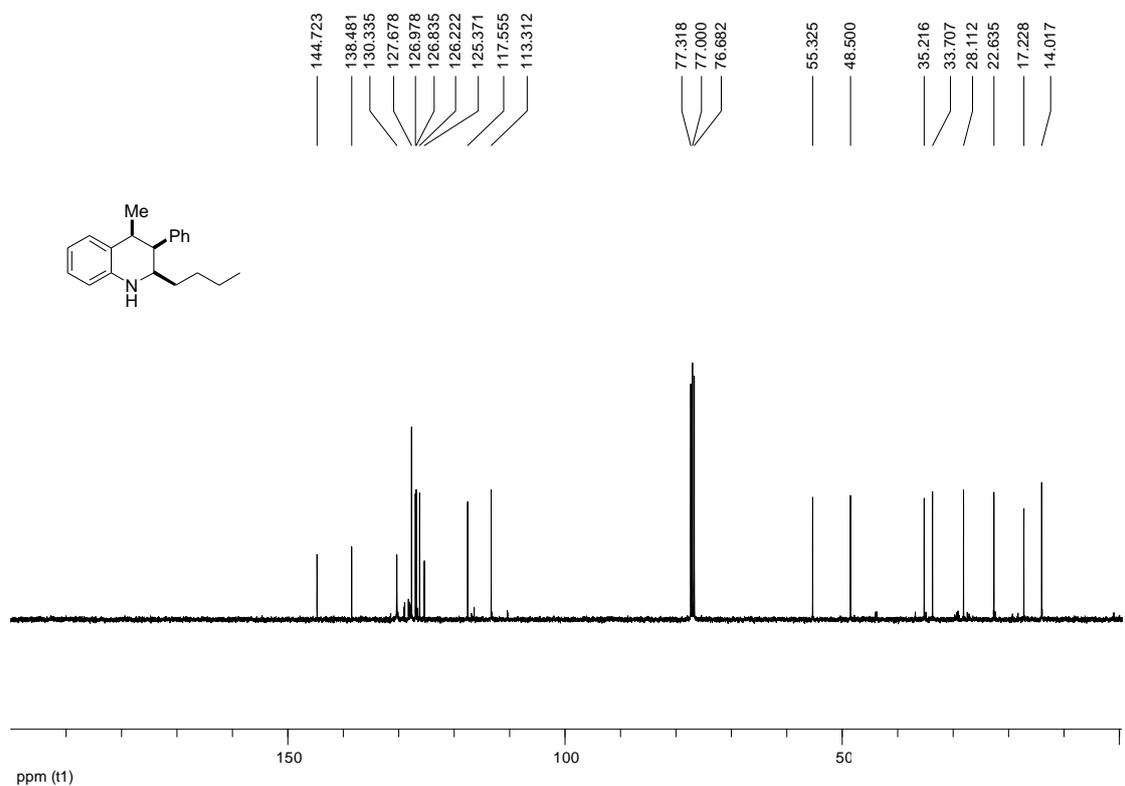
¹³C NMR (100MHz, CDCl₃) spectrum of 4af



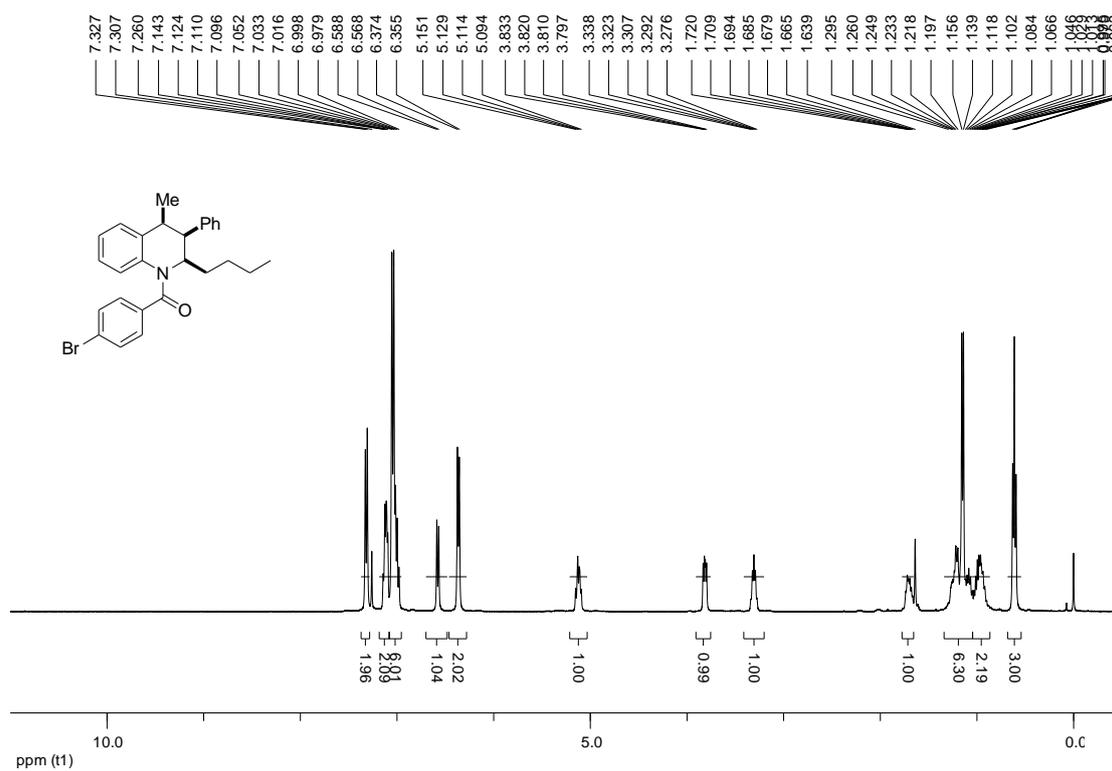
¹H NMR (400 MHz, CDCl₃) spectrum of 4ag



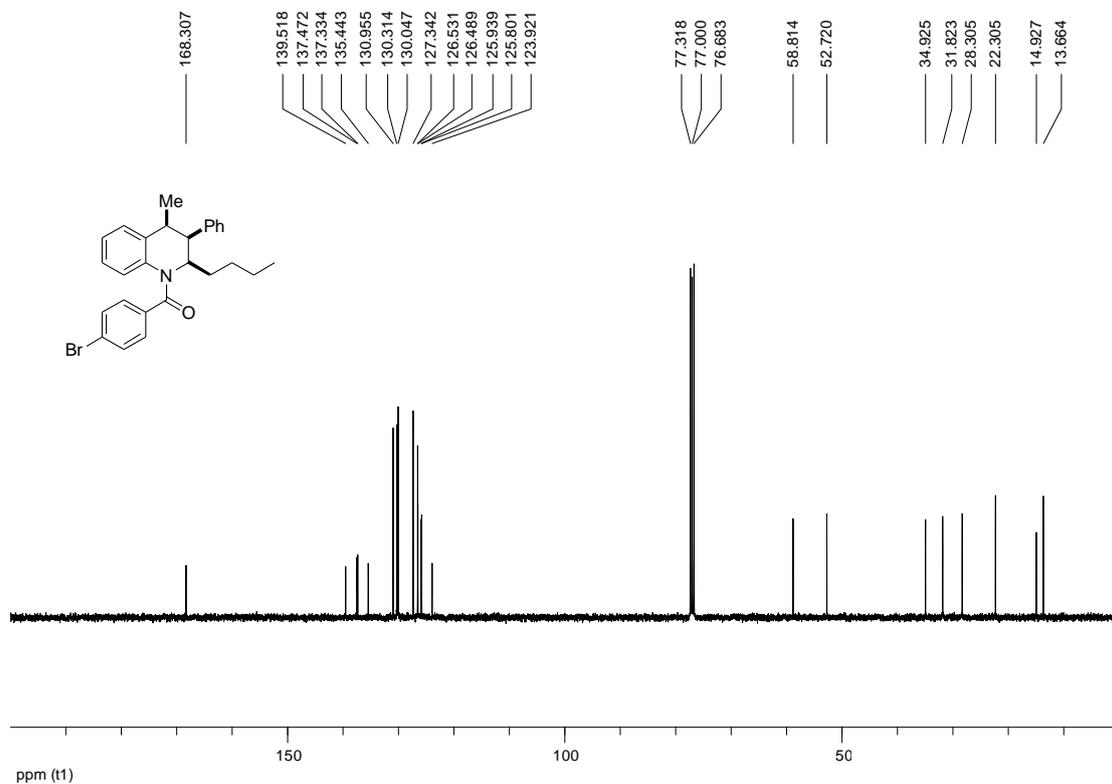
¹³C NMR (100MHz, CDCl₃) spectrum of 4ag



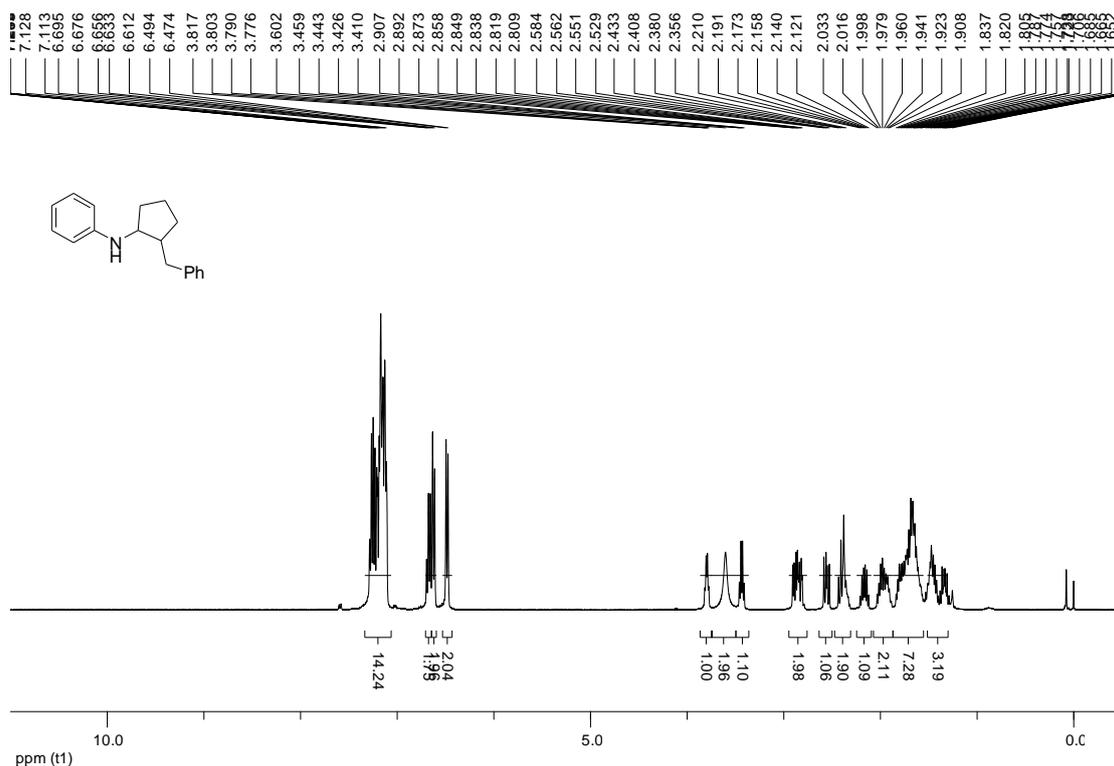
¹H NMR (400 MHz, CDCl₃) spectrum of 4ag'



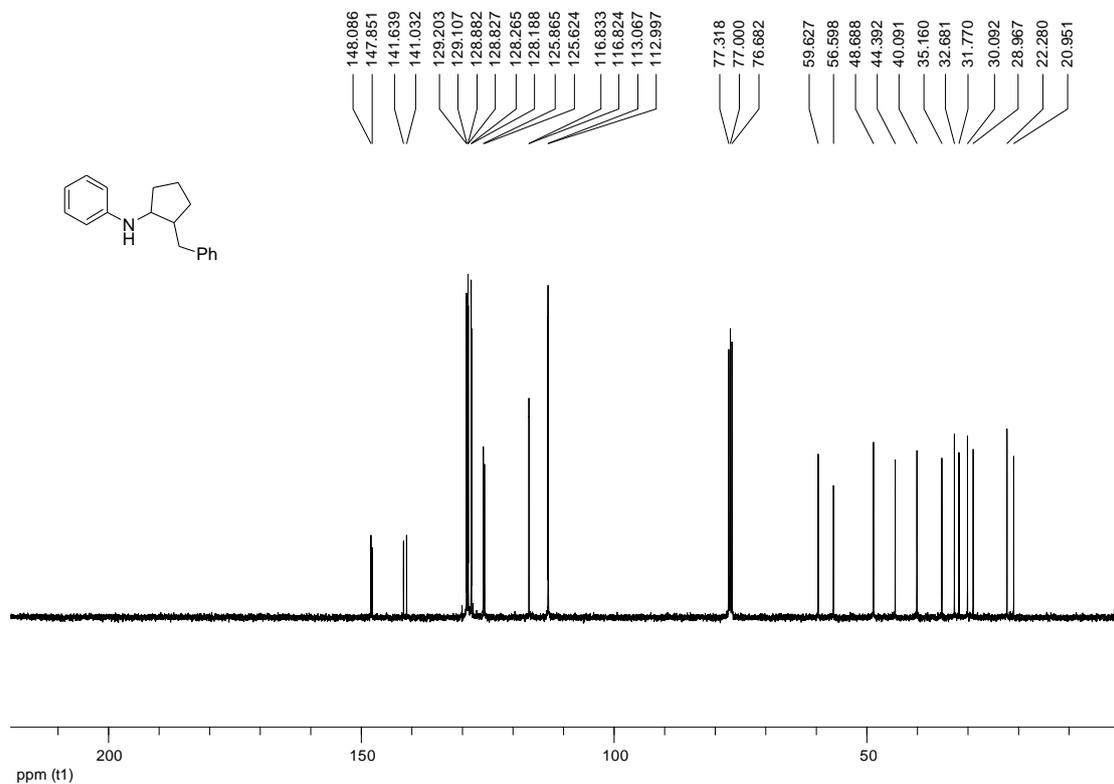
¹³C NMR (100MHz, CDCl₃) spectrum of 4ag'



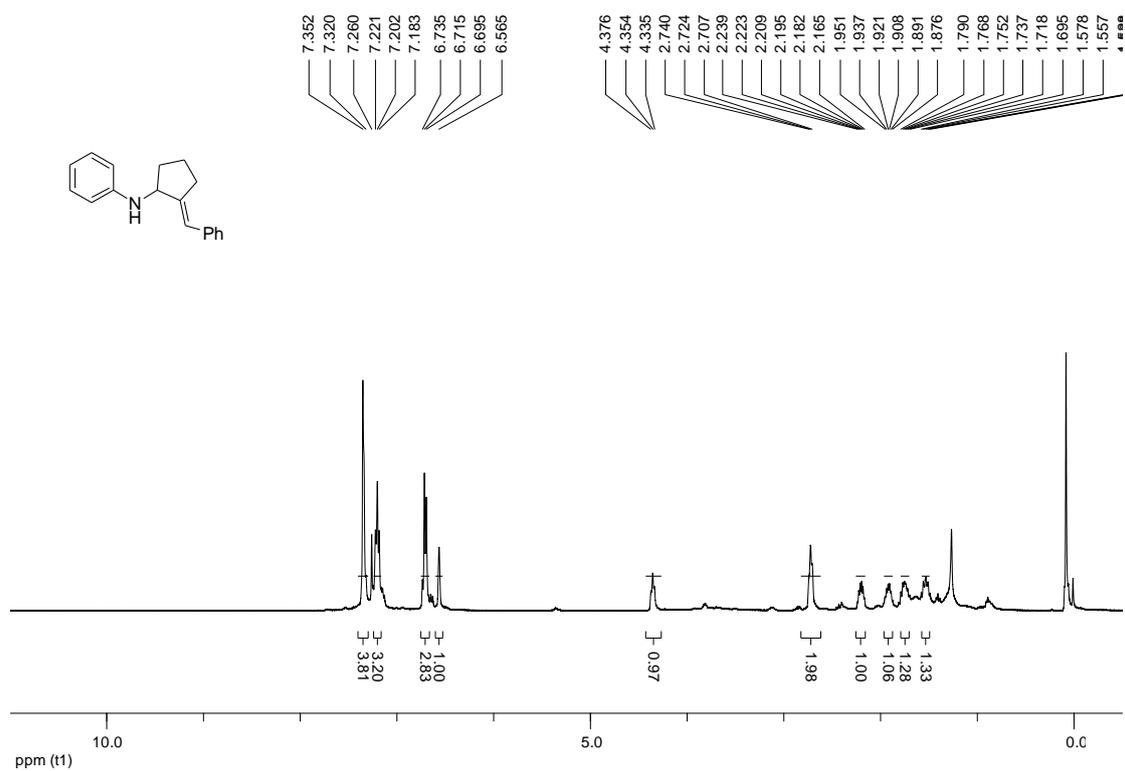
¹H NMR (400 MHz, CDCl₃) spectrum of 4ah



¹³C NMR (100MHz, CDCl₃) spectrum of 4ah



¹H NMR (400 MHz, CDCl₃) spectrum of 4ai



¹³C NMR (100MHz, CDCl₃) spectrum of 4ai

