

## Supporting Information

### **Photo-Switchable Regiodivergent Azidation of Olefins with Sulfonium Iodate(I) Reagent**

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**Abstract:** Photo-switchable strategy for selective azidation of structurally diverse olefins under transition metal-free conditions is reported. The unprecedented reactivity of trimethylsulfonium [bis(azido)iodate(I)] species under visible-light allows radical azidooxygenation of C=C  $\pi$  bond with distinctive selectivity. In the absence of visible-light, the reaction proceeds through an ionic intermediate which led to complementary regioselectivity ought to provide  $\alpha$ -alkylazides. Mechanistic studies reveal that light-controlled regiodivergent azidation involving radical or else ionic pathway can be accomplished with exclusive regioselectivity.

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## Supporting Material

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### A. General Experimental Information

#### General Synthesis Information:

Reactions were run in screw capped glass vials (4 mL) stirred with Teflon®-coated magnetic stir bars. Moisture and air-sensitive reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via nitrogen-flushed syringe. Experiments were monitored by thin layer chromatography (TLC). Melting points were obtained in open capillary tubes using a micro melting point apparatus and were uncorrected.

#### Materials:

Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Removal of solvent under reduced pressure refers to distillation with a Büchi rotary evaporator attached to a vacuum pump (~3 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (~1 mmHg).

#### Chromatography:

Analytical TLC was performed using Whatman 250-micron aluminum backed UV F254 pre-coated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for visualization of UV active materials. Staining with p-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization.

#### Physical Data:

Proton and Carbon nuclear magnetic resonance spectra ( $^1\text{H}$ ,  $^{13}\text{C}$  NMR) were recorded on Avance 300, 400 or 500 MHz and ECS 4000 MHz (JEOL) NMR spectrometers. The proton resonances are annotated as: chemical shift ( $\delta$ ) relative to tetramethylsilane ( $\delta$  0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d ( $\delta$  7.26, singlet), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant ( $J$ , Hz), and number of protons for a given resonance is indicated by nH. The chemical shifts of  $^{13}\text{C}$  NMR are reported in ppm relative to the central line of the triplet at  $\delta$  77.00 ppm for  $\text{CDCl}_3$ . IR spectra were recorded on a PerkinElmer FT-IR spectrometer and wave numbers of maximum absorption peaks are presented in  $\text{cm}^{-1}$ . Mass analyses (ESI-MS) and HRMS were performed on Xevo G2-S QTOF (Waters, USA) Spectrometer.

#### Abbreviations used:

MeCN: acetonitrile, DCE: dichloroethane, DCM: dichloromethane, MeOH: methanol, AcOH: acetic acid, THF: tetrahydrofuran, TLC: thin layer chromatography, CFL: compact fluorescent lamp, LED:

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light emitting diode, TMSN<sub>3</sub>: azidotrimethylsilane, TEMPO: 2,2,6,6-tetramethylpiperidin-1-yl)oxyl, EtOAc: ethylacetate, PPh<sub>3</sub>: triphenylphosphine, Boc<sub>2</sub>O: di-*tert*-butyl dicarbonate, *t*-BuOK: potassium *tert*-butoxide, *t*-Bu: *tert*-butyl, *t*-BuOH: *tert*-butyl alcohol, Tf<sub>2</sub>O: triflic anhydride, BHT: 2,6-di-*tert*-butyl-4-methylphenol.

### B. Optimizations Studies

**Table S1.** Optimization of selective azidation using sulfonium iodate reagent.<sup>[a]</sup>

The reaction scheme shows styrene (1a) reacting with Me<sub>3</sub>SI(OAc)<sub>2</sub> reagents under either light or dark conditions in a solvent at room temperature under N<sub>2</sub>. This yields two regioisomeric products: 2 (where X = I) and 3 (where X = I). Product 2 has the iodine atom on the benzylic carbon and the azide group on the terminal carbon. Product 3 has the azide group on the benzylic carbon and the iodine atom on the terminal carbon.

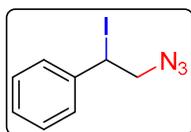
Entry	Solvent/Azide/Radical source	Visible Light	Product(s) Yields % <sup>[b]</sup> (Ratio) <sup>[c]</sup>
1	MeCN/NaN <sub>3</sub>	CFL (27 W)	<b>2:3</b> ; 66 (1:4)
2	DCE/NaN <sub>3</sub>	CFL (27 W)	<b>2:3</b> ; 54 (1:2.5)
3	MeOH/NaN <sub>3</sub>	CFL (27 W)	<b>2:3</b> ; 58 (1:2)
4 <sup>[d]</sup>	AcOH/NaN <sub>3</sub>	CFL (27 W)	<b>2:3</b> ; 59 (1:2)
5	H <sub>2</sub> O/NaN <sub>3</sub>	CFL (27 W)	<b>2:3</b> ; 43 (1:2)
6	Toluene/NaN <sub>3</sub>	CFL (27 W)	<b>2</b> ; 88
7	<b>Toluene/NaN<sub>3</sub></b>	<b>DARK</b>	<b>3</b> ; <b>94</b>
8	Toluene/NaN <sub>3</sub> /TEMPO	CFL (27 W)	<b>4</b> ; 65
9	Toluene/NaN <sub>3</sub> /TEMPO	White-LEDs (7 W)	<b>4</b> ; 72
10	Toluene/NaN <sub>3</sub> /TEMPO	Green-LEDs (7 W)	<b>4</b> ; 78
11	Toluene/NaN <sub>3</sub> /TEMPO	Blue-LEDs (7 W)	<b>4</b> ; 82
12	Toluene/TMSN <sub>3</sub> /TEMPO	Blue-LEDs (7 W)	<b>4</b> ; 85
<b>13</b>	<b>DCM/TMSN<sub>3</sub>/TEMPO</b>	<b>Blue-LEDs (7 W)</b>	<b>4</b> ; <b>92</b>
14	MeCN/TMSN <sub>3</sub> /TEMPO	Blue-LEDs (7 W)	<b>4</b> ; 63
15	THF/TMSN <sub>3</sub> /TEMPO	Blue-LEDs (7 W)	<b>4</b> ; 58

[a] Reaction conditions: **1a** (1.0 mmol, 1.0 equiv.), Me<sub>3</sub>SI(OAc)<sub>2</sub> (1.1 equiv.), TMSN<sub>3</sub> or NaN<sub>3</sub> (2.5 equiv.), TEMPO (2.5 equiv.), solvent (2 mL), stirred at 35 °C for 12 h, irradiated with a CFL (27 W) or LEDs (7 W), unless otherwise noted. [b] The isolated yields. [c] Determined by <sup>1</sup>H NMR spectroscopy. [d] Mixture of iodoacetoxy compound, observed by <sup>1</sup>H NMR.

### C. Synthesis and Spectroscopic Characterization Data.

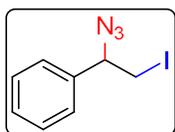
**Preparation of  $\text{Me}_3\text{SI}(\text{OAc})_2$ :** An equimolar mixture of trimethylsulfoniumiodide (500 mg, 2.45 mmol, 1.0 equiv.) and PIDA (790 mg, 2.45 mmol, 1.0 equiv.) in  $\text{CH}_2\text{Cl}_2$  was stirred at room temperature. The resulting turbid dark yellow mixture turned into dark brown then a dark red homogeneous solution after 15 min. The reaction mixture was cooled to 0 °C. Diethyl ether was added to give a yellow precipitate. This material was collected by filtration, washed with diethyl ether, and dried in vacuo to give analytically pure Sulfonium bis(acetoxy)iodate(I) complex.<sup>[1]</sup>

#### **Radical Azidation:**



**(2-azido-1-iodoethyl)benzene (2):** A preformed solution of  $\text{Me}_3\text{SI}(\text{OAc})_2$  (354 mg, 1.1 mmol, 1.1 equiv.),  $\text{NaN}_3$  (162 mg, 2.5 mmol, 2.5 equiv.) in toluene (5 mL) was treated with styrene **1a** (104 mg, 1.0 mmol, 1.0 equiv.) at room temperature. The mixture was stirred under nitrogen atmosphere and irradiated with visible light (27 W CFL). The distance between the light source and the reaction flask was approximately 3-4 cm, resulted in the temperature increasing up to 35 °C. For safety reasons, the reaction was carried out behind an *anti*-blast shield. The reaction was stirred until the completion of starting material, typically for 12 h (adjudged by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated  $\text{NaHCO}_3$  (5 mL) and saturated aqueous sodium thiosulfate (2 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated *in vacuo* and purified by silica gel column chromatography using hexanes as eluent to afford the compound **2** as pale yellow oil (240 mg, 0.88 mmol, 88%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (dd,  $J = 8.1, 1.2$  Hz, 2H), 7.36-7.28 (m, 3H), 5.14 (t,  $J = 7.7$  Hz, 1H), 3.93 (d,  $J = 7.7$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.3, 129.0, 128.8, 127.6, 58.8, 27.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[2]</sup>

#### **Ionic Azidation:**

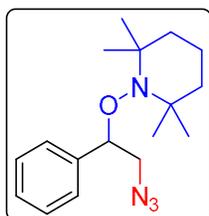


**(1-azido-2-iodoethyl)benzene (3):** A preformed solution of  $\text{Me}_3\text{SI}(\text{OAc})_2$  (354 mg, 1.1 mmol, 1.1 equiv.),  $\text{NaN}_3$  (162 mg, 2.5 mmol, 2.5 equiv.) in toluene (5 mL) was treated with styrene **1a** (104 mg,

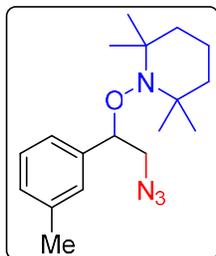
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1.0 mmol, 1.0 equiv.) at room temperature under completely dark condition. The reaction was stirred under nitrogen atmosphere for 12 h or until the completion of starting material (adjudged by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated NaHCO<sub>3</sub> (5 mL) and saturated aqueous sodium thiosulfate (2 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified by silica gel column chromatography to afford the title compound **3** (256 mg, 0.94 mmol, 94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.37 (m, 3H), 7.33-7.29 (m, 2H), 4.71 (t, *J* = 7.0 Hz, 1H), 3.39 (d, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.9, 129.0, 126.6, 67.1, 8.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3]</sup>

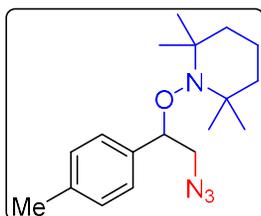
### Radical Azidooxygenation:



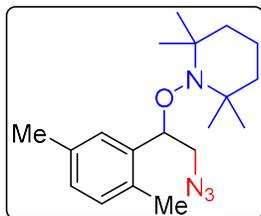
**1-(2-azido-1-phenylethoxy)-2,2,6,6-tetramethylpiperidine (4):** A preformed solution of Me<sub>3</sub>Si(OAc)<sub>2</sub> (354 mg, 1.1 mmol, 1.1 equiv.), TMSN<sub>3</sub> (287 mg, 328 μL, 2.5 mmol, 2.5 equiv.) and 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (390 mg, 2.5 mmol, 2.5 equiv.) in DCM (5 mL) was treated with styrene (104 mg, 1.0 mmol, 1.0 equiv.) at room temperature. The mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED). The distance between the light source and the reaction flask was approximately 3-4 cm, resulted in the temperature increasing up to 35 °C. For safety reasons, the reaction was carried out behind an *anti*-blast shield. The reaction was stirred until the completion of starting material, typically for 15 h (adjudged by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated NaHCO<sub>3</sub> (5 mL) and saturated aqueous sodium thiosulfate (2 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified by silica gel column chromatography using hexanes as eluent to afford the compound **4** as pale-yellow oil (278 mg, 0.920 mmol, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41-7.19 (m, 5H), 4.82 (dd, *J* = 6.8, 4.7 Hz, 1H), 3.73 (dd, *J* = 12.3, 4.6 Hz, 1H), 3.64 (dd, *J* = 12.2, 6.9 Hz, 1H), 1.56-1.34 (m, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.69 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.6, 128.1, 127.8, 127.5, 84.9, 60.0, 55.2, 40.3, 34.3, 33.9, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4]</sup>



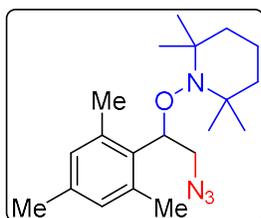
**1-(2-azido-1-(*m*-tolyl)ethoxy)-2,2,6,6-tetramethylpiperidine (5):** Following general radical azidooxygenation procedure using 1-methyl-3-vinylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless oil (195 mg, 0.617 mmol, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (t,  $J = 7.4$  Hz, 1H), 7.12 (dd,  $J = 16.5, 7.9$  Hz, 3H), 4.78 (dd,  $J = 6.8, 4.7$  Hz, 1H), 3.75 (dd,  $J = 12.3, 4.6$  Hz, 1H), 3.63 (dd,  $J = 12.3, 6.9$  Hz, 1H), 2.36 (s, 3H), 1.54 - 1.34 (m, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.72 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 137.6, 128.6, 128.2, 128.0, 124.6, 84.9, 60.0, 55.2, 40.4, 34.3, 34.0, 29.7, 21.5, 20.3, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



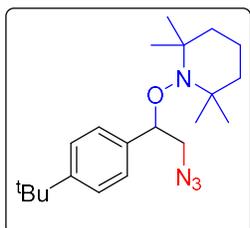
**1-(2-azido-1-(*p*-tolyl)ethoxy)-2,2,6,6-tetramethylpiperidine (6):** Following general radical azidooxygenation procedure using 1-methyl-4-vinylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (197 mg, 0.624 mmol, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 8.0$  Hz, 2H), 7.15 (d,  $J = 7.9$  Hz, 2H), 4.79 (dd,  $J = 6.9, 4.8$  Hz, 1H), 3.74 (dd,  $J = 12.2, 4.6$  Hz, 1H), 3.62 (dd,  $J = 12.2, 7.0$  Hz, 1H), 2.35 (s, 3H), 1.56-1.36 (m, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.72 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 137.4, 128.8, 127.4, 84.6, 60.0, 55.2, 40.3, 34.3, 34.0, 21.2, 20.3, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



**1-(2-azido-1-(2,5-dimethylphenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (7):** Following general radical azidooxygenation procedure using 1,4-dimethyl-2-vinylbenzene (90 mg, 0.681 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (164 mg, 0.497 mmol, 73%). IR (Film): 2923, 2097, 1731, 1500, 1451, 1248, 1173, 1037, 935, 812, 731, 611, 529  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (s, 1H), 7.03-6.97 (m, 2H), 5.05 (t,  $J = 5.7$  Hz, 1H), 3.68 (d,  $J = 5.4$  Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 1.58-1.36 (m, 6H), 1.34 (s, 3H), 1.20 (s, 3H), 1.02 (s, 3H), 0.72 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.0, 135.2, 131.9, 130.0, 128.2, 128.1, 81.8, 60.0, 59.9, 54.8, 40.4, 34.4, 33.3, 21.2, 20.3, 20.2, 19.1, 17.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{19}\text{H}_{31}\text{N}_4\text{O}]^+$ : 331.2492; found: 331.2495.

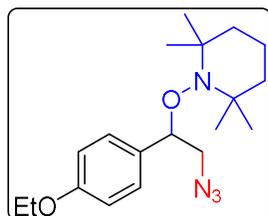


**1-(2-azido-1-(mesitylethoxy)-2,2,6,6-tetramethylpiperidine (8):** Following general radical azidooxygenation procedure using 1,3,5-trimethyl-2-vinylbenzene (90 mg, 0.616 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless semi solid (148 mg, 0.431 mmol, 70%). IR (Film): 2926, 2826, 2096, 1739, 1452, 1366, 1219, 1132, 1026, 925, 851, 799, 523  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.81 (d,  $J = 17.0$  Hz, 2H), 5.22 (dd,  $J = 8.9, 5.1$  Hz, 1H), 3.89 (dd,  $J = 12.0, 5.1$  Hz, 1H), 3.70 (dd,  $J = 11.9, 8.9$  Hz, 1H), 2.49 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H), 1.56-1.35 (m, 6H), 1.33 (s, 3H), 1.16 (s, 3H), 0.99 (s, 3H), 0.69 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.8, 136.7, 134.1, 134.0, 82.6, 59.9, 59.7, 54.2, 40.5, 40.3, 34.4, 33.4, 31.9, 29.7, 29.6, 29.4, 20.9, 17.1, 14.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{20}\text{H}_{33}\text{N}_4\text{O}]^+$ : 345.2649; found: 345.2651.

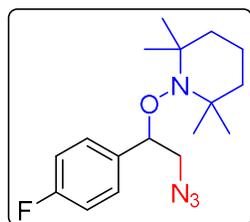


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**1-(2-azido-1-(4-(tert-butyl)phenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (9):** Following general radical azidooxygenation procedure using 1-(tert-butyl)-4-vinylbenzene (90 mg, 0.562 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as Pale yellow oil (158 mg, 0.443 mmol, 79 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.3$  Hz, 2H), 7.26 (d,  $J = 8.3$  Hz, 2H), 4.81 (dd,  $J = 6.8, 4.7$  Hz, 1H), 3.76 (dd,  $J = 12.3, 4.7$  Hz, 1H), 3.62 (dd,  $J = 12.2, 6.9$  Hz, 1H), 1.61-1.36 (m, 6H), 1.31 (s, 12H), 1.19 (s, 3H), 1.05 (s, 3H), 0.72 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 137.4, 127.2, 125.0, 84.4, 60.0, 55.2, 40.4, 34.5, 34.3, 33.9, 31.3, 20.4, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4]</sup>



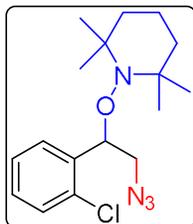
**1-(2-azido-1-(4-ethoxyphenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (10):** Following general radical azidooxygenation procedure using 1-ethoxy-4-vinylbenzene (100 mg, 0.675 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as transparent semi solid (152 mg, 0.438 mmol, 65%). IR (Film): 2929, 2097, 1739, 1611, 1511, 1451, 1366, 1235, 1176, 1117, 1046, 923, 826, 704, 545  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (d,  $J = 9.8$  Hz, 2H), 6.80 (d,  $J = 8.6$  Hz, 2H), 4.70 (dd,  $J = 7.0, 4.9$  Hz, 1H), 3.96 (q,  $J = 7.0$  Hz, 2H), 3.67 (dd,  $J = 12.2, 4.9$  Hz, 1H), 3.52 (dd,  $J = 12.2, 7.1$  Hz, 1H), 1.48-1.27 (m, 9H), 1.24 (s, 3H), 1.11 (s, 3H), 0.95 (s, 3H), 0.61 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 132.7, 128.8, 114.1, 84.4, 63.3, 60.0, 55.2, 40.4, 34.4, 34.1, 20.3, 17.1, 14.8; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{19}\text{H}_{31}\text{N}_4\text{O}_2]^+$ : 347.2442; found: 347.2443.



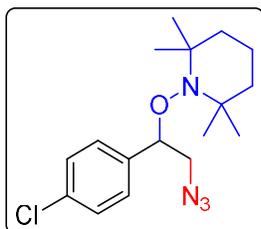
**1-(2-azido-1-(4-fluorophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (11):** Following general radical azidooxygenation procedure using 1-fluoro-4-vinylbenzene (100 mg, 0.819 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (204 mg, 0.638 mmol, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 14.1$  Hz, 2H), 7.04 (d,  $J = 17.4$  Hz, 2H), 4.81 (dd,  $J = 7.0, 4.7$  Hz, 1H), 3.72 (dd,  $J = 12.3, 4.7$  Hz, 1H), 3.61 (dd,  $J = 12.3, 7.0$  Hz, 1H), 1.60-1.34 (m, 6H), 1.31 (s, 3H), 1.18 (s, 3H), 1.02 (s, 3H), 0.67 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$

## SUPPORTING INFORMATION

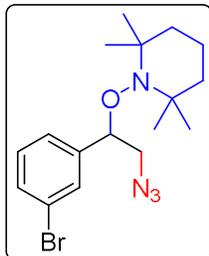
162.4 (d,  $^1J_{CF} = 245.9$  Hz), 136.5 (d,  $^4J_{CF} = 2.9$  Hz), 129.2 (d,  $^3J_{CF} = 7.9$  Hz), 115.1 (d,  $^2J_{CF} = 21.2$  Hz), 84.2, 60.0, 55.1, 40.3, 34.3, 34.0, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



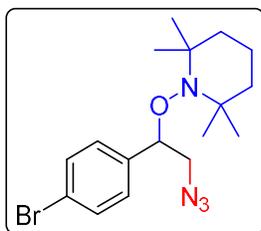
**1-(2-azido-1-(2-chlorophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (12):** Following general radical azidooxygenation procedure using 1-chloro-2-vinylbenzene (110 mg, 0.797 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (214 mg, 0.637 mmol, 80%). IR (Film): 2970, 2928, 2098, 1739, 1470, 1439, 1376, 1230, 1066, 1034, 990, 879, 829, 780, 739, 755, 721, 666, 630  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 7.7$  Hz, 1H), 7.32 (t,  $J = 7.5$  Hz, 2H), 7.26 - 7.20 (m, 1H), 5.34 (dd,  $J = 5.0, 3.4$  Hz, 1H), 3.95 (dd,  $J = 12.8, 5.2$  Hz, 1H), 3.55 (dd,  $J = 12.8, 3.2$  Hz, 1H), 1.46 (d,  $J = 36.6$  Hz, 6H), 1.35 (s, 3H), 1.20 (s, 3H), 1.04 (s, 3H), 0.78 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.5, 131.8, 129.4, 129.1, 128.7, 126.7, 82.1, 60.4, 59.6, 53.6, 40.4, 34.6, 33.1, 29.7, 20.6, 20.3, 17.1, 17.0; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{17}\text{H}_{26}\text{ClN}_4\text{O}]^+$ : 337.1790; found 337.1792.



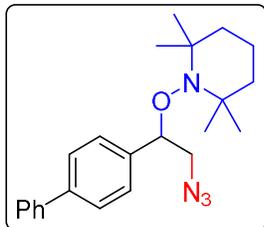
**1-(2-azido-1-(4-chlorophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (13):** Following general radical azidooxygenation procedure using 1-chloro-4-vinylbenzene (110 mg, 0.797 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (203 mg, 0.605 mmol, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.5$  Hz, 2H), 7.28 (d,  $J = 8.5$  Hz, 2H), 4.80 (dd,  $J = 6.6, 4.7$  Hz, 1H), 3.70 (dd,  $J = 12.3, 4.6$  Hz, 1H), 3.64 (dd,  $J = 12.3, 6.8$  Hz, 1H), 1.58-1.32 (m, 6H), 1.30 (s, 3H), 1.18 (s, 3H), 1.02 (s, 3H), 0.68 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 133.6, 128.8, 128.4, 84.3, 60.0, 55.0, 40.3, 34.4, 34.1, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4]</sup>



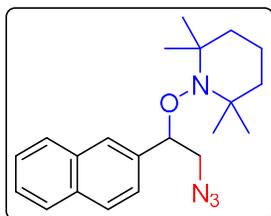
**1-(2-azido-1-(3-bromophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (14):** Following general radical azidooxygenation procedure using 1-bromo-3-vinylbenzene (140 mg, 0.769 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as semi solid (225 mg, 0.592 mmol, 77%). IR (Film): 2970, 2829, 2098, 1740, 1595, 1570, 1469, 1428, 1376, 1362, 1258, 1231, 1132, 1068, 1045, 995, 956, 922, 880, 826, 764, 697, 663, 628, 593, 551, 440  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (s, 1H), 7.43 (d,  $J = 7.8$  Hz, 1H), 7.25 (dt,  $J = 19.8, 7.7$  Hz, 2H), 4.78 (dd,  $J = 6.2, 5.0$  Hz, 1H), 3.71 (dd,  $J = 12.4, 4.6$  Hz, 1H), 3.64 (dd,  $J = 12.3, 6.7$  Hz, 1H), 1.56-1.36 (m, 6H), 1.31 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.70 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 130.9, 130.5, 129.8, 126.2, 122.3, 84.3, 60.1, 55.0, 40.3, 34.3, 34.0, 29.7, 20.3, 17.0; HRMS (ESI)  $m/z$   $[\text{M}]^+$  calculated for  $[\text{C}_{17}\text{H}_{25}\text{BrN}_4\text{O}]^+$ : 381.3255; found: 381.3251.



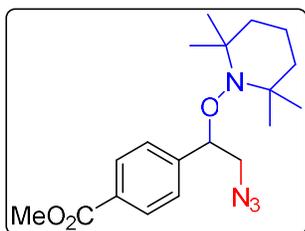
**1-(2-azido-1-(4-bromophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (15):** Following general radical azidooxygenation procedure using 1-bromo-4-vinylbenzene (140 mg, 0.769 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oily viscous (219 mg, 0.576 mmol, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.3$  Hz, 2H), 7.22 (d,  $J = 8.3$  Hz, 2H), 4.78 (dd,  $J = 6.6, 4.7$  Hz, 1H), 3.70 (dd,  $J = 12.3, 4.6$  Hz, 1H), 3.64 (dd,  $J = 12.3, 6.8$  Hz, 1H), 1.54-1.33 (m, 6H), 1.31 (s, 3H), 1.18 (s, 3H), 1.03 (s, 3H), 0.69 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 131.3, 129.2, 121.8, 84.4, 60.1, 55.0, 40.4, 34.4, 34.1, 29.7, 20.3, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



**1-(1-((1,1'-biphenyl)-4-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine (16):** Following general radical azidoxygenation procedure using 4-vinyl-1,1'-biphenyl (100 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (159 mg, 0.421 mmol, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67-7.55 (m, 5H), 7.51-7.37 (m, 4H), 4.93-4.85 (m, 1H), 3.78 (dd,  $J = 11.9, 4.3$  Hz, 1H), 3.69 (dd,  $J = 12.1, 6.8$  Hz, 1H), 1.55-1.24 (m, 9H), 1.07 (s, 3H), 0.88 (s, 3H), 0.75 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 140.6, 139.7, 128.7, 127.9, 127.2, 127.1, 126.9, 84.6, 60.1, 55.2, 40.4, 34.4, 34.1, 29.7, 20.3, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>

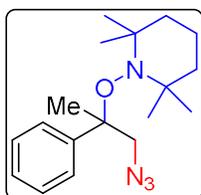


**1-(2-azido-1-(naphthalen-2-yl)ethoxy)-2,2,6,6-tetramethylpiperidine (17):** Following general radical azidoxygenation procedure using 2-vinylnaphthalene (100 mg, 0.649 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (191 mg, 0.545 mmol, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87-7.81 (m, 3H), 7.78 (s, 1H), 7.52-7.44 (m, 3H), 4.99 (dd,  $J = 6.6, 4.9$  Hz, 1H), 3.81 (dd,  $J = 12.4, 4.6$  Hz, 1H), 3.74 (dd,  $J = 12.3, 6.9$  Hz, 1H), 1.61-1.30 (m, 9H), 1.23 (s, 3H), 1.05 (s, 3H), 0.66 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 133.1, 133.0, 128.0, 127.9, 127.7, 126.8, 126.0, 125.9, 125.2, 85.2, 60.1, 55.2, 40.4, 34.4, 34.1, 32.8, 20.3, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>

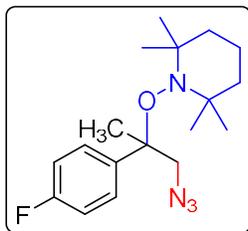


## SUPPORTING INFORMATION

**methyl 4-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)benzoate (18):** Following general radical azidooxygenation procedure using methyl-4-vinylbenzoate (100 mg, 0.617 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (142 mg, 0.394 mmol, 64%). IR (Film): 2935, 2098, 1722, 1612, 1438, 1360, 1273, 1107, 1018, 960, 923, 771, 711, 643, 546, 422  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.2$  Hz, 2H), 7.43 (d,  $J = 8.2$  Hz, 2H), 4.88 (t,  $J = 5.5$  Hz, 1H), 3.91 (s, 3H), 3.71 (d,  $J = 5.5$  Hz, 2H), 1.53-1.35 (m, 6H), 1.33 (s, 3H), 1.20 (s, 3H), 1.03 (s, 3H), 0.66 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 145.5, 129.1, 127.0, 84.3, 59.6, 54.5, 51.7, 39.9, 34.0, 33.6, 19.8, 16.6; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{19}\text{H}_{29}\text{N}_4\text{O}_3]^+$ : 361.2234; found: 361.2235.



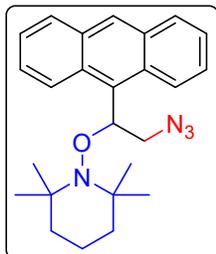
**1-((1-azido-2-phenylpropan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (19):** Following general radical azidooxygenation procedure using prop-1-en-2-ylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (168 mg, 0.533 mmol, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dd,  $J = 8.1, 1.2$  Hz, 2H), 7.38-7.32 (m, 2H), 7.30-7.24 (m, 1H), 3.62 (d,  $J = 11.8$  Hz, 1H), 3.44 (d,  $J = 11.8$  Hz, 1H), 1.73 (s, 3H), 1.58-1.32 (m, 6H), 1.20 (s, 6H), 1.04 (s, 3H), 0.49 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 127.6, 126.9, 126.2, 81.4, 62.0, 59.6, 59.4, 40.7, 40.5, 34.0, 33.0, 20.5, 20.4, 19.1, 16.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



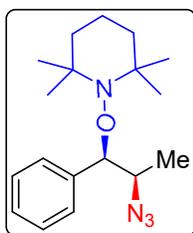
**1-((1-azido-2-(4-fluorophenyl)propan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (20):** Following general radical azidooxygenation procedure using 1-fluoro-4-(prop-1-en-2-yl)benzene (100 mg, 0.735 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as orange sticky liquid (179 mg, 0.536 mmol, 73%). IR (Film): 2934, 2098, 1687, 1601, 1507, 1369, 1231, 1014, 919, 729, 676, 535  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 14.3$  Hz, 2H), 7.03 (d,  $J = 17.5$  Hz, 2H), 3.59 (d,  $J = 11.8$  Hz, 1H), 3.43 (d,  $J = 11.8$  Hz, 1H), 1.71 (s, 3H), 1.58-1.32 (m, 6H), 1.19

## SUPPORTING INFORMATION

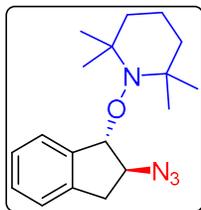
(s, 3H), 1.19 (s, 3H), 1.03 (s, 3H), 0.49 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9 (d,  $^1J_{\text{CF}} = 245.8$  Hz), 141.6 (d,  $^4J_{\text{CF}} = 3.3$  Hz), 128.0 (d,  $^3J_{\text{CF}} = 7.9$  Hz), 114.6 (d,  $^2J_{\text{CF}} = 21.1$  Hz), 81.3, 62.1, 62.0, 59.8, 59.6, 40.9, 40.7, 34.2, 33.3, 20.7, 20.6, 19.5, 16.8; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{18}\text{H}_{28}\text{FN}_4\text{O}]^+$ : 335.4469; found: 335.4471.



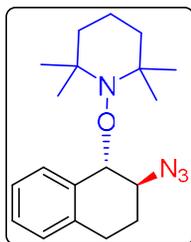
**1-(1-(anthracen-9-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine (21):** Following general radical azidooxygenation procedure using 9-vinylanthracene (100 mg, 0.490 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown solid (118 mg, 0.294 mmol, 60%). Mp: 97-98 °C; IR (Film): 2932, 2101, 1738, 1450, 1367, 1219, 1131, 1043, 886, 786, 732, 526  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (s, 2H), 8.02 (d,  $J = 8.4$  Hz, 2H), 7.58-7.52 (m, 2H), 7.50-7.44 (m, 2H), 6.31 (dd,  $J = 9.2, 4.1$  Hz, 1H), 4.72 (t,  $J = 9.6$  Hz, 1H), 4.12 (dd,  $J = 9.9, 4.1$  Hz, 1H), 1.48-1.36 (m, 6H), 1.33 (s, 3H), 1.23 (s, 3H), 1.08 (s, 3H), 0.97 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  129.7, 129.4, 129.0, 127.5, 124.9, 79.1, 60.9, 60.1, 59.8, 39.6, 39.5, 33.1, 33.0, 20.1, 20.0, 17.0; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{25}\text{H}_{31}\text{N}_4\text{O}]^+$ : 403.2492; found: 403.2495.



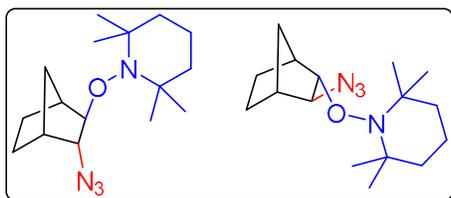
**1-(2-azido-1-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (22):** Following general radical azidooxygenation procedure using (*E*)-prop-1-en-1-ylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (173 mg, 0.548 mmol, 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.27 (m, 5H), 4.61 (d,  $J = 3.2$  Hz, 1H), 4.45 (qd,  $J = 6.8, 3.3$  Hz, 1H), 1.55-1.34 (m, 6H), 1.28 (s, 6H), 1.03 (s, 3H), 0.96 (d,  $J = 6.9$  Hz, 3H), 0.61 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 129.0, 127.6, 127.5, 90.4, 60.1, 59.3, 40.5, 34.7, 34.1, 20.2, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



**1-((2-azido-2,3-dihydro-1H-inden-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (23):** Following general radical azidooxygenation procedure using indene (100 mg, 0.862 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (203 mg, 0.646 mmol, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.2$  Hz, 1H), 7.30-7.18 (m, 3H), 5.33 (d,  $J = 4.1$  Hz, 1H), 4.40 (dt,  $J = 7.0, 4.7$  Hz, 1H), 3.35 (dd,  $J = 16.1, 7.2$  Hz, 1H), 2.87 (dd,  $J = 16.2, 5.2$  Hz, 1H), 1.60-1.38 (m, 6H), 1.29 (s, 3H), 1.19 (s, 3H), 1.10 (s, 3H), 1.04 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.3, 140.0, 128.8, 126.6, 126.5, 124.5, 90.1, 66.5, 60.6, 59.7, 40.1, 36.5, 34.2, 33.6, 17.1, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4]</sup>

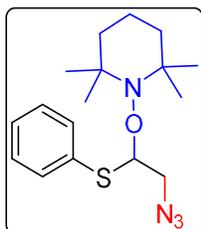


**1-(((1S,2S)-2-azido-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (24):** Following general radical azidooxygenation procedure using 1,2-dihydronaphthalene (100 mg, 0.769 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as dark yellow oil (209 mg, 0.638 mmol, 83%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 7.5$  Hz, 1H), 7.25-7.19 (m, 1H), 7.17-7.07 (m, 2H), 4.78 (d,  $J = 2.7$  Hz, 1H), 4.28 (dd,  $J = 7.0, 3.2$  Hz, 1H), 2.94-2.74 (m, 2H), 2.36-2.25 (m, 1H), 1.98 (ddd,  $J = 10.0, 6.3, 3.2$  Hz, 1H), 1.70-1.35 (m, 6H), 1.33 (s, 3H), 1.15 (s, 3H), 0.97 (s, 3H), 0.35 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.5, 133.2, 132.9, 128.1, 128.0, 124.9, 78.5, 60.6, 59.4, 58.2, 40.1, 40.0, 34.3, 32.9, 24.0, 22.2, 20.5, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>

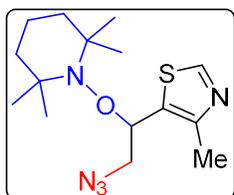


## SUPPORTING INFORMATION

**1-(((1*S*,2*R*,3*S*,4*R*)-3-azidobicyclo[2.2.1]heptan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (25):** Following general radical azidooxygenation procedure using norbornene (100 mg, 1.063 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless oil (214 mg, 0.733 mmol, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.00 (dd, *J* = 6.8, 1.4 Hz, 1H), 3.97-3.94 (m, 1H), 3.27 (t, *J* = 2.5 Hz, 1H), 3.19 (d, *J* = 6.3 Hz, 1H), 2.70 (d, *J* = 2.8 Hz, 1H), 2.59 (bs, 1H), 2.36 (bs, 1H), 2.30 (d, *J* = 4.6 Hz, 1H), 1.90-1.81 (m, 1H), 1.79 (dd, *J* = 8.8, 1.6 Hz, 1H), 1.62 (ddd, *J* = 7.6, 6.2, 2.8 Hz, 2H), 1.58-1.51 (m, 2H), 1.51-1.41 (m, 12H), 1.40-1.25 (m, 6H), 1.23 (s, 6H), 1.18-1.11 (s, 6H), 1.09 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 92.8, 90.1, 70.7, 66.8, 61.2, 59.9, 59.4, 58.9, 42.1, 41.9, 40.7, 40.3, 40.2, 40.1, 39.9, 35.1, 34.6, 34.1, 33.9, 33.5, 33.3, 26.9, 26.6, 24.6, 20.6, 20.5, 20.4, 20.3, 17.2, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4a]</sup>



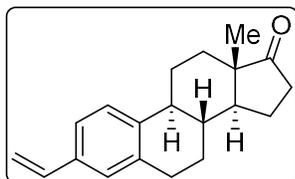
**1-(2-azido-1-(phenylthio)ethoxy)-2,2,6,6-tetramethylpiperidine (26):** Following general radical azidooxygenation procedure using phenyl(vinyl)sulfane (100 mg, 0.735 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow oil (181 mg, 0.543 mmol, 74%). IR (Film): 2920, 2853, 2101, 1740, 1580, 1458, 1373, 1227, 1071, 1023, 902, 840, 738, 690, 550 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, *J* = 6.6, 1.4 Hz, 2H), 7.34-7.25 (m, 3H), 5.31 (td, *J* = 6.0, 1.6 Hz, 1H), 3.70 (ddd, *J* = 12.8, 5.7, 1.4 Hz, 1H), 3.46 (ddd, *J* = 12.8, 6.2, 1.4 Hz, 1H), 1.58-1.46 (m, 6H), 1.31 (s, 3H), 1.19 (s, 3H), 1.15 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 133.8, 133.2, 128.9, 127.5, 91.9, 60.9, 60.4, 53.7, 40.4, 34.6, 33.8, 29.7, 20.7, 17.1; HRMS (ESI) *m/z* [M + H]<sup>+</sup> calculated for [C<sub>17</sub>H<sub>27</sub>N<sub>4</sub>OS]<sup>+</sup>: 335.1900; found: 335.1904.



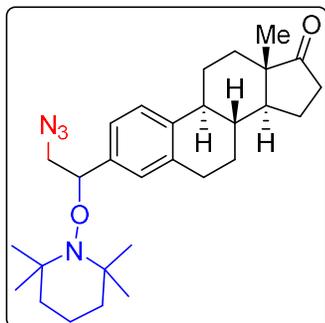
**5-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-4-methylthiazole (27):** Following general radical azidooxygenation procedure using 4-methyl-5-vinylthiazole (110 mg, 0.88 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil

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(233 mg, 0.721 mmol, 82%). IR (Film): 2930, 2099, 1737, 1539, 1455, 1366, 1258, 1131, 1016, 924, 845, 797, 730, 658, 554, 509, 441 $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (s, 1H), 5.23 (t,  $J = 5.6$  Hz, 1H), 3.67 (d,  $J = 5.6$  Hz, 2H), 2.51 (s, 3H), 1.54-1.36 (m, 6H), 1.33 (s, 3H), 1.17 (s, 3H), 1.01 (s, 3H), 0.67 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.6, 150.8, 131.0, 60.3, 59.8, 55.1, 40.2, 34.0, 32.8, 20.0, 16.8, 15.7; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{15}\text{H}_{26}\text{N}_5\text{OS}]^+$ : 324.1853; found: 324.1855.

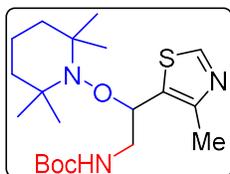


**3-vinylestrone: First step:** A 100 mL round bottom flask was dried and charged with estrone (200 mg, 0.740 mmol, 1.0 equiv.),  $\text{CH}_2\text{Cl}_2$  (10 mL), and  $\text{Et}_3\text{N}$  (205  $\mu\text{L}$ , 150 mg, 1.481 mmol, 2.0 equiv.). The mixture was cooled to 0  $^\circ\text{C}$  and  $\text{Tf}_2\text{O}$  (149  $\mu\text{L}$ , 251 mg, 0.888 mmol, 1.2 equiv.) was added over 3 min drop wise. The mixture was allowed to warm to room temperature and stirred at room temperature under nitrogen for 3 h. The resulting brown mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , washed with sat.  $\text{NH}_4\text{Cl}$  and the aqueous layer were extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 5 mL). The combined organic layers were dried over  $\text{MgSO}_4$ , and the filtrate was concentrated. The crude was purified with column chromatography to afford 3-(trifluoromethanesulfonyl)estrone as white solid (250 mg, 0.621 mmol, 84%). **Second step:** A 100 mL two neck round bottom flask was charged with 3-(trifluoromethanesulfonyl)estrone (200 mg, 0.497 mmol, 1.0 equiv.), potassium vinyl trifluoroborate (65 mg, 0.497 mmol, 1.0 equiv.),  $\text{PdCl}_2$  (2 mg, 0.009 mmol, 0.02 equiv.), and the round bottom flask was brought into a  $\text{N}_2$ -filled glove box.  $\text{PPh}_3$  (8 mg, 0.029 mmol, 0.06 equiv.),  $\text{Cs}_2\text{CO}_3$  (485 mg, 1.492 mmol, 3.0 equiv.) and THF (1.8 mL) were added, and the round bottom flask was sealed.  $\text{H}_2\text{O}$  (0.2 mL) was added, degas the reaction mixture using nitrogen and the mixture was stirred at 85  $^\circ\text{C}$  for 24 h. The resulting dark brown mixture was allowed to cool to room temperature, diluted with  $\text{CH}_2\text{Cl}_2$ , and washed with  $\text{H}_2\text{O}$ . The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 mL). The combined organic layers were dried over  $\text{MgSO}_4$ , and the filtrate was concentrated. The crude was purified with column chromatography to afford 3-vinylestrone as white solid (108 mg, 0.387 mmol, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.24 (m, 1H), 7.21 (d,  $J = 8.2$  Hz, 1H), 7.14 (s, 1H), 6.66 (dd,  $J = 17.6, 10.9$  Hz, 1H), 5.70 (d,  $J = 17.6$  Hz, 1H), 5.19 (d,  $J = 10.9$  Hz, 1H), 2.92 (dd,  $J = 8.7, 3.9$  Hz, 2H), 2.51 (dd,  $J = 18.7, 8.7$  Hz, 1H), 2.42 (dt,  $J = 8.9, 3.5$  Hz, 1H), 2.29 (dd,  $J = 13.6, 7.0$  Hz, 1H), 2.16 (dd,  $J = 18.4, 9.4$  Hz, 1H), 2.11 - 1.93 (m, 3H), 1.68-1.39 (m, 6H), 0.91 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  220.8, 139.5, 136.5, 135.2, 126.8, 125.5, 123.6, 113.2, 50.5, 48.0, 44.4, 38.1, 35.8, 31.6, 29.4, 26.5, 25.7, 21.6, 13.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[5]</sup>



**(8R,9S,13S,14S)-3-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-13-methyl**

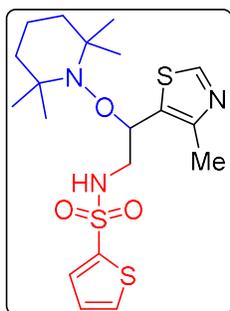
**6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (28):** Following general radical azidooxygenation procedure using 3-vinylestrone (100 mg, 0.357 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (126 mg, 0.264 mmol, 74%). Mp:159-160 °C; IR (Film): 2924, 2098, 1737, 1454, 1363, 1289, 1257, 1132, 1051, 1012, 962, 920, 805, 727, 639, 581, 511, 447  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19 (s, 1H), 7.05 (t,  $J$  = 7.5 Hz, 1H), 6.97 (d,  $J$  = 7.9 Hz, 1H), 4.70 (dd,  $J$  = 6.8, 4.5 Hz, 1H), 3.75-3.65 (m, 1H), 3.57 (dd,  $J$  = 12.2, 7.0 Hz, 1H), 2.86 (dd,  $J$  = 7.8, 3.1 Hz, 2H), 2.44 (dd,  $J$  = 18.7, 8.7 Hz, 1H), 2.39-2.32 (m, 1H), 2.24 (td,  $J$  = 11.0, 3.3 Hz, 1H), 2.13-1.87 (m, 4H), 1.60-1.32 (m, 12H), 1.25 (s, 3H), 1.12 (s, 3H), 0.99 (s, 3H), 0.85 (s, 3H), 0.72 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 137.8, 136.1, 136.0, 127.9, 127.9, 125.0, 124.8, 124.6, 84.4, 84.3, 60.1, 59.9, 55.1, 50.5, 47.9, 44.3, 40.3, 40.0, 35.8, 34.3, 34.1, 31.5, 29.6, 29.3, 26.5, 25.6, 25.5, 21.5, 20.3, 17.0, 13.8; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{29}\text{H}_{43}\text{N}_4\text{O}_2]^+$ : 479.3381; found 479.3383.



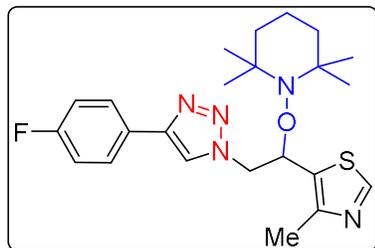
**tert-butyl(2-(4-methylthiazol-5-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)carbamate (29):** A preformed solution of  $\text{PPh}_3$  (178 mg, 0.681 mmol, 2.2 equiv.) and  $\text{H}_2\text{O}$  (28  $\mu\text{L}$ , 1.547 mmol, 5 equiv.) in THF (5 mL) was treated with compound **27** (100 mg, 0.309 mmol, 1.0 equiv., prepared by oxyazidation of 4-methyl-5-vinylthiazole) at 0 °C. The reaction was stirred at room temperature until the complete conversion of starting material as observed by TLC. Subsequently, a solution of di-*tert*-butyl dicarbonate (Boc anhydride) (213  $\mu\text{L}$ , 0.928 mmol, 202 mg, 3.0 equiv.) in THF (2 mL) was added to the above reaction mixture drop wise at room temperature. The resulting mixture was then stirred until amine intermediates were fully consumed (monitored by TLC). The reaction mixture was concentrated *in vacuo*, the residue was subsequently purified by column chromatography (Hexane/EtOAc: from 10:1

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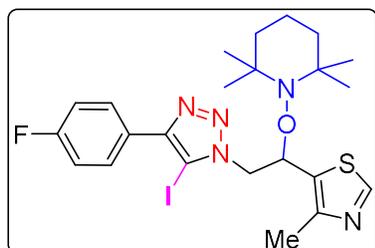
to 2:1) to afford the protected amine **29** as white solid (102 mg, 0.256 mmol, 83%). Mp: 101-102 °C; IR (Film): 3267, 2927, 1707, 1504, 1456, 1366, 1251, 1166, 1077, 976, 854, 788, 729, 640, 557, 441 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (s, 1H), 5.21 (t, *J* = 6.2 Hz, 1H), 4.80 (s, 1H), 3.90-3.79 (m, 1H), 3.34-3.25 (m, 1H), 2.47 (s, 3H), 1.54-1.38 (m, 15H), 1.33 (s, 3H), 1.14 (s, 3H), 1.00 (s, 3H), 0.72 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.6, 151.4, 150.5, 132.1, 79.4, 77.8, 60.2, 60.1, 40.4, 34.1, 33.0, 28.3, 20.3, 20.1, 17.0, 15.7, 14.1; HRMS (ESI) *m/z* [M]<sup>+</sup> calculated for [C<sub>20</sub>H<sub>36</sub>N<sub>3</sub>O<sub>3</sub>S]<sup>+</sup>: 398.2472; found: 398.2475.



***N*-(2-(4-methylthiazol-5-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)thiophene-2-sulfonamide (30)**: A preformed solution of PPh<sub>3</sub> (178 mg, 0.681 mmol, 2.2 equiv.) and H<sub>2</sub>O (28 μL, 1.547 mmol, 5 equiv.) in THF (5 mL) was treated with compound **27** (100 mg, 0.309 mmol, 1.0 equiv., prepared by oxyazidation of 4-methyl-5-vinylthiazole) at 0 °C. The reaction was stirred at room temperature until the complete conversion of starting material as observed by TLC. The reaction mixture was concentrated *in vacuo*, the crude amine was added to a preformed solution of thiophene-2-sulfonyl chloride (67 mg, 0.371, 1.2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> drop wise at 0 °C, followed by Et<sub>3</sub>N (64 μL, 47 mg, 0.464, 1.5 equiv.) The resulting mixture was then stirred until amine intermediate was fully consumed (monitored by TLC). The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), quenched with saturated NaHCO<sub>3</sub> (5 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified by silica gel column chromatography (Hexane/EtOAc: from 10:1 to 10:3) to afford the sulfonamide **30** as white solid (141 mg, 0.319 mmol, 82%). Mp: 144-146 °C; IR (Film): 3081, 2968, 2918, 2859, 1455, 1338, 1229, 1157, 1088, 1043, 1014, 939, 847, 663, 581, 537 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (s, 1H), 7.65-7.53 (m, 2H), 7.14-7.04 (m, 1H), 6.07 (s, 1H), 5.36 (t, *J* = 6.1 Hz, 1H), 3.71-3.57 (m, 1H), 3.38-3.24 (m, 1H), 2.42 (s, 3H), 1.46 (d, *J* = 12.3 Hz, 6H), 1.17 (s, 3H), 1.09 (s, 3H), 1.02 (s, 3H), 0.91 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.6, 150.2, 140.7, 131.9, 131.8, 130.3, 127.3, 60.7, 60.2, 48.5, 40.2, 40.0, 33.2, 20.3, 20.2, 16.9, 15.5, 14.0; HRMS (ESI) *m/z* [M + H]<sup>+</sup> calculated for [C<sub>19</sub>H<sub>30</sub>N<sub>3</sub>O<sub>3</sub>S<sub>3</sub>]<sup>+</sup>: 444.1444; found: 444.1443.



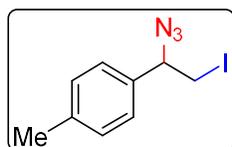
**5-(2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-4-methylthiazole (31):** Compound **27** (100 mg, 0.309 mmol, 1 equiv., prepared by oxyazidation of 4-methyl-5-vinylthiazole), 1-ethynyl-4-fluorobenzene (42  $\mu$ L 0.371 mmol, 44 mg, 1.2 equiv.), CuSO<sub>4</sub> (10 mg, 0.619 mmol, 0.2 equiv.), sodium ascorbate (24 mg, 0.123 mmol, 0.4 equiv.) were suspended in <sup>t</sup>BuOH: H<sub>2</sub>O (2 mL:1mL) (2:1) and the reaction mixture was stirred at room temperature for 3h. The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated NaHCO<sub>3</sub> (5 mL) and extracted with EtOAc (3  $\times$  30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated *in vacuo* and purified by silica gel column chromatography (Hexane/EtOAc: from 10:1 to 10:2) to afford the triazole **31** as white solid (123 mg, 0.278 mmol, 90%). Mp:141-142 °C; IR (Film): 2960, 2020, 1710, 1630, 1510, 1490, 1350, 1220, 1170, 1060, 990, 840, 648, 560, 490 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.70 (s, 1H), 7.70 (d, *J* = 13.9 Hz, 2H), 7.38 (s, 1H), 7.09 (d, *J* = 17.3 Hz, 2H), 5.57 (dd, *J* = 7.5, 5.8 Hz, 1H), 5.22 (dd, *J* = 13.5, 5.6 Hz, 1H), 4.49 (dd, *J* = 13.5, 7.8 Hz, 1H), 2.17 (s, 3H), 1.56-1.38 (m, 6H), 1.13 (s, 3H), 1.05 (s, 3H), 0.89 (s, 3H), 0.79 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.7 (d, <sup>1</sup>*J*<sub>CF</sub> = 247.3 Hz), 151.9, 151.7, 146.8, 130.2, 127.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.1 Hz), 126.5 (d, <sup>4</sup>*J*<sub>CF</sub> = 3.1 Hz), 120.4, 115.8 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.8 Hz), 115.7, 78.2, 60.4, 54.7, 40.4, 37.1, 34.2, 33.1, 31.9, 30.1, 30.0, 29.3, 22.7, 20.4, 17.0, 15.2, 14.1; HRMS (ESI) *m/z* [M + H]<sup>+</sup> calculated for [C<sub>23</sub>H<sub>31</sub>FN<sub>5</sub>OS]<sup>+</sup>: 444.2228; found: 444.2231.



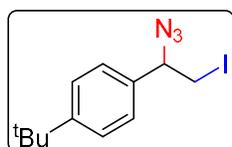
**5-(2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-2-iodo-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-4-methylthiazole (32):** Following the standard triazole procedure using 1-fluoro-4-(iodoethynyl)benzene<sup>[6]</sup> (91 mg, 0.371 mmol, 1.2 equiv.) and purified by silica gel column chromatography, eluting with a gradient of Hexane/EtOAc: from 10:1 to 10:2 afforded the title triazole **32** as white solid (147 mg, 0.259 mmol, 84%).Mp: 131-132 °C; IR (Film): 2930, 2050, 1740, 1685,

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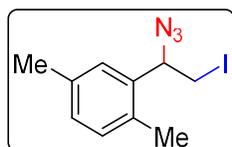
1540, 1450, 1380, 1250, 1140, 1060, 970, 810, 648, 529, 459  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (s, 1H), 7.82 (d,  $J = 14.0$  Hz, 2H), 7.14 (d,  $J = 17.3$  Hz, 2H), 5.70 (dd,  $J = 7.8, 6.5$  Hz, 1H), 5.25 (dd,  $J = 13.4, 6.2$  Hz, 1H), 4.55 (dd,  $J = 13.4, 8.2$  Hz, 1H), 2.12 (s, 3H), 1.56 - 1.40 (m, 6H), 1.08 (s, 3H), 1.07 (s, 3H), 0.87 (s, 3H), 0.83 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9 (d,  $^1J_{\text{CF}} = 248.6$  Hz), 151.8, 151.6, 149.0, 130.1, 129.4 (d,  $^3J_{\text{CF}} = 8.3$  Hz), 126.2 (d,  $^4J_{\text{CF}} = 2.9$  Hz), 115.6 (d,  $^2J_{\text{CF}} = 21.8$  Hz), 78.1, 78.0, 60.4, 54.3, 40.4, 37.1, 34.2, 33.2, 31.9, 30.1, 30.0, 29.3, 28.9, 22.7, 20.4, 17.0, 15.2, 14.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{23}\text{H}_{30}\text{FIN}_5\text{OS}]^+$ : 570.1194; found: 570.1196.



**1-(1-azido-2-iodoethyl)-4-methylbenzene (33):** Following general ionic azidation procedure using 1-methyl-4-vinylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (166 mg, 0.579 mmol, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.15 (m, 4H), 4.67 (t,  $J = 7.1$  Hz, 1H), 3.36 (d,  $J = 7.1$  Hz, 2H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9, 134.8, 129.6, 126.5, 66.9, 21.2, 8.2; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3]</sup>



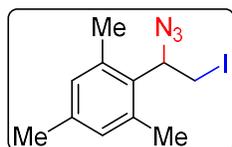
**1-(1-azido-2-iodoethyl)-4-(tert-butyl)benzene (34):** Following general ionic azidation procedure using 1-(tert-butyl)-4-vinylbenzene (90 mg, 0.562 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown-color oil (149 mg, 0.455 mmol, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.36 (m, 2H), 7.28-7.16 (m, 2H), 4.70 (dd,  $J = 7.8, 6.3$  Hz, 1H), 3.44-3.33 (m, 2H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.1, 134.9, 126.3, 126.0, 67.1, 34.7, 31.2, 8.3; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[7]</sup>



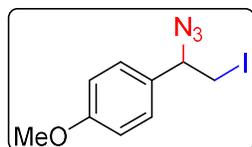
**2-(1-azido-2-iodoethyl)-1,4-dimethylbenzene(35):** Following general ionic azidation procedure using 1,4-dimethyl-2-vinylbenzene (90 mg, 0.681 mmol) and purified by silica gel column chromatography,

## SUPPORTING INFORMATION

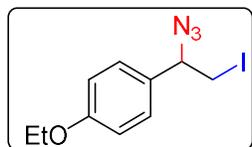
eluting with hexanes afforded the title compound as semi solid (164 mg, 0.544 mmol, 80%). IR (Film): 2923, 2097, 1731, 1614, 1500, 1451, 1332, 1248, 1173, 1037, 935, 812, 731, 648, 611, 529, 459  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19-6.99 (m, 3H), 4.93 (t,  $J = 7.1$  Hz, 1H), 3.35 (d,  $J = 7.6$  Hz, 2H), 2.33 (d,  $J = 2.8$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.3, 135.9, 132.1, 130.9, 129.5, 126.3, 63.9, 21.1, 18.8, 7.3; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{10}\text{H}_{13}\text{IN}_3]^+$ : 302.0149; found: 302.0147.



**2-(1-azido-2-iodoethyl)-1,3,5-trimethylbenzene (36):** Following general ionic azidation procedure using 1,3,5-trimethyl-2-vinylbenzene (90 mg, 0.616 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale-yellow oil (137 mg, 0.437 mmol, 71%). IR (Film): 2950, 2097, 1609, 1450, 1243, 611  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.86 (s, 2H), 5.27 (dd,  $J = 10.0, 5.3$  Hz, 1H), 3.53 (t,  $J = 10.3$  Hz, 1H), 3.36 (dd,  $J = 10.5, 5.3$  Hz, 1H), 2.40 (s, 6H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 136.3, 130.8, 130.5, 64.0, 20.8, 20.7, 5.7; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{11}\text{H}_{15}\text{IN}_3]^+$ : 316.0305; found: 316.0308.



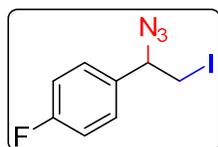
**1-(1-azido-2-iodoethyl)-4-methoxybenzene (37):** Following general ionic azidation procedure using 1-methoxy-4-vinylbenzene (100 mg, 0.746 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless oil (194 mg, 0.641 mmol, 86%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (d,  $J = 8.7$  Hz, 2H), 6.92 (d,  $J = 8.8$  Hz, 2H), 4.67 (dd,  $J = 7.6, 6.6$  Hz, 1H), 3.82 (s, 3H), 3.36 (dd,  $J = 7.1, 1.7$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 129.8, 127.9, 114.3, 66.7, 55.3, 8.4; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3,7]</sup>



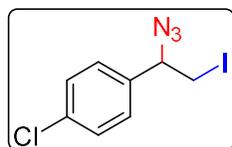
**1-(1-azido-2-iodoethyl)-4-ethoxybenzene (38):** Following general ionic azidation procedure using 1-ethoxy-4-vinylbenzene (100 mg, 0.675 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow semi solid (179 mg, 0.567 mmol, 84%). IR

## SUPPORTING INFORMATION

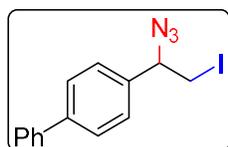
(Film): 2970, 2105, 1738, 1610, 1511, 1442, 1367, 1229, 1216, 1115, 1014,  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dd,  $J = 9.7, 7.8$  Hz, 2H), 6.95-6.88 (m, 2H), 4.75-4.61 (m, 1H), 4.04 (q,  $J = 7.0$  Hz, 2H), 3.41-3.32 (m, 2H), 1.42 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 129.6, 127.9, 114.8, 66.8, 63.5, 14.8, 8.5; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{10}\text{H}_{13}\text{IN}_3\text{O}]^+$ : 318.0098; found: 318.0011.



**1-(1-azido-2-iodoethyl)-4-fluorobenzene (39):** Following general ionic azidation procedure using 1-fluoro-4-vinylbenzene (100 mg, 0.819 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless oil (178 mg, 0.614 mmol, 75%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 8.3, 5.4$  Hz, 2H), 7.10 (t,  $J = 8.5$  Hz, 2H), 4.78-4.61 (m, 1H), 3.28 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $^1J_{\text{CF}} = 248.4$  Hz), 133.7 (d,  $^4J_{\text{CF}} = 2.7$  Hz), 128.5 (d,  $^3J_{\text{CF}} = 8.4$  Hz), 116.0 (d,  $^2J_{\text{CF}} = 21.8$  Hz), 66.3, 8.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3]</sup>



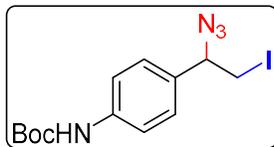
**1-(1-azido-2-iodoethyl)-4-chlorobenzene (40):** Following general ionic azidation procedure using 1-chloro-4-vinylbenzene (110 mg, 0.797 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (225 mg, 0.733 mmol, 92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.4$  Hz, 2H), 7.26 (d,  $J = 8.5$  Hz, 2H), 4.70 (t,  $J = 6.9$  Hz, 1H), 3.46-3.22 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.4, 134.9, 129.2, 128.1, 66.3, 7.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3,7]</sup>



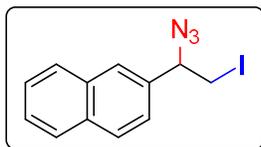
**4-(1-azido-2-iodoethyl)-1,1'-biphenyl (41):** Following general ionic azidation procedure using 4-vinyl-1,1'-biphenyl (100 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown color oil (158 mg, 0.455 mmol, 82%). IR (Film): 3029, 2102, 1694, 1485, 1380, 1245, 1220, 1170, 1060, 960, 830, 680, 550  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

## SUPPORTING INFORMATION

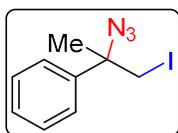
$\delta$  7.73-7.54 (m, 4H), 7.53-7.31 (m, 5H), 4.76 (t,  $J = 7.0$  Hz, 1H), 3.50-3.36 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.0, 140.2, 136.8, 128.8, 128.0, 127.7, 127.6, 127.3, 127.1, 66.9, 8.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{14}\text{H}_{13}\text{IN}_3]^+$ : 350.0149; found: 350.0152.



**tert-butyl (4-(1-azido-2-iodoethyl)phenyl)carbamate (42):** Following general ionic azidation procedure using *tert*-butyl (4-vinylphenyl)carbamate (100 mg, 0.456 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (153 mg, 0.396 mmol, 87%). Mp:79-80 °C; IR (Film): 3321, 2979, 2926, 2099, 1698, 1598, 1524, 1409, 1366, 1317, 1239, 1157, 1053, 833, 775, 732, 688, 629, 560, 515, 466  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.3$  Hz, 2H), 7.24 (dd,  $J = 9.3, 5.9$  Hz, 2H), 6.66 (s, 1H), 4.67 (t,  $J = 7.0$  Hz, 1H), 3.48-3.15 (m, 2H), 1.52 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 139.0, 132.1, 127.4, 118.7, 80.8, 66.6, 28.2, 8.2; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{13}\text{H}_{18}\text{IN}_4\text{O}_2]^+$ : 389.0469; found 389.0472.



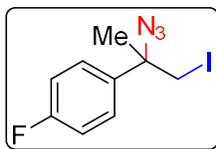
**2-(1-azido-2-iodoethyl)naphthalene (43):** Following general ionic azidation procedure using 2-vinylnaphthalene (100 mg, 0.649 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (153 mg, 0.473 mmol, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93-7.84 (m, 3H), 7.80 (s, 1H), 7.53 (dd,  $J = 6.2, 3.2$  Hz, 2H), 7.41 (dd,  $J = 8.5, 1.8$  Hz, 1H), 4.89 (t,  $J = 7.0$  Hz, 1H), 3.48 (d,  $J = 6.9$  Hz, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  135.2, 133.5, 133.1, 129.2, 128.1, 127.8, 126.7, 126.4, 123.6, 67.4, 7.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[7]</sup>



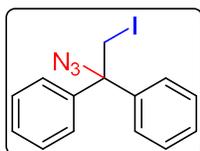
**(2-azido-1-iodopropan-2-yl)benzene (44):** Following general ionic azidation procedure using prop-1-en-2-ylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless oil (170 mg, 0.594 mmol, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.28 (m, 5H), 3.47 (q,  $J = 7.3$  Hz, 2H), 1.88 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

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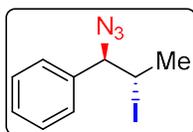
$\delta$ 140.7, 128.7, 128.2, 125.5, 65.0, 25.1, 17.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3]</sup>



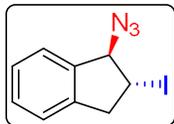
**1-(2-azido-1-iodopropan-2-yl)-4-fluorobenzene (45):** Following general ionic azidation procedure using 1-fluoro-4-(prop-1-en-2-yl)benzene (100 mg, 0.735 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (186 mg, 0.610 mmol, 83%). IR (Film): 2976, 2471, 2101, 1890, 1739, 1601, 1507, 1467, 1374, 1231, 1164, 1013, 831, 730, 684, 546, 499, 449  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.39 (m, 2H), 7.10-7.06 (m, 2H), 3.56-3.35 (m, 2H), 1.88 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $^1J_{\text{CF}} = 247.8$  Hz), 136.6 (d,  $^4J_{\text{CF}} = 3.2$  Hz), 127.5 (d,  $^3J_{\text{CF}} = 8.4$  Hz), 115.6 (d,  $^2J_{\text{CF}} = 21.5$  Hz), 64.6, 25.1, 17.5; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_9\text{H}_{10}\text{FIN}_3]^+$ : 305.9898; found 305.9895.



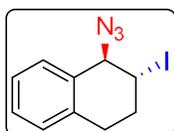
**(1-azido-2-iodoethane-1,1-diyl)dibenzene (46):** Following general ionic azidation procedure using ethene-1,1-diyl dibenzene (100 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless solid (149 mg, 0.427 mmol, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45-7.24 (m, 10H), 4.07 (s, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 128.5, 128.2, 127.2, 71.2, 15.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[8]</sup>



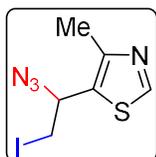
**(1-azido-2-iodopropyl)benzene (47):** Following general ionic azidation procedure using (*E*)-prop-1-en-1-ylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as colorless oil (185 mg, 0.647 mmol, 85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.26 (m, 4H), 4.76 (d,  $J = 6.3$  Hz, 1H), 4.40-4.24 (m, 2H), 1.87 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 128.8, 128.7, 128.4, 127.3, 72.7, 28.8, 23.4; spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3,11]</sup>



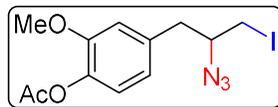
**1-azido-2-iodo-2,3-dihydro-1H-indene (48):** Following general ionic azidation procedure using indene (100 mg, 0.862 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown oil (186 mg, 0.655 mmol, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.22 (m, 4H), 5.11 (d,  $J = 5.5$  Hz, 1H), 4.37 (td,  $J = 6.5, 5.6$  Hz, 1H), 3.64 (dd,  $J = 16.7, 7.0$  Hz, 1H), 3.34 (dd,  $J = 16.7, 6.4$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 138.5, 129.4, 127.7, 124.7, 124.4, 74.9, 43.5, 25.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[9]</sup>



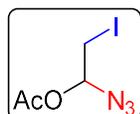
**1-azido-2-iodo-1,2,3,4-tetrahydronaphthalene (49):** Following general ionic azidation procedure using 1,2-dihydronaphthalene (100 mg, 0.769 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown oil (181 mg, 0.607 mmol, 79%). IR (Film): 2926, 2087, 1604, 1452, 1330, 1269, 1223, 1185, 1074, 990, 850, 630, 540  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39-7.16 (m, 4H), 4.82 (d,  $J = 4.0$  Hz, 1H), 4.59 (dd,  $J = 5.4, 3.7$  Hz, 1H), 3.09-2.96 (m, 1H), 2.89 (dd,  $J = 17.5, 4.9$  Hz, 1H), 2.28-2.15 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.3, 130.4, 129.8, 129.3, 128.9, 126.6, 66.3, 28.7, 28.6, 27.6; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{10}\text{H}_{11}\text{IN}_3]^+$ : 299.9992; found 299.9995.



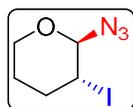
**5-(1-azido-2-iodoethyl)-4-methylthiazole (50):** Following general ionic azidation procedure using 4-methyl-5-vinylthiazole (110 mg, 0.88 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale-yellow oil (224 mg, 0.765 mmol, 87%). IR (Film): 2930, 2099, 1739, 1538, 1455, 1366, 1257, 1131, 1016, 929, 844, 797, 718, 663, 554, 510, 441  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (s, 1H), 5.06 (t,  $J = 7.1$  Hz, 1H), 3.40 (ddd,  $J = 17.0, 10.4, 7.1$  Hz, 2H), 2.51 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.9, 151.5, 129.0, 59.7, 15.6, 7.07; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_6\text{H}_8\text{IN}_4\text{S}]^+$ : 294.9509; found: 294.9512.



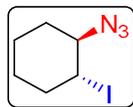
**4-(2-azido-3-iodopropyl)-2-methoxyphenyl acetate (51):** Following general ionic azidation procedure using 4-allyl-2-methoxyphenyl acetate (100 mg, 0.485 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow semi solid (152 mg, 0.407 mmol, 84%). IR (Film): 2936, 2101, 1760, 1509, 1410, 1330, 1220, 1160, 1060, 910, 810, 650, 590  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.99 (dd,  $J = 8.0, 3.0$  Hz, 1H), 6.88-6.79 (m, 2H), 3.88-3.81 (m, 3H), 3.64 (dd,  $J = 12.7, 6.0$  Hz, 1H), 3.28 (dd,  $J = 10.6, 5.3$  Hz, 1H), 3.22 (dd,  $J = 10.5, 5.5$  Hz, 1H), 2.96 (dd,  $J = 13.9, 6.3$  Hz, 1H), 2.88 (dd,  $J = 13.9, 7.1$  Hz, 1H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 151.1, 138.9, 135.1, 123.0, 121.4, 113.4, 63.1, 55.9, 40.2, 20.7, 8.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{12}\text{H}_{14}\text{IN}_3\text{O}_3]^+$ : 376.0153; found: 376.0155.



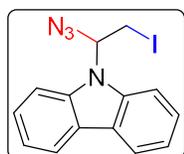
**1-azido-2-iodoethyl acetate (52):** Following general ionic azidation procedure using vinyl acetate (90 mg, 1.046 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (226 mg, 0.889 mmol, 85%). IR (Film): 3474, 3027, 2970, 2114, 1748, 1571, 1471, 1418, 1371, 1310, 1245, 941, 898, 790, 685, 640, 556, 497  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.70 (t,  $J = 4.9$  Hz, 1H), 3.37 (d,  $J = 4.9$  Hz, 2H), 2.13 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 88.0, 20.7, 2.3; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_4\text{H}_7\text{IN}_3\text{O}_2]^+$ : 255.9577; found: 255.9581.



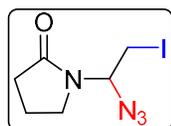
**2-azido-3-iodotetrahydro-2H-pyran (53):** Following general ionic azidation procedure using 3,4-dihydro-2H-pyran (90 mg, 1.071 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown oil (197 mg, 0.781 mmol, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.95 (d,  $J = 7.2$  Hz, 1H), 4.12 (dd,  $J = 11.4, 4.5$  Hz, 1H), 3.94 (ddd,  $J = 9.7, 7.2, 4.3$  Hz, 1H), 3.76-3.61 (m, 1H), 2.50-2.32 (m, 1H), 2.15-1.98 (m, 1H), 1.69 (dd,  $J = 9.7, 4.7$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  92.3, 66.1, 33.8, 27.3, 26.2; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3,10]</sup>



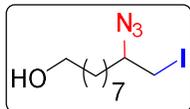
**1-azido-2-iodocyclohexane (54):** Following general ionic azidation procedure using cyclohexene (80 mg, 0.975 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as brown oil (217 mg, 0.867 mmol, 89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.96 (ddd,  $J = 11.1, 9.8, 4.2$  Hz, 1H), 3.59-3.42 (m, 1H), 2.54-2.40 (m, 1H), 2.17 (ddd,  $J = 7.6, 4.3, 2.2$  Hz, 1H), 2.08-1.96 (m, 1H), 1.92-1.83 (m, 1H), 1.65-1.53 (m, 1H), 1.53-1.36 (m, 2H), 1.31 (dd,  $J = 8.4, 6.7$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  67.2, 38.4, 33.2, 31.9, 27.0, 23.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3,10]</sup>



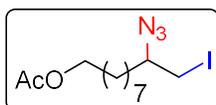
**9-(1-azido-2-iodoethyl)-9H-carbazole (55):** Following general ionic azidation procedure using 9-vinylcarbazole (100 mg, 0.518 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (163 mg, 0.450 mmol, 87%). IR (Film): 2924, 2098, 1597, 1480, 1340, 1210, 1140, 1080, 900, 810, 650, 580  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.8$  Hz, 2H), 7.56 (d,  $J = 8.3$  Hz, 2H), 7.45 (ddd,  $J = 8.3, 7.2, 1.2$  Hz, 2H), 7.34-7.21 (m, 2H), 6.38 (dd,  $J = 7.8, 6.7$  Hz, 1H), 3.83-3.67 (m, 1H), 3.66-3.55 (m, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 126.2, 123.9, 120.6, 120.3, 110.5, 110.1, 72.8, 2.8; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{14}\text{H}_{11}\text{IN}_4]^+$ : 363.0101; found: 363.0104.



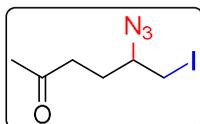
**1-(1-azido-2-iodoethyl)pyrrolidin-2-one (56):** Following general ionic azidation procedure using 1-vinyl-2-pyrrolidone (100 mg, 0.900 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (234 mg, 0.837 mmol, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.87 (dd,  $J = 8.9, 6.1$  Hz, 1H), 3.51-3.30 (m, 3H), 3.19 (dd,  $J = 10.6, 9.1$  Hz, 1H), 2.50 (t,  $J = 8.1$  Hz, 2H), 2.25-2.04 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 68.1, 41.3, 30.6, 18.0, 1.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3]</sup>



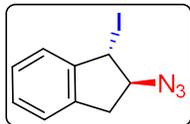
**9-azido-10-iododecan-1-ol (57):** Following general ionic azidation procedure using undec-10-en-1-ol (100 mg, 0.641 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow semi-solid (154 mg, 0.474 mmol, 74%). IR (Film): 3336, 3075, 2924, 2853, 2102, 1739, 1640, 1572, 1461, 1438, 1367, 1230, 1055, 994, 908, 730, 685, 653, 549, 449  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, )  $\delta$  3.64 (t,  $J$  = 6.6 Hz, 2H), 3.45-3.33 (m, 2H), 3.26 (dd,  $J$  = 5.7, 4.2 Hz, 2H), 1.68 (dd,  $J$  = 9.2, 5.0 Hz, 1H), 1.57 (dd,  $J$  = 10.4, 7.3 Hz, 1H), 1.47-1.27 (m, 12H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  63.0, 62.7, 37.1, 34.4, 32.7, 29.4, 29.3, 29.3, 29.1, 25.8, 25.7, 8.6; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{10}\text{H}_{20}\text{IN}_3\text{O}]^+$ : 326.0724; found: 326.0721.



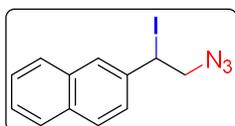
**9-azido-10-iododecyl acetate (58):** Following general ionic azidation procedure using undec-10-en-1-yl acetate (100 mg, 0.505 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow semi-solid (142 mg, 0.388 mmol, 77%). IR (Film): 3459, 2925, 2854, 2103, 1738, 1640, 1572, 1465, 1438, 1365, 1232, 1036, 995, 909, 732, 653, 605, 449  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.05 (t,  $J$  = 6.7 Hz, 2H), 3.40 (dd,  $J$  = 11.3, 8.1 Hz, 1H), 3.32-3.21 (m, 2H), 2.05 (s, 3H), 1.90-1.48 (m, 2H), 1.30 (s, 12H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 64.5, 62.6, 34.4, 29.3, 29.2, 29.1, 29.0, 28.5, 25.8, 25.7, 21.0, 8.5; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_{12}\text{H}_{22}\text{IN}_3\text{O}_2]^+$ : 368.0829; found: 368.0832.



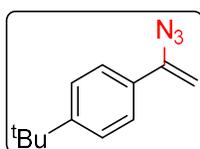
**5-azido-6-iodohexan-2-one (59):** Following general ionic azidation procedure using 5-hexene-2-one (80 mg, 0.816 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (198 mg, 0.742 mmol, 91%). IR (Film): 3953, 2938, 2100, 1717, 1424, 1358, 1235, 1066, 1002, 736, 598, 446  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.55-3.43 (m, 1H), 3.29 (d,  $J$  = 5.9 Hz, 2H), 2.60 (t,  $J$  = 7.1 Hz, 2H), 2.19 (s, 3H), 2.03 (dd,  $J$  = 11.5, 7.5, Hz, 1H), 1.81-1.64 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.1, 61.7, 39.3, 30.0, 28.4, 7.7; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_6\text{H}_{11}\text{IN}_3\text{O}]^+$ : 267.9941; found: 267.9945.



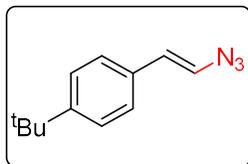
**2-azido-1-iodo-2,3-dihydro-1H-indene (60):** Following general radical azidation procedure using indene (100 mg, 0.862 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (226 mg, 0.793 mmol, 92%). IR (Film): 2922, 2088, 1452, 1350, 1290, 1225, 1150, 1074, 910, 747, 664, 590  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.22 (m, 4H), 4.77 (d,  $J = 5.6$  Hz, 1H), 4.17 (td,  $J = 6.7, 5.7$  Hz, 1H), 3.35 (dd,  $J = 16.0, 7.3$  Hz, 1H), 2.94 (dd,  $J = 16.0, 6.6$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 137.7, 129.5, 127.8, 125.1, 124.6, 70.3, 67.7, 36.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_9\text{H}_9\text{IN}_3]^+$ : 285.9836; found: 285.9838.



**2-(2-azido-1-iodoethyl)naphthalene (61):** Following general radical azidation procedure using 2-vinylnaphthalene (100 mg, 0.649 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow oil (188 mg, 0.584 mmol, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.75 (m, 4H), 7.55 (d,  $J = 1.6$  Hz, 1H), 7.52 (dd,  $J = 9.7, 7.4$  Hz, 2H), 5.35 (t,  $J = 7.8$  Hz, 1H), 4.05 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.4, 133.3, 133.1, 129.1, 128.0, 127.8, 126.8, 126.7, 126.3, 125.2, 58.5, 28.5; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. <sup>[2]</sup>

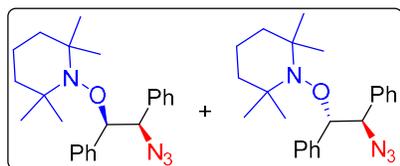


**1-(1-azidovinyl)-4-(tert-butyl)benzene (62):** 1-(1-azido-2-iodoethyl)-4-(tert-butyl)benzene (100 mg, 0.303 mmol, 1 equiv.) in THF (2 mL) was slowly added to a suspension of *t*-BuOK (40 mg, 0.364 mmol, 1.2 equiv.) in dry THF under  $\text{N}_2$  atmosphere and allowed to stir for 2 h at room temperature. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with water. Finally, the compound was purified by column chromatography and affords the compound **62** as pale yellow oil (48 mg, 0.236 mmol, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 8.4$  Hz, 2H), 7.37 (d,  $J = 8.4$  Hz, 2H), 5.39 (d,  $J = 2.1$  Hz, 1H), 4.91 (d,  $J = 2.2$  Hz, 1H), 1.32 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 144.9, 131.5, 125.4, 125.3, 97.3, 34.7, 31.2; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. <sup>[7]</sup>

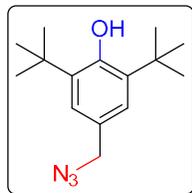


**(E)-1-(2-azidovinyl)-4-(tert-butyl)benzene (63):** 1-(2-azido-1-iodoethyl)-4-(tert-butyl)benzene (100 mg, 0.303 mmol, 1 equiv.) in THF (2 mL) was slowly added to a suspension of *t*-BuOK (40 mg, 0.364 mmol, 1.2 equiv.) in dry THF under N<sub>2</sub> atmosphere and allowed to stir for 2 h at room temperature. The crude product was dissolved in dichloromethane and washed with water. Finally the compound was purified by column chromatography and affords the compound **63** as Pale yellow oil (46 mg, 0.23 mmol, 75%). IR (Film): 3310, 2956, 2865, 2103, 1671, 1609, 1503, 1464, 1400, 1364, 1273, 1114, 1017, 833, 775, 736, 701, 559 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 13.8 Hz, 1H), 6.26 (d, *J* = 13.8 Hz, 1H), 1.31 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.6, 132.2, 125.9, 125.7, 125.5, 119.6, 34.6, 31.2; HRMS (ESI) *m/z* [M]<sup>+</sup> calculated for [C<sub>12</sub>H<sub>16</sub>N<sub>3</sub>]<sup>+</sup>: 202.1339; found 202.1338.

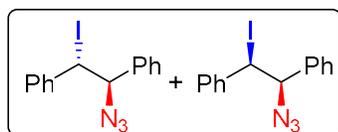
## D. Mechanistic Studies



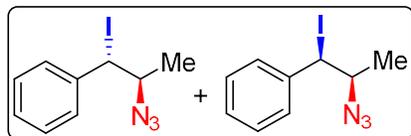
**1-(2-azido-1,2-diphenylethoxy)-2,2,6,6-tetramethylpiperidine (64):** Following general radical azidooxygenation procedure using *trans*-stilbene (100 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound (*dr* = 2.6:1) as colorless oil (165 mg, 0.438 mmol, 79%). The azidooxygenation reaction of *cis*-stilbene (100 mg, 0.555 mmol) gave **64** (159 mg, 0.421 mmol, 76%) with *dr* = 3.4:1. **Syn-isomer;** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.24 (m, 6H), 7.16-7.11 (m, 4H), 5.11 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 8.0 Hz, 1H), 1.83-1.31 (m, 12H), 1.20 (s, 3H), 0.44 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.7, 136.7, 129.5, 128.0, 127.9, 127.2, 89.0, 69.2, 60.1, 59.4, 40.8, 35.1, 34.1, 20.2, 17.0; **Anti-isomer;** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34-7.30 (m, 6H), 7.10-7.06 (m, 4H), 5.62 (d, *J* = 3.3 Hz, 1H), 4.88 (d, *J* = 3.4 Hz, 1H), 1.83-1.34 (m, 12H), 1.20 (s, 3H), 0.75 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.1, 137.0, 129.1, 127.7, 127.6, 126.9, 91.4, 67.9, 61.1, 59.3, 40.6, 35.1, 34.1, 20.5, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[4]</sup>



**4-(azidomethyl)-2,6-di-tert-butylphenol (65):** A preformed solution of  $\text{Me}_3\text{SI}(\text{OAc})_2$  (354 mg, 1.1 mmol, 1.1 equiv.),  $\text{TMSN}_3$  (287 mg, 328  $\mu\text{L}$ , 2.5 mmol, 2.5 equiv.), 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (171 mg, 1.1 mmol, 1.5 equiv.) and BHT (660 mg, 3.0 mmol, 3 equiv.) in DCM (5 mL) was treated with *trans*-stilbene (**1b**) (180 mg, 1.0 mmol, 1.0 equiv.) at room temperature. The mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED). The distance between the light source and the reaction flask was approximately 3-4 cm, resulted in the temperature increasing up to 35  $^\circ\text{C}$ . For safety reasons, the reaction was carried out behind an *anti*-blast shield. The reaction was stirred until the completion of starting material, typically for 15 h (adjudged by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated  $\text{NaHCO}_3$  (5 mL) and saturated aqueous sodium thiosulfate (2 mL) and extracted with EtOAc (3  $\times$  30 mL). The combined organic layers were washed with brine solution, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , concentrated *in vacuo* and purified by silica gel column chromatography using hexanes as eluent to afford the compound **65** as pale yellow oil (375 mg, 1.44 mmol, 48%). IR (Film): 3559, 2956, 2922, 2871, 2108, 2084, 1433, 1236, 1197, 1116, 1025, 933, 1025, 855, 789, 703, 609, 555, 497  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (s, 2H), 5.27 (s, 1H), 4.25 (s, 2H), 1.45 (s, 18H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.8, 136.2, 126.1, 125.2, 55.4, 30.2; HRMS (ESI)  $m/z$   $[\text{M}]^+$  calculated for  $[\text{C}_{15}\text{H}_{24}\text{N}_3\text{O}]^+$ : 262.1914; found 262.1916.

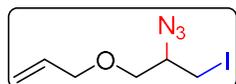


**1,2-diiodo-1,2-diphenylethane (67):** Following general radical azidation procedure using *trans*-stilbene (100 mg, 0.555 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the compound **67** as colorless oil (141 mg, 0.405 mmol, 73%, *dr*; 2:1). **Anti-isomer**;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.33 (m, 6H), 7.37-7.25 (m, 4H), 5.22 (d,  $J = 9.2$  Hz, 1H), 5.10 (d,  $J = 9.2$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 137.6, 128.7, 128.6, 128.5, 127.6, 71.8, 34.4; **Syn-isomer**;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.33 (m, 6H), 7.37-7.25 (m, 4H), 5.18 (d,  $J = 9.6$  Hz, 1H), 4.92 (d,  $J = 9.6$  Hz, 1H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 136.2, 129.0, 128.6, 128.2, 127.2, 72.7, 36.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[3]</sup>

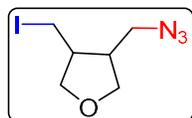


**(2-azido-1-iodopropyl)benzene (68):** Following general radical azidation procedure using (*E*)-prop-1-en-1-ylbenzene (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the compound **68** as yellow oil (192 mg, 0.670 mmol, 88%, *dr* = 1:1). **Both-Isomers;**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44-7.37 (m, 10H), 4.99 (d,  $J$  = 7.9 Hz, 1H), 4.93 (d,  $J$  = 7.8 Hz, 1H), 3.98-3.90 (m, 1H), 3.85-3.79 (m, 1H), 1.52 (d,  $J$  = 6.5 Hz, 3H), 1.24 (d,  $J$  = 6.5 Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6, 140.4, 128.8, 128.7, 128.5, 128.4, 128.1, 63.7, 63.1, 37.4, 36.3, 19.8, 18.4; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.<sup>[2,3,11]</sup>

**Experiment for carbocation trapping using Radical azidation of allyl ether:** Following general radical azidation procedure using allyl ether (40 mg, 0.408 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the 1:1 mixture of vicinal azidoiodo compound **69** and rearranged cyclic product **70** (*dr* 2:1) in 72% overall yields.



**3-(2-azido-3-iodopropoxy)prop-1-ene (69):** Yellow oil; (39 mg, 0.146 mmol, 36%). IR (Film): 2926, 2859, 2095, 1710, 1672, 1452, 1360, 1269, 1223, 1185, 1074, 914, 800, 664, 590  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.90 (ddd,  $J$  = 21.8, 10.6, 5.4 Hz, 1H), 5.36-5.12 (m, 2H), 4.04 (d,  $J$  = 5.6 Hz, 2H), 3.83-3.67 (m, 1H), 3.66 (d,  $J$  = 25.4 Hz, 2H), 3.40-3.19 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.9, 117.6, 72.3, 71.5, 61.3, 3.7; HRMS (ESI)  $m/z$   $[\text{M}]^+$  calculated for  $[\text{C}_6\text{H}_{11}\text{IN}_3\text{O}]^+$ : 267.9941; found: 267.9946.



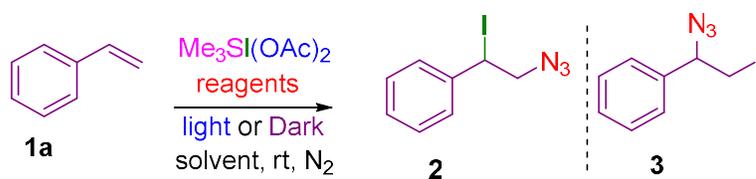
**3-(azidomethyl)-4-(iodomethyl)tetrahydrofuran (70):** Pale yellow oil; (39 mg, 0.146 mmol, 36%). IR (Film): 2900, 2830, 2010, 1760, 1690, 1380, 1280, 1210, 1150, 1090, 960, 840, 690, 540  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.07-3.94 (m, 6H), 3.79 (dd,  $J$  = 9.0, 4.9 Hz, 2H), 3.67-3.60 (m, 3H), 3.57-3.11 (m, 13H), 2.91-2.80 (m, 2H), 2.54 (dd,  $J$  = 13.3, 6.8 Hz, 2H), 2.34 (dd,  $J$  = 12.8, 6.9 Hz, 1H), 2.20 (dd,  $J$  = 12.3, 5.3 Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  74.3, 73.3, 71.4, 71.1, 53.3, 49.3, 46.1, 45.6, 44.7, 42.2, 8.0, 2.1; HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  calculated for  $[\text{C}_6\text{H}_{11}\text{IN}_3\text{O}]^+$ : 267.9941; found: 267.9944.

**E. References for Supporting Information**

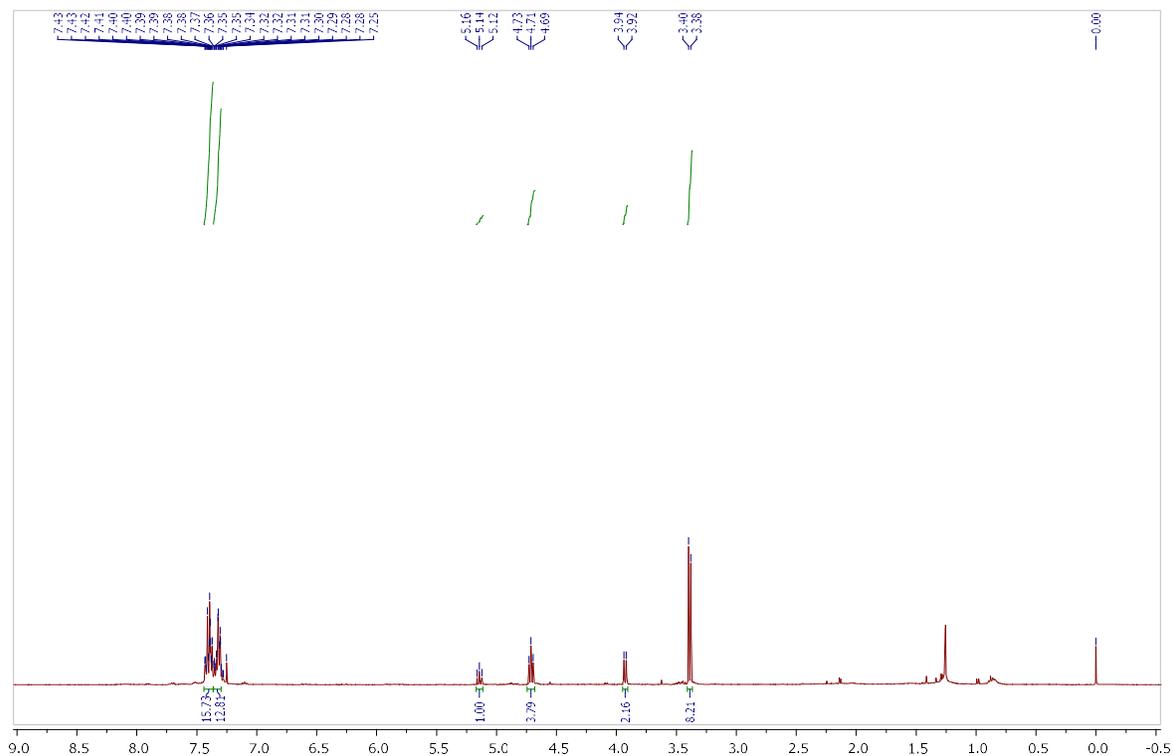
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## SUPPORTING INFORMATION

### F. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

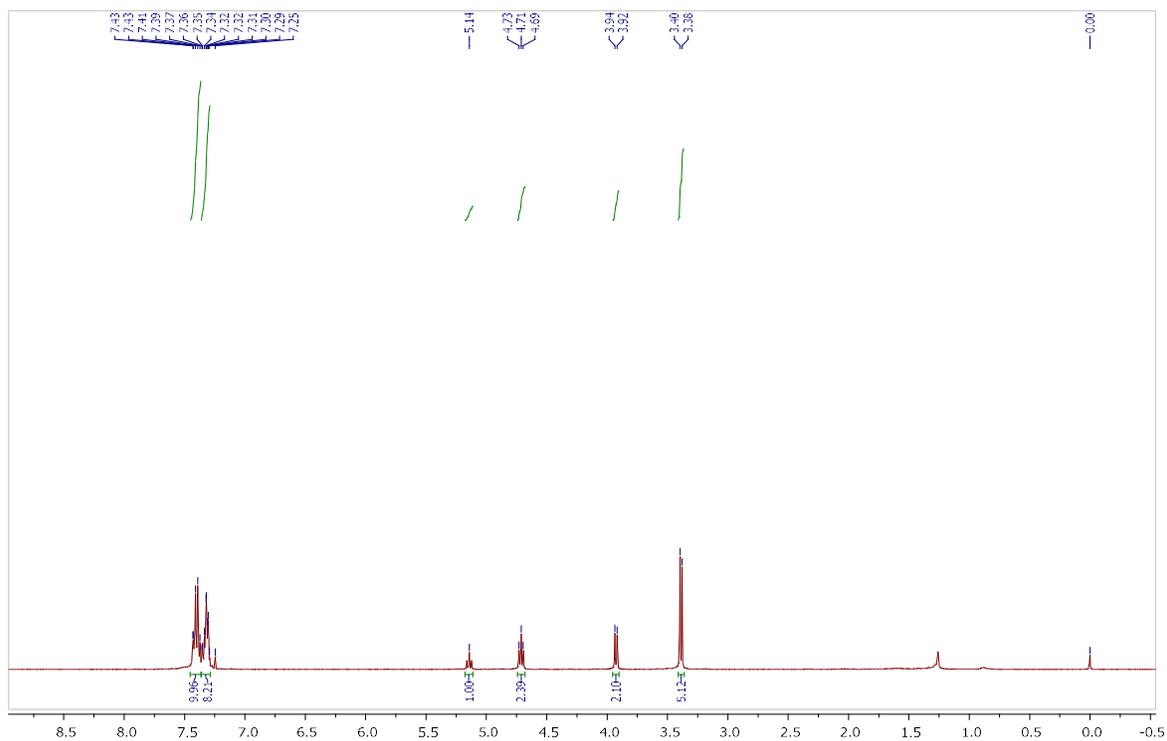


$^1\text{H}$  NMR Spectrum of compound **2:3** (**1:4**) in  $\text{CDCl}_3$  (Table 1, entry 1)

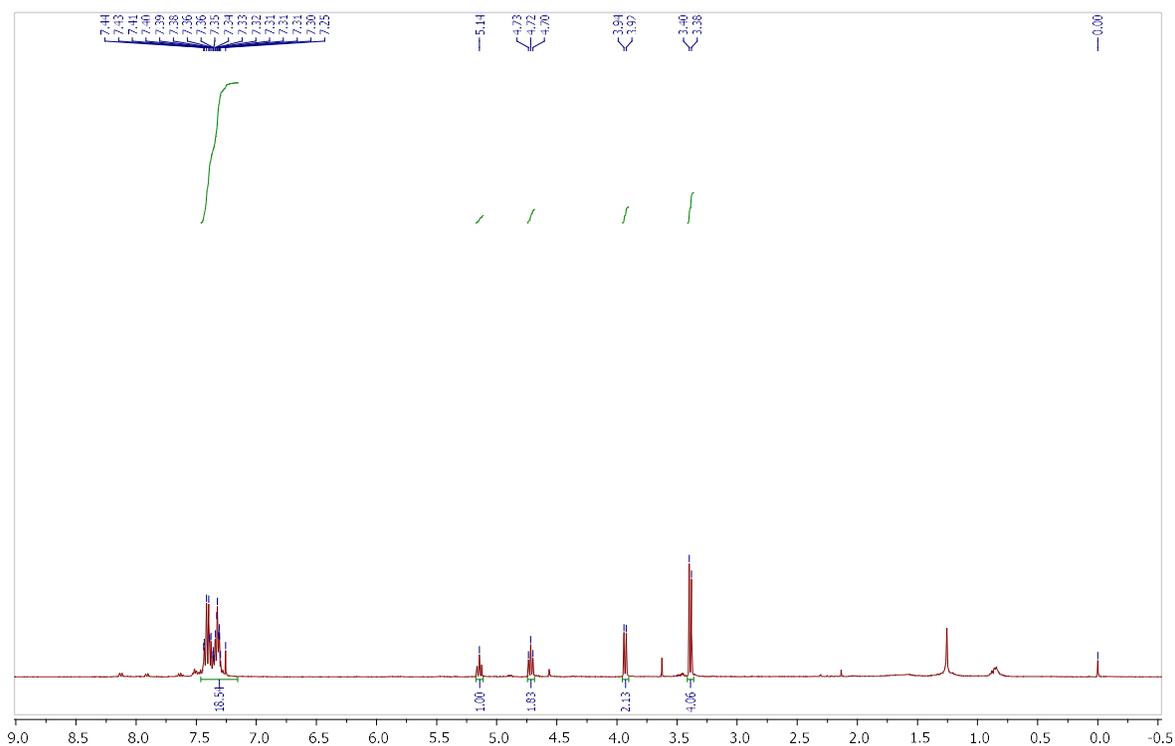


## SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **2:3** (**1:2.5**) in  $\text{CDCl}_3$  (Table 1, entry 2)

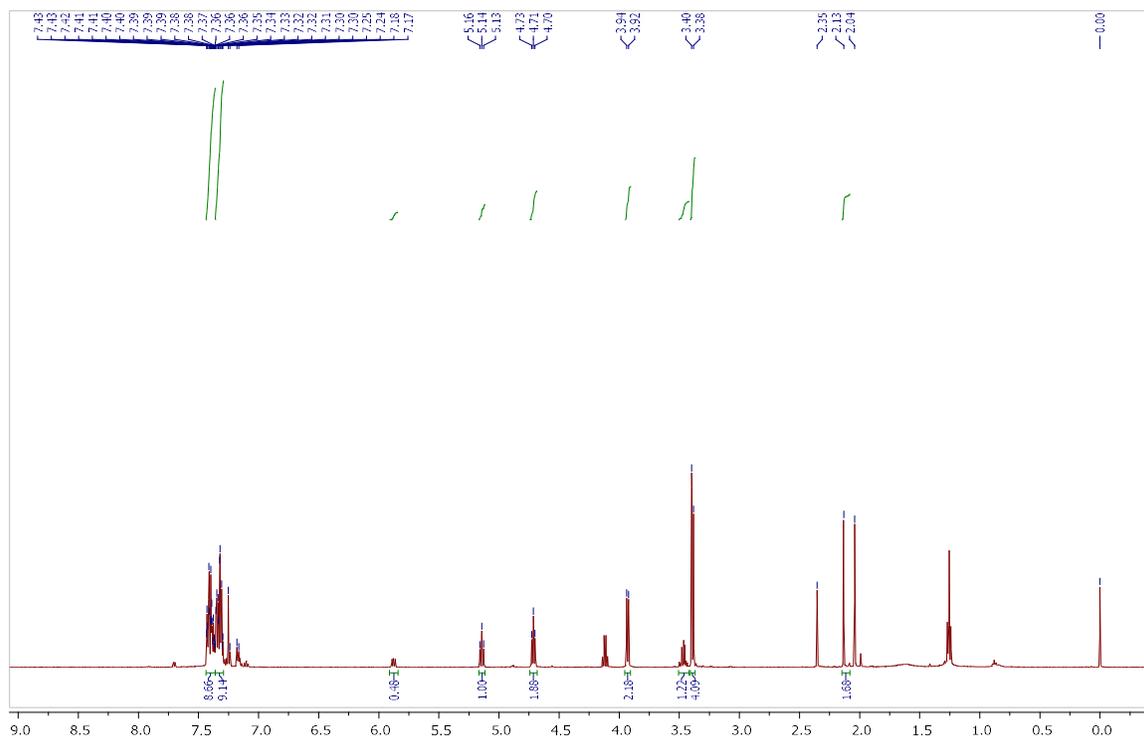


$^1\text{H}$  NMR Spectrum of compound **2:3** (**1:2**) in  $\text{CDCl}_3$  (Table 1, entry 3)

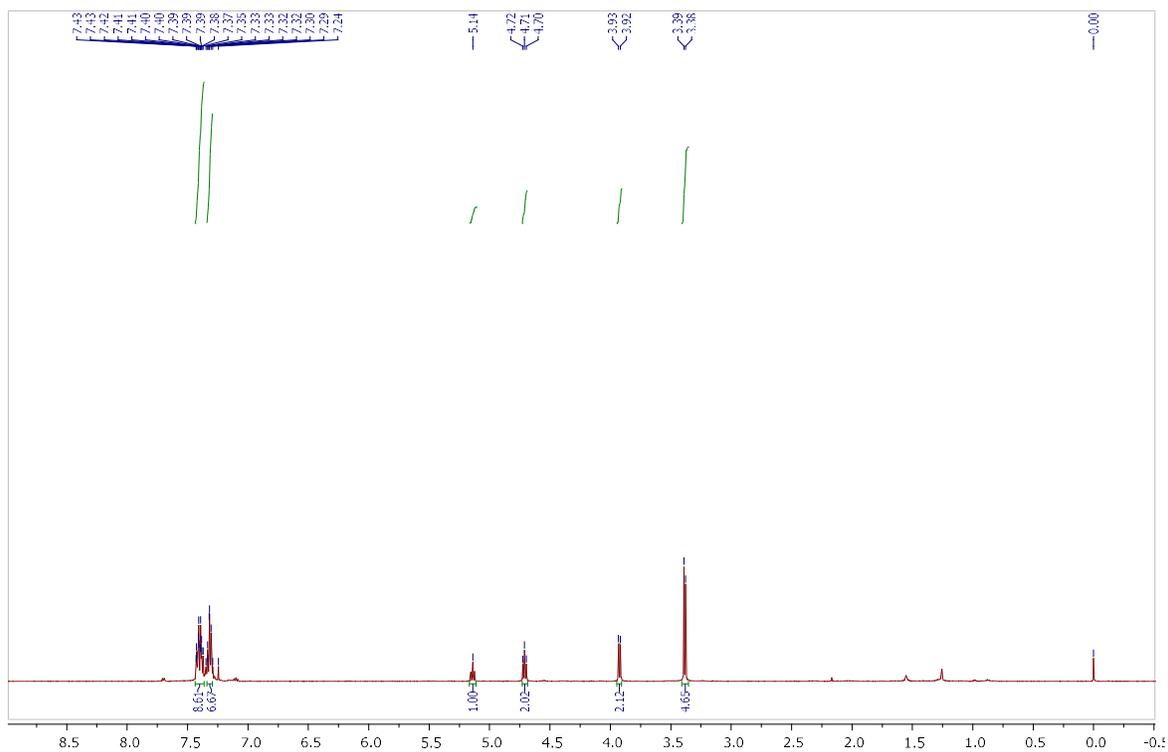


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **2:3 (1:2)** in CDCl<sub>3</sub> (Table 1, entry 4)

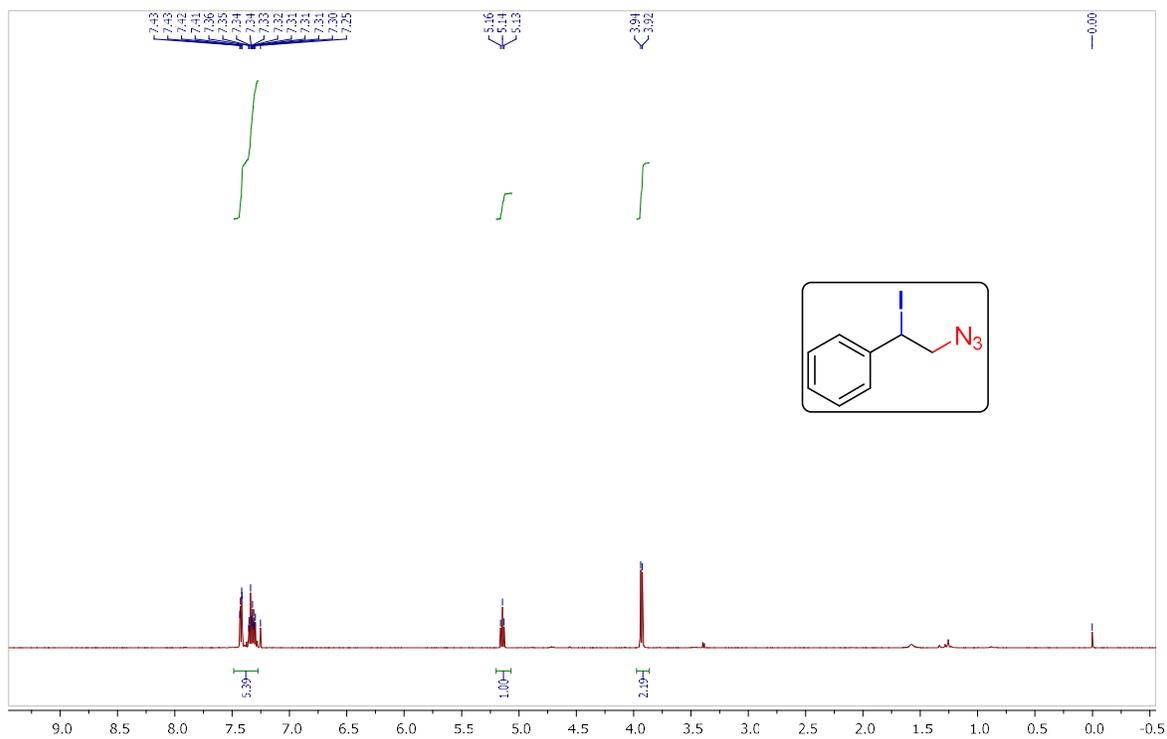


<sup>1</sup>H NMR Spectrum of compound **2:3 (1:2)** in CDCl<sub>3</sub> (Table 1, entry 5)

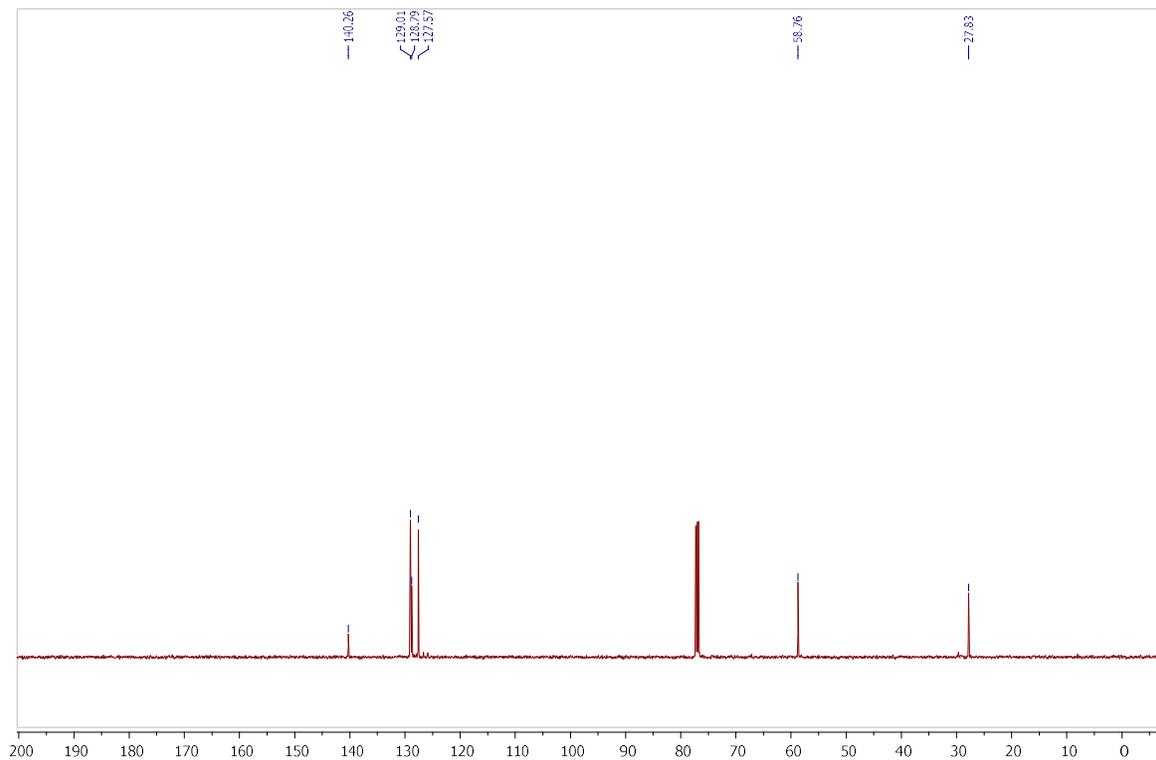


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **2** in $\text{CDCl}_3$

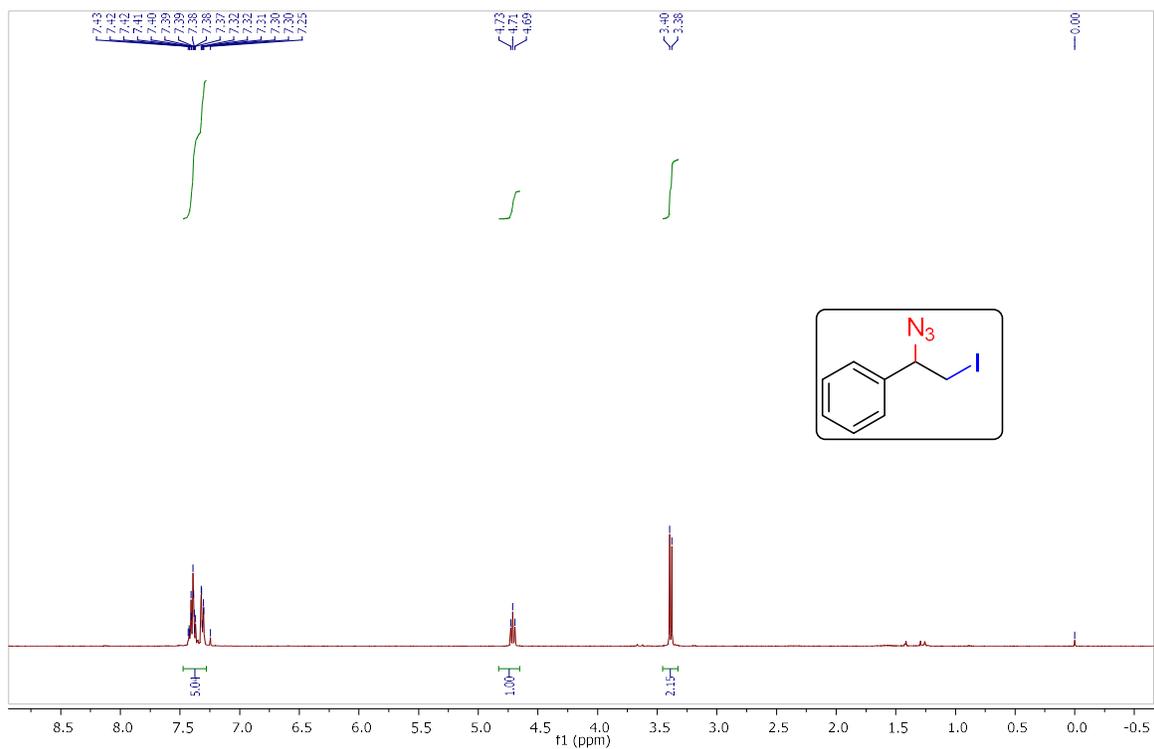


## $^{13}\text{C}$ NMR Spectrum of compound **2** in $\text{CDCl}_3$

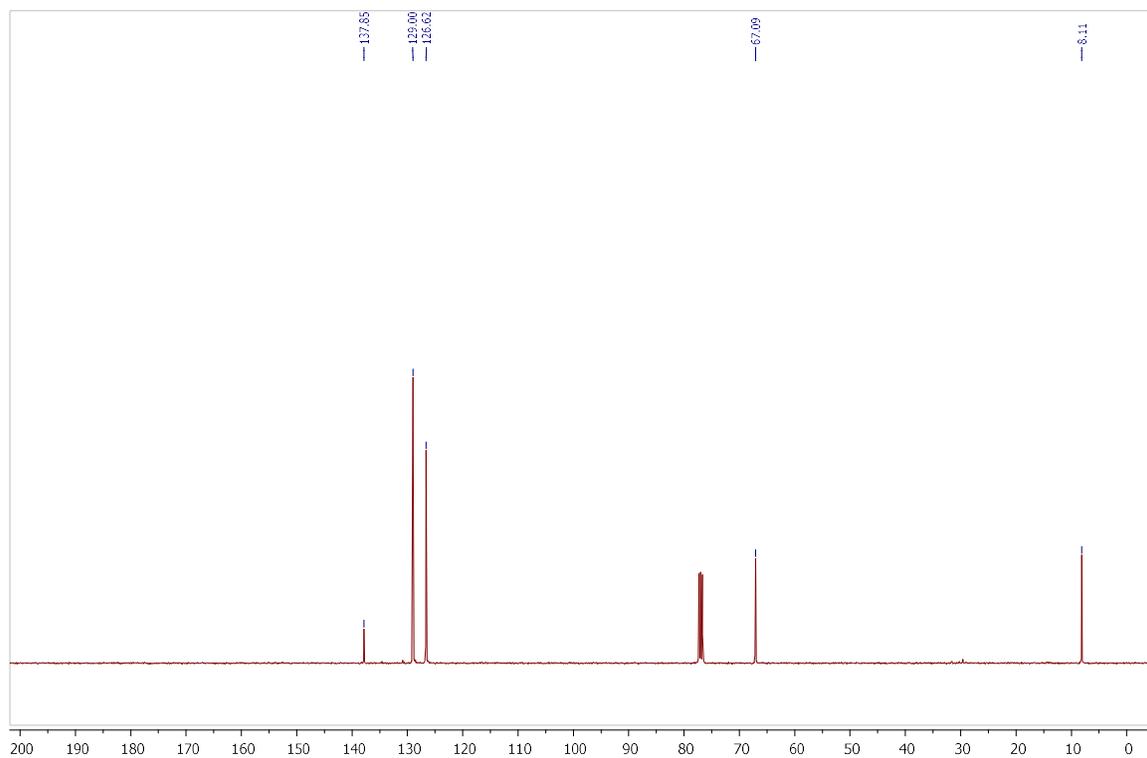


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **3** in $\text{CDCl}_3$

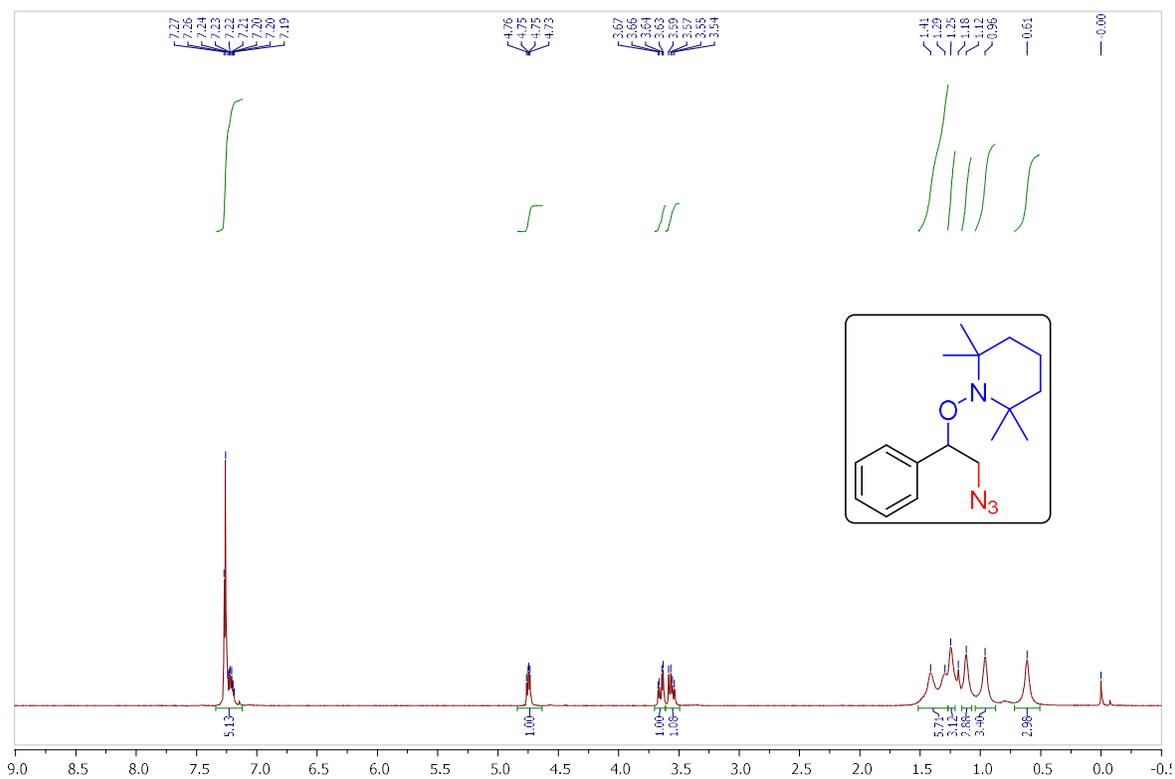


## $^{13}\text{C}$ NMR Spectrum of compound **3** in $\text{CDCl}_3$

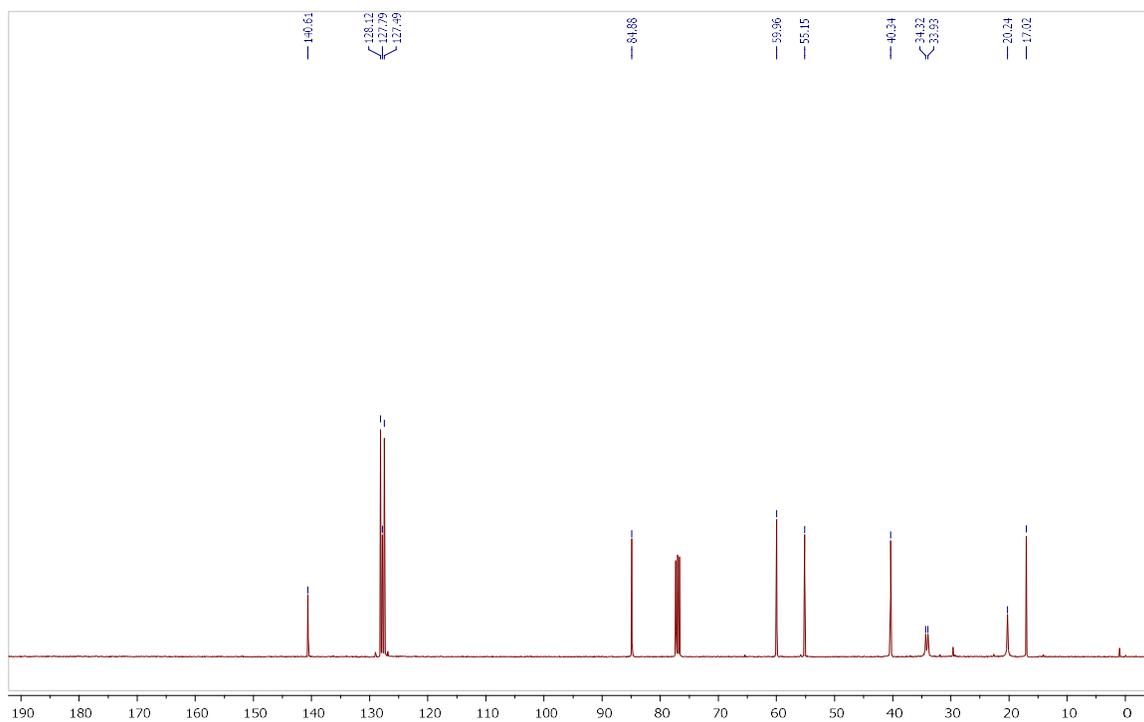


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **4** in $\text{CDCl}_3$

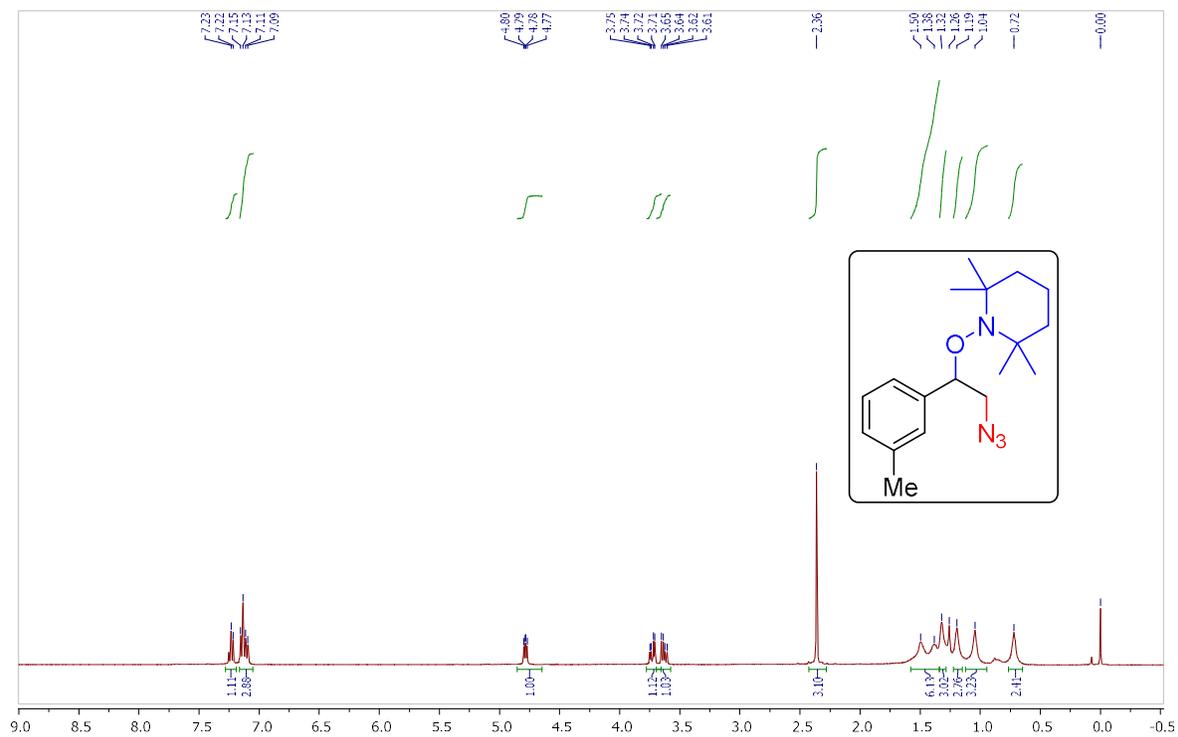


## $^{13}\text{C}$ NMR Spectrum of compound **4** in $\text{CDCl}_3$

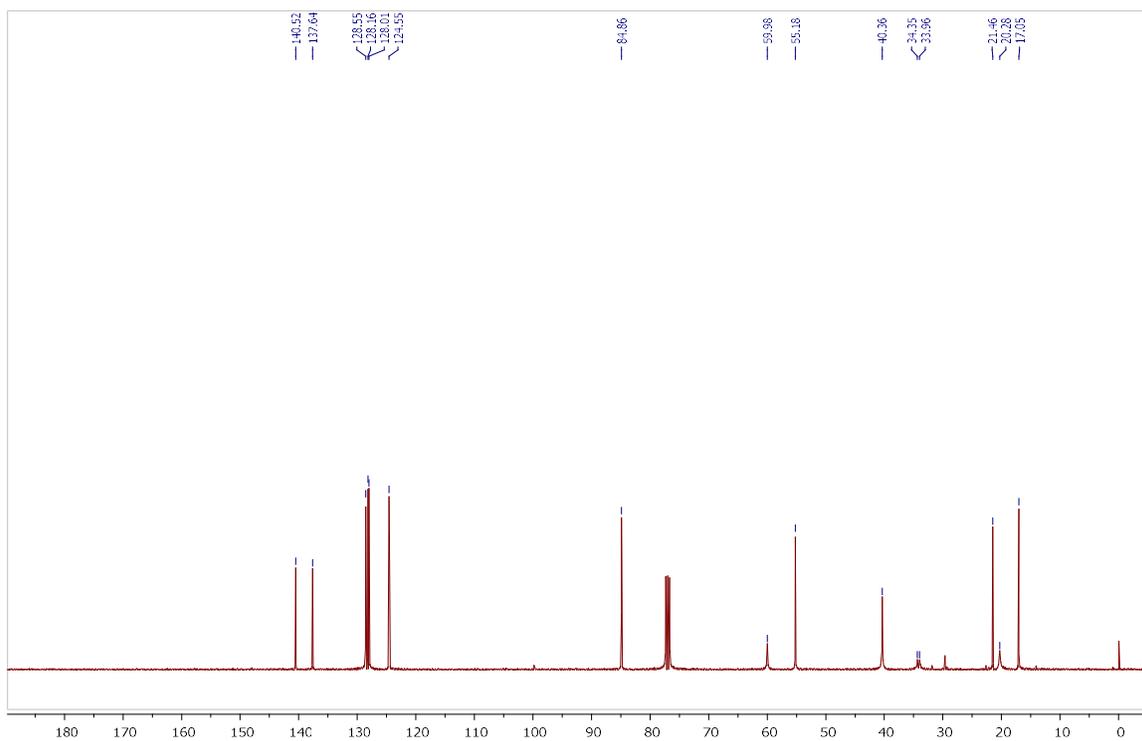


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **5** in CDCl<sub>3</sub>

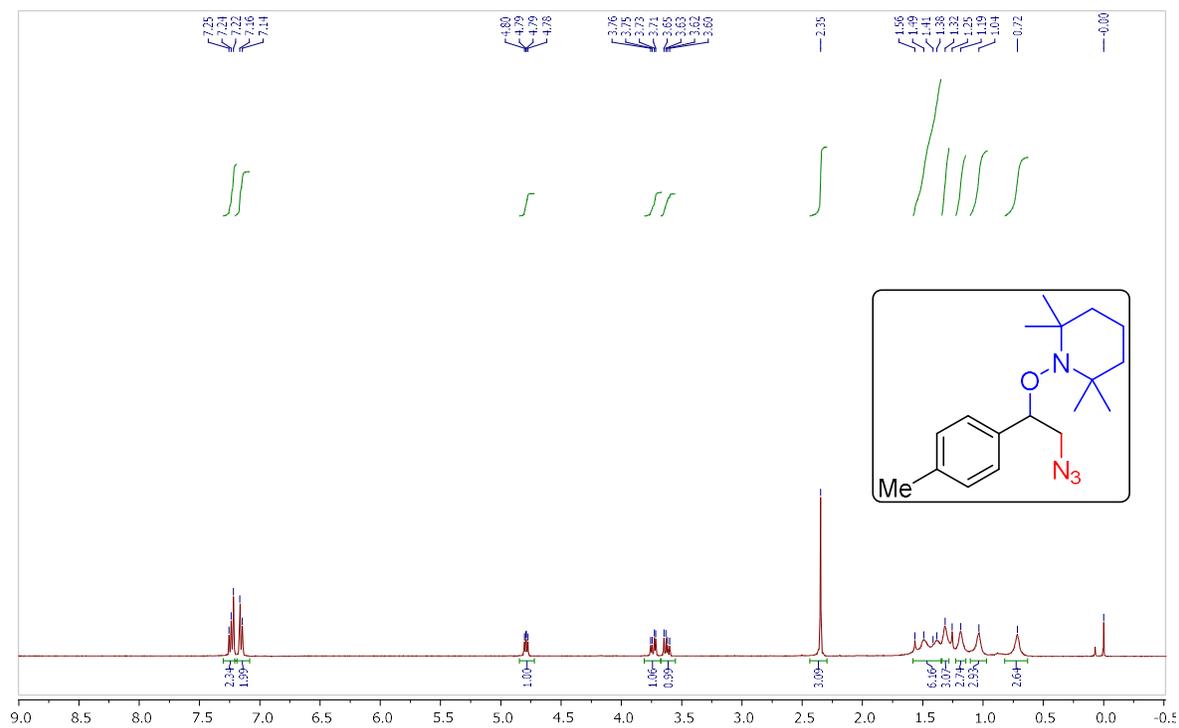


## <sup>13</sup>C NMR Spectrum of compound **5** in CDCl<sub>3</sub>

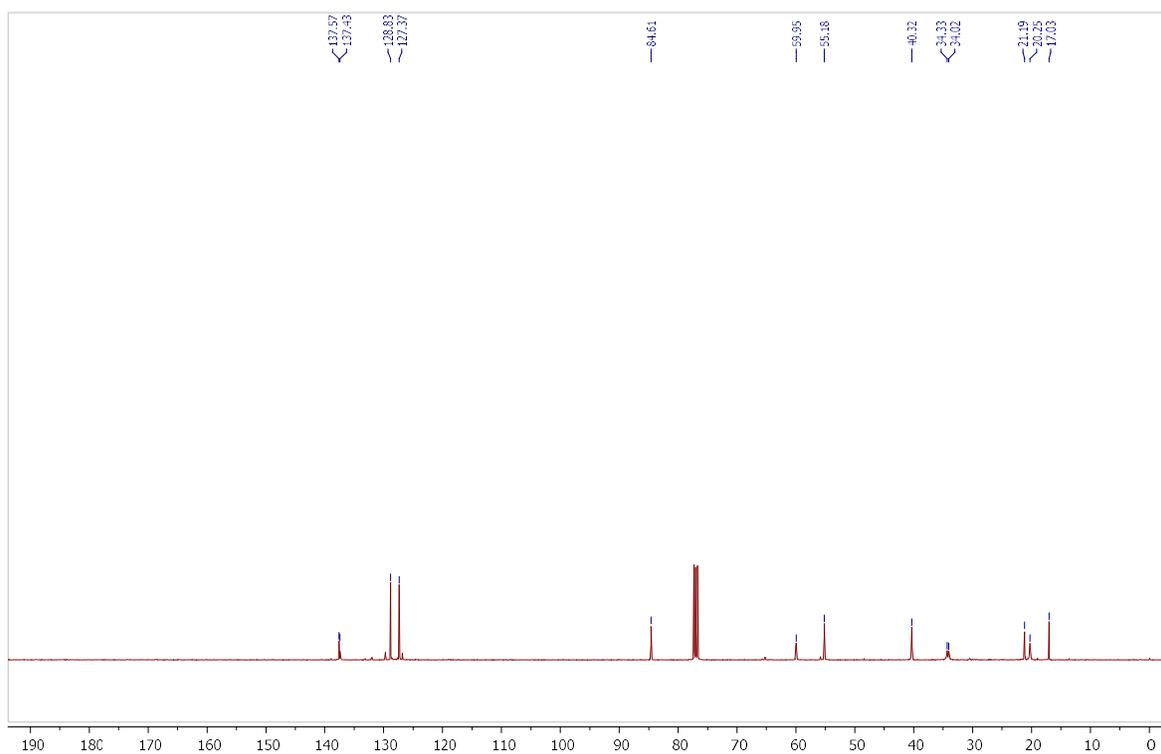


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **6** in $\text{CDCl}_3$

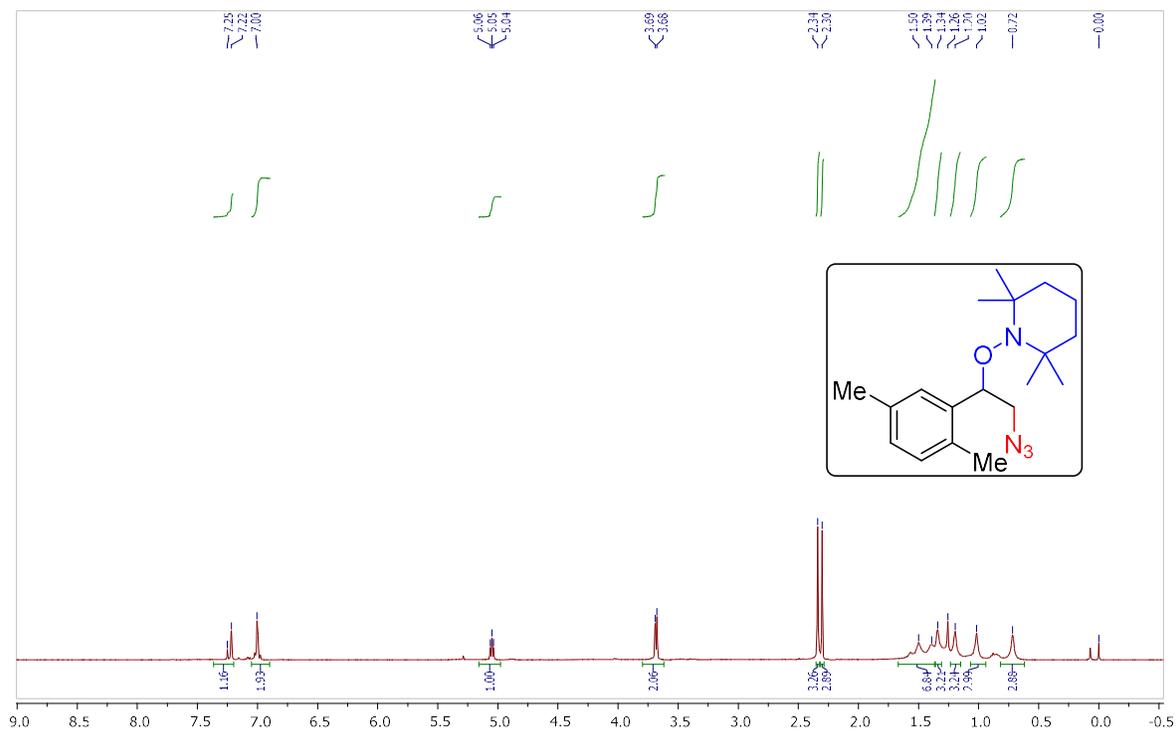


## $^{13}\text{C}$ NMR Spectrum of compound **6** in $\text{CDCl}_3$

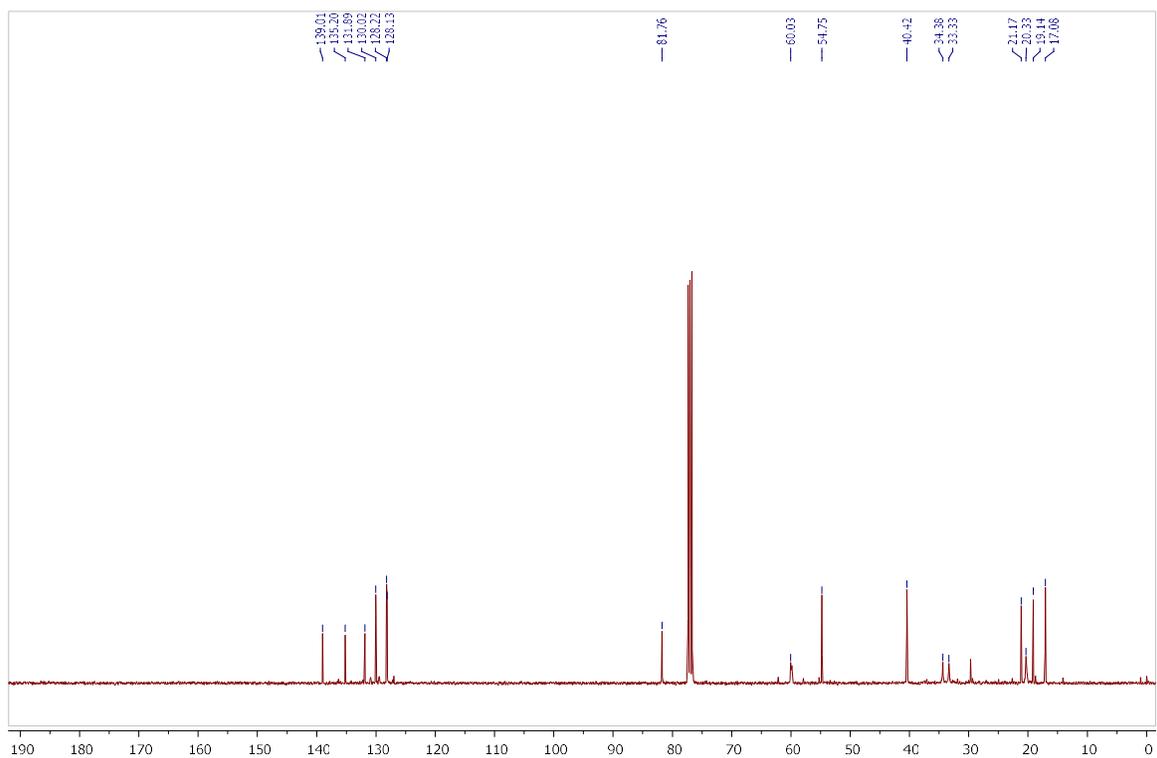


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **7** in $\text{CDCl}_3$

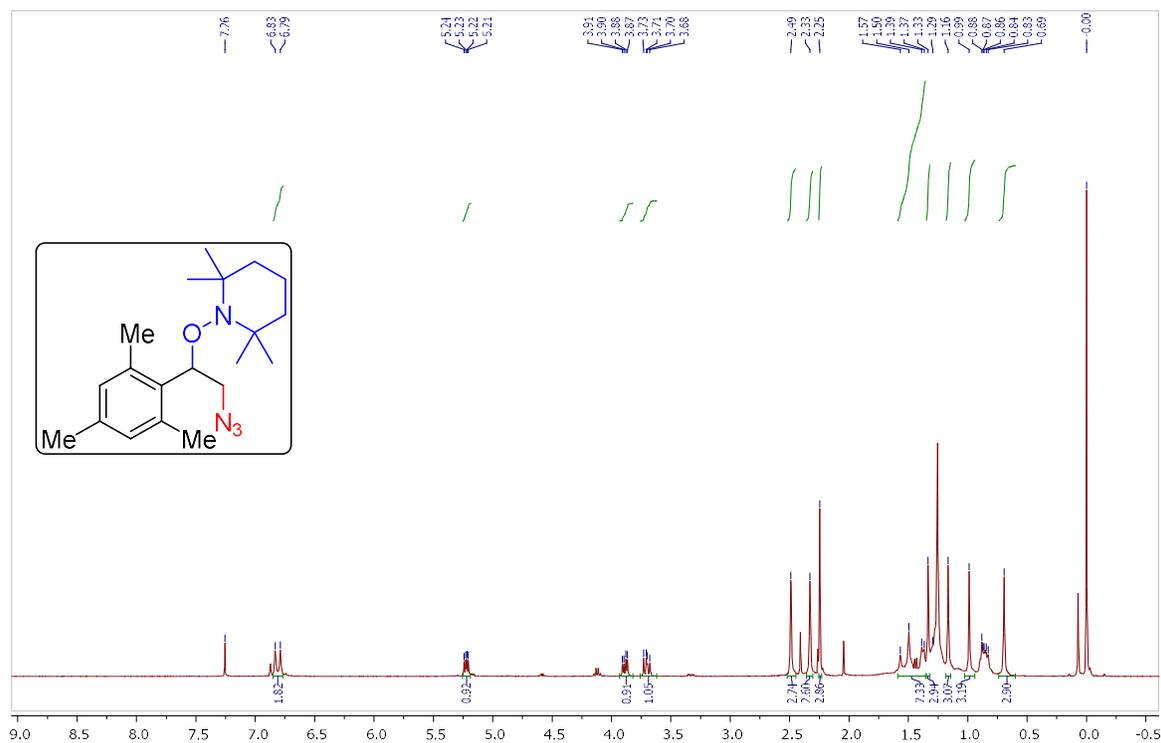


## $^{13}\text{C}$ NMR Spectrum of compound **7** in $\text{CDCl}_3$

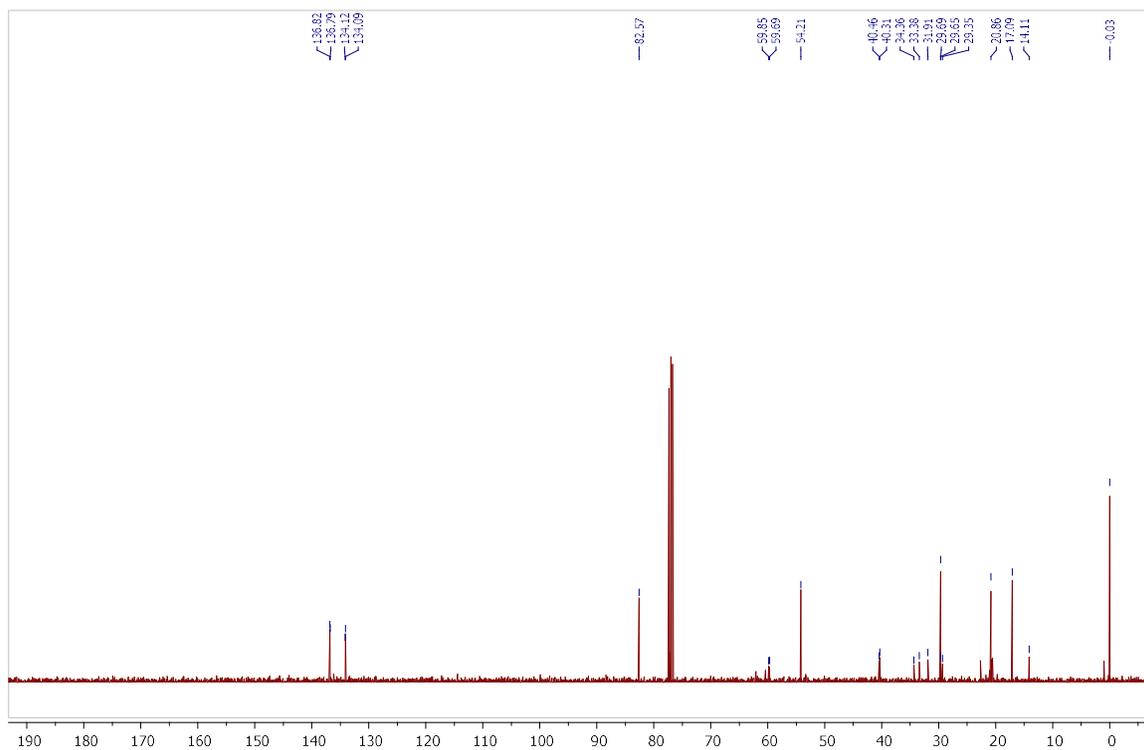


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **8** in CDCl<sub>3</sub>

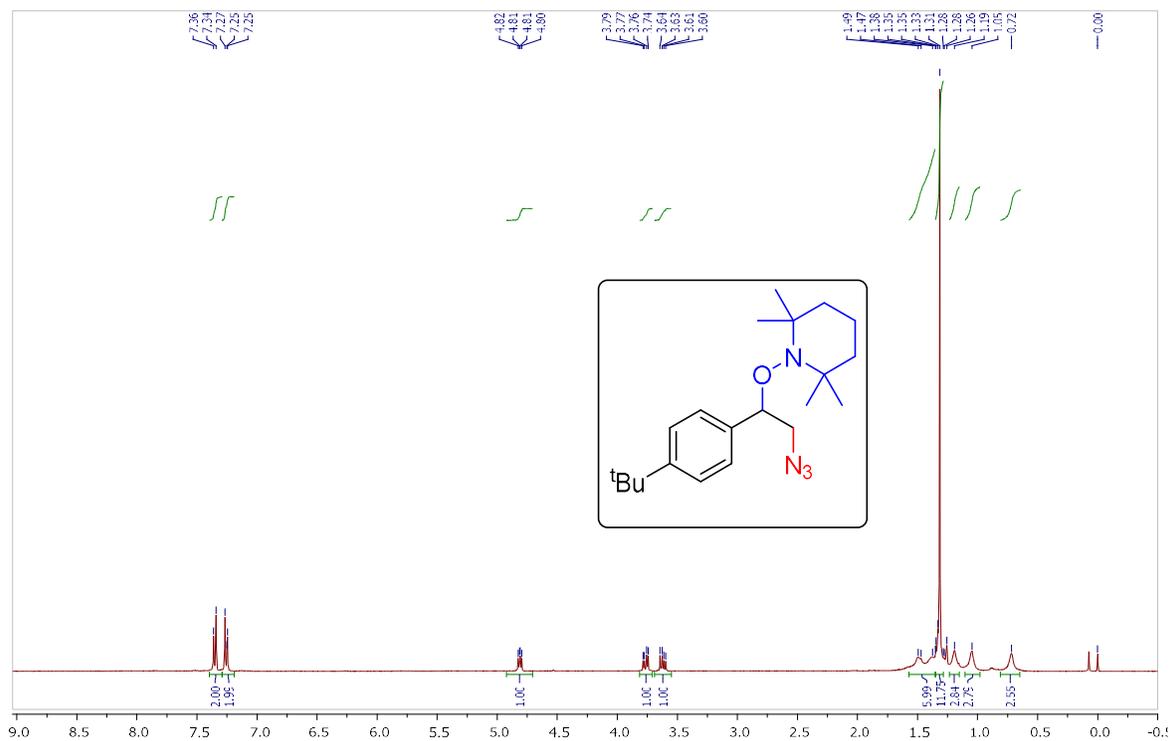


## <sup>13</sup>C NMR Spectrum of compound **8** in CDCl<sub>3</sub>

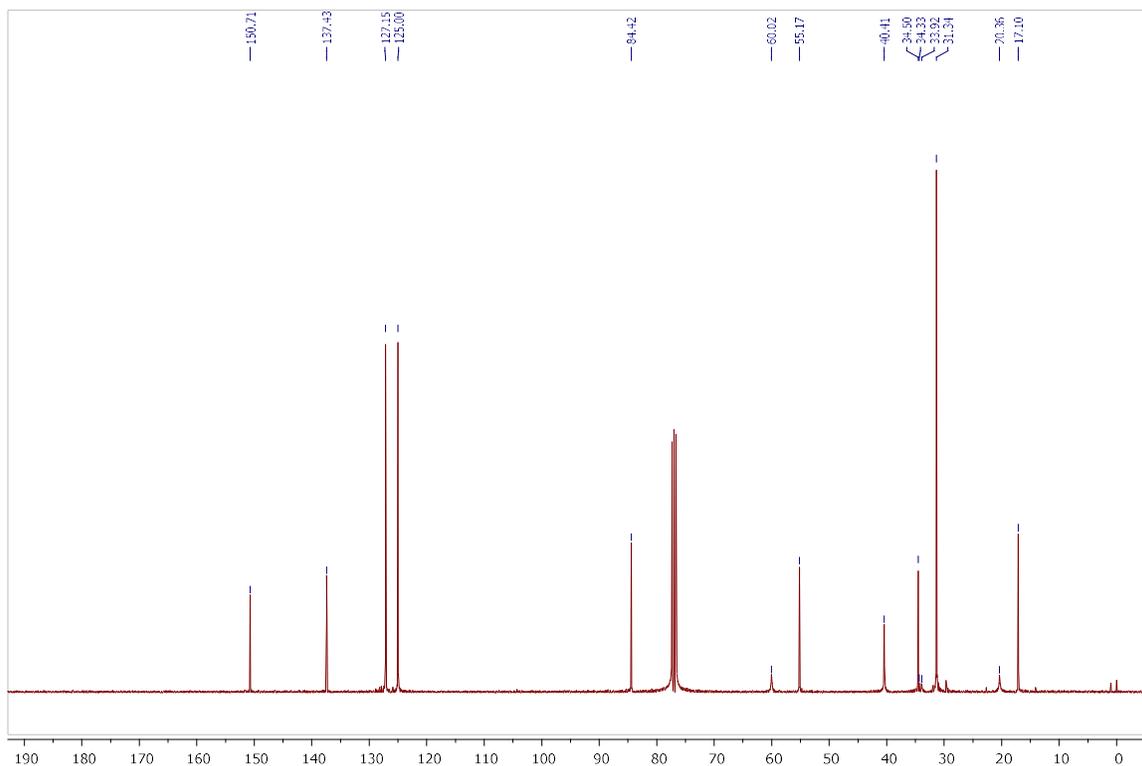


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **9** in CDCl<sub>3</sub>

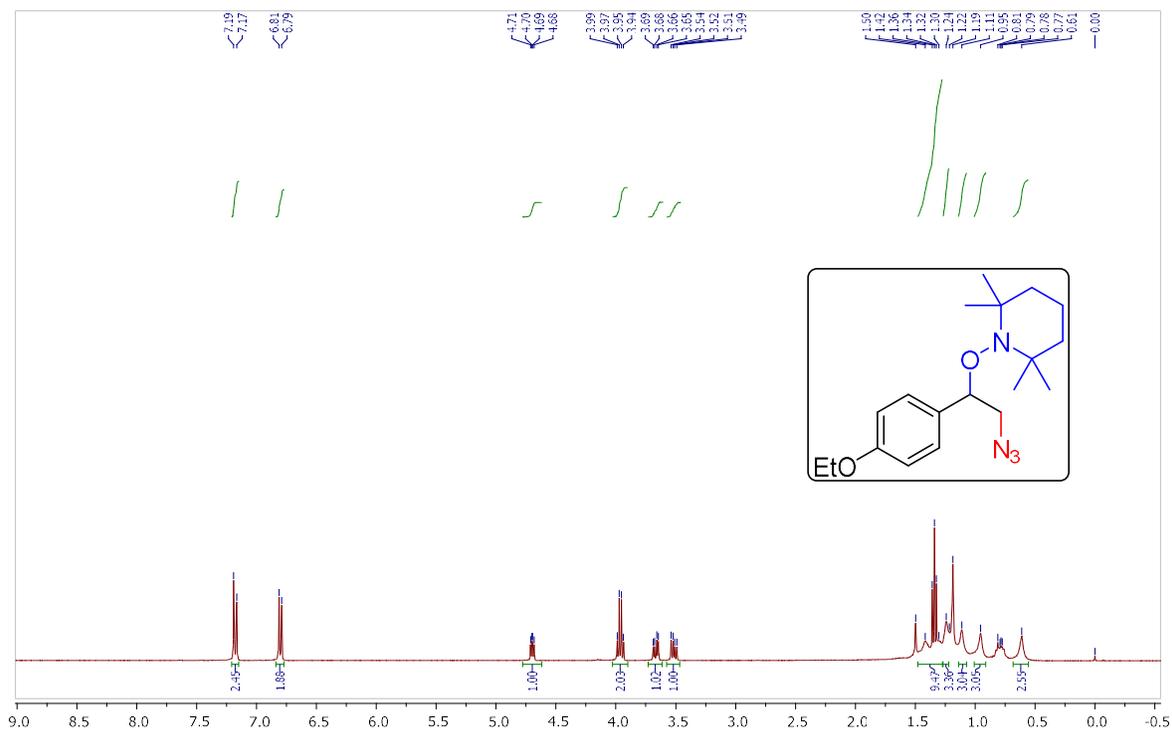


## <sup>13</sup>C NMR Spectrum of compound **9** in CDCl<sub>3</sub>

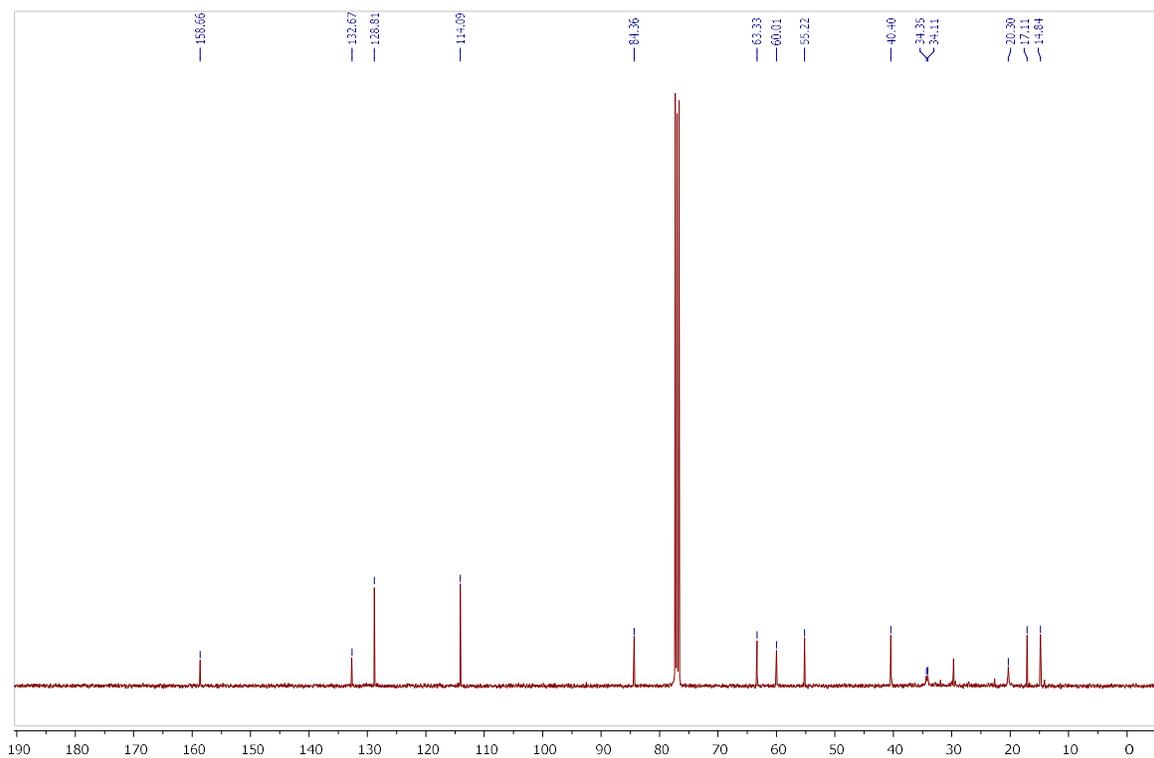


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **10** in $\text{CDCl}_3$

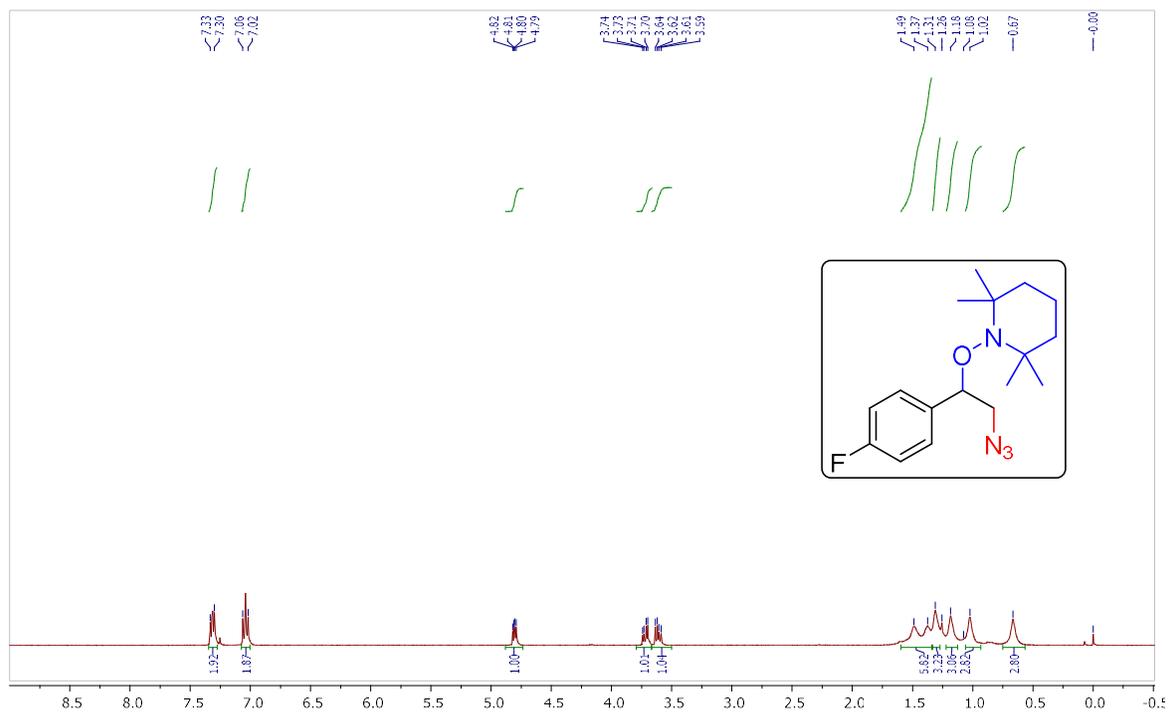


## $^{13}\text{C}$ NMR Spectrum of compound **10** in $\text{CDCl}_3$

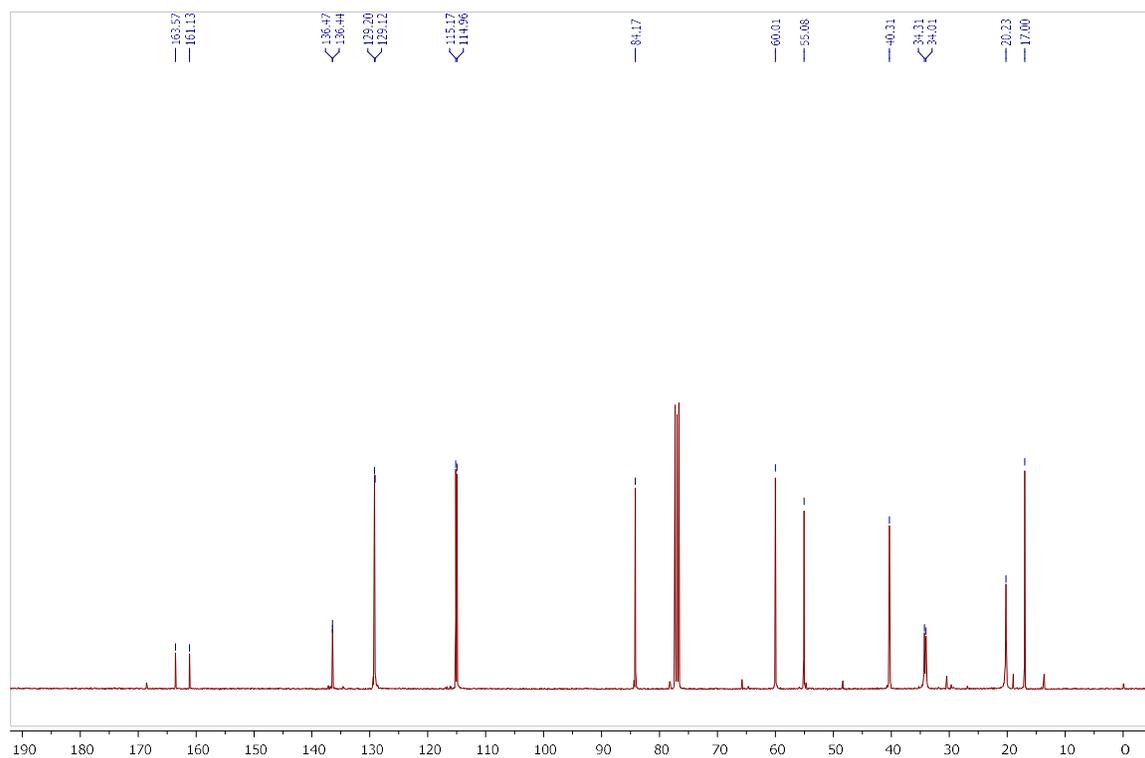


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **11** in CDCl<sub>3</sub>

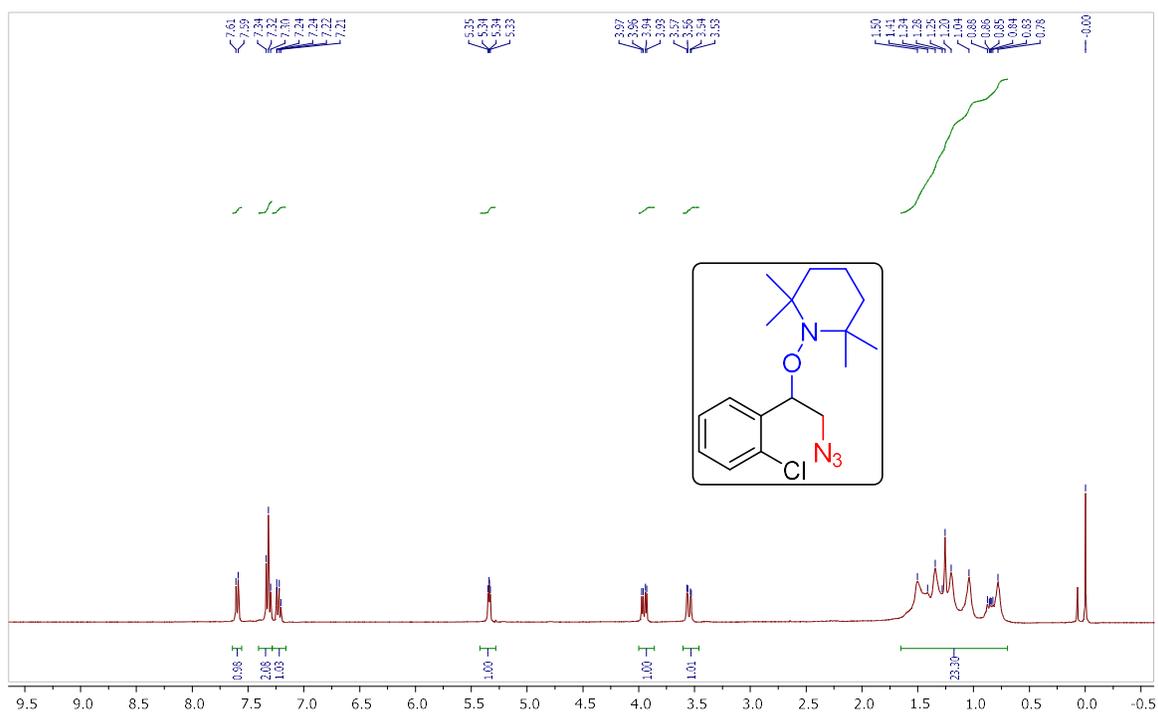


## <sup>13</sup>C NMR Spectrum of compound **11** in CDCl<sub>3</sub>

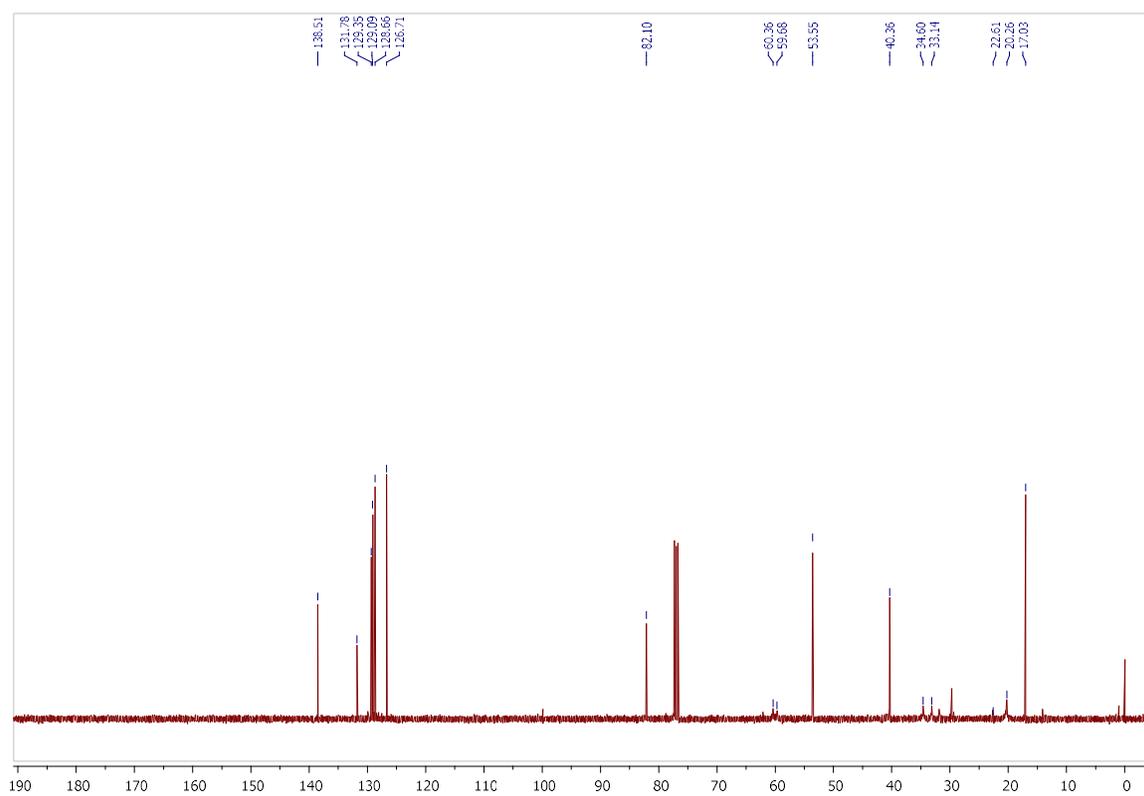


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **12** in $\text{CDCl}_3$

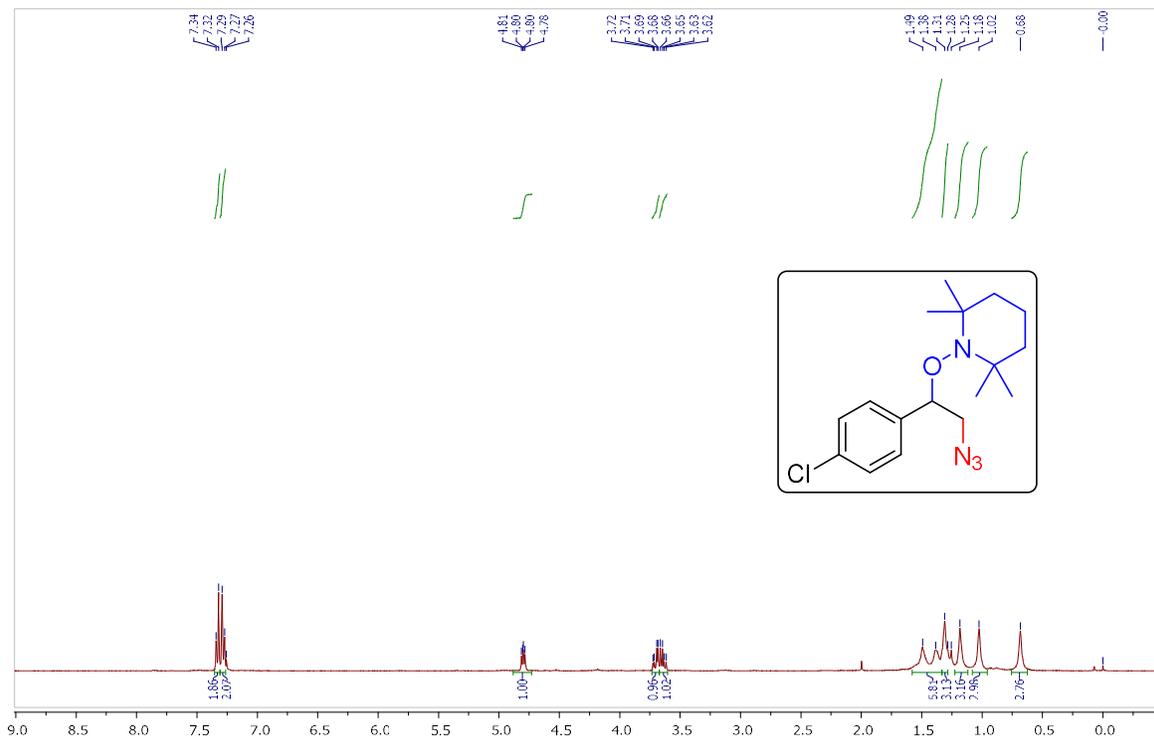


## $^{13}\text{C}$ NMR Spectrum of compound **12** in $\text{CDCl}_3$

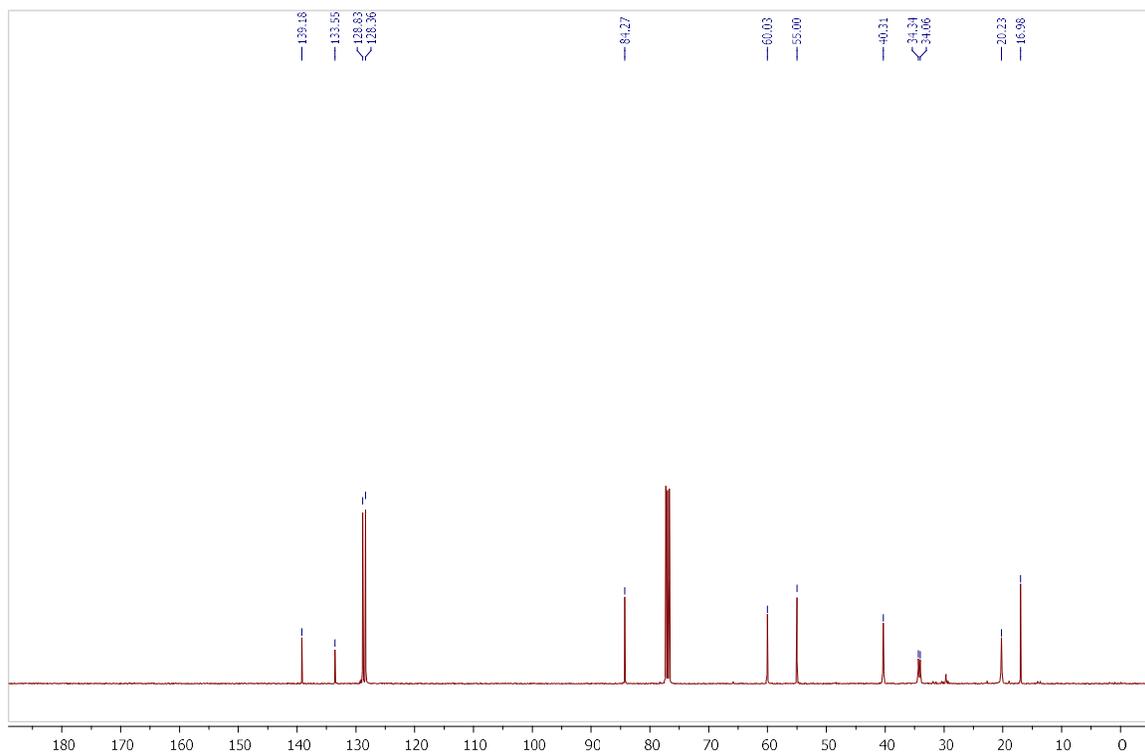


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **13** in $\text{CDCl}_3$

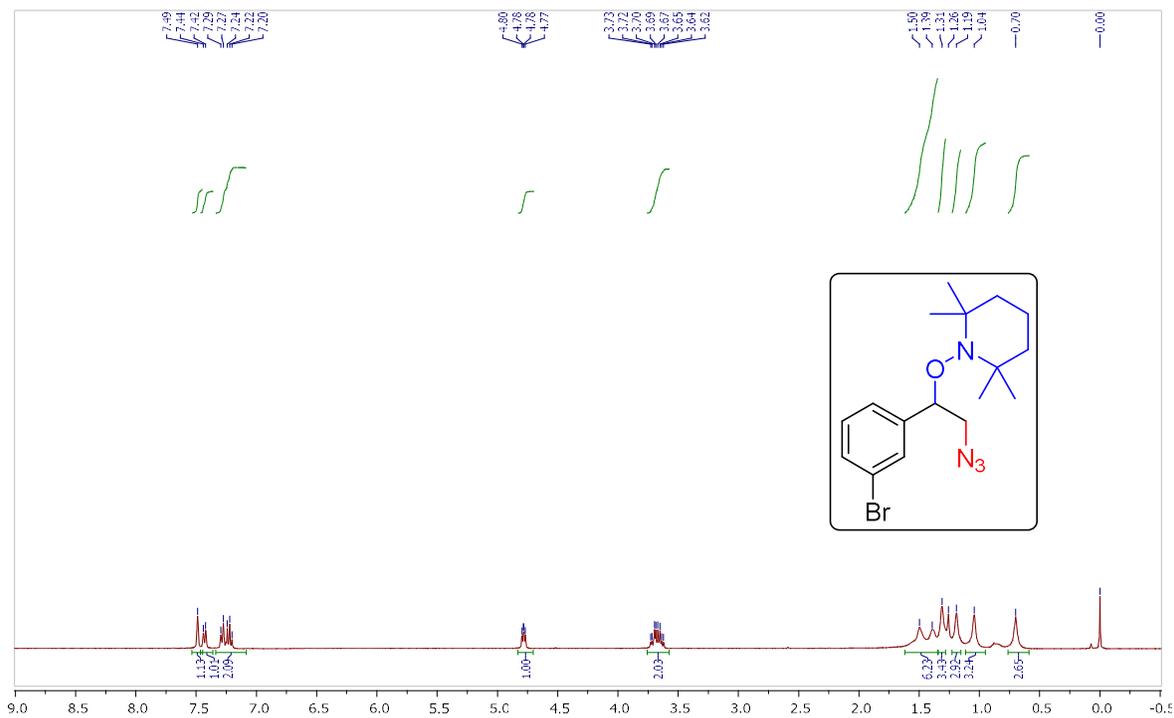


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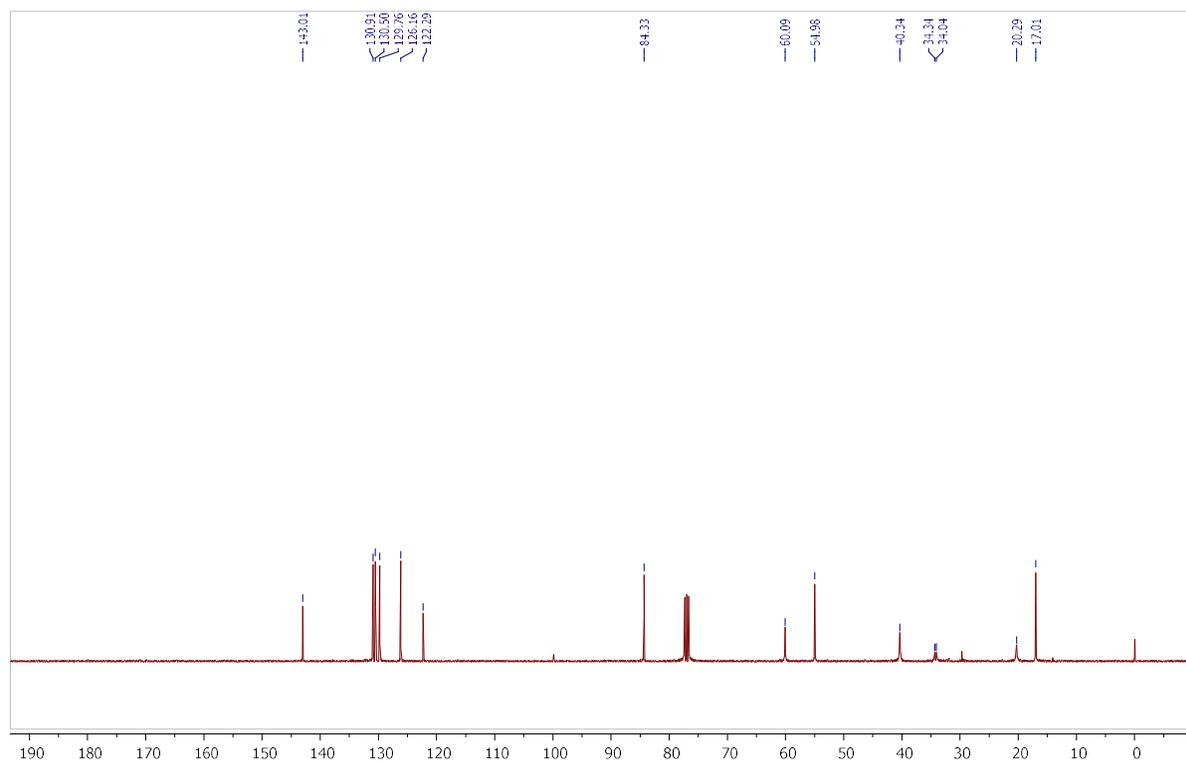


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **14** in CDCl<sub>3</sub>

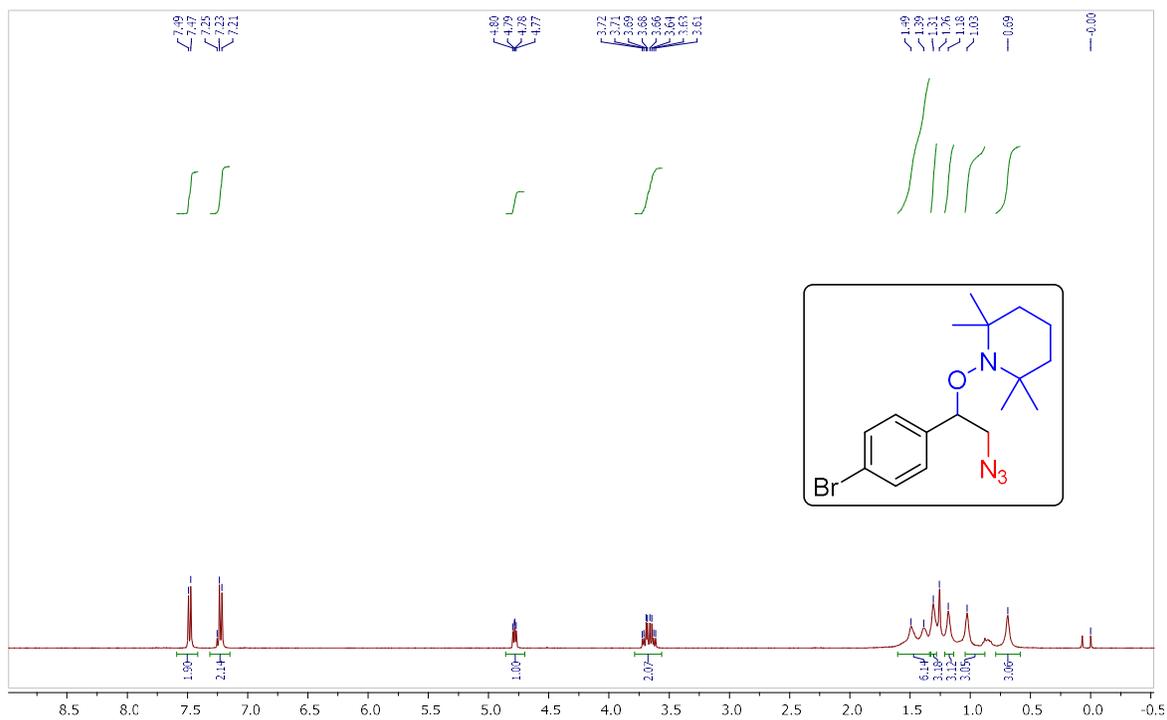


## <sup>13</sup>C NMR Spectrum of compound **14** in CDCl<sub>3</sub>

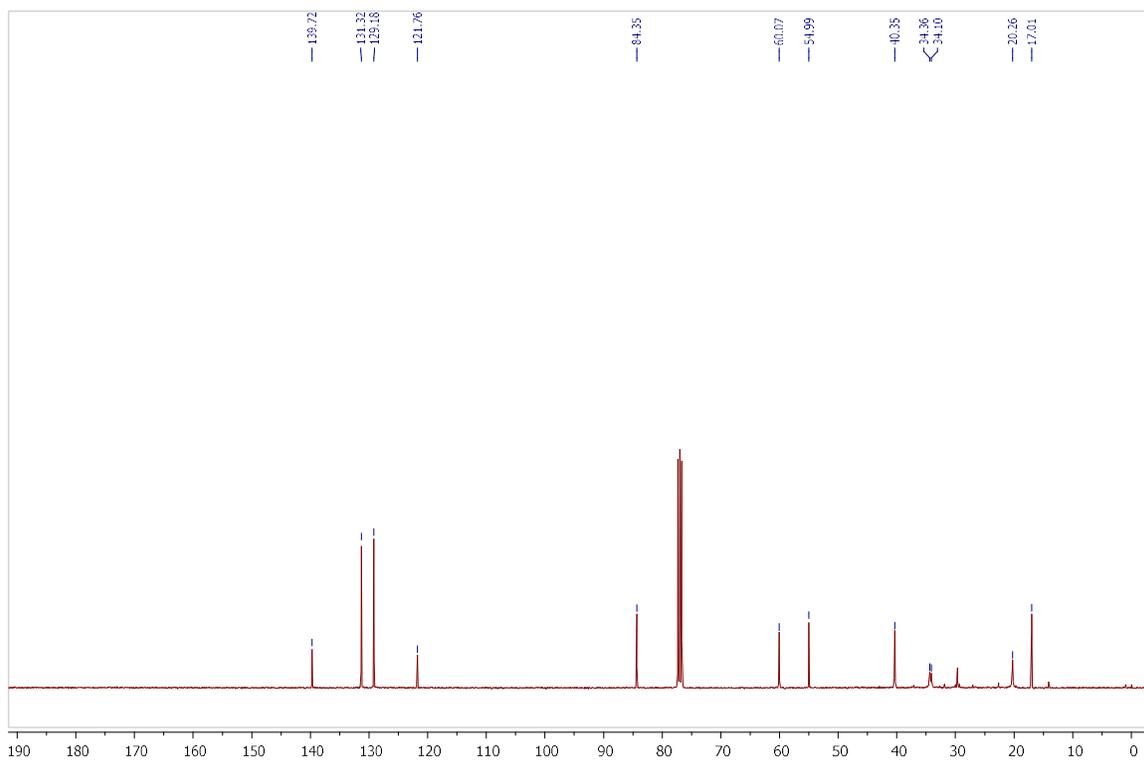


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **15** in CDCl<sub>3</sub>

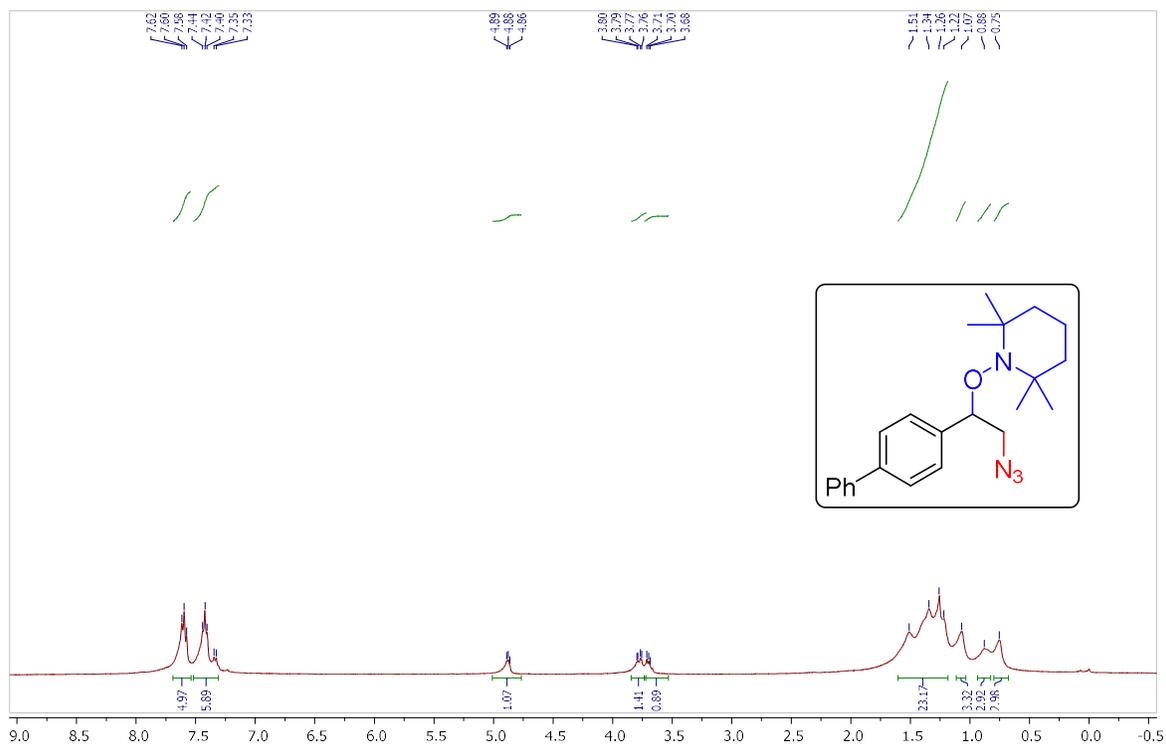


<sup>13</sup>C NMR Spectrum of compound **15** in CDCl<sub>3</sub>

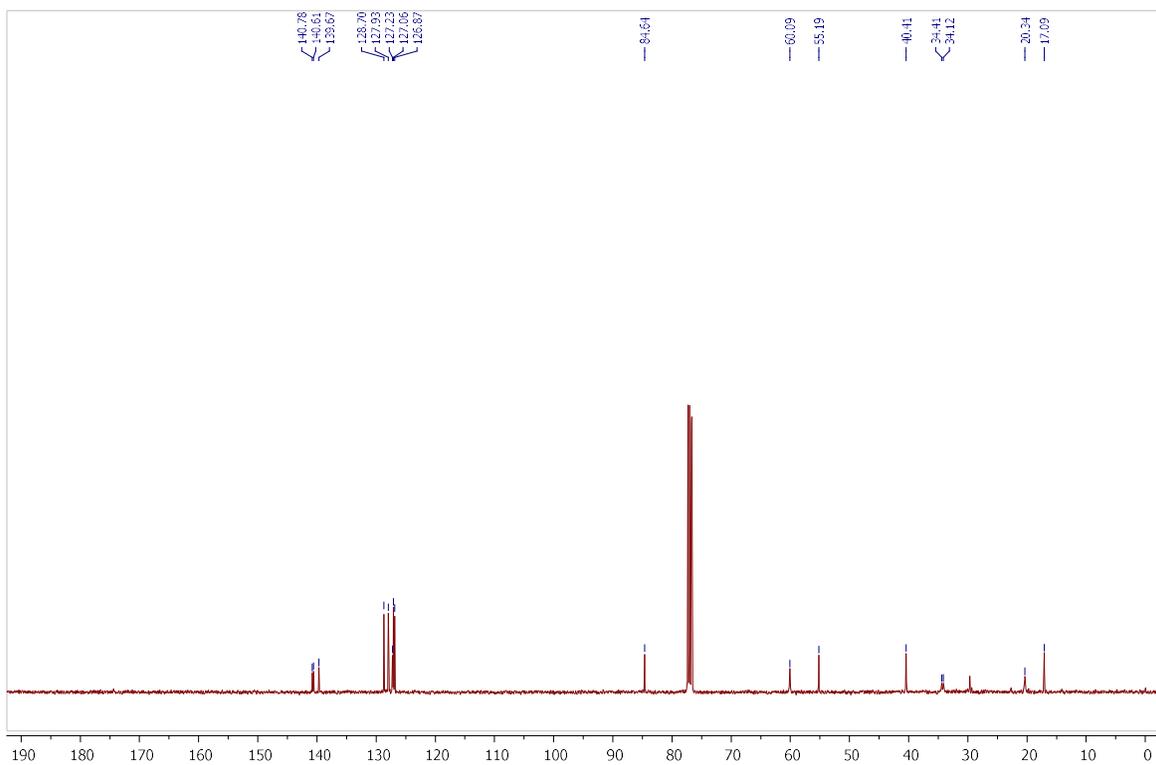


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **16** in CDCl<sub>3</sub>

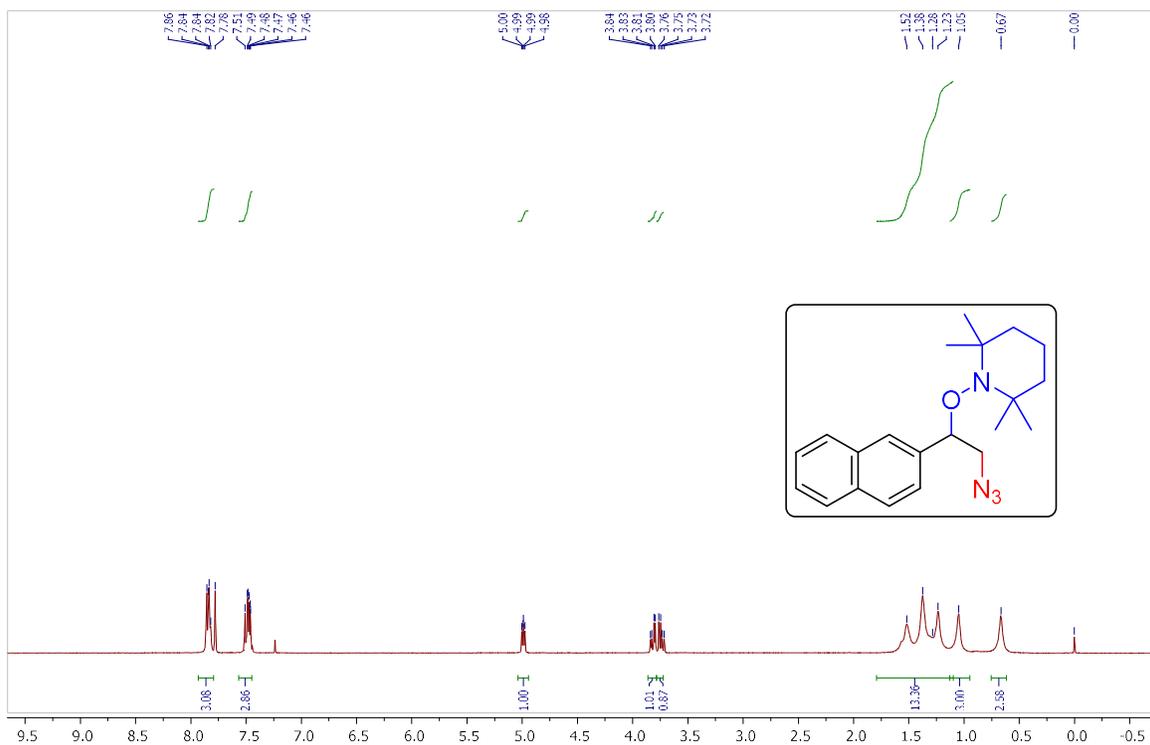


## <sup>13</sup>C NMR Spectrum of compound **16** in CDCl<sub>3</sub>

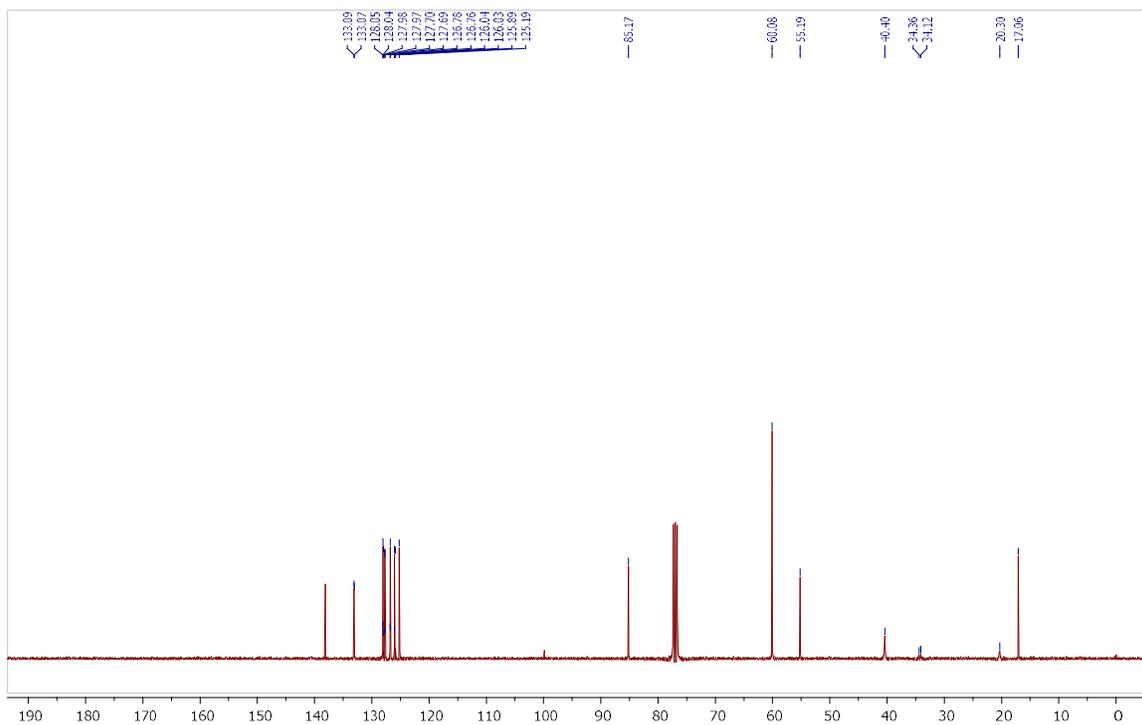


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **17** in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR Spectrum of compound **17** in  $\text{CDCl}_3$

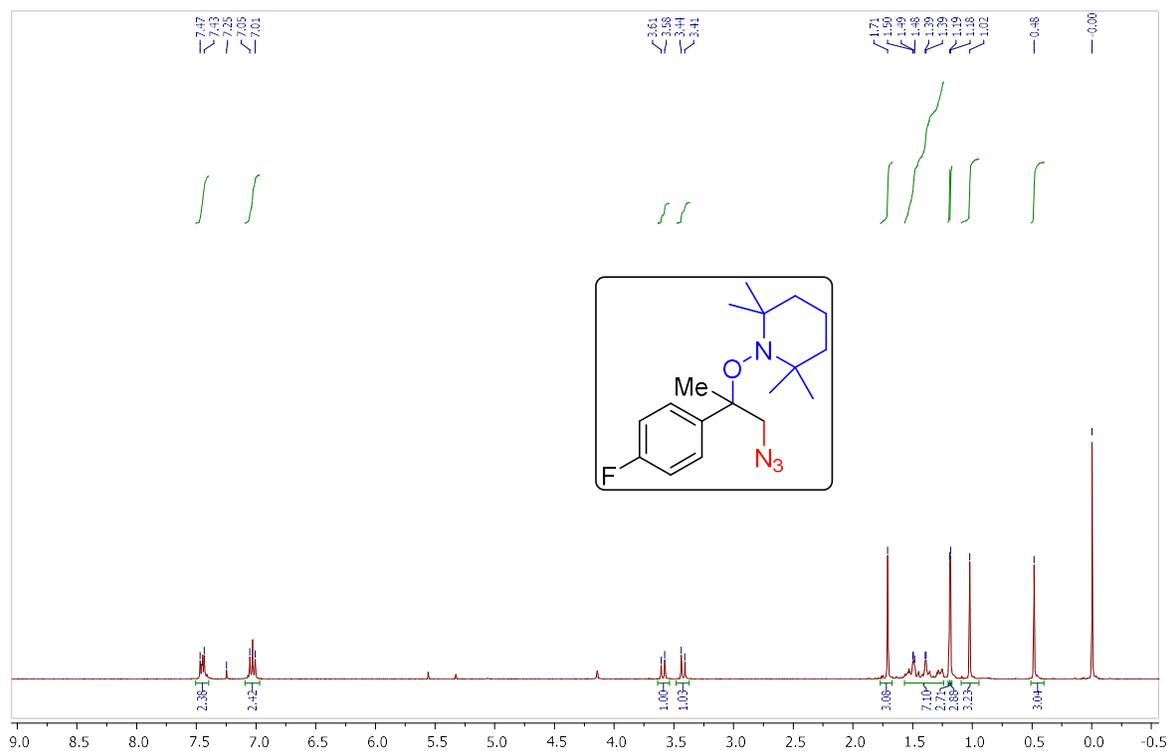




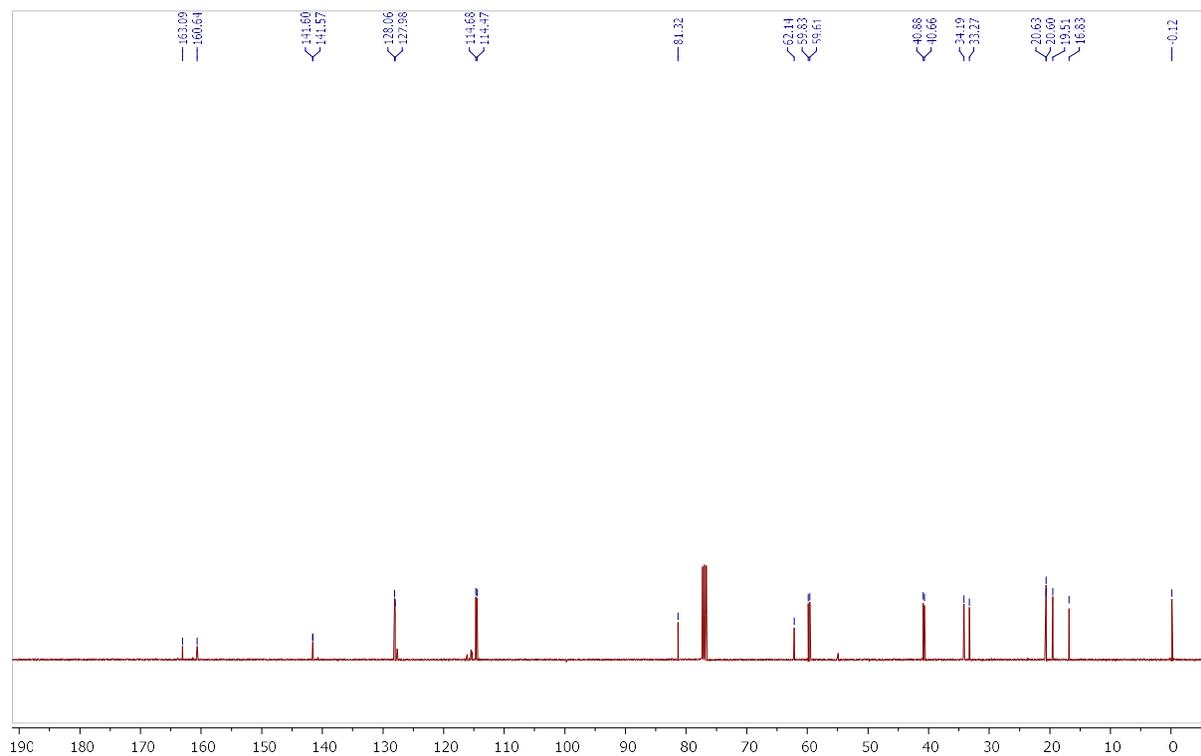


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **20** in $\text{CDCl}_3$

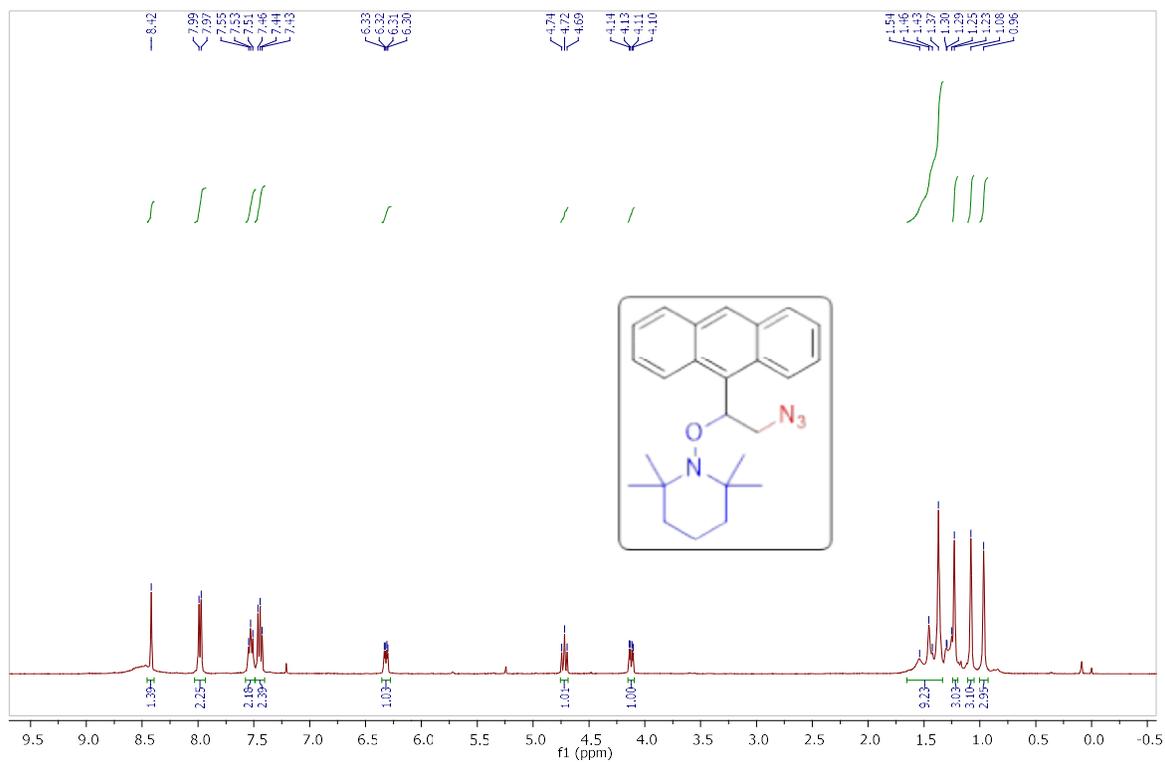


## $^{13}\text{C}$ NMR Spectrum of compound **20** in $\text{CDCl}_3$

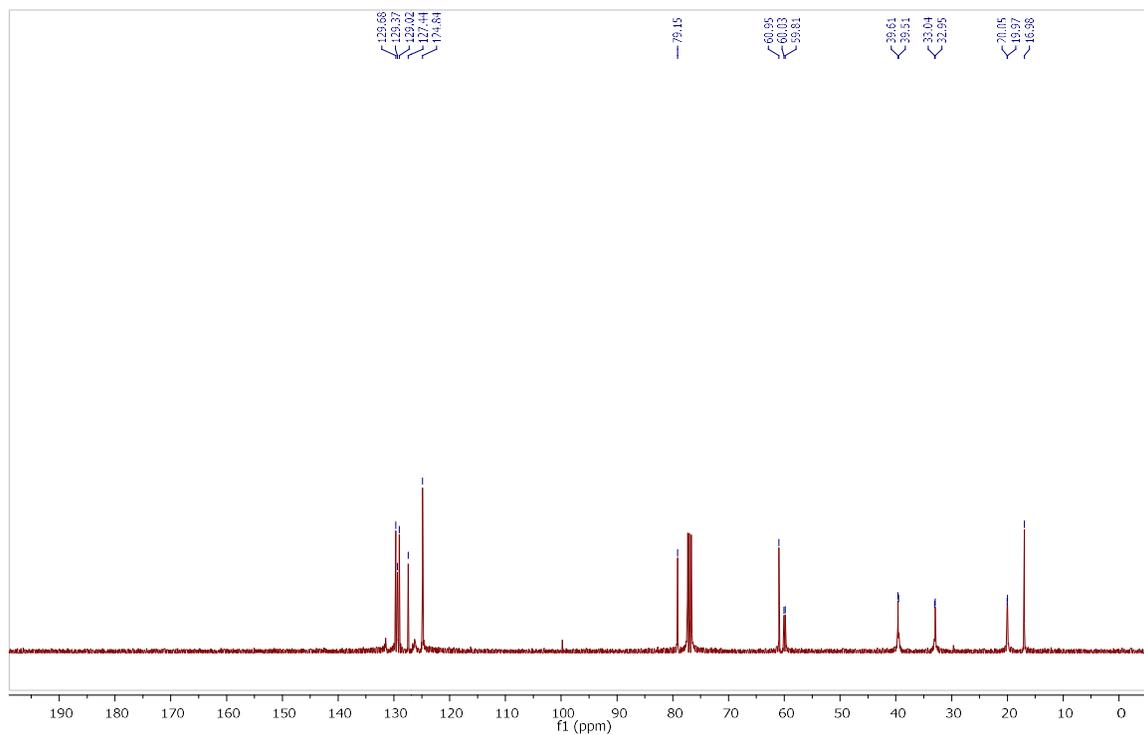


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **21** in $\text{CDCl}_3$

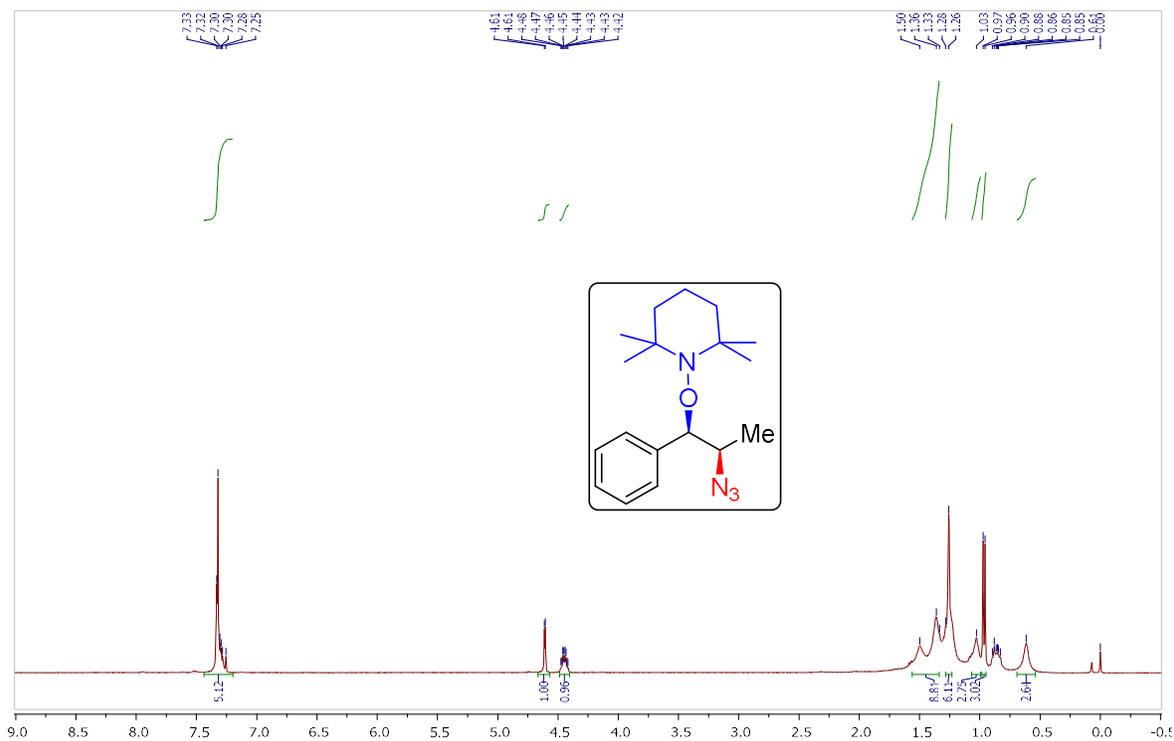


## $^{13}\text{C}$ NMR Spectrum of compound **21** in $\text{CDCl}_3$

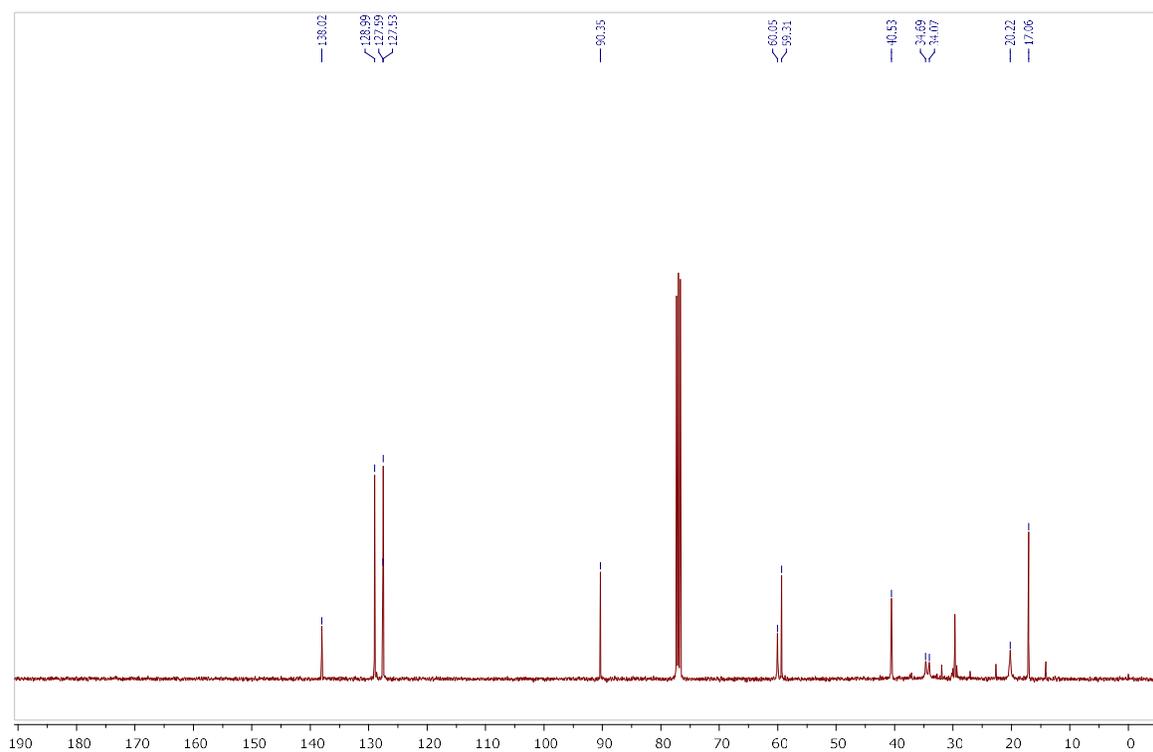


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **22** in $\text{CDCl}_3$

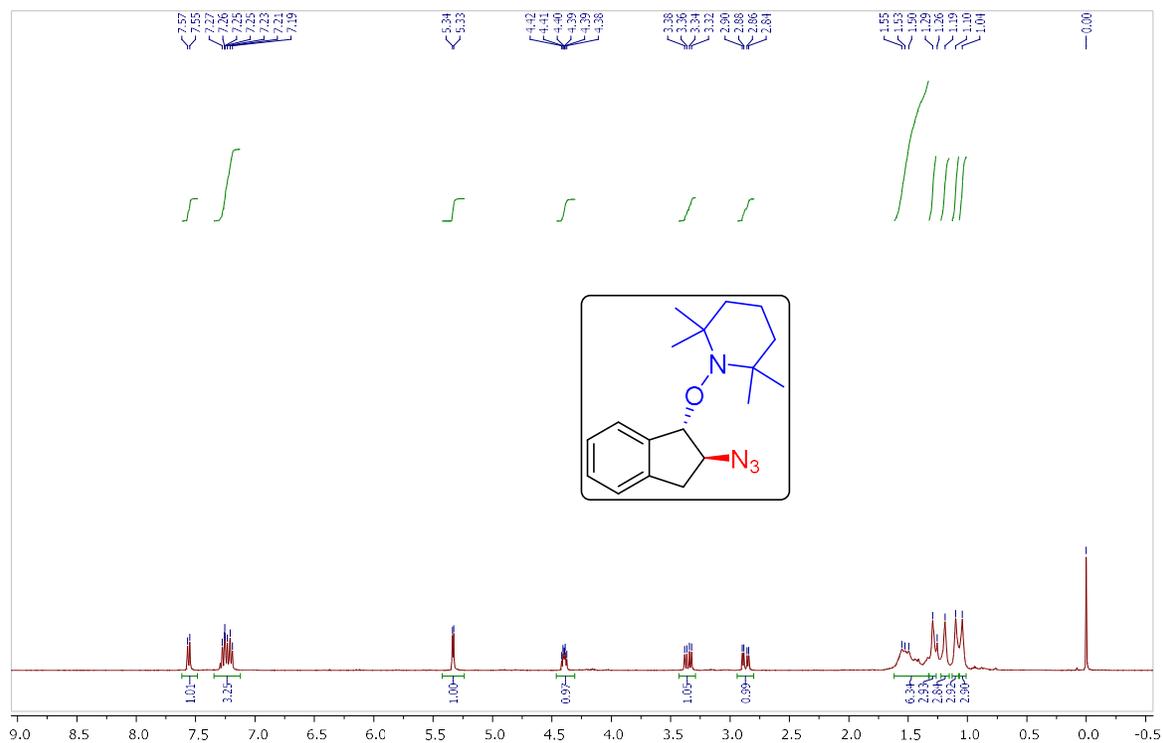


## $^{13}\text{C}$ NMR Spectrum of compound **22** in $\text{CDCl}_3$

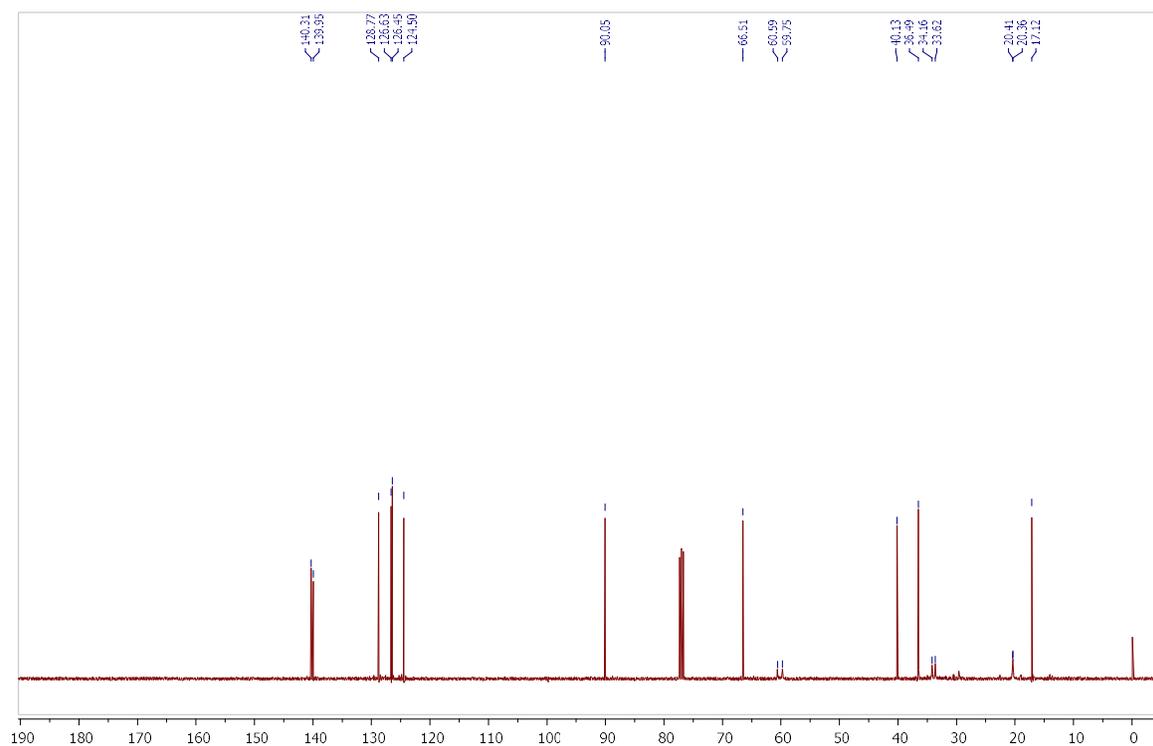


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **23** in $\text{CDCl}_3$

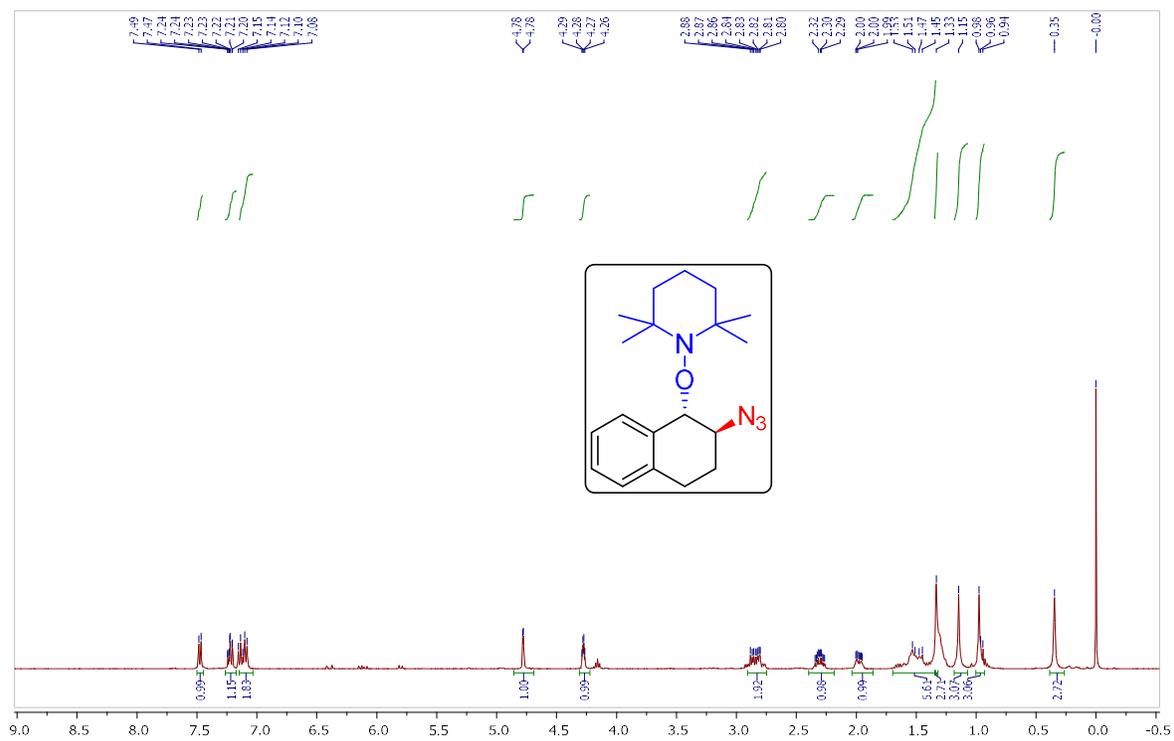


## $^{13}\text{C}$ NMR Spectrum of compound **23** in $\text{CDCl}_3$

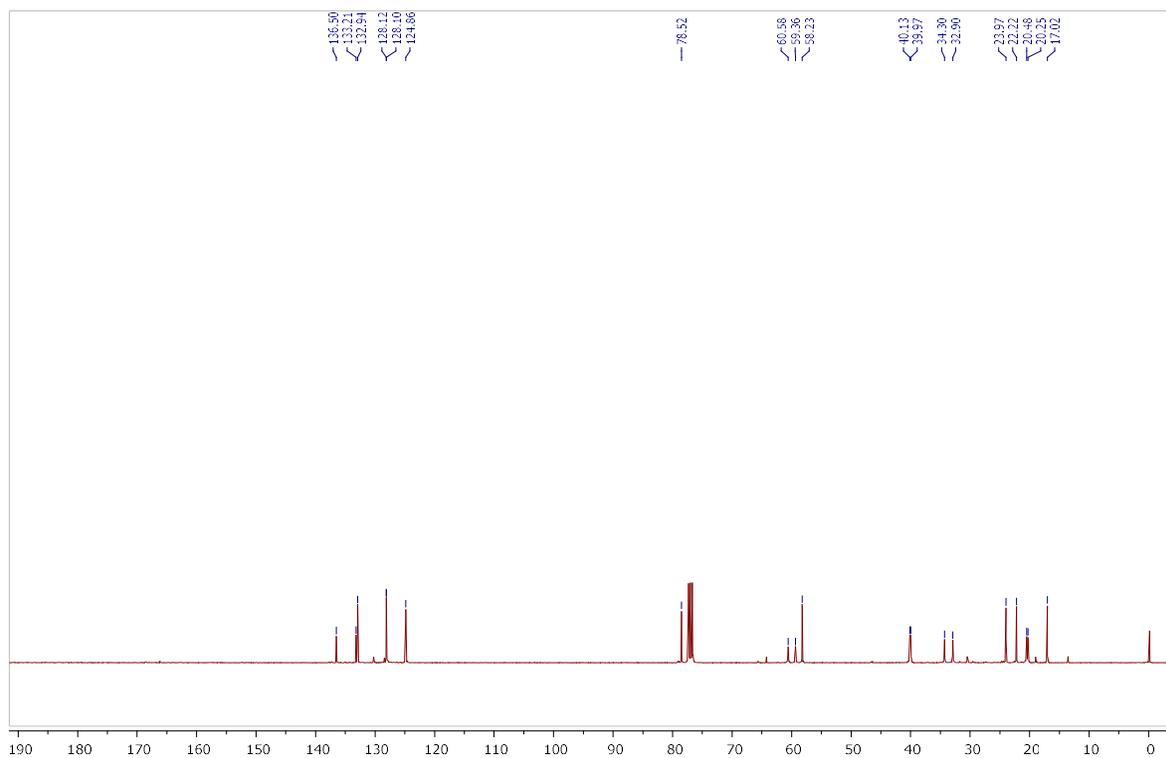


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **24** in CDCl<sub>3</sub>

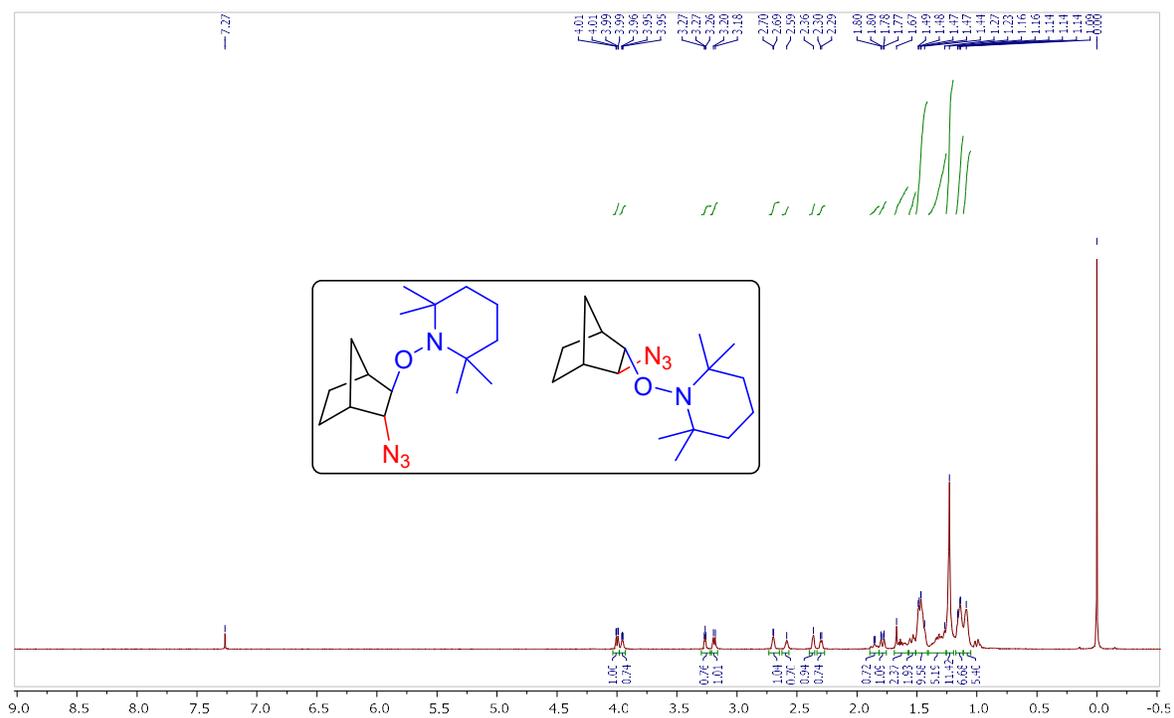


## <sup>13</sup>C NMR Spectrum of compound **24** in CDCl<sub>3</sub>

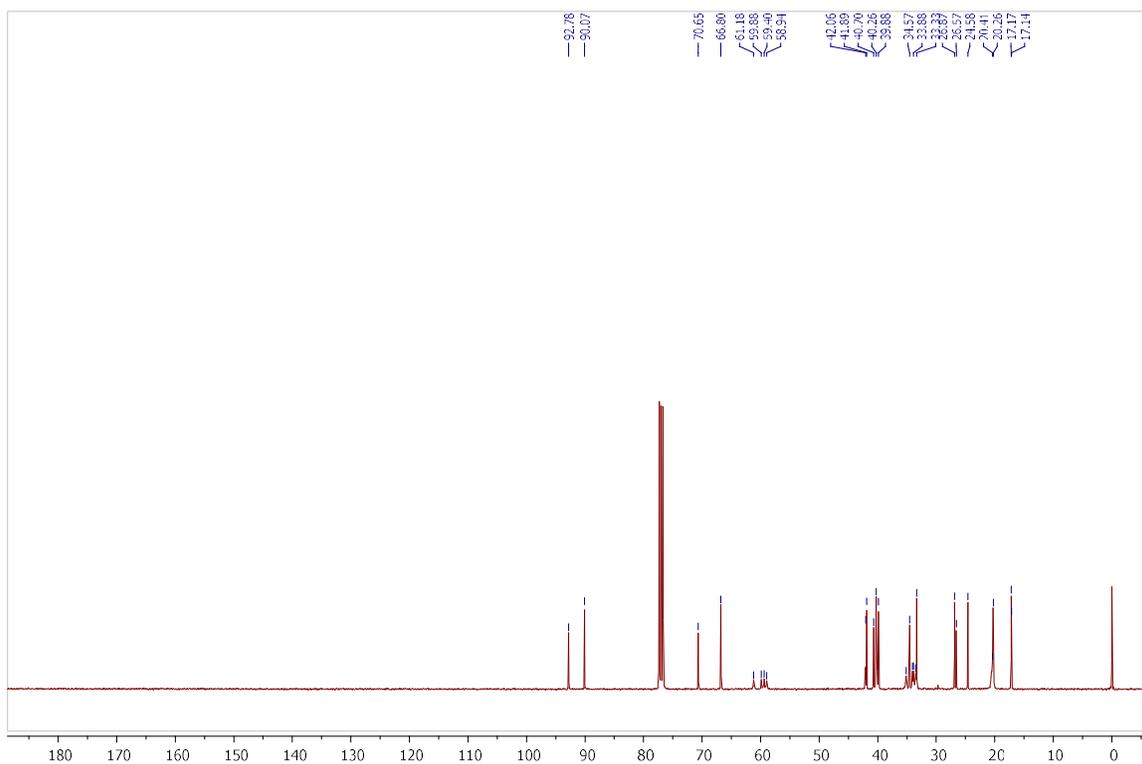


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **25** in CDCl<sub>3</sub>

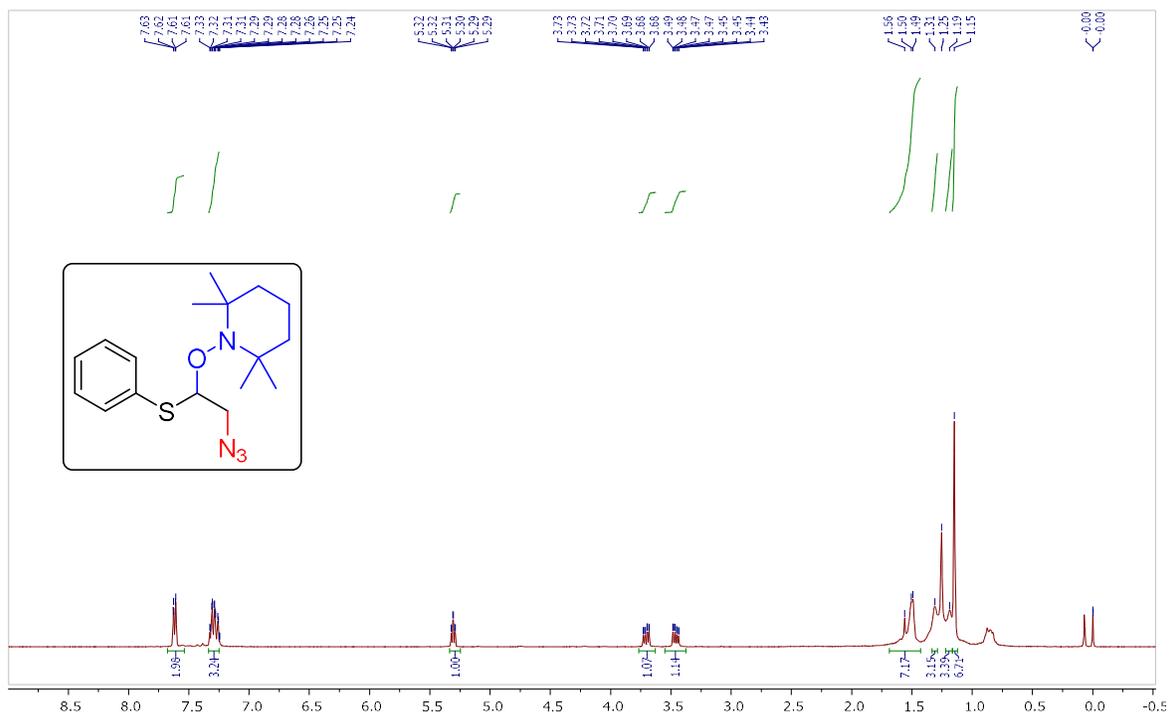


## <sup>13</sup>C NMR Spectrum of compound **25** in CDCl<sub>3</sub>

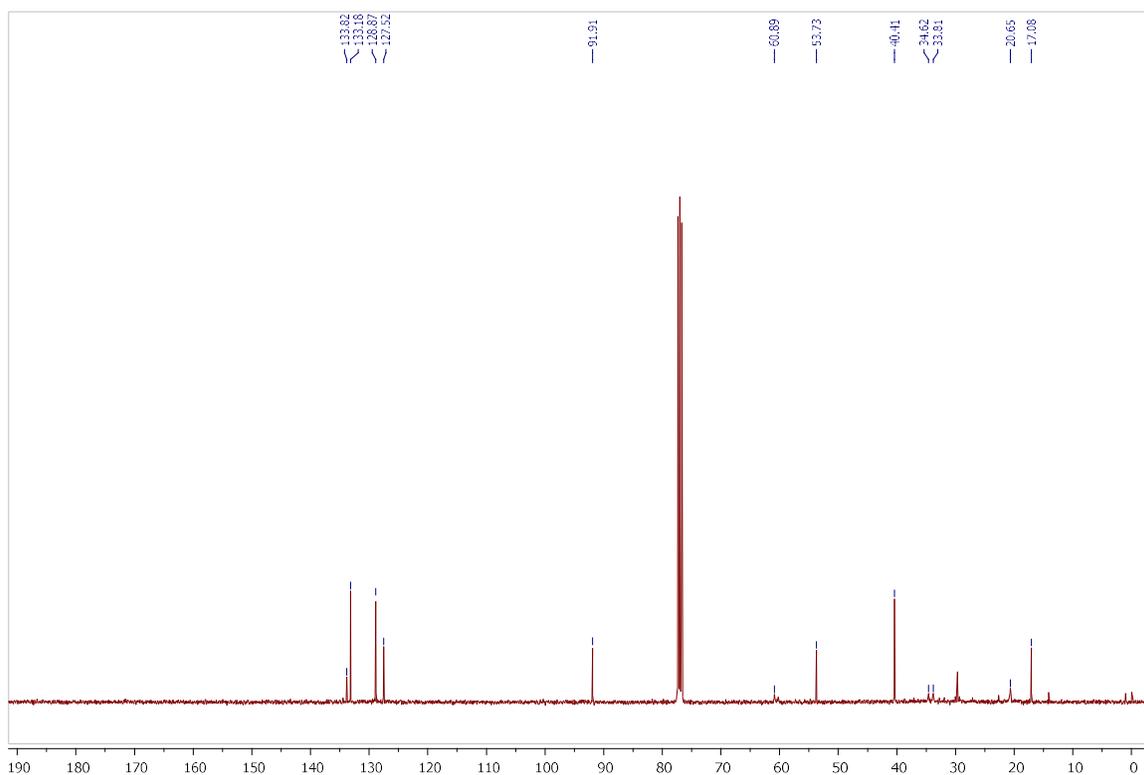


# SUPPORTING INFORMATION

## <sup>1</sup>H NMR Spectrum of compound **26** in CDCl<sub>3</sub>

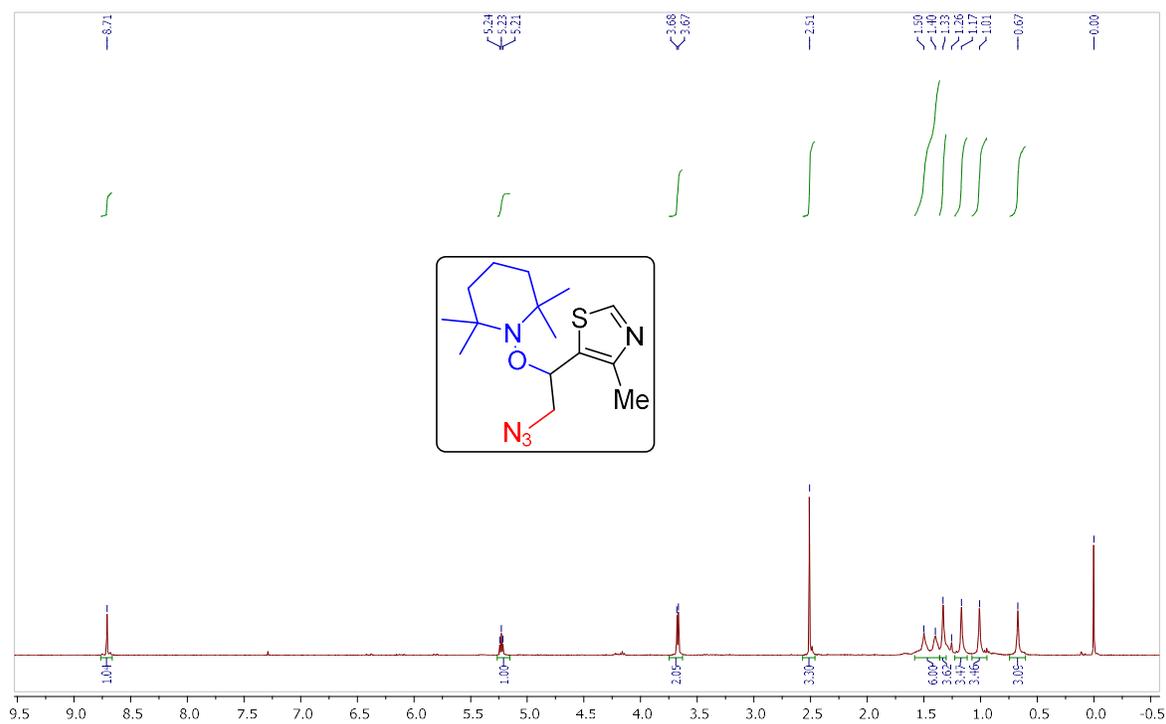


## <sup>13</sup>C NMR Spectrum of compound **26** in CDCl<sub>3</sub>

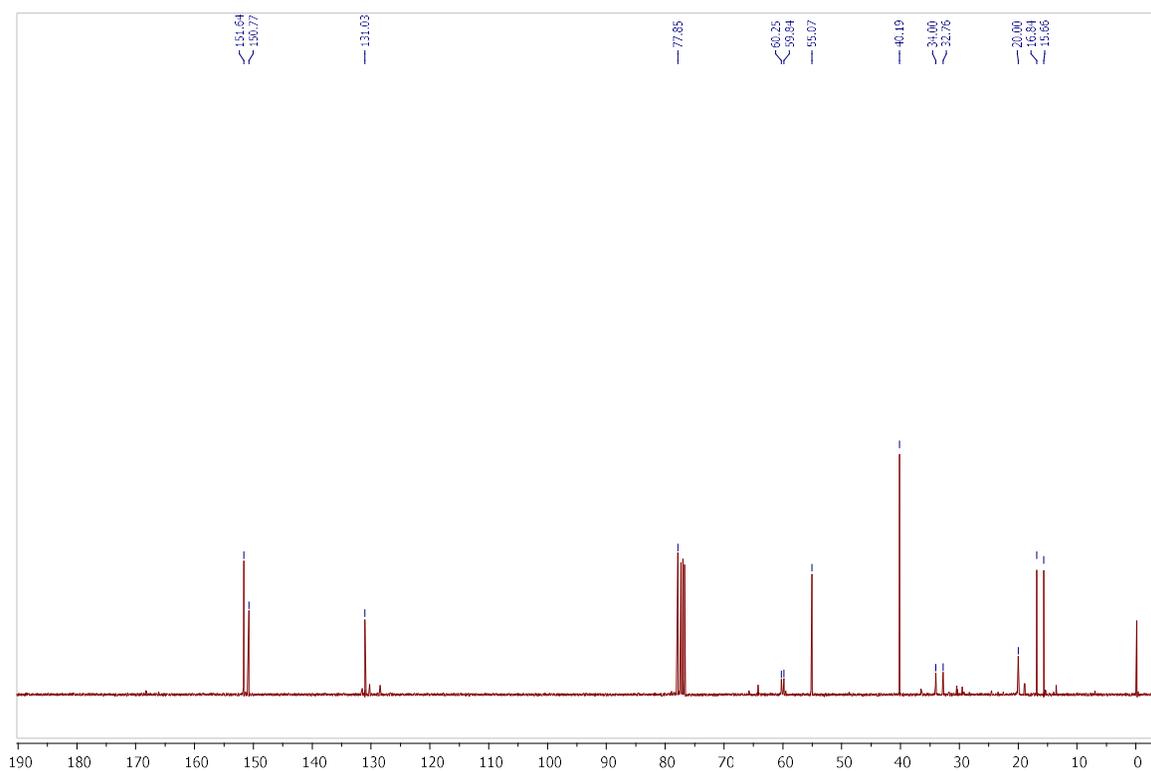


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **27** in $\text{CDCl}_3$

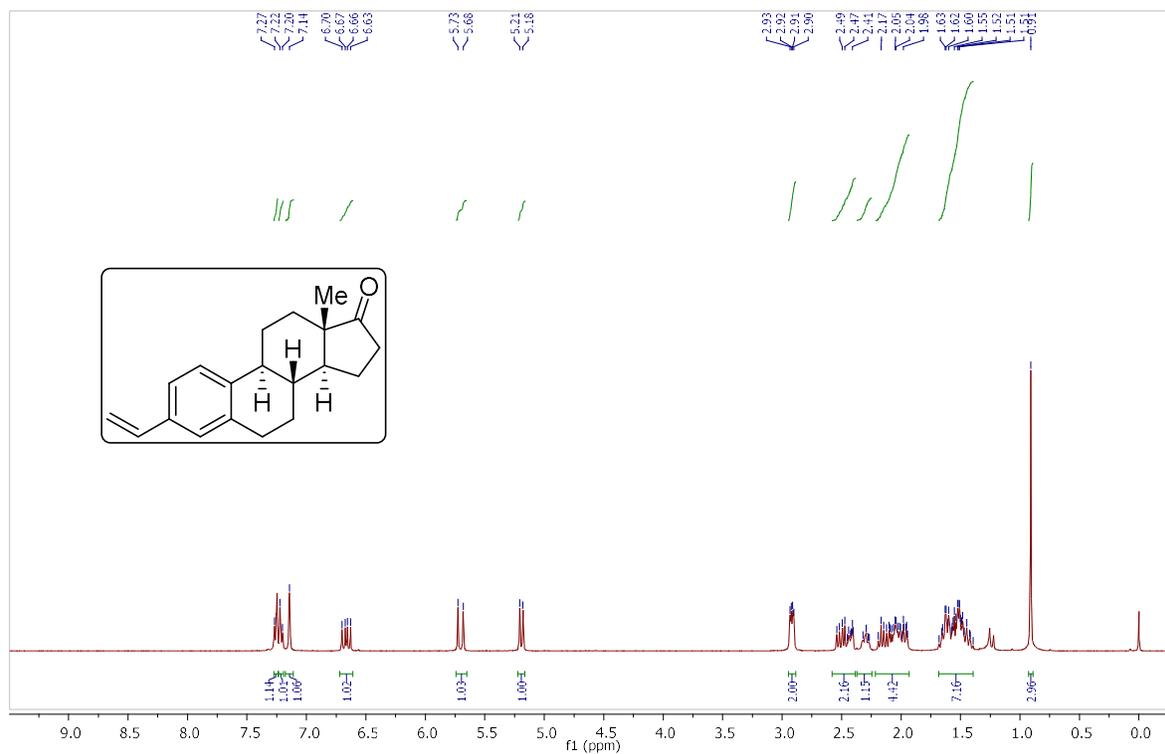


## $^{13}\text{C}$ NMR Spectrum of compound **27** in $\text{CDCl}_3$

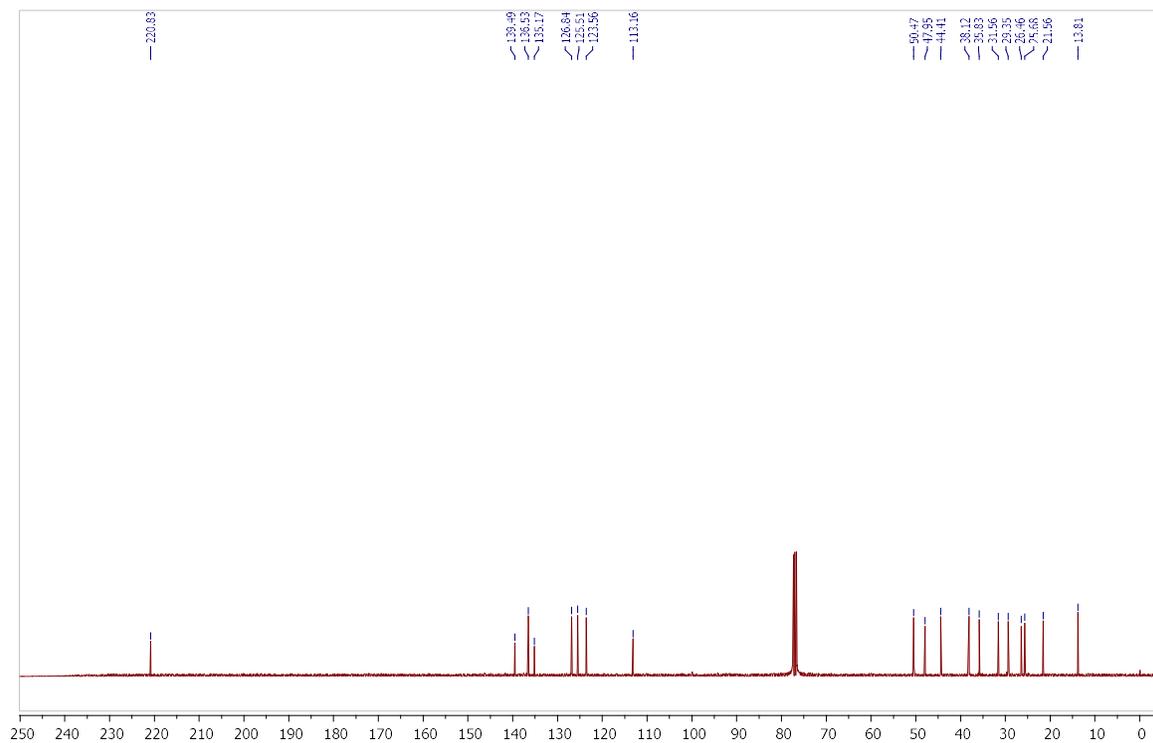


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **vinyl-estrone** in $\text{CDCl}_3$

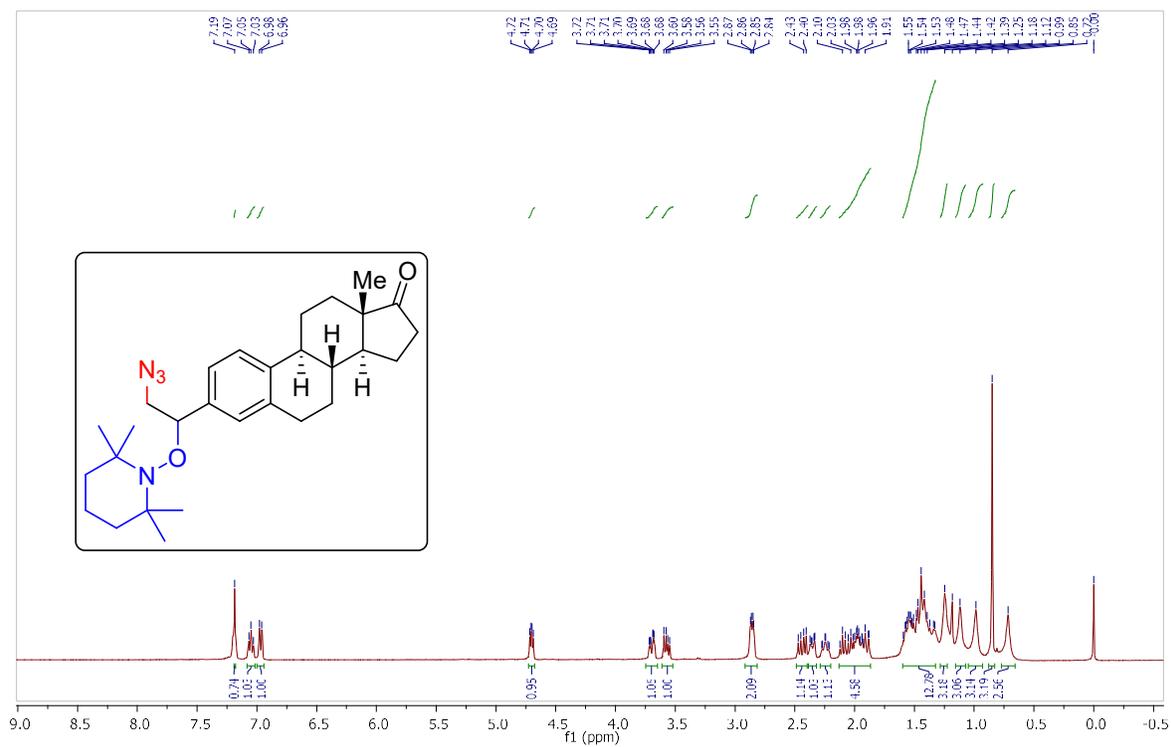


## $^{13}\text{C}$ NMR Spectrum of compound **vinyl-estrone** in $\text{CDCl}_3$

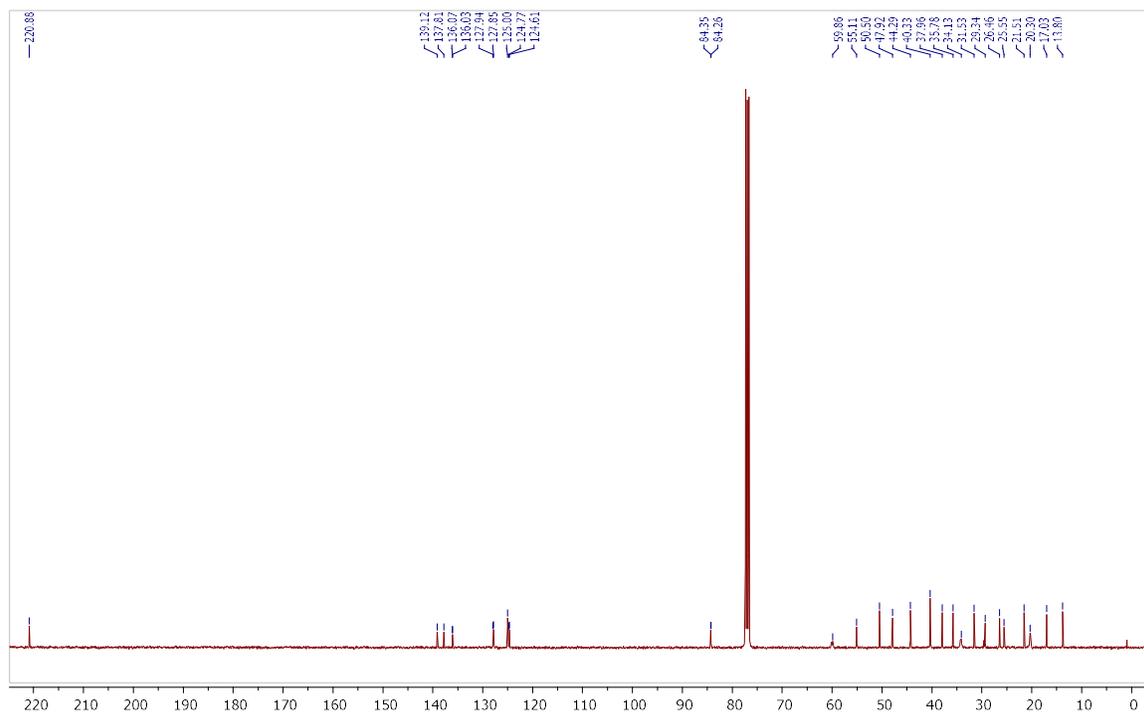


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **28** in $\text{CDCl}_3$



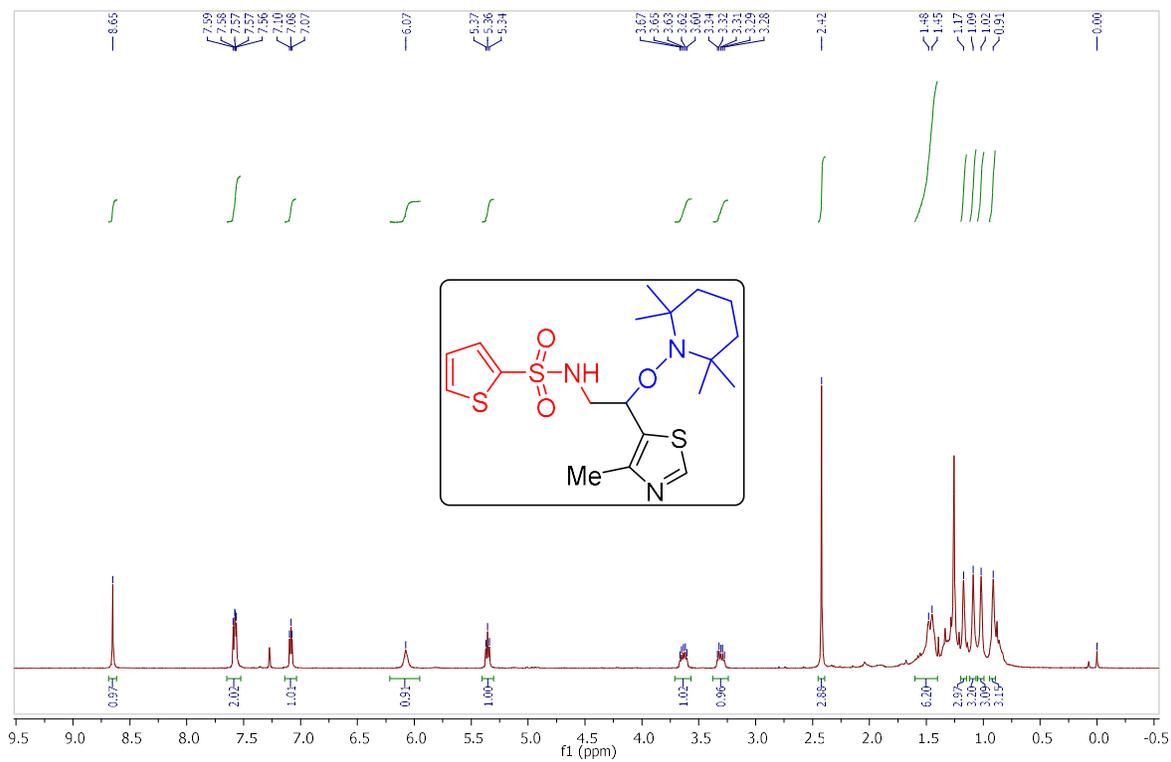
## $^{13}\text{C}$ NMR Spectrum of compound **28** in $\text{CDCl}_3$



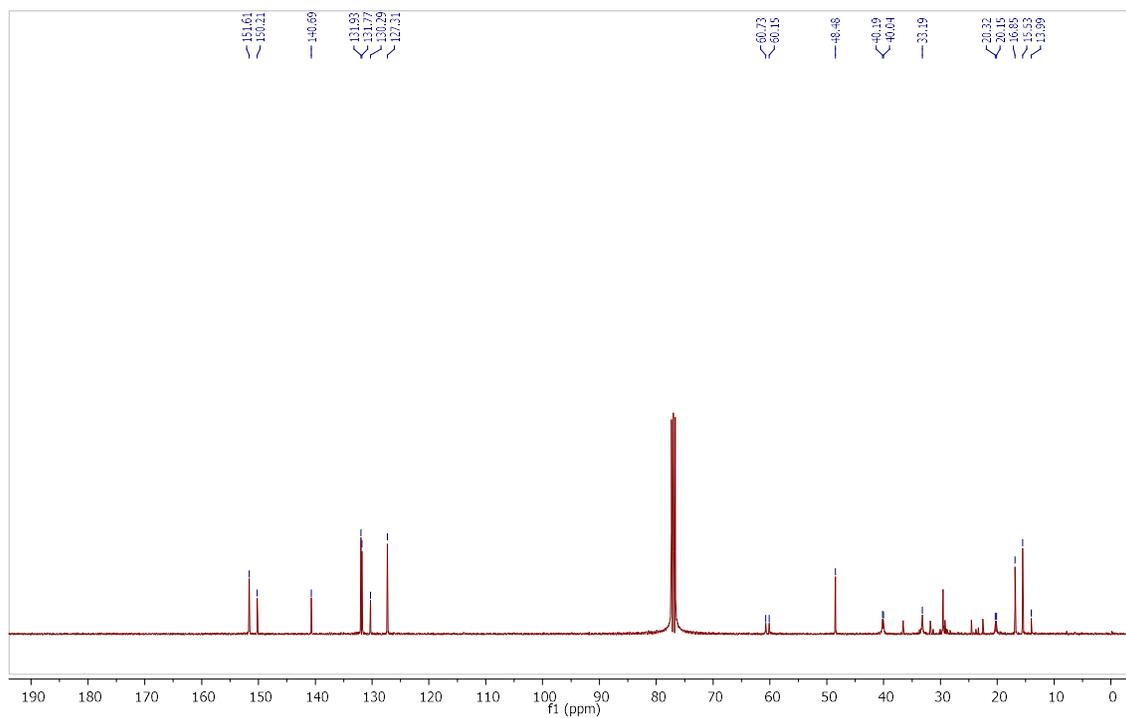


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **30** in $\text{CDCl}_3$

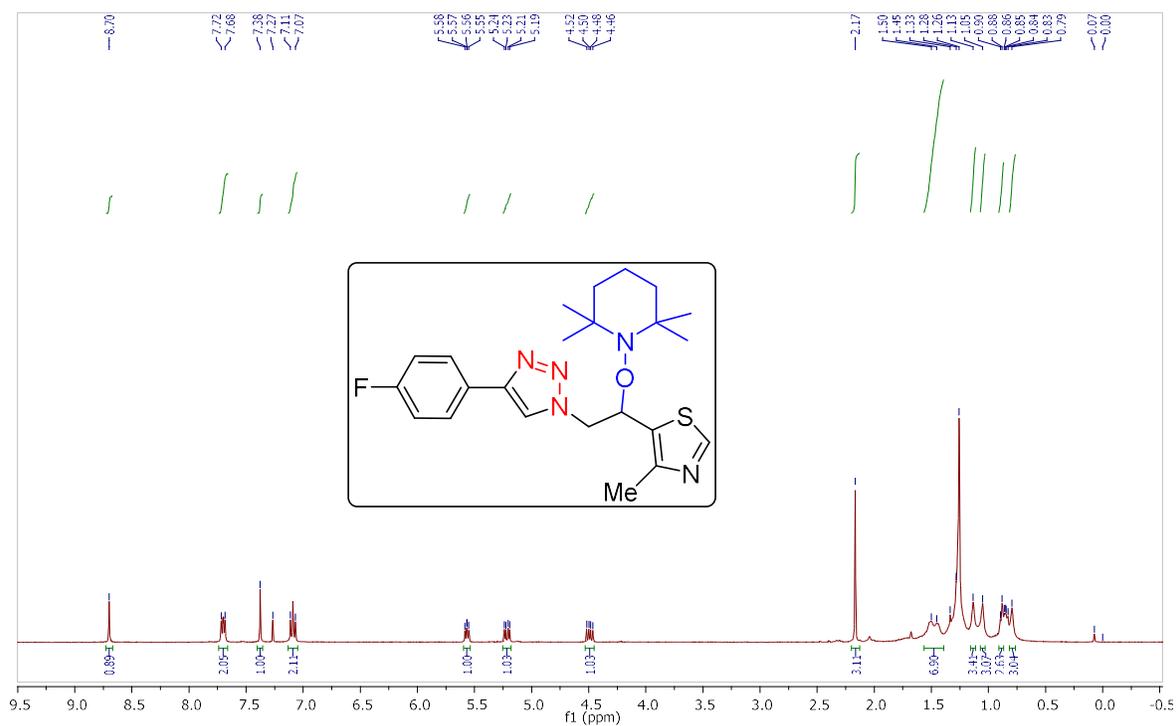


## $^{13}\text{C}$ NMR Spectrum of compound **30** in $\text{CDCl}_3$

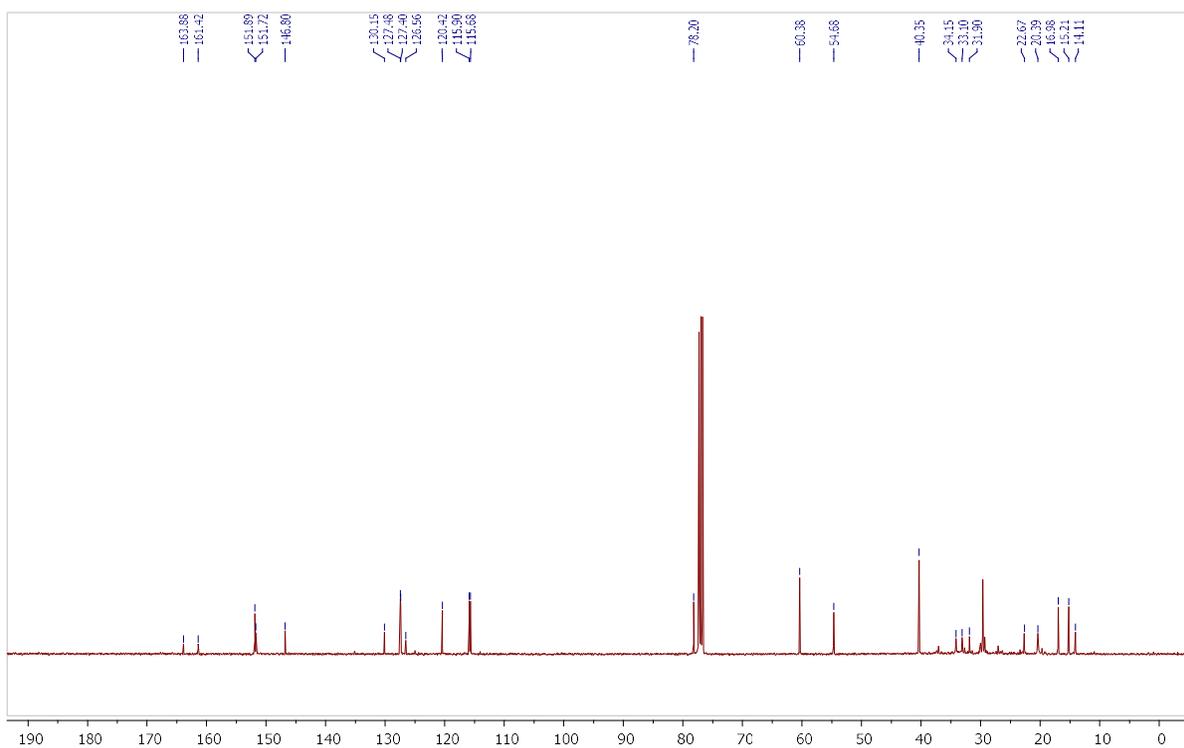


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **31** in $\text{CDCl}_3$

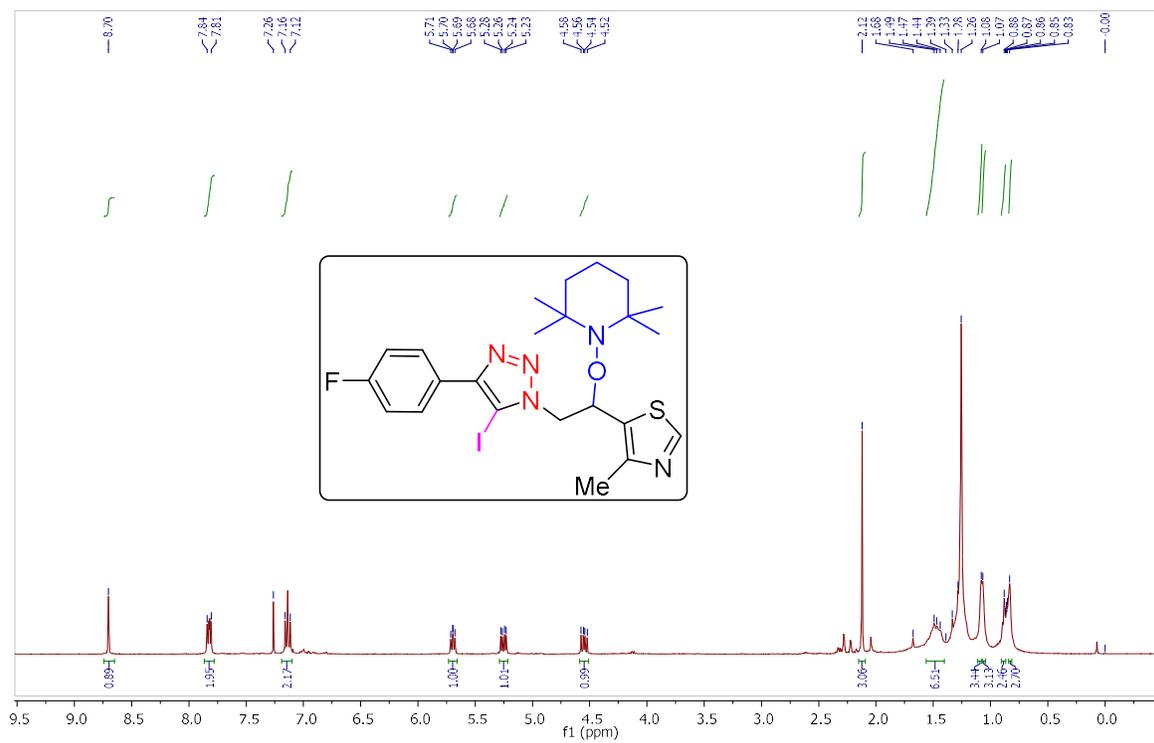


## $^{13}\text{C}$ NMR Spectrum of compound **31** in $\text{CDCl}_3$

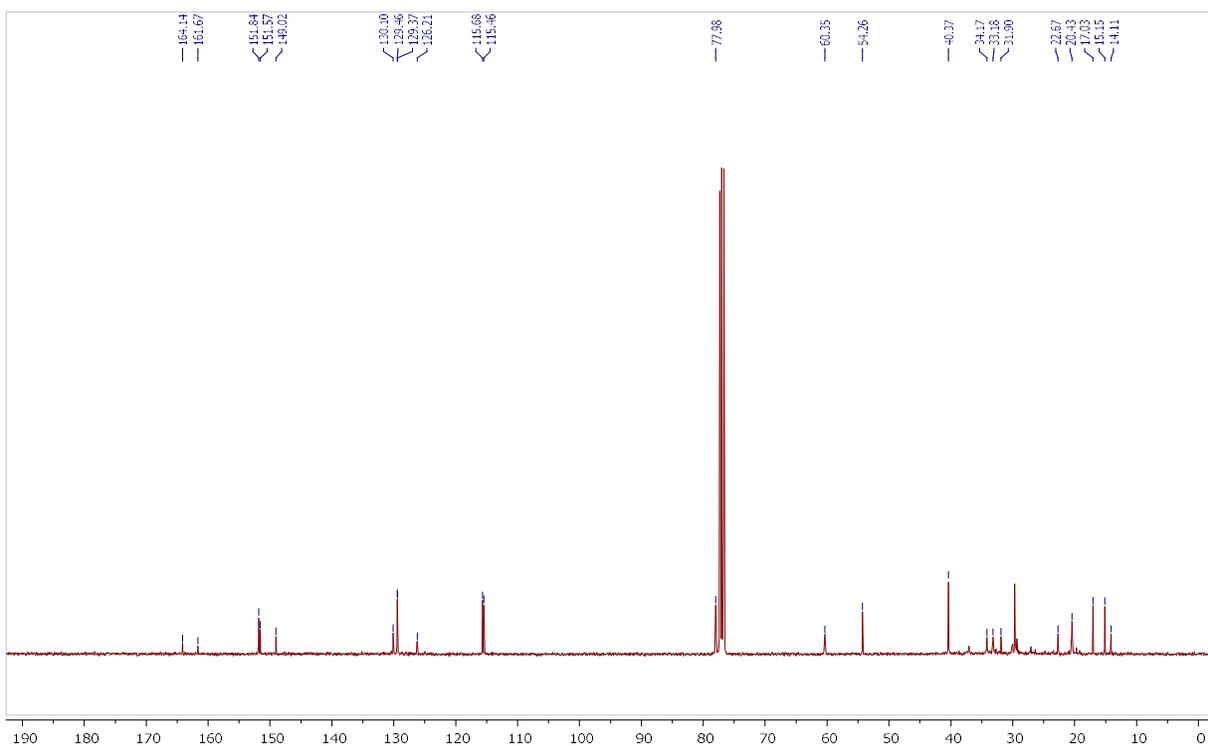


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **32** in $\text{CDCl}_3$

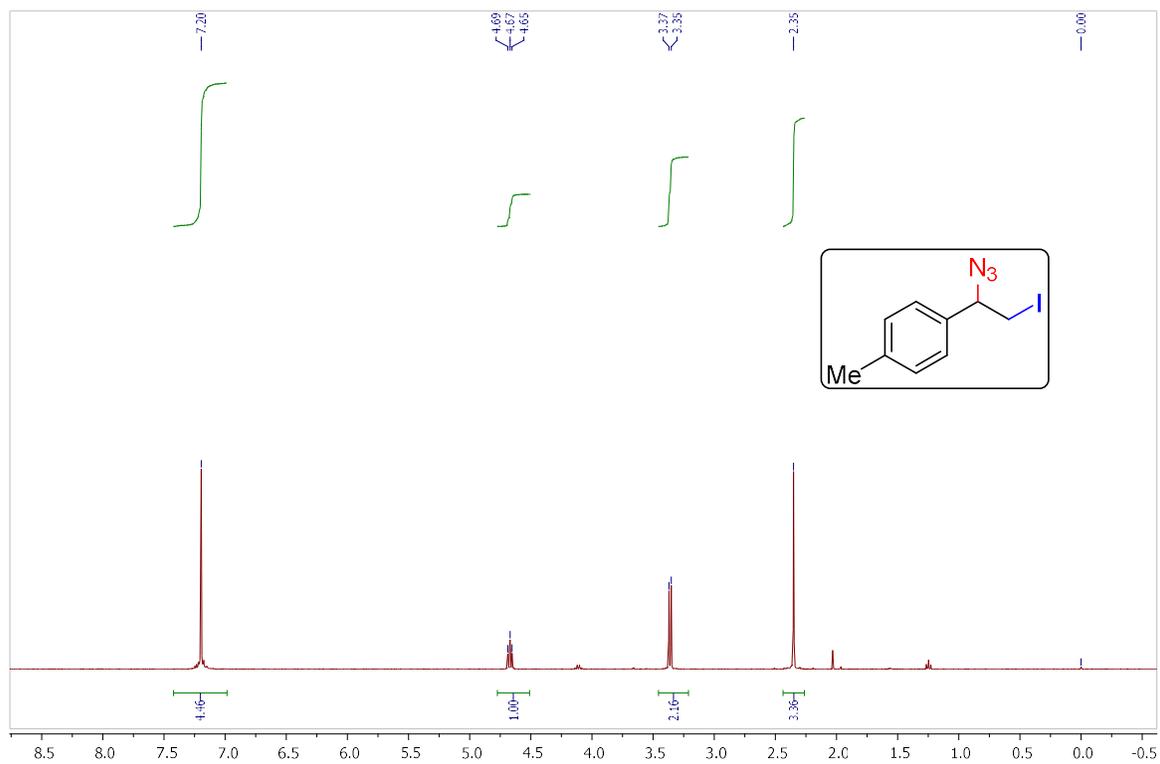


## $^{13}\text{C}$ NMR Spectrum of compound **32** in $\text{CDCl}_3$

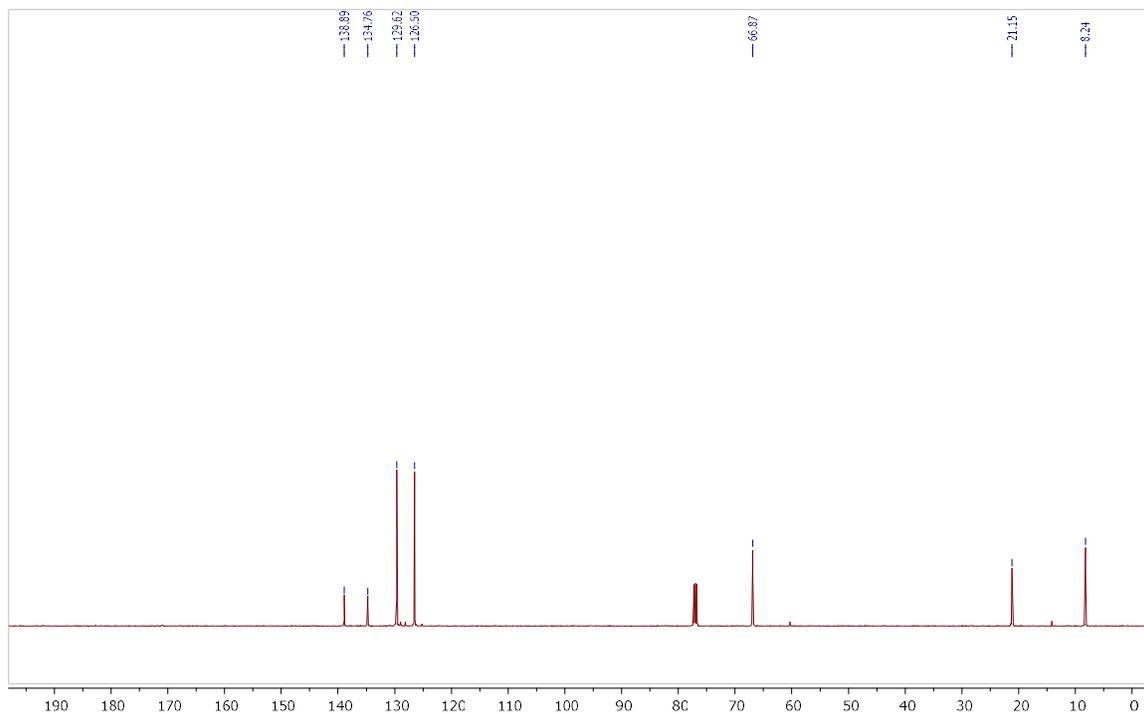


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **33** in $\text{CDCl}_3$

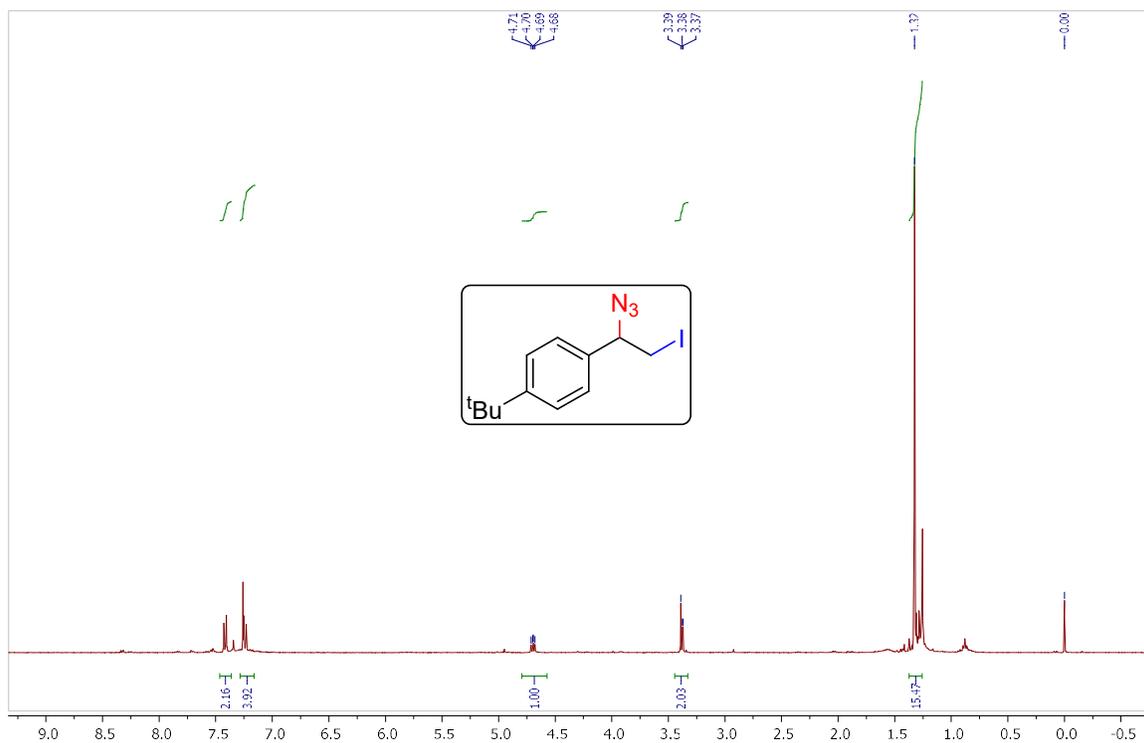


## $^{13}\text{C}$ NMR Spectrum of compound **33** in $\text{CDCl}_3$

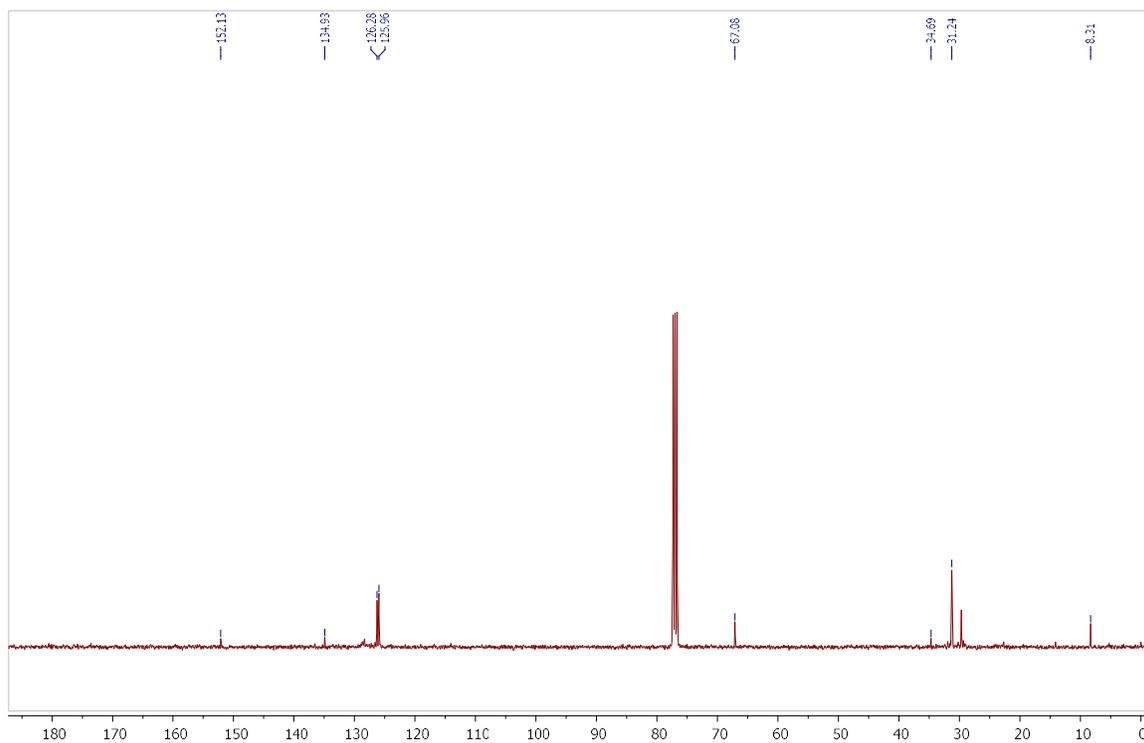


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **34** in  $\text{CDCl}_3$

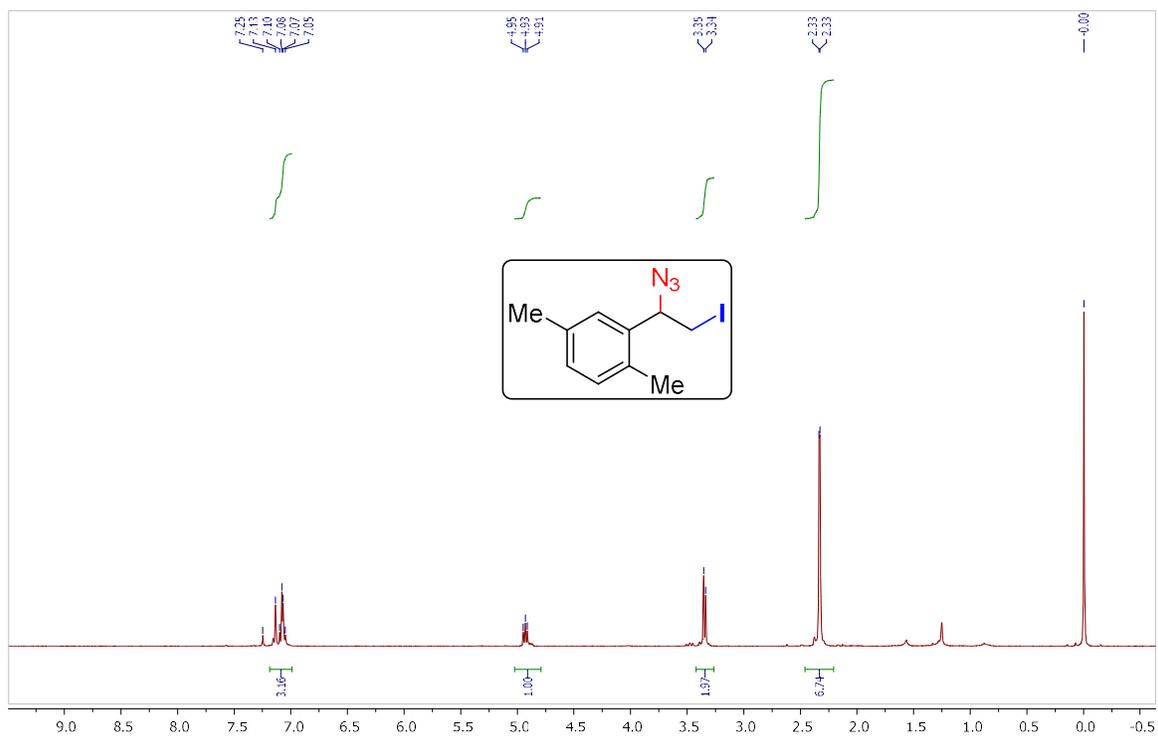


$^{13}\text{C}$  NMR Spectrum of compound **34** in  $\text{CDCl}_3$

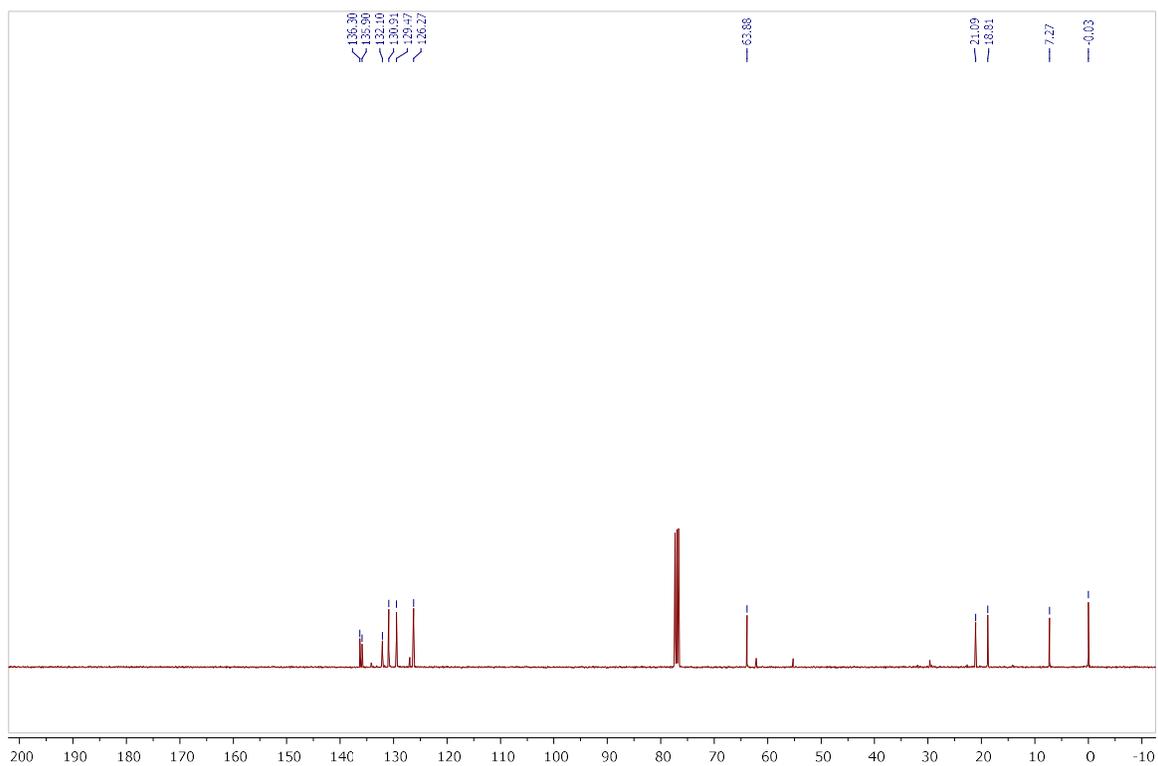


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **35** in $\text{CDCl}_3$

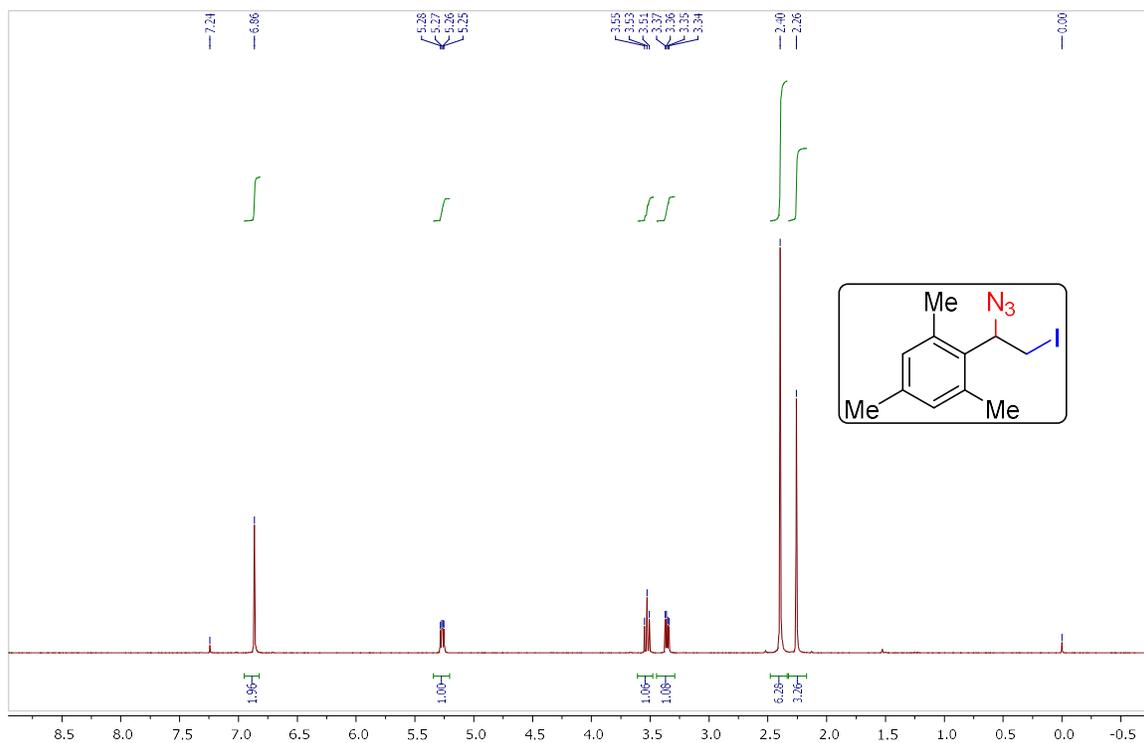


## $^{13}\text{C}$ NMR Spectrum of compound **35** in $\text{CDCl}_3$

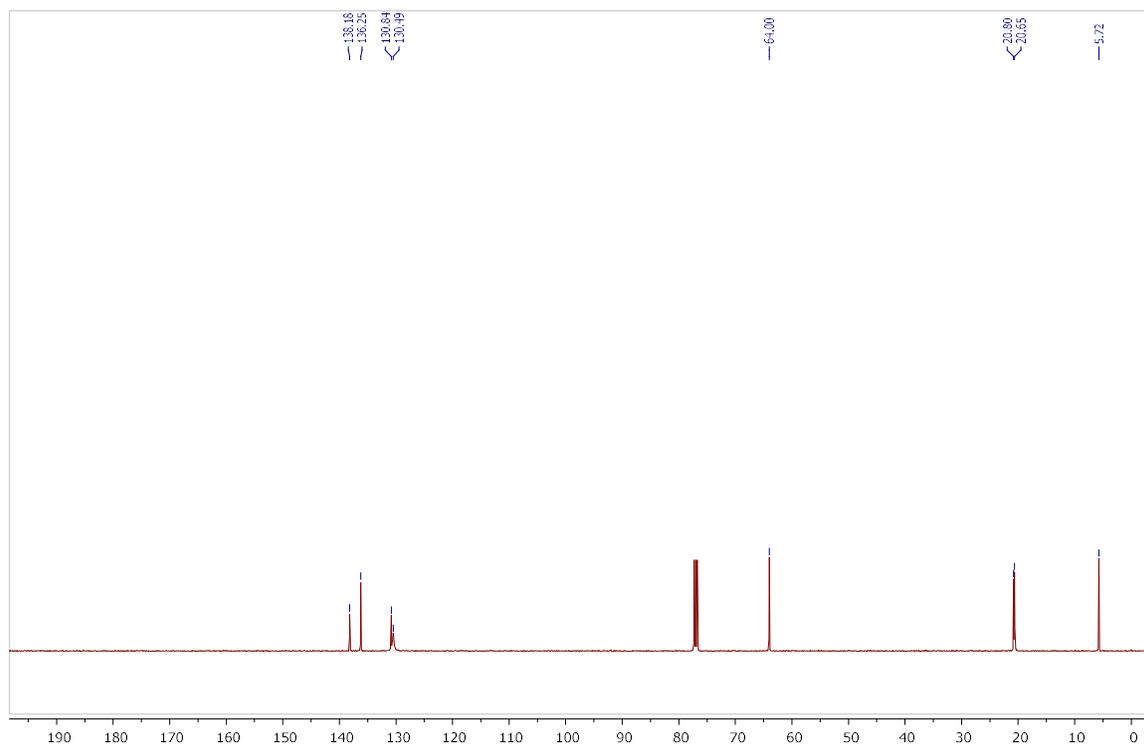


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **36** in  $\text{CDCl}_3$

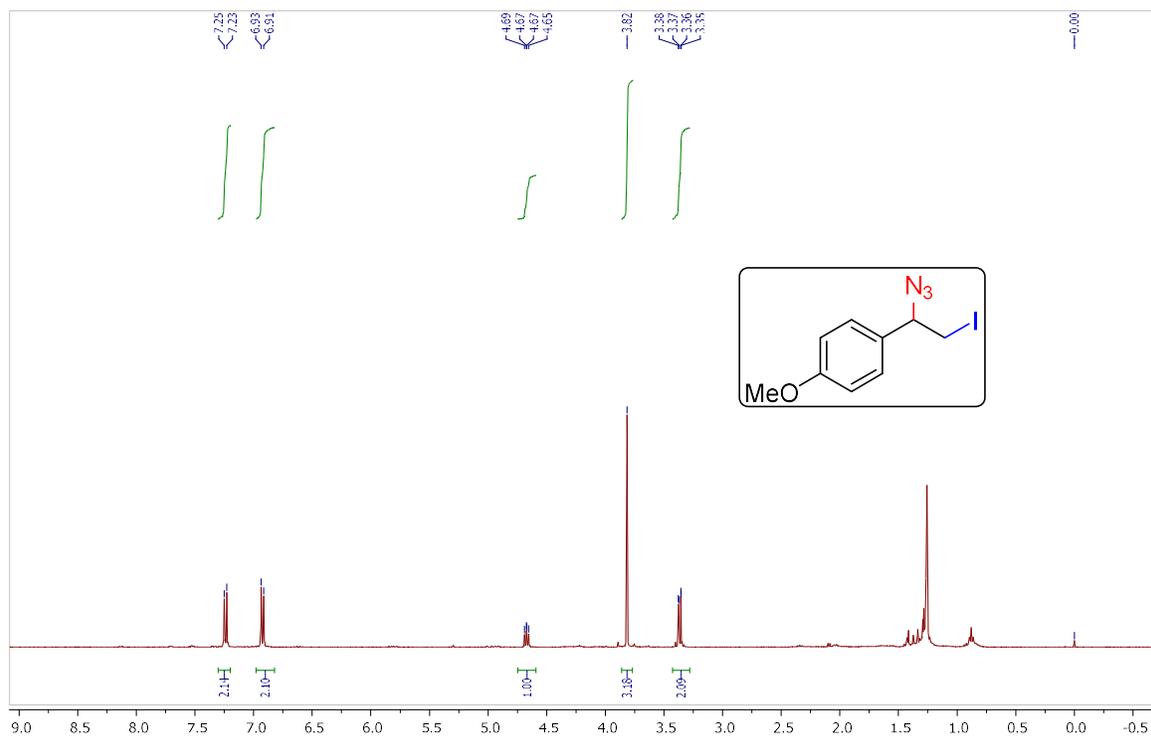


$^{13}\text{C}$  NMR Spectrum of compound **36** in  $\text{CDCl}_3$

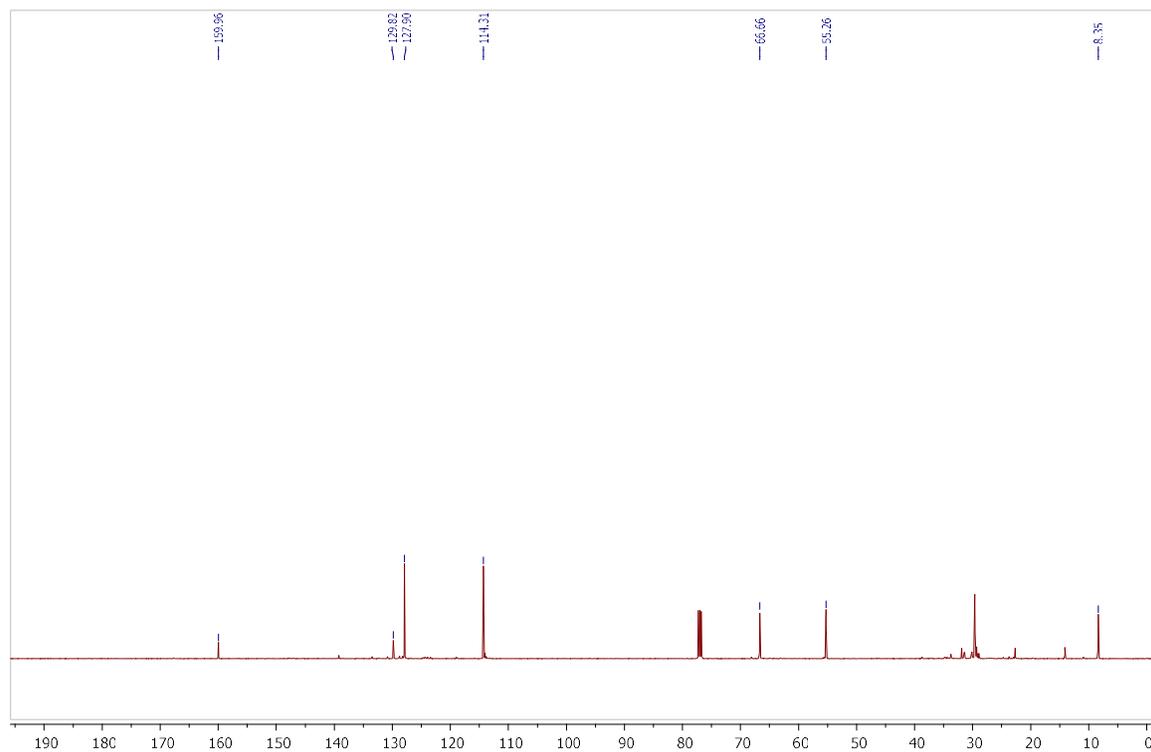


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **37** in $\text{CDCl}_3$

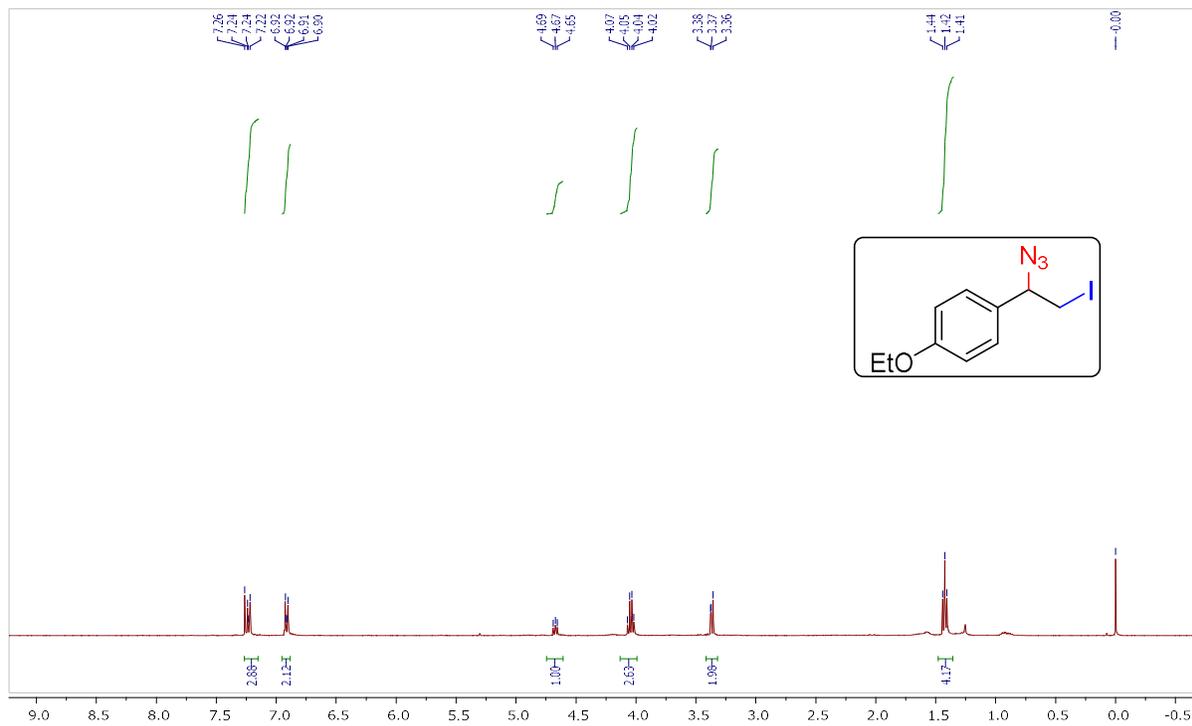


## $^{13}\text{C}$ NMR Spectrum of compound **37** in $\text{CDCl}_3$

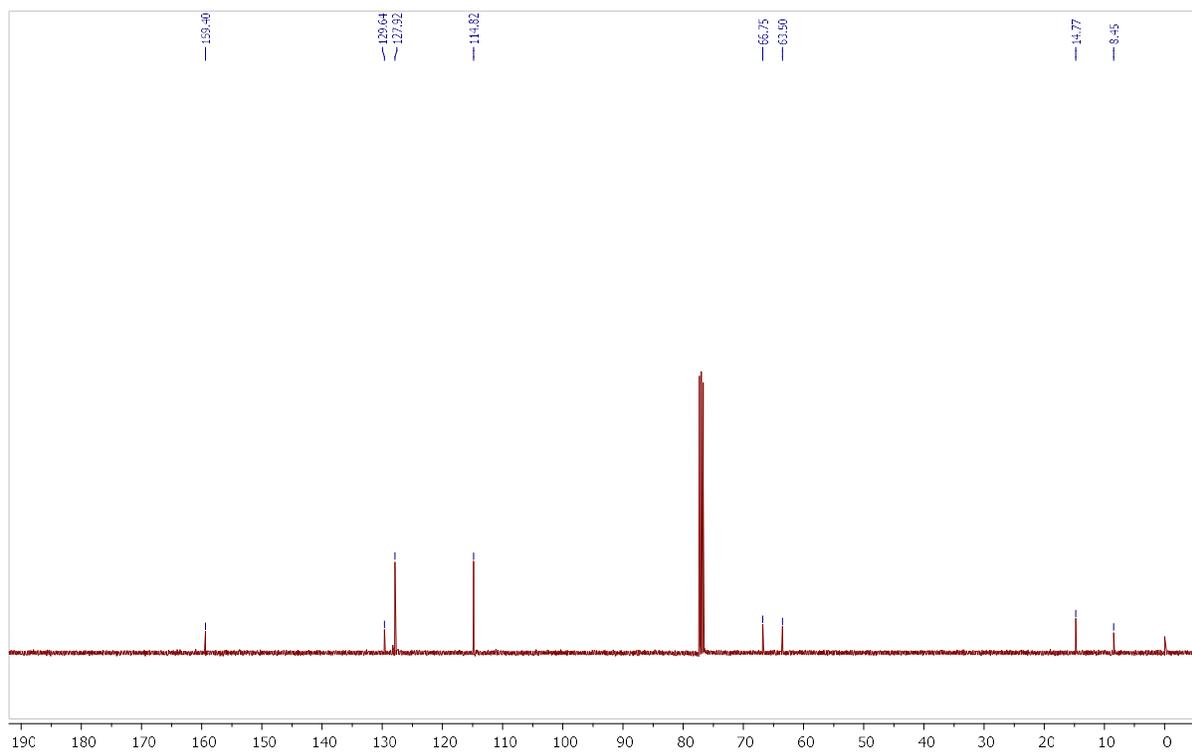


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **38** in $\text{CDCl}_3$

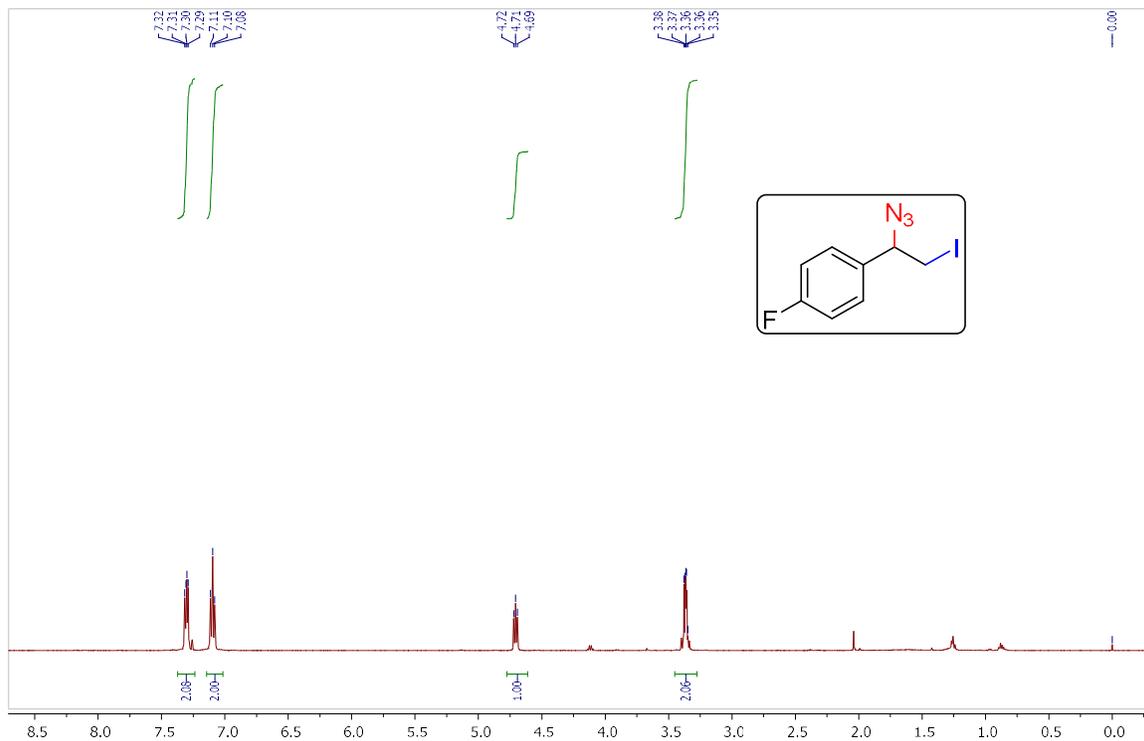


## $^{13}\text{C}$ NMR Spectrum of compound **38** in $\text{CDCl}_3$

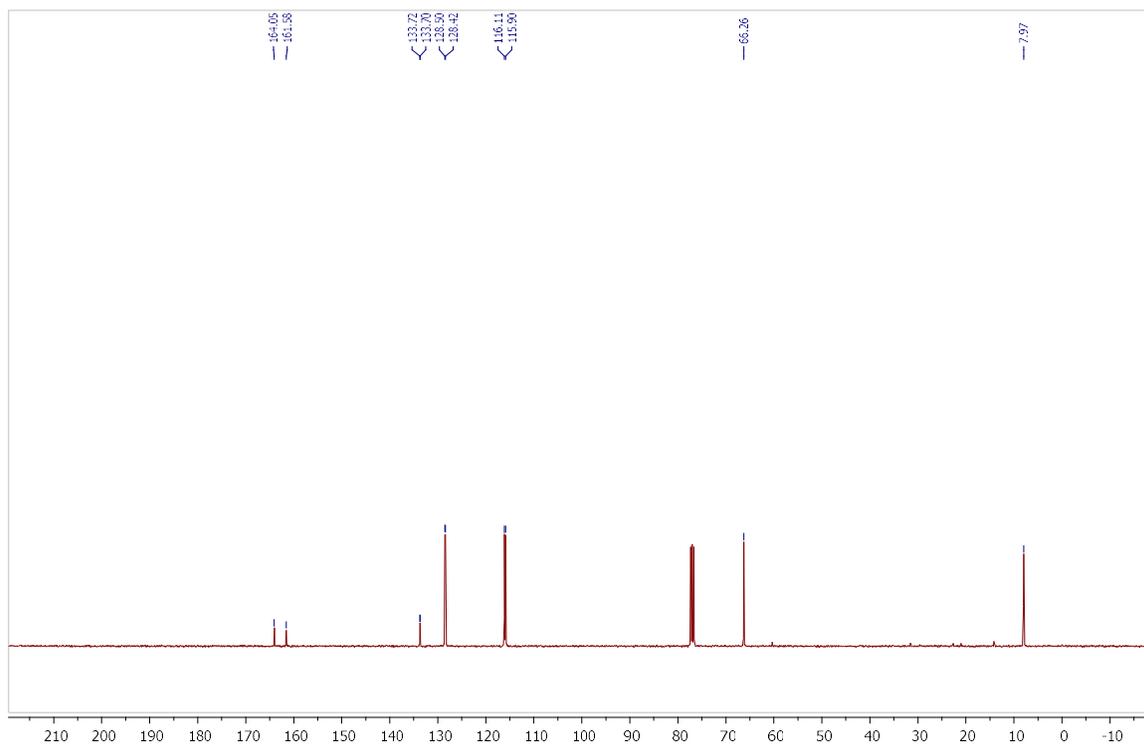


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **39** in $\text{CDCl}_3$

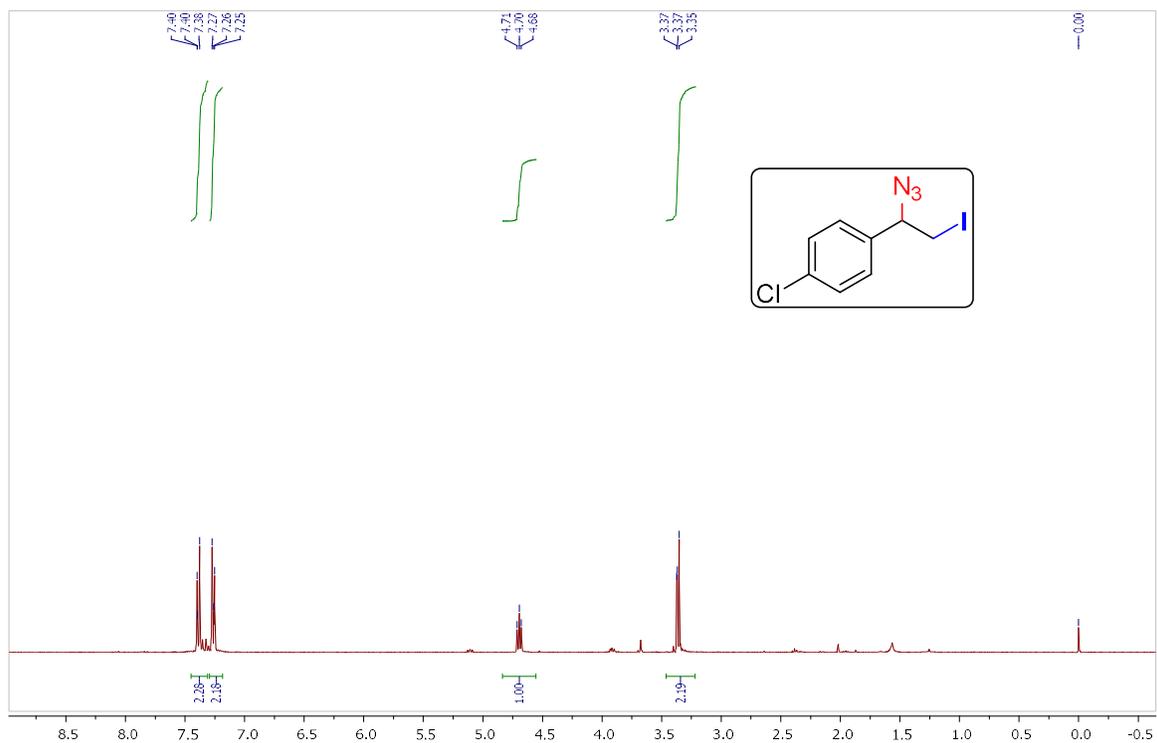


## $^{13}\text{C}$ NMR Spectrum of compound **39** in $\text{CDCl}_3$

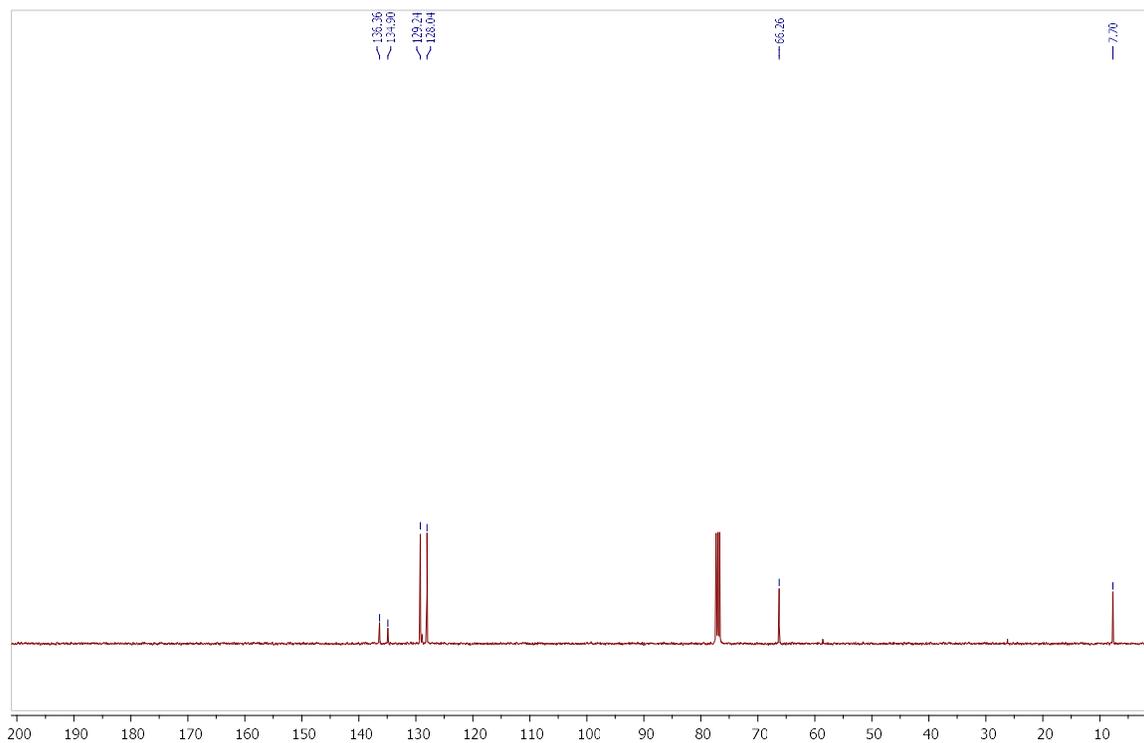


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **40** in  $\text{CDCl}_3$

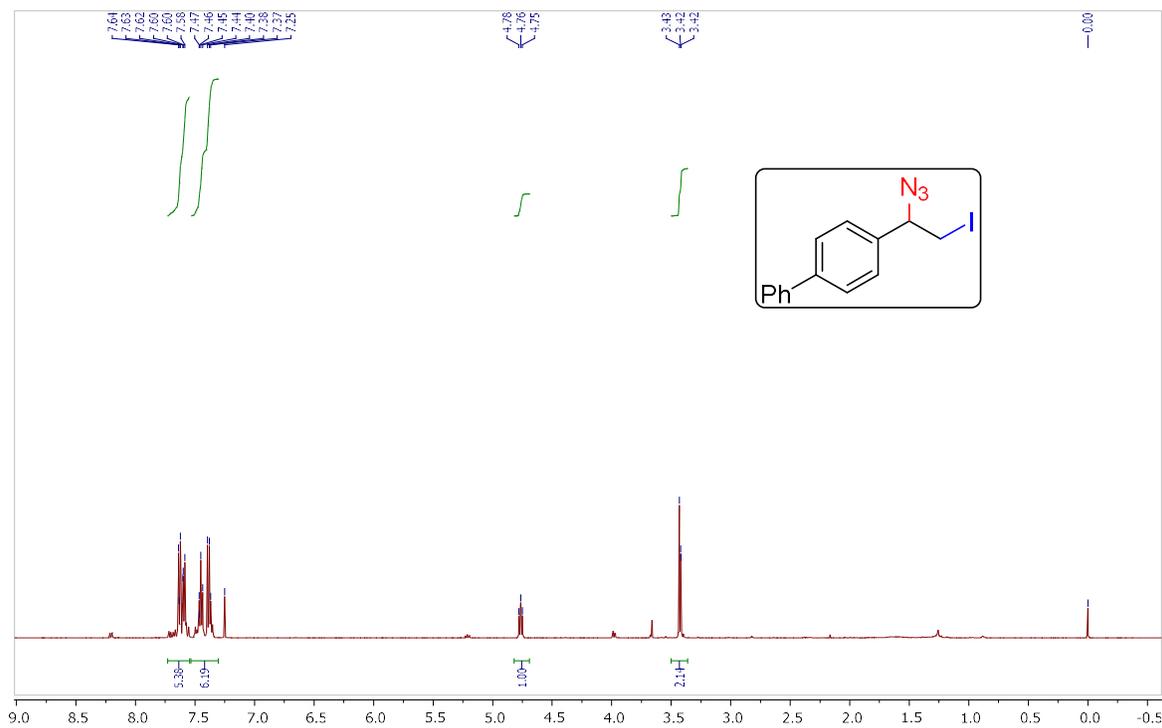


$^{13}\text{C}$  NMR Spectrum of compound **40** in  $\text{CDCl}_3$

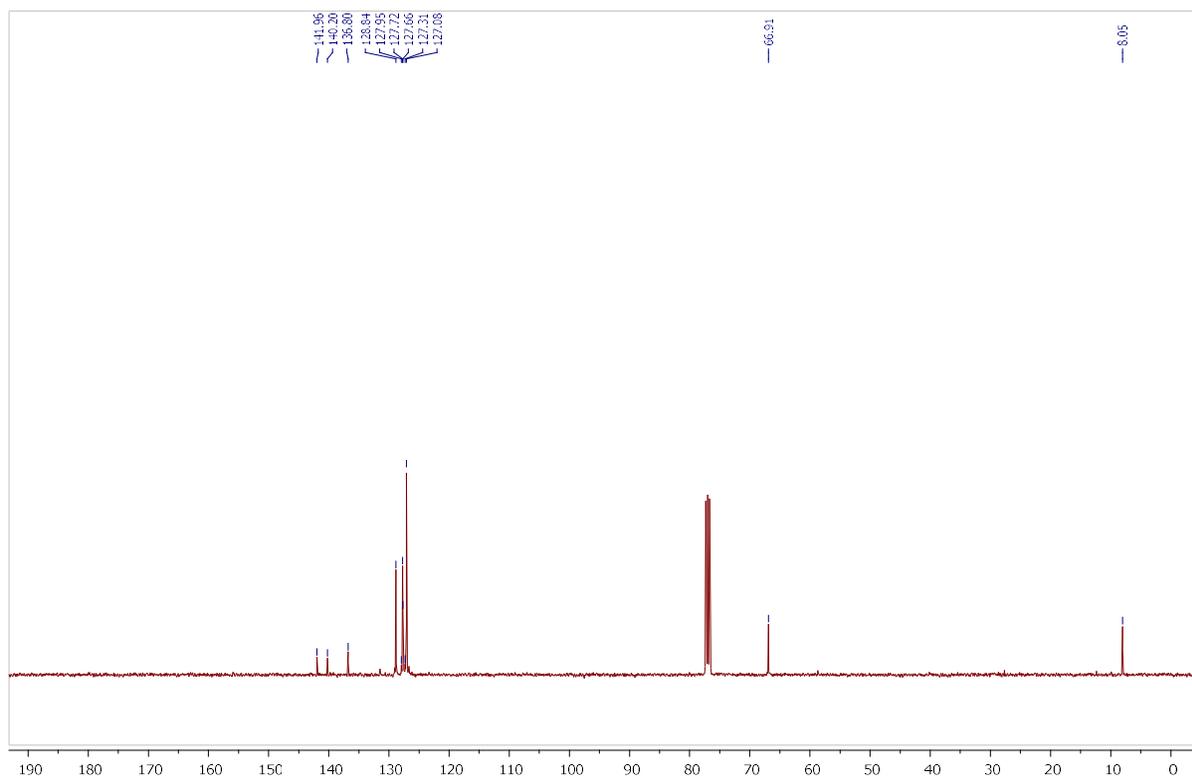


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **41** in  $\text{CDCl}_3$

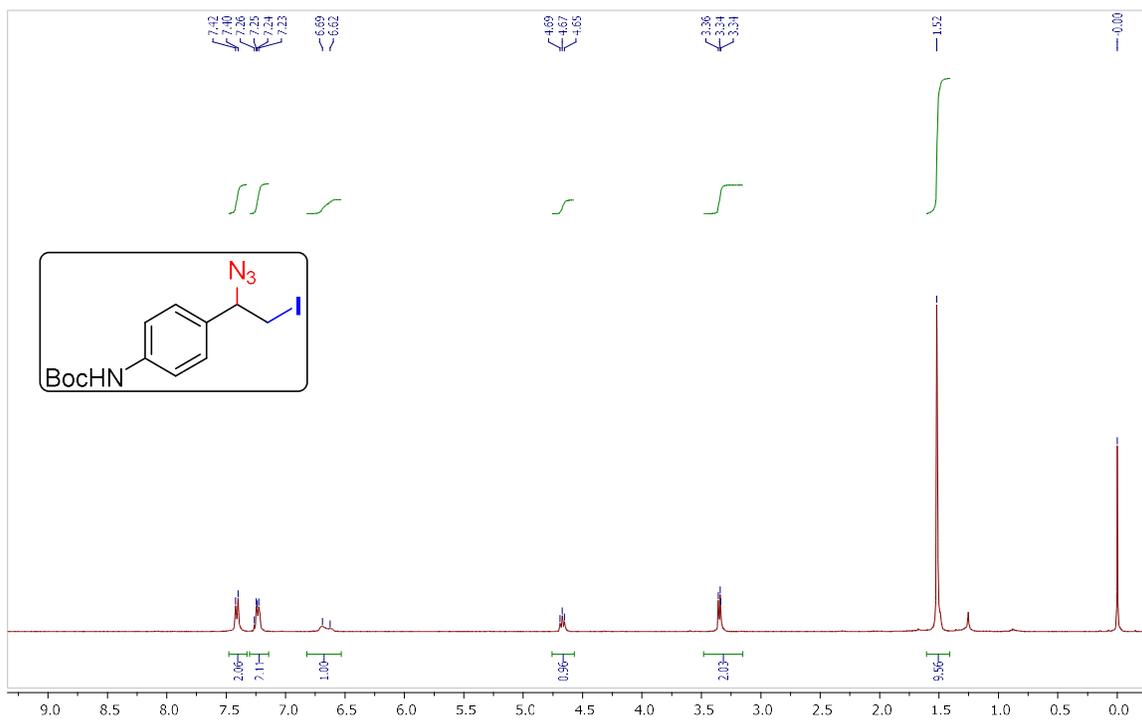


$^{13}\text{C}$  NMR Spectrum of compound **41** in  $\text{CDCl}_3$

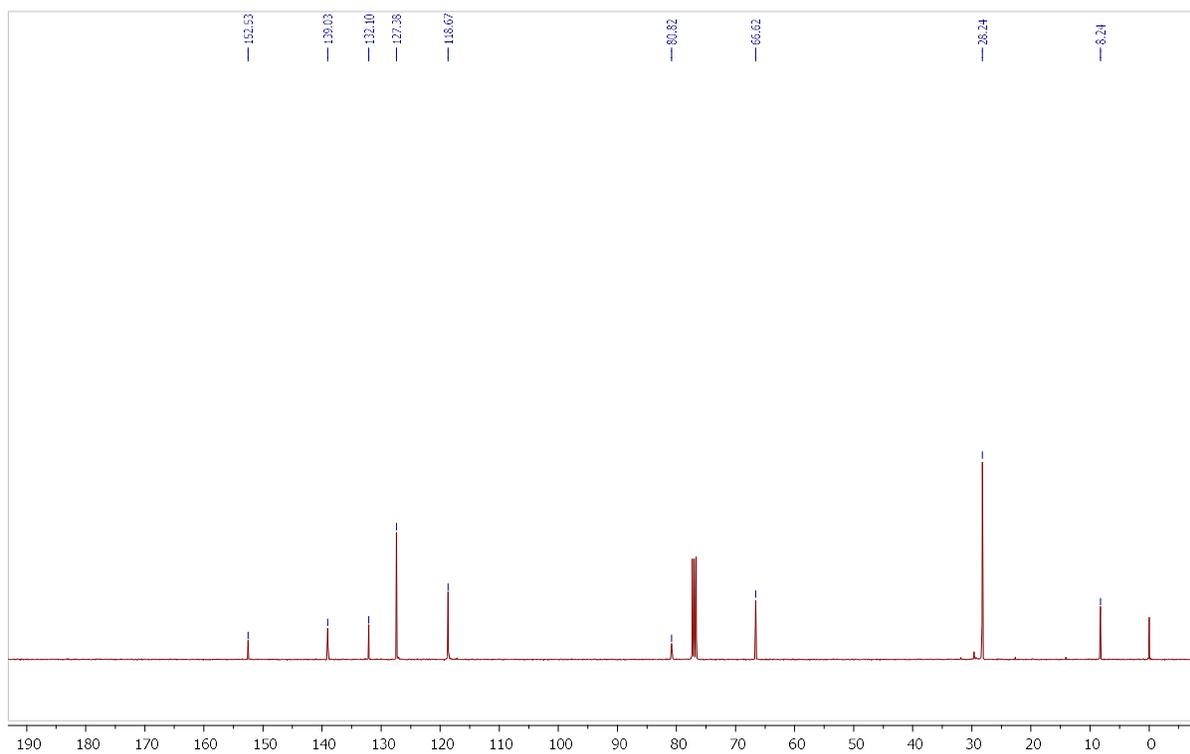


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **42** in $\text{CDCl}_3$

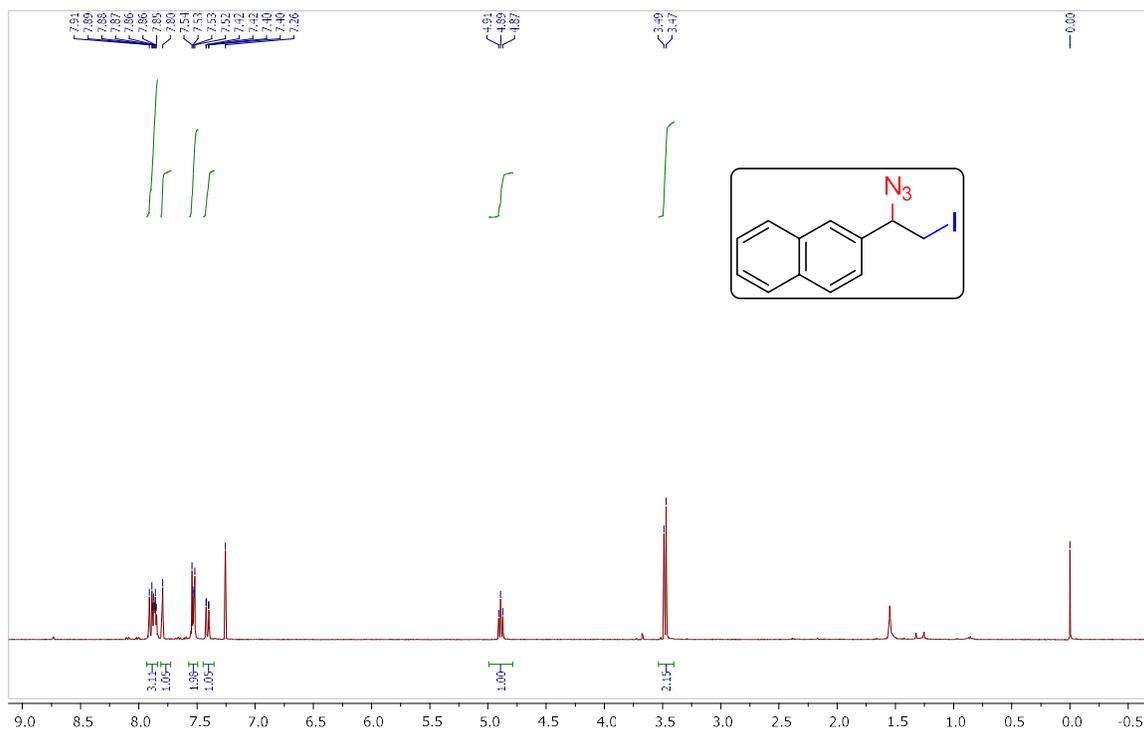


## $^{13}\text{C}$ NMR Spectrum of compound **42** in $\text{CDCl}_3$

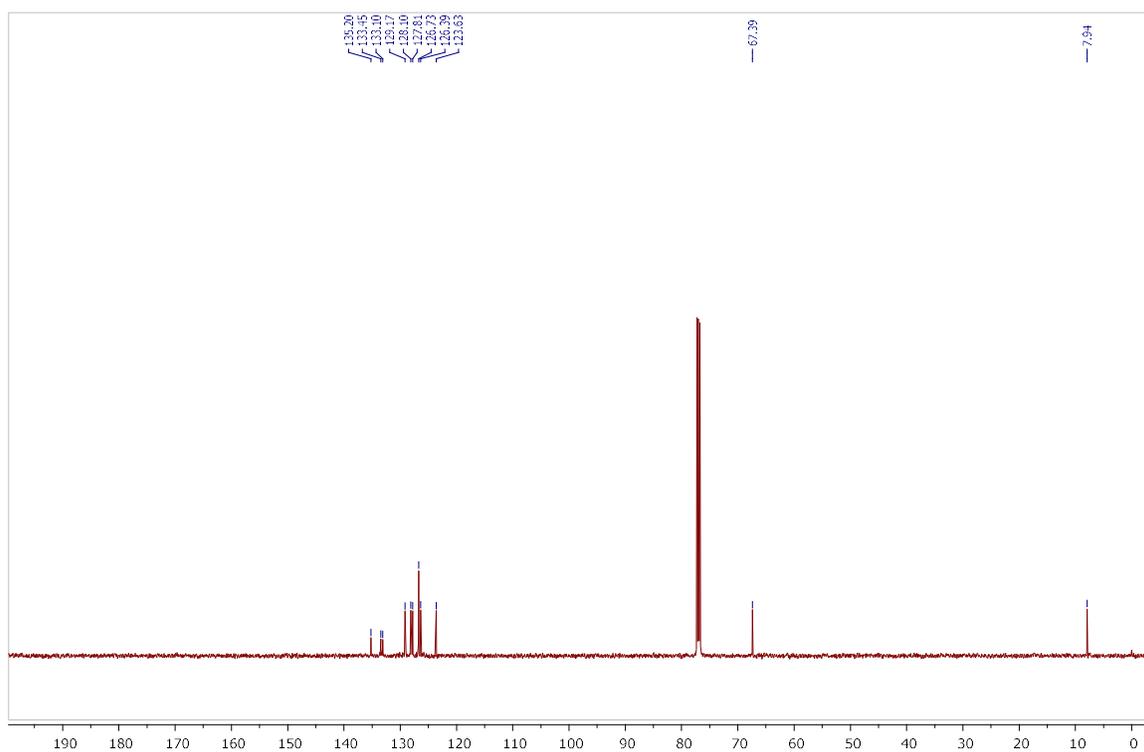


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **43** in $\text{CDCl}_3$

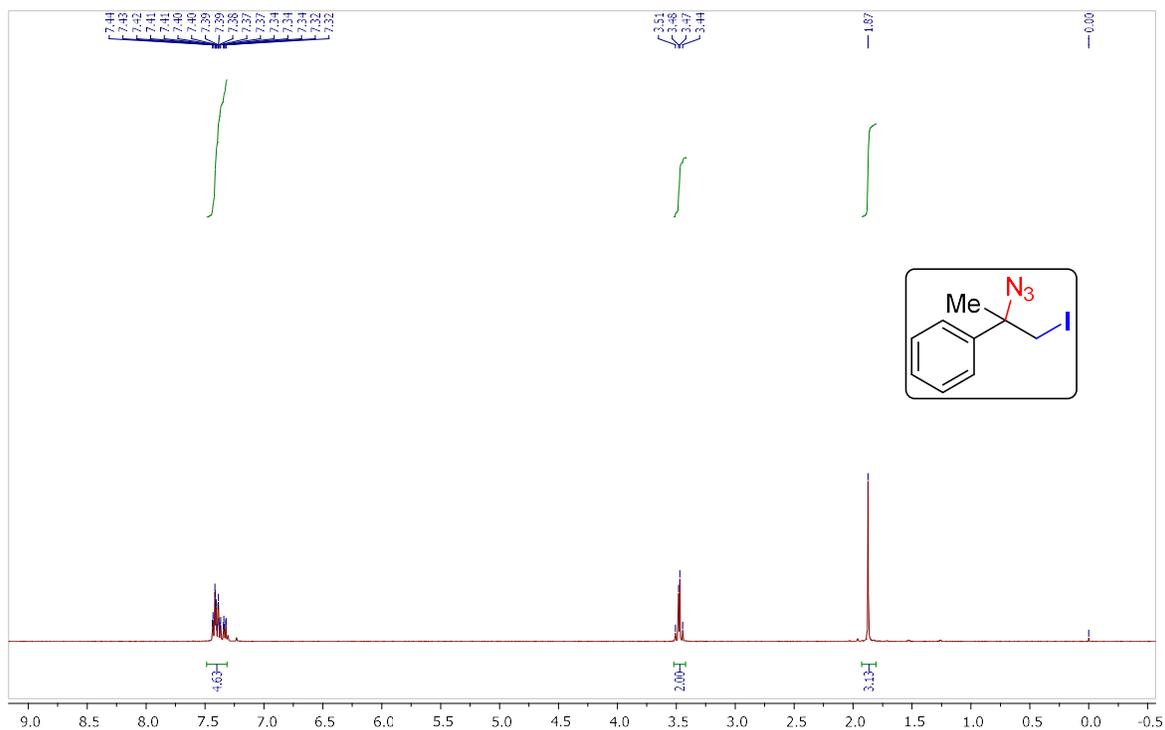


## $^{13}\text{C}$ NMR Spectrum of compound **43** in $\text{CDCl}_3$

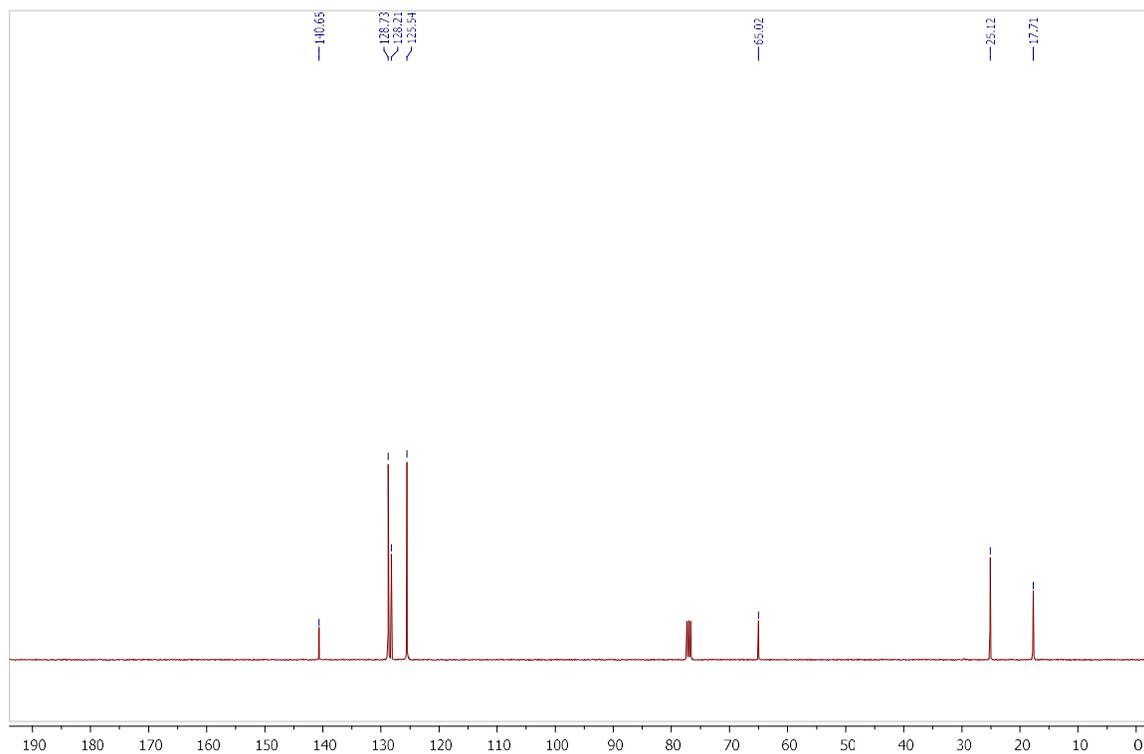


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **44** in $\text{CDCl}_3$

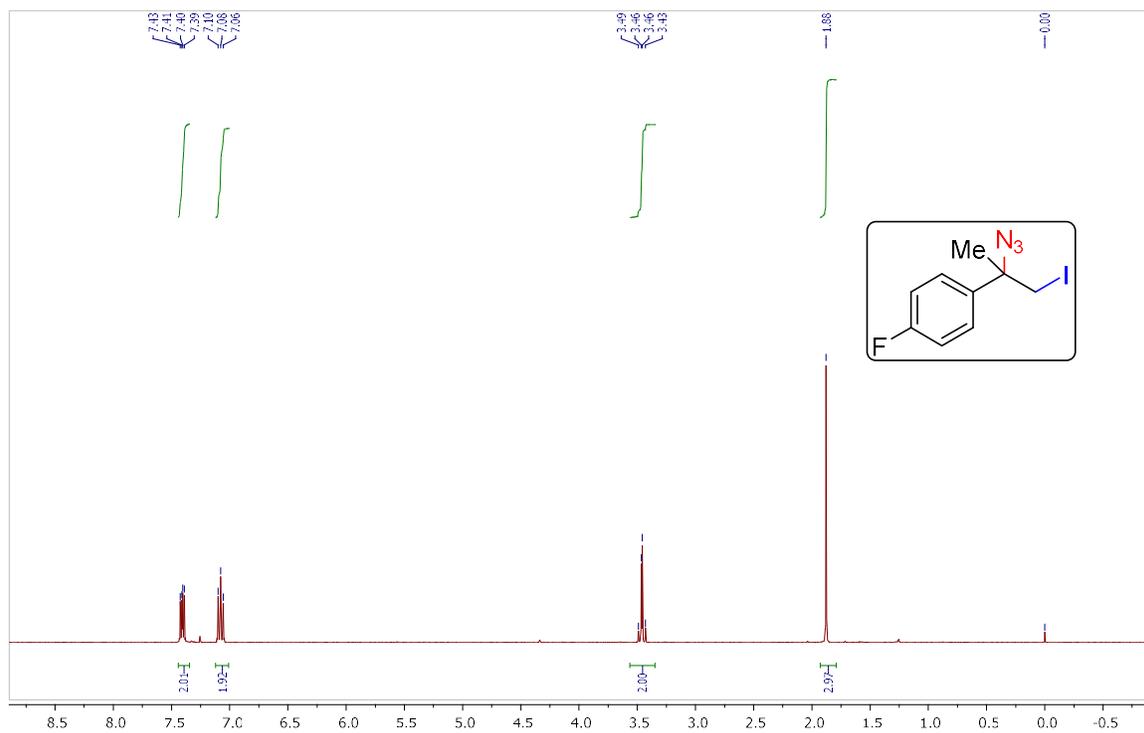


## $^{13}\text{C}$ NMR Spectrum of compound **44** in $\text{CDCl}_3$

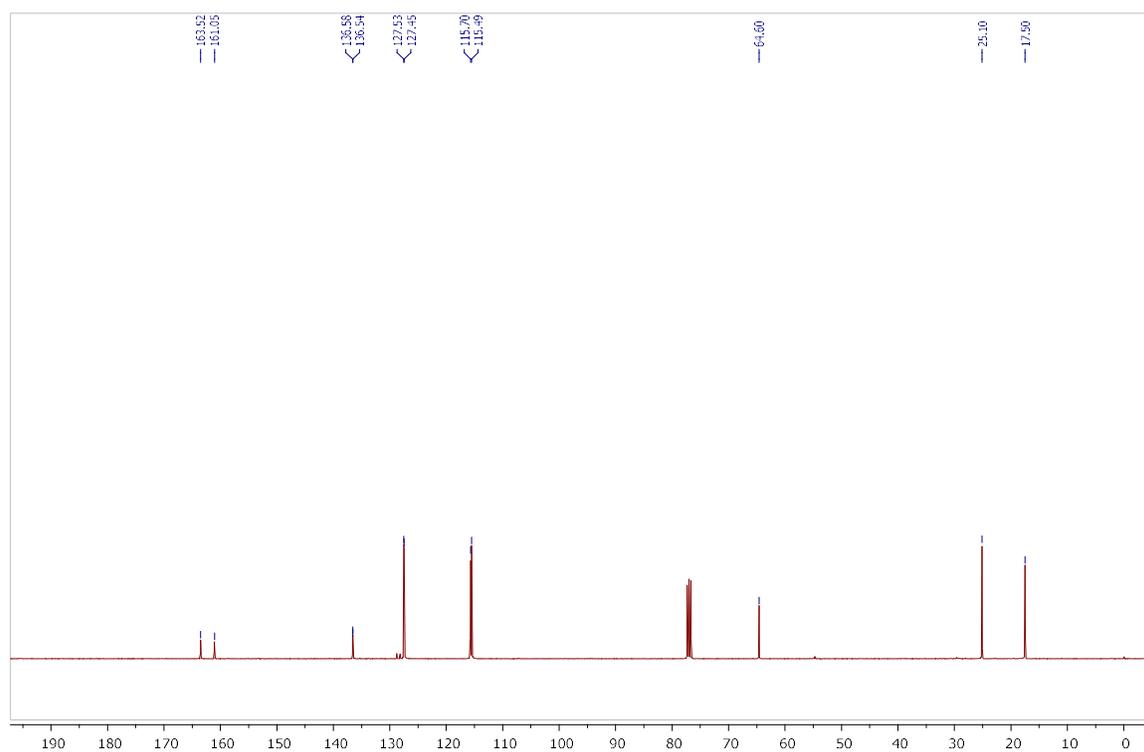


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **45** in $\text{CDCl}_3$

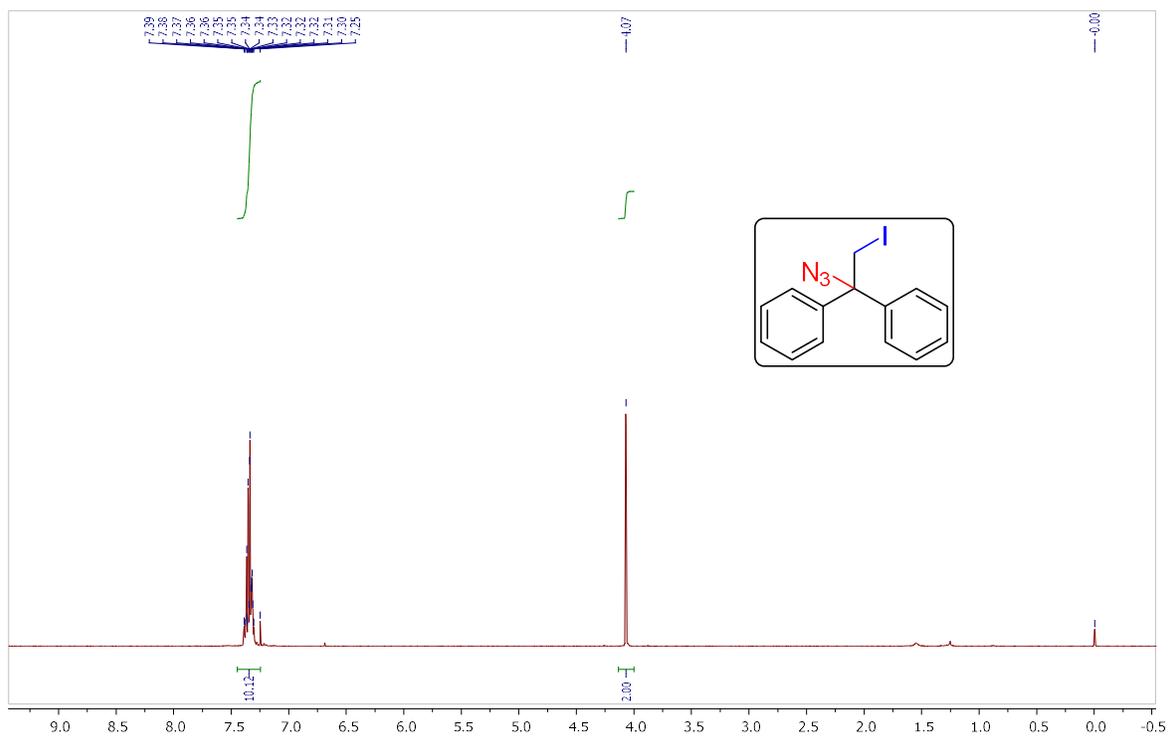


## $^{13}\text{C}$ NMR Spectrum of compound **45** in $\text{CDCl}_3$

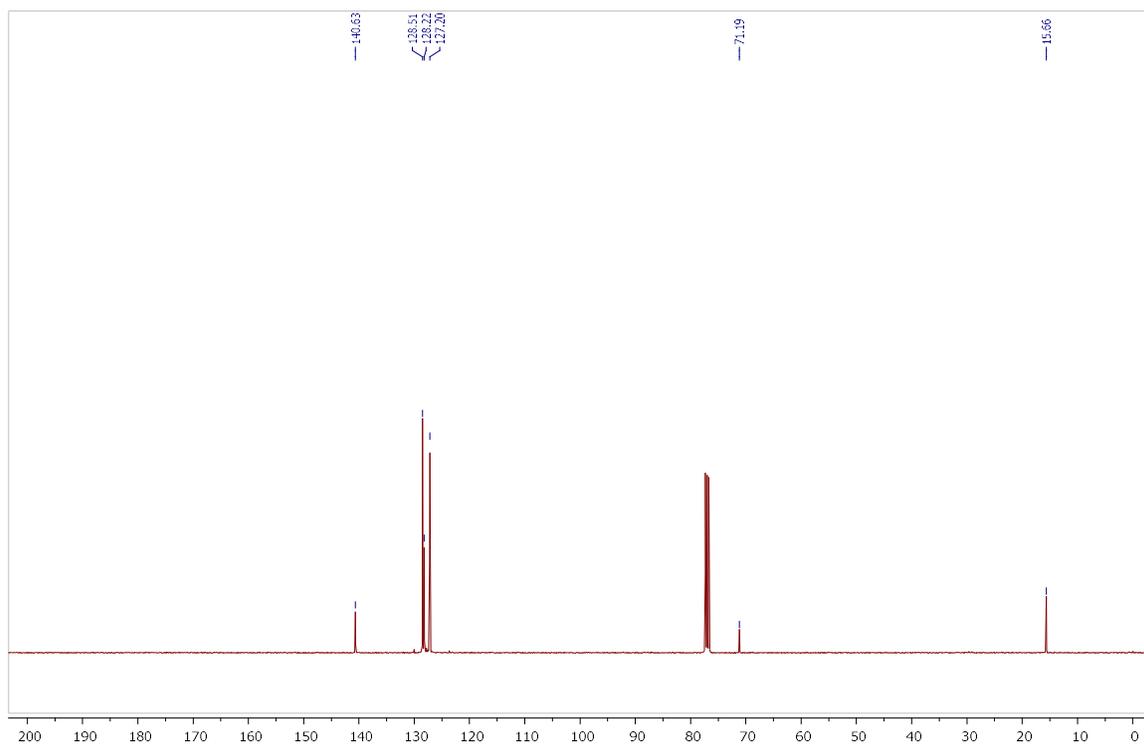


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **46** in $\text{CDCl}_3$

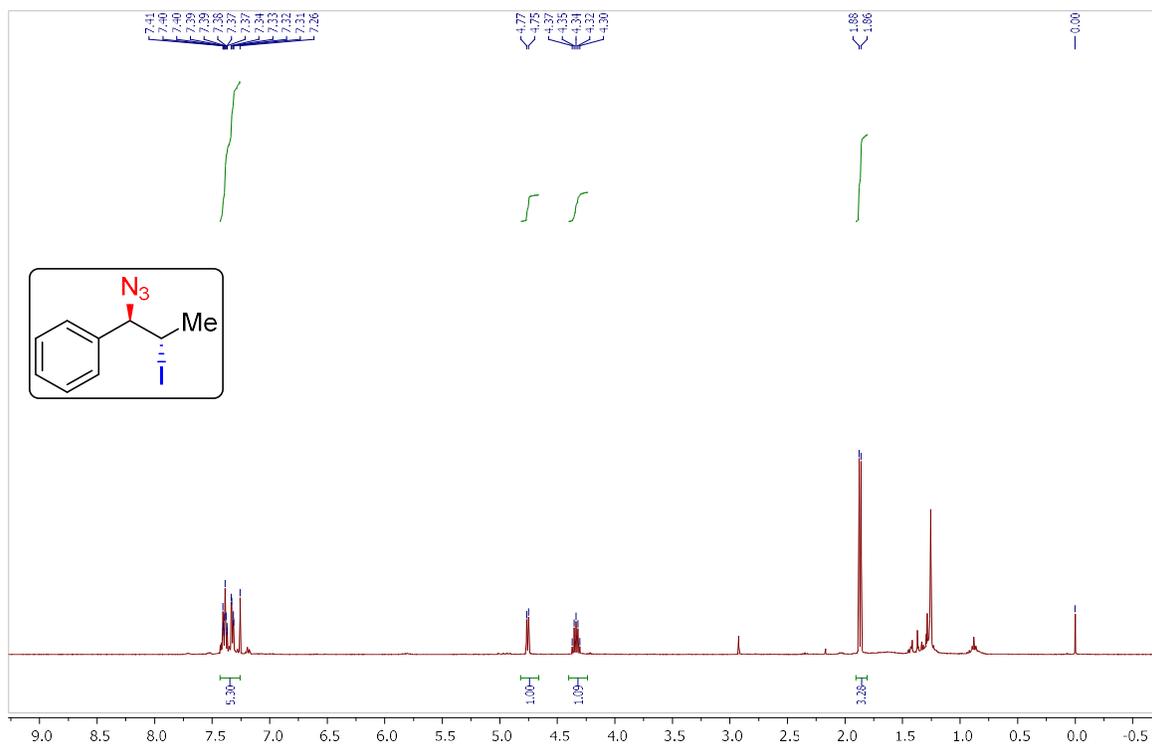


## $^{13}\text{C}$ NMR Spectrum of compound **46** in $\text{CDCl}_3$

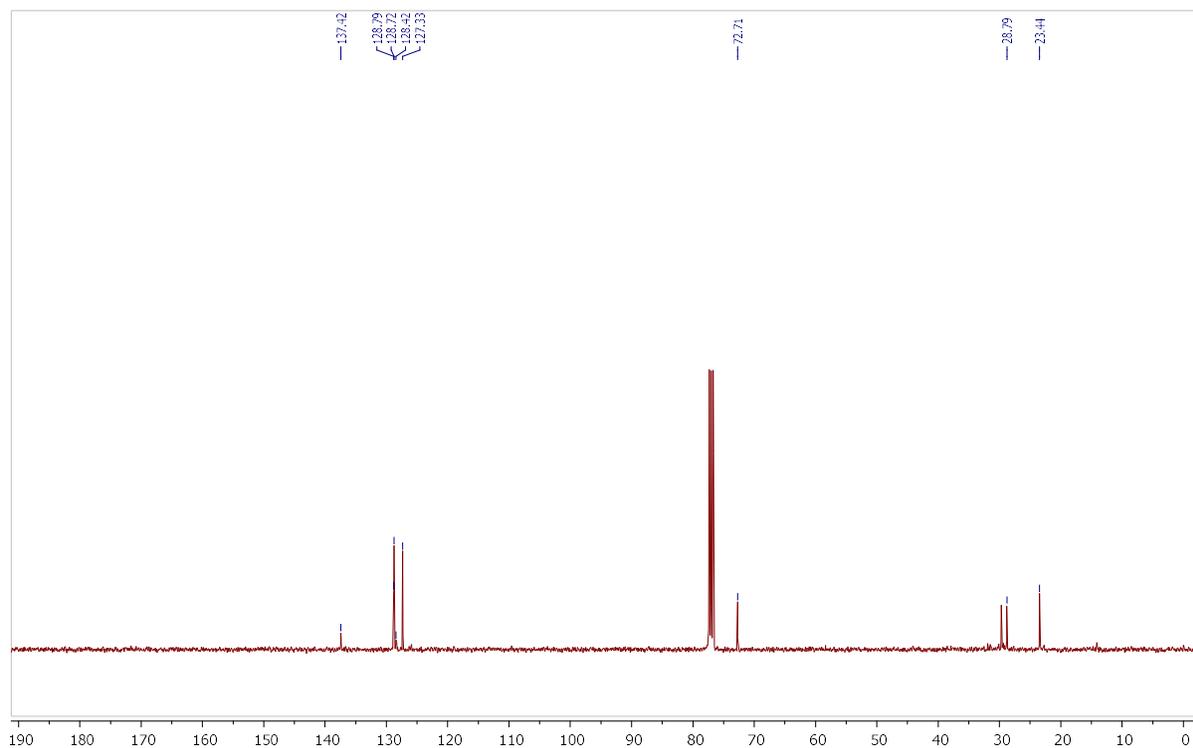


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **47** in  $\text{CDCl}_3$

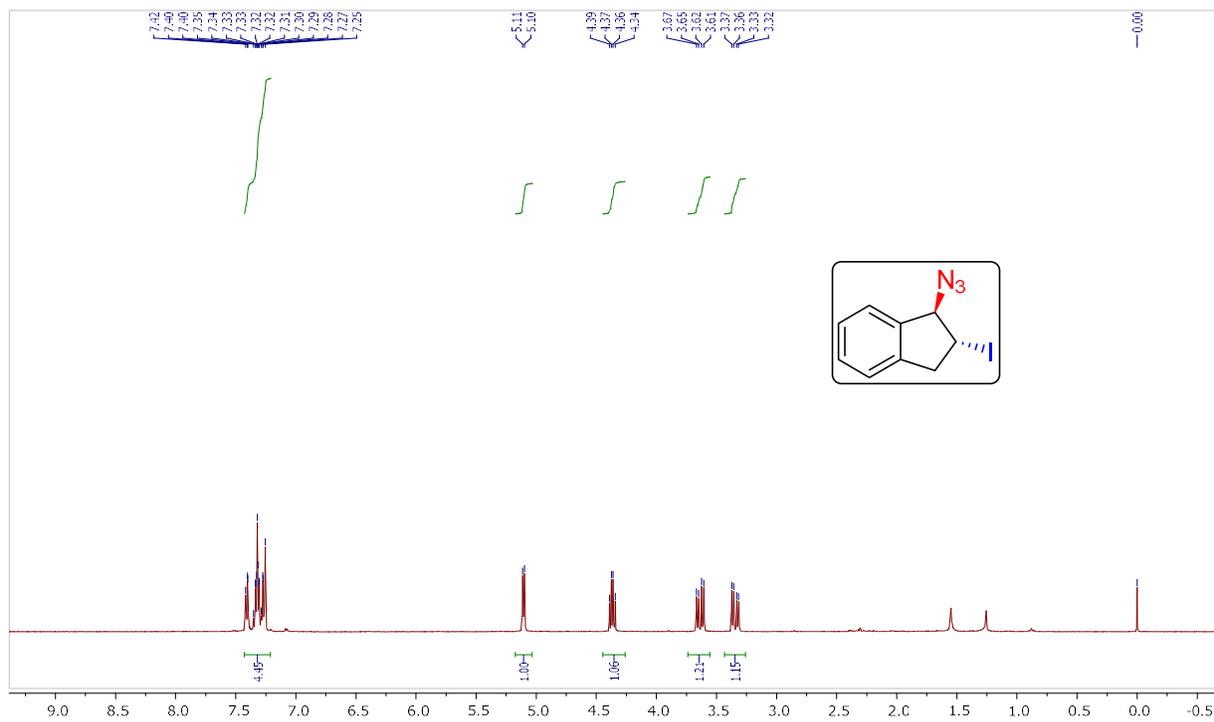


$^{13}\text{C}$  NMR Spectrum of compound **47** in  $\text{CDCl}_3$

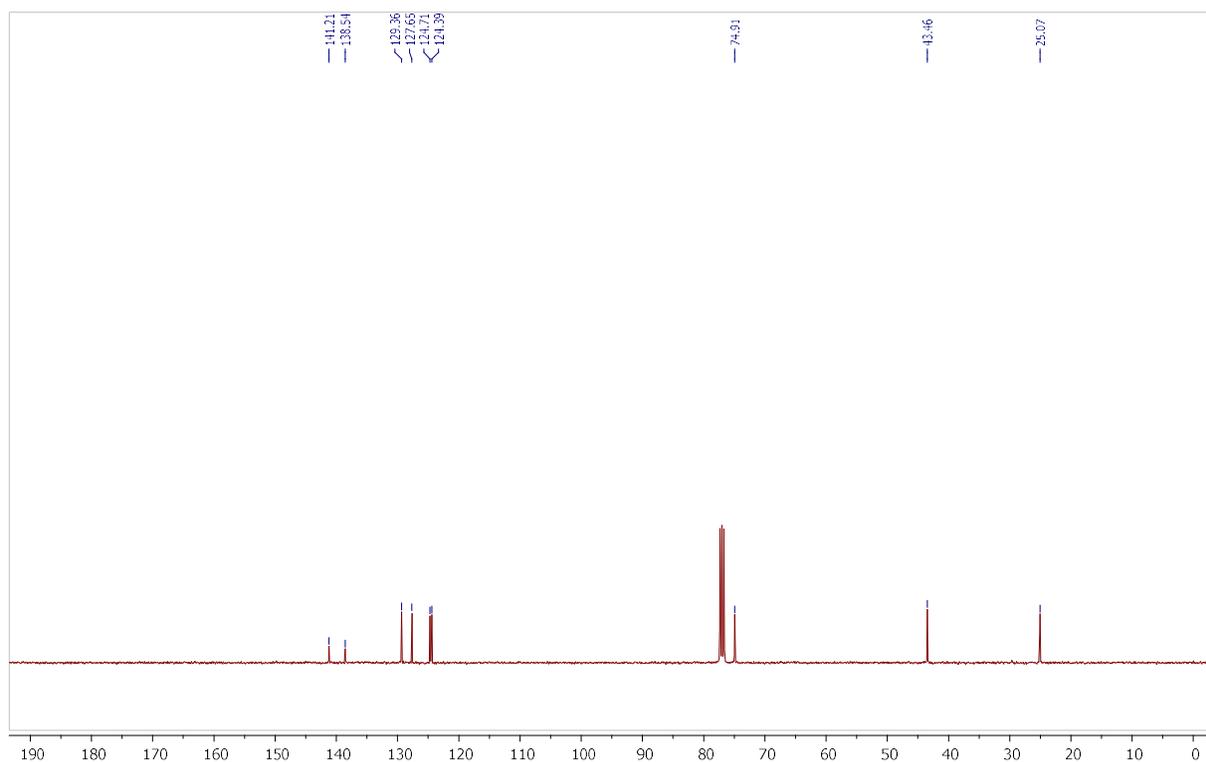


SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **48** in  $\text{CDCl}_3$

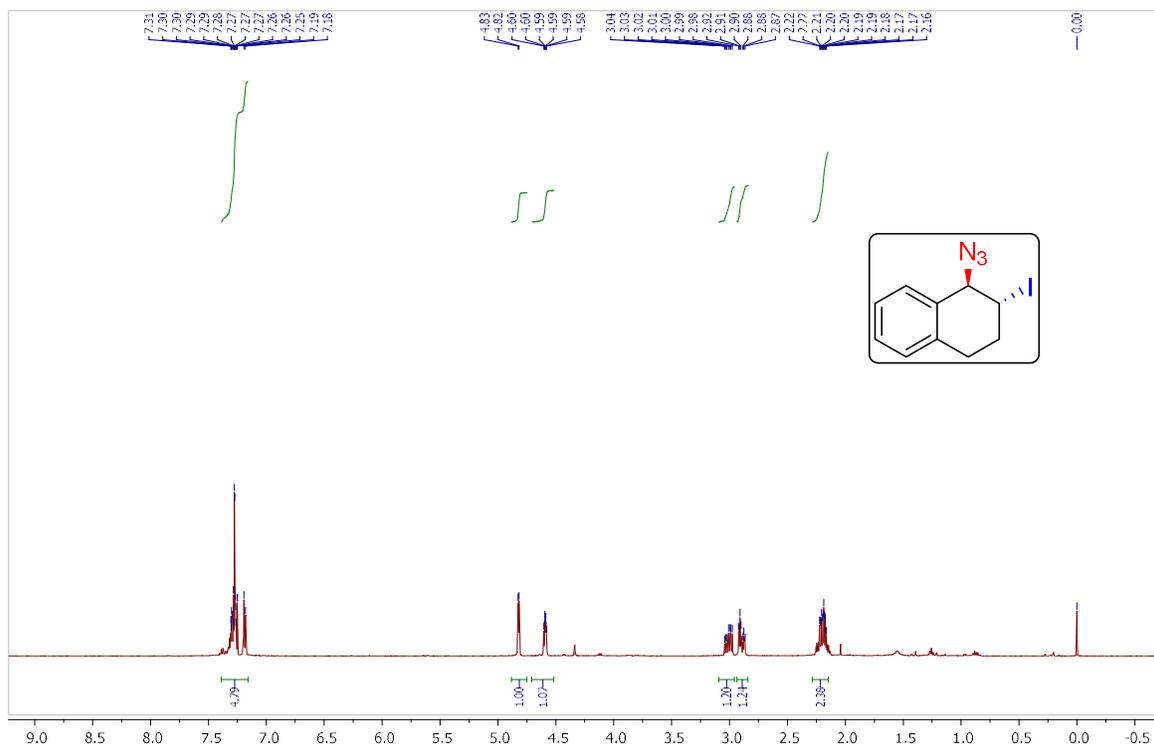


$^{13}\text{C}$  NMR Spectrum of compound **48** in  $\text{CDCl}_3$

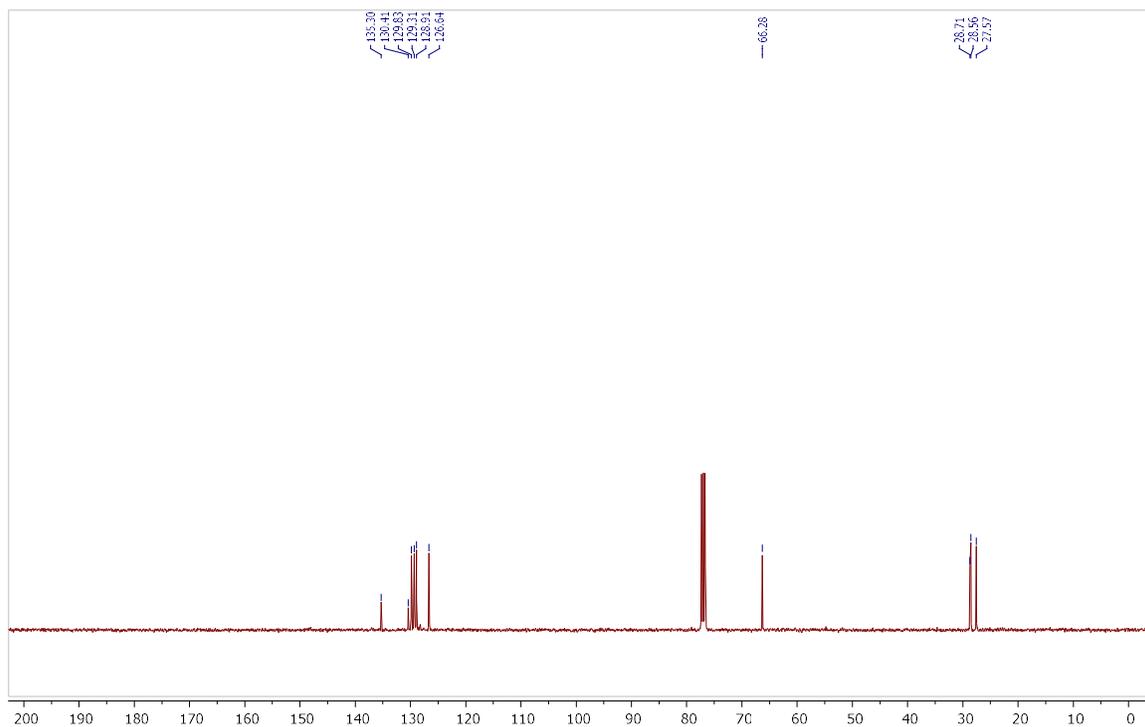


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **49** in  $\text{CDCl}_3$

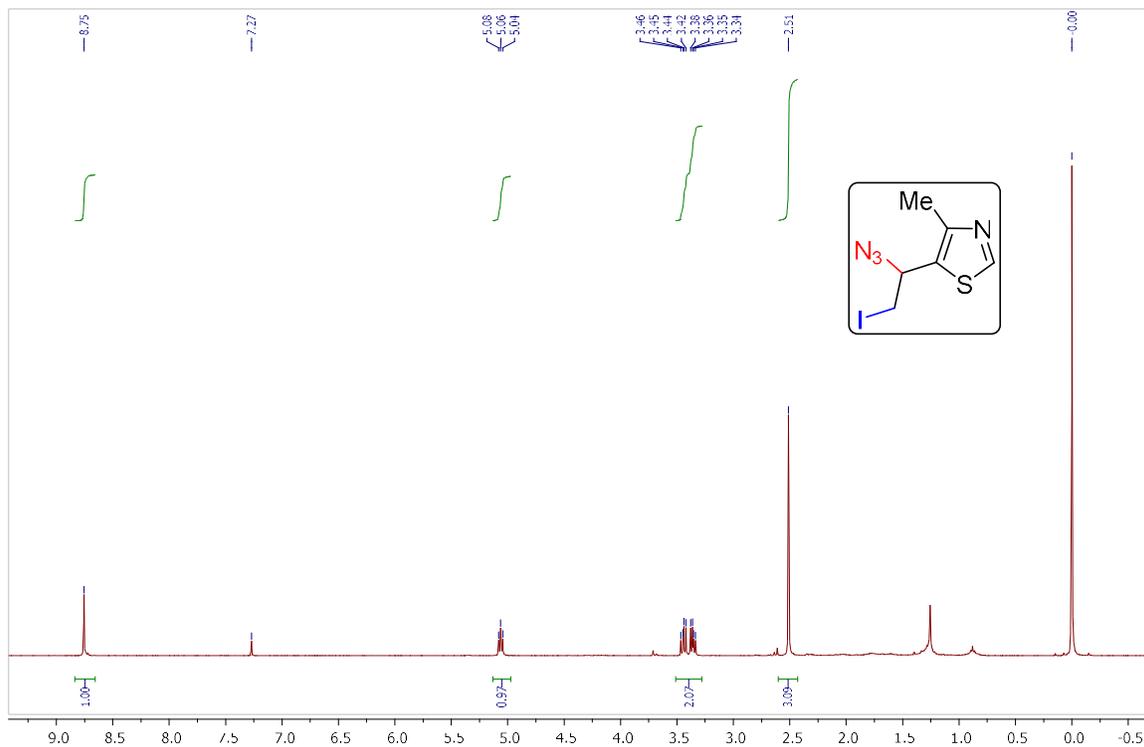


$^{13}\text{C}$  NMR Spectrum of compound **49** in  $\text{CDCl}_3$

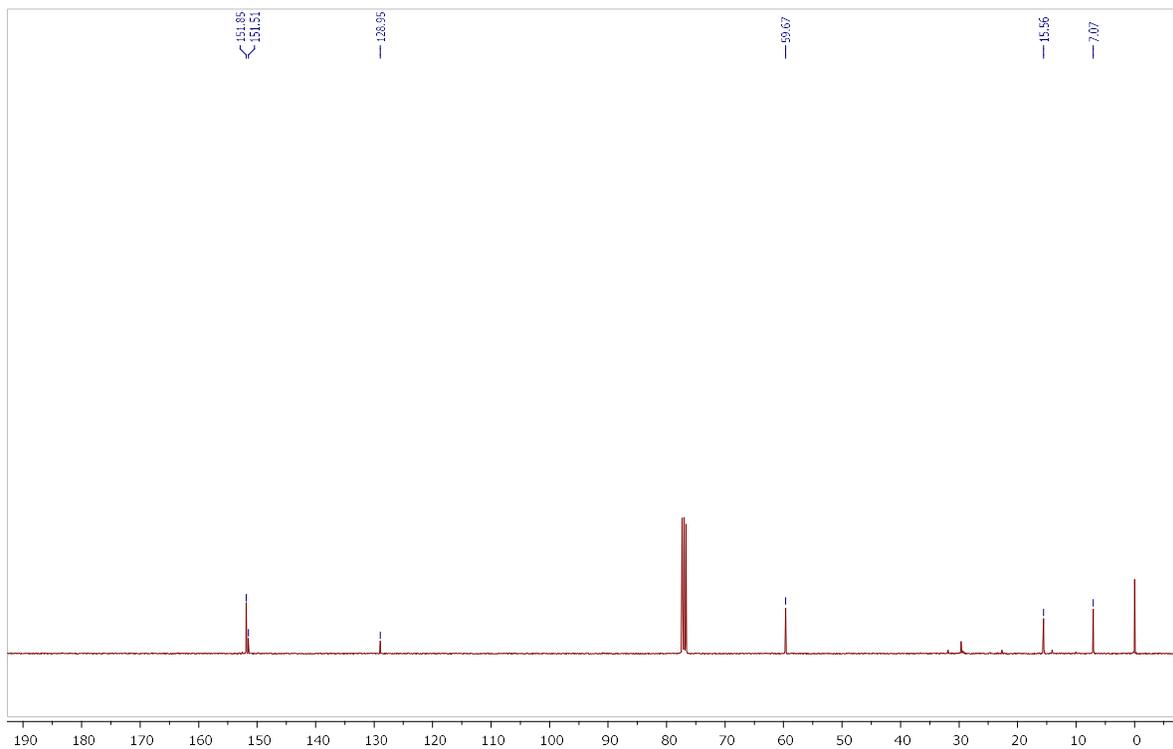


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **50** in $\text{CDCl}_3$

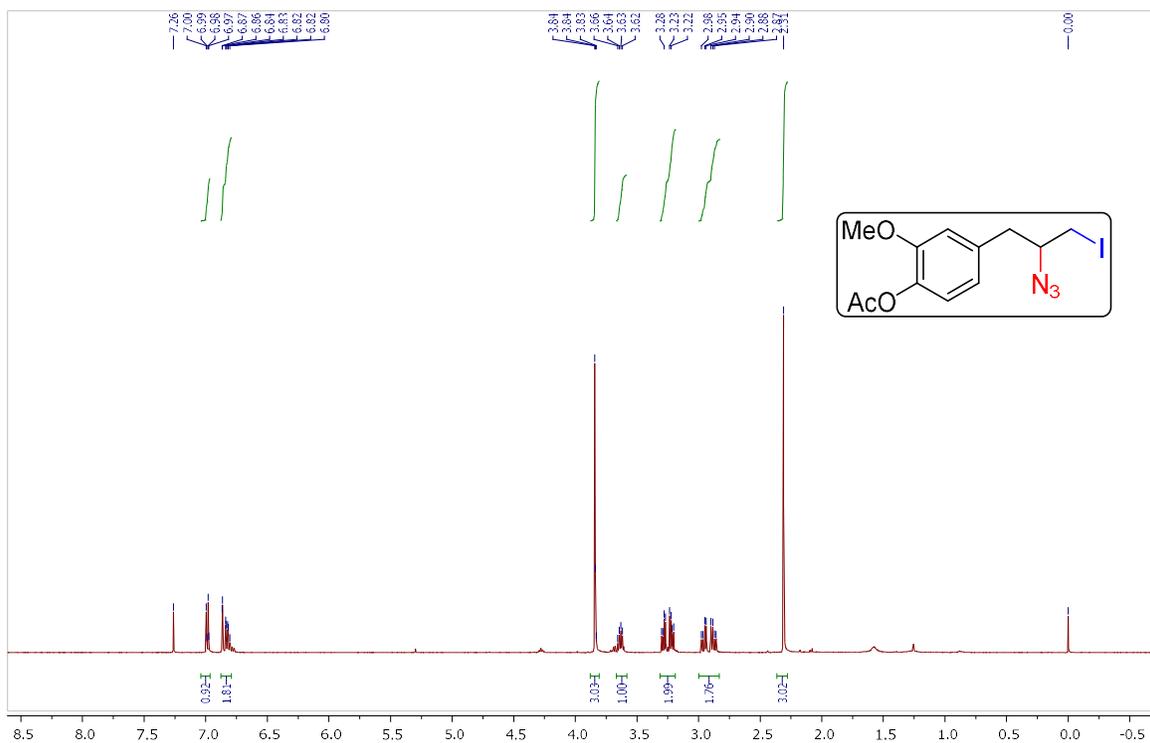


## $^{13}\text{C}$ NMR Spectrum of compound **50** in $\text{CDCl}_3$

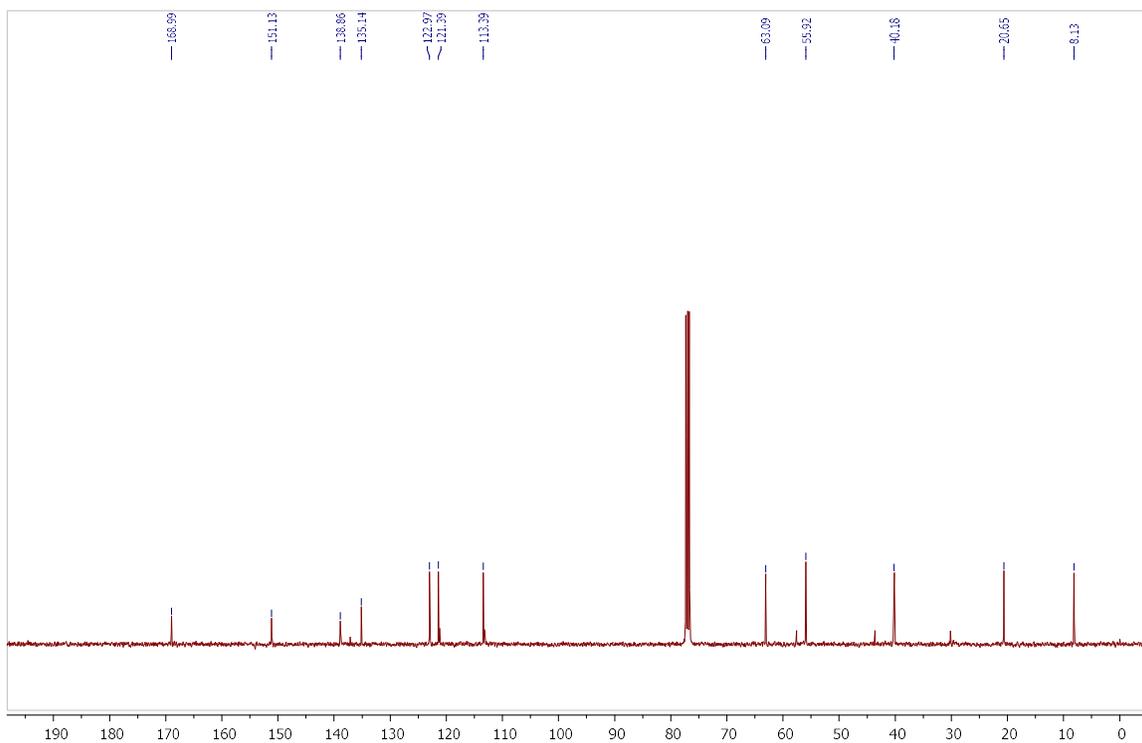


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **51** in CDCl<sub>3</sub>

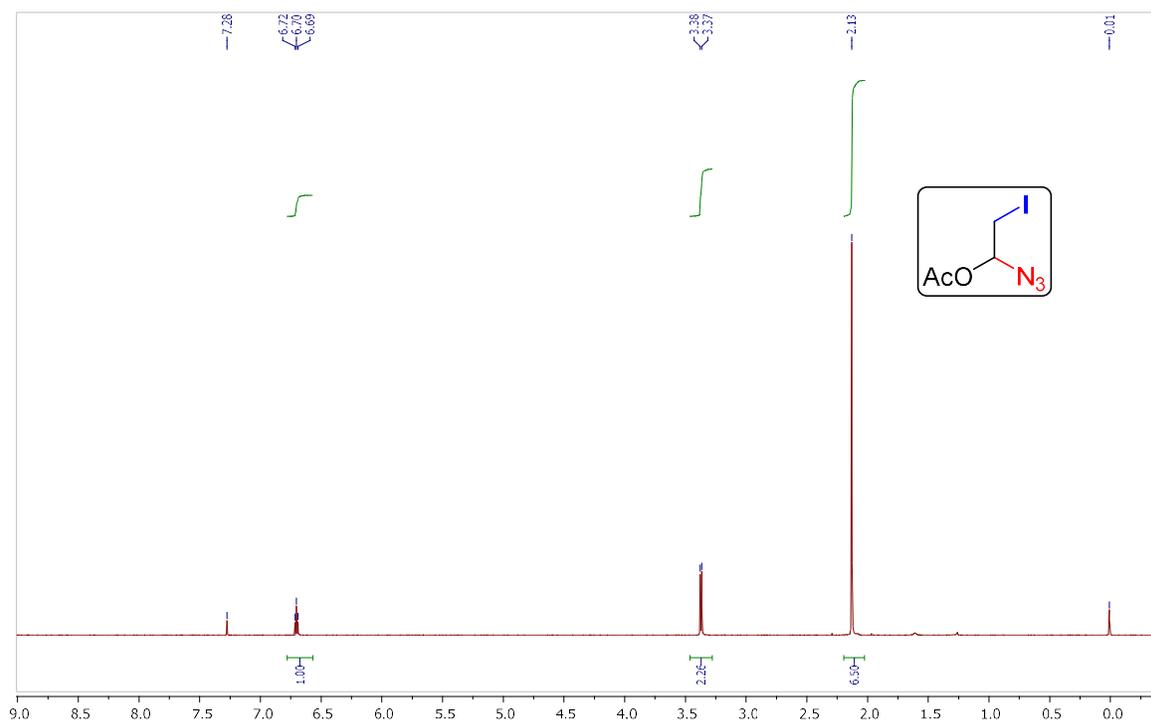


<sup>13</sup>C NMR Spectrum of compound **51** in CDCl<sub>3</sub>

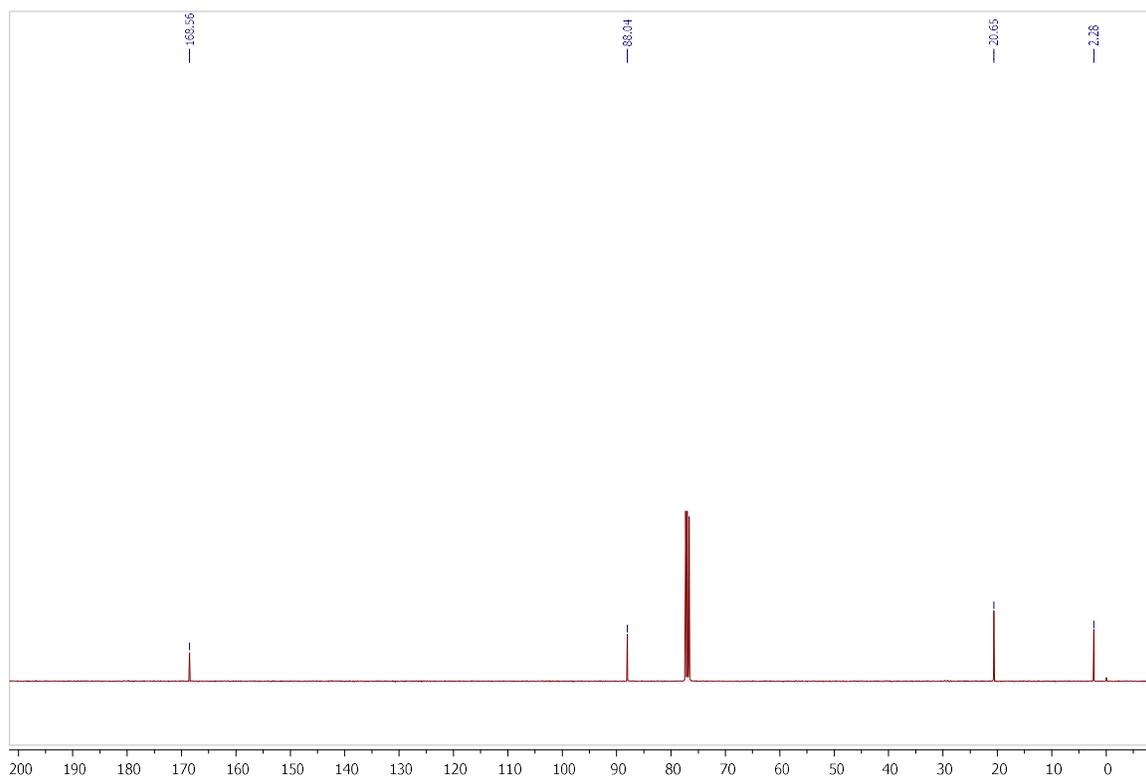


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **52** in  $\text{CDCl}_3$

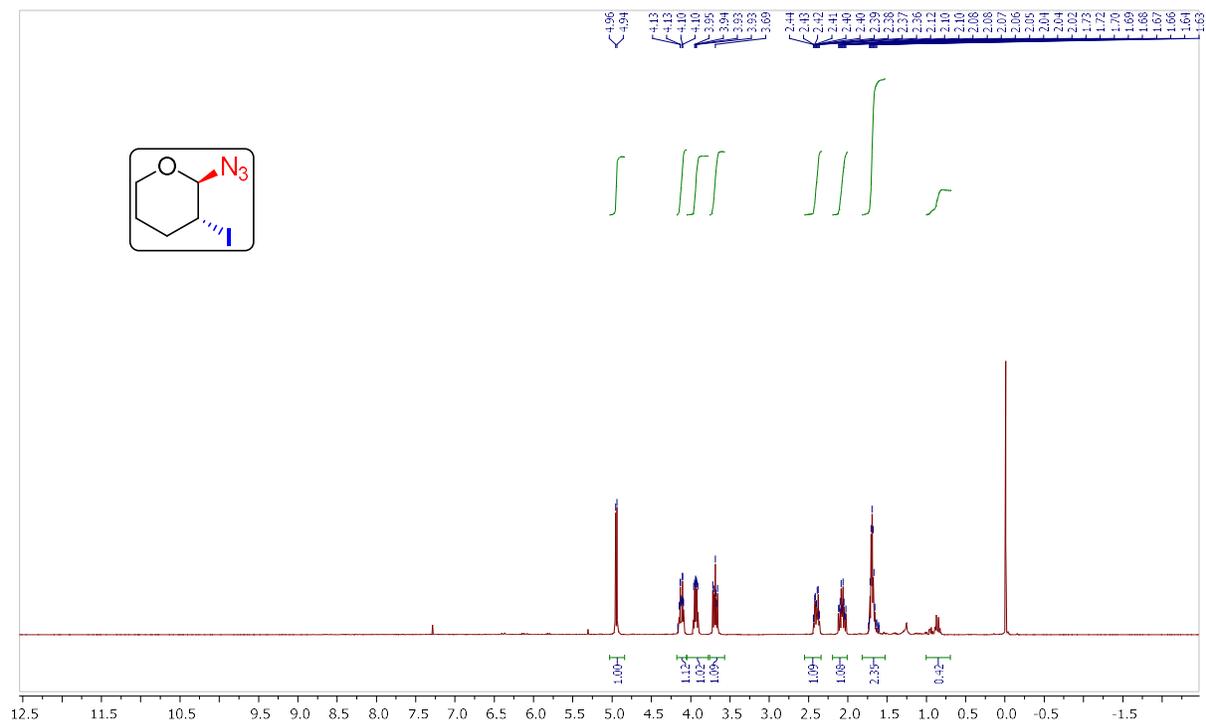


$^{13}\text{C}$  NMR Spectrum of compound **52** in  $\text{CDCl}_3$

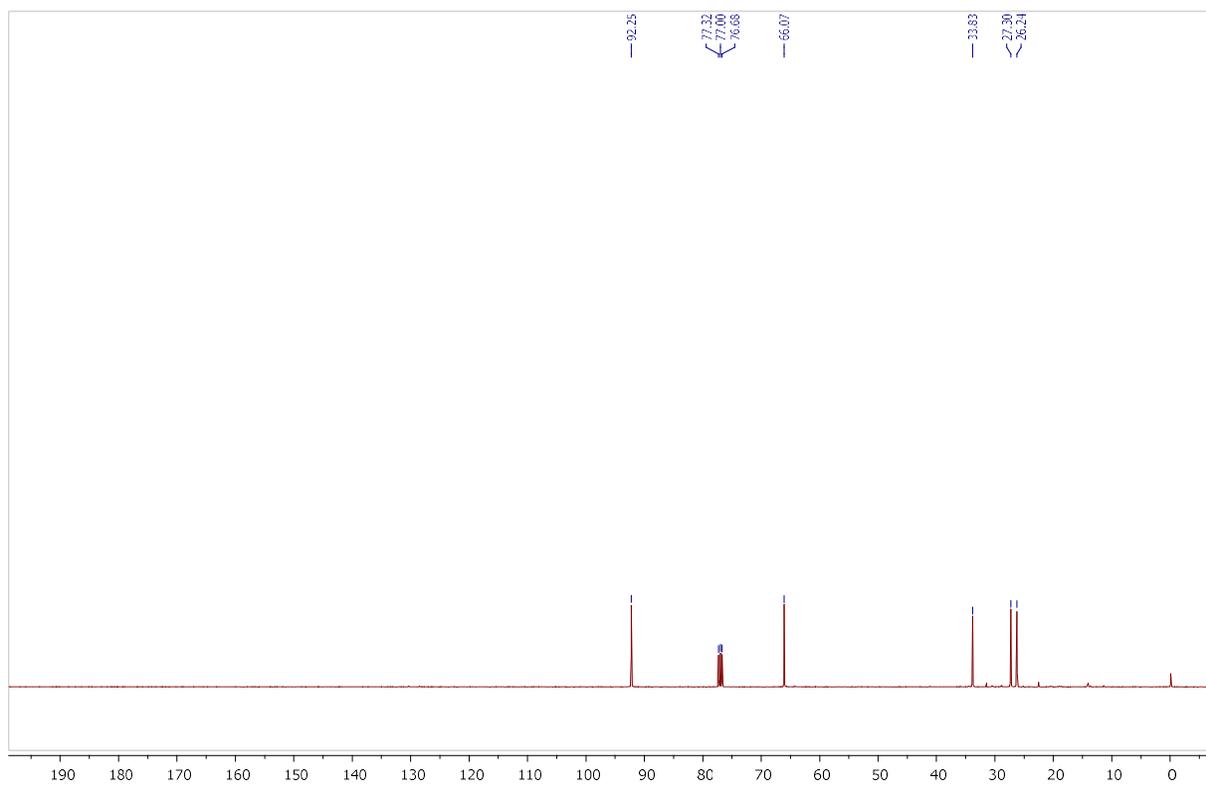


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **53** in $\text{CDCl}_3$

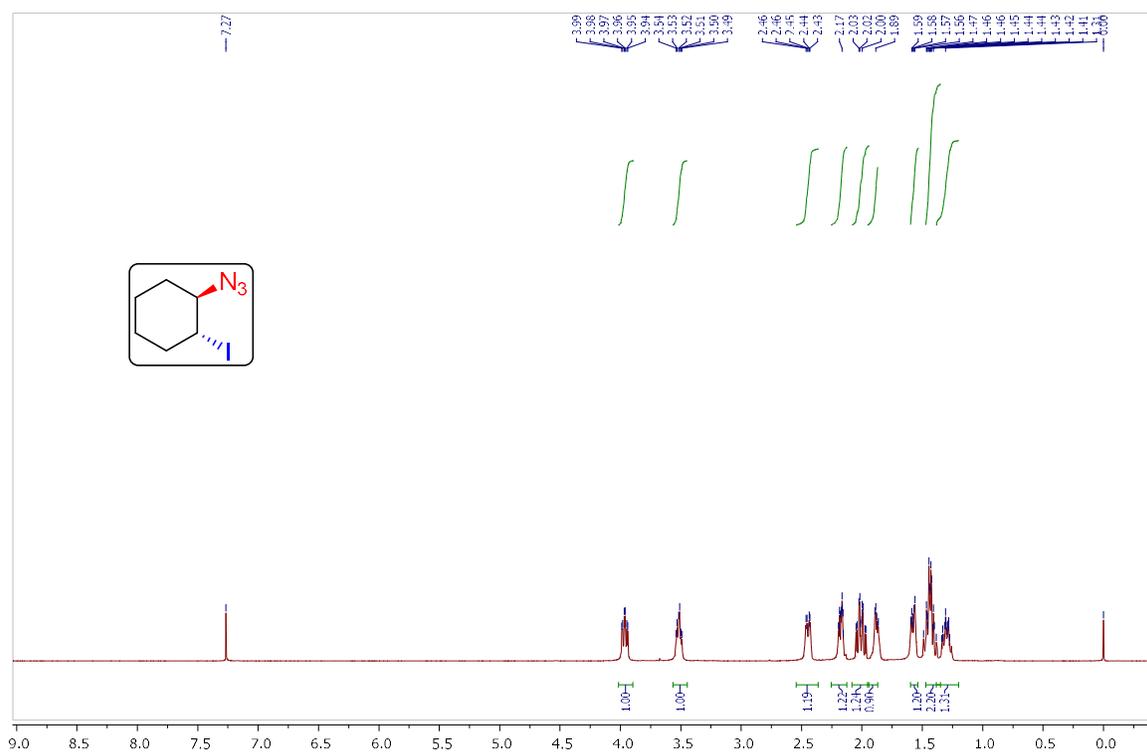


## $^{13}\text{C}$ NMR Spectrum of compound **53** in $\text{CDCl}_3$

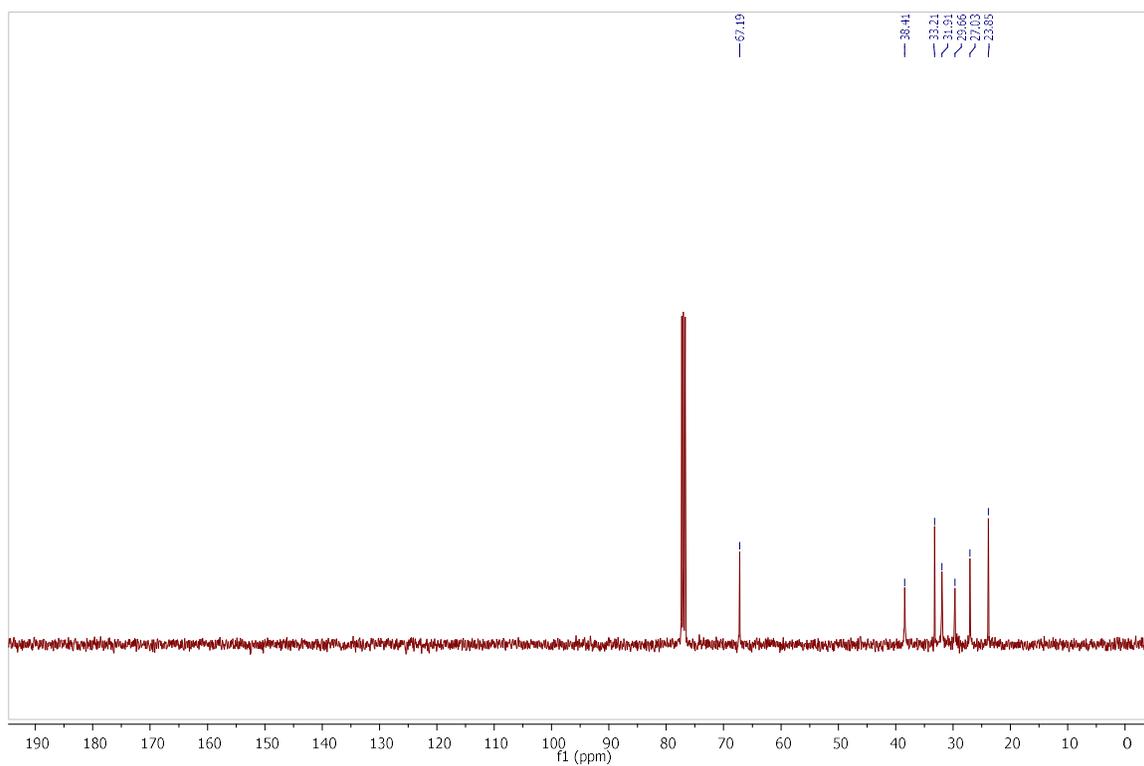


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **54** in $\text{CDCl}_3$

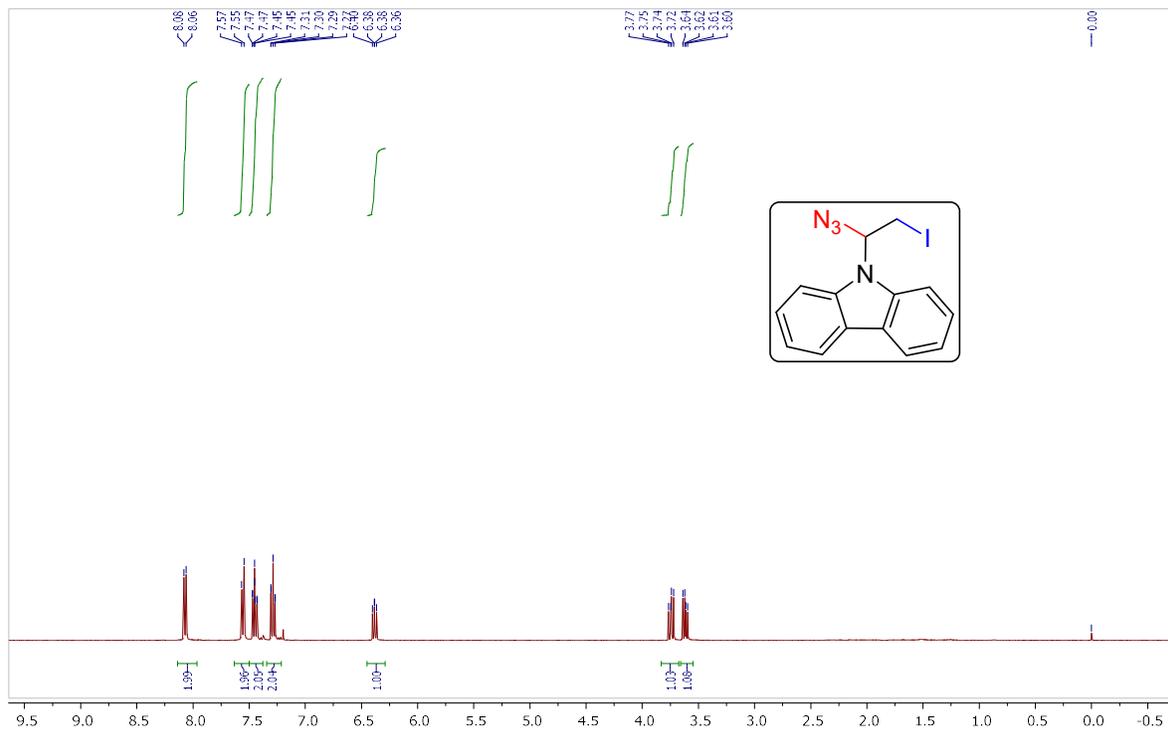


## $^{13}\text{C}$ NMR Spectrum of compound **54** in $\text{CDCl}_3$

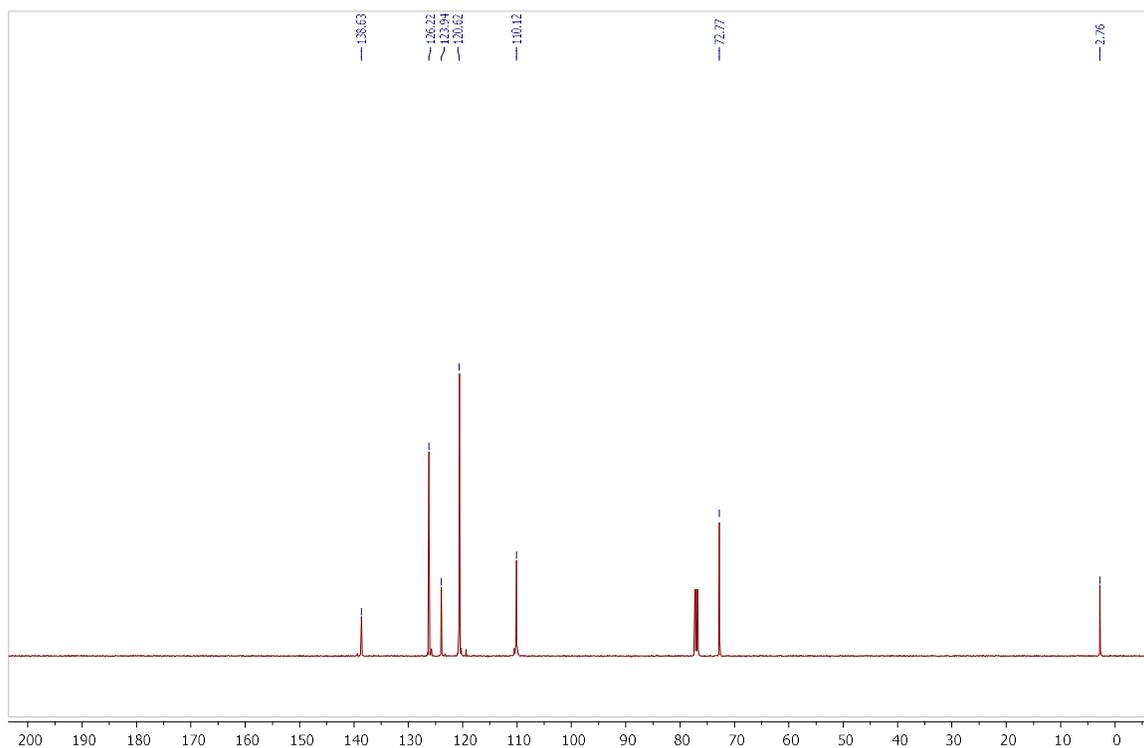


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **55** in $\text{CDCl}_3$

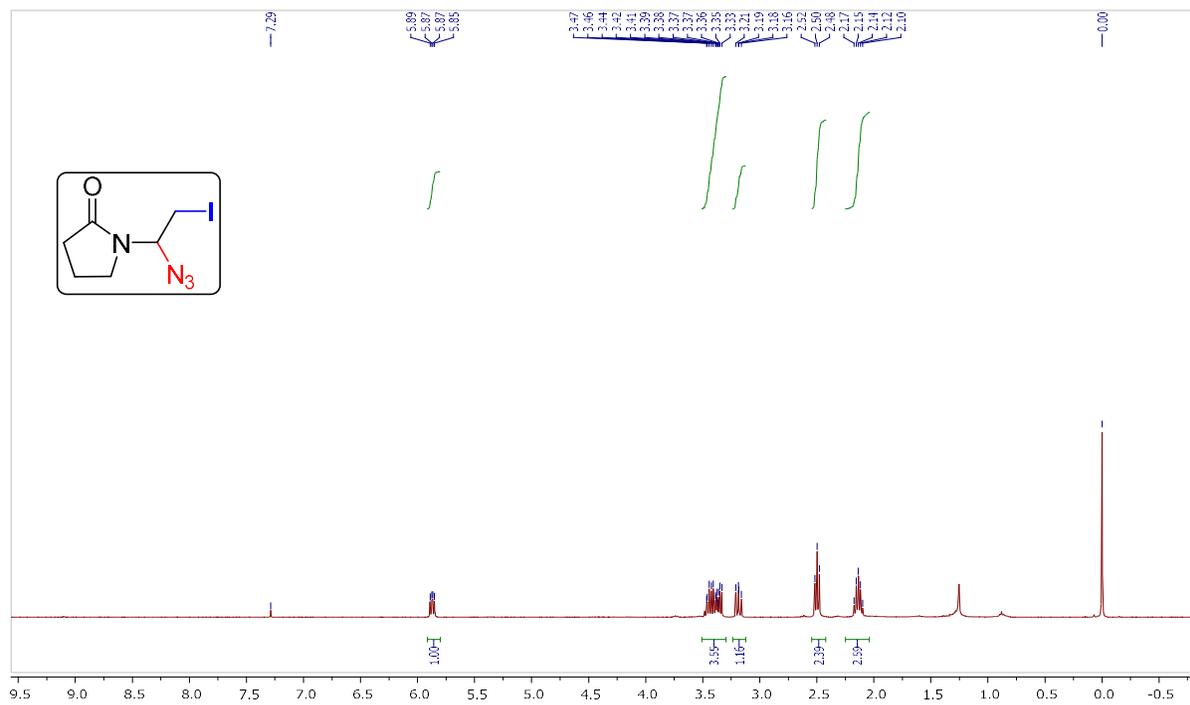


## $^{13}\text{C}$ NMR Spectrum of compound **55** in $\text{CDCl}_3$

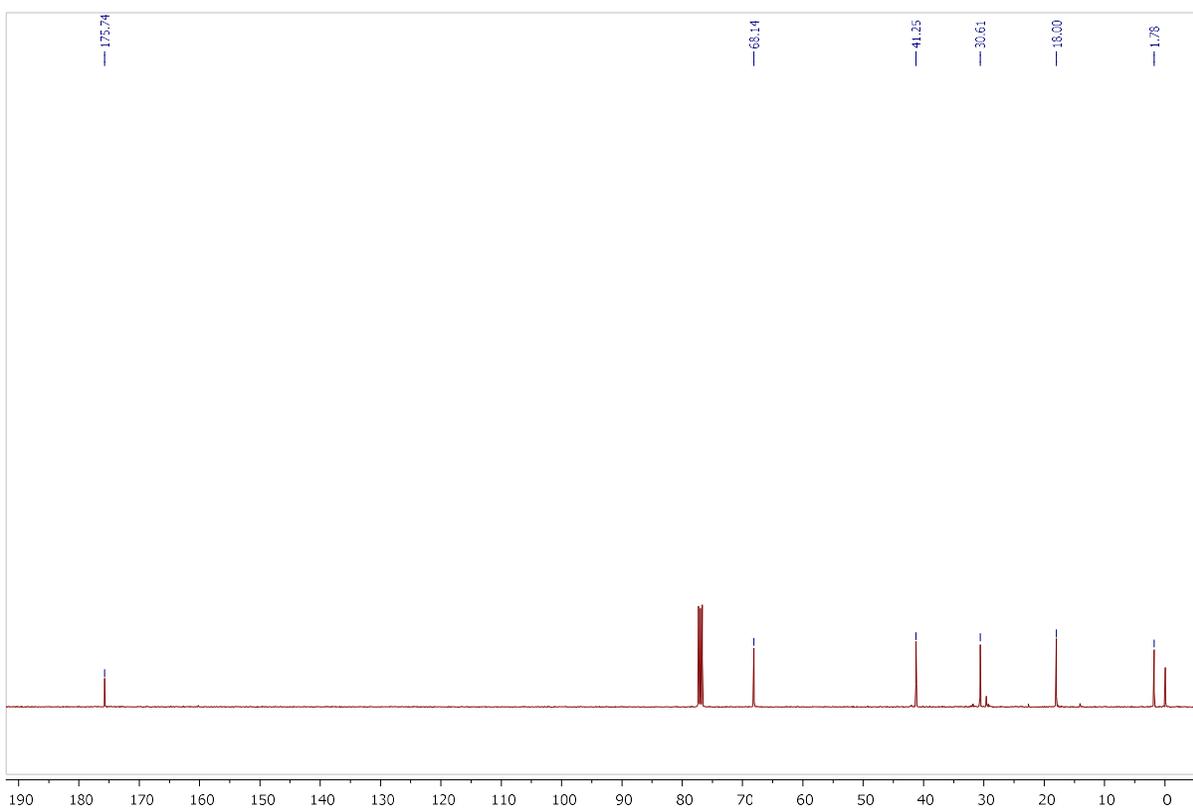


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **56** in CDCl<sub>3</sub>

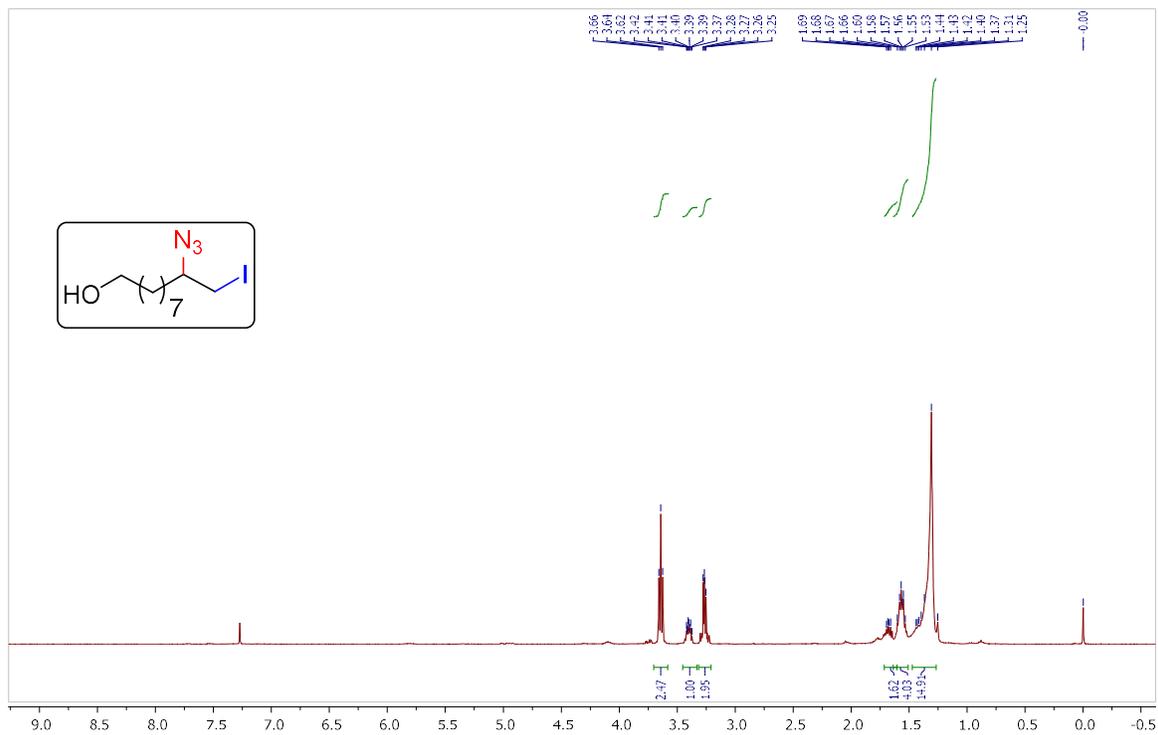


<sup>13</sup>C NMR Spectrum of compound **56** in CDCl<sub>3</sub>

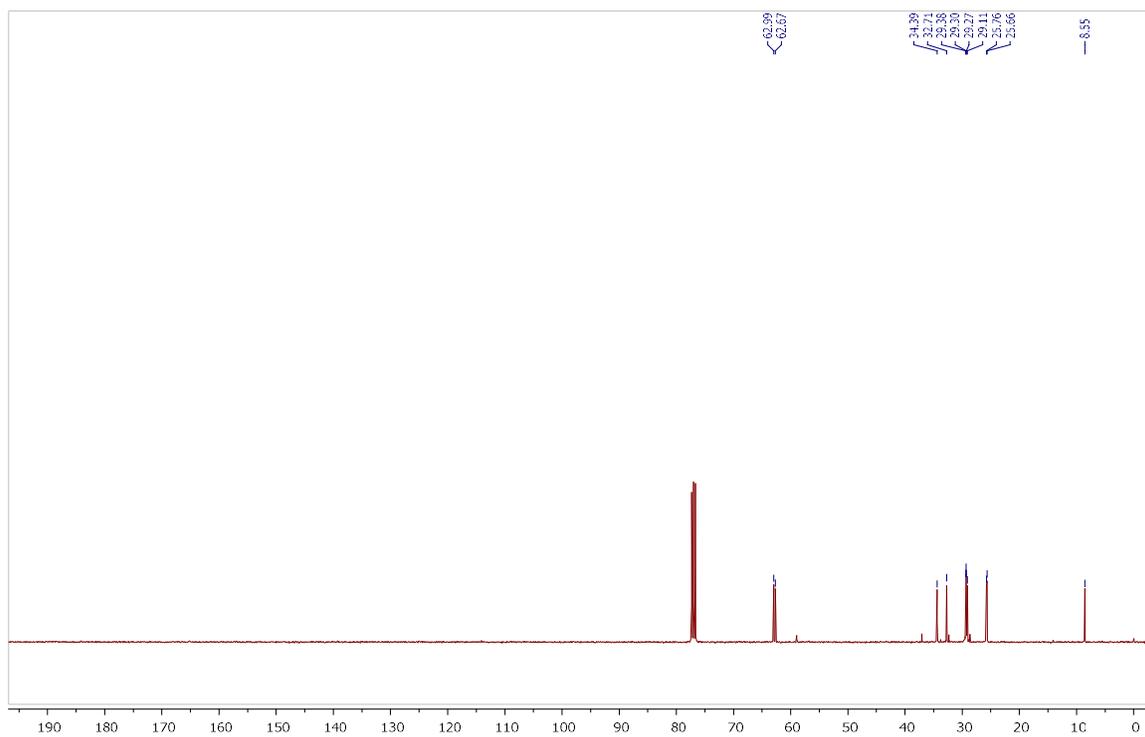


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **57** in  $\text{CDCl}_3$

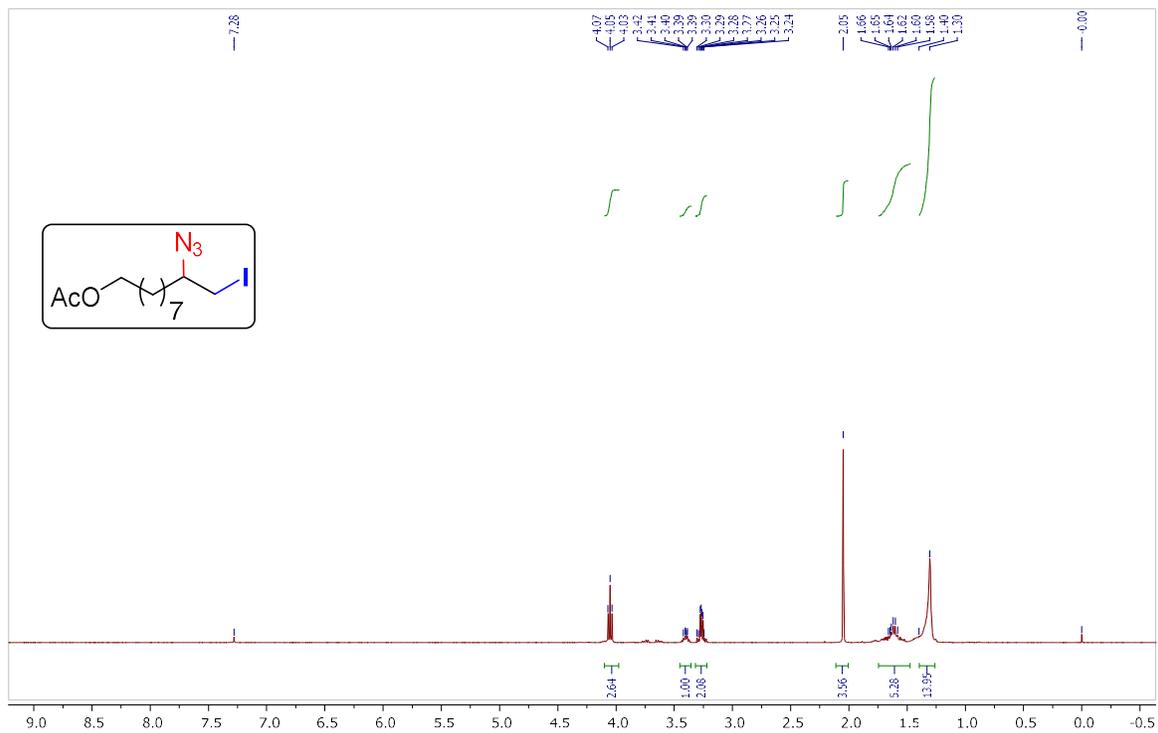


$^{13}\text{C}$  NMR Spectrum of compound **57** in  $\text{CDCl}_3$

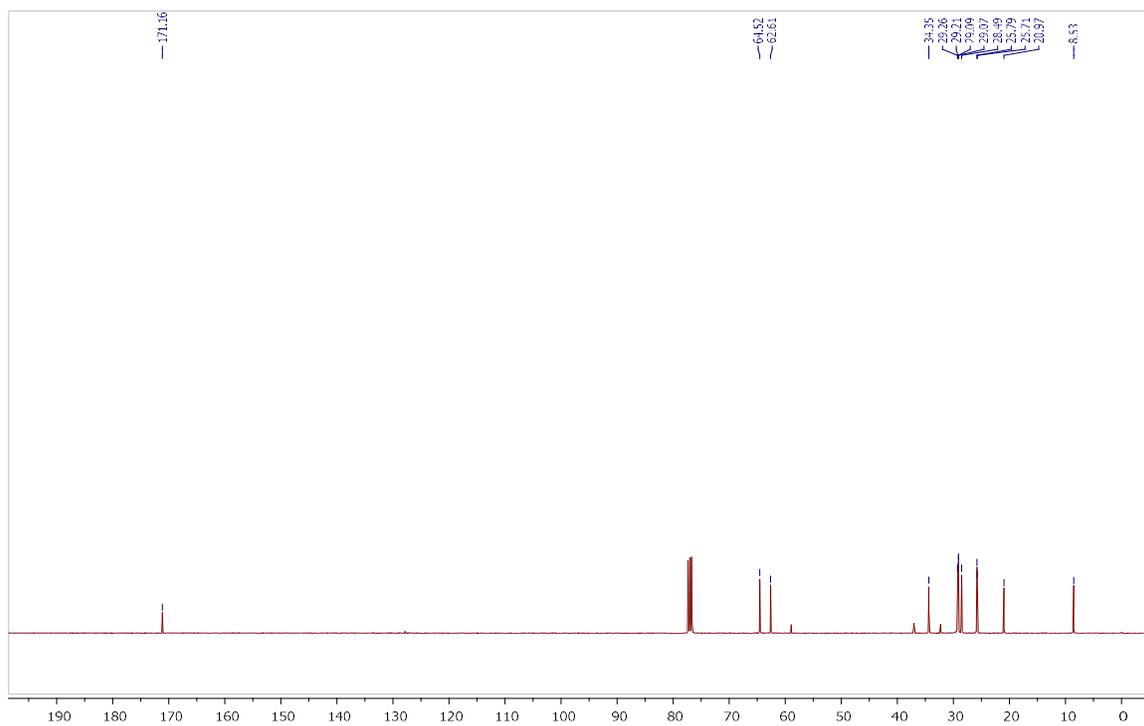


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **58** in CDCl<sub>3</sub>

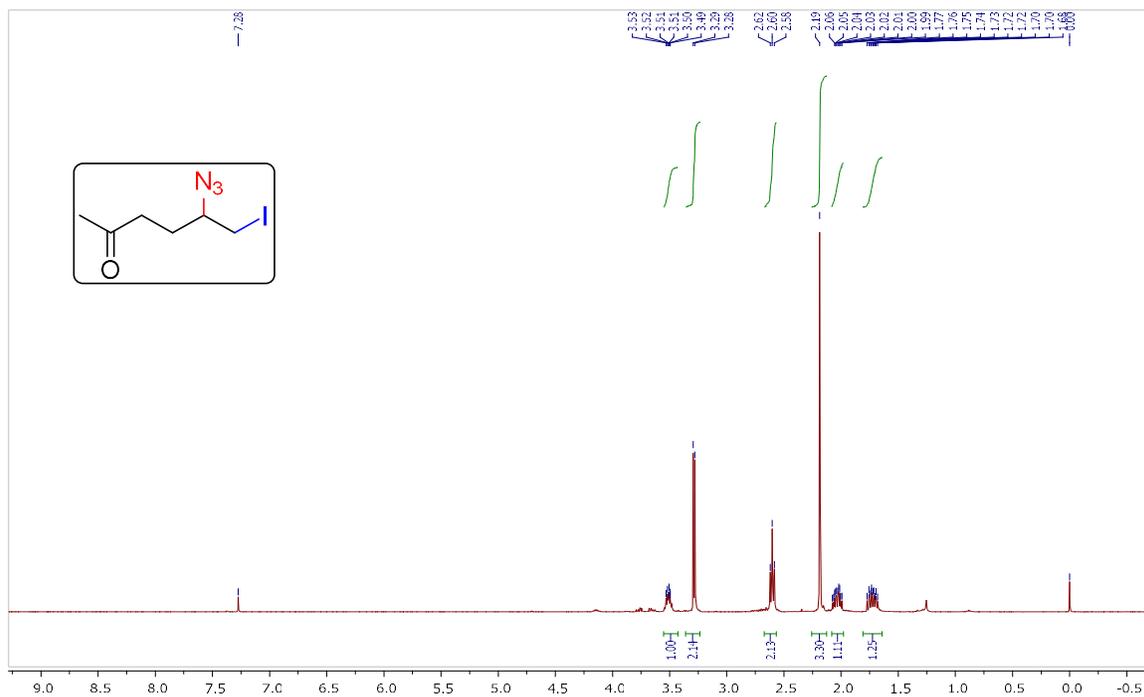


<sup>13</sup>C NMR Spectrum of compound **58** in CDCl<sub>3</sub>

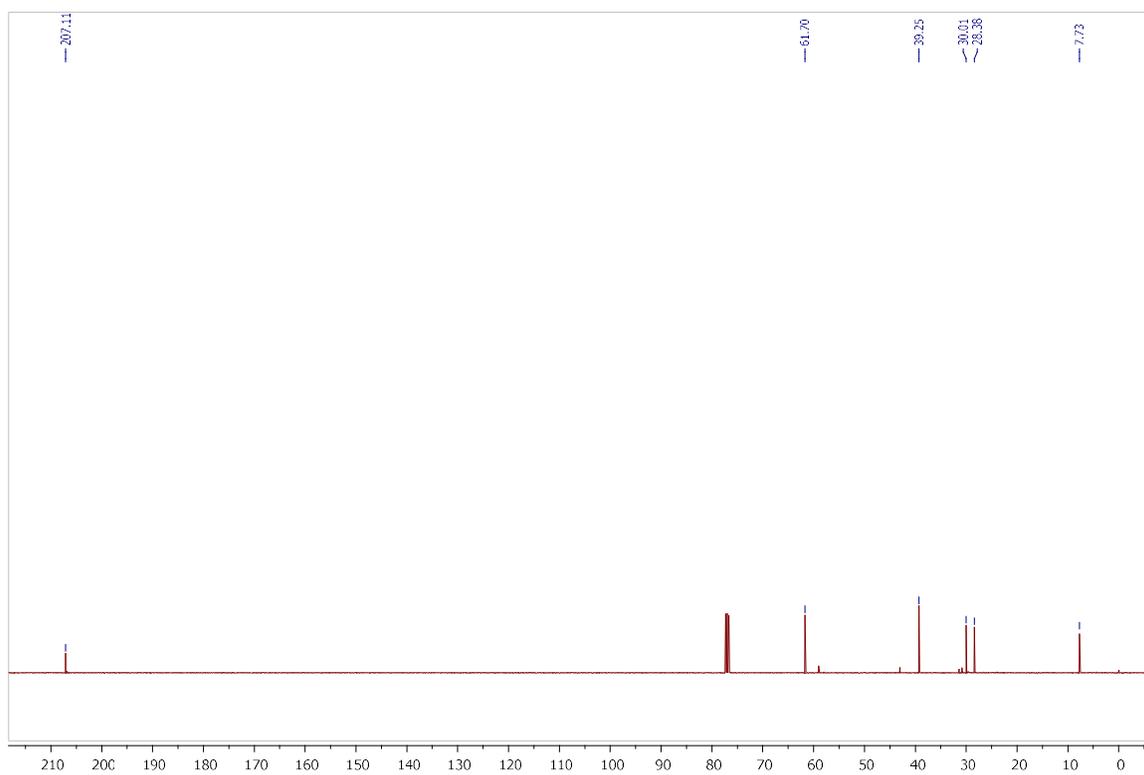


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **59** in CDCl<sub>3</sub>

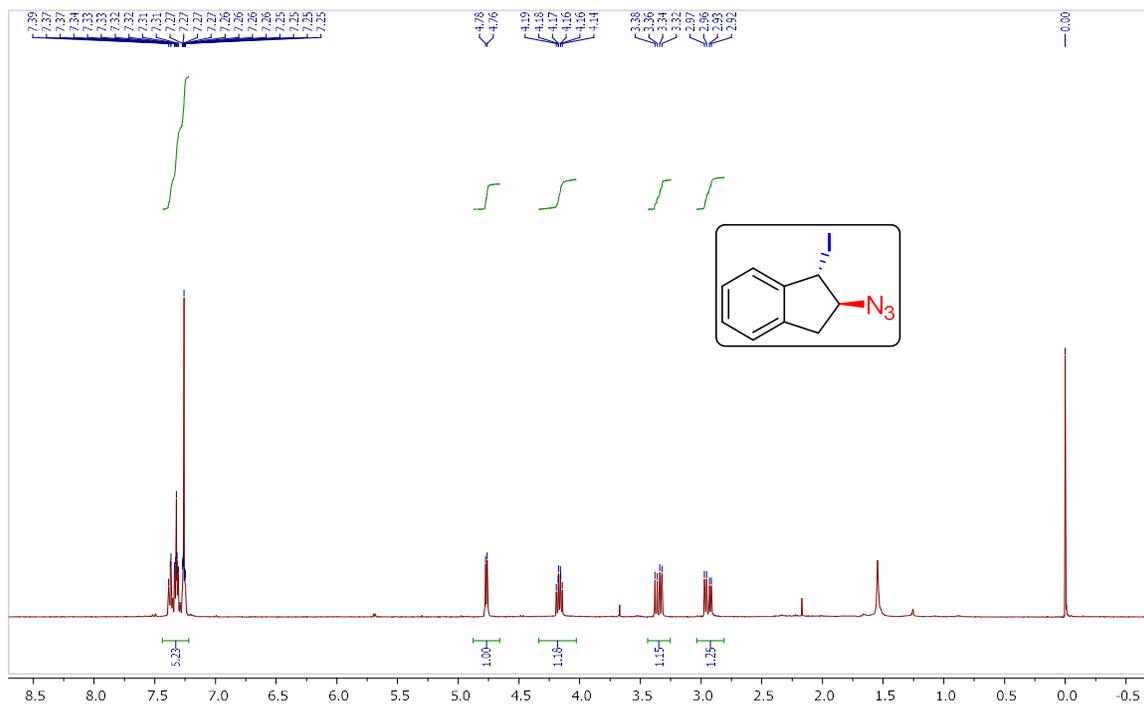


<sup>13</sup>C NMR Spectrum of compound **59** in CDCl<sub>3</sub>

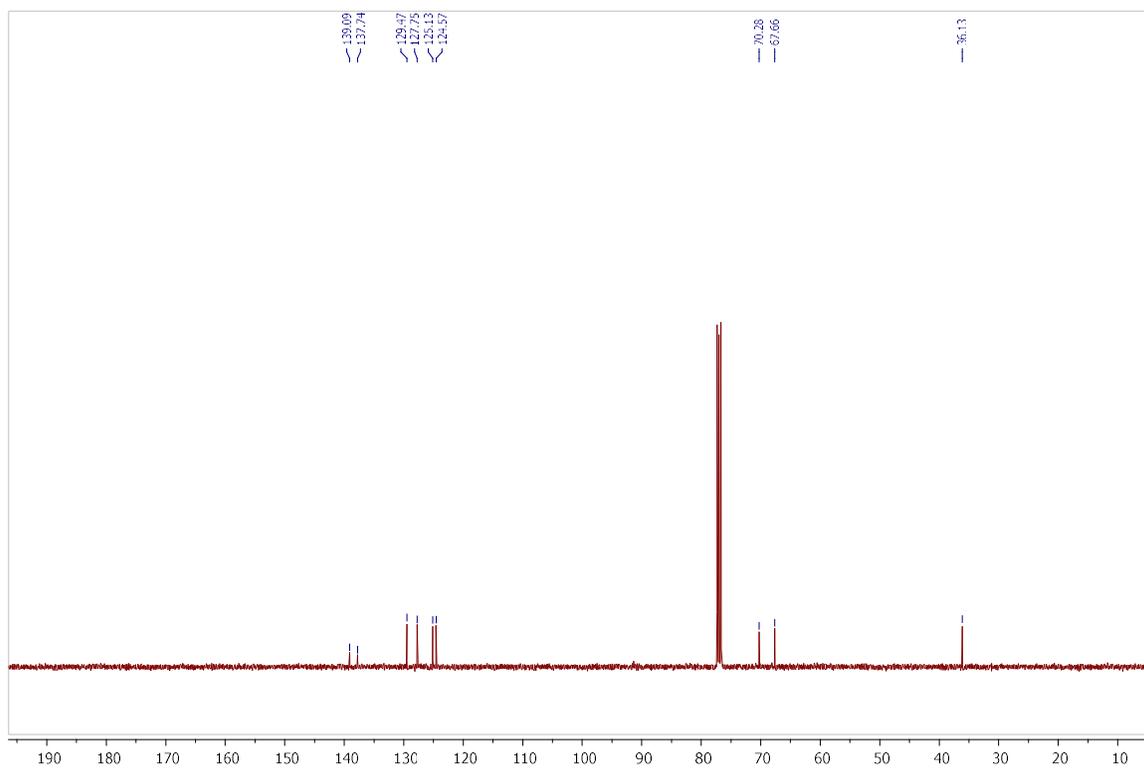


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **60** in $\text{CDCl}_3$

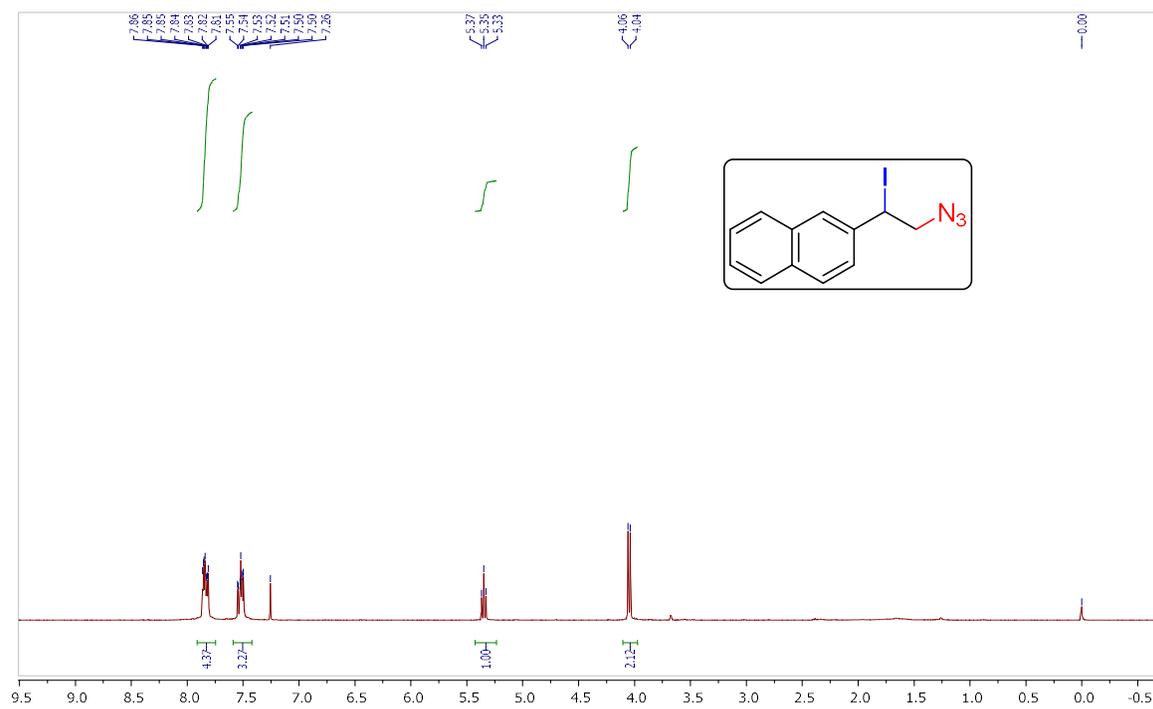


## $^{13}\text{C}$ NMR Spectrum of compound **60** in $\text{CDCl}_3$

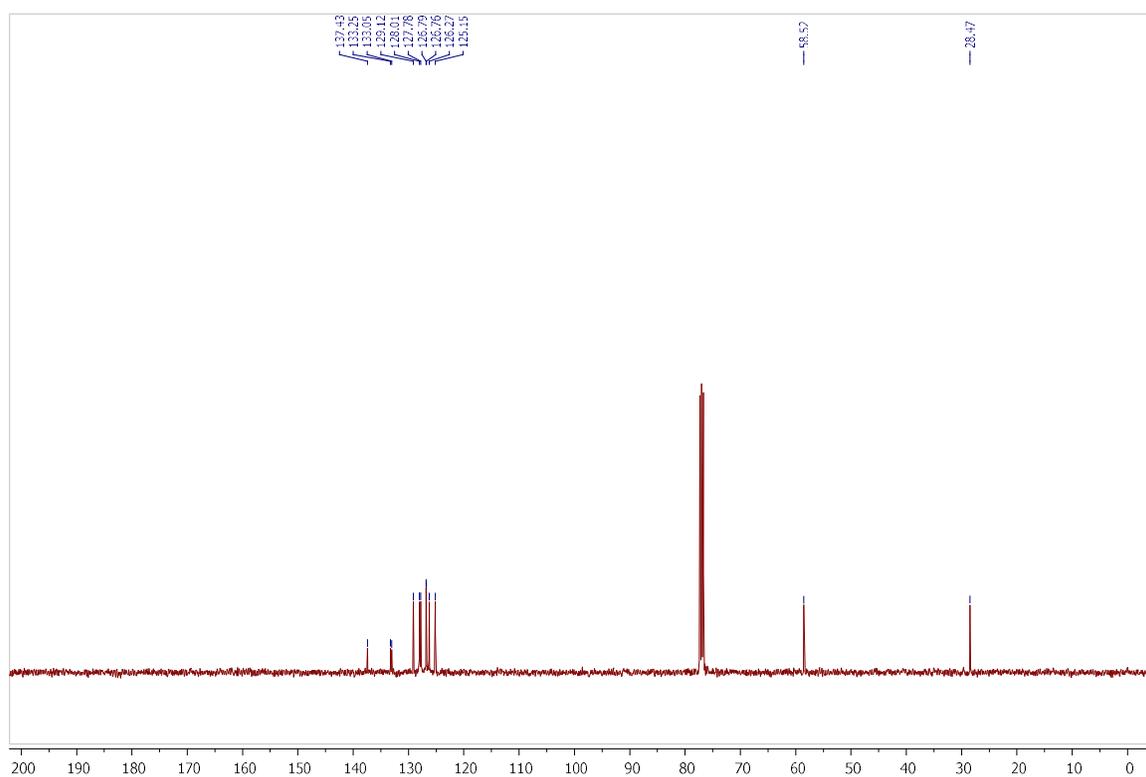


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **61** in $\text{CDCl}_3$

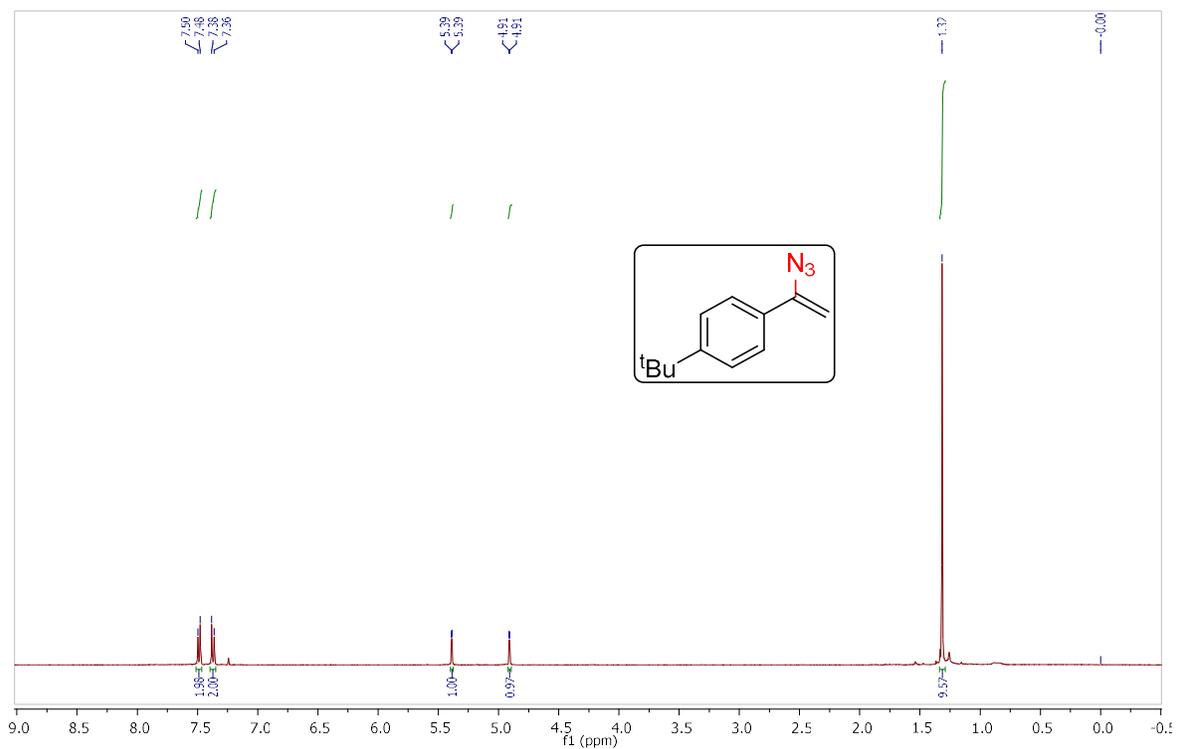


## $^{13}\text{C}$ NMR Spectrum of compound **61** in $\text{CDCl}_3$

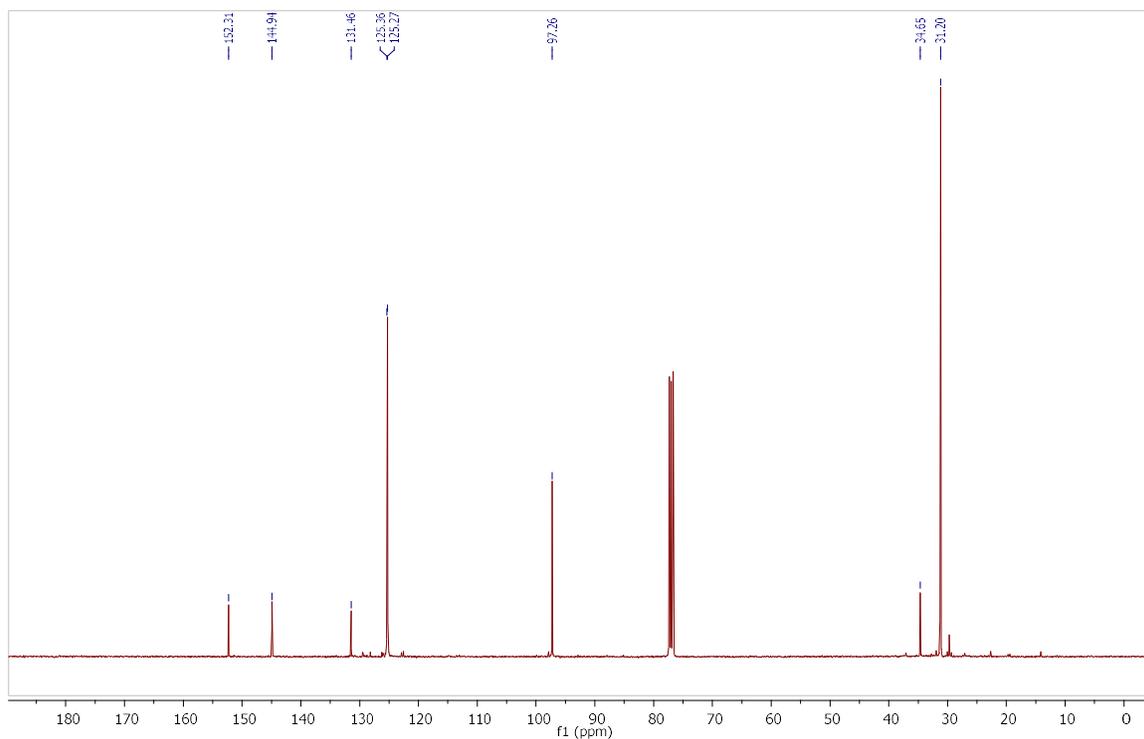


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **62** in $\text{CDCl}_3$

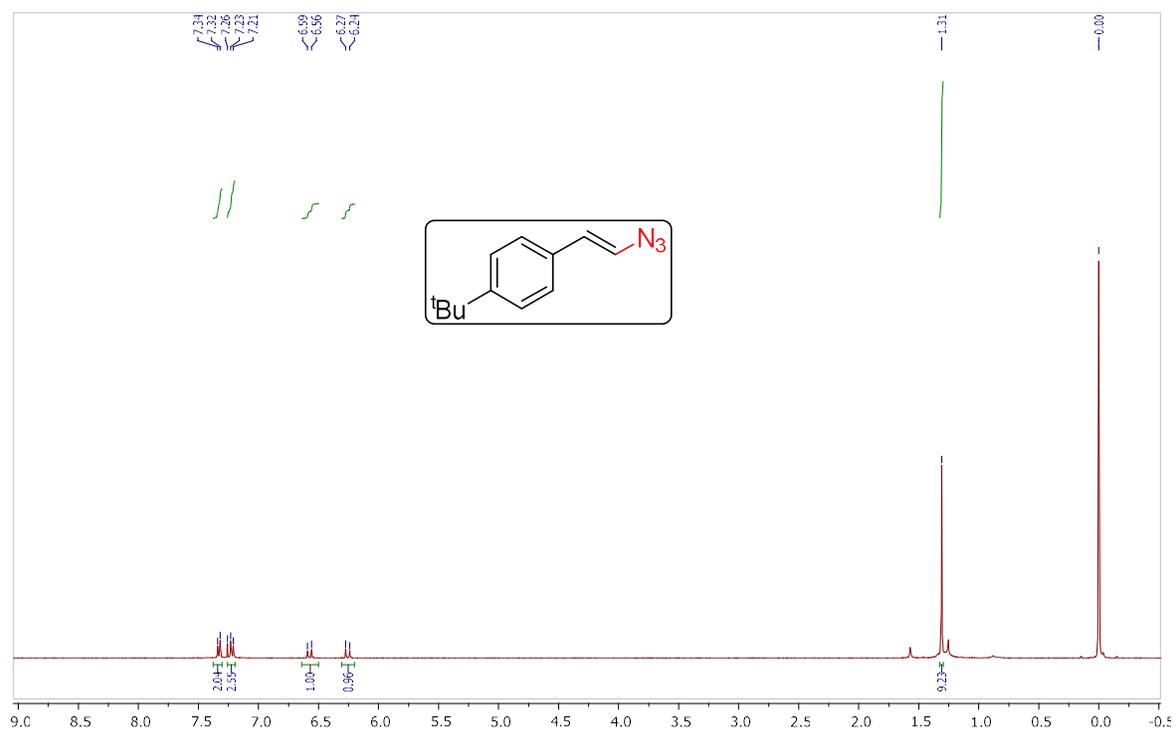


## $^{13}\text{C}$ NMR Spectrum of compound **62** in $\text{CDCl}_3$

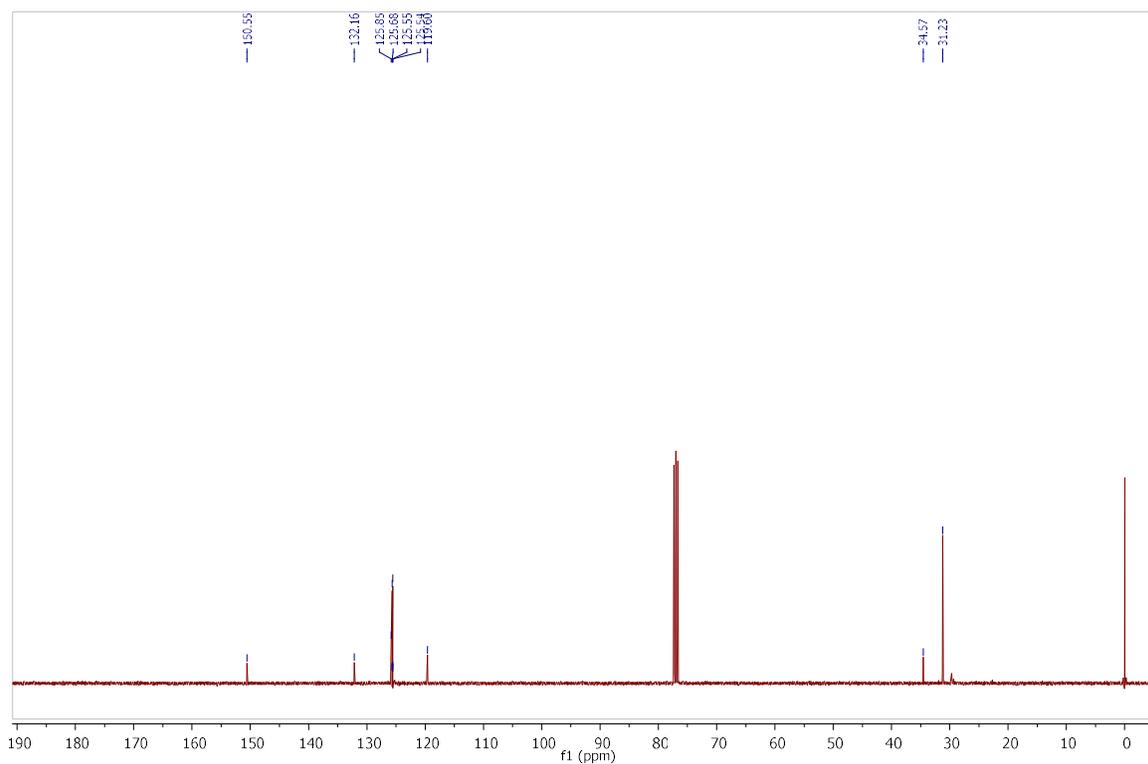


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **63** in $\text{CDCl}_3$

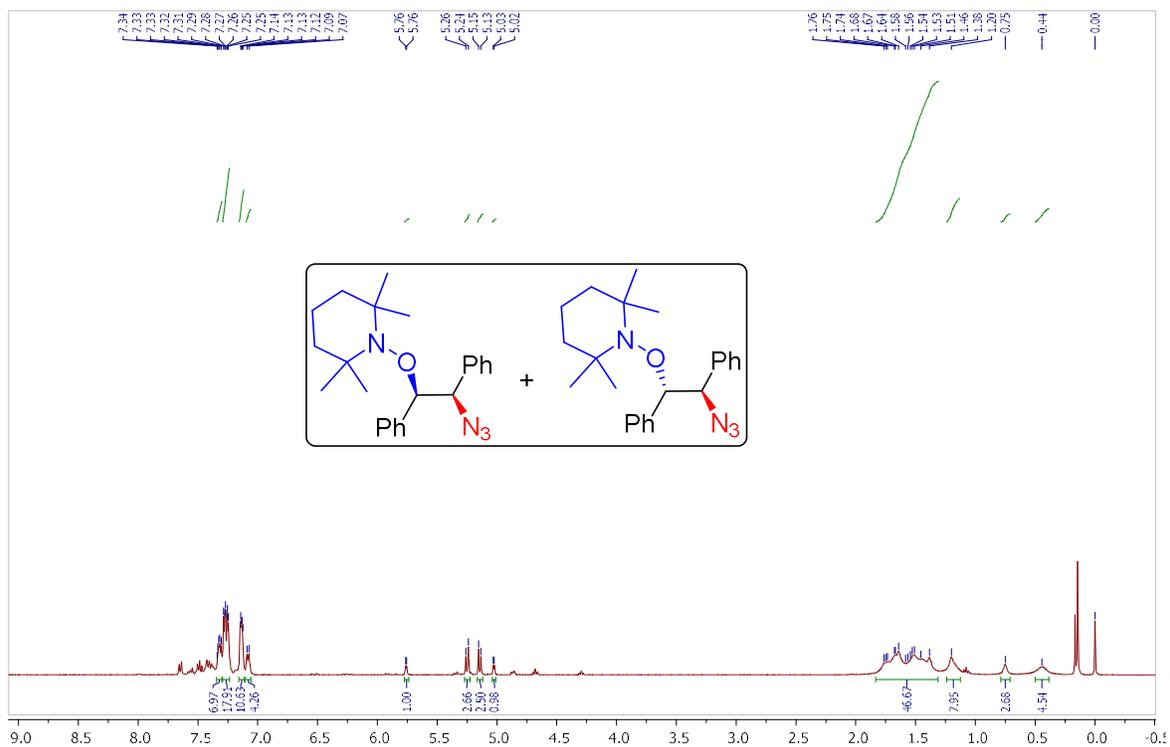


## $^{13}\text{C}$ NMR Spectrum of compound **63** in $\text{CDCl}_3$

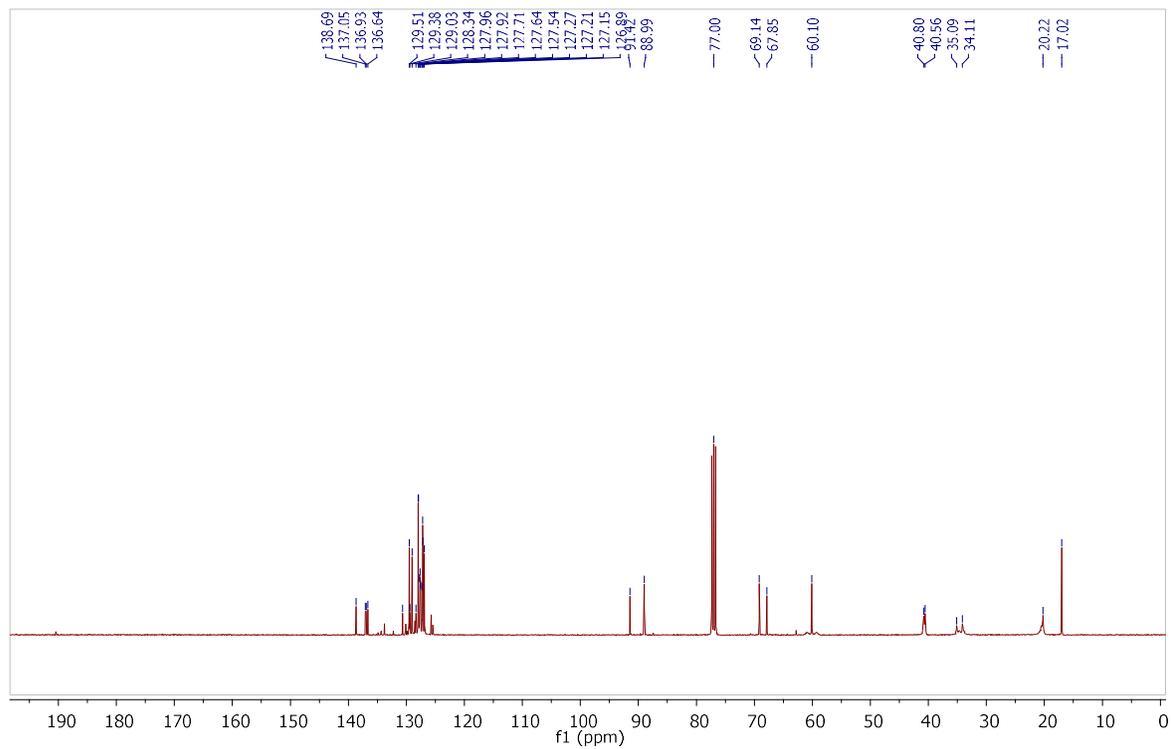


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **64** (from *trans*-Stilbene) in  $\text{CDCl}_3$

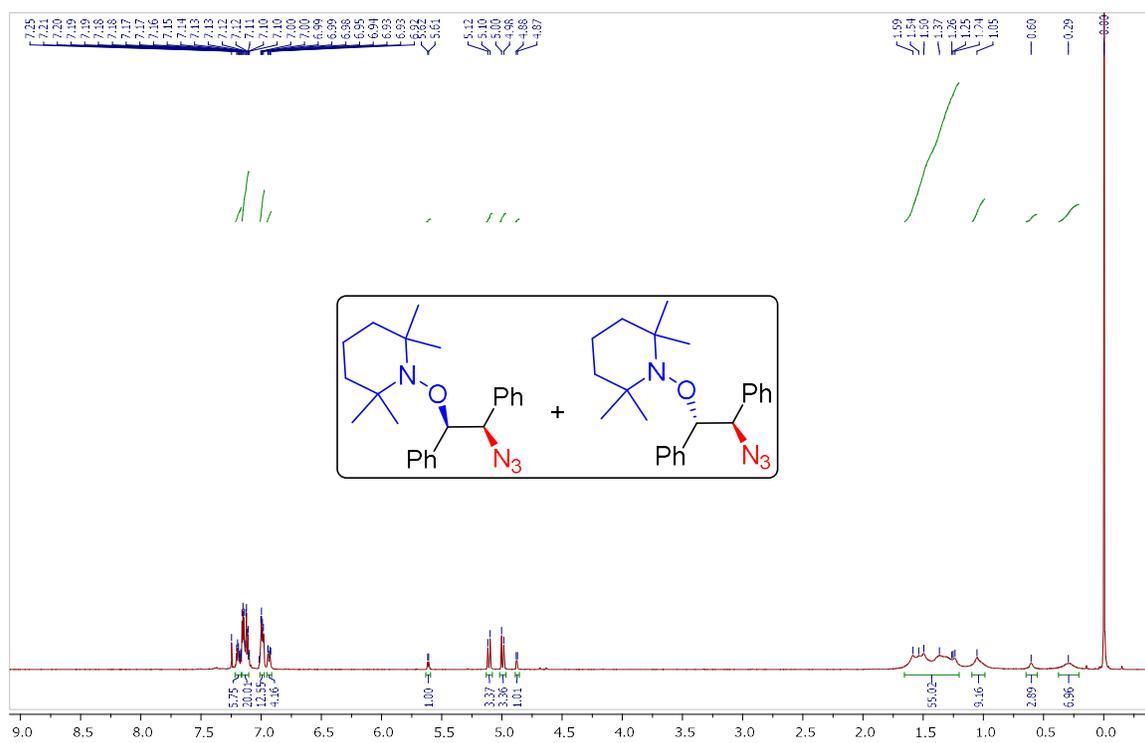


$^{13}\text{C}$  NMR Spectrum of compound **64** in  $\text{CDCl}_3$

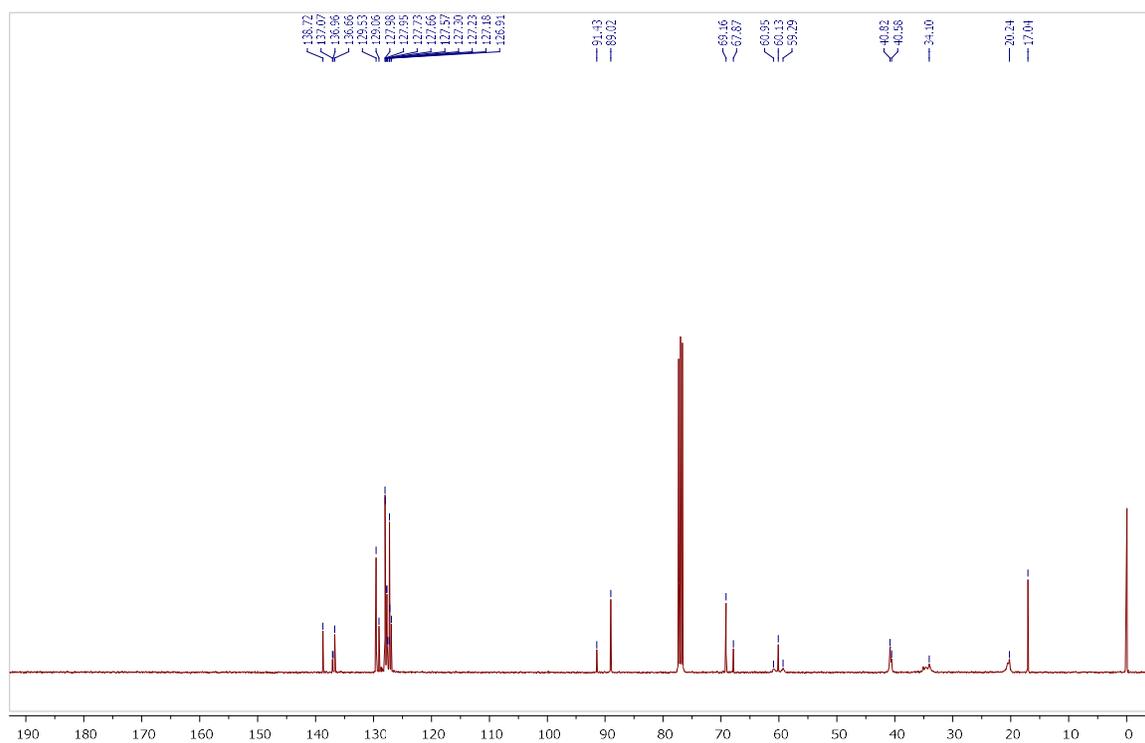


# SUPPORTING INFORMATION

<sup>1</sup>H NMR Spectrum of compound **64** (from *cis*-Stilbene) in CDCl<sub>3</sub>

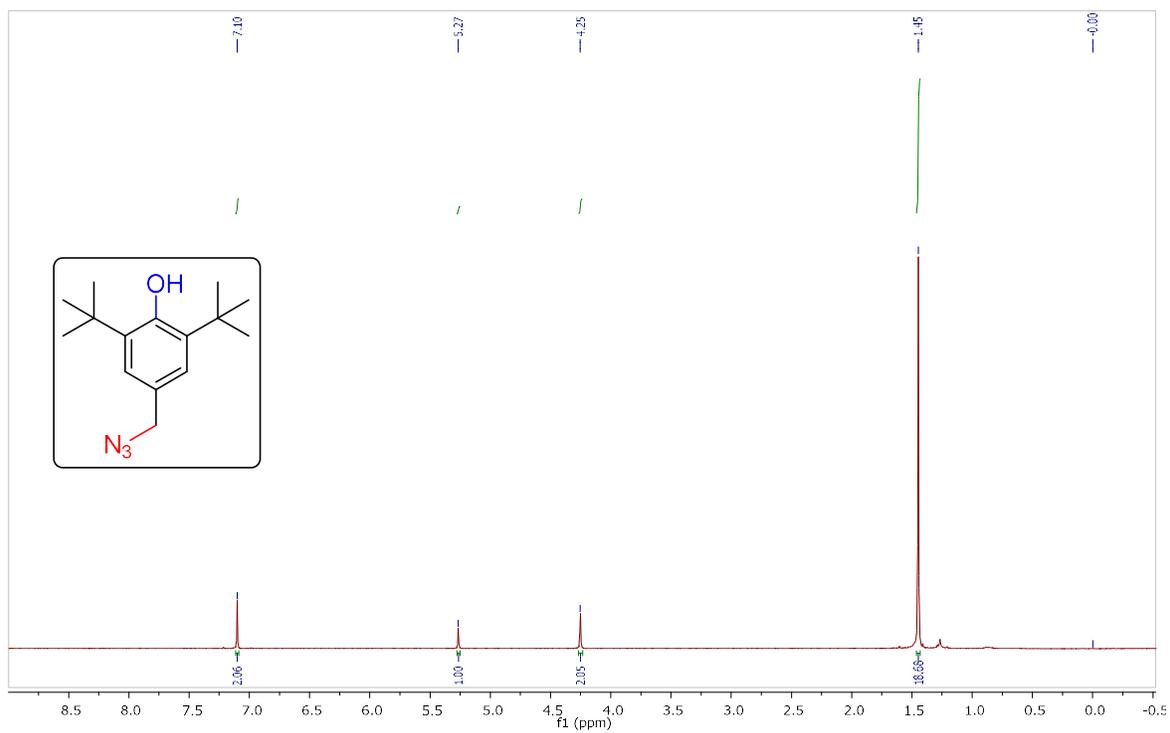


<sup>13</sup>C NMR Spectrum of compound **64** in CDCl<sub>3</sub>

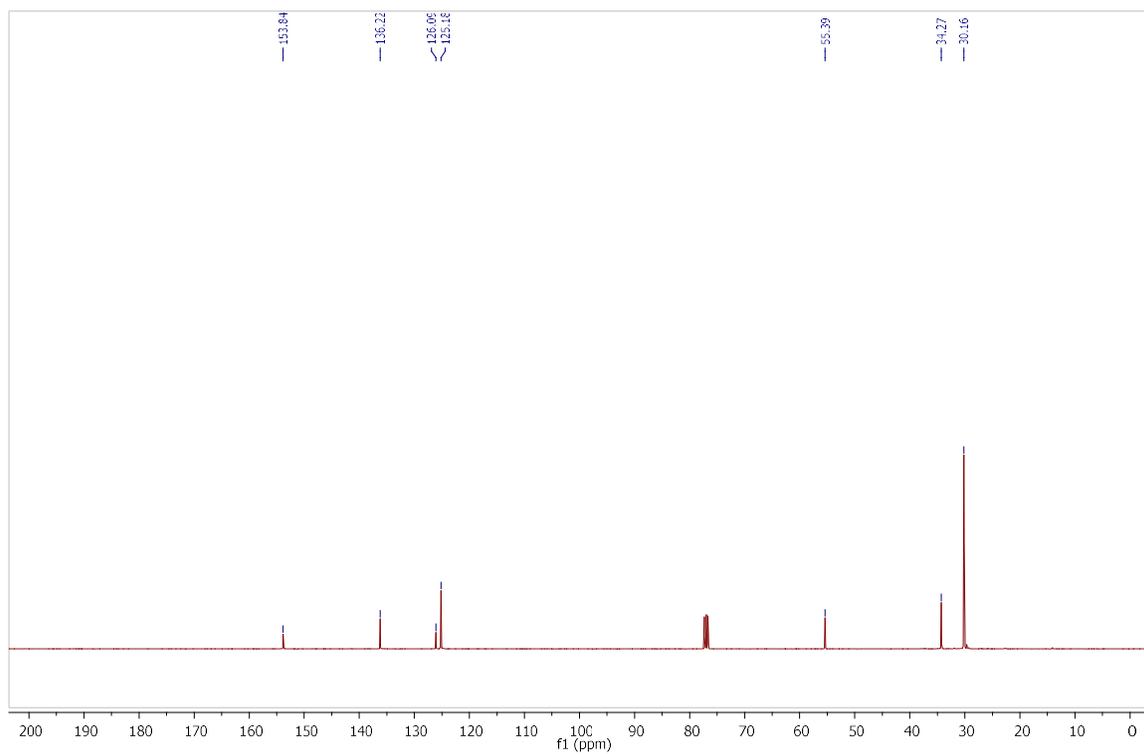


# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **65** in $\text{CDCl}_3$

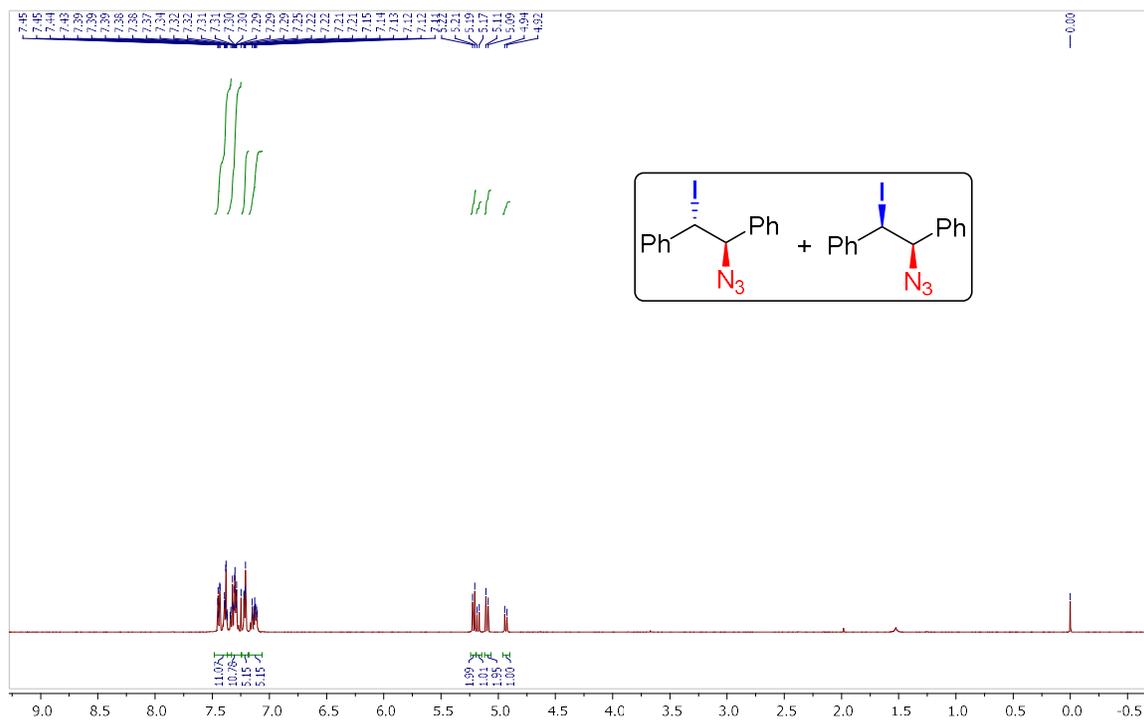


## $^{13}\text{C}$ NMR Spectrum of compound **65** in $\text{CDCl}_3$

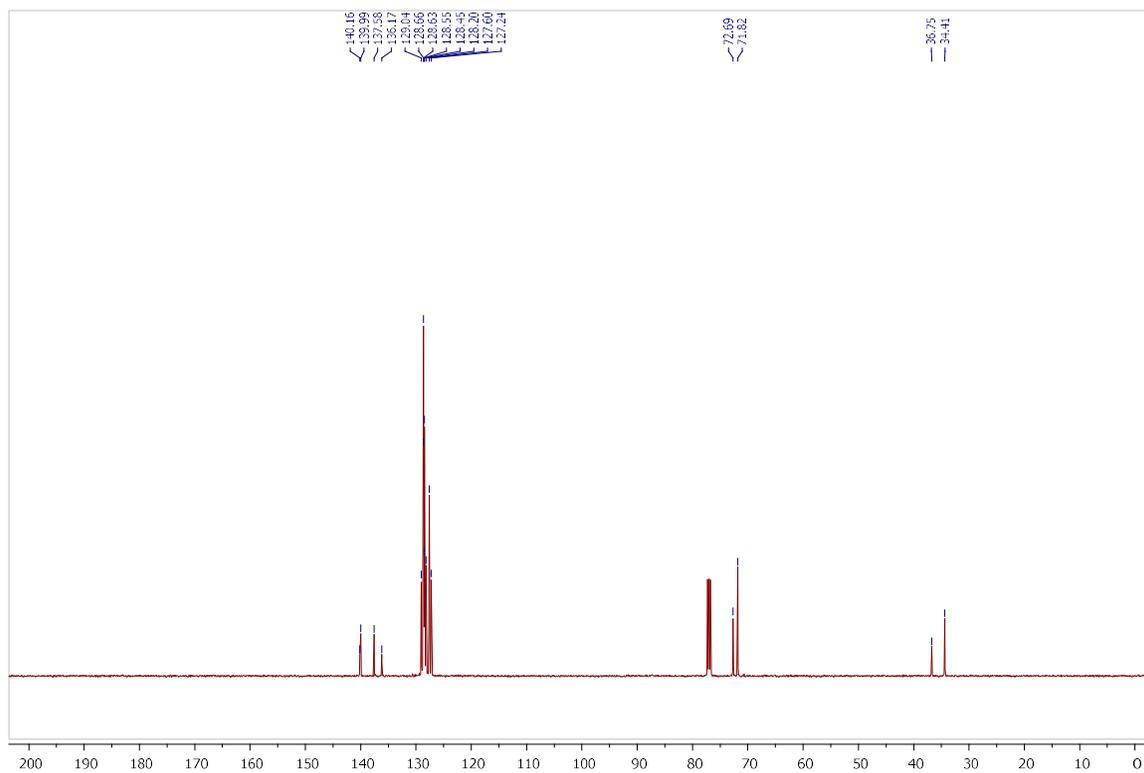


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **67** in  $\text{CDCl}_3$



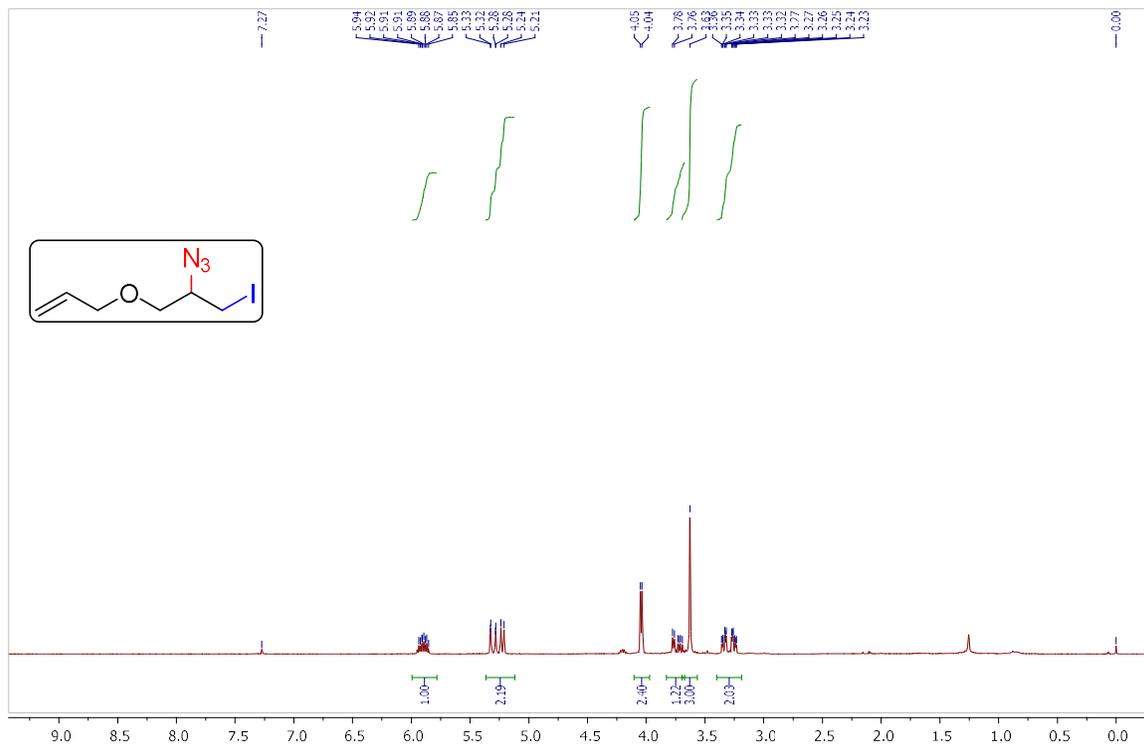
$^{13}\text{C}$  NMR Spectrum of compound **67** in  $\text{CDCl}_3$



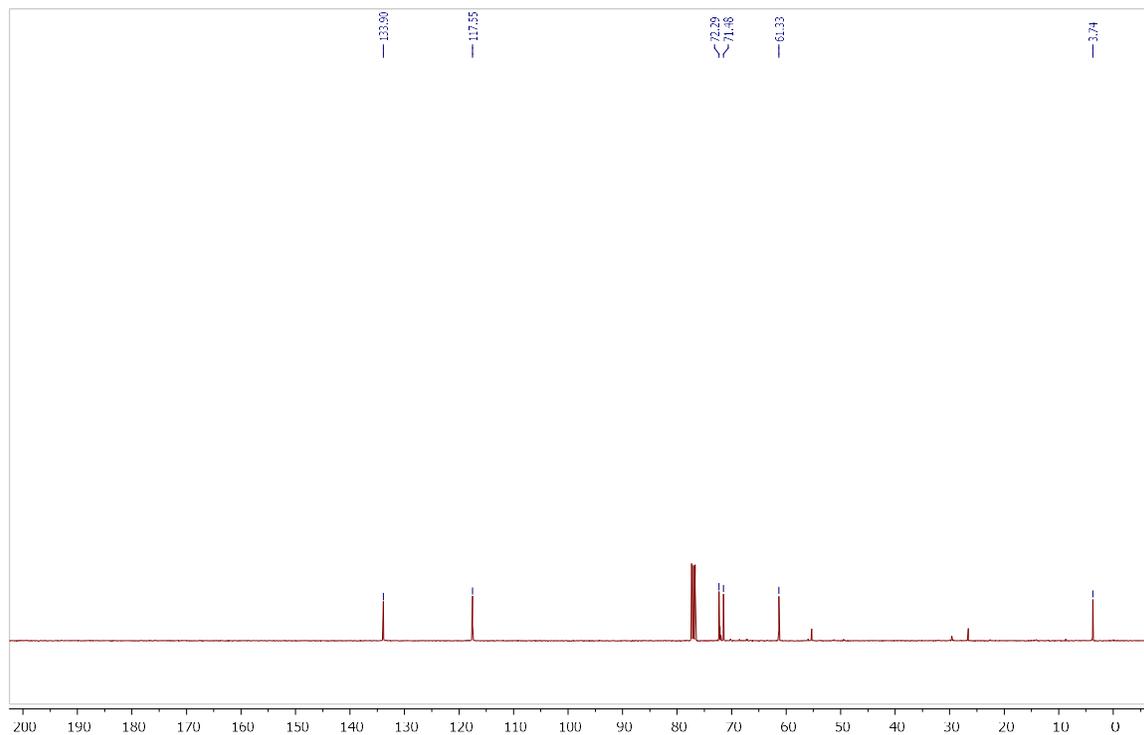


# SUPPORTING INFORMATION

$^1\text{H}$  NMR Spectrum of compound **69** in  $\text{CDCl}_3$

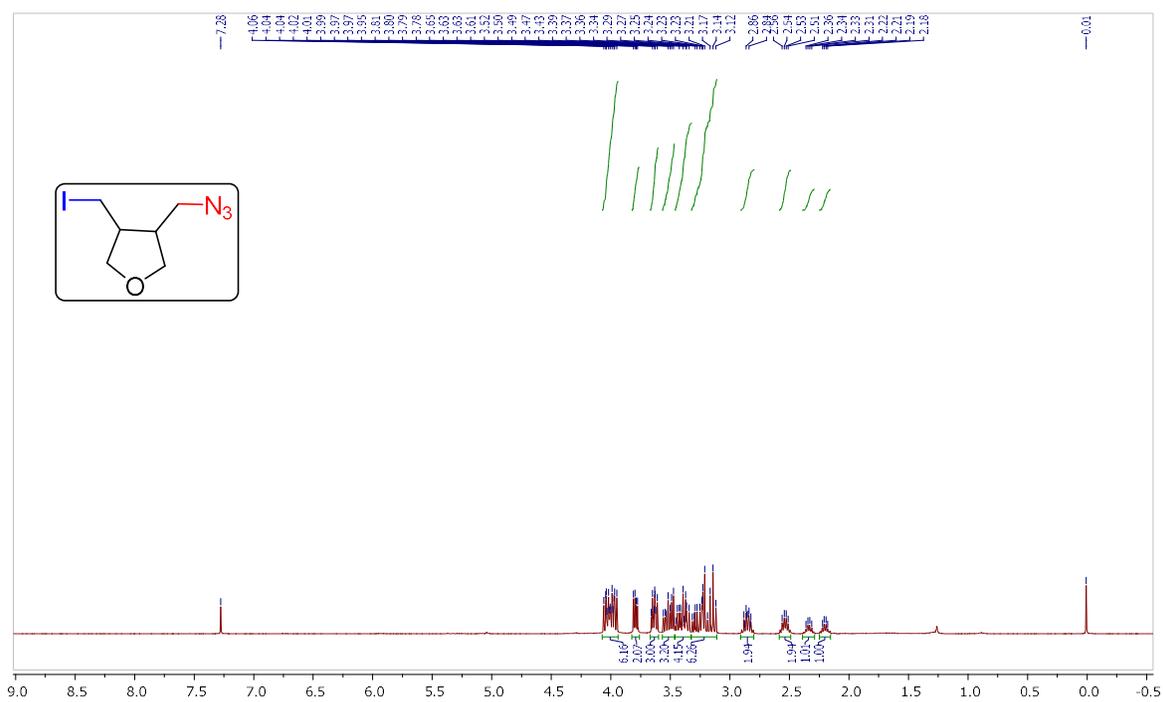


$^{13}\text{C}$  NMR Spectrum of compound **69** in  $\text{CDCl}_3$



# SUPPORTING INFORMATION

## $^1\text{H}$ NMR Spectrum of compound **70** in $\text{CDCl}_3$



## $^{13}\text{C}$ NMR Spectrum of compound **70** in $\text{CDCl}_3$

