Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for

Organocatalytic electrochemical amination of benzylic C–H bonds

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Contents

1. General Information

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. Flash column chromatography was performed with silica gel (200–300 mesh). NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H NMR and $CDCl_3$ (77.2 ppm) for ^{13}C NMR. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (ESI HRMS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Cyclic voltammograms were obtained on a CHI 660E potentiostat.

2. General Procedure for the Electrolysis

General Procedure for the model reaction： A 20 mL three-necked beaker-type cell (Figure S1A) was charged with DDQ (5 mol%), alkylarene (0.30 mmol), nitrogen-containing nucleophiles (0.60 mmol) and *n*-Bu_4NBF_4 (0.15 mmol). The cell was equipped with a reticulated vitreous carbon (RVC, 100 PPI, 1.2 cm x 0.8 cm x 0.8 cm) anode and a platinum plate (1 cm x 1 cm x 0.1 mm) cathode (Figure S1B) and then flushed with argon. MeCN (3.0 mL) and DCE (3.0 mL) were added. The electrolysis was carried out at room temperature using a constant current of 10 mA for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product.

General Procedure for the Gram-scale Synthesis of 3： The gram-scale electrolysis of **1** was conducted in a 100 mL three-necked round-bottomed flask (Figure S1C) with a piece of RVC (1.2 cm x 2 cm x 2 cm) as the anode, a Pt plate as the cathode (1.5 cm x 1.5 cm x 0.3 mm), and a constant current of 66 mA for 8 h at room temperature. The reaction mixture consisted 1-ethyl-4-methoxybenzene **1** (1.09 g, 8.0 mmol), 4-chloropyrazole **2** (1.64 g, 16.0 mmol), DDQ (91 mg, 0.015 mmol), *n*Bu_4NBF_4 (263 mg, 0.80 mmol), MeCN (40 mL) and DCE (40 mL). When the reaction was complete, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product **3** (1.49 g, 79% yield).

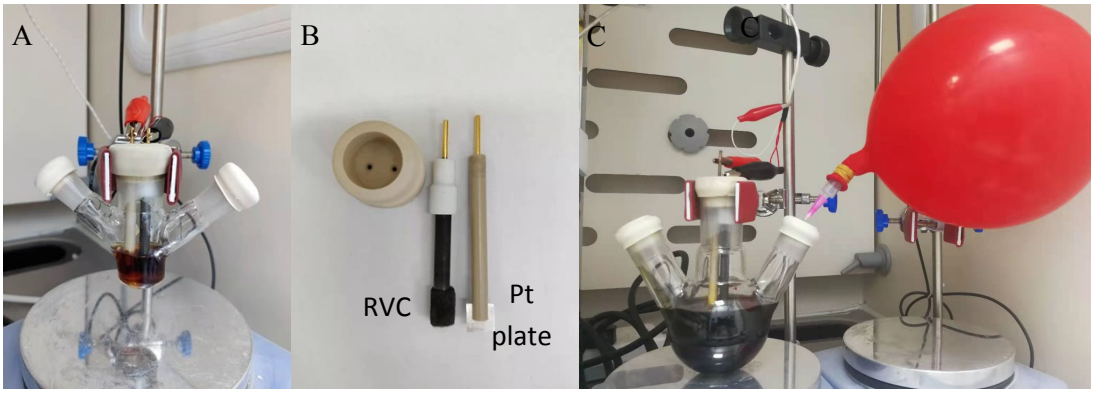
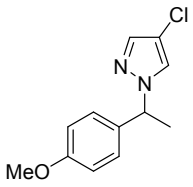


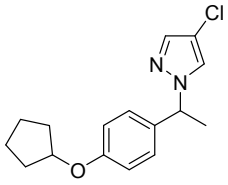
Figure S1. The electrolysis setup. The RVC is fixed on a sharpened graphite rod (⌀ 6 mm).

3. Characterization Data for the Electrolysis Products

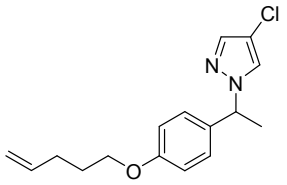
The products **3**,[1] **16**,[1] **39**,[2] **40**[3] and **43**[4] have been reported.



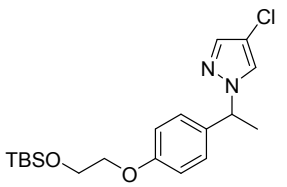
4-Chloro-1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (3). Yield = 86%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.30 (s, 1H), 7.20 – 7.14 (m, 2H), 6.90 – 6.84 (m, 2H), 5.40 (q, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 1.84 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 137.5, 133.1, 127.9, 125.9, 114.3, 109.9, 61.5, 55.5, 21.3.



4-Chloro-1-(1-(4-(cyclopentyloxy)phenyl)ethyl)-1*H*-pyrazole (4). Yield = 78%; White solid; m.p. = 67.2−68.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44 (s, 1H), 7.29 (s, 1H), 7.17–7.11 (m, 2H), 6.86–6.80 (m, 2H), 5.39 (q, *J* = 7.0 Hz, 1H), 4.76–4.69 (m, 1H), 1.93–1.82 (m, 7H), 1.81–1.75 (m, 2H), 1.66–1.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 158.2, 137.5, 132.4, 127.8, 125.9, 115.8, 109.8, 79.4, 61.5, 33.0, 24.2, 21.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 313.1078, obsd 313.1084.

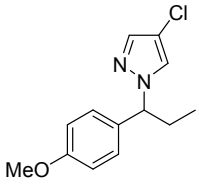


4-Chloro-1-(1-(4-(pent-4-en-1-yloxy)phenyl)ethyl)-1*H*-pyrazole (5). Yield = 77%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44 (d, *J* = 0.7 Hz, 1H), 7.30 (d, *J* = 0.7 Hz, 1H), 7.18–7.12 (m, 2H), 6.89–6.83 (m, 2H), 5.90–5.78 (m, 1H), 5.39 (q, *J* = 6.7 Hz, 1H), 5.09–4.97 (m, 2H), 3.95 (t, *J* = 6.7 Hz, 2H), 2.26–2.19 (m, 2H), 1.90–1.82 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.0, 137.9, 137.5, 132.9, 127.9, 125.9, 115.4, 114.9, 109.8, 67.3, 61.5, 30.2, 28.5, 21.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 313.1078, obsd 313.1080.

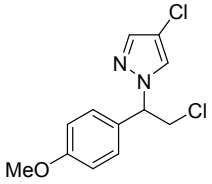


1-(1-(4-(2-((*tert*-Butyldimethylsilyl)oxy)ethoxy)phenyl)ethyl)-4-chloro-1*H*-pyrazole (6). Yield = 68%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.44 (d, *J* = 0.7 Hz, 1H), 7.29 (d, *J* = 0.7 Hz, 1H), 7.18–7.13 (m, 2H), 6.90–6.86 (m, 2H), 5.39 (q, *J* = 7.1 Hz, 1H), 4.04–4.00 (m, 2H),

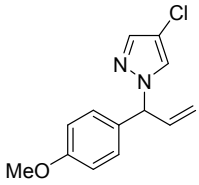
3.97–3.94 (m, 2H), 1.84 (d, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.0, 137.5, 133.1, 127.9, 125.9, 115.0, 109.9, 69.5, 62.1, 61.5, 26.1, 21.3, 18.6, −5.0; ESI HRMS *m/z* $(M+Na)^+$ calcd 403.1579, obsd 403.1584.



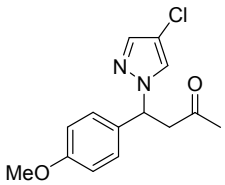
4-Chloro-1-(1-(4-methoxyphenyl)propyl)-1*H*-pyrazole (7). Yield = 81%; White solid; m.p. = 56.8−57.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (d, *J* = 0.7 Hz, 1H), 7.35 (d, *J* = 0.7 Hz, 1H), 7.24–7.19 (m, 2H), 6.88–6.84 (m, 2H), 5.09–5.00 (m, 1H), 3.78 (s, 3H), 2.43–2.32 (m, 1H), 2.19–2.08 (m, 1H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.5, 137.5, 132.0, 128.3, 126.2, 114.2, 109.8, 68.2, 55.4, 28.3, 11.2; ESI HRMS *m/z* $(M+Na)^+$ calcd 273.0765, obsd 273.0768.



4-Chloro-1-(2-chloro-1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (8). Yield = 75%; White solid; m.p. = 52.6−53.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51 (d, *J* = 0.7 Hz, 1H), 7.41 (d, *J* = 0.7 Hz, 1H), 7.27–7.23 (m, 2H), 6.91–6.85 (m, 2H), 5.35 (dd, *J* = 9.0, 5.4 Hz, 1H), 4.40 (dd, *J* = 11.5, 9.0 Hz, 1H), 3.98 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.2, 138.5, 128.9, 128.5, 127.7, 114.5, 110.3, 67.4, 55.5, 45.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 293.0219, obsd 293.0218.

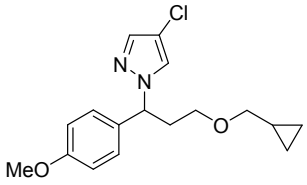


4-Chloro-1-(1-(4-methoxyphenyl)allyl)-1*H*-pyrazole (9). Yield = 47%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.47 (d, *J* = 0.7 Hz, 1H), 7.30 (d, *J* = 0.7 Hz, 1H), 7.19–7.14 (m, 2H), 6.92–6.87 (m, 2H), 6.30 (ddd, *J* = 17.0, 10.3, 6.1 Hz, 1H), 5.89 (dt, *J* = 6.1, 1.6 Hz, 1H), 5.39 (dt, *J* = 10.3, 1.0 Hz, 1H), 5.06 (ddd, *J* = 17.0, 1.6, 1.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.8, 138.0, 135.9, 130.2, 129.2, 126.7, 118.9, 114.4, 110.1, 68.3, 55.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 271.0609, obsd 271.0609.

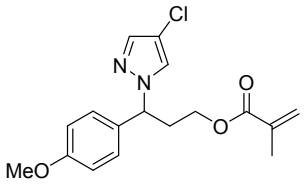


4-(4-Chloro-1*H*-pyrazol-1-yl)-4-(4-methoxyphenyl)butan-2-one (10). Yield = 75%; Light

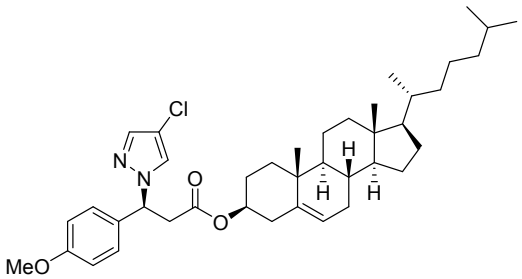
yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 0.8 Hz, 1H), 7.34 (d, J = 0.8 Hz, 1H), 7.21–7.15 (m, 2H), 6.87–6.82 (m, 2H), 5.72 (dd, J = 8.9, 5.1 Hz, 1H), 3.85–3.77 (m, 4H), 3.02 (dd, J = 17.4, 5.1 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1, 159.7, 137.6, 131.7, 128.1, 127.6, 114.4, 110.2, 61.0, 55.4, 48.3, 30.6; ESI HRMS *m/z* $(M+Na)^+$ calcd 301.0714, obsd 301.0719.



4-Chloro-1-(3-(cyclopropylmethoxy)-1-(4-methoxyphenyl)propyl)-1*H*-pyrazole (11). Yield = 61%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 0.7 Hz, 1H), 7.36 (d, J = 0.7 Hz, 1H), 7.30–7.17 (m, 2H), 6.91–6.82 (m, 2H), 5.69 (dd, J = 9.0, 6.0 Hz, 1H), 3.87 (d, J = 7.3 Hz, 2H), 3.78 (s, 3H), 3.56 (dd, J = 16.2, 9.0 Hz, 1H), 3.06 (dd, J = 16.2, 6.0 Hz, 1H), 1.11–0.96 (m, 1H), 0.57–0.44 (m, 2H), 0.22–0.17 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 159.8, 137.9, 131.0, 128.3, 127.2, 114.4, 110.1, 69.9, 62.2, 55.4, 40.3, 9.8, 3.4 (2C); ESI HRMS *m/z* $(M+Na)^+$ calcd 357.0976, obsd 357.0988.

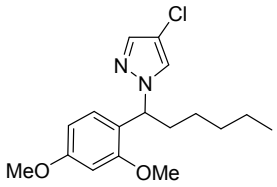


3-(4-Chloro-1*H*-pyrazol-1-yl)-3-(4-methoxyphenyl)propyl methacrylate (12). Yield = 49%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 0.7 Hz, 1H), 7.36 (d, J = 0.7 Hz, 1H), 7.25–7.20 (m, 2H), 6.90–6.84 (m, 2H), 6.11–6.07 (m, 1H), 5.59–5.55 (m, 1H), 5.32 (dd, J = 8.6, 6.8 Hz, 1H), 4.16–4.05 (m, 2H), 3.79 (s, 3H), 2.86–2.76 (m, 1H), 2.54–2.44 (m, 1H), 1.94 (t, J = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 159.8, 137.9, 136.2, 131.3, 128.3, 126.8, 125.9, 114.4, 110.2, 63.3, 61.5, 55.5, 34.2, 18.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 357.0976, obsd 357.0988.

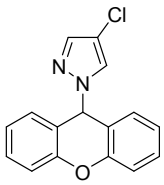


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl (*S*)-3-(4-chloro-1*H*-pyrazol-1-yl)-3-(4-methoxyphenyl)propanoate (13). Yield = 56%; White solid; m.p. = 135.5−137.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.34 (s, 1H), 7.25–7.20 (m, 2H), 6.89–6.84 (m, 2H), 5.67 (dd, J = 9.0, 6.1 Hz, 1H), 5.36–5.30 (m, 1H), 4.63–4.49 (m, 1H), 3.78 (s, 3H), 3.50 (ddd, J = 16.1, 9.0, 2.4 Hz, 1H), 3.02 (ddd, J = 16.1, 6.1, 1.4 Hz, 1H), 2.27–2.15 (m, 2H), 2.03–1.92 (m, 2H), 1.88–1.79 (m, 2H), 1.75–1.69 (m, 1H), 1.57–1.01 (m, 20H),

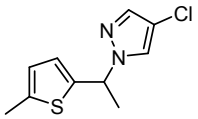
0.99 (s, 3H), 0.98–0.94 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88–0.83 (m, 6H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 169.7, 159.8, 139.6, 137.8, 131.0, 128.3, 127.2, 122.9, 114.4, 110.1, 74.8, 62.3, 56.8, 56.3, 55.4, 50.2, 42.5, 40.6, 39.9, 39.7, 38.0, 37.1, 36.7, 36.3, 36.0, 32.0, 28.4, 28.2, 27.7, 24.4, 24.0, 23.0, 22.7, 21.2, 19.4, 18.9, 12.0; ESI HRMS *m/z* $(M+Na)^+$ calcd 671.3950, obsd 671.3957.



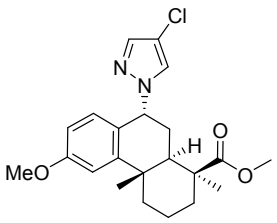
4-Chloro-1-(1-(2,4-dimethoxyphenyl)hexyl)-1*H*-pyrazole (14). Yield = 56%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (d, *J* = 0.8 Hz, 1H), 7.39 (d, *J* = 0.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.50–6.41 (m, 2H), 5.58 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 2.38–2.28 (m, 1H), 2.09–2.00 (m, 1H), 1.32–1.21 (m, 6H), 0.88–0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.7, 157.8, 137.3, 128.1, 127.0, 121.0, 109.0, 104.6, 98.7, 59.7, 55.6, 55.5, 34.2, 31.5, 26.3, 22.6, 14.1; ESI HRMS *m/z* $(M+Na)^+$ calcd 345.1340, obsd 345.1345.



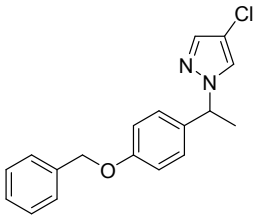
4-Chloro-1-(9*H*-xanthen-9-yl)-1*H*-pyrazole (15). Yield = 90%; White solid; m.p. = 188.5−190.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.42 (s, 1H), 7.39–7.30 (m, 4H), 7.24–7.18 (m, 2H), 7.13–7.08 (m, 2H), 7.03 (s, 1H), 6.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 151.0, 137.6, 130.4, 129.6, 126.0, 124.0, 118.6, 117.3, 111.2, 58.4; ESI HRMS *m/z* $(M+Na)^+$ calcd 305.0452, obsd 305.0453.



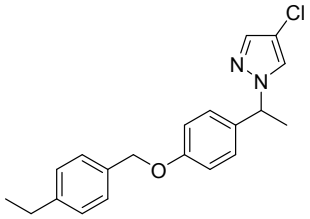
4-Chloro-1-(1-(5-methylthiophen-2-yl)ethyl)-1*H*-pyrazole (16). Yield = 62%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 0.7 Hz, 1H), 7.36 (d, *J* = 0.7 Hz, 1H), 6.79 (dd, *J* = 3.4, 1.0 Hz, 1H), 6.60 (dq, *J* = 3.4, 1.0 Hz, 1H), 5.60 (q, *J* = 7.0 Hz, 1H), 2.44 (d, *J* = 1.0 Hz, 3H), 1.88 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.6, 137.6, 125.5, 125.5, 125.0, 110.1, 57.9, 22.1, 15.5.



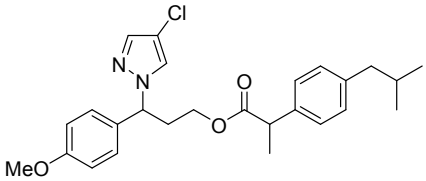
Methyl (1*S*,4a*S*,9*R*,10a*R*)-9-(4-chloro-1*H*-pyrazol-1-yl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (17). Yield = 76%; White solid; m.p. = 152.1−154.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 0.7 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.84 (d, *J* = 0.7 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.48 (dd, *J* = 4.7, 2.0 Hz, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 2.71 (dt, *J* = 14.9, 2.0 Hz, 1H), 2.45–2.36 (m, 1H), 2.30–2.21 (m, 2H), 1.99–1.90 (m, 1H), 1.68–1.60 (m, 1H), 1.46–1.36 (m, 2H), 1.03 (s, 3H), 1.02–0.93 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 160.3, 151.4, 137.9, 132.4, 127.4, 122.4, 112.4, 111.4, 108.6, 61.4, 55.4, 51.5, 46.3, 43.4, 39.2, 38.9, 37.3, 28.3, 28.2, 22.3, 19.9; ESI HRMS *m/z* $(M+Na)^+$ calcd 425.1602, obsd 425.1600.



1-(1-(4-(Benzyloxy)phenyl)ethyl)-4-chloro-1*H*-pyrazole (18). Yield = 60%; White solid; m.p. = 91.6−93.0 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 0.7 Hz, 1H), 7.42–7.35 (m, 4H), 7.34–7.28 (m, 2H), 7.18–7.13 (m, 2H), 6.96–6.91 (m, 2H), 5.39 (q, *J* = 7.0 Hz, 1H), 5.04 (s, 2H), 1.83 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 137.5, 136.9, 133.3, 128.8, 128.2, 127.9, 127.6, 125.9, 115.2, 109.9, 70.2, 61.5, 21.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 335.0922, obsd 335.0928.

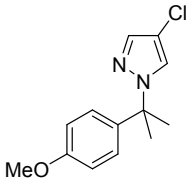


4-Chloro-1-(1-(4-((4-ethylbenzyl)oxy)phenyl)ethyl)-1*H*-pyrazole (19). Yield = 57%; White solid; m.p. = 62.7−63.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 0.7 Hz, 1H), 7.36–7.31 (m, 2H), 7.30 (d, *J* = 0.7 Hz, 1H), 7.23–7.19 (m, 2H), 7.18–7.13 (m, 2H), 6.97–6.90 (m, 2H), 5.39 (q, *J* = 7.1 Hz, 1H), 5.00 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.83 (d, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 144.4, 137.5, 134.1, 133.2, 128.3, 127.9, 127.8, 125.9, 115.2, 109.9, 70.2, 61.5, 28.8, 21.3, 15.8; ESI HRMS *m/z* $(M+Na)^+$ calcd 363.1235, obsd 363.1242.

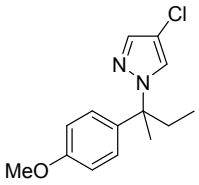


3-(4-Chloro-1*H*-pyrazol-1-yl)-3-(4-methoxyphenyl)propyl 2-(4-isobutylphenyl)propanoate (20). Yield = 55%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.38 (m, 1H), 7.25–7.21 (m, 2H), 7.18–7.14 (m, 2H), 7.12–7.07 (m, 1.5H), 7.01–6.96 (m, 1H), 6.89–6.86 (m, 0.5H), 6.84–6.76 (m, 2H), 4.96–4.89 (m, 1H), 4.07–3.94 (m, 1H), 3.92–3.84 (m, 1H), 3.78–3.74 (m, 3H),

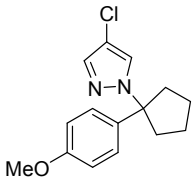
3.73–3.67 (m, 1H), 2.72–2.61 (m, 1H), 2.50–2.45 (m, 2H), 2.38–2.28 (m, 1H), 1.90–1.82 (m, 1H), 1.51–1.47 (m, 3H), 0.92–0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 174.4, 159.6 (2C), 141.0 (2C), 138.1, 137.9, 131.4, 131.2, 129.7, 129.6, 128.2, 127.4 (2C), 127.3, 127.1, 114.3, 114.2, 109.9, 109.8, 62.5, 62.4, 61.2, 55.4 (2C), 45.3, 45.2 (2C), 34.0 (2C), 30.4, 30.3, 22.6, 22.5, 18.2, 18.1; ESI HRMS *m/z* $(M+Na)^+$ calcd 477.1915, obsd 477.1920.



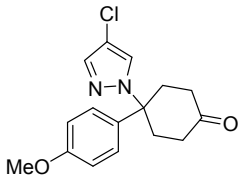
4-Chloro-1-(2-(4-methoxyphenyl)propan-2-yl)-1*H*-pyrazole (21). Yield = 71%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 0.8 Hz, 1H), 7.35 (d, J = 0.8 Hz, 1H), 7.07–7.02 (m, 2H), 6.86–6.81 (m, 2H), 3.78 (s, 3H), 1.91 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 137.8, 137.2, 126.6, 126.0, 114.0, 109.7, 64.1, 55.4, 29.7; ESI HRMS *m/z* $(M+Na)^+$ calcd 273.0765, obsd 273.0772.



4-Chloro-1-(2-(4-methoxyphenyl)butan-2-yl)-1*H*-pyrazole (22). Yield = 62%; Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.45 (m, 1H), 7.38–7.33 (m, 1H), 7.04–6.99 (m, 2H), 6.86–6.81 (m, 2H), 3.78 (s, 3H), 2.45 (dq, J = 14.5, 7.4 Hz, 1H), 2.24 (dq, J = 14.5, 7.4 Hz, 1H), 1.83 (s, 3H), 0.78 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 137.4, 137.2, 127.0, 126.5, 113.9, 109.6, 67.3, 55.4, 33.9, 26.1, 8.7; ESI HRMS *m/z* $(M+Na)^+$ calcd 287.0922, obsd 287.0926.

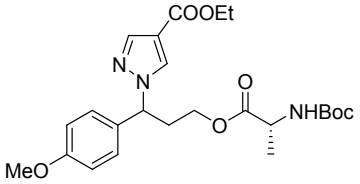


4-Chloro-1-(1-(4-methoxyphenyl)cyclopentyl)-1*H*-pyrazole (23). Yield = 54%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.39 (m, 2H), 7.14–7.08 (m, 2H), 6.84–6.79 (m, 2H), 3.77 (s, 3H), 2.84–2.76 (m, 2H), 2.31–2.23 (m, 2H), 1.88–1.72 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 137.1, 136.3, 127.1, 126.1, 113.9, 110.0, 75.3, 55.4, 38.8, 22.9; ESI HRMS *m/z* $(M+Na)^+$ calcd 299.0922, obsd 299.0927.

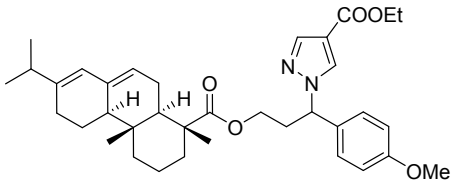


4-(4-Chloro-1*H*-pyrazol-1-yl)-4-(4-methoxyphenyl)cyclohexan-1-one (24). Yield = 60%; White solid; m.p. = 90.8−92.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 0.7 Hz, 1H), 7.46 (d,

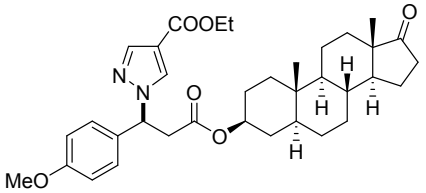
J = 0.7 Hz, 1H), 7.02–6.97 (m, 2H), 6.87–6.83 (m, 2H), 3.79 (s, 3H), 3.04–2.96 (m, 2H), 2.63–2.53 (m, 4H), 2.47–2.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 159.4, 137.7, 135.6, 126.3 (2C), 114.4, 111.2, 65.2, 55.5, 37.7, 36.2; ESI HRMS *m/z* $(M+Na)^+$ calcd 327.0871, obsd 327.0872.



Ethyl 1-(3-(((*tert*-butoxycarbonyl)-*D*-alanyl)oxy)-1-(4-methoxyphenyl)propyl)-1*H*-pyrazole-4-carboxylate (25). Yield = 61%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.89 (m, 2H), 7.29–7.25 (m, 2H), 6.91–6.83 (m, 2H), 5.44–5.34 (m, 1H), 5.06 (s, 1H), 4.33–4.23 (m, 3H), 4.17–4.00 (m, 2H), 3.79 (s, 3H), 2.90–2.72 (m, 1H), 2.58–2.42 (m, 1H), 1.45 (s, 9H), 1.38 (d, *J* = 7.2 Hz, 3H), 1.34–1.30 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 163.1, 159.8, 155.3, 141.3, 132.5, 130.9, 128.4, 115.2, 114.5, 80.1, 62.7, 61.9, 60.3, 55.4, 49.4, 34.3, 28.5, 18.5, 14.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 498.2211, obsd 498.2216.

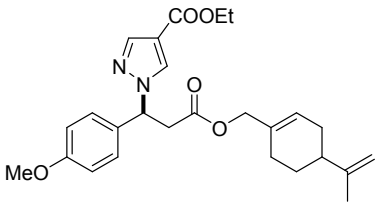


Ethyl 1-(3-(((1*R*,4a*R*,4b*R*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carbonyl)oxy)-1-(4-methoxyphenyl)propyl)-1*H*-pyrazole-4-carboxylate (26). Yield = 45%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.92 (m, 1H), 7.92–7.85 (m, 1H), 7.14–7.04 (m, 2H), 6.87–6.79 (m, 2H), 6.10–5.92 (m, 1H), 5.60–5.27 (m, 1H), 4.33–4.24 (m, 2H), 4.14–4.00 (m, 2H), 3.80–3.77 (m, 3H), 2.68–2.56 (m, 2H), 2.34–2.05 (m, 2H), 1.98–1.70 (m, 12H), 1.65–1.54 (m, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.27–1.06 (m, 6H), 1.01–0.81 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 163.5, 158.1, 140.6, 140.3, 134.7, 133.4, 130.9, 129.5, 126.0, 125.1, 114.7, 114.0, 65.0, 63.9, 60.3, 55.4, 50.7, 46.7, 45.1, 38.4, 37.4, 34.6, 31.4, 30.7, 27.4, 26.7, 26.0, 25.4, 22.5, 18.2, 17.2, 14.6, 14.2; ESI HRMS *m/z* $(M+Na)^+$ calcd 611.3455, obsd 611.3458.

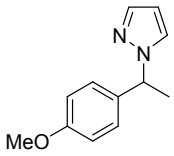


Ethyl 1-(3-(((3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-1-(4-methoxyphenyl)-3-oxopropyl)-1*H*-pyrazole-4-carboxylate (27). Yield = 66%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87 (s, 1H), 7.28–7.24 (m, 2H), 6.90–6.85 (m, 2H), 5.73 (dd, *J* = 9.0, 6.1 Hz, 1H), 4.70–4.57 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.52 (dd, *J* = 16.1, 9.0 Hz, 1H), 3.10–3.00 (m, 1H), 2.43 (dd, *J* = 19.1, 9.0 Hz, 1H), 2.09–2.01 (m, 1H), 1.95–1.89 (m, 1H), 1.80–1.61 (m, 5H), 1.55–1.39 (m, 4H), 1.33–1.16 (m, 10H), 1.01–0.91 (m, 2H), 0.85 (s, 3H), 0.82 (s, 3H), 0.72–0.65 (m, 1H);

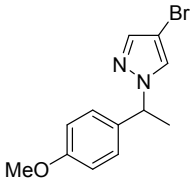
^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 169.7, 163.1, 159.9, 141.2, 132.6, 130.5, 128.4, 115.1, 114.4, 74.3, 62.2, 60.3, 55.4, 54.4, 51.5, 47.9, 44.7, 40.6, 36.7, 36.0, 35.7, 35.1, 33.8, 31.6, 30.9, 28.4, 27.3, 21.9, 20.6, 14.5, 13.9, 12.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 613.3248, obsd 613.3251.



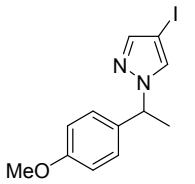
Ethyl 1-(1-(4-methoxyphenyl)-3-oxo-3-((4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)methoxy) propyl)-1*H*-pyrazole-4-carboxylate (28). Yield = 52%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87 (s, 1H), 7.27–7.24 (m, 2H), 6.90–6.84 (m, 2H), 5.78–5.72 (m, 1H), 5.67–5.61 (m, 1H), 4.74–4.68 (m, 2H), 4.43 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.65–3.57 (m, 1H), 3.14–3.07 (m, 1H), 2.15–2.05 (m, 2H), 1.97–1.76 (m, 4H), 1.73 (s, 3H), 1.45–1.37 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 163.1, 159.9, 149.6, 141.2, 132.6, 132.3, 130.5, 128.4, 126.3, 115.2, 114.5, 108.9, 69.1, 62.2, 60.3, 55.5, 40.9, 40.3, 30.6, 27.4, 26.3, 20.9, 14.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 475.2203, obsd 475.2206.



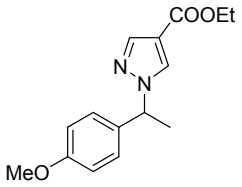
1-(1-(4-Methoxyphenyl)ethyl)-1*H*-pyrazole (29). Yield = 54%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.1Hz, 1H), 7.36 (d, *J* = 2.1 Hz, 1H), 7.19–7.12 (m, 2H), 6.89–6.82 (m, 2H), 6.24 (t, *J* = 2.1 Hz, 1H), 5.49 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 1.87 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 139.1, 134.1, 127.8, 127.7, 114.2, 105.4, 60.6, 55.4, 21.7; ESI HRMS *m/z* $(M+Na)^+$ calcd 225.0998, obsd 225.0997.



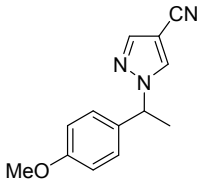
4-Bromo-1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (30). Yield = 83%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 0.7 Hz, 1H), 7.33 (d, *J* = 0.7 Hz, 1H), 7.20–7.14 (m, 2H), 6.90–6.84 (m, 2H), 5.42 (q, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 1.84 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 139.6, 133.0, 128.0, 127.9, 114.3, 93.0, 61.5, 55.4, 21.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 303.0103, obsd 303.0109.



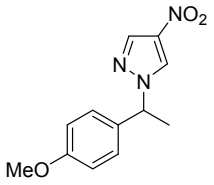
4-Iodo-1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (31). Yield = 73%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 0.7 Hz, 1H), 7.36 (d, J = 0.7 Hz, 1H), 7.20–7.14 (m, 2H), 6.89–6.84 (m, 2H), 5.45 (q, J = 7.1 Hz, 1H), 3.79 (s, 3H), 1.84 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 144.2, 133.1, 132.3, 128.0, 114.3, 61.3, 56.1, 55.5, 21.4; ESI HRMS *m/z* $(M+Na)^+$ calcd 350.9965, obsd 350.9969.



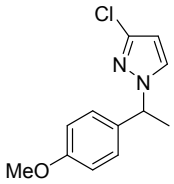
Ethyl 1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole-4-carboxylate (32). Yield = 76%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.85 (s, 1H), 7.23–7.16 (m, 2H), 6.91–6.84 (m, 2H), 5.47 (q, J = 7.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.88 (d, J = 7.1 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 159.6, 140.9, 132.6, 131.2, 128.0, 115.0, 114.4, 61.3, 60.2, 55.4, 21.4, 14.5; ESI HRMS *m/z* $(M+Na)^+$ calcd 297.1210, obsd 297.1218.



1-(1-(4-Methoxyphenyl)ethyl)-1*H*-pyrazole-4-carbonitrile (33). Yield = 71%; White solid; m.p. = 74.8−76.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 0.7 Hz, 1H), 7.71 (d, J = 0.7 Hz, 1H), 7.23–7.18 (m, 2H), 6.92–6.88 (m, 2H), 5.48 (q, J = 7.0 Hz, 1H), 3.81 (s, 3H), 1.89 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 142.2, 133.0, 131.7, 128.1, 114.5, 113.7, 92.1, 61.9, 55.5, 21.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 250.0951, obsd 250.0956.

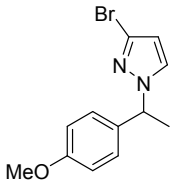


1-(1-(4-Methoxyphenyl)ethyl)-4-nitro-1*H*-pyrazole (34). Yield = 51%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$)^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.00 (s, 1H), 7.27–7.22 (m, 2H), 6.94–6.90 (m, 2H), 5.47 (q, J = 7.0 Hz, 1H), 3.82 (s, 3H), 1.91 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 135.8, 131.1, 128.4, 128.3, 127.3, 114.7, 62.5, 55.5, 21.1; ESI HRMS *m/z* $(M+Na)^+$ calcd 270.0849, obsd 270.0856.

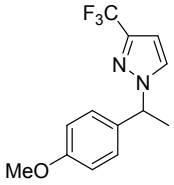


3-Chloro-1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (35). Yield = 65%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 1.9 Hz, 1H), 7.21–7.17 (m, 2H), 6.86–6.81 (m, 2H), 6.19 (d, J =

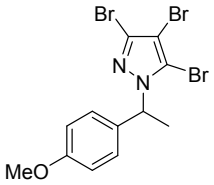
1.9 Hz, 1H), 5.61 (q, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 1.88 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.2, 139.3, 133.6, 127.8, 126.6, 114.1, 104.9, 57.1, 55.4, 21.4; ESI HRMS *m/z* $(M+Na)^+$ calcd 259.0609, obsd 259.0612.



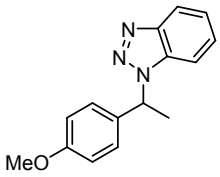
3-Bromo-1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (36). Yield = 62%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.55 (d, *J* = 1.9 Hz, 1H), 7.21–7.17 (m, 2H), 6.86–6.82 (m, 2H), 6.28 (d, *J* = 1.9 Hz, 1H), 5.64 (q, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 1.88 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.2, 140.2, 133.7, 127.8, 114.1, 112.6, 108.6, 58.1, 55.4, 21.6; ESI HRMS *m/z* $(M+Na)^+$ calcd 303.0103, obsd 303.0106.



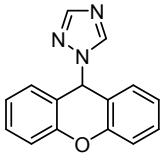
1-(1-(4-Methoxyphenyl)ethyl)-3-(trifluoromethyl)-1*H*-pyrazole (37). Yield = 37%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.55 (d, *J* = 1.8 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 2H), 6.88–6.82 (m, 2H), 6.58 (d, *J* = 1.8 Hz, 1H), 5.59 (q, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 1.90 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.4, 138.7, 133.1, 131.5 (q, J_{C-F} = 39.2 Hz), 128.0, 120.5 (q, J_{C-F} = 268.8 Hz), 114.0, 107.4 (q, J_{C-F} = 2.4 Hz), 59.3, 55.4, 22.1; ^{19}F NMR (377 MHz, $CDCl_3$) *δ* −58.7; ESI HRMS *m/z* $(M+Na)^+$ calcd 293.0872, obsd 293.0881.



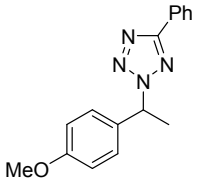
3,4,5-Tribromo-1-(1-(4-methoxyphenyl)ethyl)-1*H*-pyrazole (38). Yield = 58%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.24–7.20 (m, 2H), 6.87–6.83 (m, 2H), 5.59 (q, *J* = 7.0 Hz, 1H), 3.78 (s, 3H), 1.87 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 159.5, 132.5, 128.0, 127.9, 116.0, 114.2, 99.9, 60.8, 55.5, 21.4; ESI HRMS *m/z* $(M+Na)^+$ calcd 458.8314, obsd 458.8323.



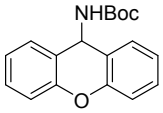
1-(1-(4-Methoxyphenyl)ethyl)-1*H*-benzo[d][1,2,3]triazole (39). Yield = 60%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–7.99 (m, 1H), 7.35–7.28 (m, 2H), 7.27–7.21 (m, 3H), 6.88–6.81 (m, 2H), 6.02 (q, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 2.14 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 146.6, 132.5, 132.3, 127.8, 127.1, 123.9, 120.1, 114.4, 110.4, 58.8, 55.4, 21.3.



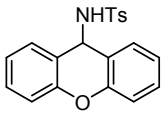
1-(9*H*-Xanthen-9-yl)-1*H*-1,2,4-triazole (40). Yield = 88%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.78 (s, 1H), 7.41 – 7.33 (m, 4H), 7.26 – 7.20 (m, 2H), 7.15 – 7.09 (m, 2H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 151.3, 142.1, 130.6, 129.6, 124.0, 117.7, 117.4, 56.0.



1-(1-(4-Methoxyphenyl)ethyl)-5-phenyl-1*H*-tetrazole (41). Yield = 42%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.17–8.10 (m, 2H), 7.49–7.42 (m, 3H), 7.41–7.34 (m, 2H), 6.92–6.84 (m, 2H), 6.07 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 2.07 (d, *J* = 7.1 Hz, 3H)：^{13}C NMR (101 MHz, $CDCl_3$) *δ* 165.1, 159.9, 131.1, 130.3, 128.9, 128.2, 127.8, 127.0, 114.3, 63.3, 55.5, 21.3; ESI HRMS *m/z* $(M+Na)^+$ calcd 303.1216, obsd 303.1227.



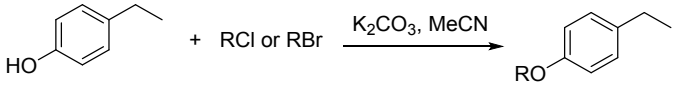
***tert*-Butyl (9*H*-xanthen-9-yl)carbamate (42).** Yield = 70%; White solid; m.p. = 139.5−142.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51–7.46 (m, 2H), 7.29–7.24 (m, 2H), 7.12–7.06 (m, 4H), 6.11 (d, *J* = 9.6 Hz, 1H), 5.11 (d, *J* = 9.6 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 155.7, 151.1, 129.6, 129.2, 123.6, 121.8, 116.7, 80.0, 45.4, 28.6; ESI HRMS *m/z* $(M+Na)^+$ calcd 320.1257, obsd 320.1265.



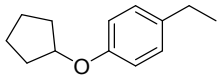
4-Methyl-*N*-(9*H*-xanthen-9-yl)benzenesulfonamide (43). Yield = 51%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.34–7.29 (m, 2H), 7.27–7.22 (m, 2H), 7.16–7.10 (m, 2H), 7.08–7.03 (m, 2H), 7.00–6.95 (m, 2H), 5.75 (d, *J* = 8.6 Hz, 1H), 4.97 (d, *J* = 8.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 143.7, 138.8, 130.0, 129.6, 129.6, 127.3, 123.7, 120.6, 116.9, 49.3, 21.8.

4. Synthesis and Characterization of Substrates

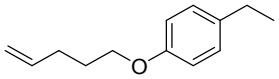
General Procedure A for the Synthesis of Substrates



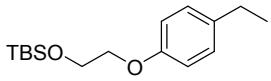
To a mixture of 4-ethylphenol (5.0 mmol, 1.0 equiv.) and K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv.) in 15 mL MeCN was added RCl or RBr (6.0 mmol, 1.2 equiv.). The reaction mixture was stirred for 12 h at 70 °C. Water (20 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the product.



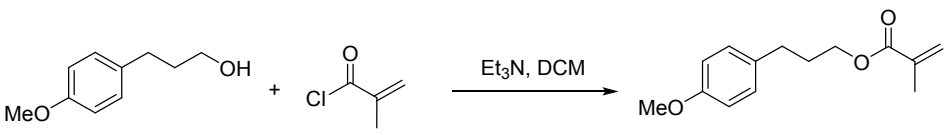
1-(Cyclopentyloxy)-4-ethylbenzene (S1). The title compound was prepared starting from 4-ethylphenol and bromocyclopentane by following the General Procedure A. Yield = 64%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.05 (m, 2H), 6.82–6.77 (m, 2H), 4.74–4.69 (m, 1H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.93–1.74 (m, 6H), 1.63–1.55 (m, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 136.1, 128.8, 115.6, 79.3, 33.0, 28.1, 24.2, 16.0; ESI HRMS *m/z* $(M+Na)^+$ calcd 213.1250, obsd 213.1255.



1-Ethyl-4-(pent-4-en-1-yloxy)benzene (S2). The title compound was prepared starting from 4-ethylphenol and 5-bromopent-1-ene by following the General Procedure A. Yield = 65%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.06 (m, 2H), 6.85–6.79 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09–4.96 (m, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.26–2.19 (m, 2H), 1.90–1.83 (m, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 138.1, 136.5, 128.8, 115.3, 114.6, 67.4, 30.3, 28.7, 28.2, 16.1; ESI HRMS *m/z* $(M+Na)^+$ calcd 213.1250, obsd 213.1254.

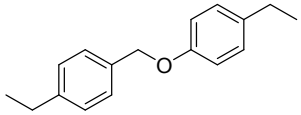


***tert*-Butyl(2-(4-ethylphenoxy)ethoxy)dimethylsilane (S3).** The title compound was prepared starting from 4-ethylphenol and (2-bromoethoxy)(*tert*-butyl)dimethylsilane by following the General Procedure A. Yield = 75%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12–7.06 (m, 2H), 6.85–6.80 (m, 2H), 4.03–3.99 (m, 2H), 3.97–3.94 (m, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 136.6, 128.8, 114.6, 69.5, 62.3, 28.2, 26.1, 18.6, 16.1, −5.0; ESI HRMS *m/z* $(M+Na)^+$ calcd 303.1761, obsd 303.1761.

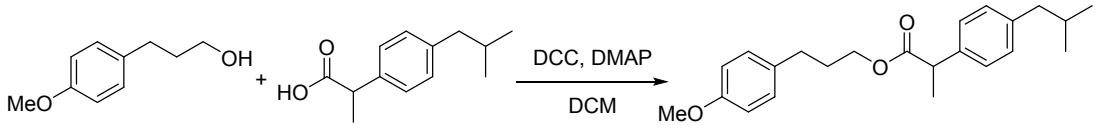


3-(4-Methoxyphenyl)propyl methacrylate (S4). To a solution of 3-(4-methoxyphenyl)propan-1-ol (0.49 mL, 3.0 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) was added

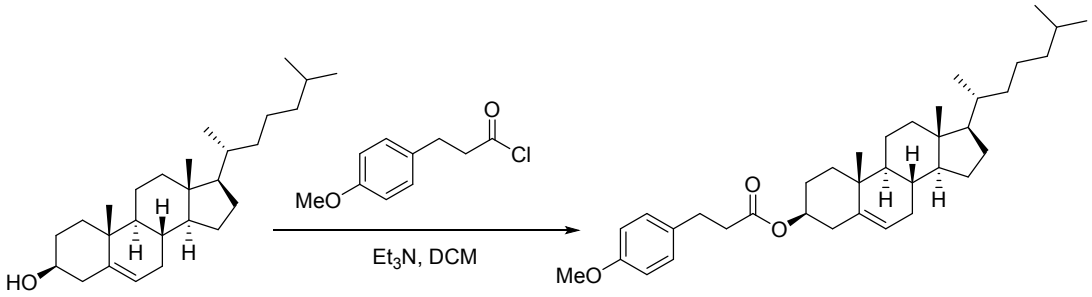
triethylamine (0.83 mL, 6.0 mmol, 2.0 equiv.). The resulting mixture was cooled down to 0 °C and methacryloyl chloride (0.35 mL, 3.6 mmol, 1.2 equiv.) was added slowly. The reaction mixture was allowed to warm up to r.t. and stirred overnight. A saturated solution of $NaHCO_3$ was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic solution was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography to afford the product as a colorless oil (600 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.07 (m, 2H), 6.86–6.80 (m, 2H), 6.12–6.09 (m, 1H), 5.57–5.54 (m, 1H), 4.15 (t, J = 6.5 Hz, 2H), 3.78 (s, 3H), 2.70–2.61 (m, 2H), 2.01–1.93 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 158.1, 136.6, 133.4, 129.5, 125.4, 114.0, 64.1, 55.4, 31.4, 30.6, 18.5; ESI HRMS m/z $(M+Na)^+$ calcd 257.1148, obsd 257.1156.



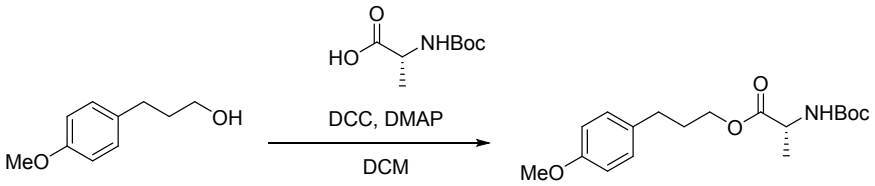
1-Ethyl-4-((4-ethylbenzyl)oxy)benzene (S5). The title compound was prepared starting from 4-ethylphenol and 1-(chloromethyl)-4-ethylbenzene by following the General Procedure A. Yield = 58%; White solid; m.p. = 41.6–42.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.32 (m, 2H), 7.22–7.19 (m, 2H), 7.13–7.07 (m, 2H), 6.92–6.86 (m, 2H), 4.99 (s, 2H), 2.65 (q, J = 7.6 Hz, 2H), 2.58 (q, J = 7.6 Hz, 2H), 1.26–1.18 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 144.2, 136.7, 134.6, 128.9, 128.2, 127.9, 114.9, 70.2, 28.8, 28.2, 16.0, 15.8; ESI HRMS m/z $(M+Na)^+$ calcd 263.1406, obsd 263.1412.



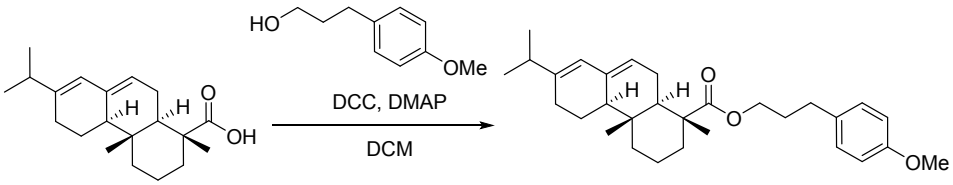
3-(4-Methoxyphenyl)propyl 2-(4-*iso*-butylphenyl)propanoate (S6). To a solution of Ibuprofen (619 mg, 3.0 mmol, 1.0 equiv.), 3-(4-methoxyphenyl)propan-1-ol (0.60 mL, 3.6 mmol, 1.2 equiv.) and DMAP (37 mg, 0.3 mmol, 0.1 equiv.) in CH_2Cl_2 (10 mL) was added DCC (0.74 mL, 4.5 mmol, 1.5 equiv.). The reaction mixture was stirred for 12 h at r.t. A saturated solution of $NaHCO_3$ was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (3 x 10 mL). The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired product as a colorless oil (550 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 2H), 7.13–7.07 (m, 2H), 6.99–6.93 (m, 2H), 6.81–6.75 (m, 2H), 4.09–4.00 (m, 2H), 3.77 (s, 3H), 3.70 (q, J = 7.1 Hz, 1H), 2.49 (t, J = 7.1 Hz, 2H), 2.44 (d, J = 7.1 Hz, 2H), 1.89–1.80 (m, 3H), 1.49 (d, J = 7.1 Hz, 3H), 0.88 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 158.0, 140.7, 138.1, 133.4, 129.5, 129.5, 127.4, 113.9, 63.9, 55.4, 45.4, 45.2, 31.2, 30.6, 30.4, 22.6, 18.5; ESI HRMS m/z $(M+Na)^+$ calcd 377.2092, obsd 377.2092.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-(4-methoxyphenyl) propanoate (S7). The title compound was prepared starting from Cholesterol and 3-(4-methoxyphenyl)propanoyl chloride by following the procedure described for the synthesis of **S4**. Yield = 82%; White solid; m.p. = 114.5−116.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.09 (m, 2H), 6.84–6.80 (m, 2H), 5.38–5.34 (m, 1H), 4.65–4.56 (m, 1H), 3.78 (s, 3H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.59–2.53 (m, 2H), 2.31–2.25 (m, 2H), 2.03–1.93 (m, 2H), 1.87–1.78 (m, 3H), 1.61–1.02 (m, 20H), 1.01 (s, 3H), 0.98–0.95 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.88–0.85 (m, 6H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 158.2, 139.8, 132.9, 129.4, 122.8, 114.0, 56.9, 56.3, 55.4, 50.2, 42.5, 39.9, 39.7, 38.3, 37.2, 36.8, 36.7, 36.4, 36.0, 32.1, 32.0, 30.4, 28.4, 28.2, 27.9, 24.5, 24.0, 23.0, 22.8, 21.2, 19.5, 18.9, 12.0; ESI HRMS *m/z* $(M+Na)^+$ calcd 571.4125, obsd 571.4125.

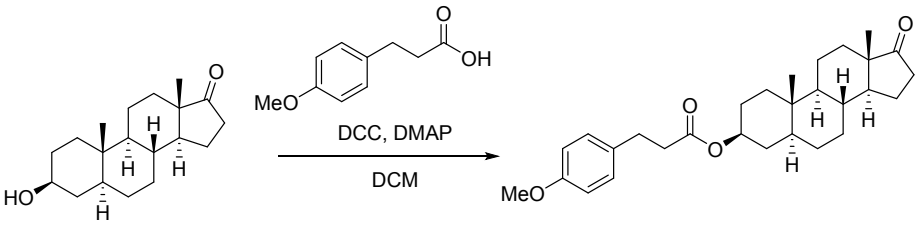


3-(4-Methoxyphenyl)propyl (*tert*-butoxycarbonyl)-*D*-alaninate (S8). The title compound was prepared starting from 3-(4-methoxyphenyl)propan-1-ol and (*tert*-butoxycarbonyl)-*D*-alanine by following the procedure described for the synthesis of **S6**. Yield = 81%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.06 (m, 2H), 6.85–6.81 (m, 2H), 5.19–4.94 (m, 1H), 4.40–4.23 (m, 1H), 4.17–4.11 (m, 2H), 3.78 (s, 3H), 2.66–2.60 (m, 2H), 1.98–1.90 (m, 2H), 1.45 (s, 9H), 1.39 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 158.1, 155.3, 133.2, 129.5, 114.0, 80.0, 64.7, 55.4, 49.4, 31.2, 30.5, 28.5, 18.9; ESI HRMS *m/z* $(M+Na)^+$ calcd 360.1781, obsd 360.1786.

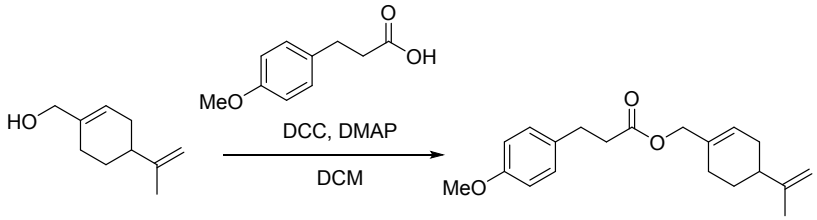


3-(4-Methoxyphenyl)propyl (1*R*,4a*R*,4b*R*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxylate (S9). The title compound was prepared starting from 3-(4-methoxyphenyl)propan-1-ol and abietic acid by following the procedure described for the synthesis of **S6**. Yield = 52%; Colorless oil; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.10–7.06 (m, 2H), 6.84–6.80 (m, 2H), 5.77 (s, 1H), 5.40–5.35 (m, 1H), 4.08–3.98 (m, 2H), 3.78 (s, 3H), 2.64–2.58 (m, 2H), 2.27–2.18 (m, 1H), 2.09–1.73 (m, 11H), 1.64–1.55 (m, 3H), 1.26 (s, 3H), 1.24–1.14 (m, 2H), 1.04–0.98 (m, 6H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 158.0, 145.4, 135.7, 133.4, 129.5, 122.6, 120.8, 114.0, 63.9, 55.4, 51.1, 46.8, 45.3, 38.5, 37.4, 35.0, 34.7, 31.4, 30.7, 27.6, 25.8, 22.7, 21.6, 21.0, 18.3, 17.2, 14.2; ESI HRMS *m/z* $(M+Na)^+$ calcd 473.3026, obsd 473.3032.



(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 3-(4-methoxyphenyl)propanoate (S10). The title compound was prepared starting from 3-(4-methoxyphenyl)propanoic acid and epiandrosterone by following the procedure described for the synthesis of **S6**. Yield = 52%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.09 (m, 2H), 6.85–6.80 (m, 2H), 4.74–4.64 (m, 1H), 3.78 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 2.55 (t, *J* = 7.8 Hz, 2H), 2.43 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.11–2.01 (m, 1H), 1.96–1.89 (m, 1H), 1.81–1.65 (m, 5H), 1.60–1.44 (m, 4H), 1.35–1.17 (m, 7H), 1.06–0.95 (m, 2H), 0.85 (s, 3H), 0.84 (s, 3H), 0.75–0.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 172.7, 158.2, 132.8, 129.4, 114.0, 73.6, 55.4, 54.5, 51.5, 47.9, 44.8, 36.9, 36.7, 36.0, 35.8, 35.2, 34.1, 31.7, 31.0, 30.4, 28.4, 27.5, 21.9, 20.6, 14.0, 12.4; ESI HRMS *m/z* $(M+Na)^+$ calcd 475.2819, obsd 475.2821.



(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methyl 3-(4-methoxyphenyl)propanoate (S11). The title compound was prepared starting from 3-(4-methoxyphenyl)propanoic acid and perillyl alcohol by following the procedure described for the synthesis of **S6**. Yield = 65%; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.09 (m, 2H), 6.85–6.80 (m, 2H), 5.75–5.66 (m, 1H), 4.75–4.68 (m, 2H), 4.45 (s, 2H), 3.78 (s, 3H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 2.19–2.09 (m, 2H), 2.04–1.90 (m, 3H), 1.86–1.79 (m, 1H), 1.73 (s, 3H), 1.52–1.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 158.2, 149.7, 132.8, 132.7, 129.4, 125.9, 114.0, 108.9, 68.6, 55.4, 41.0, 36.4, 30.6, 30.3, 27.5, 26.5, 20.9; ESI HRMS *m/z* $(M+H)^+$ calcd 315.1955, obsd 315.1954.

5. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN/DCE (1:1, 5 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt

wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate is 100 mV/s.

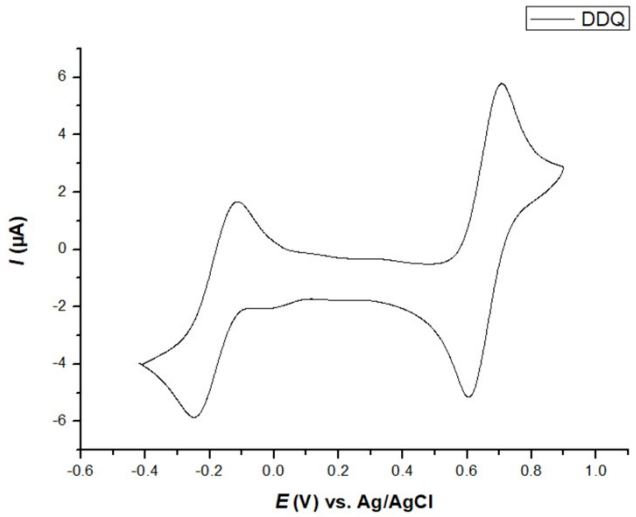


Figure S2 Cyclic voltammogram of DDQ (3 mM) in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN/DCE (1:1).

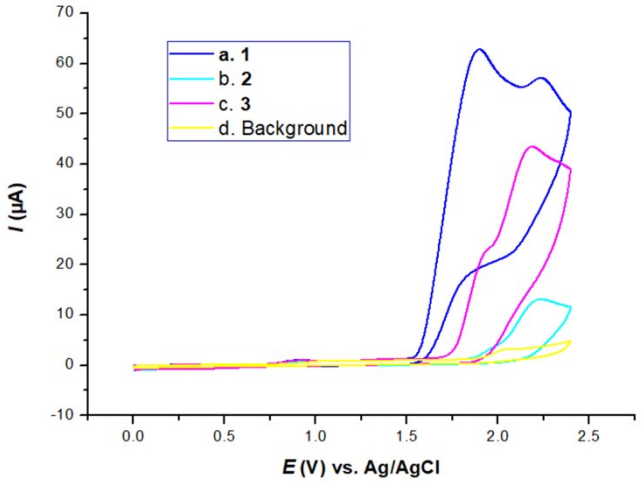


Figure S3 Cyclic voltammograms in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN/DCE (1:1, 5 mL). (a) **1** (10 mM), $E_{p/2}$ = 1.71 V.; (b) **2** (10 mM), $E_{p/2}$ = 2.07 V.; (c) **3** (10 mM), $E_{p/2}$ = 1.92 V.; (d) blank.

6. References

[1] C. Song, X. Dong, H. Yi, C.-W. Chiang and A. Lei, *ACS Catal.,* 2018, 8, 2195−2199.

[2] G. Pandey, R. Laha and D. Singh, *J. Org. Chem.,* 2016, **81**, 7161−7171.

[3] X. Shao, L. Tian and Y. Wang, *Eur. J. Org. Chem.,* 2019, **2019**, 4089–4094.

[4] Y. Liu, X. Guan, E. L.-M. Wong, P. Liu, J.-S. Huang and C.-M. Che, *J. Am. Chem. Soc.,* 2013, **135**, 7194−7204.

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and Esther Dom□nguez
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and Esther Dom□nguez
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Jokin D□az de Sarralde,
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Raul SanMartin,
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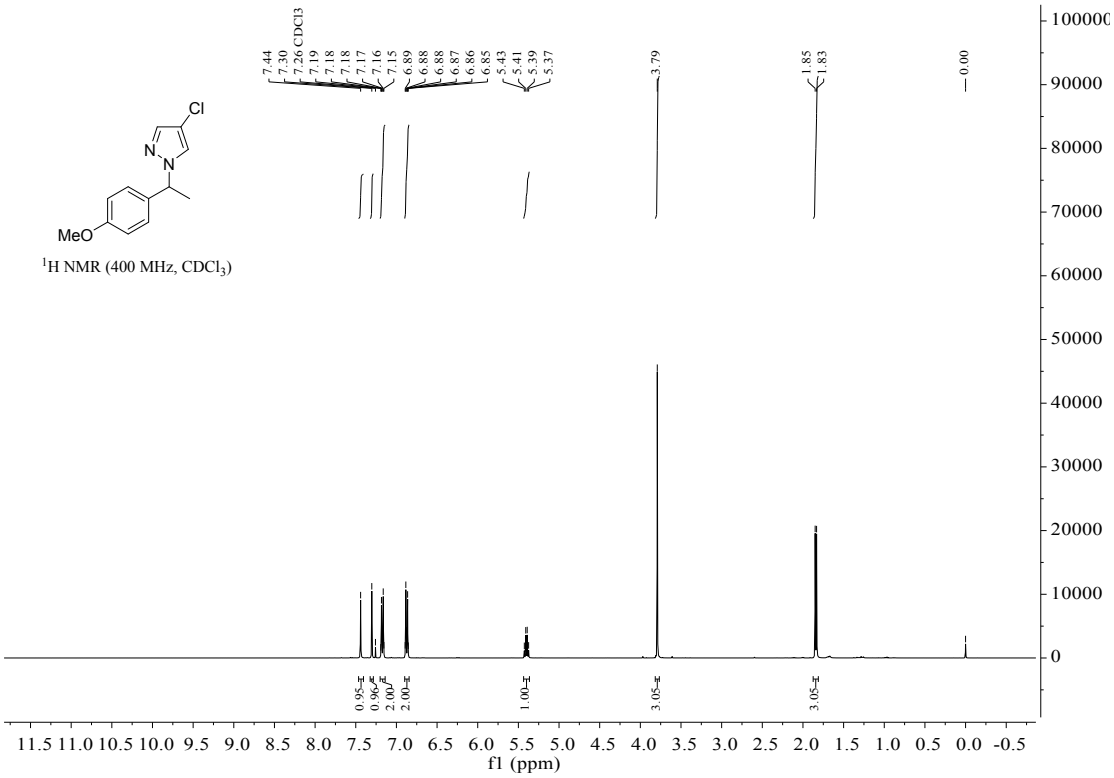
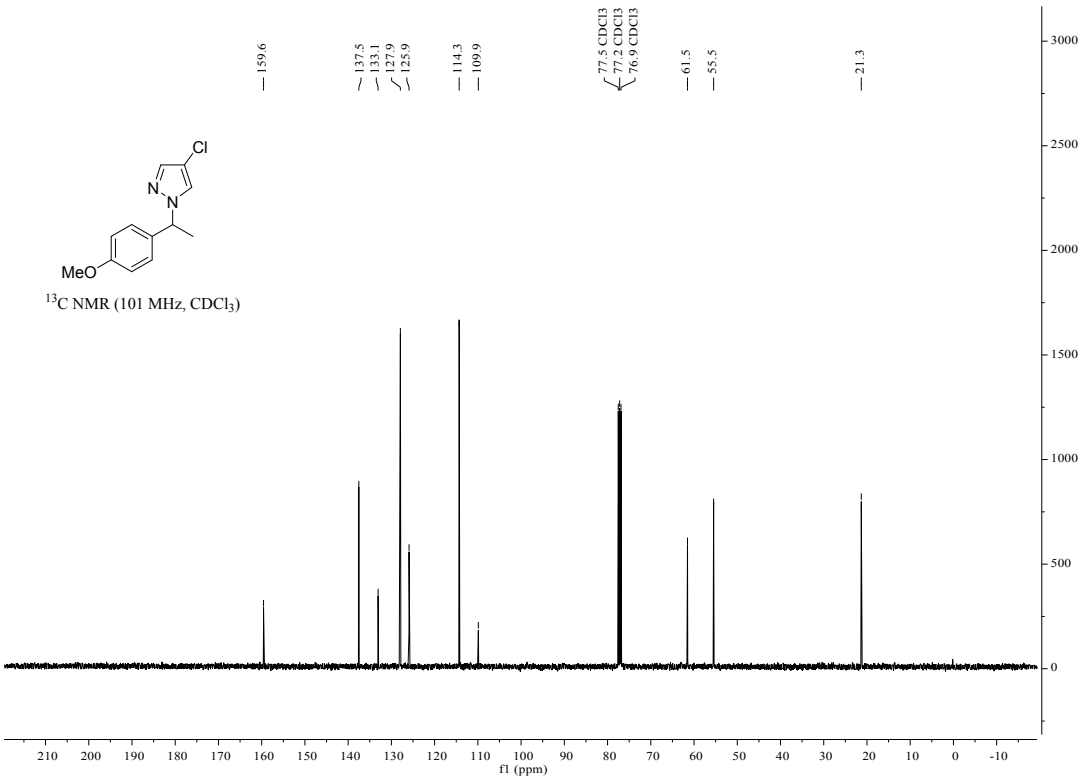
* Laura Bravo,
a
and Esther Dom□nguez

7. NMR Spectra for New Compounds

Compound 3

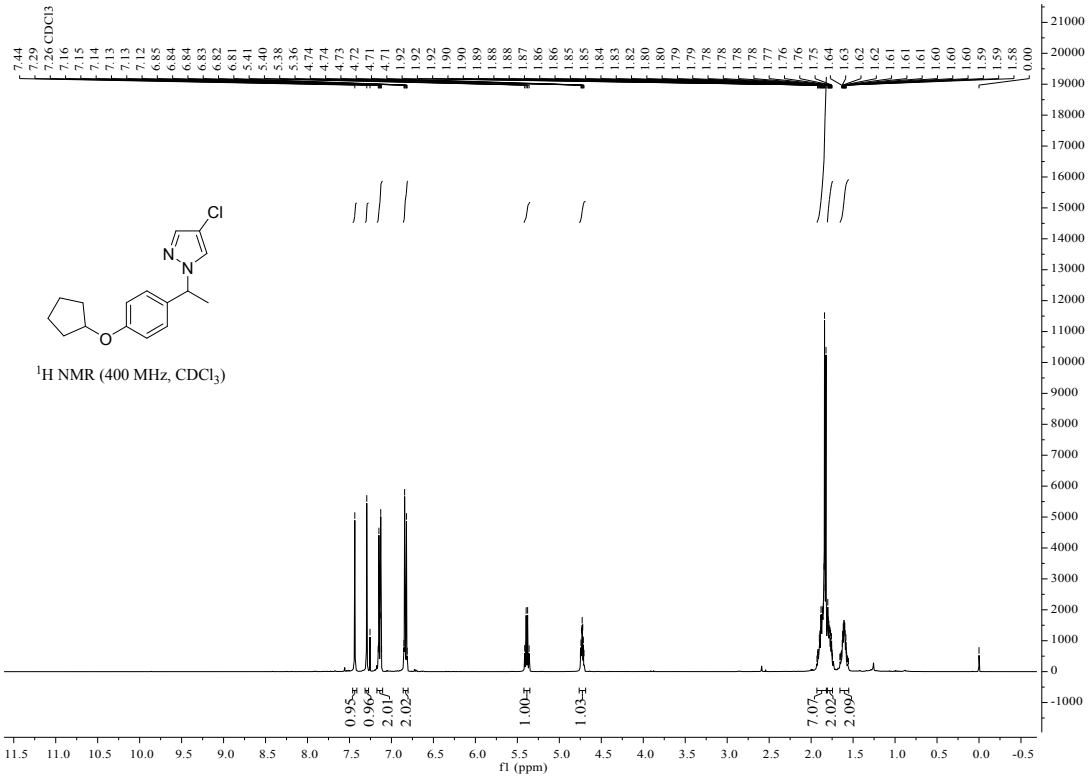


^{1}H NMR (400 MHz, $CDCl_3$)

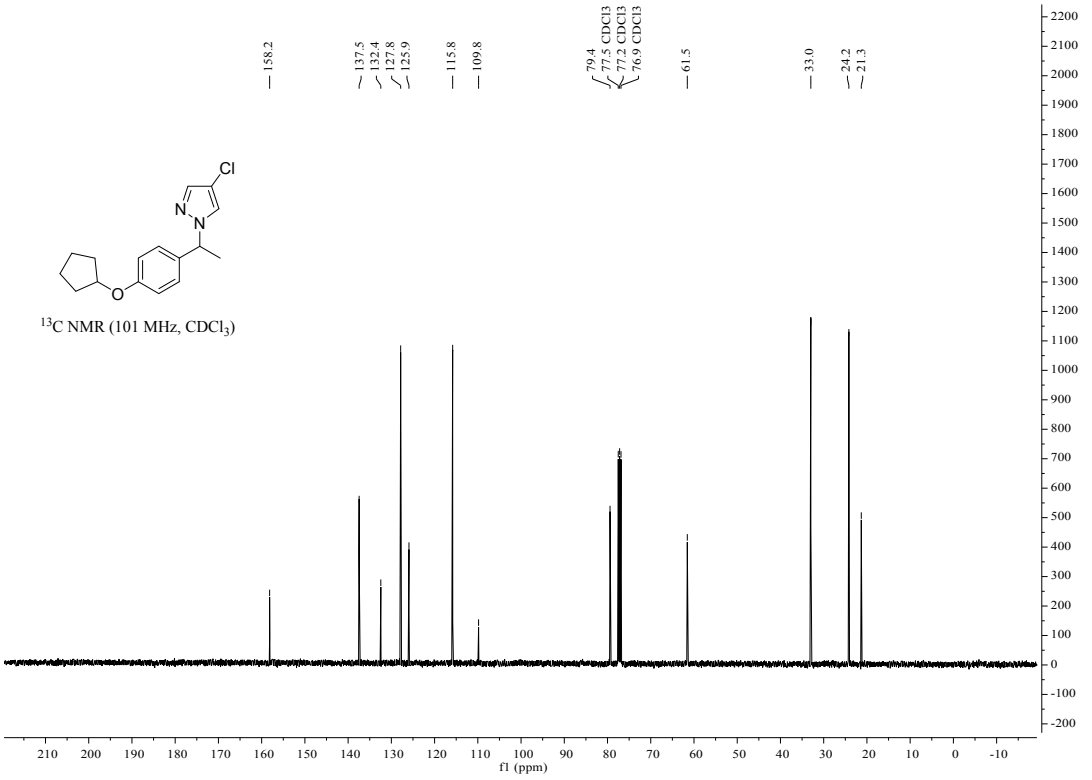


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 4

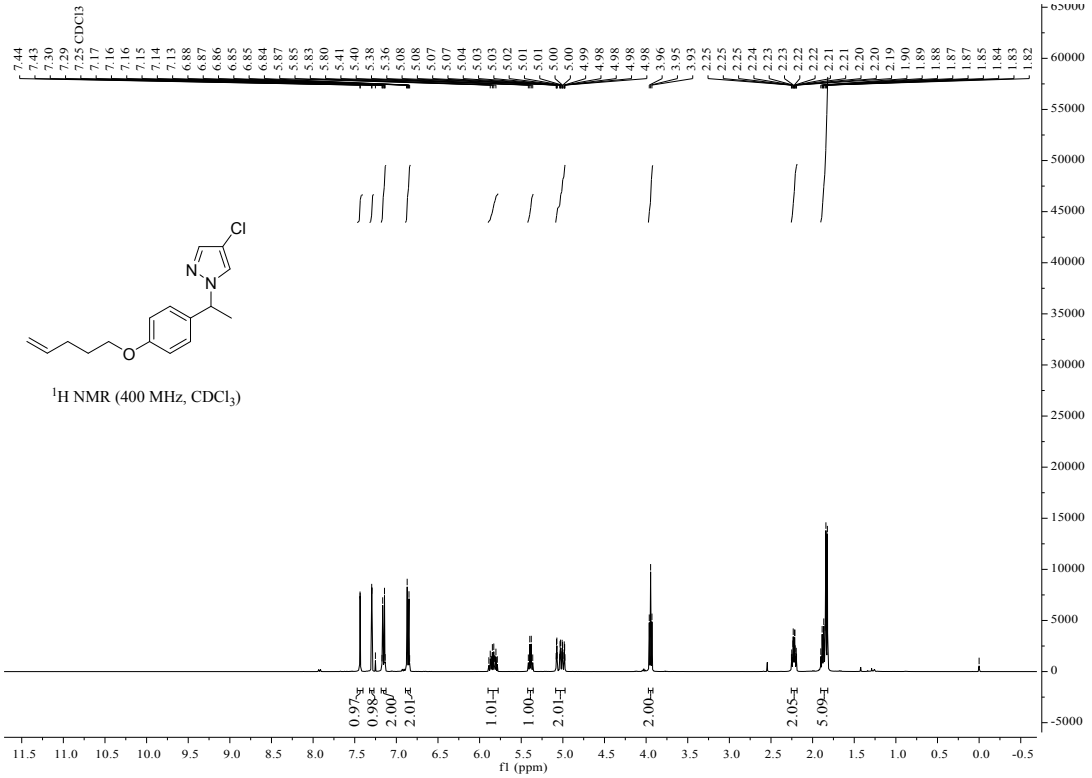


^{1}H NMR (400 MHz, $CDCl_3$)

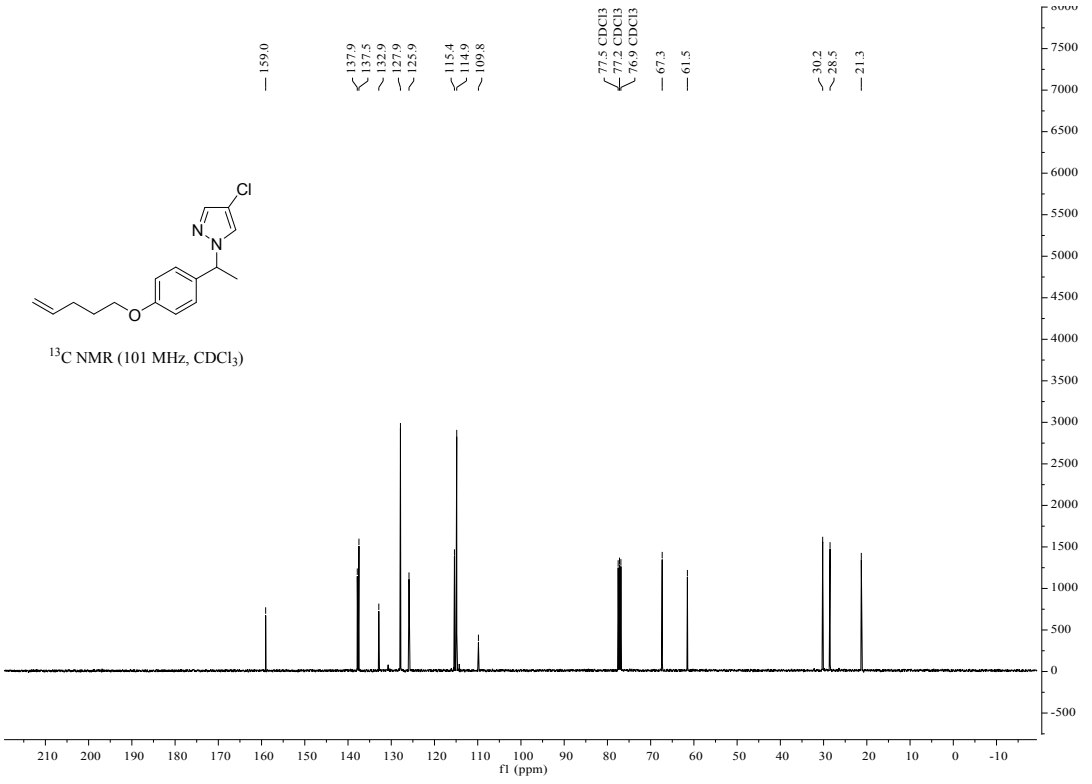


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 5

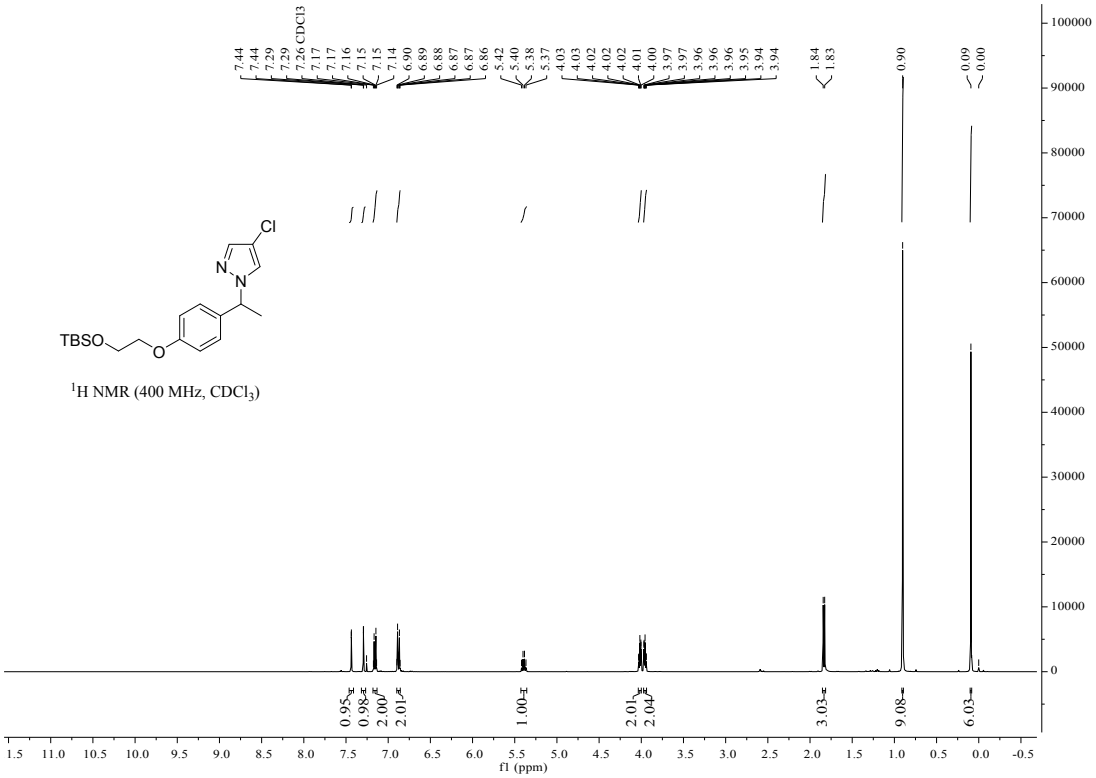


^{1}H NMR (400 MHz, $CDCl_3$)

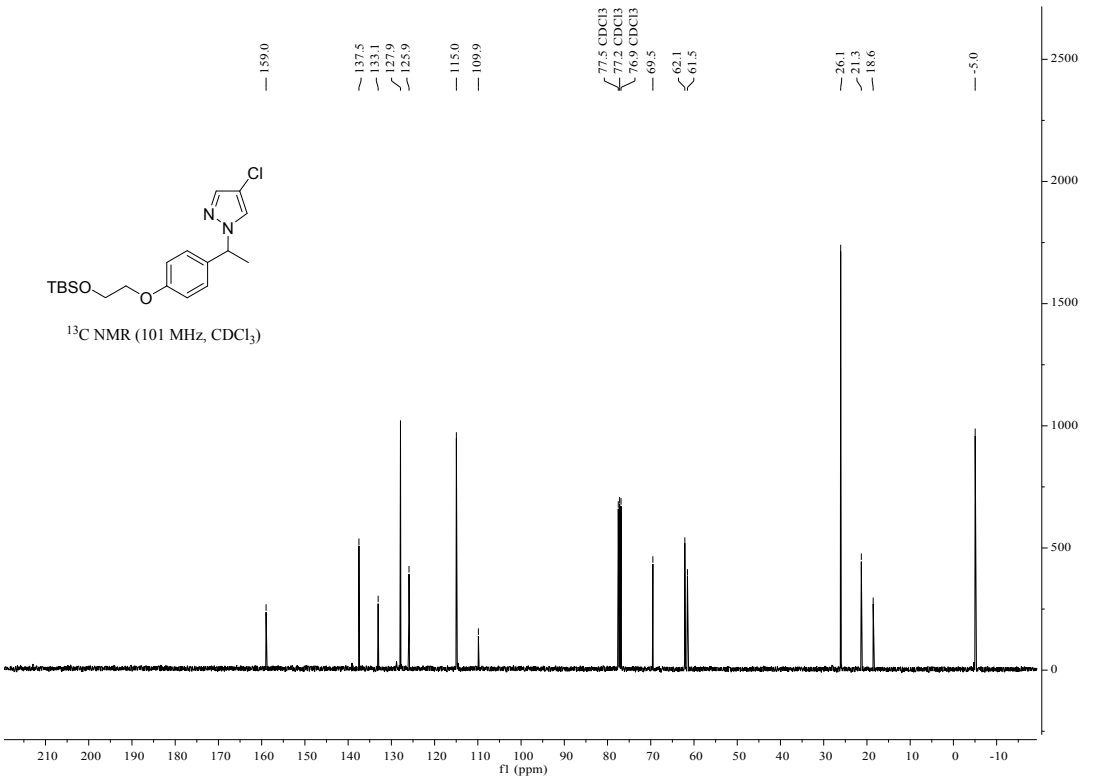


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 6

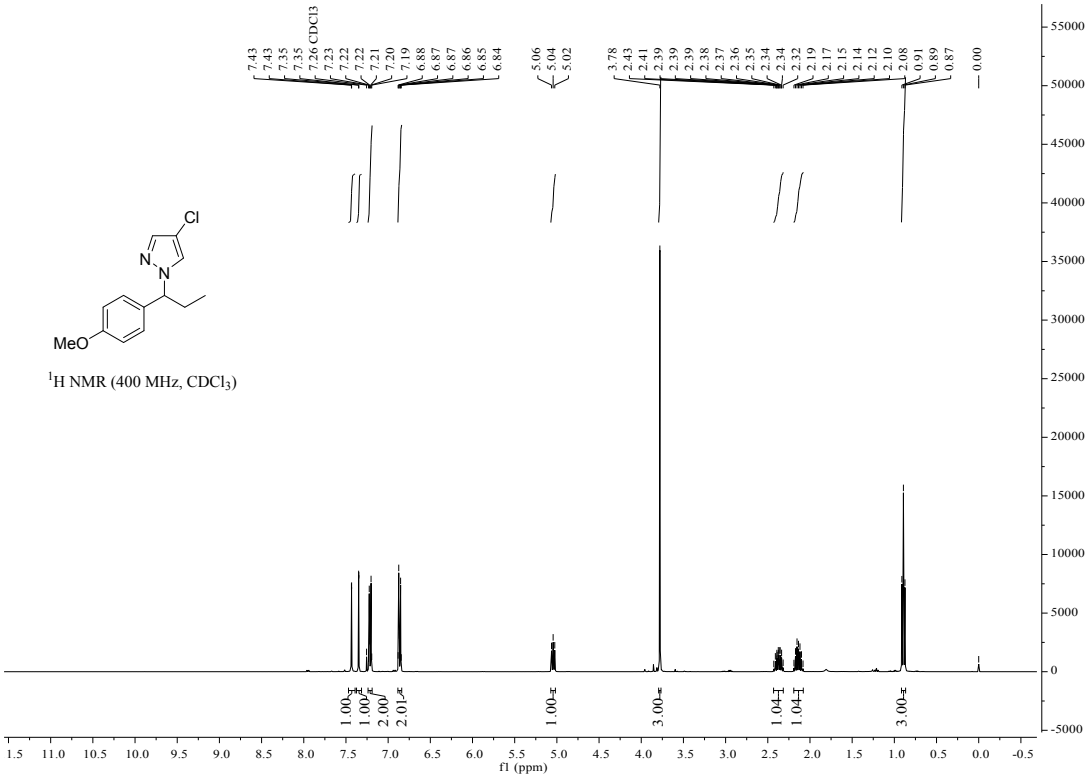


^{1}H NMR (400 MHz, $CDCl_3$)

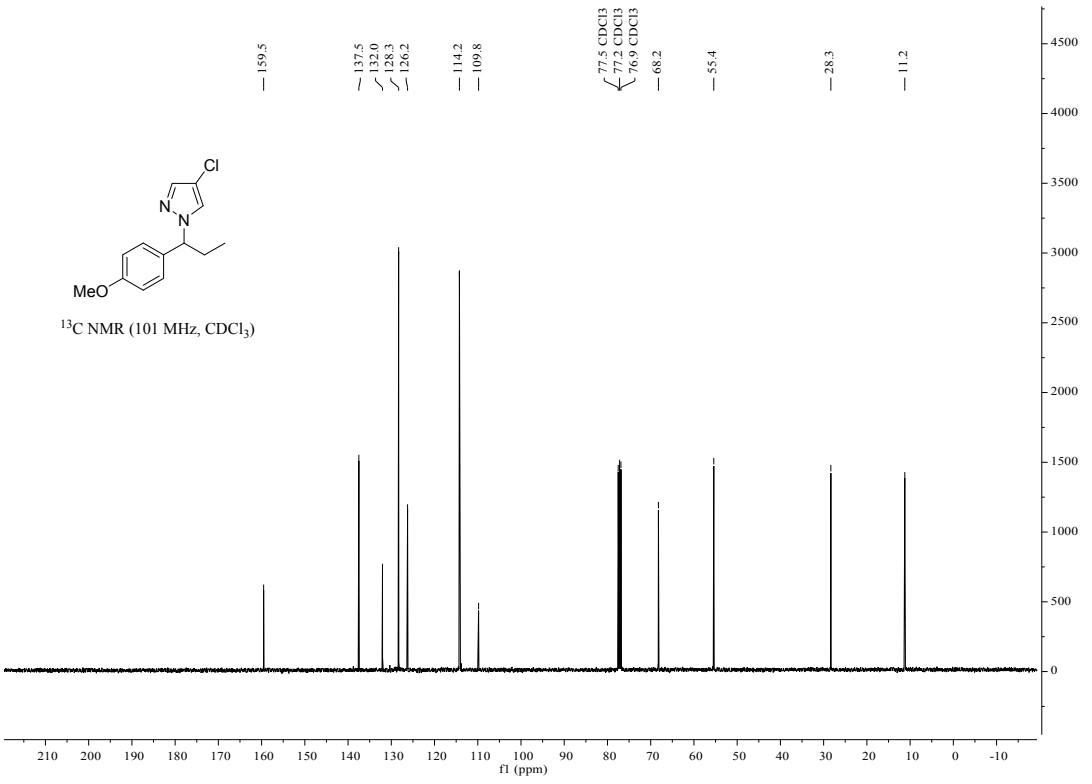


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 7

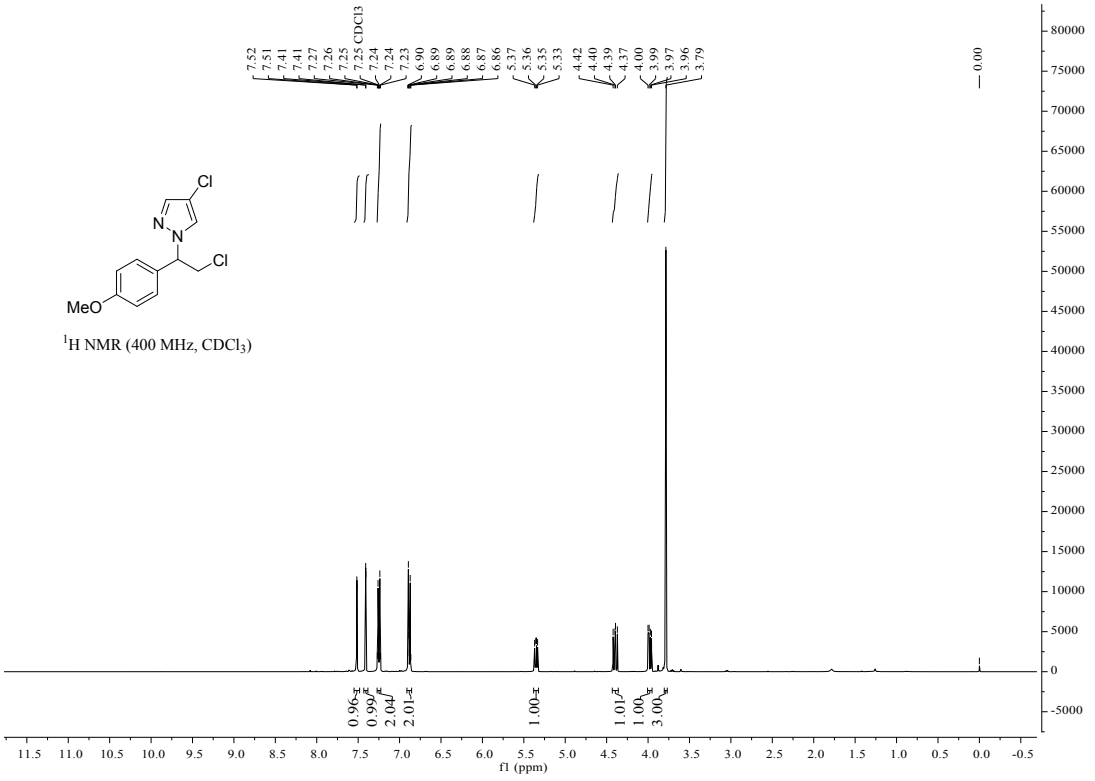


^{1}H NMR (400 MHz, $CDCl_3$)

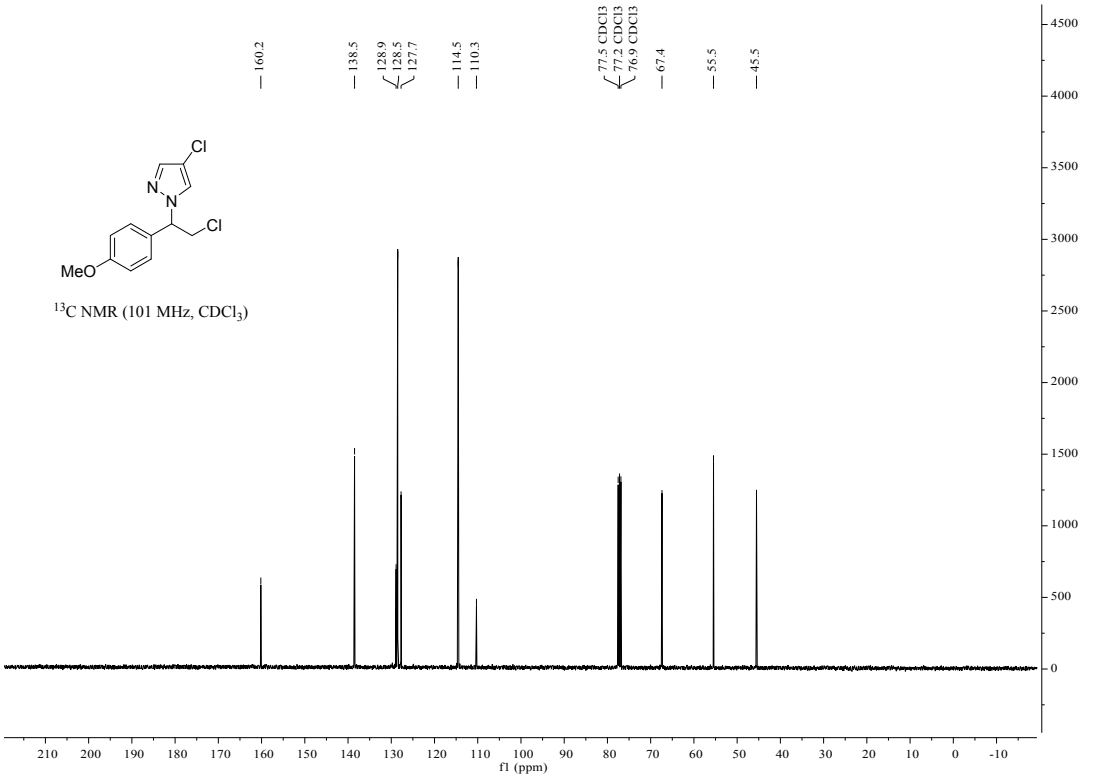


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 8

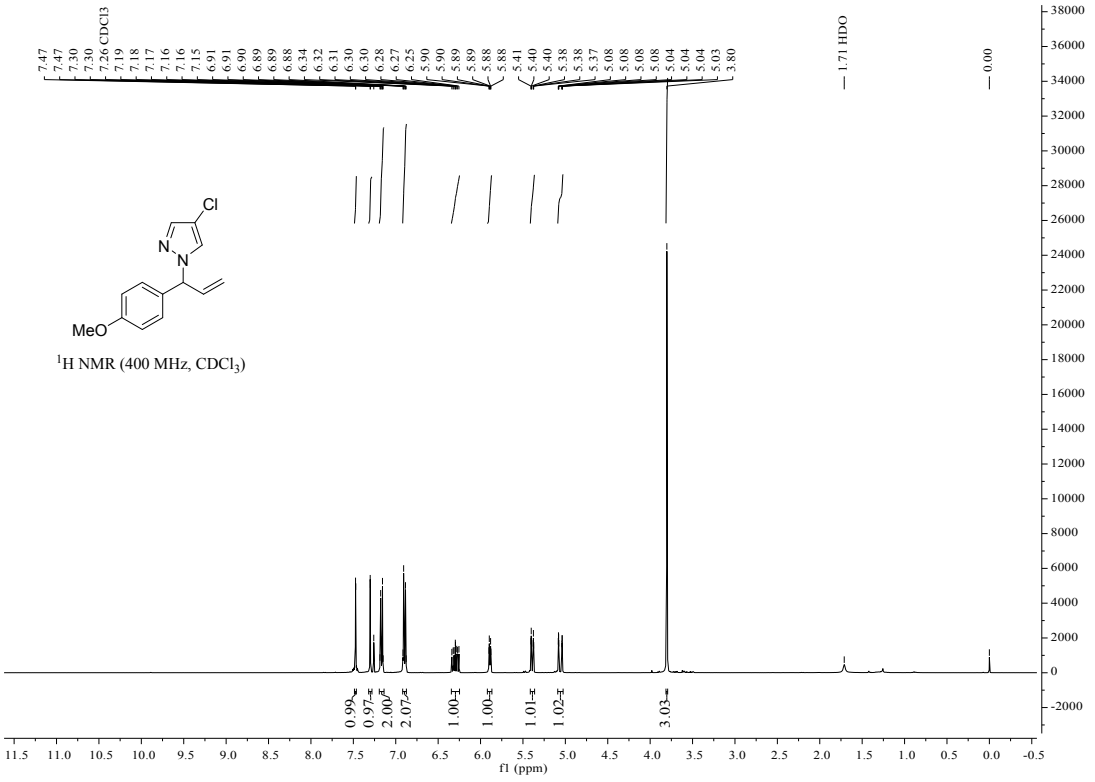


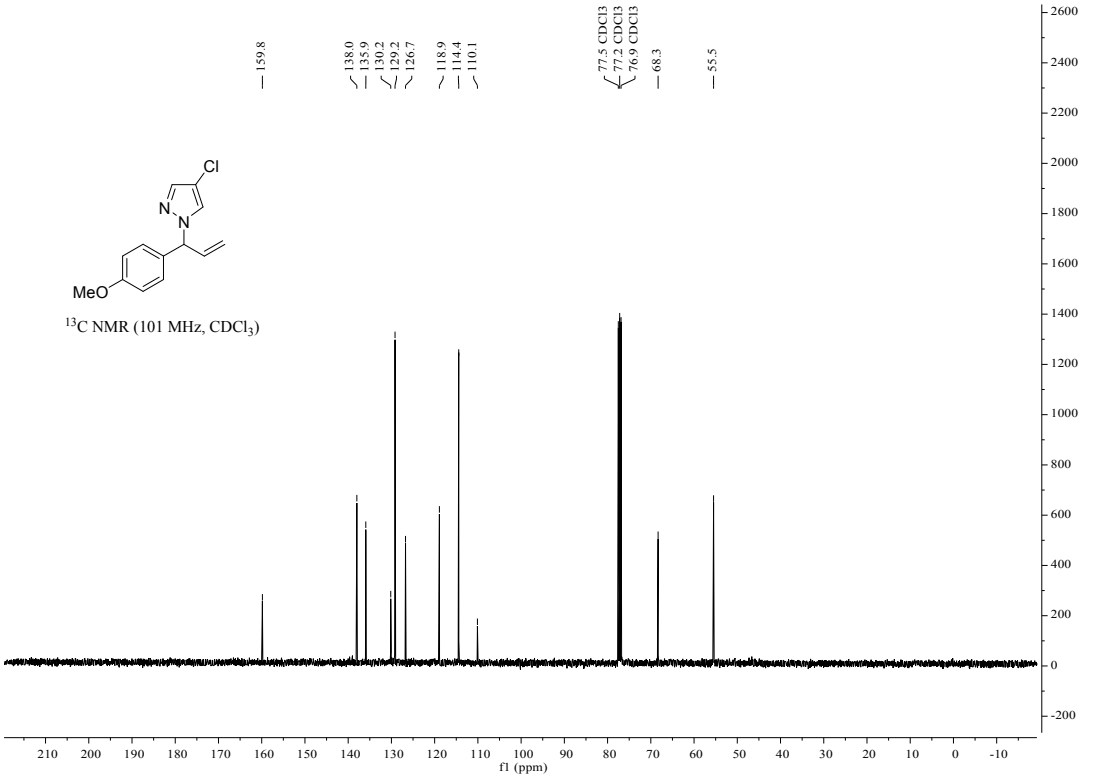
^{1}H NMR (400 MHz, $CDCl_3$)



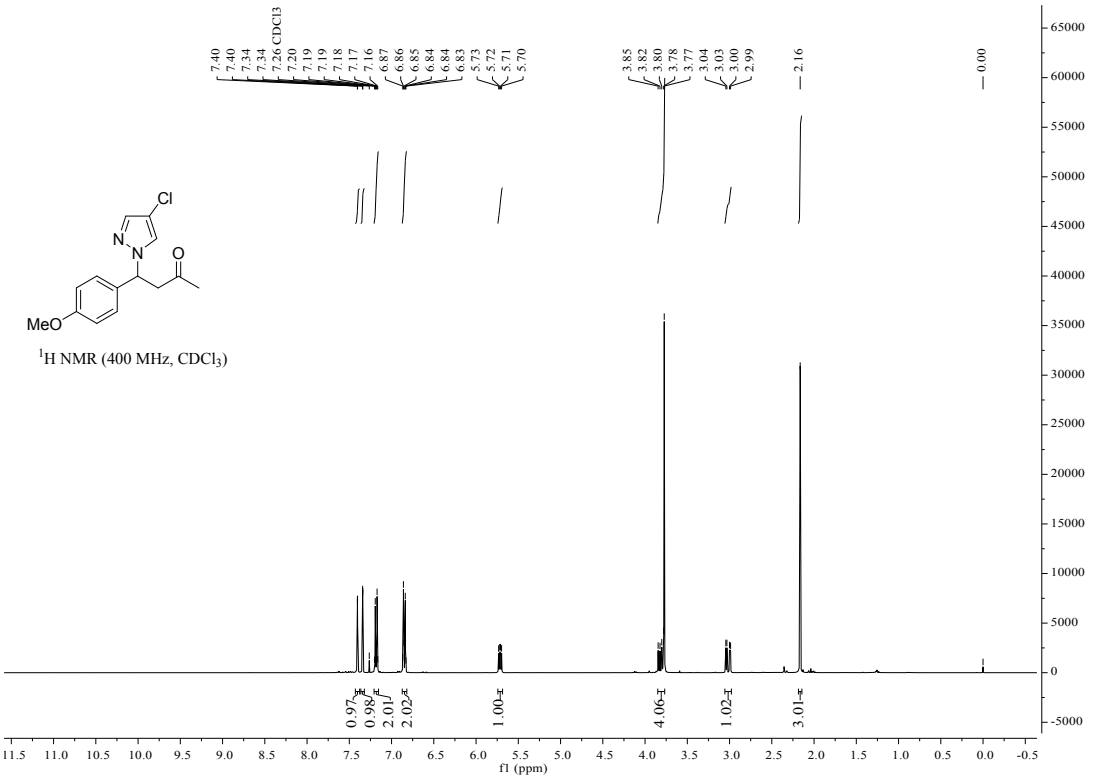
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 9

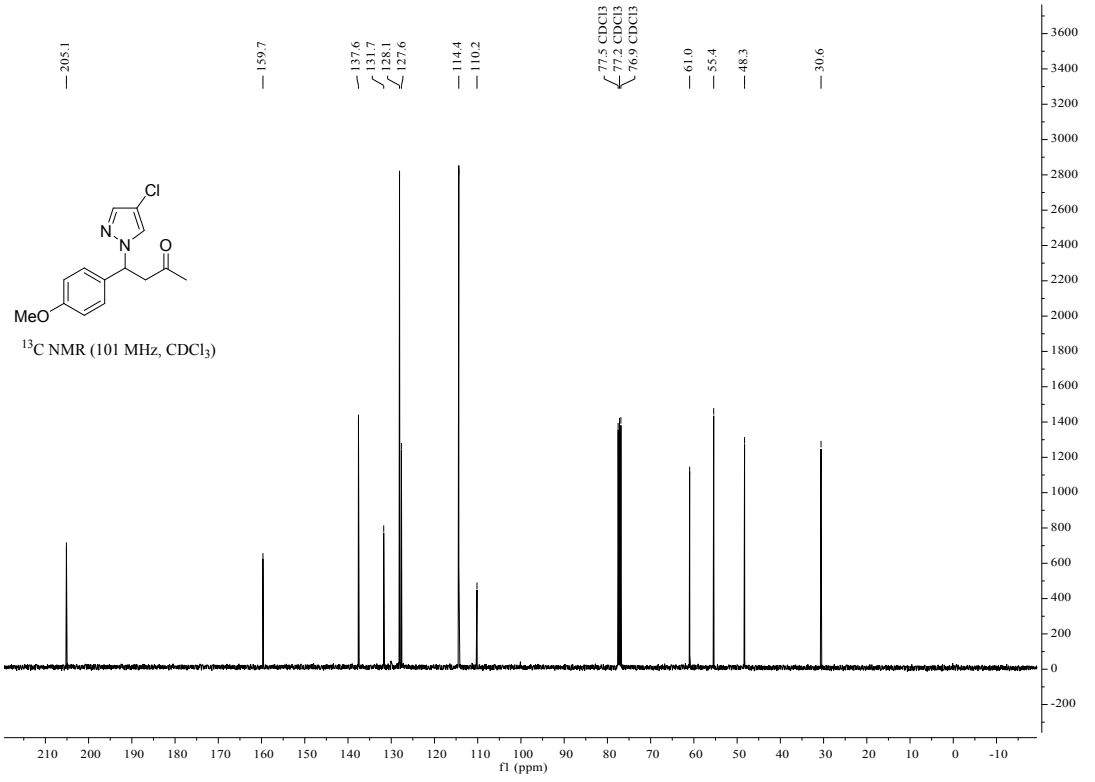

Cl
N
N
MeO
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Cl
N
N
MeO
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound 10

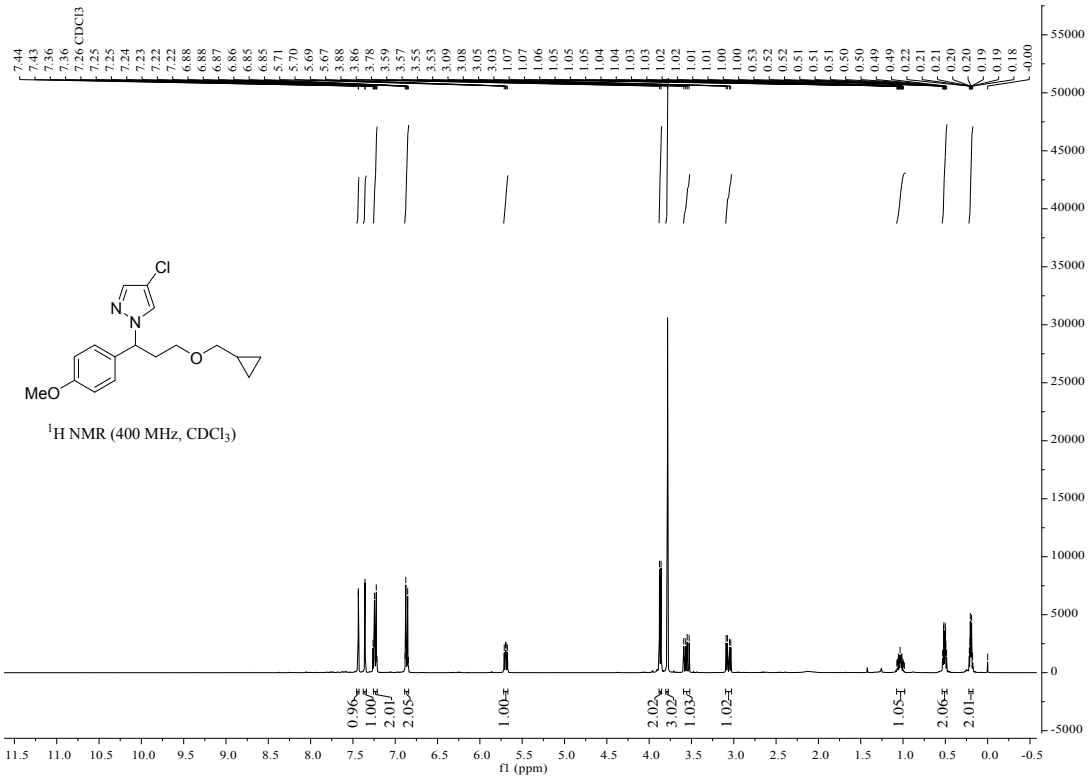


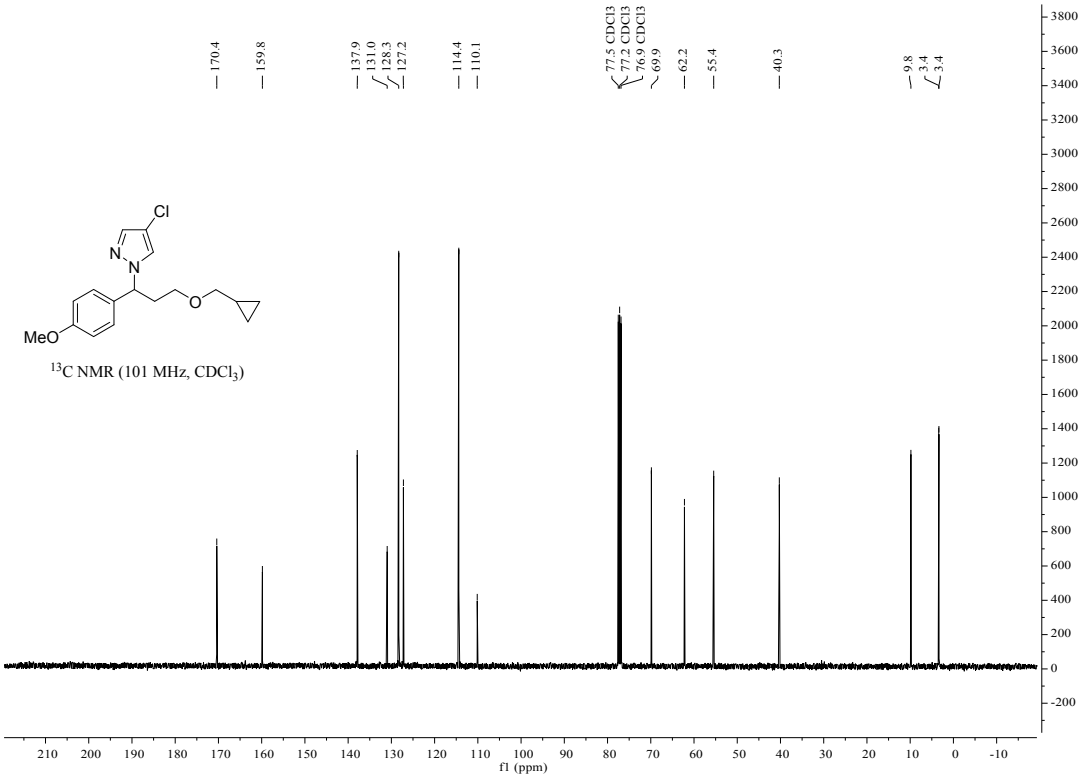
^{1}H NMR (400 MHz, $CDCl_3$)



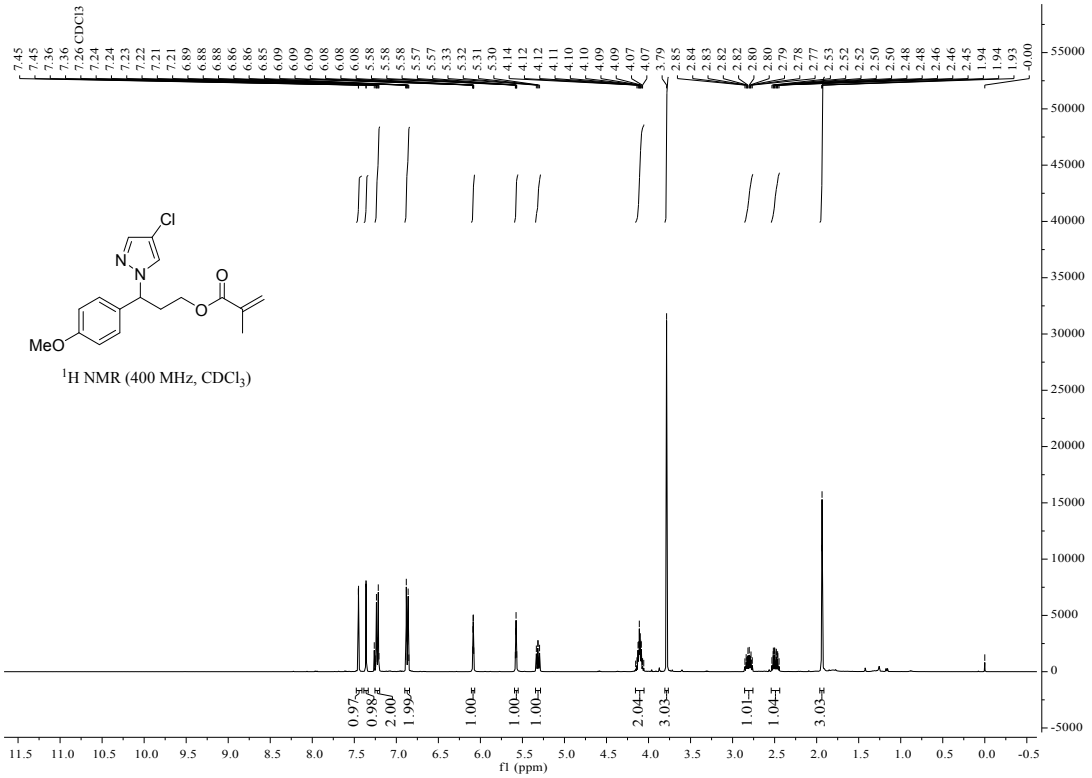
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 11

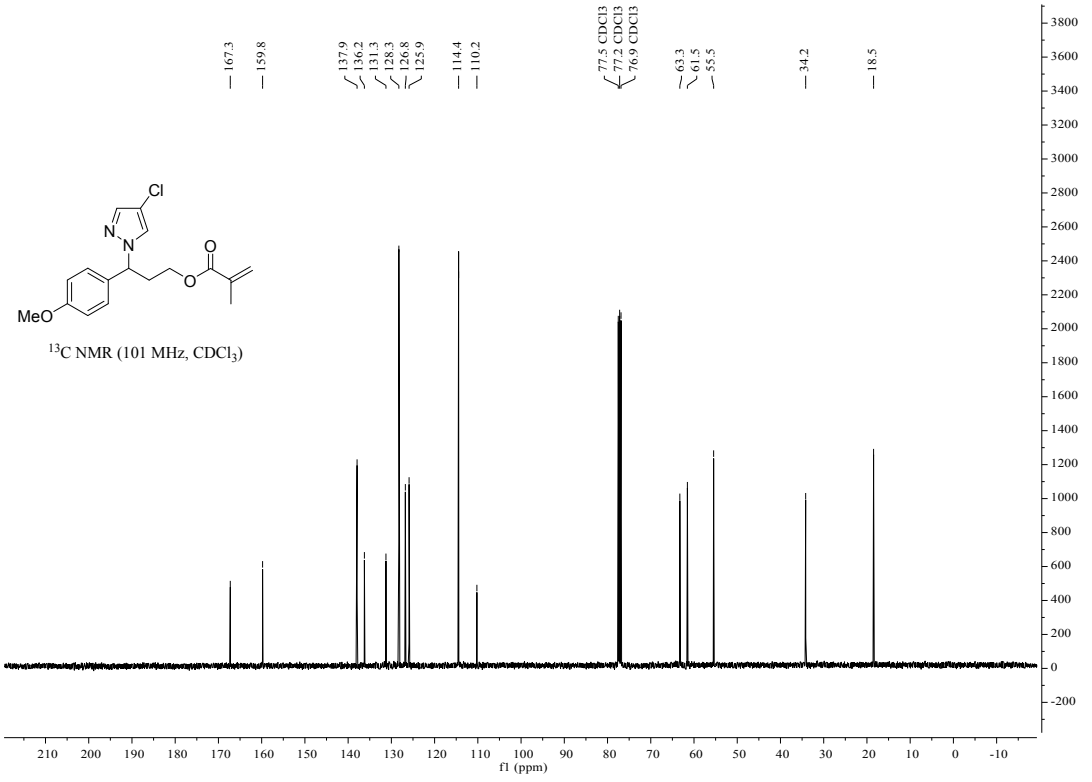

Cl
N
N
O
MeO
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Cl
N
N
O
MeO
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound 12

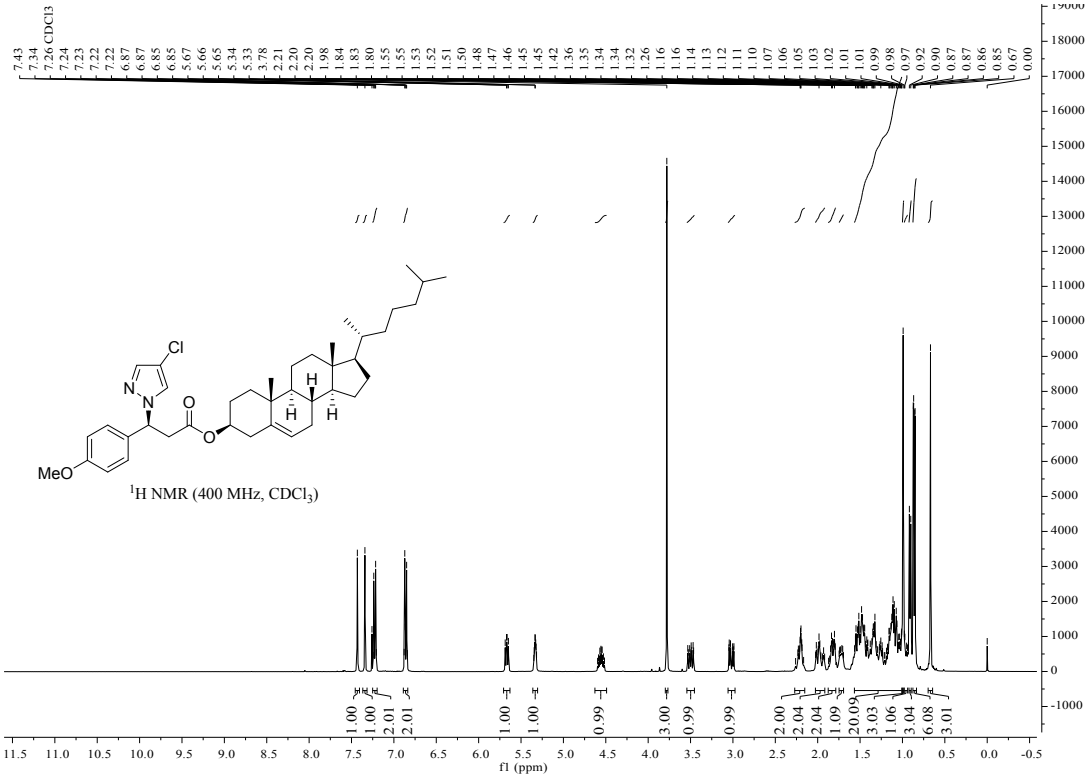


^{1}H NMR (400 MHz, $CDCl_3$)

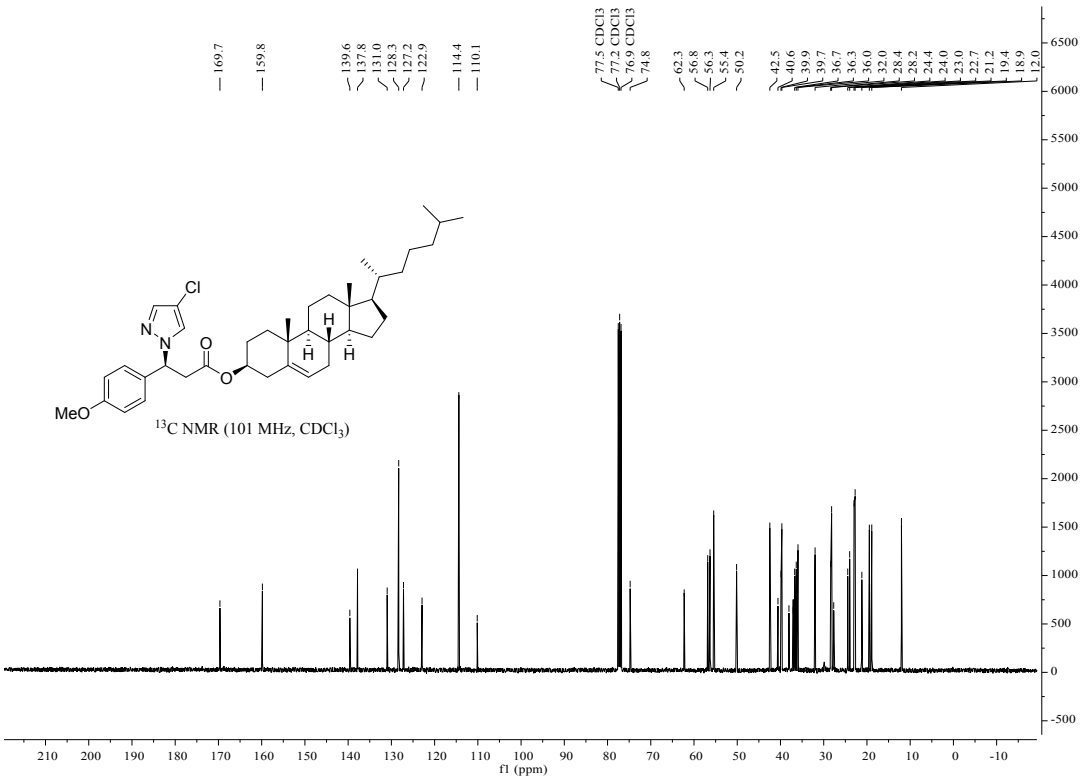


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 13

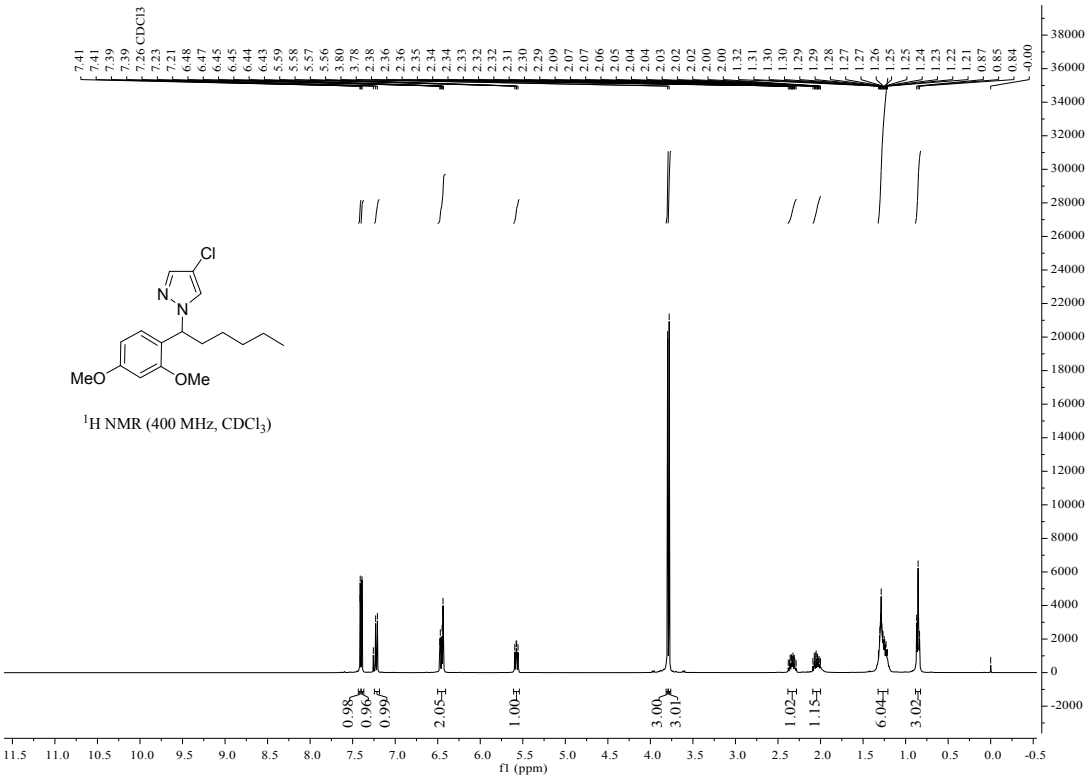


^{1}H NMR (400 MHz, $CDCl_3$)

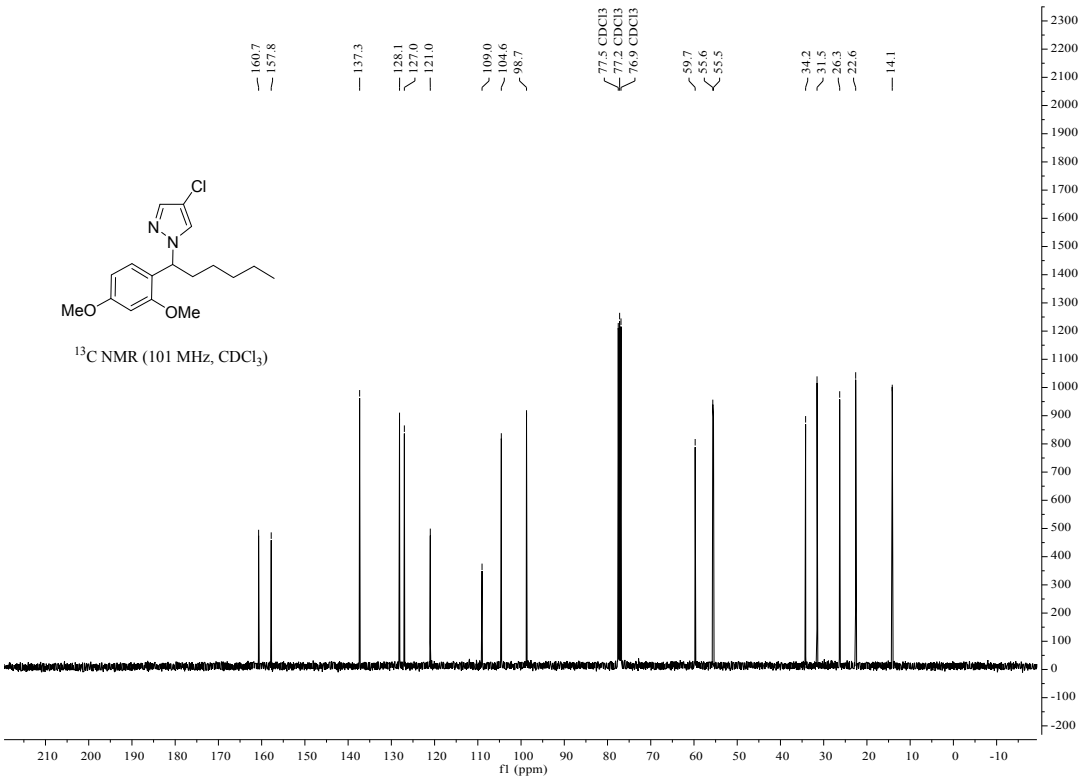


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 14

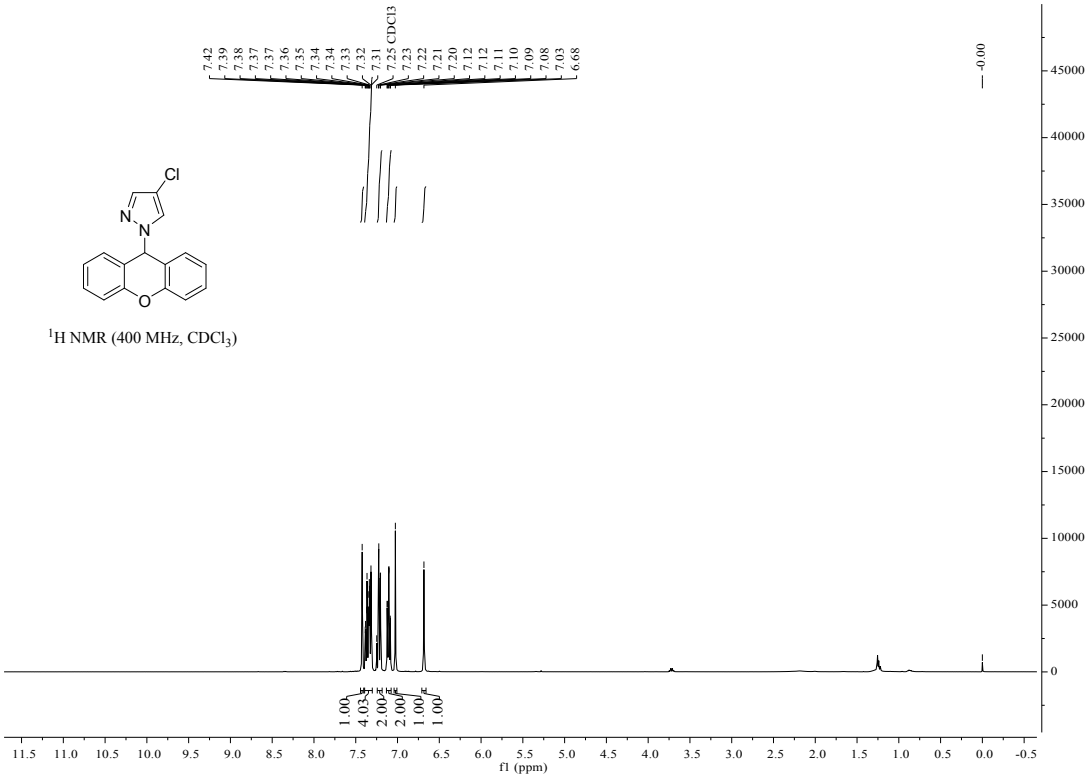


^{1}H NMR (400 MHz, $CDCl_3$)

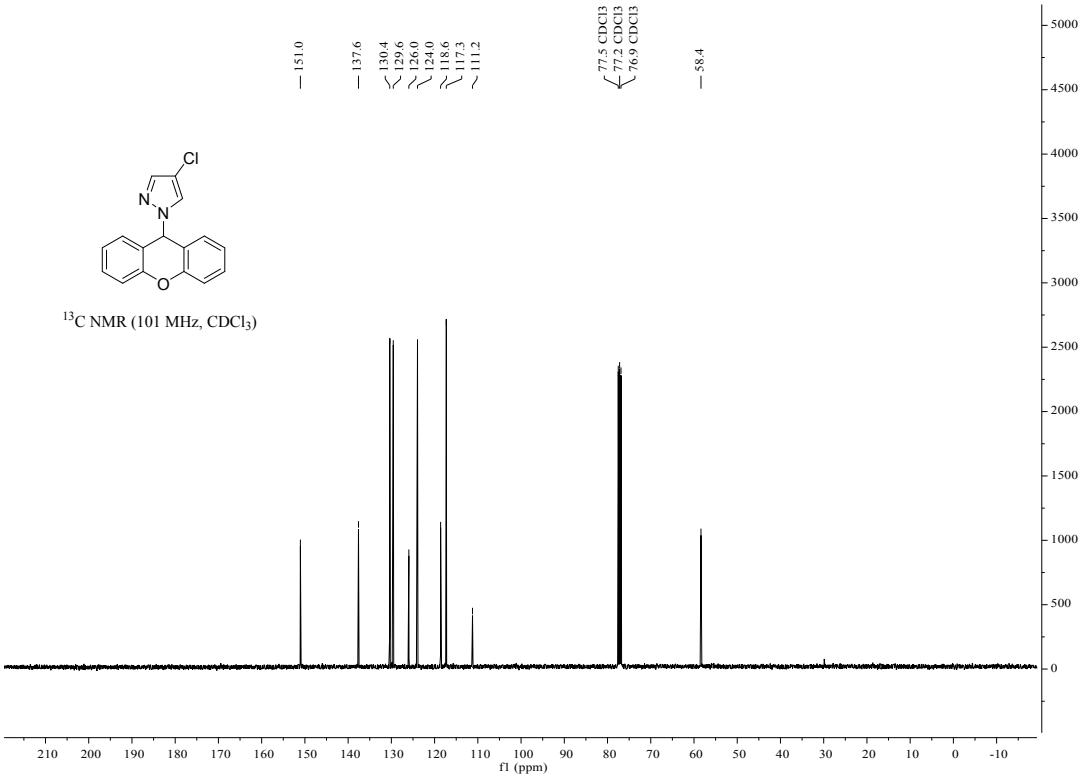


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 15

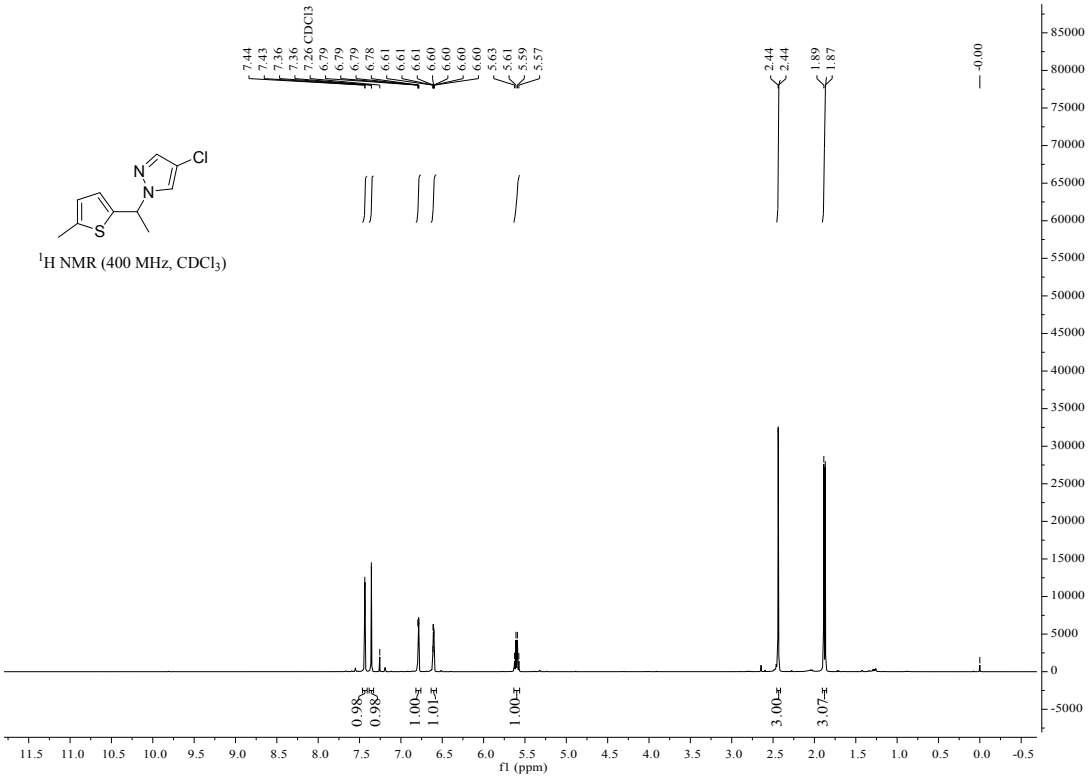


^{1}H NMR (400 MHz, $CDCl_3$)

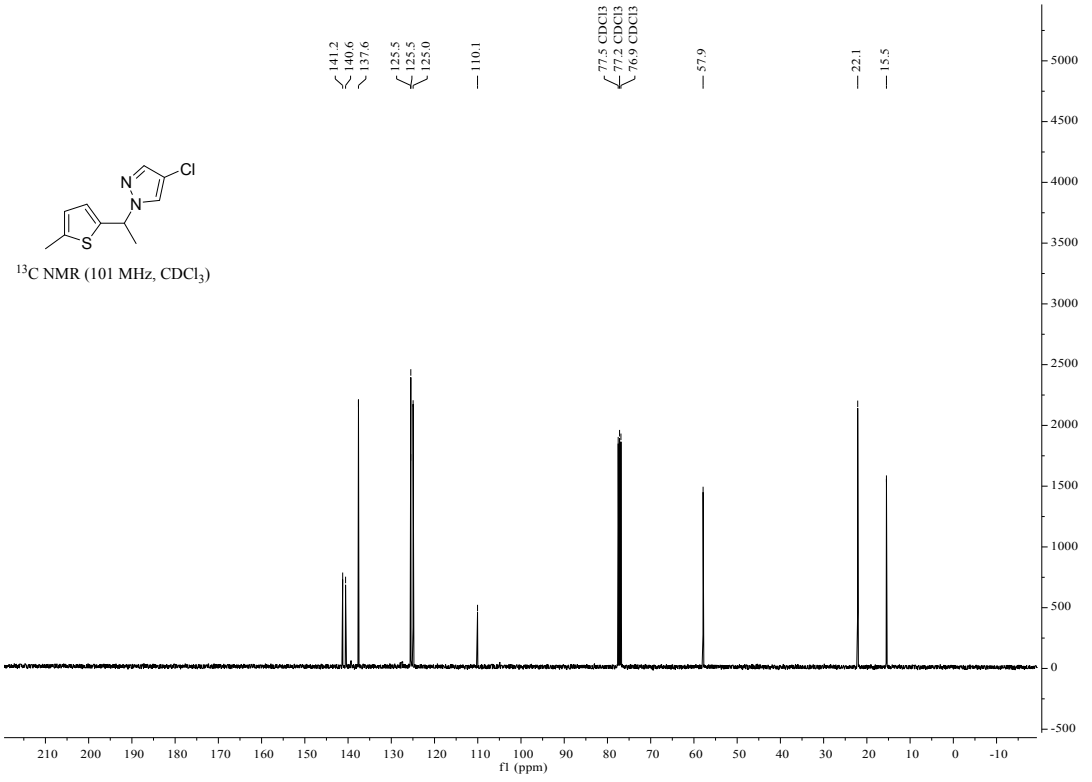


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 16

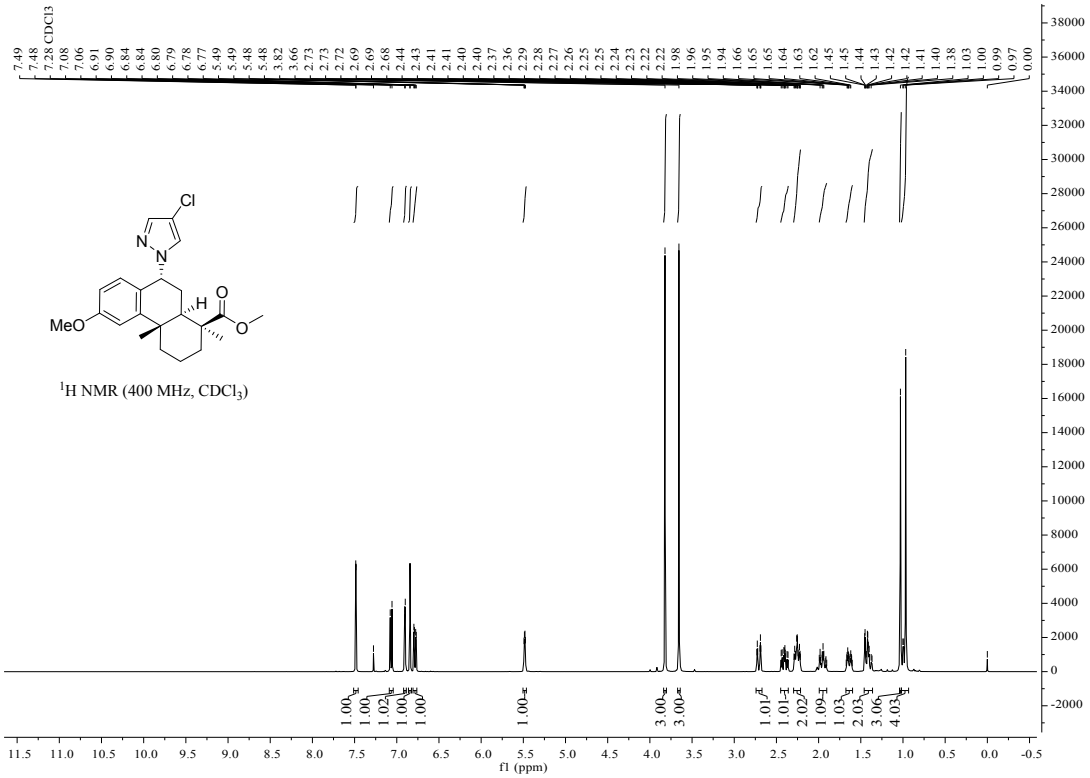


^{1}H NMR (400 MHz, $CDCl_3$)

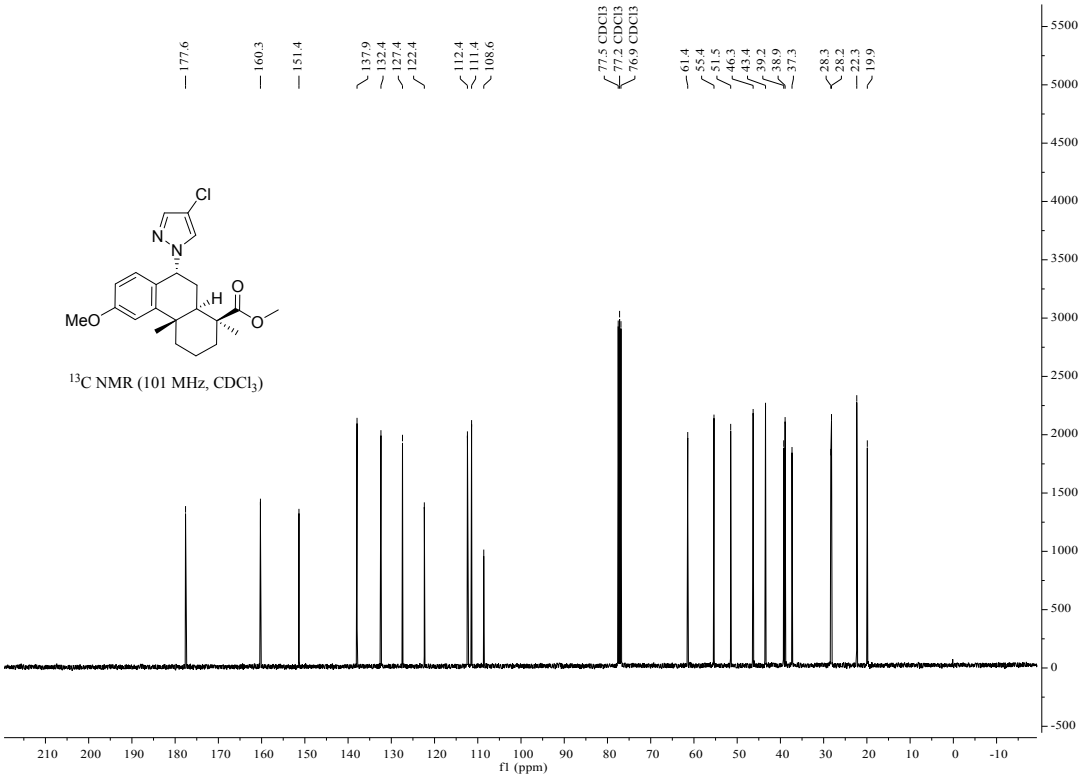


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 17

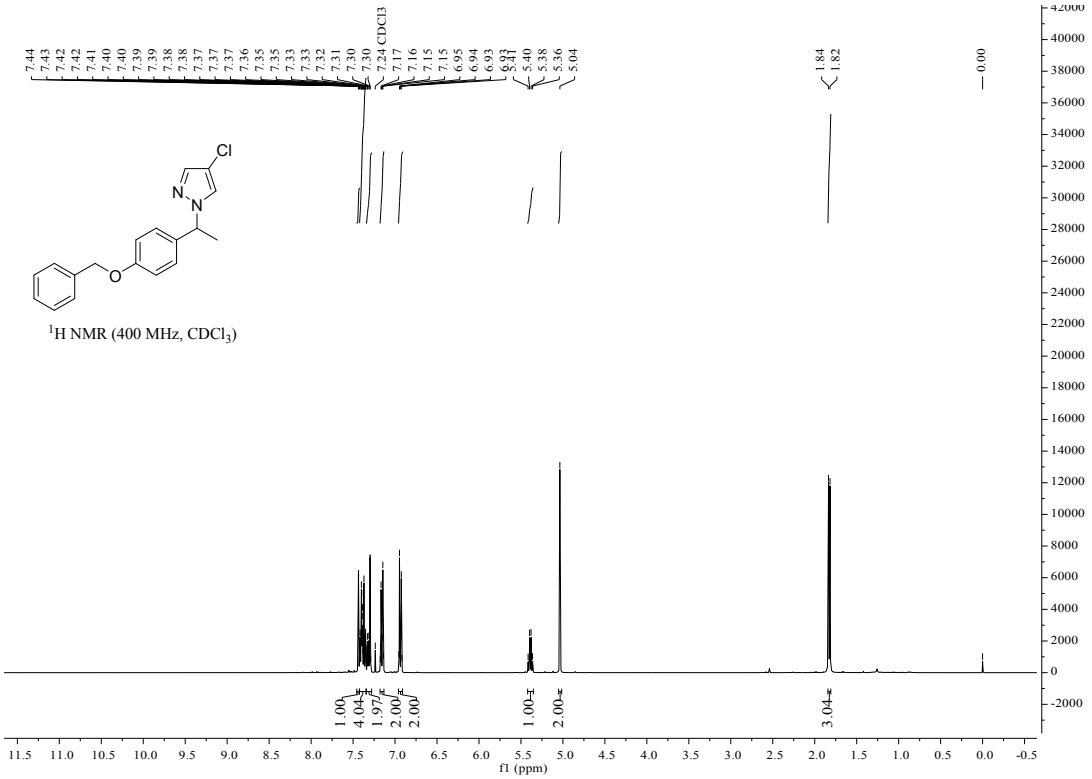


^{1}H NMR (400 MHz, $CDCl_3$)

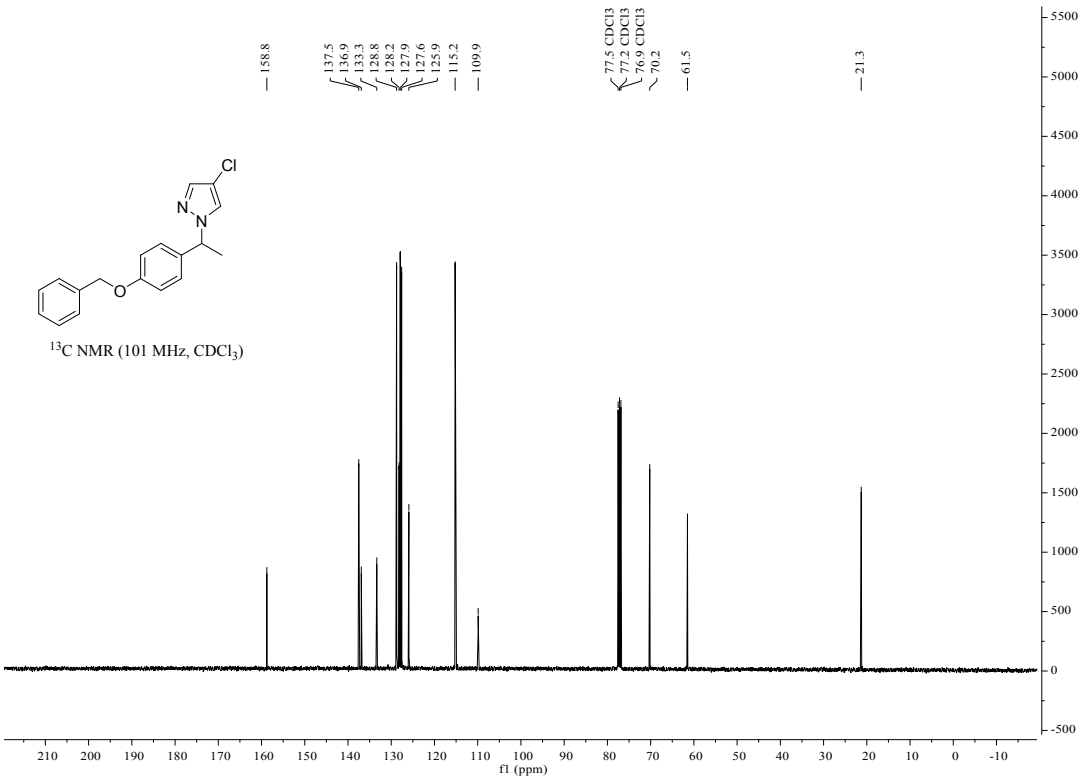


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 18

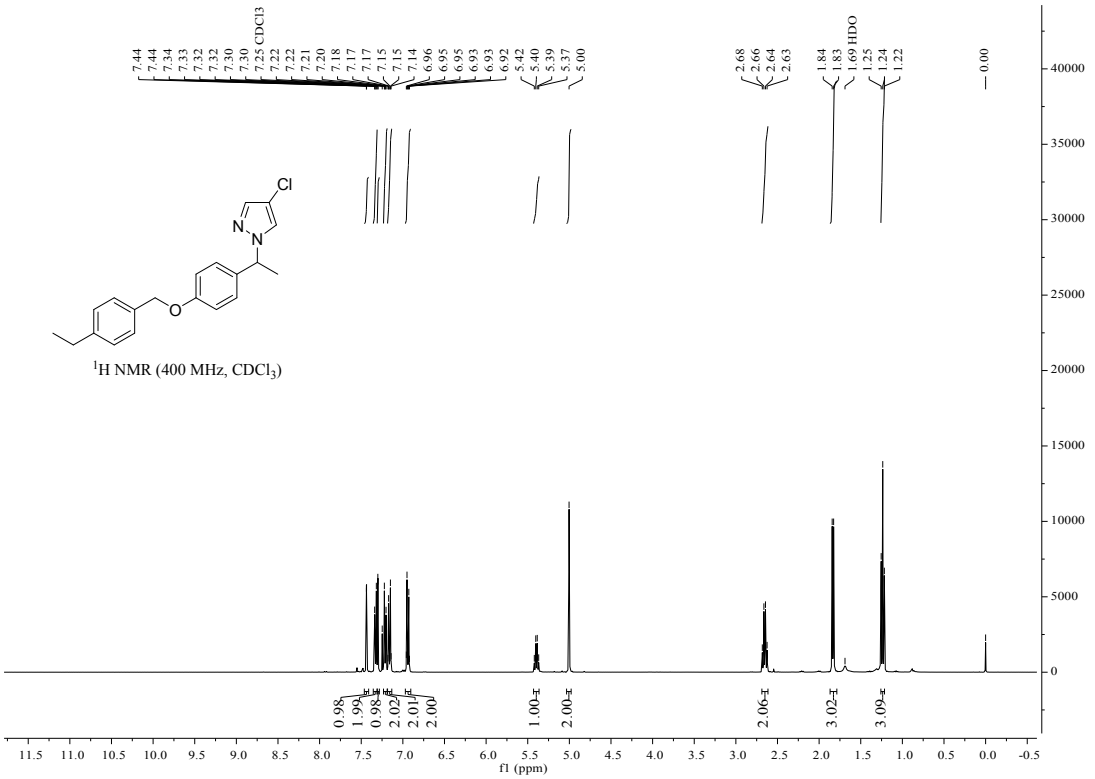


^{1}H NMR (400 MHz, $CDCl_3$)

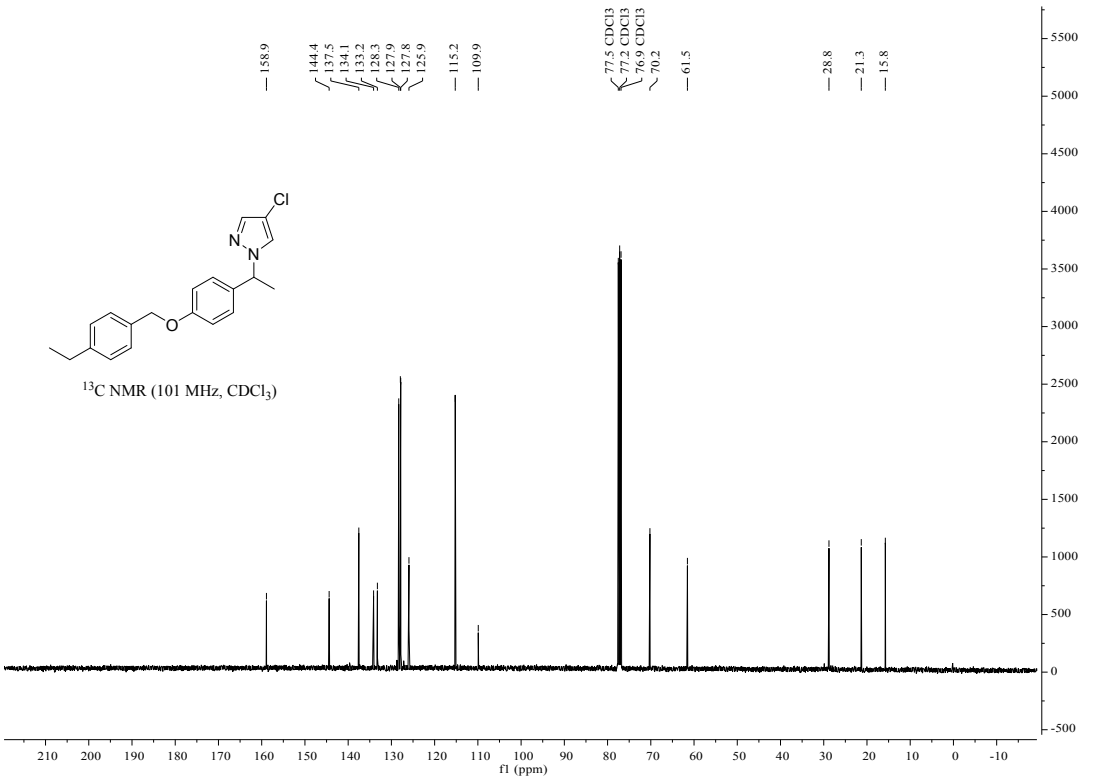


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 19

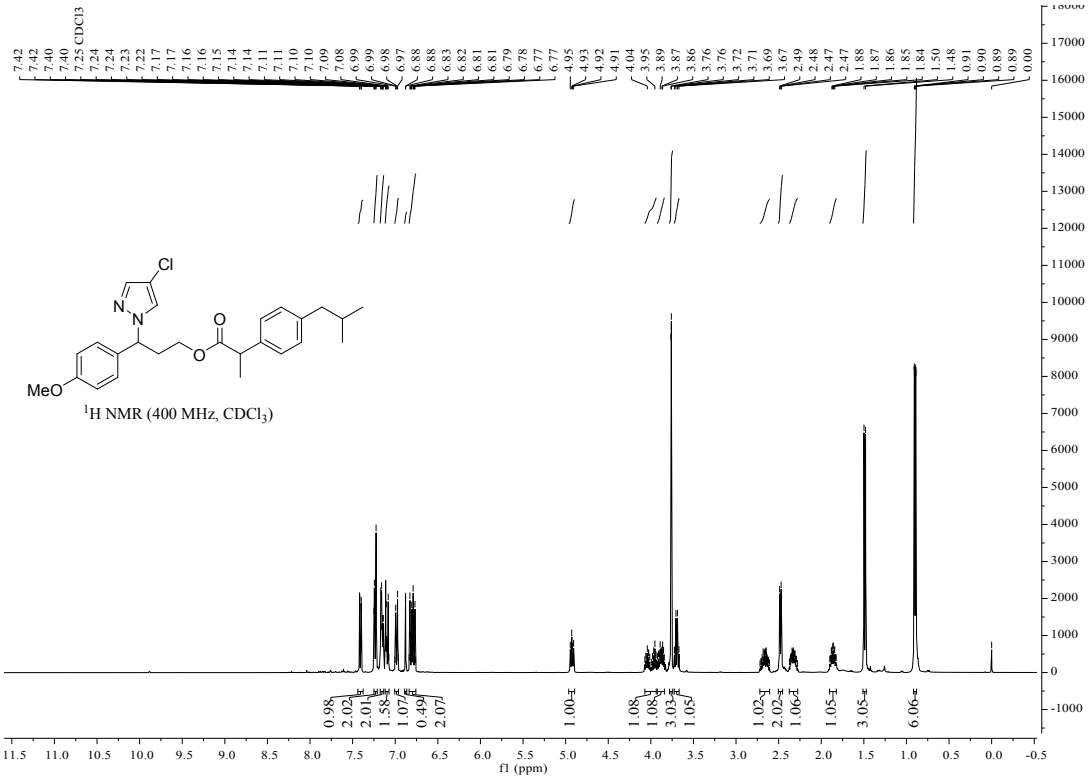


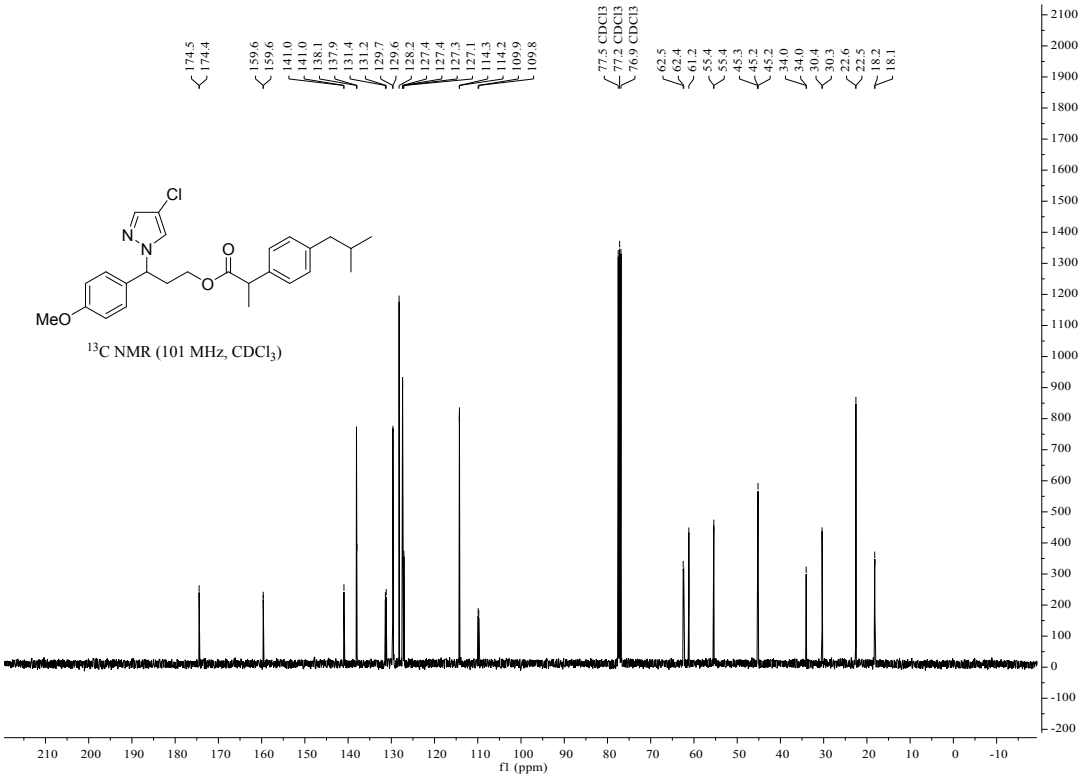
^{1}H NMR (400 MHz, $CDCl_3$)



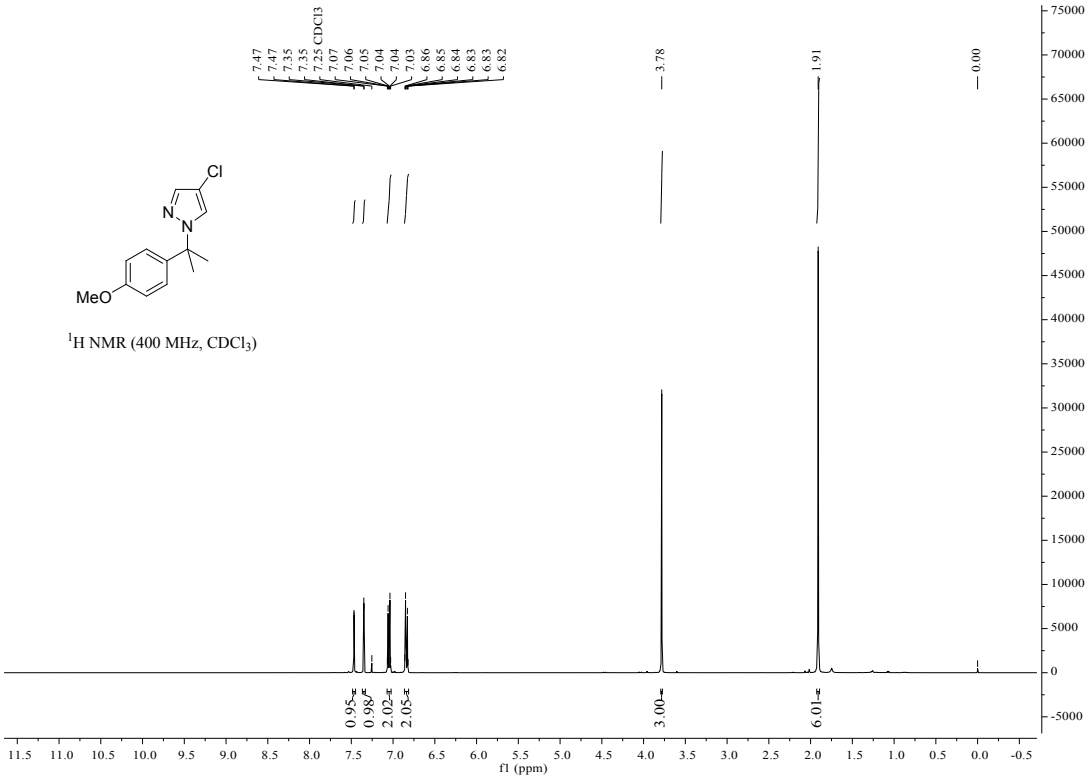
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 20

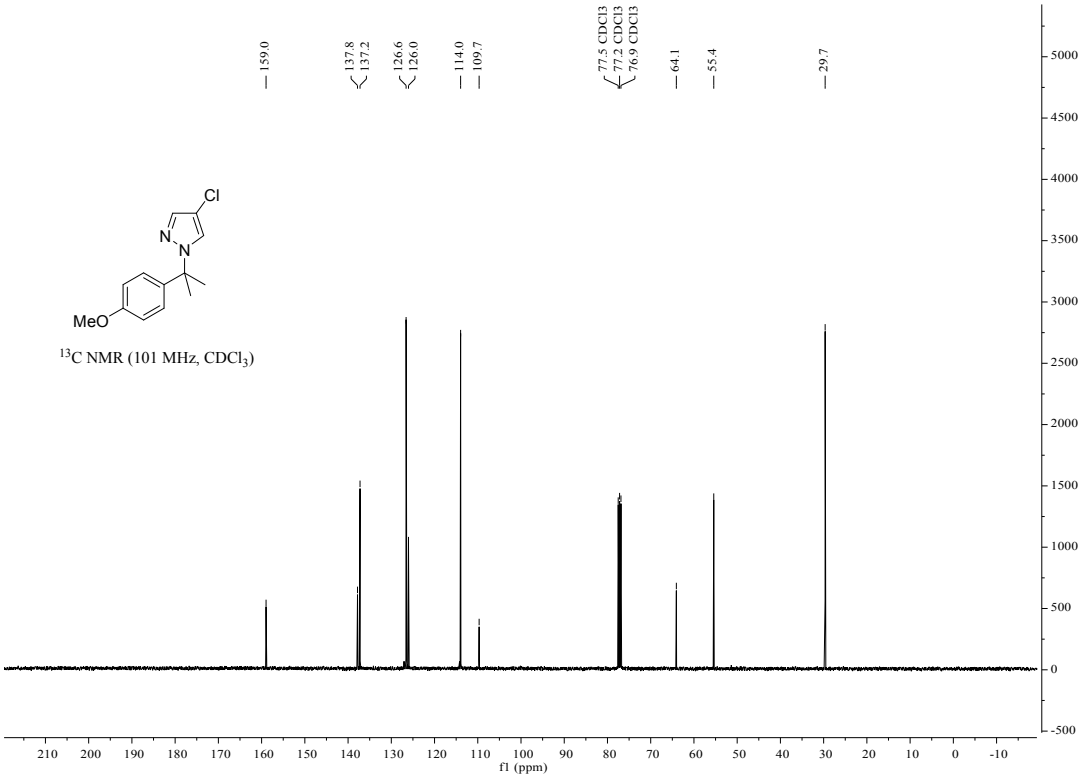

Cl
N
N
O
O
MeO
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


Cl
N
N
O
O
MeO
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound 21

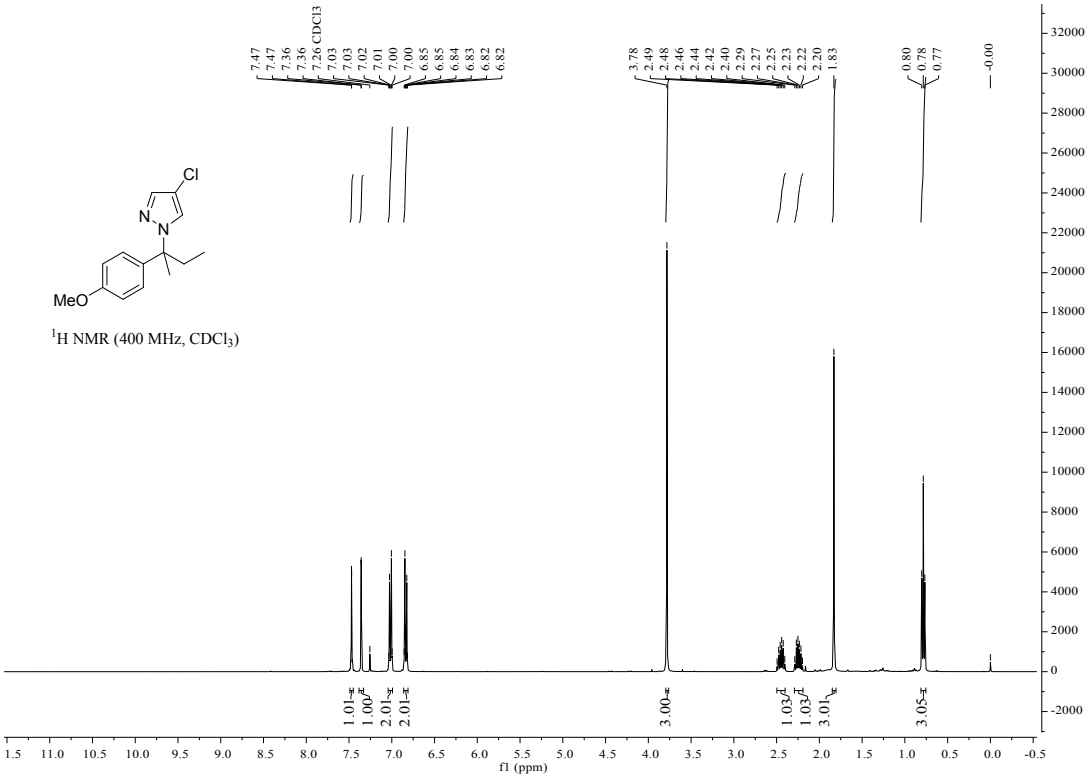


^{1}H NMR (400 MHz, $CDCl_3$)

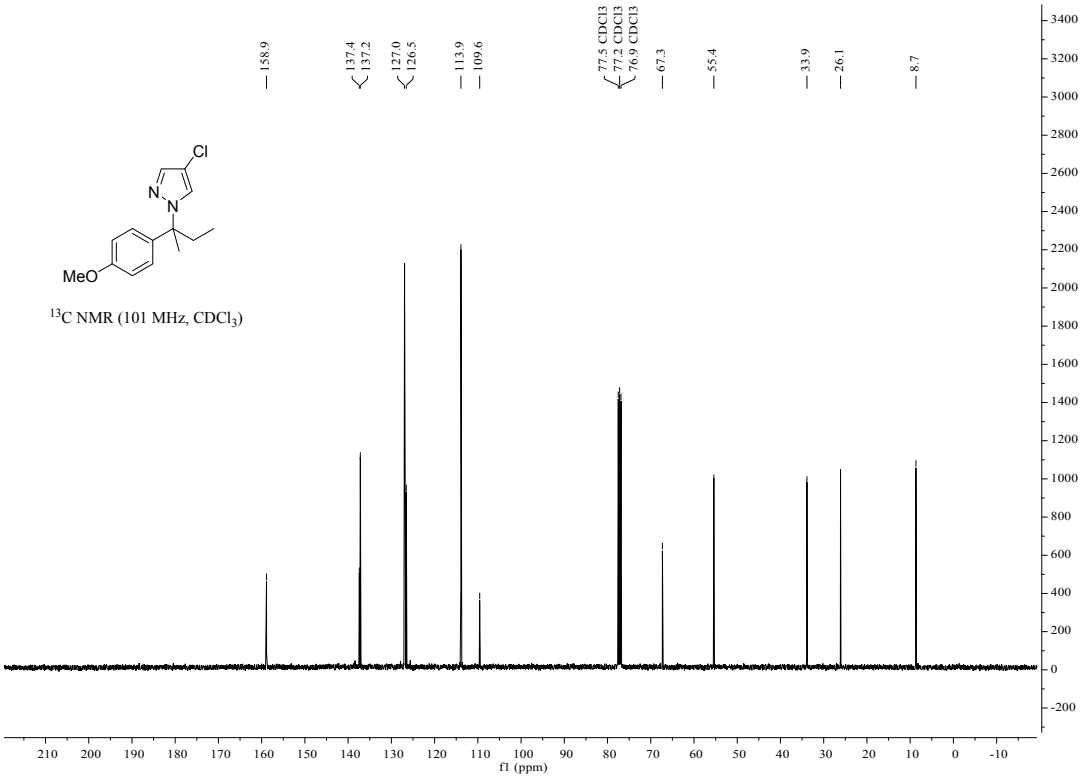


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 22

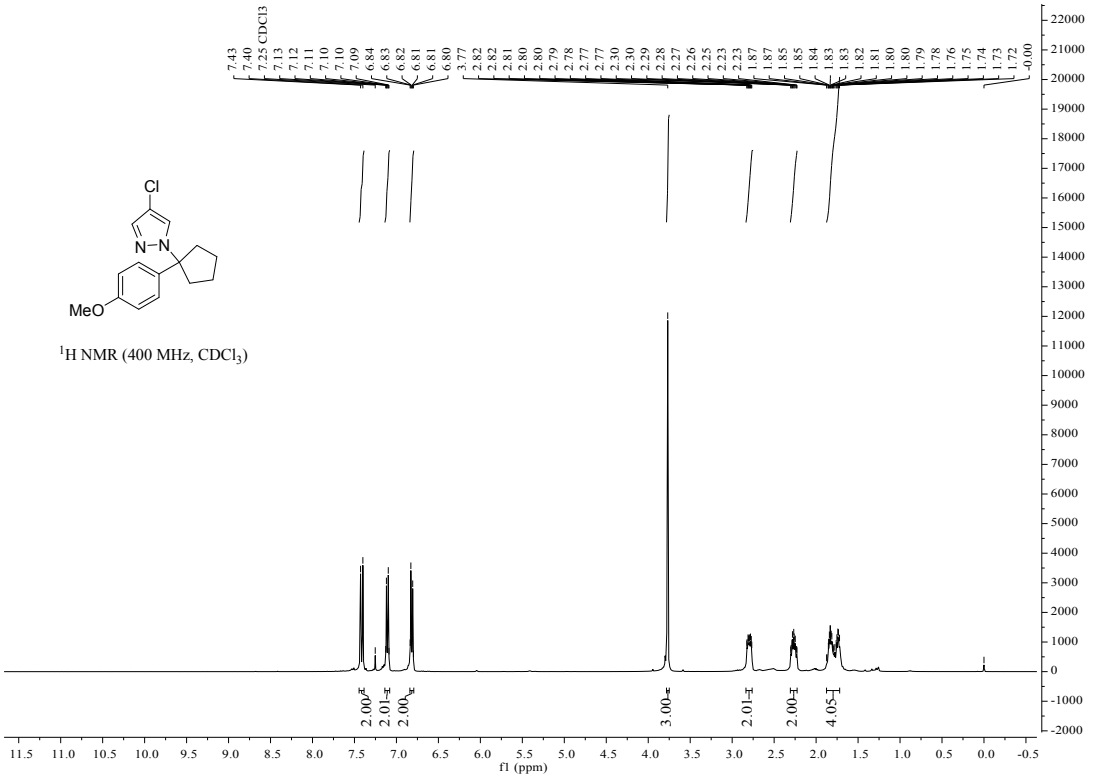


^{1}H NMR (400 MHz, $CDCl_3$)

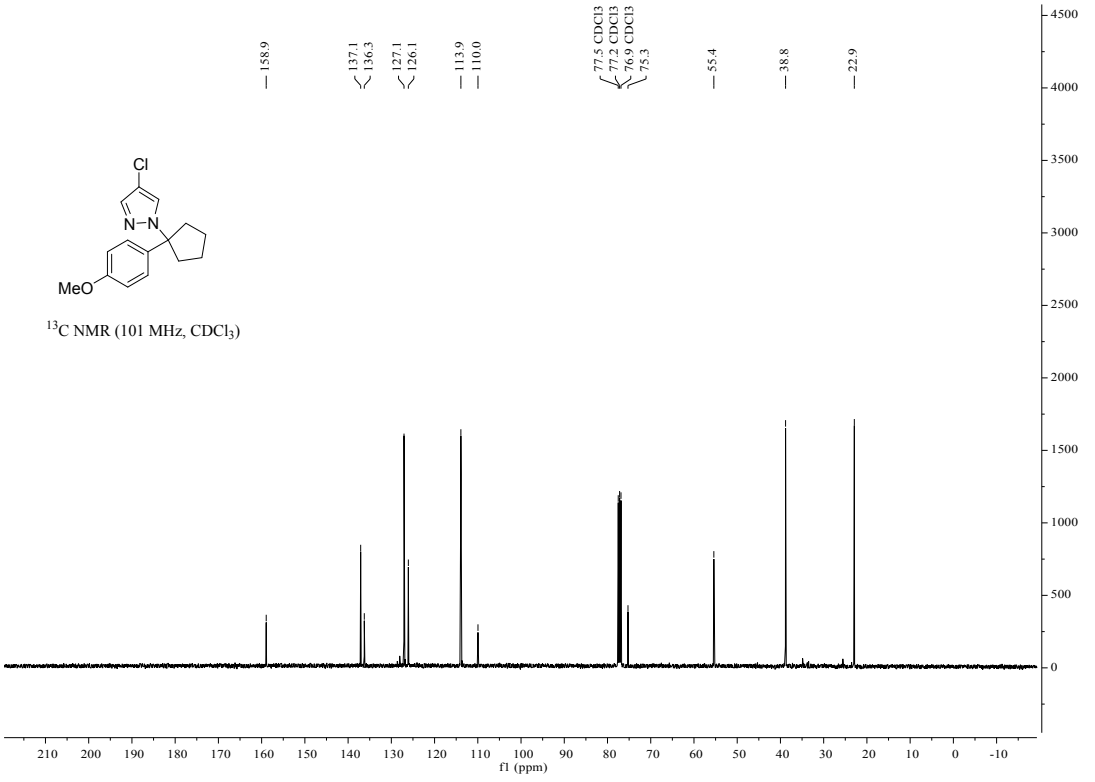


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 23

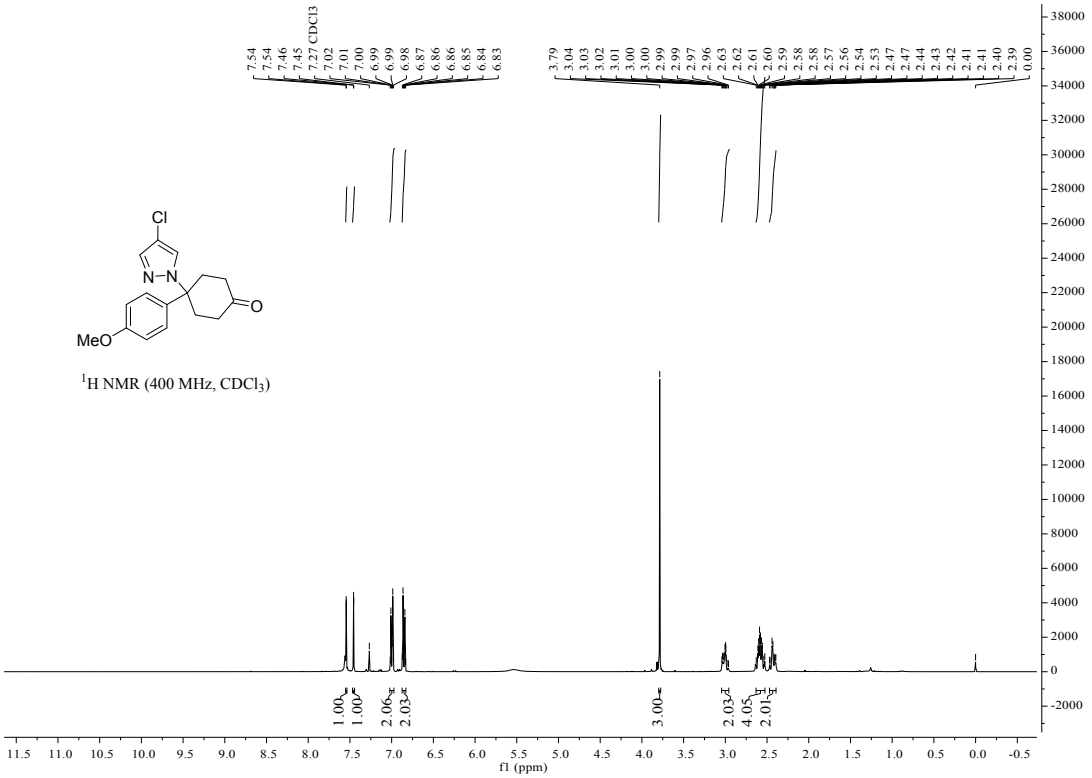


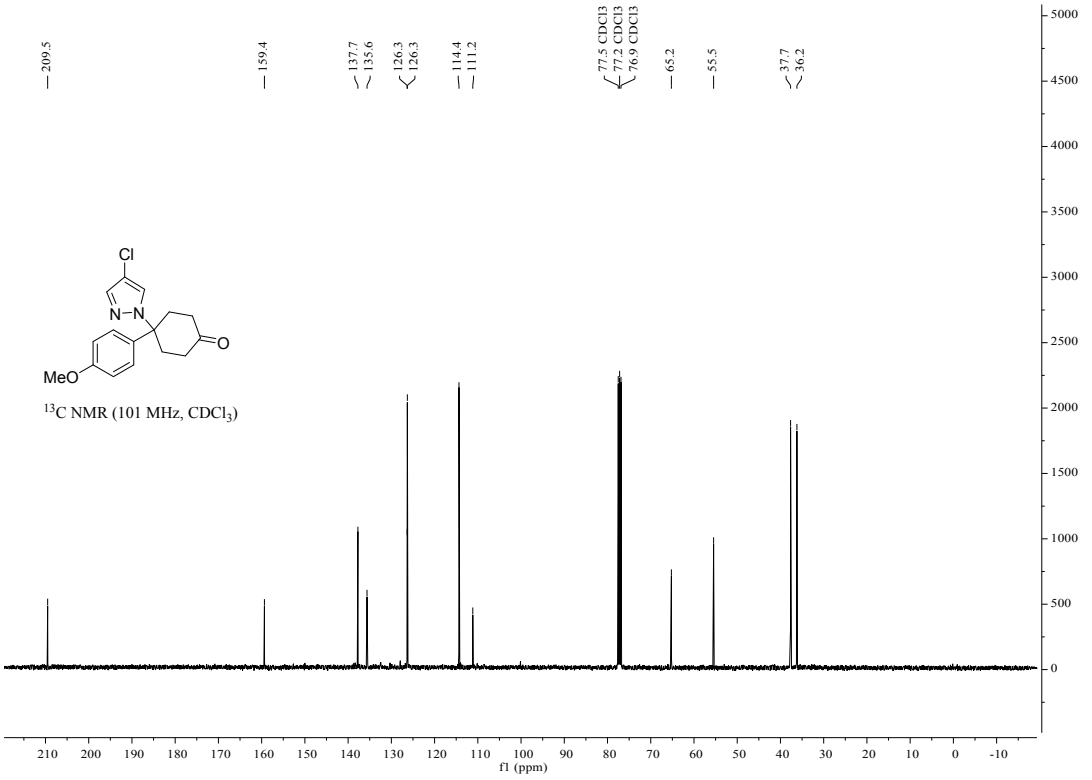
^{1}H NMR (400 MHz, $CDCl_3$)



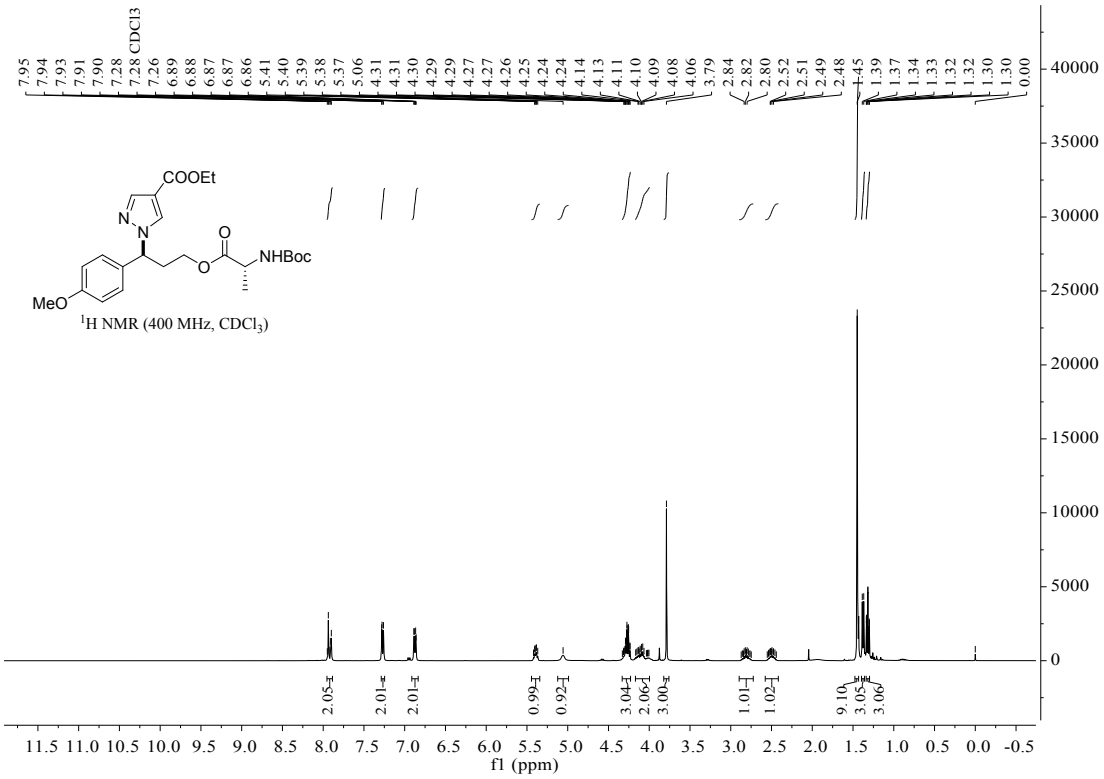
^{13}C NMR (101 MHz, $CDCl_3$)

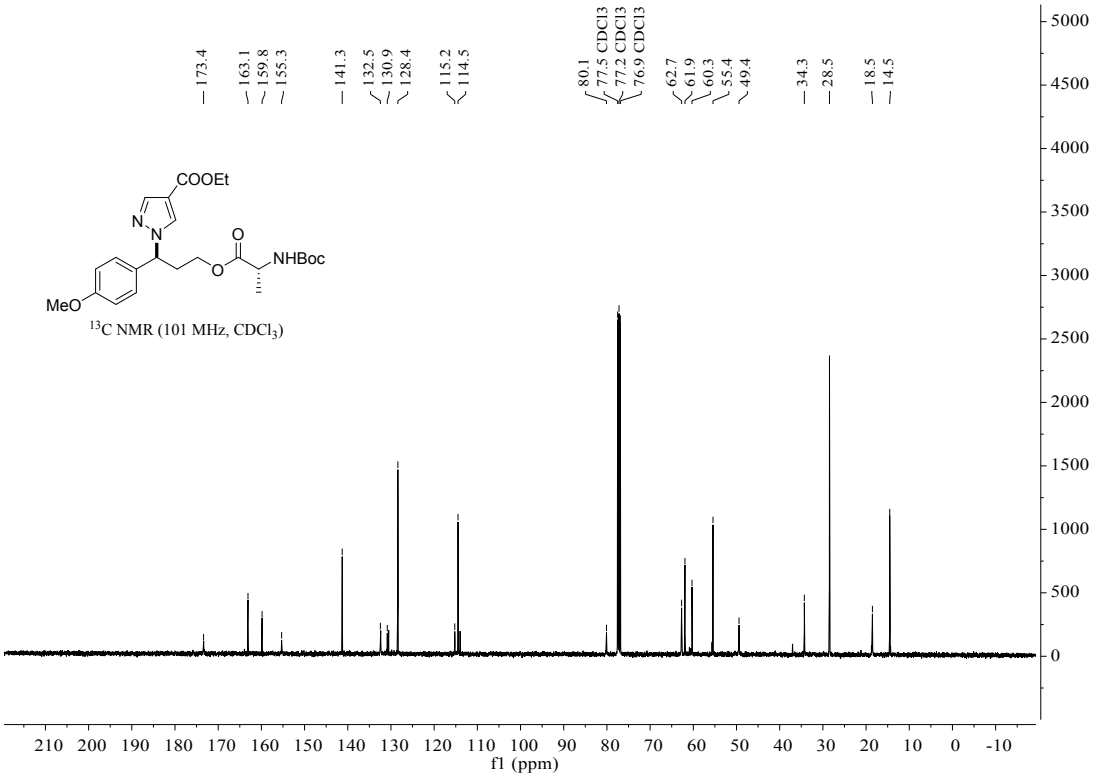
Compound 24


Cl
N–N
O
MeO
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

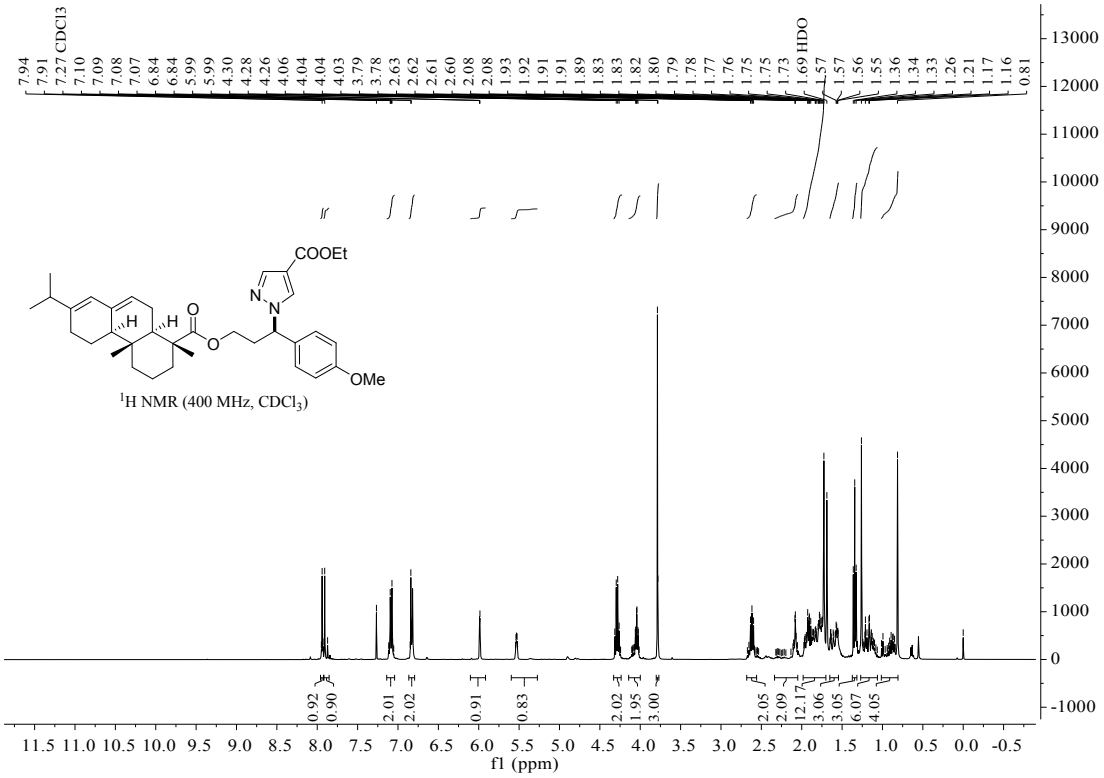

Cl
N–N
O
MeO
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound 25

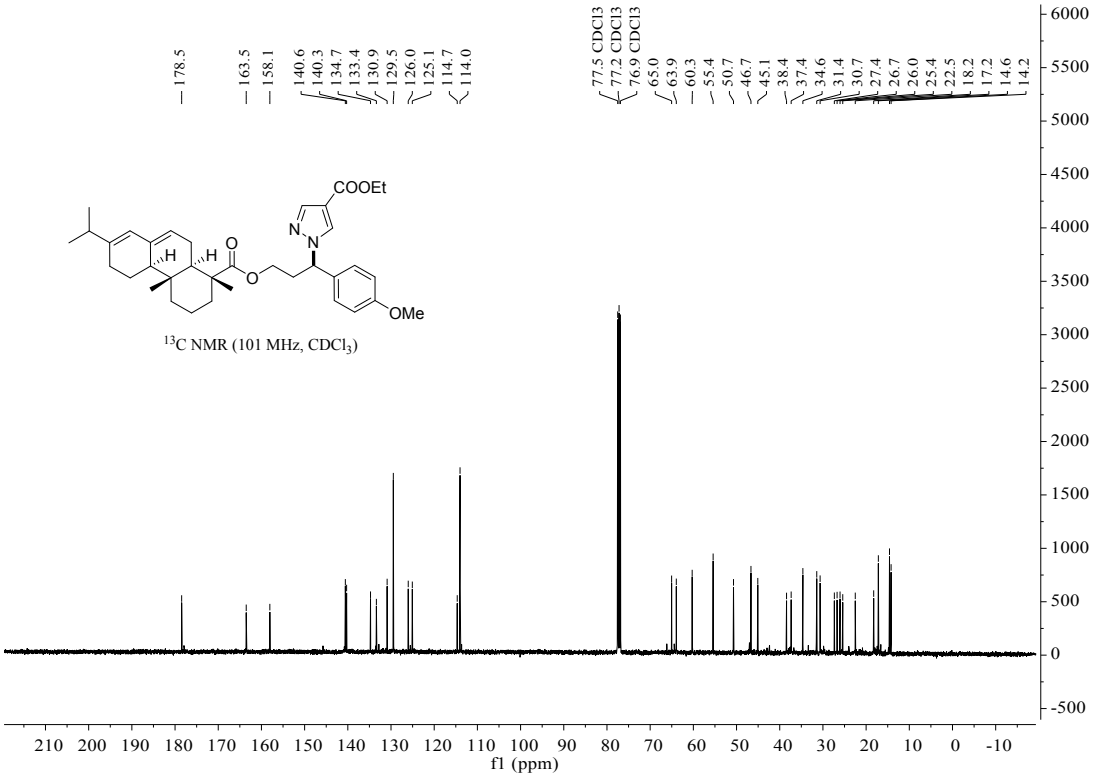

COOEt
NHBoc
MeO
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


COOEt
NHBoc
MeO
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound 26

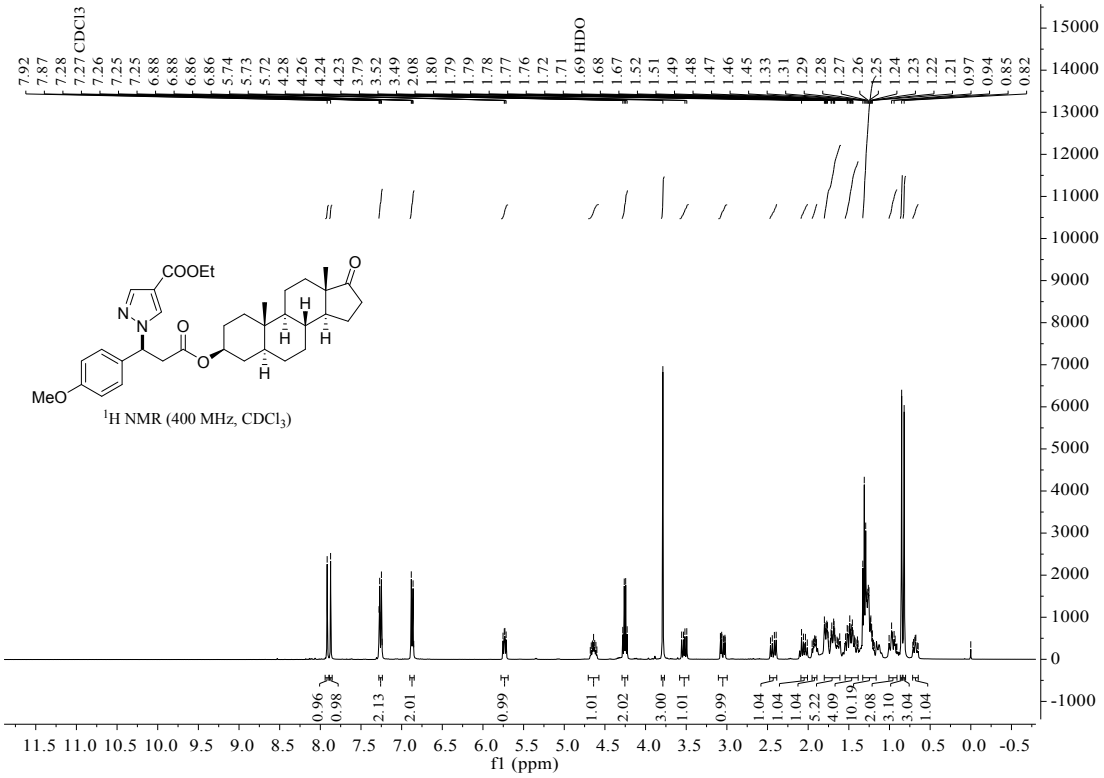


^{1}H NMR (400 MHz, $CDCl_3$)

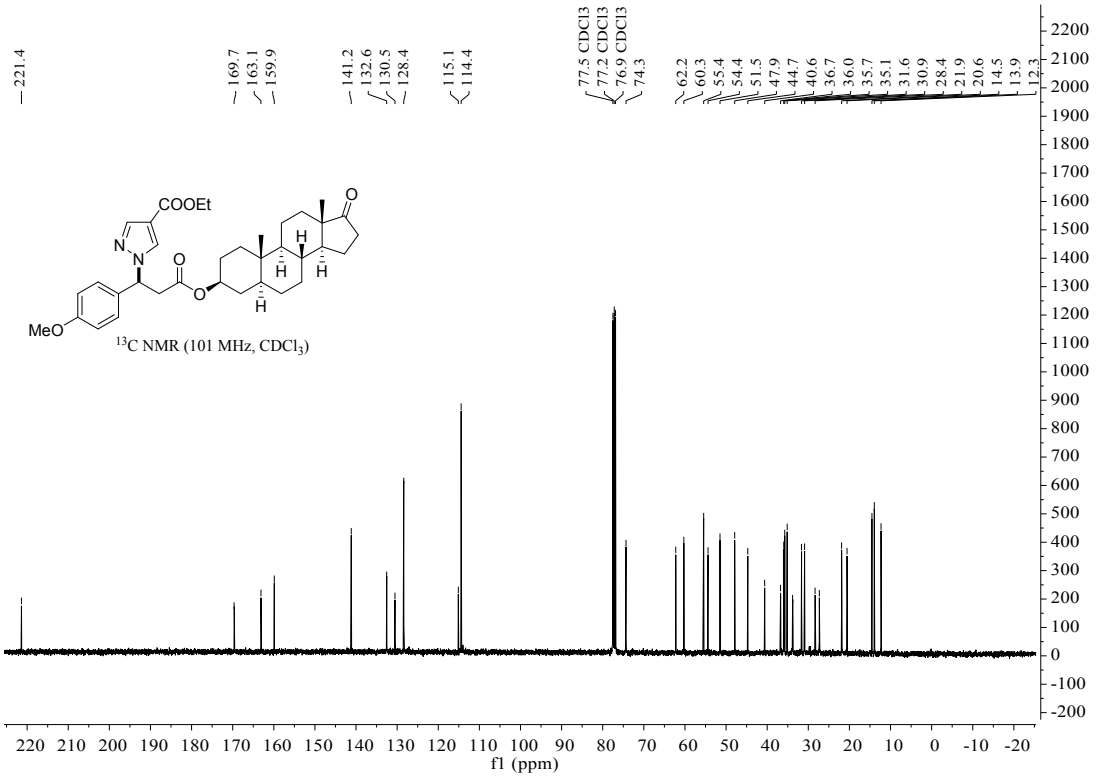


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 27

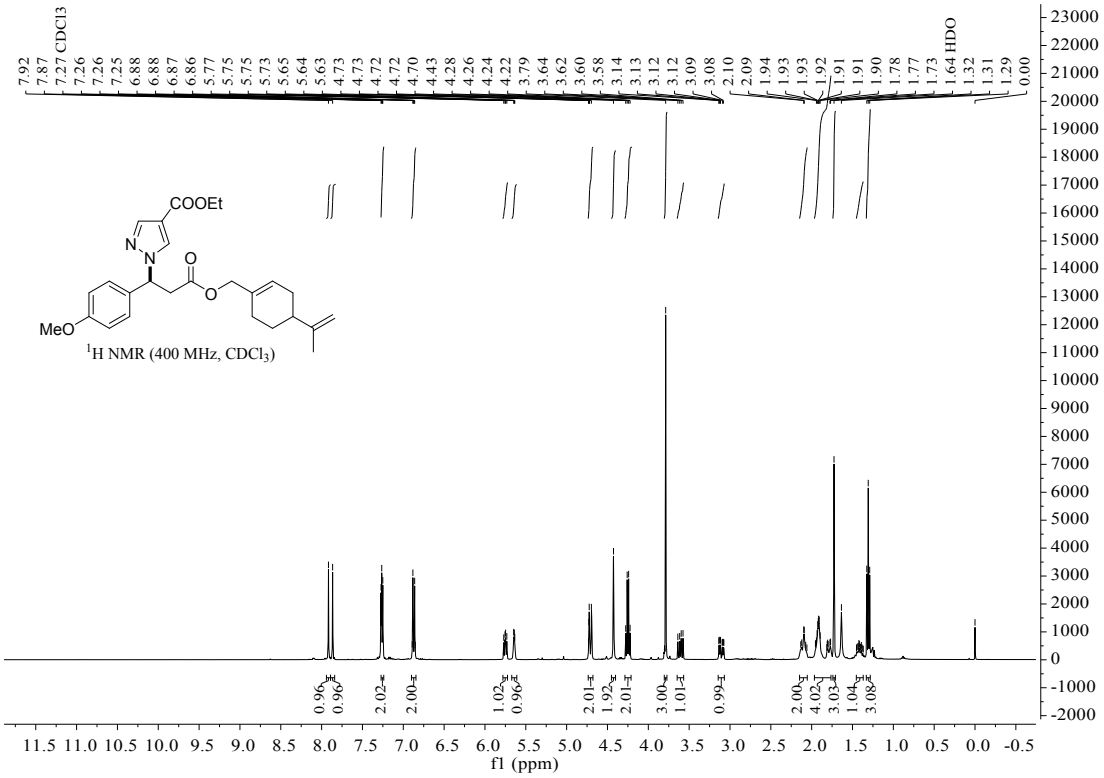


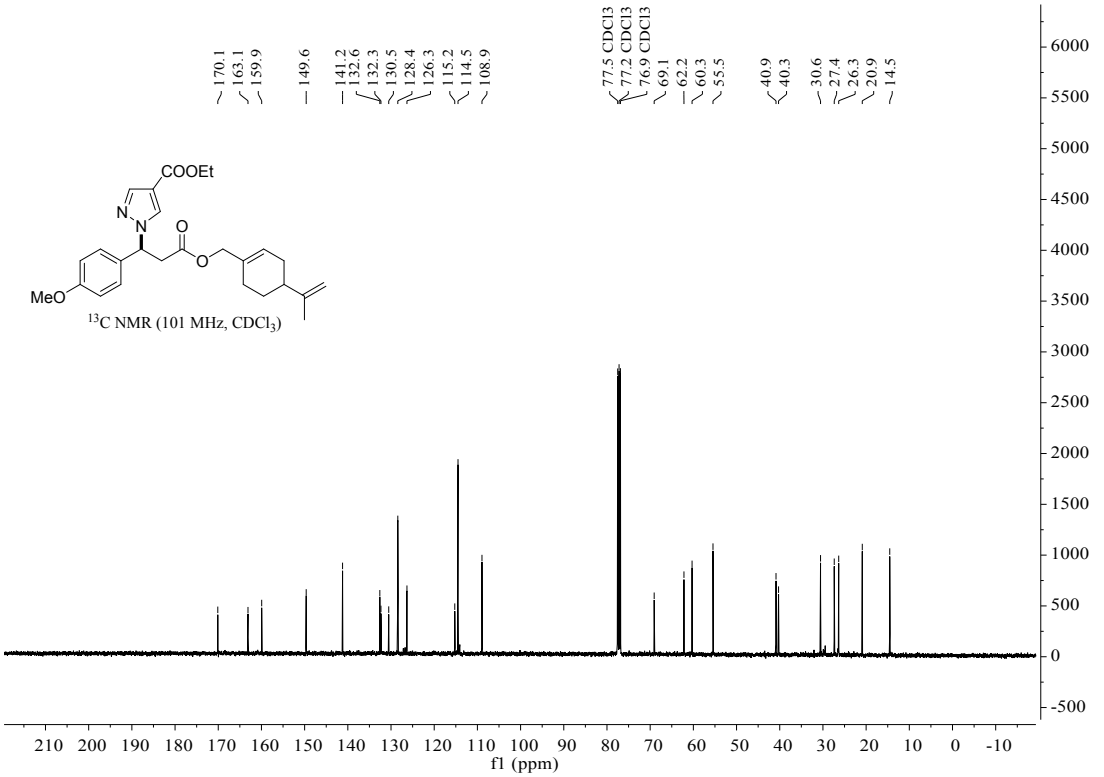
^{1}H NMR (400 MHz, $CDCl_3$)



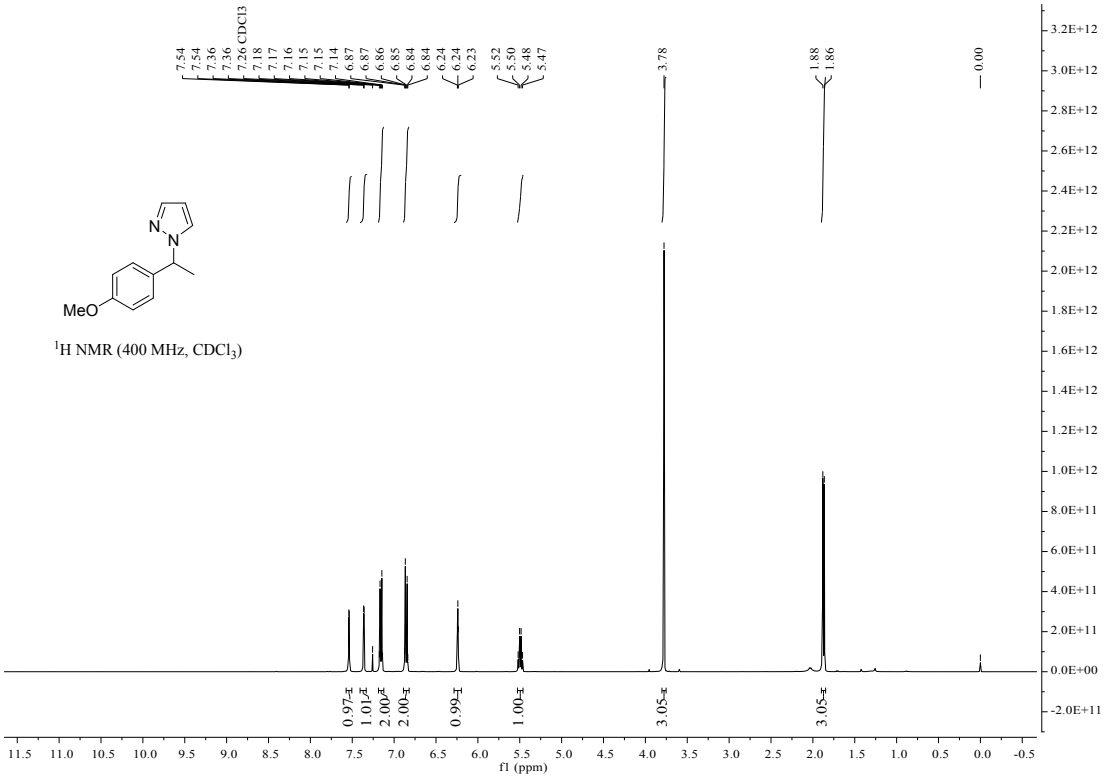
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 28

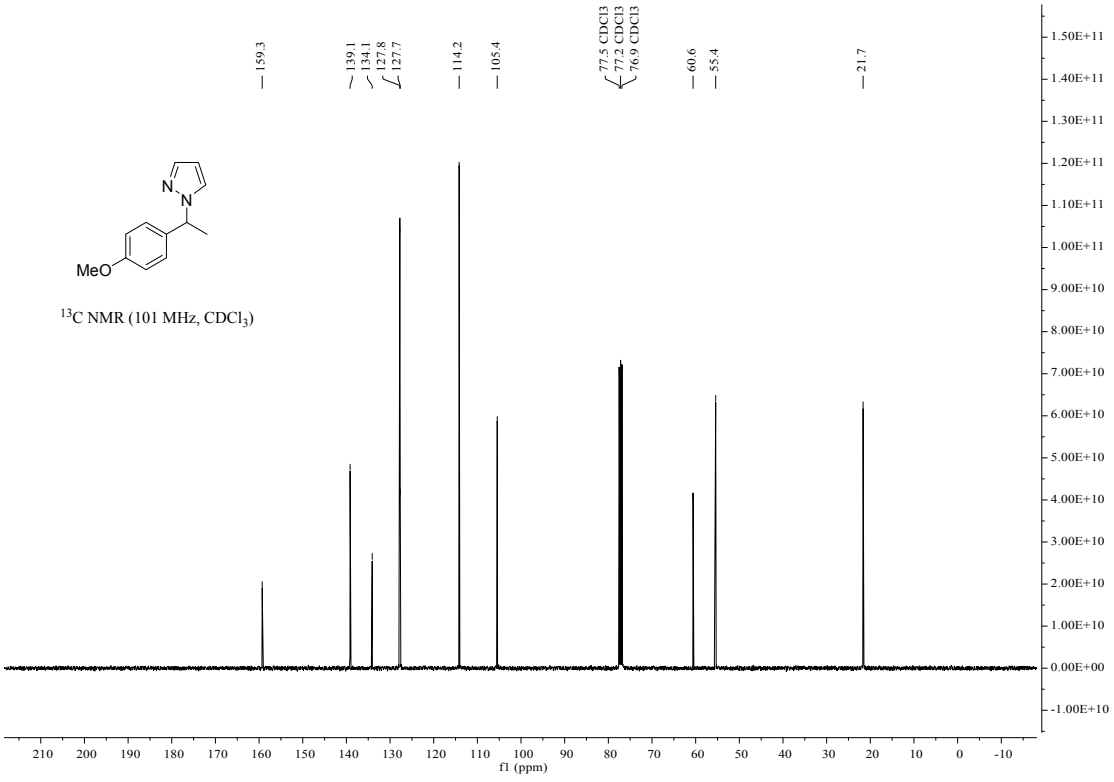

COOEt
N
N
O
O
MeO
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


COOEt
N
N
O
O
MeO
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound 29

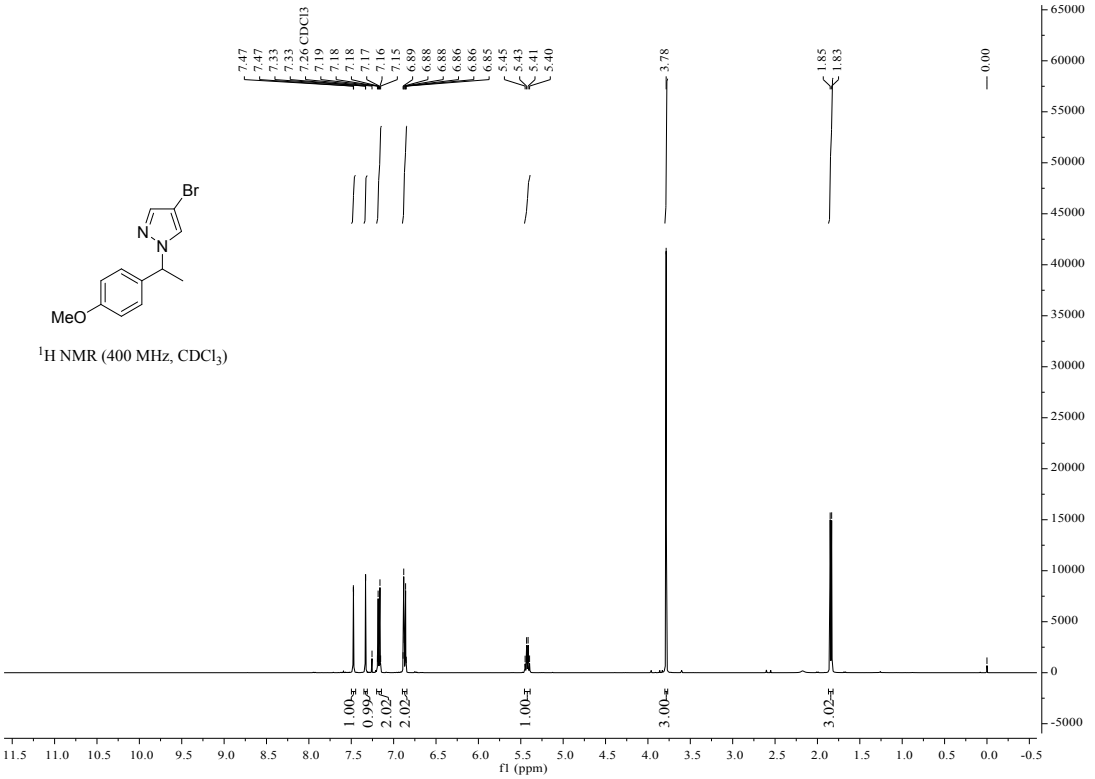


^{1}H NMR (400 MHz, $CDCl_3$)

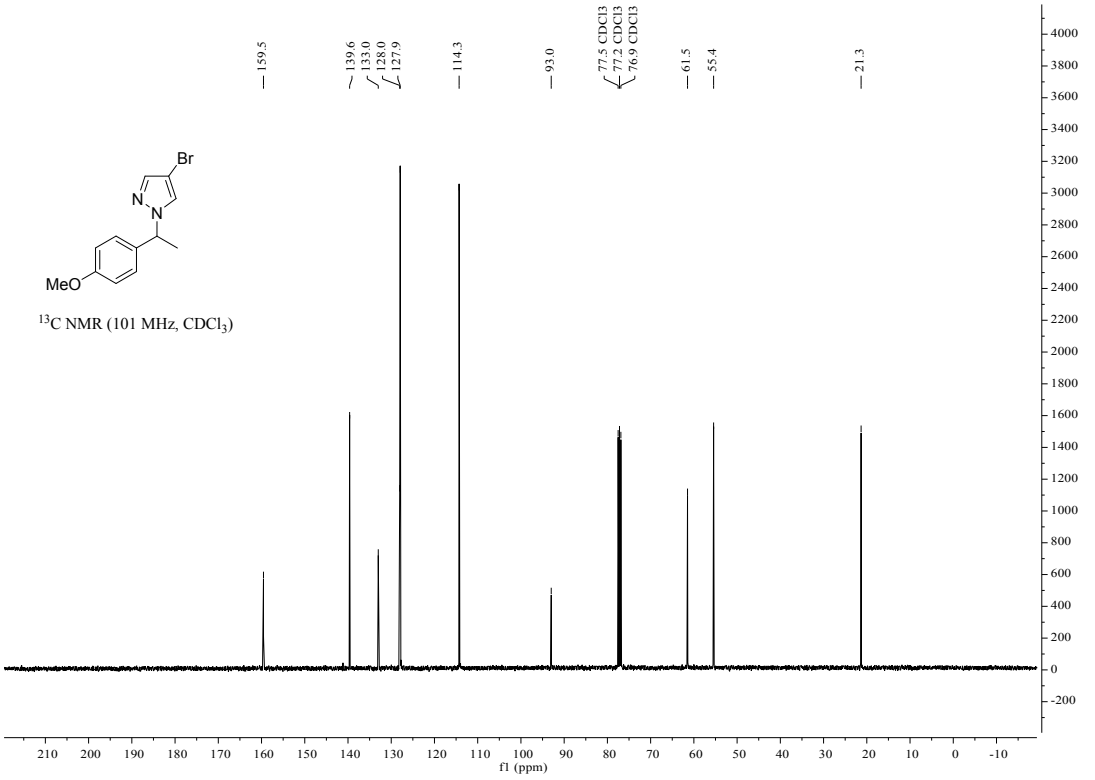


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 30

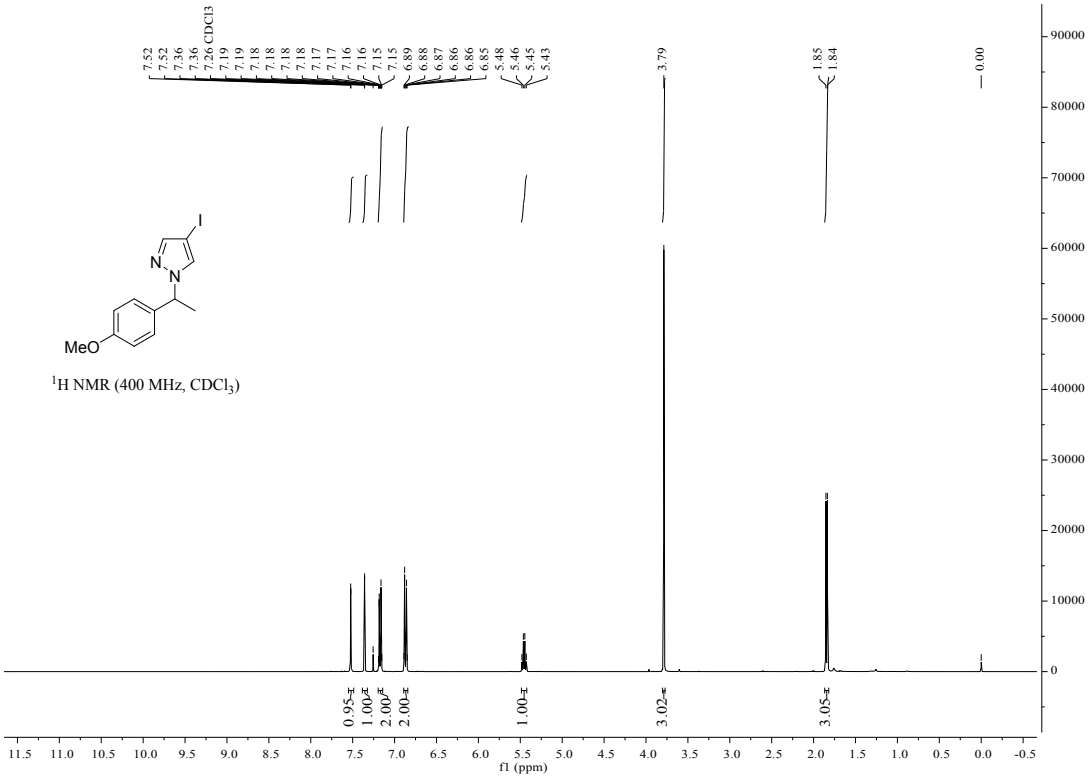


^{1}H NMR (400 MHz, $CDCl_3$)

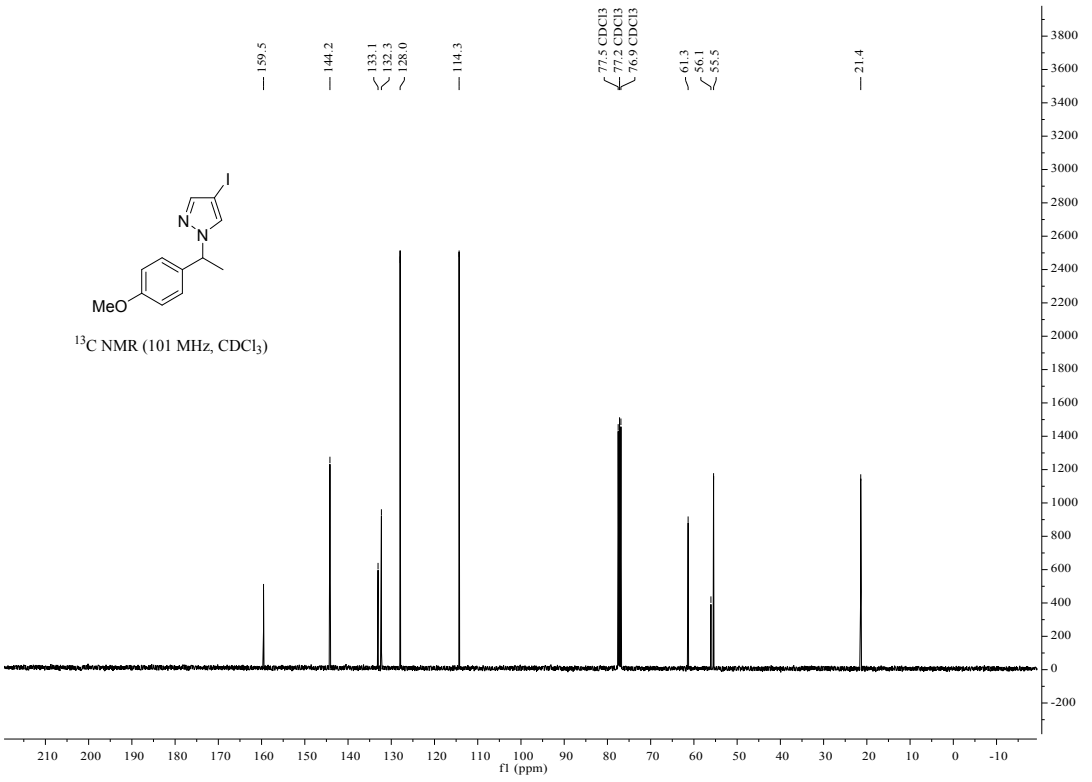


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 31

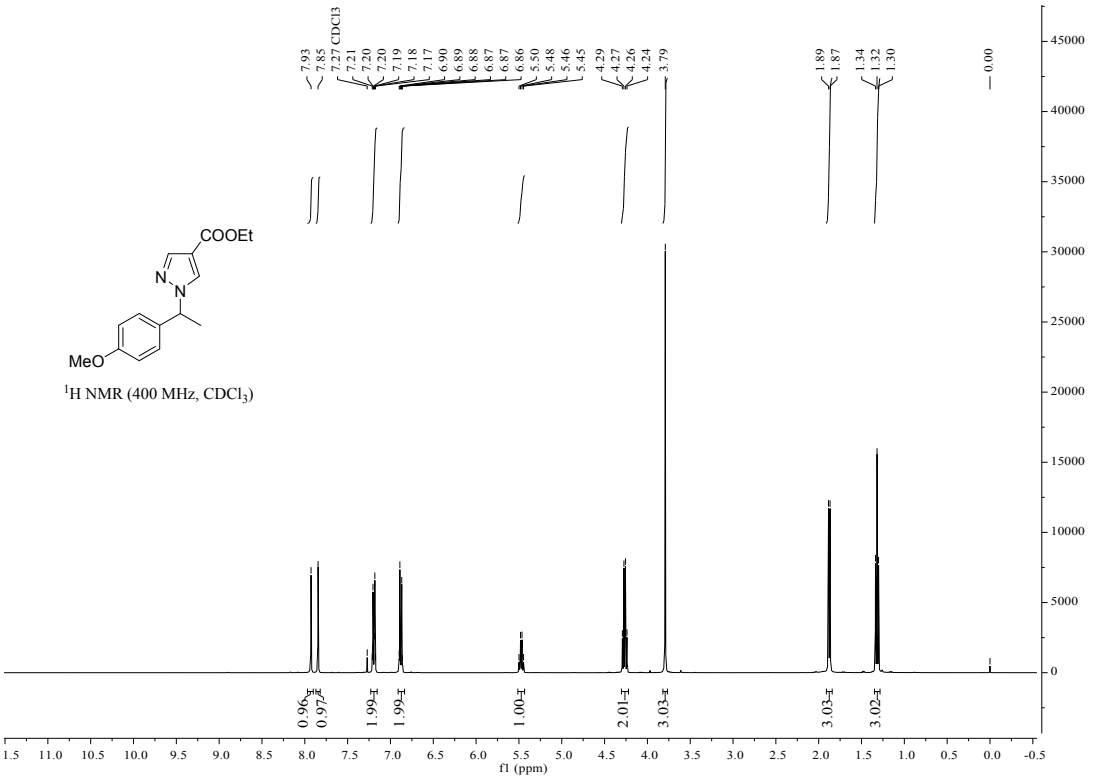


^{1}H NMR (400 MHz, $CDCl_3$)

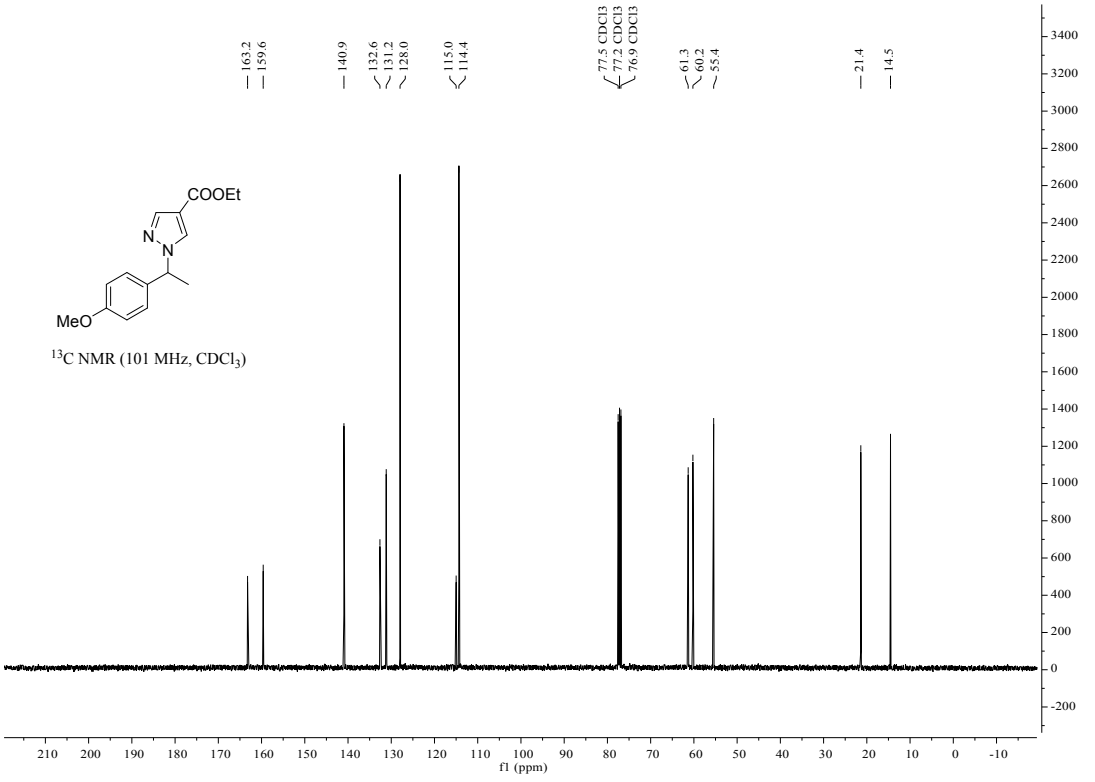


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 32

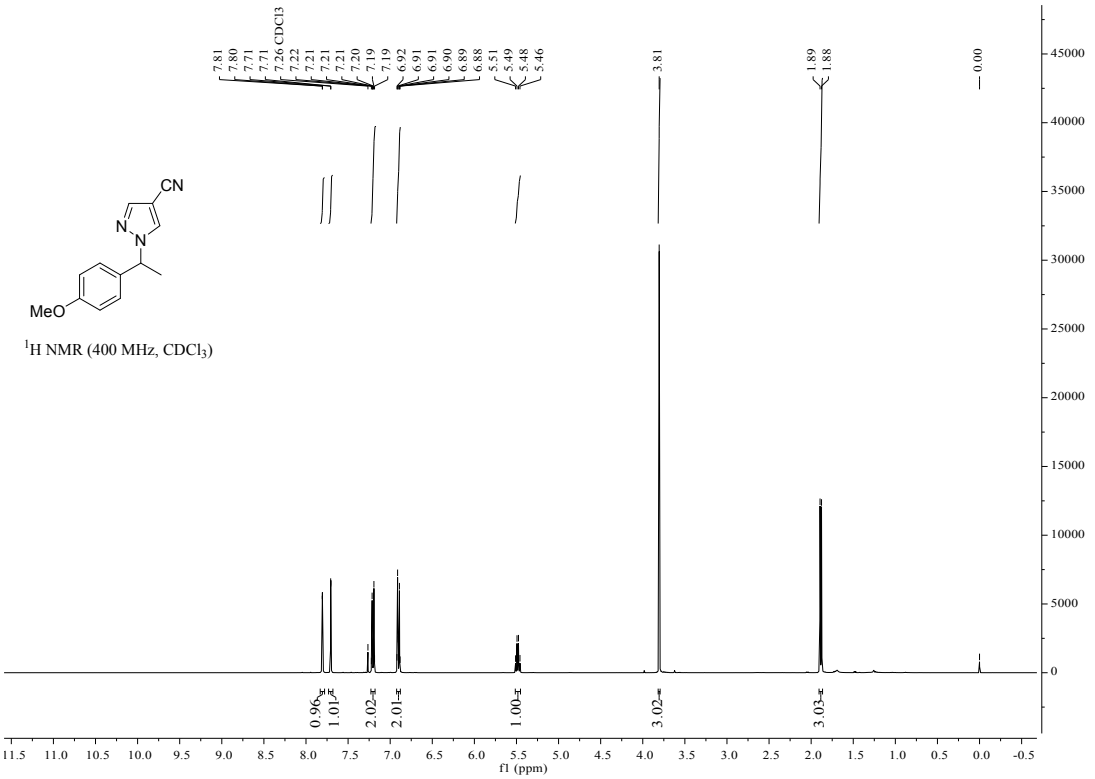


^{1}H NMR (400 MHz, $CDCl_3$)

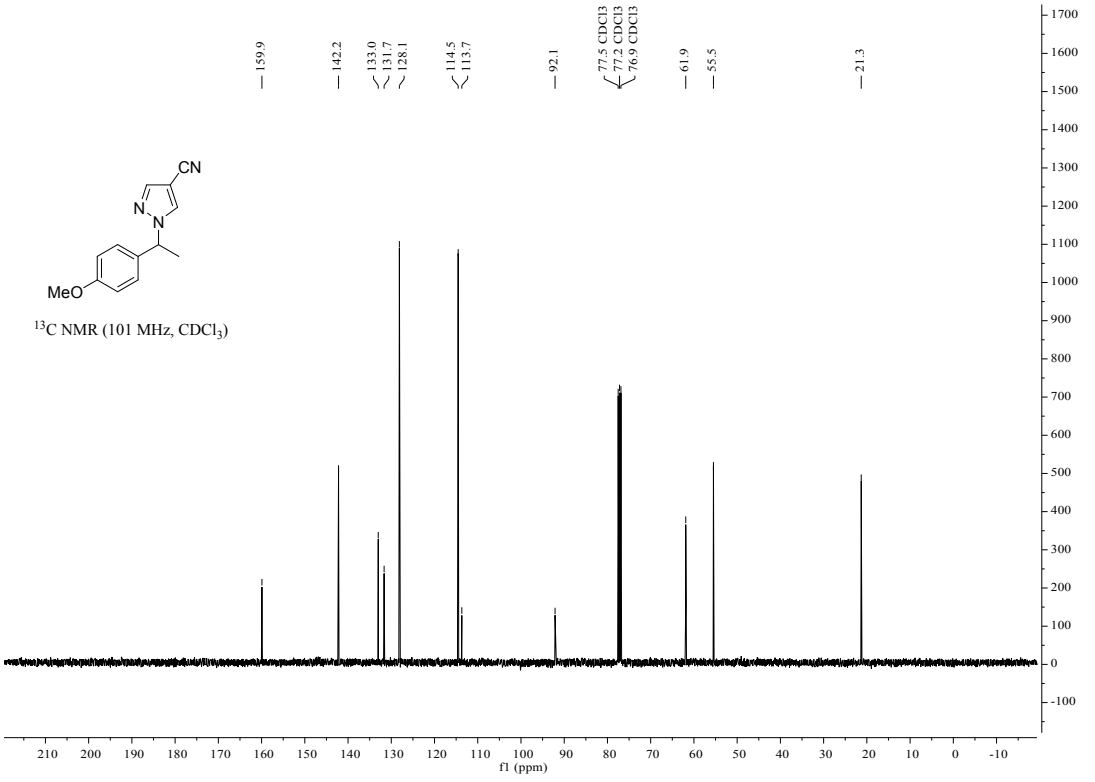


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 33

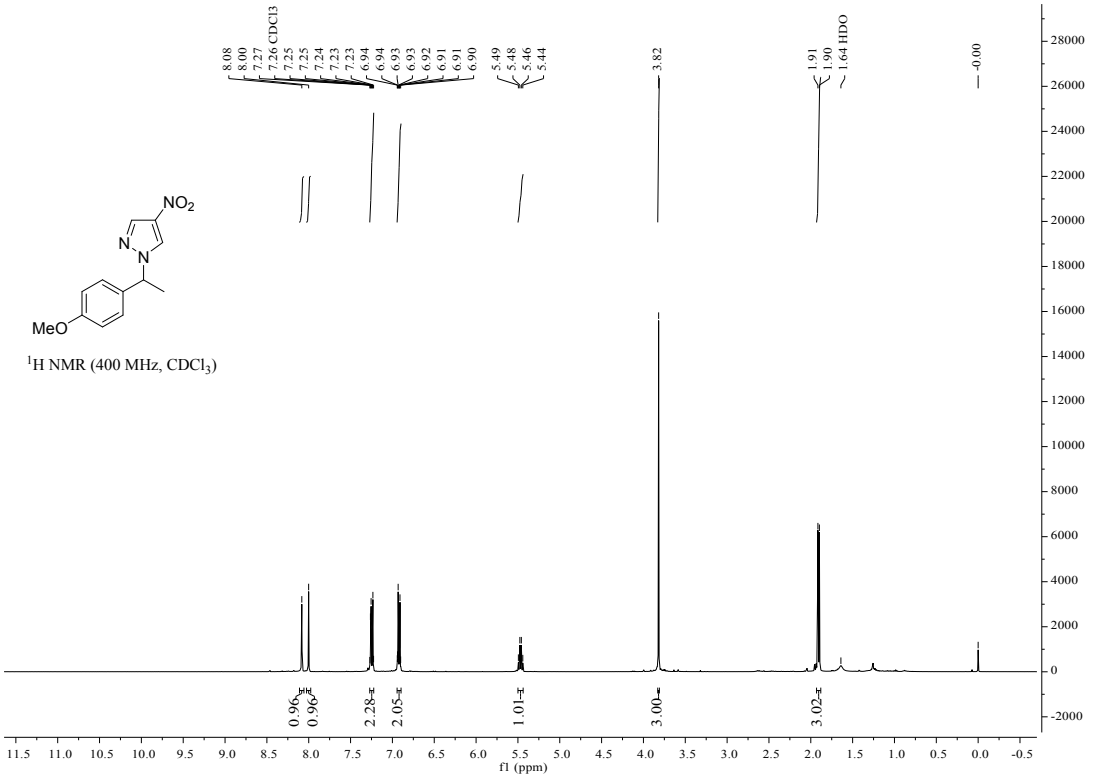


^{1}H NMR (400 MHz, $CDCl_3$)

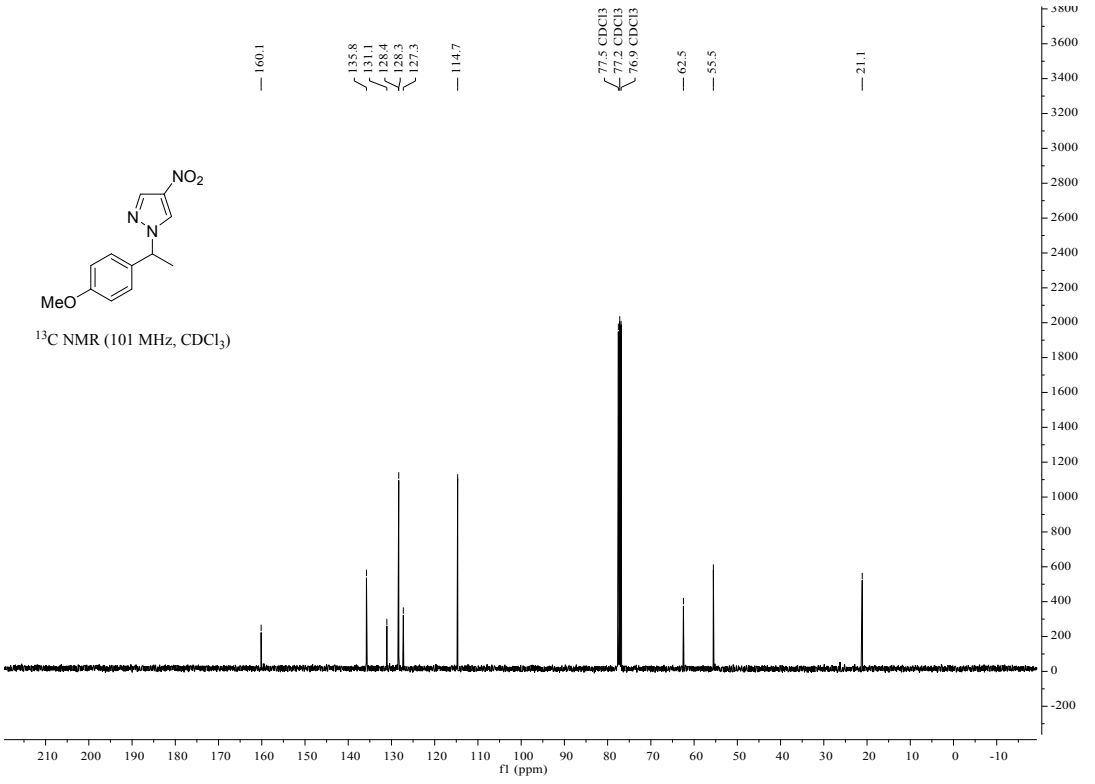


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 34

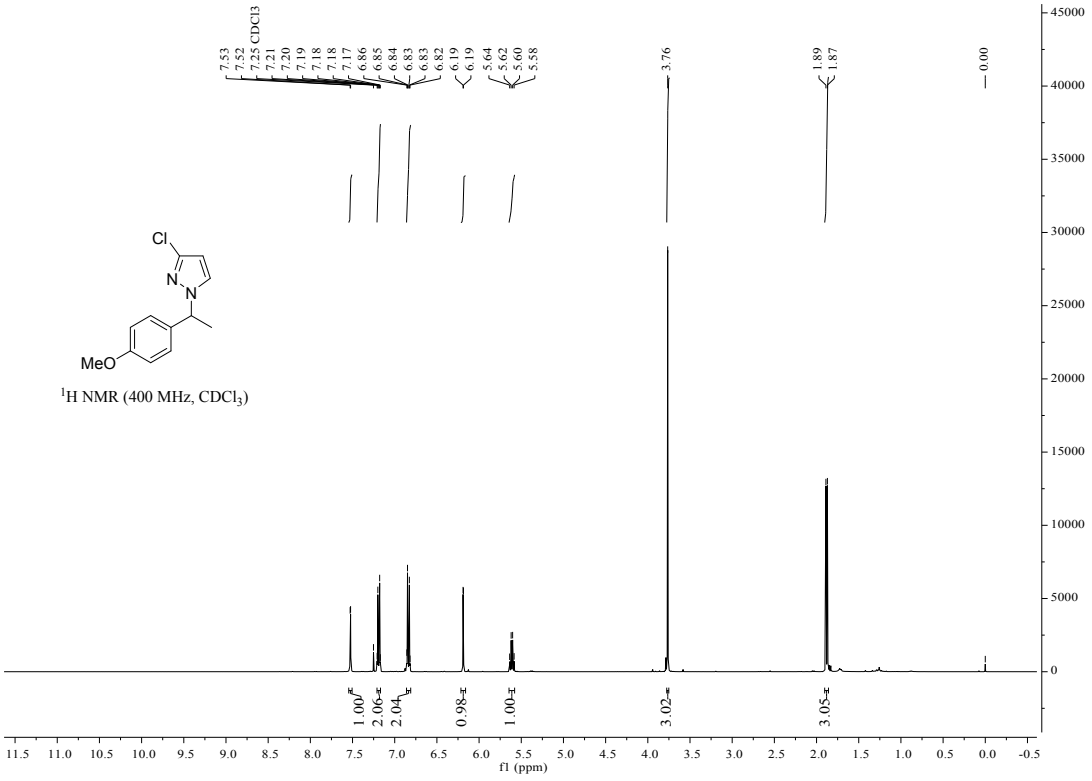


^{1}H NMR (400 MHz, $CDCl_3$)

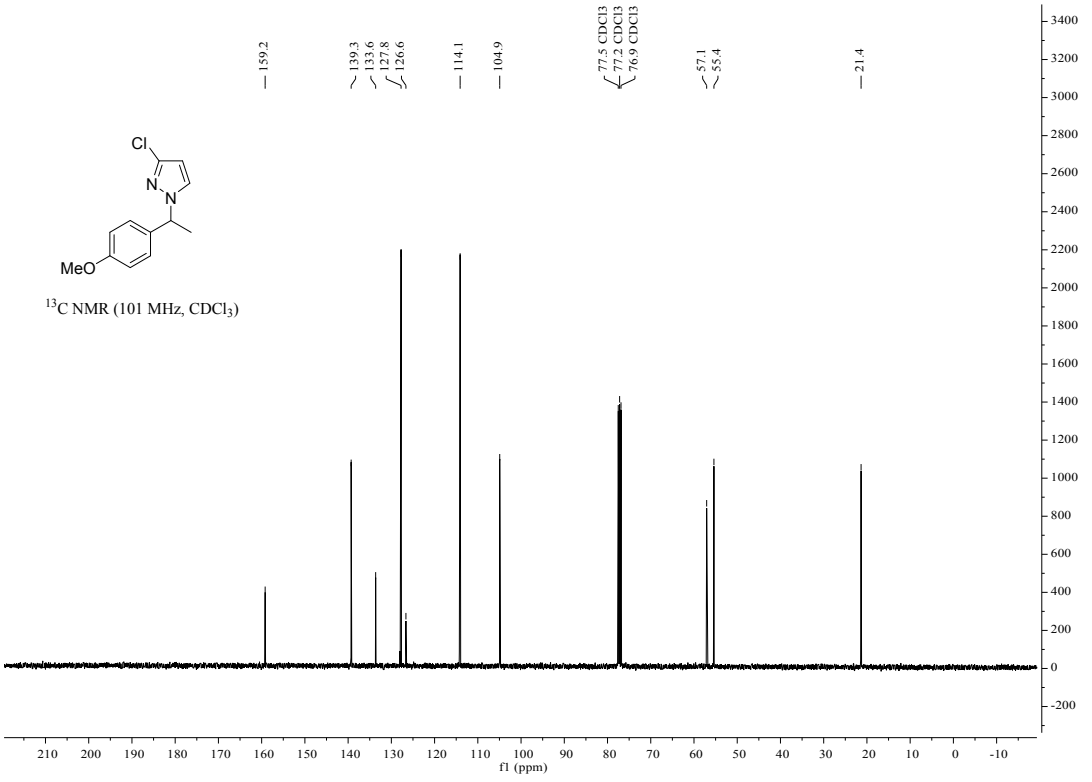


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 35

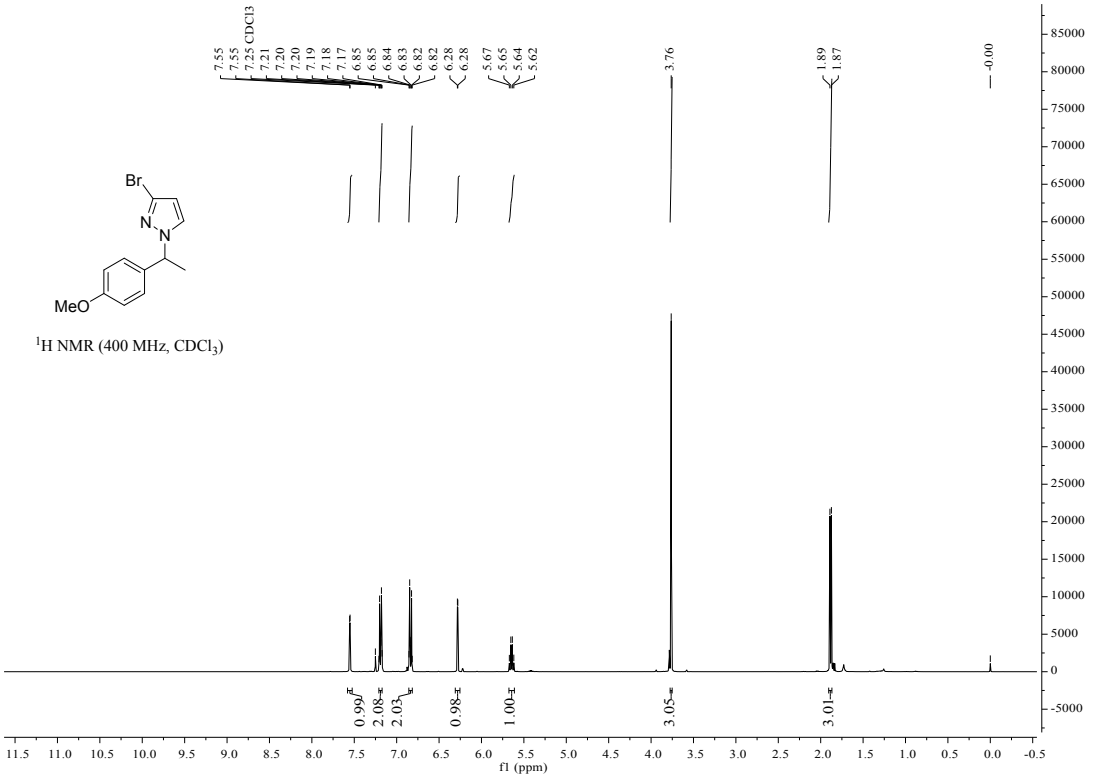


^{1}H NMR (400 MHz, $CDCl_3$)

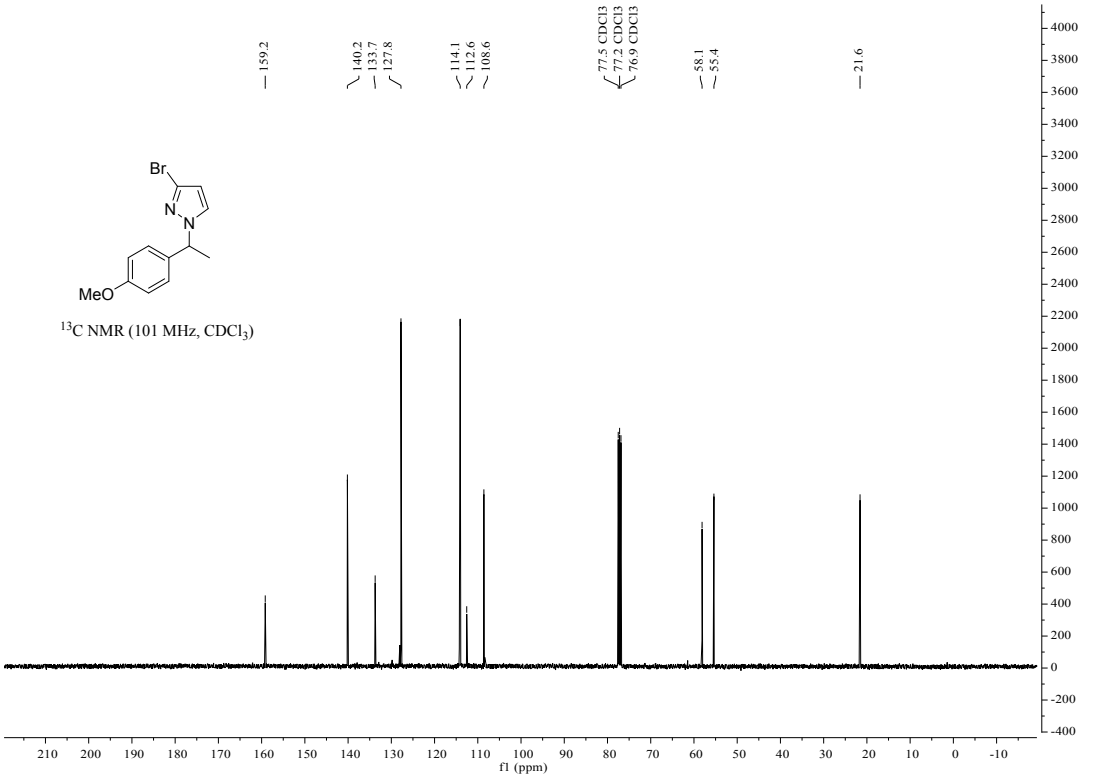


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 36

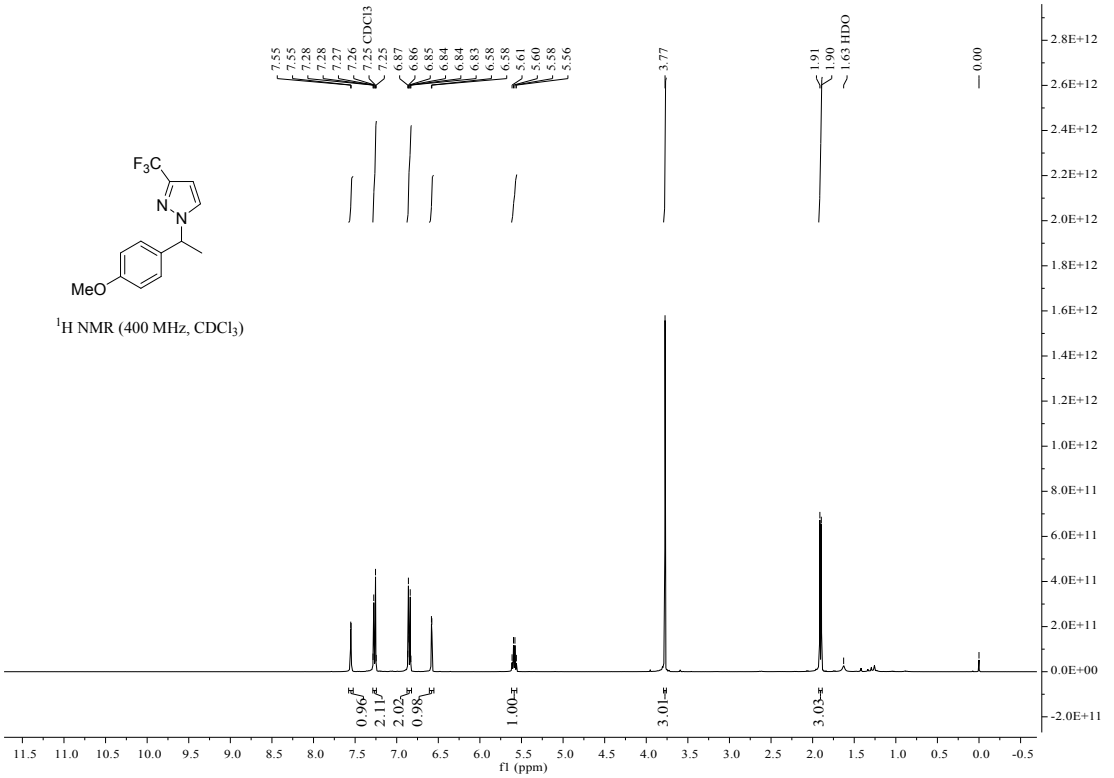


^{1}H NMR (400 MHz, $CDCl_3$)

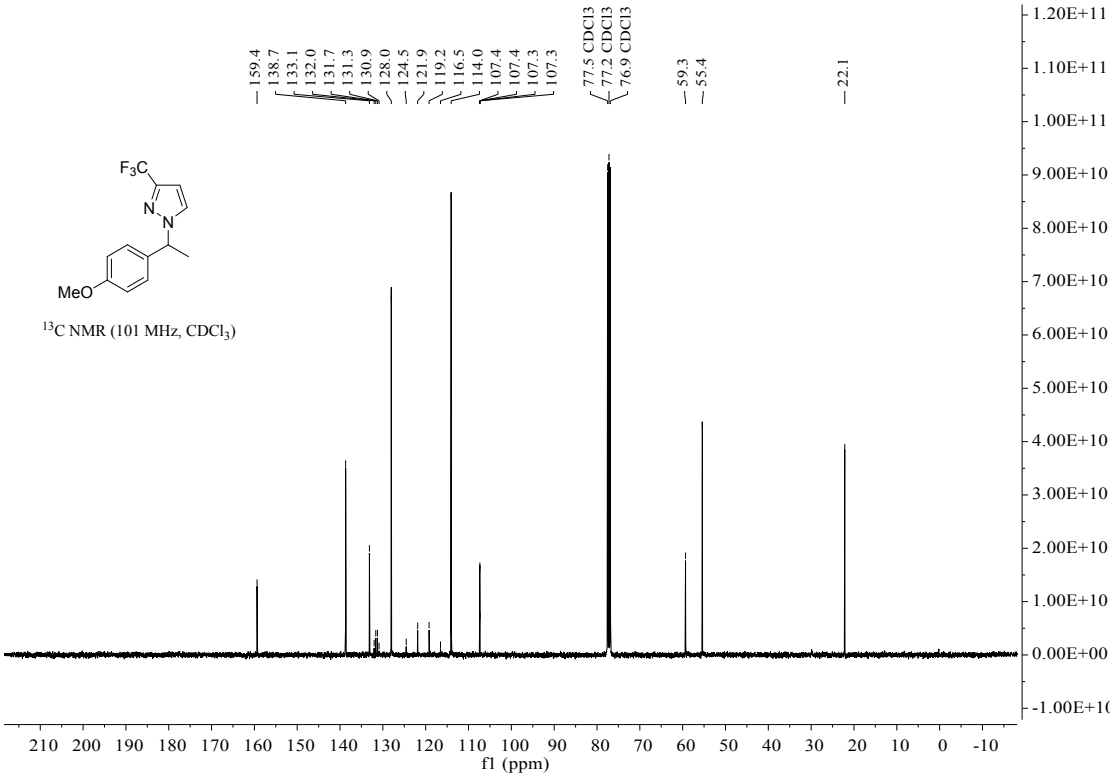


^{13}C NMR (101 MHz, $CDCl_3$)

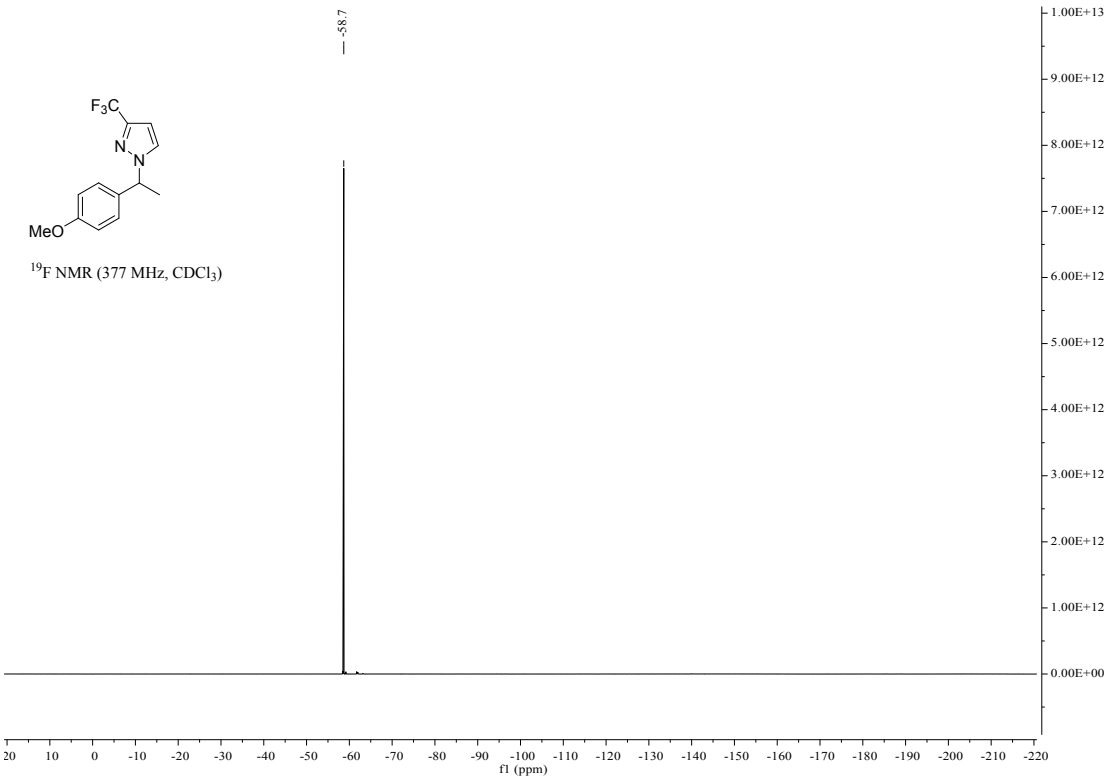
Compound 37



^{1}H NMR (400 MHz, $CDCl_3$)

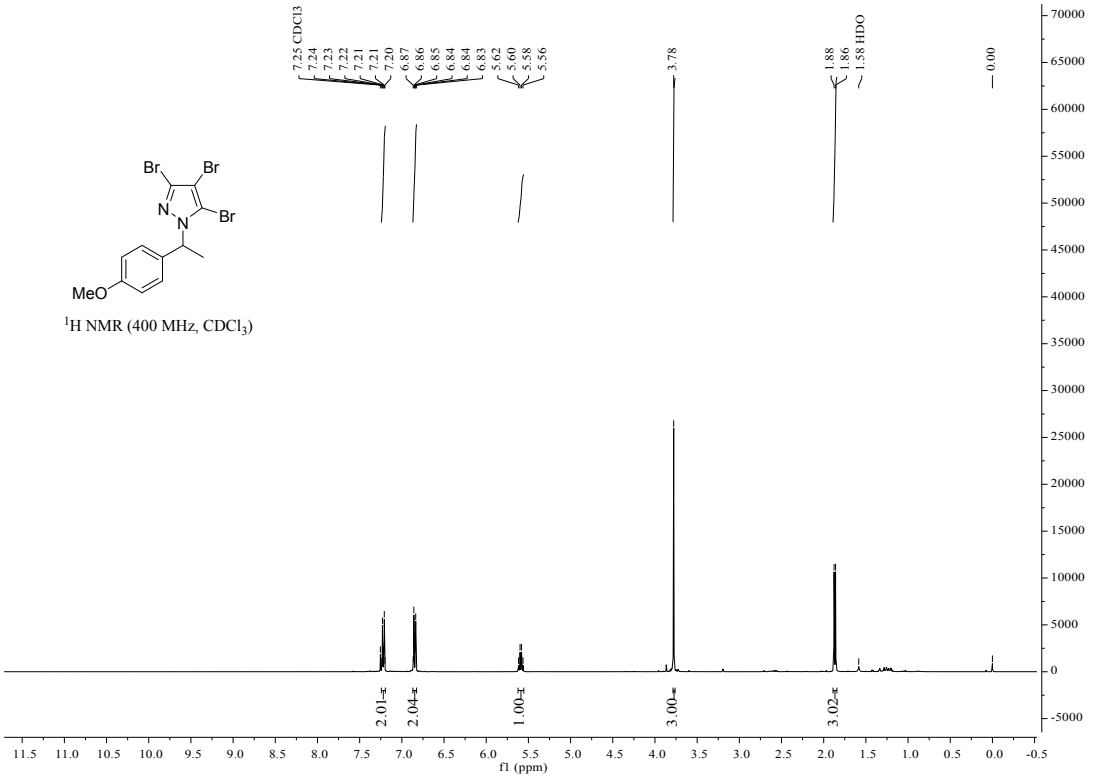


^{13}C NMR (101 MHz, $CDCl_3$)

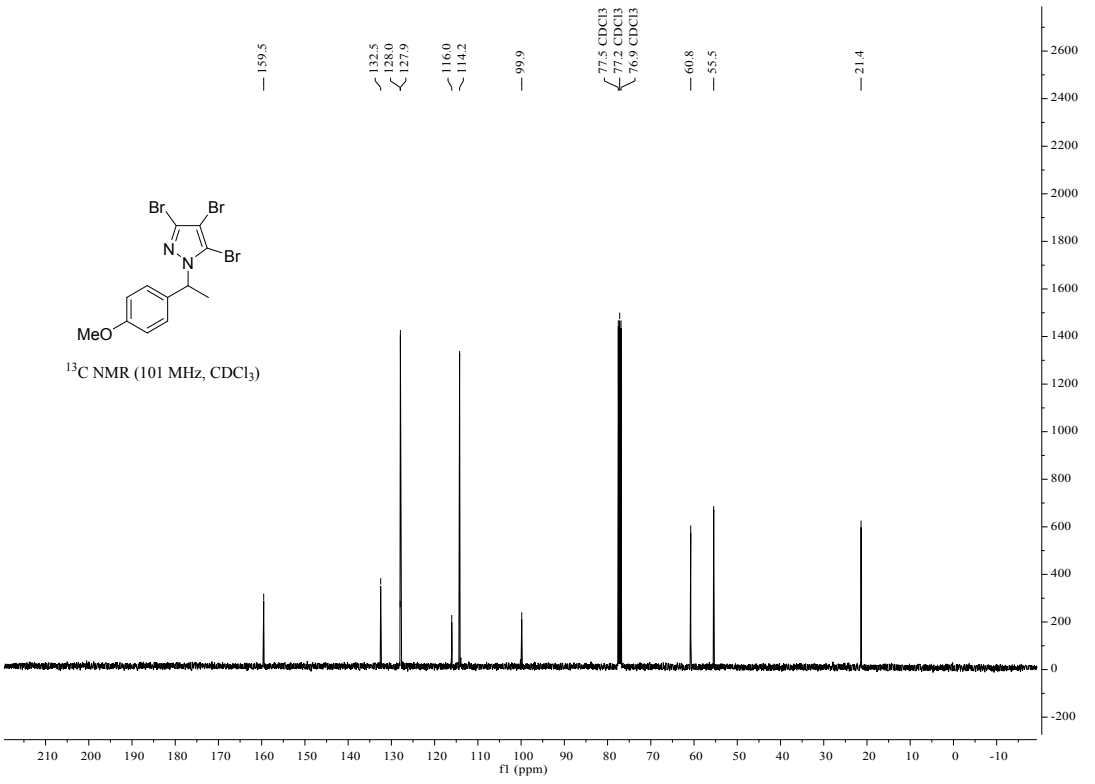


^{19}F NMR (377 MHz, $CDCl_3$)

Compound 38

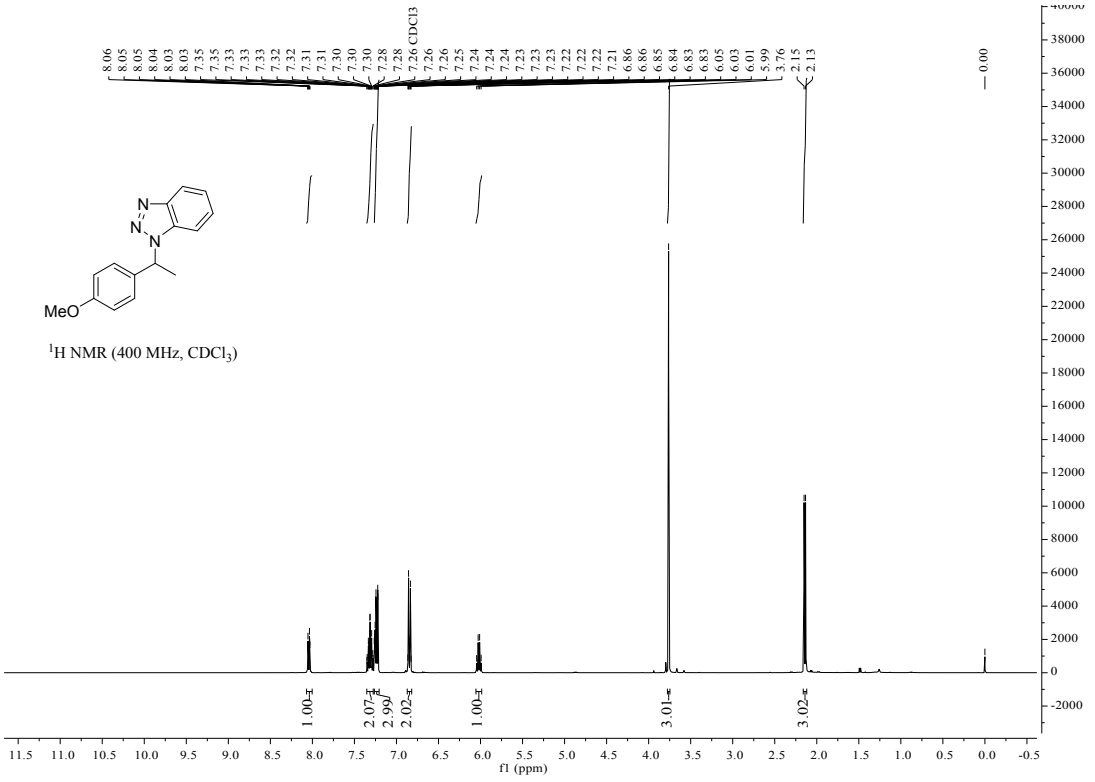


^{1}H NMR (400 MHz, $CDCl_3$)

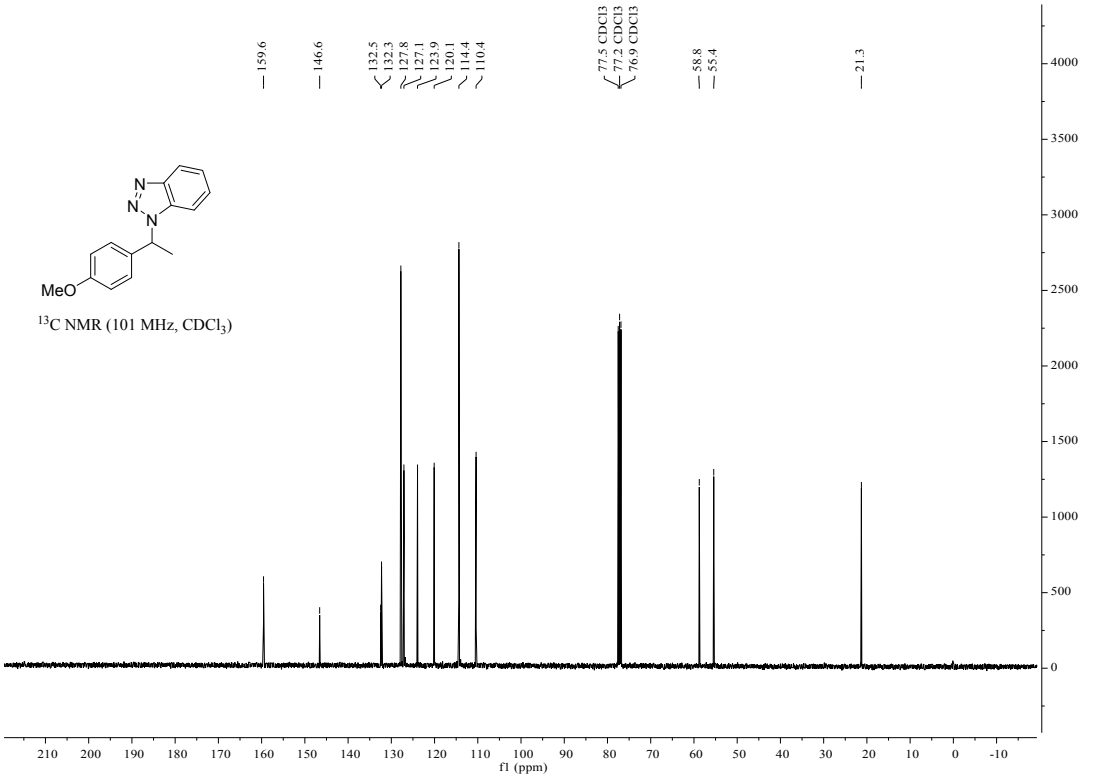


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 39

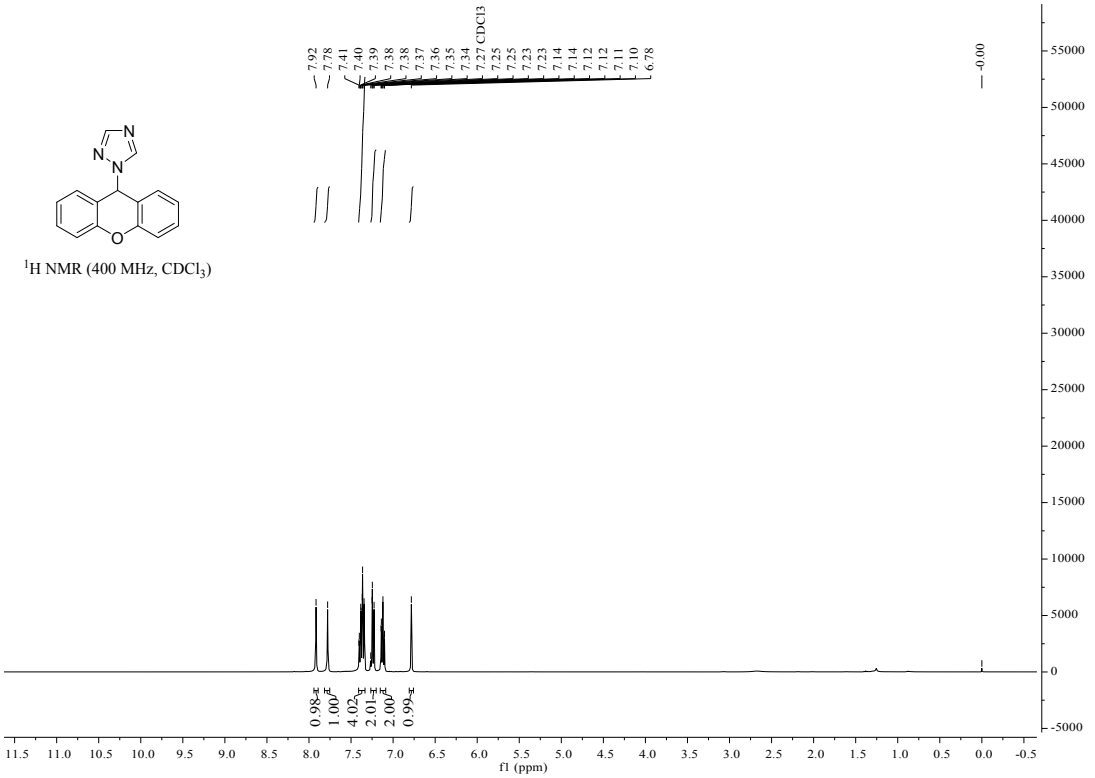


^{1}H NMR (400 MHz, $CDCl_3$)

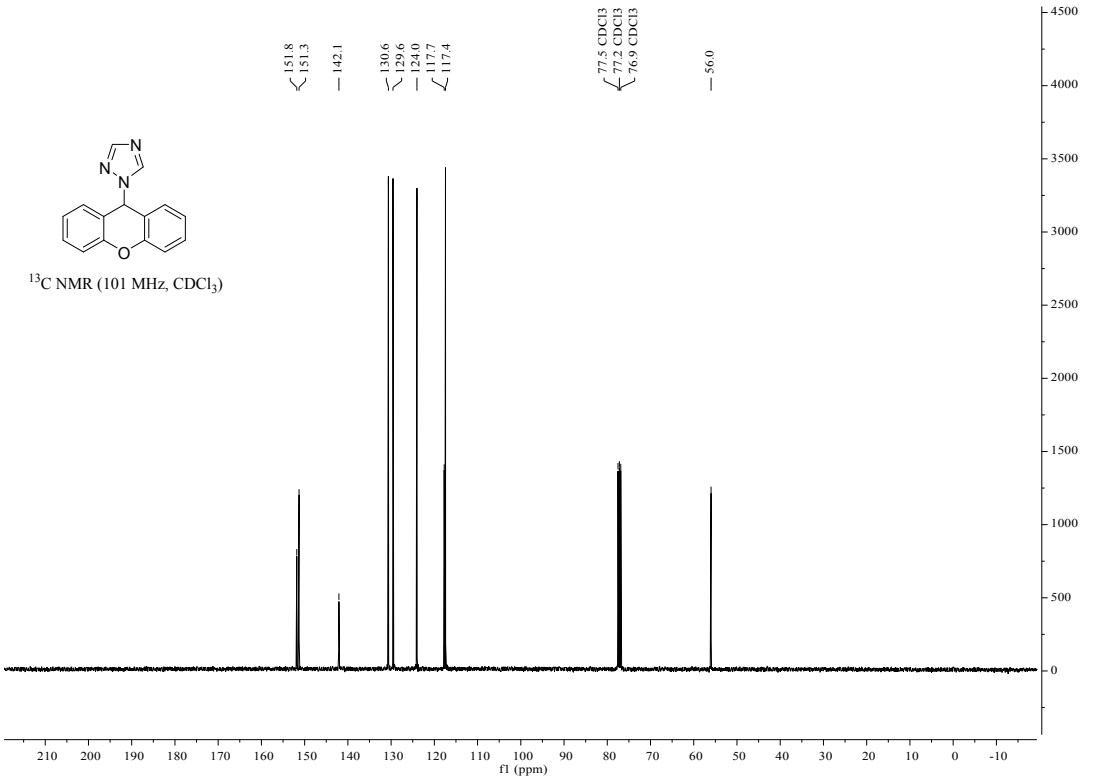


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 40

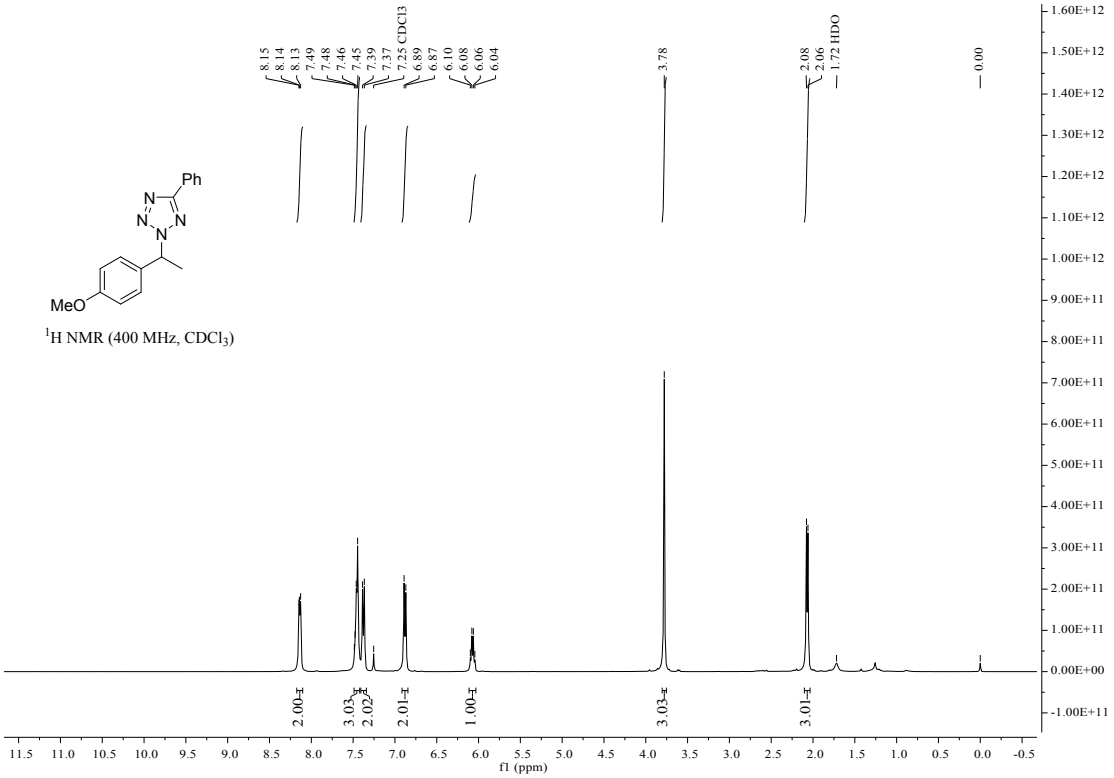


^{1}H NMR (400 MHz, $CDCl_3$)

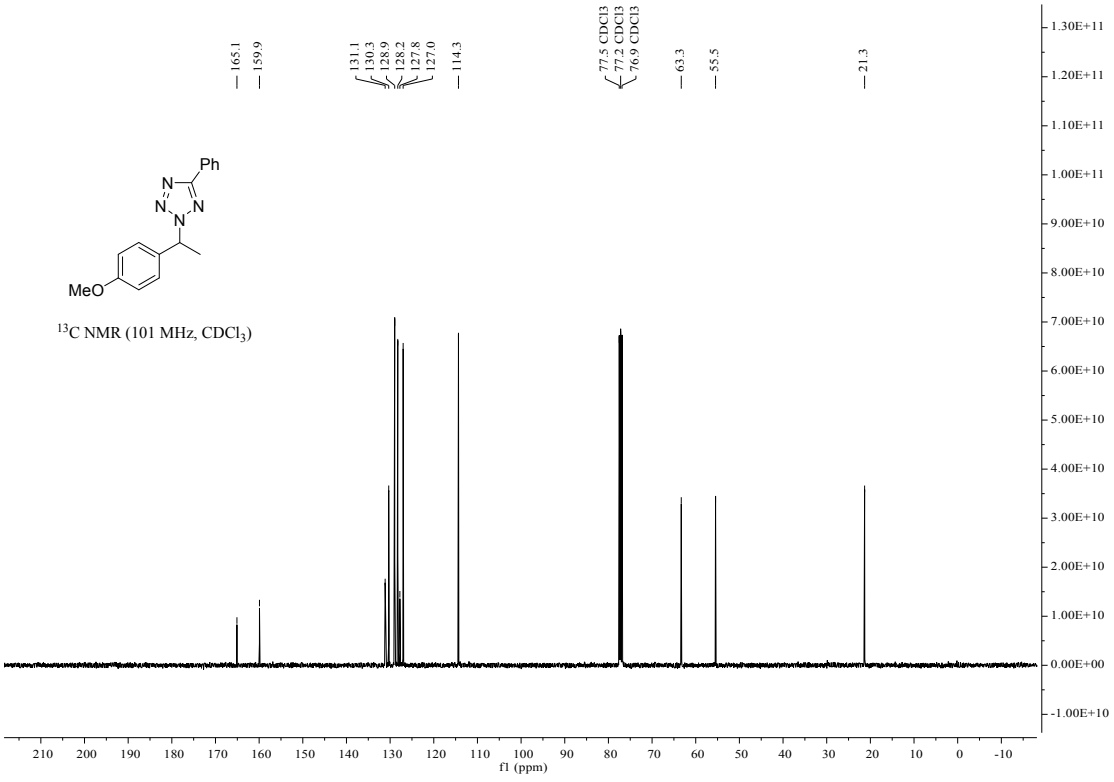


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 41

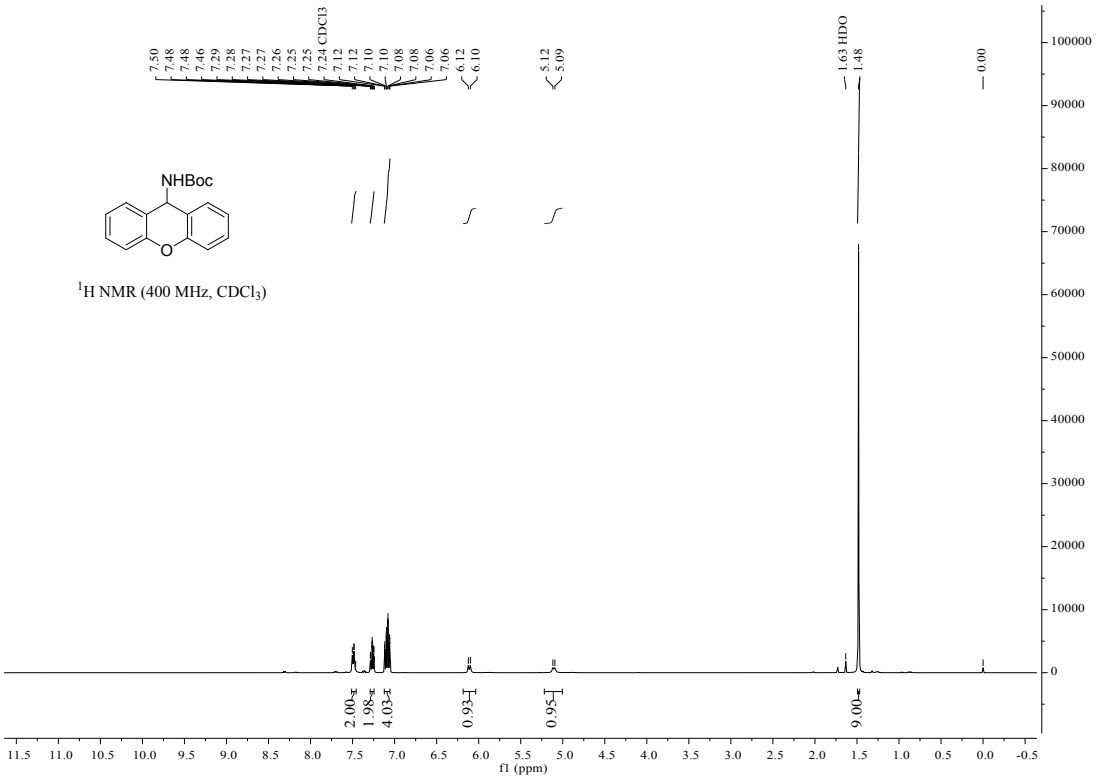


^{1}H NMR (400 MHz, $CDCl_3$)

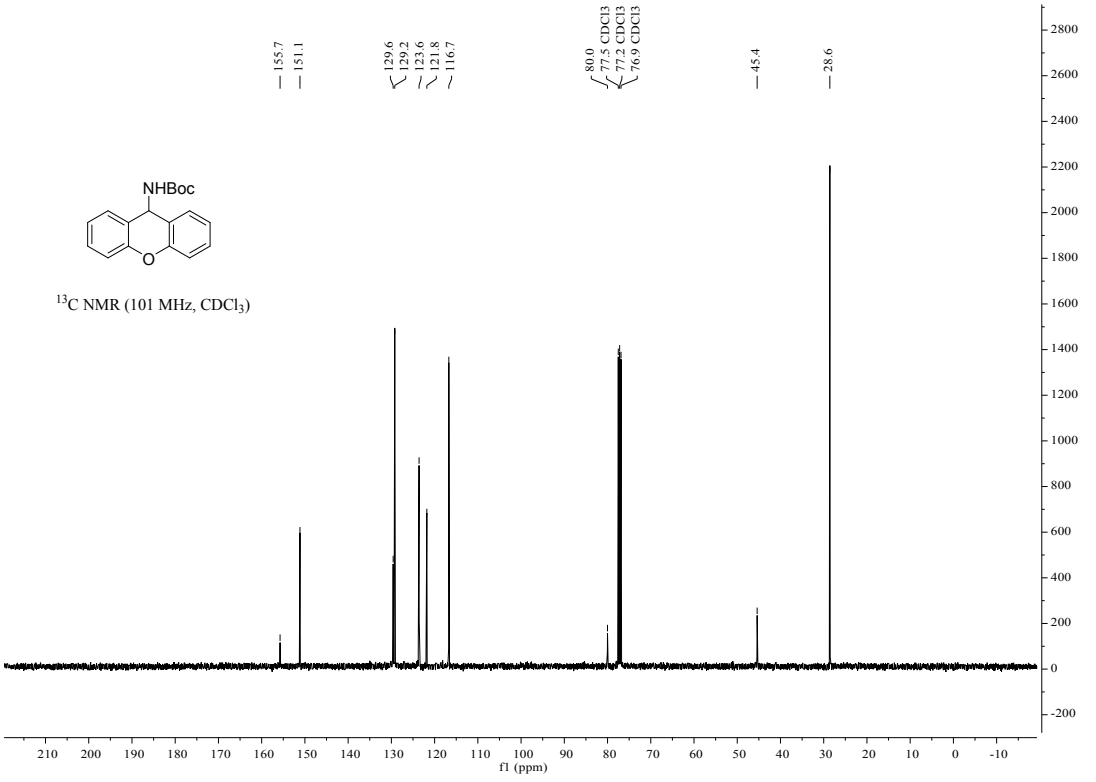


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 42

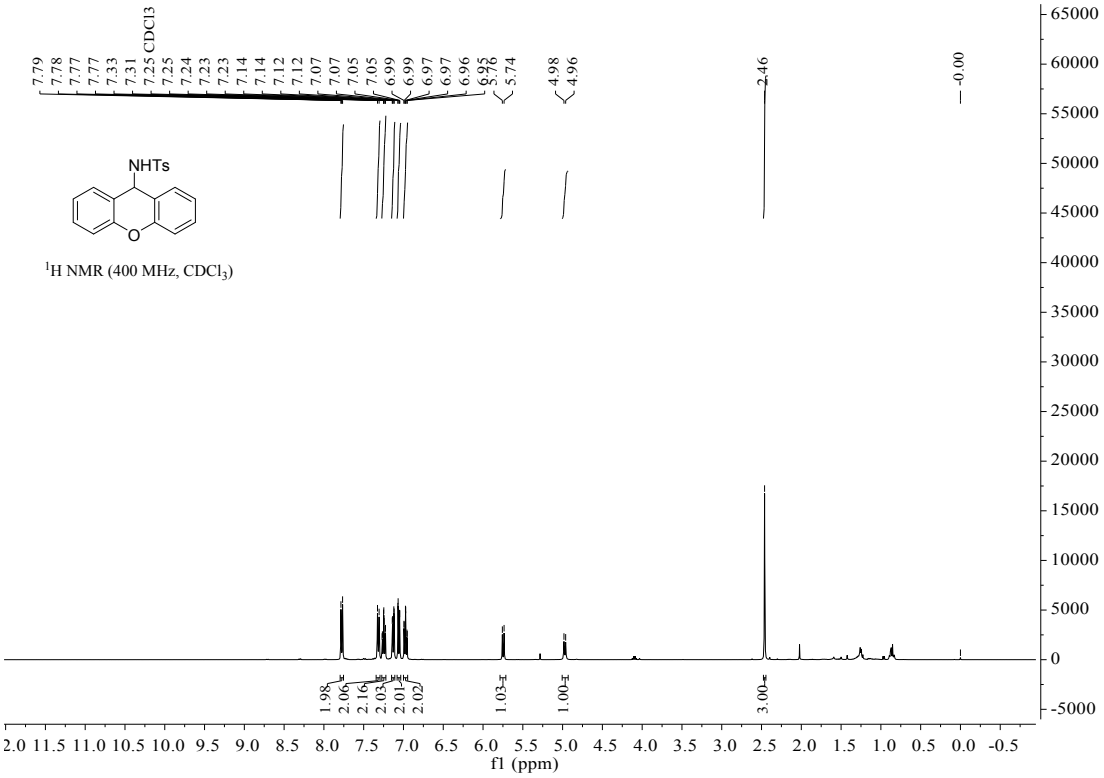


^{1}H NMR (400 MHz, $CDCl_3$)

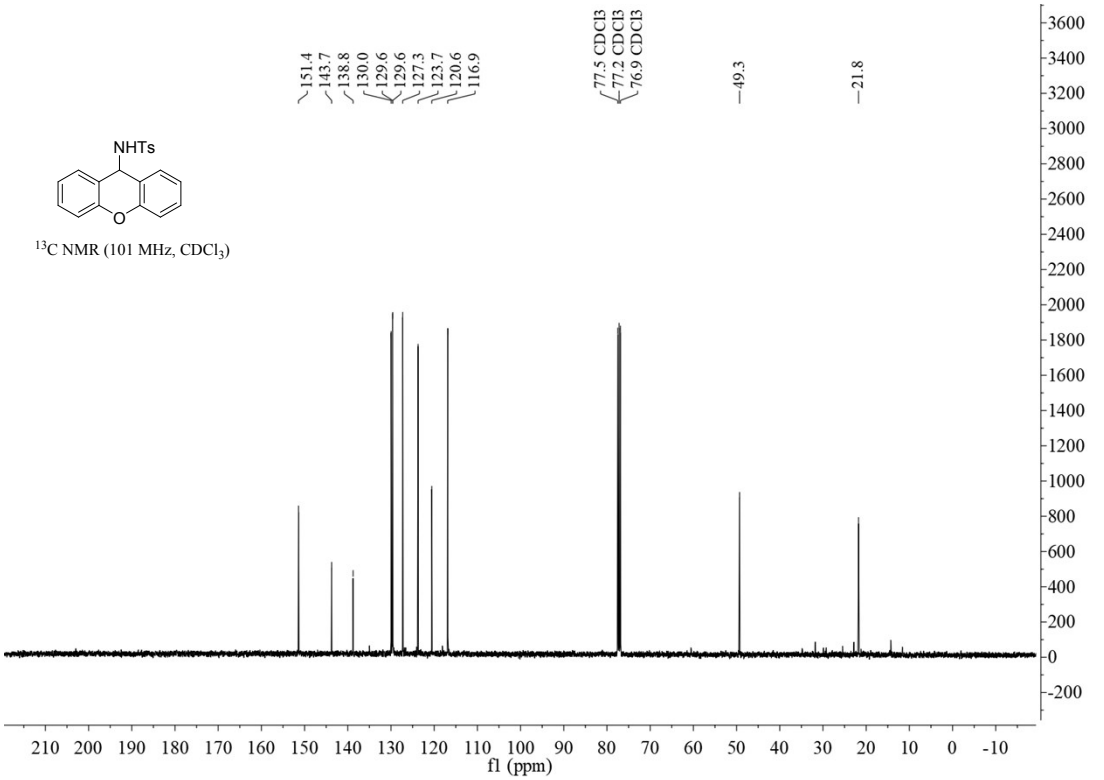


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 43

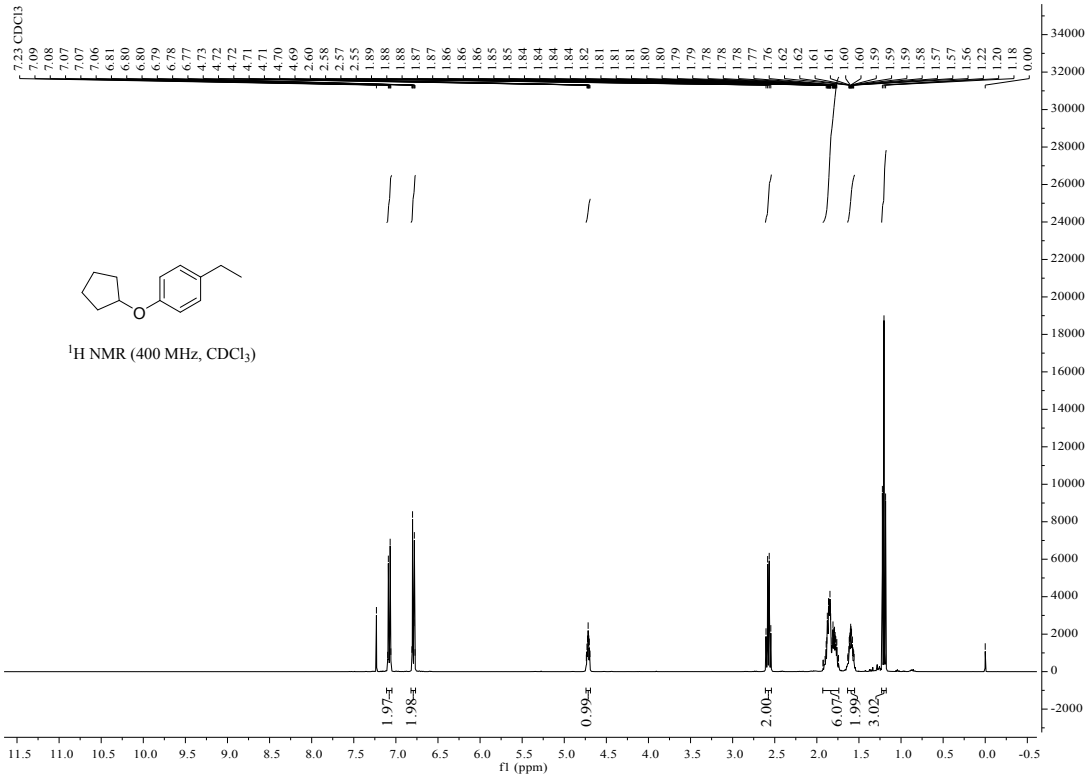


^{1}H NMR (400 MHz, $CDCl_3$)

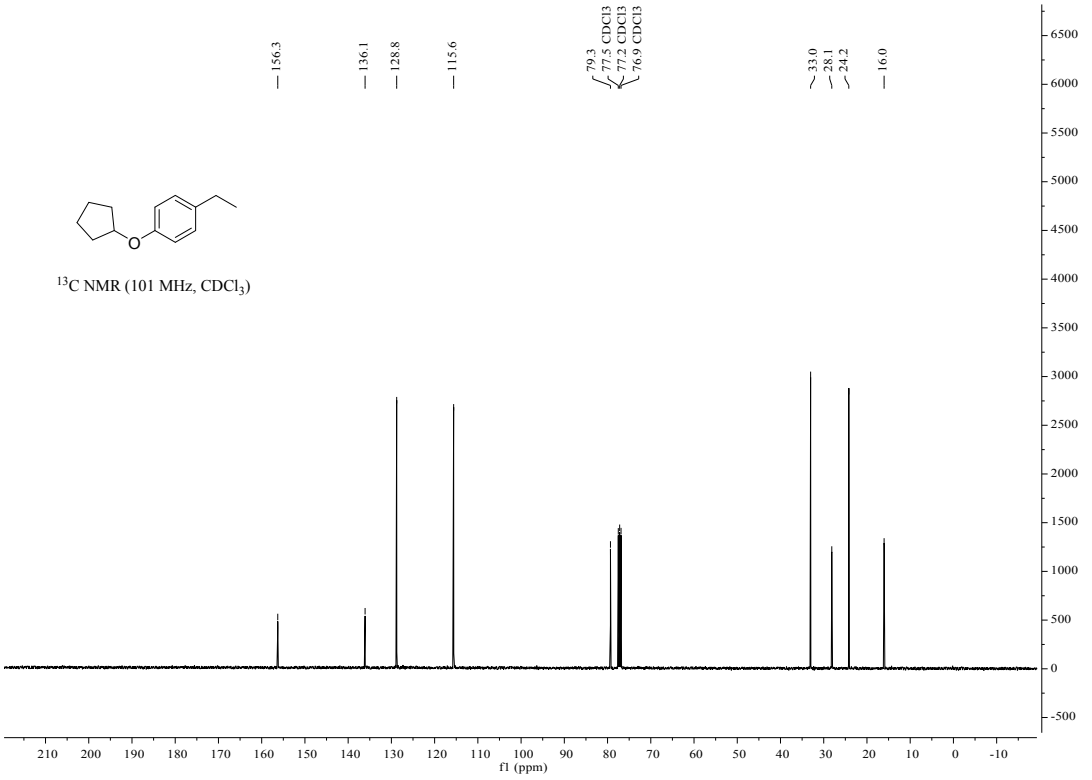


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S1

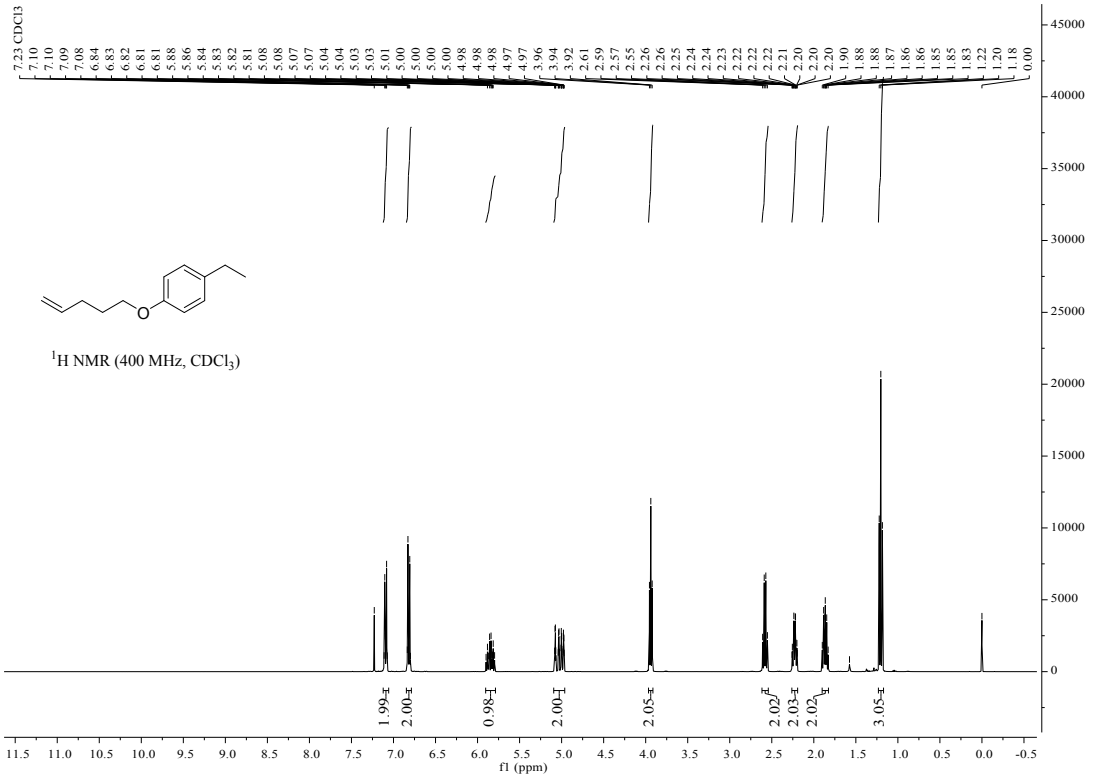


^{1}H NMR (400 MHz, $CDCl_3$)

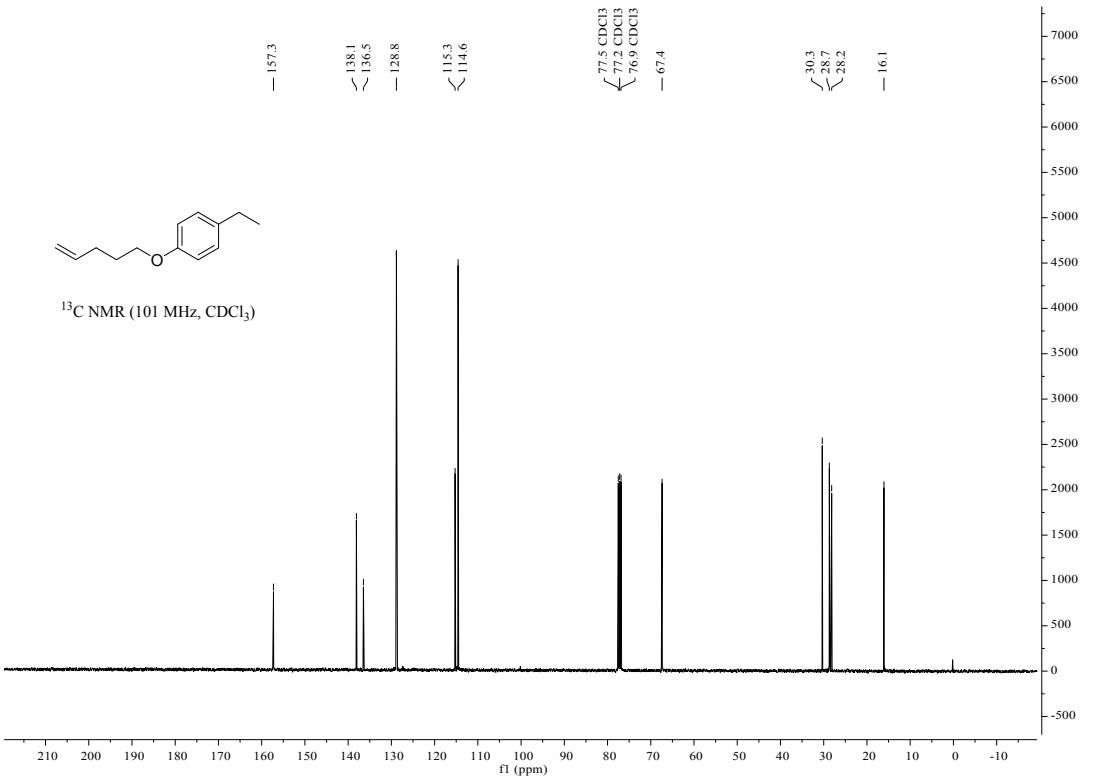


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S2

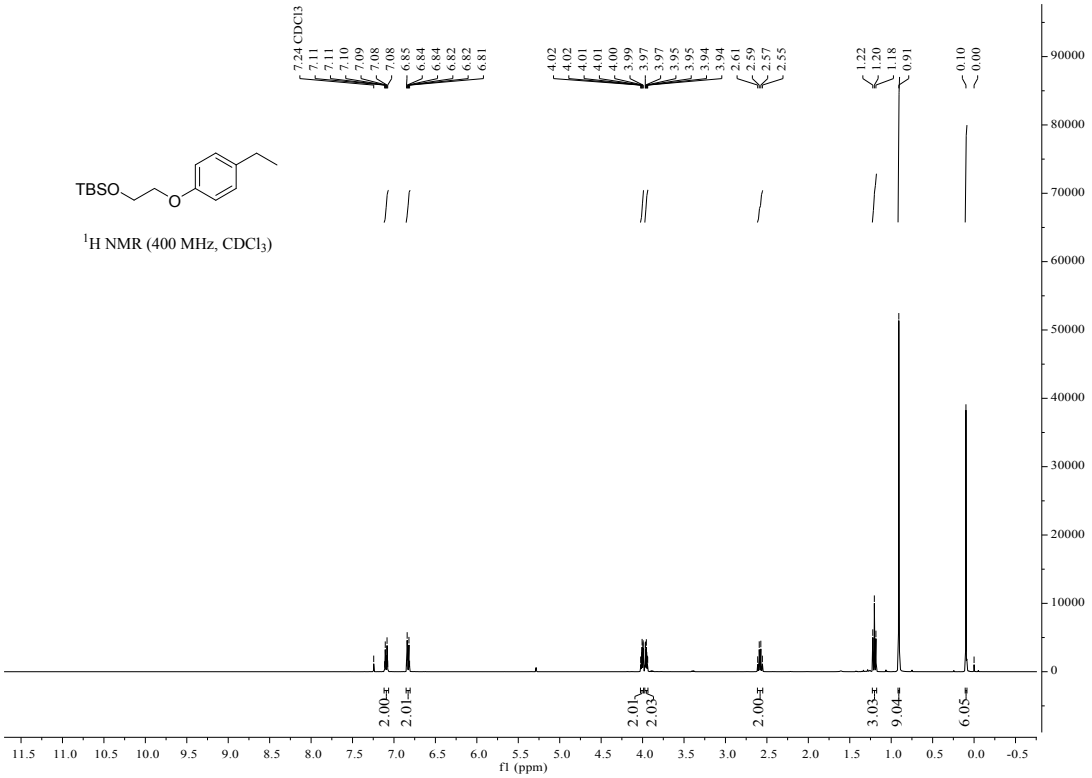


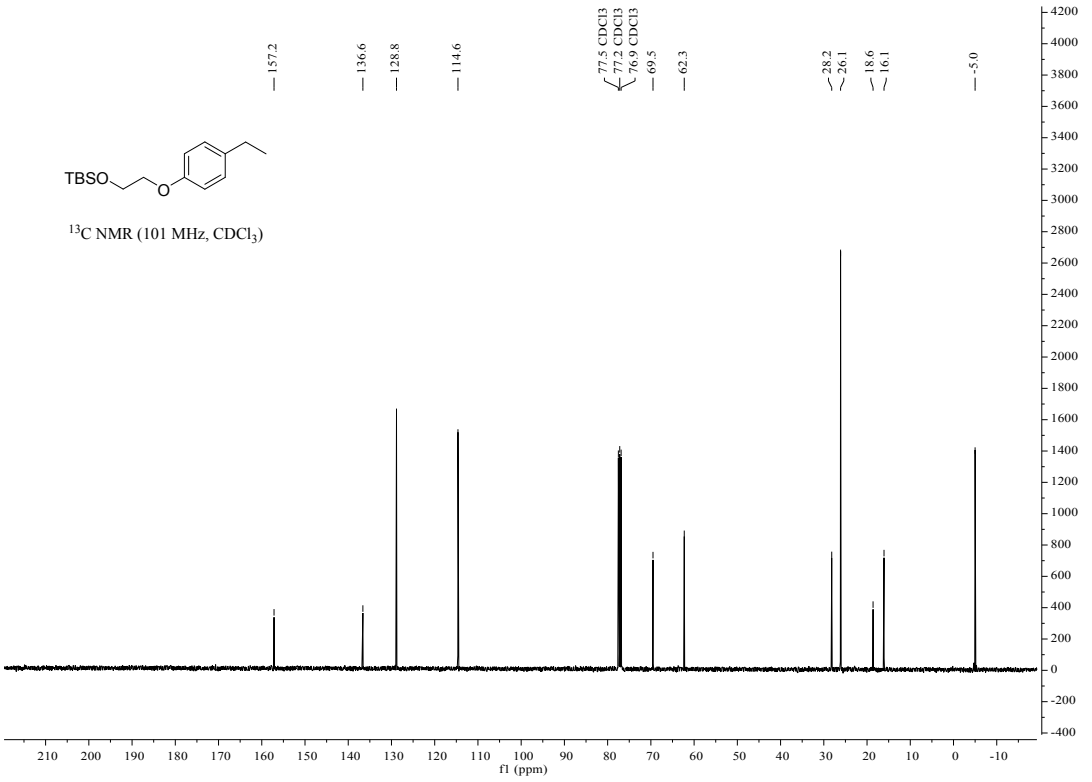
^{1}H NMR (400 MHz, $CDCl_3$)



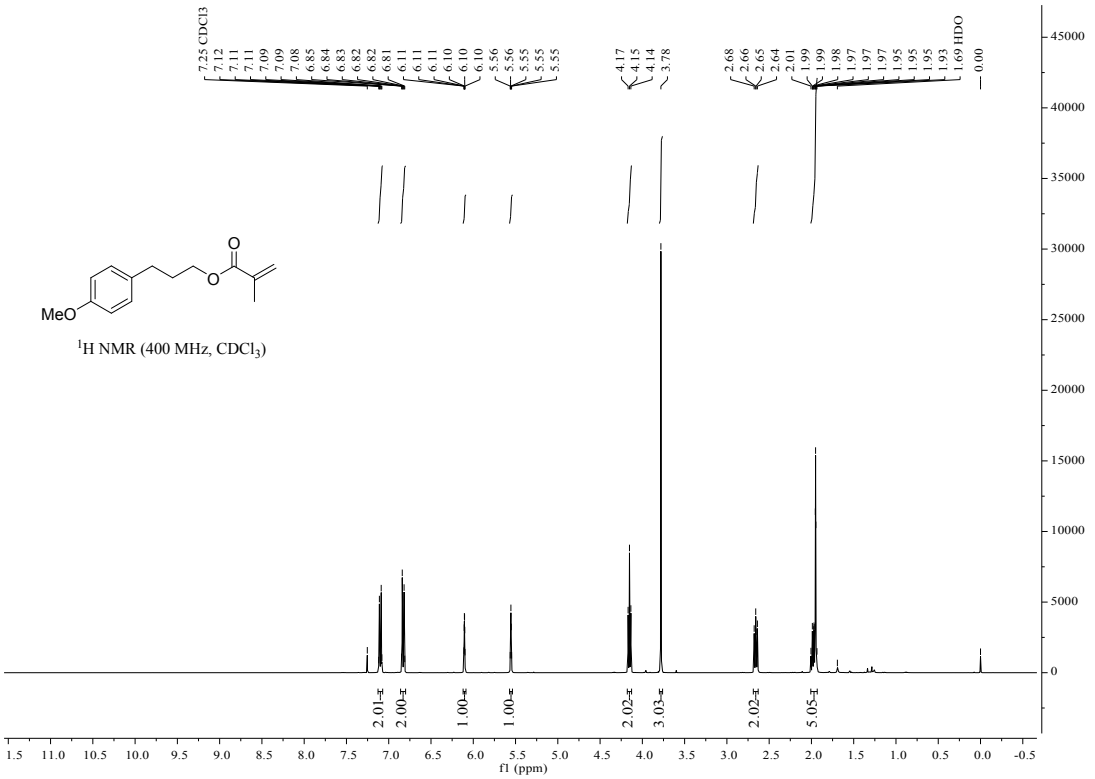
^{13}C NMR (101 MHz, $CDCl_3$)

Compound S3

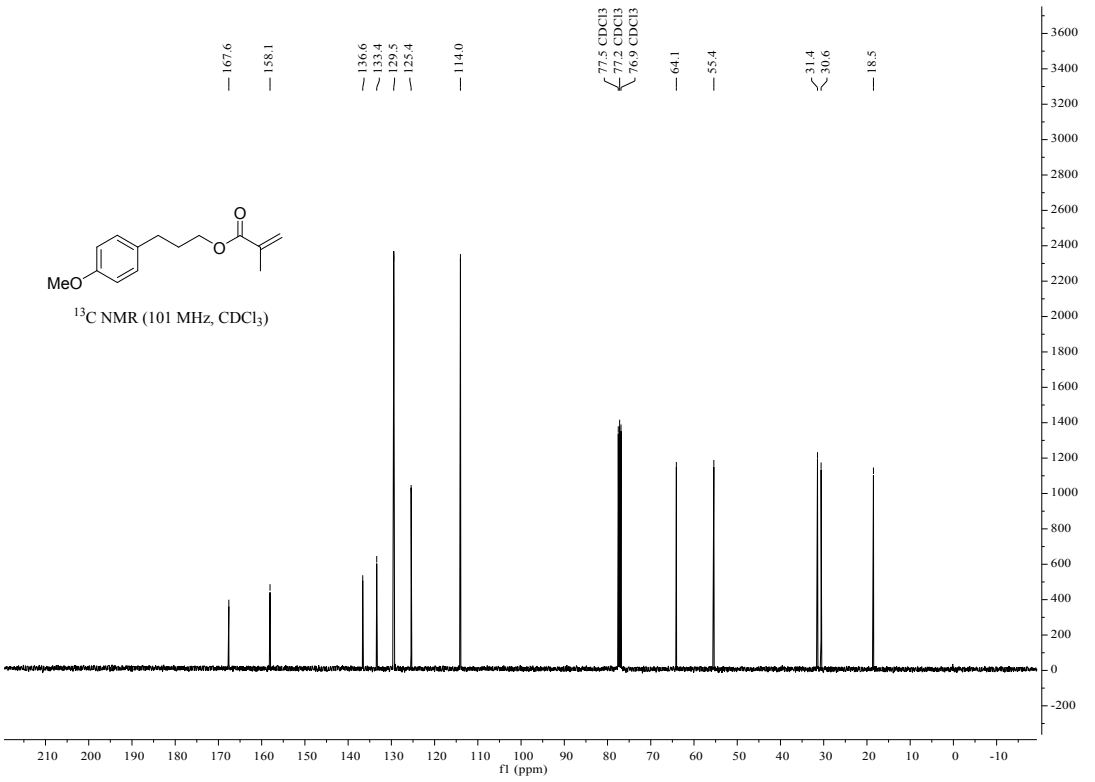

TBSO
O
^{1}H NMR (400 MHz, $CDCl_3$)
7.24 CDCl3
7.11
7.10
7.09
7.08
6.85
6.84
6.82
6.81
4.02
4.01
4.00
3.99
3.97
3.95
3.94
2.61
2.59
2.57
2.55
1.22
1.20
1.18
0.91
0.10
0.00
2.00
2.01
2.01
2.03
2.00
3.03
9.04
6.05
f1 (ppm)


TBSO
O
^{13}C NMR (101 MHz, $CDCl_3$)
157.2
136.6
128.8
114.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
69.5
62.3
28.2
26.1
18.6
16.1
-5.0
f1 (ppm)

Compound S4

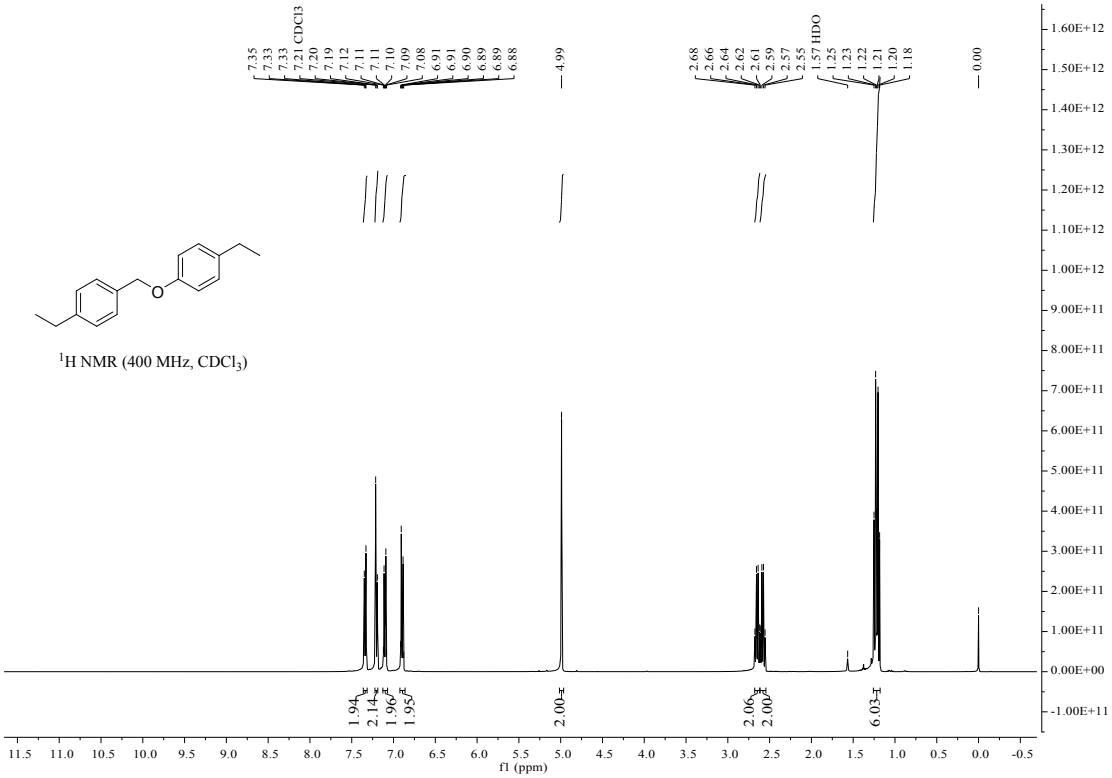


^{1}H NMR (400 MHz, $CDCl_3$)

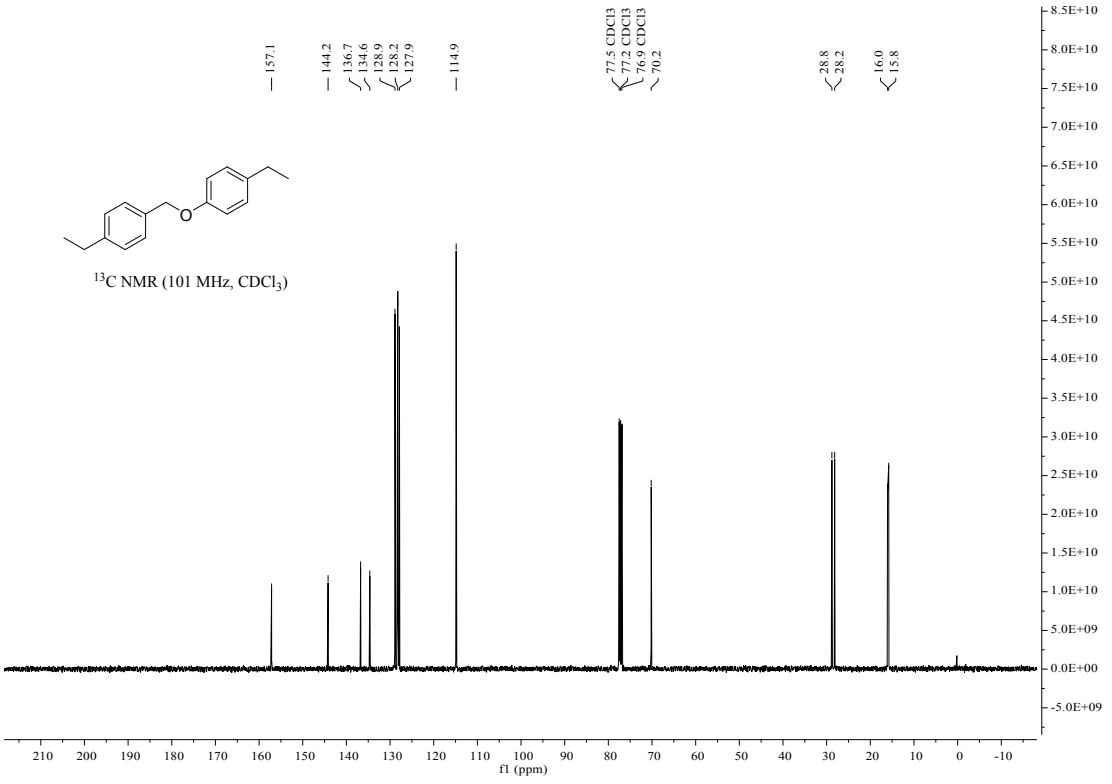


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S5

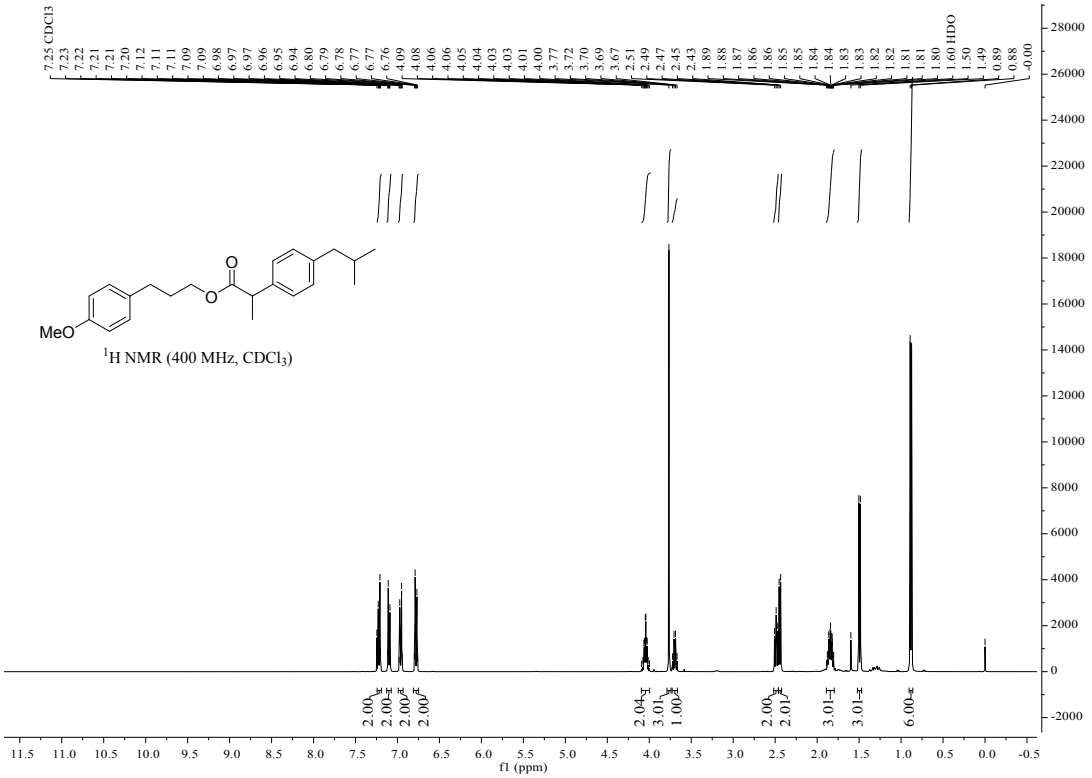


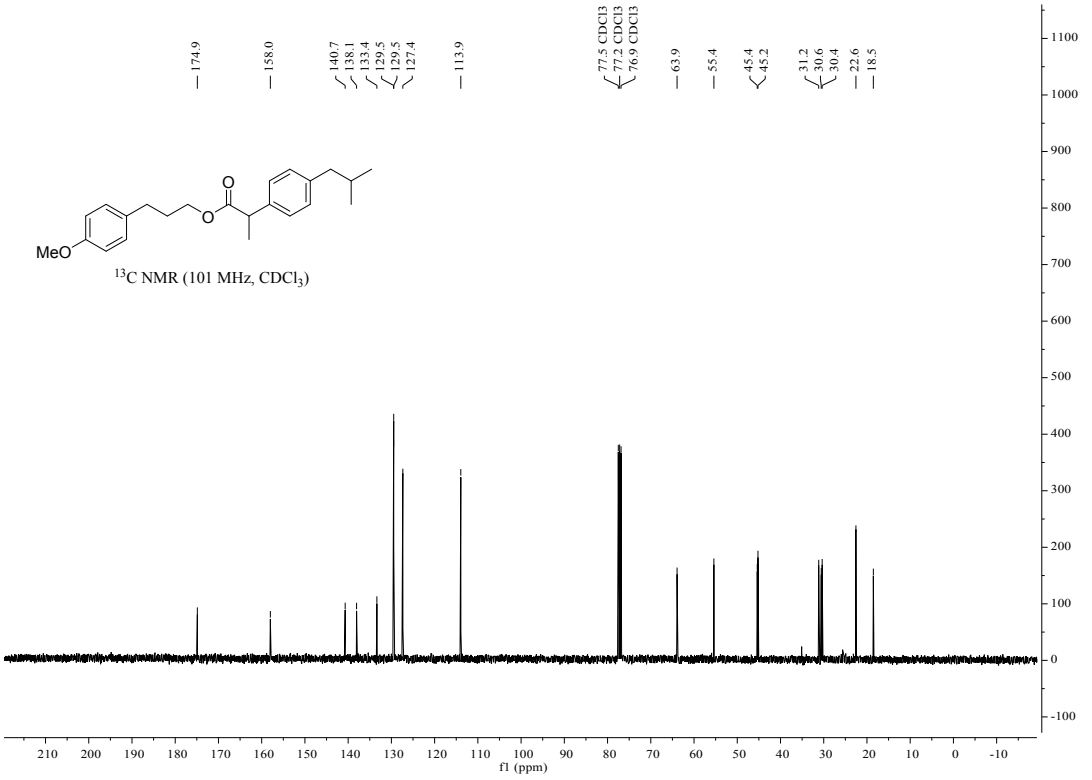
^{1}H NMR (400 MHz, $CDCl_3$)



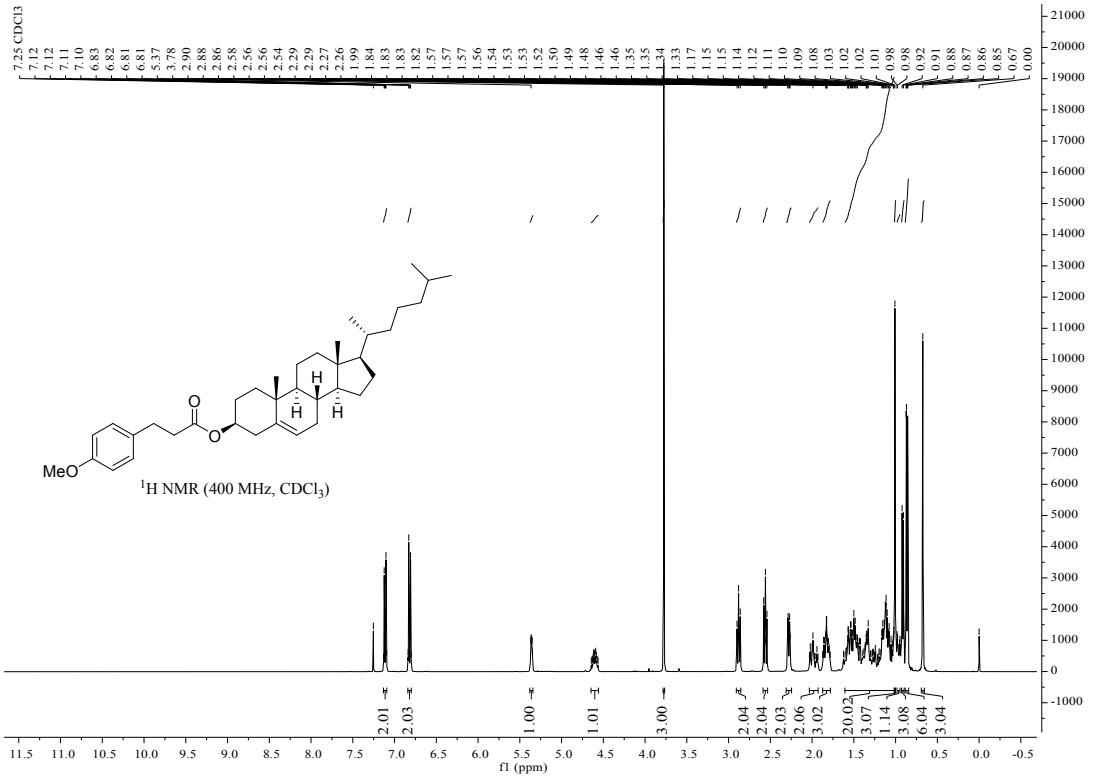
^{13}C NMR (101 MHz, $CDCl_3$)

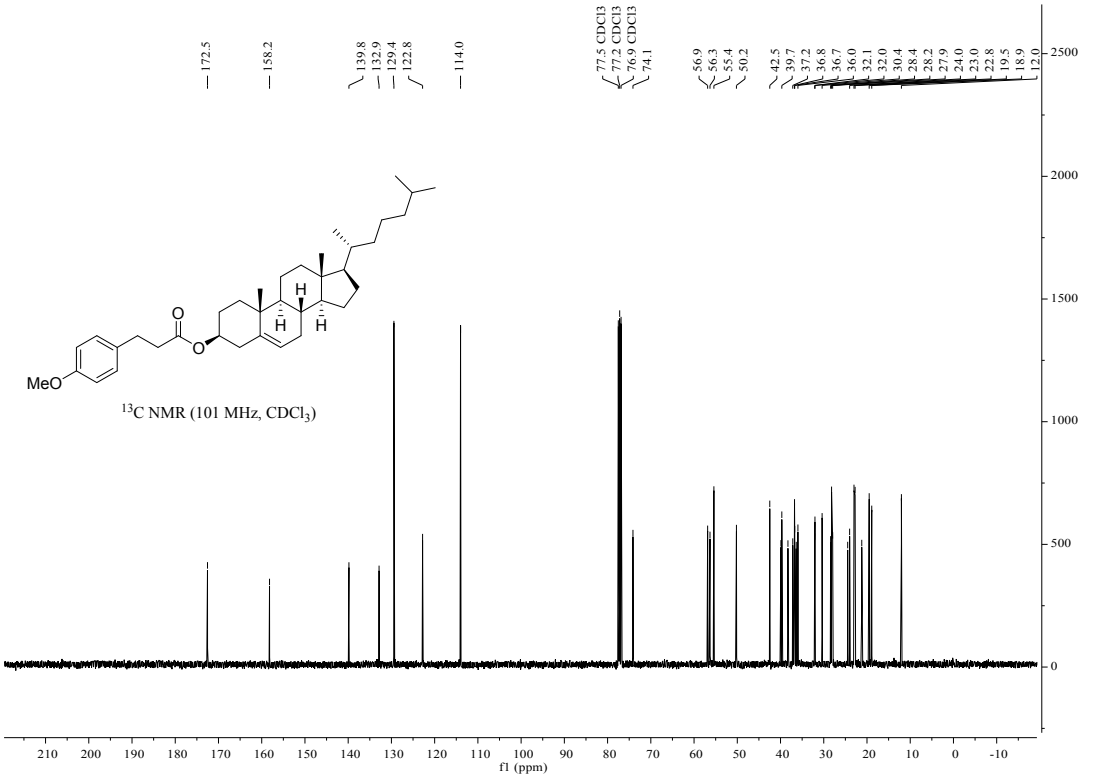
Compound S6


MeO
O
O
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

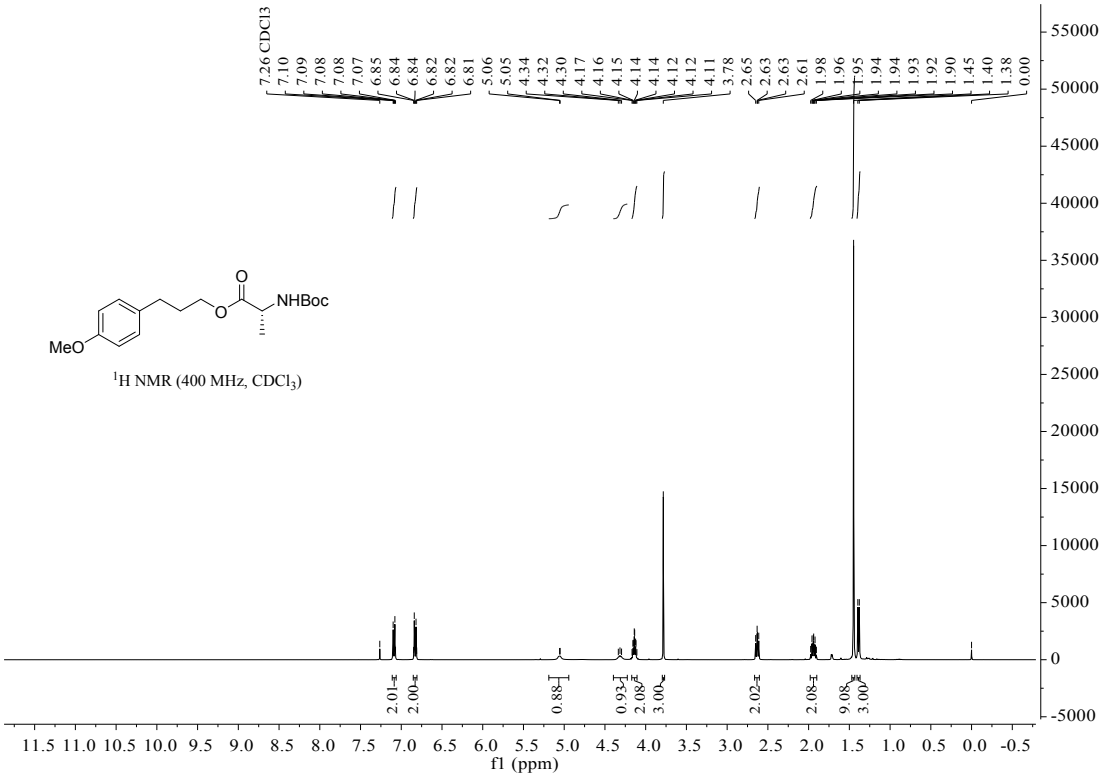

MeO
O
O
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound S7

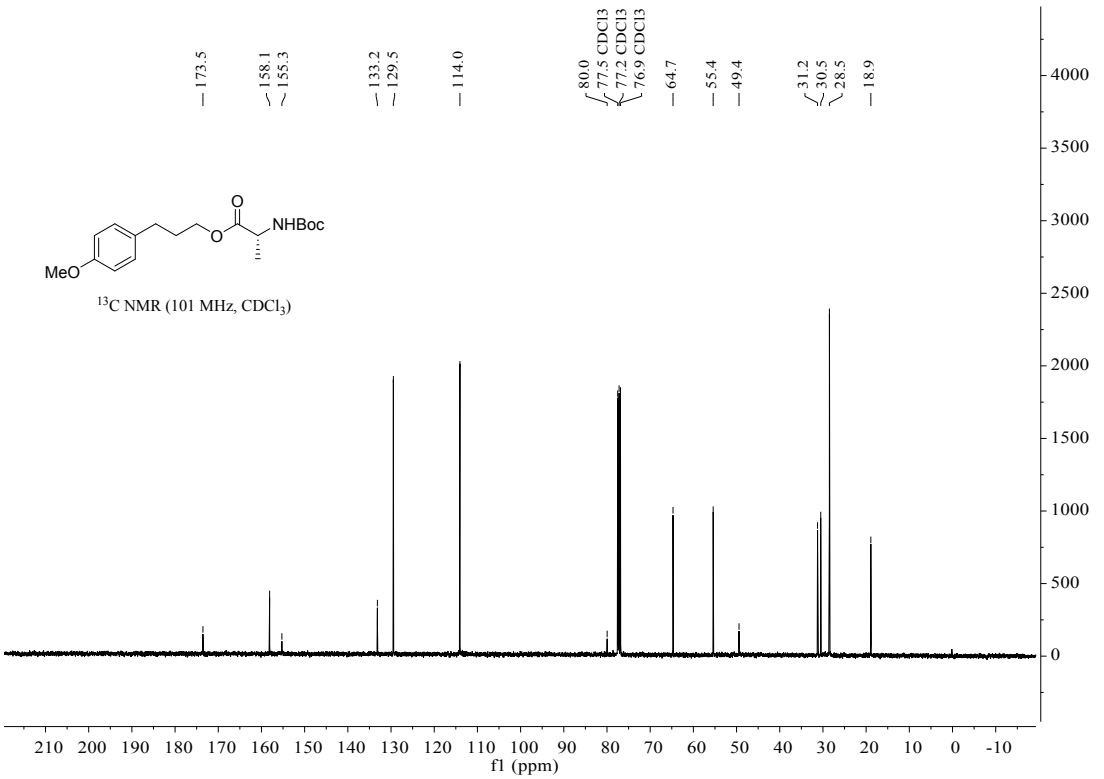

MeO
O
O
H
H
H
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


MeO
O
O
H
H
H
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

Compound S8

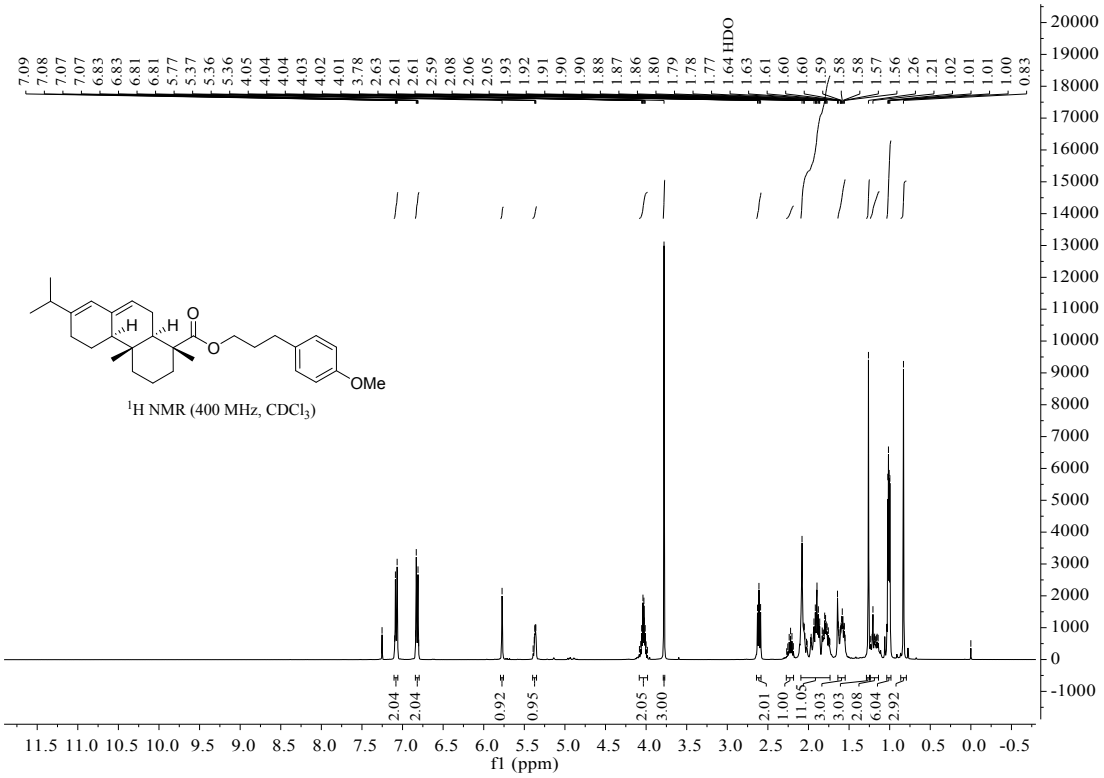


^{1}H NMR (400 MHz, $CDCl_3$)

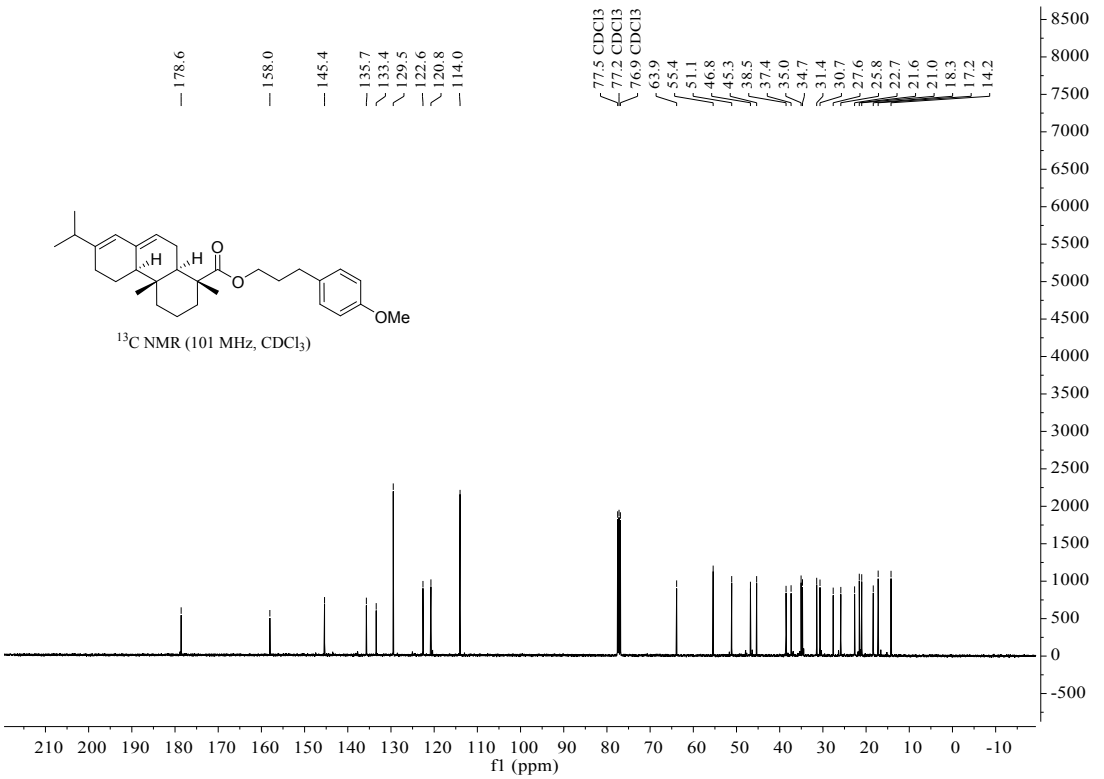


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S9

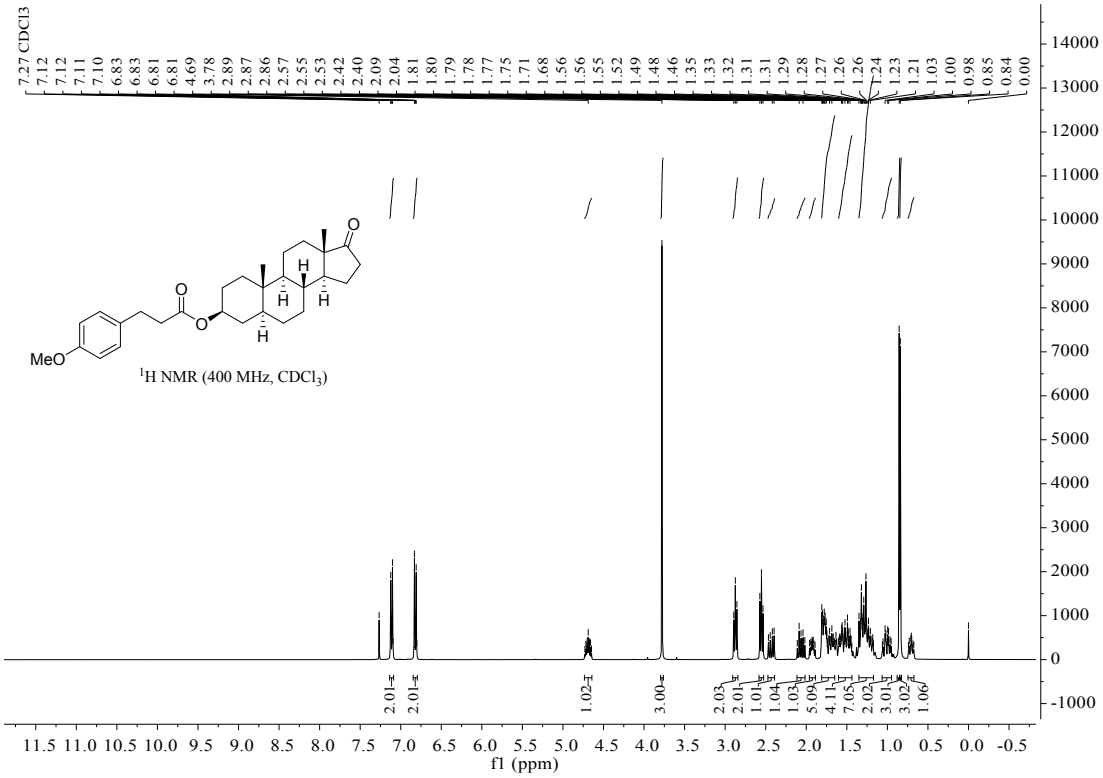


^{1}H NMR (400 MHz, $CDCl_3$)

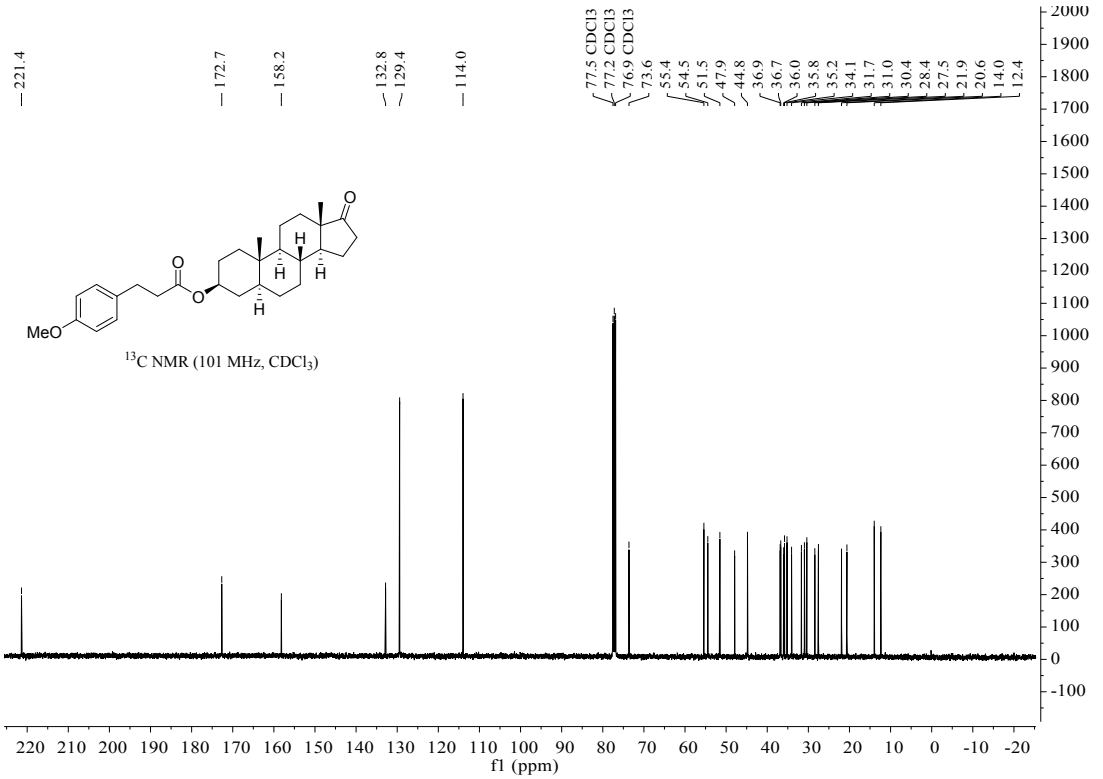


^{13}C NMR (101 MHz, $CDCl_3$)

Compound S10



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

Compound S11