Supplementary Information

Photoelectrocatalytic Arene C-H Amination

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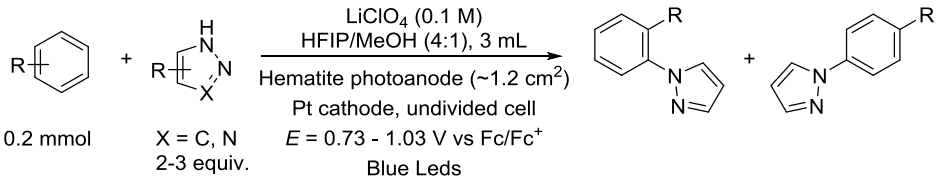
Supplementary Methods

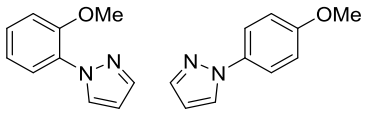
Devices for Photoelectrochemical Oxidation

The photoelectrochemical oxidation was performed in an undivided cell by a three-electrode configuration using VMP-3 instrument (Biologic Science Instrument). Hematite was used as a working electrode with a Ag/AgCl reference electrode and a Pt counter electrode. Blue led lamp (Kessil, A160We, 40W) was used as the light source. The distance between the lamp and the working electrode is ~5 cm (See Supplementary Figure 1).

C–N Coupling Reaction via Photoelectrocatalysis



General procedure for coupling of aromatic compounds and azoles in a photoelectrochemical cell: Under N_2, $LiClO_4$ (31.9 mg, 0.1 M), arene (0.2 mmol), azole (0.4 or 0.6 mmol, 2 or 3 equiv) and solvent (HFIP/MeOH = 4/1, 3 mL) were added to a 20 mL test tube equipped with a magnetic stir bar. The photoelectrochemical oxidation were performed at a constant potential (see maintext for the specific potential for each substrate) at ambient temperature for 10~24 h in a photoreactor (Supplementary Figure 1). The resulting solution was concentrated under vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/hexane to give the corresponding products.

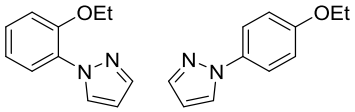


1-(2-methoxyphenyl)-1*H*-pyrazole (3a). 1-(4-methoxyphenyl)-1*H*-pyrazole (3b). 3a and **3b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (26.9 mg, 77%). The *ortho* : *para* ratio of the inseparable mixture was 6:1 as determined by ^{1}H NMR of the isolated product.

3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.1 Hz, 1H, aryl-*H*), 7.75-7.70 (m, 2H, aryl-*H*), 7.30 (td, *J* = 7.8, 1.7 Hz, 1H, aryl-*H*), 7.09-7.02 (m, 2H, aryl-*H*), 6.43 (t, *J* = 2.0 Hz, 1H, aryl-*H*), 3.87 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4 (aryl-*C*), 140.1 (aryl-*C*), 131.6 (aryl-*C*), 129.9 (aryl-*C*), 128.1 (aryl-*C*), 125.4 (aryl-*C*), 121.3 (aryl-*C*), 112.4 (aryl-*C*), 106.2 (aryl-*C*), 56.0 (O*C*H$_3$).

3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.69 (s, 1H, aryl-*H*), 7.59 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.97 (d, *J* = 8.9 Hz, 2H, aryl-*H*), 6.43 (t, *J* = 2.0 Hz, 1H, aryl-*H*), 3.83 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (aryl-*C*), 140.7 (aryl-*C*), 134.1 (aryl-*C*), 126.9 (aryl-*C*), 121.0 (aryl-*C*), 114.6 (aryl-*C*), 107.3 (aryl-*C*), 55.7 (O*C*H$_3$).

These spectroscopic data correspond to reported data.[1]

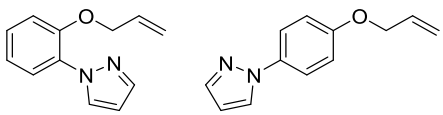


1-(2-ethoxyphenyl)-1*H*-pyrazole (4a). 1-(4-ethoxyphenyl)-1*H*-pyrazole (4b). 4a and **4b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (20:1) to give the title compound as pale yellow oil (24.5 mg, 65%). The *ortho* : *para* ratio of the inseparable mixture was 7:1 as determined by ^{1}H NMR of the isolated product.

4a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.78 (dd, *J* = 7.9, 1.7 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.26 (td, *J* = 8.0, 1.7 Hz, 1H, aryl-*H*), 7.09-7.01 (m, 2H, aryl-*H*), 6.42 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 4.10 (q, *J* = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 1.41 (t, *J* = 7.0 Hz, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4 (aryl-*C*), 140.0 (aryl-*C*), 131.6 (aryl-*C*), 130.1 (aryl-*C*), 127.8 (aryl-*C*), 125.1 (aryl-*C*), 121.3 (aryl-*C*), 113.6 (aryl-*C*), 106.2 (aryl-*C*), 64.7 (O*C*H$_2$CH$_3$), 14.9 (OCH$_2$*C*H$_3$).

4b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.69 (s, 1H, aryl-*H*), 7.58 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.96 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.42 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 4.06 (q, *J* = 6.9 Hz, 2H, OC*H*$_2$CH$_3$), 1.43 (t, *J* = 6.9 Hz, 3H, OCH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7 (aryl-*C*), 140.7 (aryl-*C*), 134.0 (aryl-*C*), 126.9 (aryl-*C*), 121.0 (aryl-*C*), 115.2 (aryl-*C*), 107.2 (aryl-*C*), 63.9 (O*C*H$_2$CH$_3$), 14.9 (OCH$_2$*C*H$_3$).

HRMS-ESI (*m/z*): Calcd for [($C_{11}H_{12}N_2O$+H)+], 189.1022; found: 189.1025.

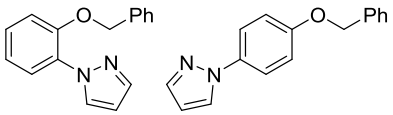


1-(2-(allyloxy)phenyl)-1*H*-pyrazole (5a). 1-(4-(allyloxy)phenyl)-1*H*-pyrazole (5b). **5a** and **5b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (30:1~10:1) to give the title compound as pale yellow oil (22.2 mg, 55%). The *ortho* : *para* ratio of the inseparable mixture was 4:1 as determined by ^{1}H NMR of the isolated product.

5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.76 (dd, *J* = 7.9, 1.7 Hz, 1H, aryl-*H*), 7.71 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.26 (td, *J* = 7.7, 1.7 Hz, 1H, aryl-*H*), 7.10-7.01 (m, 2H, aryl-*H*), 6.43 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 6.06-5.95 (m, 1H, C*H*=CH_2), 5.37 (dd, *J* = 17.3, 1.7 Hz, 1H, CH=C*H*$_2$), 5.27 (dd, *J* = 10.6, 1.7 Hz, 1H, CH=C*H*$_2$), 4.59 (d, *J* = 5.1 Hz, 2H, C*H*$_2$CH=CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2 (aryl-*C*), 140.0 (aryl-*C*), 132.7 (*C*H=CH_2), 131.7 (aryl-*C*), 130.2 (aryl-*C*), 127.9 (aryl-*C*), 125.4 (aryl-*C*), 121.6 (aryl-*C*), 117.9 (CH=*C*H_2), 114.0 (aryl-*C*), 106.3 (aryl-*C*), 69.9 (*C*H_2CH=CH_2).

5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.69 (s, 1H, aryl-*H*), 7.58 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.98 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.43 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 6.12-6.02 (m, 1H, C*H*=CH_2), 5.43 (dd, *J* = 17.2, 1.7 Hz, 1H, CH=C*H*$_2$), 5.31 (dd, *J* = 10.4, 1.6 Hz, 1H, CH=C*H*$_2$), 4.56 (d, *J* = 4.7 Hz, 2H, C*H*$_2$CH=CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (aryl-*C*), 140.7 (aryl-*C*), 134.2 (aryl-*C*), 133.1 (*C*H=CH_2), 126.9 (aryl-*C*), 121.0 (aryl-*C*), 118.0 (CH=*C*H_2), 115.5 (aryl-*C*), 107.3 (aryl-*C*), 69.2 (*C*H_2CH=CH_2).

HRMS-ESI (*m/z*): Calcd for [($C_{12}H_{12}N_2O$+H)+], 201.1022; found: 201.1026.

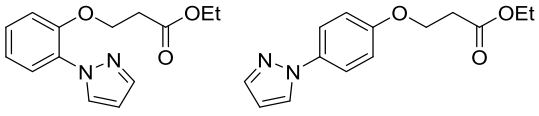


1-(2-(benzyloxy)phenyl)-1*H*-pyrazole (6a). 1-(4-(benzyloxy)phenyl)-1*H*-pyrazole (6b). 6a and **6b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (20:1) to give the title compound as colorless oil (33.1 mg, 66%). The *ortho* : *para* ratio of the inseparable mixture was 5:1 as determined by ^{1}H NMR of the isolated product.

6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.81 (dd, *J* = 7.9, 1.8 Hz, 1H, aryl-*H*), 7.73 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.48-7.30 (m, 5H, aryl-*H*), 7.27 (td, *J* = 7.8, 1.8 Hz, 1H, aryl-*H*), 7.13-7.07 (m, 2H, aryl-*H*), 6.41 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 5.13 (s, 2H, PhOC*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (aryl-*C*), 140.1 (aryl-*C*), 136.5 (aryl-*C*), 131.7 (aryl-*C*), 130.4 (aryl-*C*), 128.7 (aryl-*C*), 128.2 (aryl-*C*), 127.9 (aryl-*C*), 127.3 (aryl-*C*), 125.3 (aryl-*C*), 121.8 (aryl-*C*), 114.3 (aryl-*C*), 106.4 (aryl-*C*), 71.2 (PhO*C*H$_2$).

6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.2 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 2.0 Hz, aryl-*H*), 7.60 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 7.48-7.30 (m, 5H, aryl-*H*), 7.05 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.44 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 5.13 (s, 2H, PhOC*H*$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5 (aryl-*C*), 140.7 (aryl-*C*), 136.8 (aryl-*C*), 134.3 (aryl-*C*), 128.7 (aryl-*C*), 128.2 (aryl-*C*), 127.3 (aryl-*C*), 126.9 (aryl-*C*), 121.0 (aryl-*C*), 115.6 (aryl-*C*), 107.3 (aryl-*C*), 70.4 (PhO*C*H$_2$).

HRMS-ESI (*m/z*): Calcd for [($C_{16}H_{14}N_2O$+H)+], 251.1179; found: 251.1183.



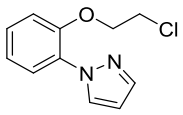
Ethyl 3-(2-(1*H*-pyrazol-1-yl)phenoxy)propanoate (7a). Ethyl 3-(4-(1*H*-pyrazol-1-yl)phenoxy)propanoate (7b). 7a and **7b** were synthesized following the general

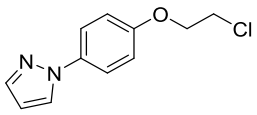
procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (4:1) to give the title compound as colorless oil (44.8 mg, 86%). The *ortho* : *para* ratio of the inseparable mixture was 6:1 as determined by ^{1}H NMR of the isolated product.

7a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.75 (dd, *J* = 7.9, 1.7 Hz, 1H, aryl-*H*), 7.67 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.26 (td, *J* = 7.9, 1.7 Hz, 1H, aryl-*H*), 7.10-7.02 (m, 2H, aryl-*H*), 6.38 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 4.30 (t, *J* = 6.3 Hz, 2H, OCH_2CH_2), 4.14 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 2.76 (t, *J* = 6.2 Hz, 2H, OCH_2CH_2), 1.24 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9 (*C*=O), 149.9 (aryl-*C*), 140.0 (aryl-*C*), 131.6 (aryl-*C*), 130.1 (aryl-*C*), 127.8 (aryl-*C*), 125.2 (aryl-*C*), 121.8 (aryl-*C*), 113.6 (aryl-*C*), 106.2 (aryl-*C*), 64.7 (OCH_2CH_2), 60.9 (OCH_2CH_3), 34.6 (OCH_2CH_2), 14.2 (OCH_2CH_3).

7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.67 (s, 1H, aryl-*H*), 7.57 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.96 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.42 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 4.27 (t, *J* = 6.4 Hz, 2H, OCH_2CH_2), 4.19 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 2.79 (t, *J* = 6.5 Hz, 2H, OCH_2CH_2), 1.27 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3).. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 (*C*=O), 157.3 (aryl-*C*), 140.7 (aryl-*C*), 134.3 (aryl-*C*), 126.8 (aryl-*C*), 120.9 (aryl-*C*), 115.4 (aryl-*C*), 107.3 (aryl-*C*), 64.0 (OCH_2CH_2), 60.9 (OCH_2CH_3), 34.7 (OCH_2CH_2), 14.3 (OCH_2CH_3).

HRMS-ESI (*m/z*): Calcd for [($C_{14}H_{16}N_2O_3$+H)+], 261.1234; found: 261.1238.





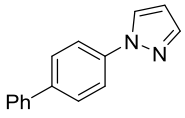
1-(2-(2-chloroethoxy)phenyl)-1*H*-pyrazole (8a). 1-(4-(2-chloroethoxy)phenyl)-1*H*-pyrazole (8b). 8a and **8b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as white solid (31.4mg, 71%). The *ortho* : *para* ratio

of the inseparable mixture was 3:1 as determined by ^{1}H NMR of the isolated product.

8a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.79 (dd, *J* = 7.9, 1.7 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.26 (td, *J* = 7.9, 1.7 Hz, 1H, aryl-*H*), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H, aryl-*H*), 6.99 (t, *J* = 8.8 Hz, 1H, aryl-*H*), 6.43 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 4.25 (t, *J* = 5.6 Hz, 2H, O*C*$H_2$$CH_2$Cl), 3.78 (t, *J* = 5.5 Hz, 2H, OCH_2*C*H_2Cl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (aryl-*C*), 140.2 (aryl-*C*), 131.9 (aryl-*C*), 130.3 (aryl-*C*), 127.9 (aryl-*C*), 125.4 (aryl-*C*), 122.3 (aryl-*C*), 113.8 (aryl-*C*), 106.5 (aryl-*C*), 69.1 (O*C*$H_2$$CH_2$Cl), 42.0 ($OCH_2$*C*$H_2$Cl).

8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.69 (d, *J* = 2.1 Hz, 1H, aryl-*H*), 7.59 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 7.00 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.43 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 4.23 (t, *J* = 5.6 Hz, 2H, O*C*$H_2$$CH_2$Cl), 3.81 (t, *J* = 5.6 Hz, 2H, OCH_2*C*H_2Cl). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (aryl-*C*), 140.8 (aryl-*C*), 134.6 (aryl-*C*), 126.9 (aryl-*C*), 121.0 (aryl-*C*), 115.5 (aryl-*C*), 107.4 (aryl-*C*), 68.5 (O*C*$H_2$$CH_2$Cl), 41.9 ($OCH_2$*C*$H_2$Cl).

HRMS-ESI (*m/z*): Calcd for [($C_{11}H_{11}ClN_2O$+H)+], 223.0633; found: 223.0638.

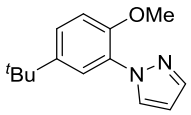


1-([1,1'-biphenyl]-4-yl)-1*H*-pyrazole (9). 9 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as white solid (21.8 mg, 50%).

9: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.78 (d, *J* = 8.8 Hz, 2H, aryl-*H*), 7.76 (s, 1H, aryl-*H*), 7.69 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 7.63 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 7.47 (t, *J* = 7.7 Hz, 2H, aryl-*H*), 7.37 (t, *J* = 7.4 Hz, 1H, aryl-*H*), 6.50 (t, *J* = 2.2 Hz, 1H, aryl-*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3 (aryl-*C*), 140.2 (aryl-*C*), 139.5 (aryl-*C*), 139.5 (aryl-*C*), 129.0 (aryl-*C*), 128.2 (aryl-*C*), 127.6 (aryl-*C*), 127.1

(aryl-*C*), 126.8 (aryl-*C*), 119.6 (aryl-*C*), 107.8 (aryl-*C*).

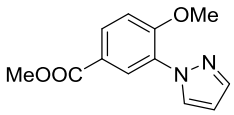
These spectroscopic data correspond to reported data.[1]



1-(5-(tert-butyl)-2-methoxyphenyl)-1*H*-pyrazole (10). 10 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (35.8 mg, 77%).

10: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.72 (d, *J* = 1.4 Hz, 2H, aryl-*H*), 7.32 (dd, *J* = 8.6, 1.8 Hz, 2H, aryl-*H*), 6.98 (d, *J* = 8.7 Hz, 1H, aryl-*H*), 6.44 (t, *J* = 1.6 Hz, 1H, aryl-*H*), 3.85 (s, 3H, OCH_3), 1.35 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3 (aryl-*C*), 144.4 (aryl-*C*), 140.0 (aryl-*C*), 131.8 (aryl-*C*), 129.2 (aryl-*C*), 125.0 (aryl-*C*), 122.7 (aryl-*C*), 112.1 (aryl-*C*), 106.2 (aryl-*C*), 56.1 (OCH_3), 34.4 (*C*(CH_3)$_3$), 31.5 (C(*C*H_3)$_3$).

HRMS-ESI (m/z): Calcd for [($C_{14}H_{18}N_2O$+H)+], 231.1492; found: 231.1496.

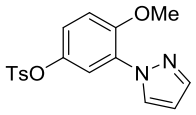


Methyl 4-methoxy-3-(1*H*-pyrazol-1-yl)benzoate (11). 11 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (20:1~5:1) to give the title compound as white solid (17.0 mg, 37%).

11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.2 Hz, 1H, aryl-*H*), 8.01 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.99 (dd, *J* = 8.7, 2.2 Hz, 2H, aryl-*H*), 7.71 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.05 (d, *J* = 8.7 Hz, 1H, aryl-*H*), 6.42 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.92 (s, 3H, COOCH_3),

3.87 (s, 3H, ArOCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (*C*OOCH$_3$), 154.8 (aryl-*C*), 140.5 (aryl-*C*), 131.6 (aryl-*C*), 129.9 (aryl-*C*), 129.5 (aryl-*C*), 126.7 (aryl-*C*), 123.3 (aryl-*C*), 111.8 (aryl-*C*), 106.6 (aryl-*C*), 56.3 (O*C*H$_3$), 52.1 (COO*C*H$_3$).

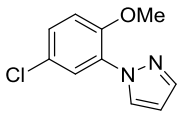
HRMS-ESI (m/z): Calcd for [($C_{12}H_{12}N_2O_3$+H)+], 233.0921; found: 233.0923.



4-methoxy-3-(1*H*-pyrazol-1-yl)phenyl 4-methylbenzenesulfonate (12). 12 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (3:1) to give the title compound as yellow oil (37.1 mg, 54%).

12: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.72 (d, *J* = 8.4 Hz, 2H, aryl-*H*), 7.64 (d, *J* = 1.6 Hz, 1H, aryl-*H*), 7.47 (t, *J* = 1.6 Hz, 1H, aryl-*H*), 7.30 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 6.91 (d, *J* = 1.7 Hz, 2H, aryl-*H*), 6.38 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.84 (s, 3H, ArOCH_3), 2.42 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (aryl-*C*), 145.6 (aryl-*C*), 143.0 (aryl-*C*), 140.4 (aryl-*C*), 132.3 (aryl-*C*), 131.5 (aryl-*C*), 130.0 (aryl-*C*), 129.9 (aryl-*C*), 128.6 (aryl-*C*), 121.1 (aryl-*C*), 119.0 (aryl-*C*), 112.7 (aryl-*C*), 106.7 (aryl-*C*), 56.4 (ArO*C*H$_3$), 21.8 (Ar*C*H$_3$).

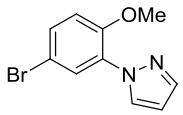
HRMS-ESI (m/z): Calcd for [($C_{17}H_{16}N_2O_4S$+H)+], 345.0904; found: 345.0909.



1-(5-chloro-2-methoxyphenyl)-1*H*-pyrazole (13). 13 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (23.2 mg, 56%).

13: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.81 (d, *J* = 2.6 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.23 (dd, *J* = 8.8, 2.6 Hz, 1H, aryl-*H*), 6.96 (d, *J* = 8.8 Hz, 1H, aryl-*H*), 6.43 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.87 (s, 3H, ArOCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7 (aryl-*C*), 140.5 (aryl-*C*), 131.7 (aryl-*C*), 130.5 (aryl-*C*), 127.4 (aryl-*C*), 126.3 (aryl-*C*), 125.0 (aryl-*C*), 113.5 (aryl-*C*), 106.8 (aryl-*C*), 56.4 (O*C*H_3).

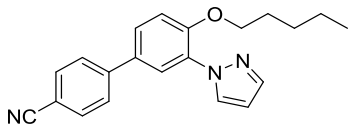
These spectroscopic data correspond to reported data.[2]



1-(5-bromo-2-methoxyphenyl)-1*H*-pyrazole (14). 14 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (25.6 mg, 51%).

14: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.94 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H, aryl-*H*), 6.90 (d, *J* = 8.8 Hz, 1H, aryl-*H*), 6.42 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.87 (s, 3H, ArOCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2 (aryl-*C*), 140.5 (aryl-*C*), 131.7 (aryl-*C*), 130.7 (aryl-*C*), 130.4 (aryl-*C*), 127.7 (aryl-*C*), 113.9 (aryl-*C*), 113.3 (aryl-*C*), 106.8 (aryl-*C*), 56.3 (O*C*H_3).

HRMS-ESI (m/z): Calcd for [($C_{10}H_9BrN_2O$+H)+], 252.9971; found: 252.9978.

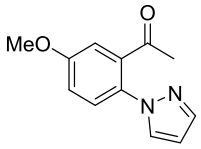


4'-(pentyloxy)-3'-(1H-pyrazol-1-yl)-[1,1'-biphenyl]-4-carbonitrile (15). 15 was synthesized following the general procedure. The residue was purified by

chromatography on silica gel, eluting with hexane/ethyl acetate (8:1) to give the title compound as white solid (34.2 mg, 52%).

15: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.6 Hz, 1H, aryl-*H*), 8.09 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.73 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.72-7.65 (m, 4H, aryl-*H*), 7.49 (dd, *J* = 8.6, 2.4 Hz, 1H, aryl-*H*), 7.12 (d, *J* = 8.6 Hz, 1H, aryl-*H*), 6.46 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 4.10 (t, *J* = 6.5 Hz, 1H, OCH_2), 1.88-1.78 (m, 2H, OCH_2CH_2), 1.47-1.32 (m, 4H, $CH_2CH_2CH_3$), 0.92 (t, *J* = 7.0 Hz, 3H, CH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8 (aryl-*C*), 144.5 (aryl-*C*), 140.3 (aryl-*C*), 132.7 (aryl-*C*), 132.1 (aryl-*C*), 131.7 (aryl-*C*), 130.4 (aryl-*C*), 127.4 (aryl-*C*), 126.2 (aryl-*C*), 123.6 (aryl-*C*), 119.1 (*C*N), 113.9 (aryl-*C*), 110.7 (aryl-*C*), 106.6 (aryl-*C*), 69.5 (OCH_2), 28.9 (OCH_2CH_2), 28.3 ($OCH_2CH_2CH_2$), 22.4 (CH_2CH_3), 14.1 (CH_2CH_3).

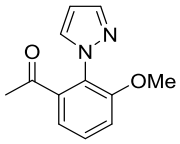
HRMS-ESI (m/z): Calcd for [($C_{21}H_{21}N_3O$+H)+], 332.1757; found: 332.1761.



1-(5-methoxy-2-(1*H*-pyrazol-1-yl)phenyl)ethan-1-one (16a). 16a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as colorless oil (14.6 mg, 34%).

16a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.64 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.34 (d, *J* = 8.5 Hz, 1H, aryl-*H*), 7.07 (d, *J* = 2.8 Hz, 1H, aryl-*H*), 7.04 (dd, *J* = 8.5, 2.9 Hz, 1H, aryl-*H*), 6.46 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.85 (s, 3H, ArOCH_3), 1.90 (s, 3H, C=OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1 (*C*=O), 159.3 (aryl-*C*), 141.2 (aryl-*C*), 137.5 (aryl-*C*), 131.8 (aryl-*C*), 130.3 (aryl-*C*), 126.4 (aryl-*C*), 117.6 (aryl-*C*), 113.0 (aryl-*C*), 107.8 (aryl-*C*), 55.9 (ArO*C*H_3), 28.8 (C=O*C*H_3).

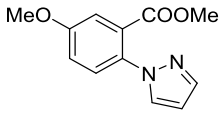
HRMS-ESI (m/z): Calcd for [($C_{12}H_{12}N_2O_2$+H)+], 217.0972; found: 217.0975.



1-(3-methoxy-2-(1*H*-pyrazol-1-yl)phenyl)ethan-1-one (16b). 16b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as white solid (6.0 mg, 14%).

16b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.71 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.41 (t, *J* = 8.0 Hz, 1H, aryl-*H*), 7.18 (d, *J* = 7.7 Hz, 1H, aryl-*H*), 7.14 (d, *J* = 8.3 Hz, 1H, aryl-*H*), 6.49 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.84 (s, 3H, ArOC*H*$_3$), 1.85 (s, 3H, C=OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9 (*C*=O), 153.5 (aryl-*C*), 140.8 (aryl-*C*), 139.4 (aryl-*C*), 132.6 (aryl-*C*), 129.4 (aryl-*C*), 127.5 (aryl-*C*), 120.2 (aryl-*C*), 114.4 (aryl-*C*), 107.2 (aryl-*C*), 56.5 (ArO*C*H$_3$), 28.7 (C=O*C*H$_3$).

HRMS-ESI (m/z): Calcd for [($C_{12}H_{12}N_2O_2$+H)+], 217.0972; found: 217.0976.

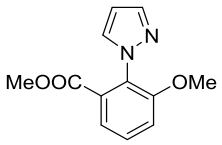


Methyl 5-methoxy-2-(1*H*-pyrazol-1-yl)benzoate (17a). 17a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as colorless oil (31.0 mg, 67%).

17a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.2 Hz, 1H, aryl-*H*), 7.60 (d, *J* = 2.3 Hz, 1H, aryl-*H*), 7.37 (d, *J* = 8.8 Hz, 1H, aryl-*H*), 7.33 (d, *J* = 3.0 Hz, 1H, aryl-*H*), 7.07 (dd, *J* = 8.7, 3.0 Hz, 1H, aryl-*H*), 6.40 (t, *J* = 2.0 Hz, 1H, aryl-*H*), 3.86 (s, 3H, ArOC*H*$_3$), 3.69 (s, 3H, COOC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (*C*OOCH$_3$), 159.0 (aryl-

C), 140.6 (aryl-*C*), 133.0 (aryl-*C*), 130.4 (aryl-*C*), 128.8 (aryl-*C*), 127.4 (aryl-*C*), 117.9 (aryl-*C*), 115.0 (aryl-*C*), 106.6 (aryl-*C*), 55.9 (ArO*C*H_3), 52.5 (COO*C*H_3).

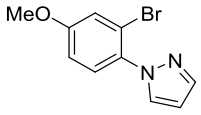
These spectroscopic data correspond to reported data.[3]



Methyl 3-methoxy-2-(1*H*-pyrazol-1-yl)benzoate (17b). 17b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as colorless oil (10.2 mg, 22%).

17b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H, aryl-*H*), 7.45-7.39 (m, 2H, aryl-*H*), 7.17 (dd, *J* = 5.7, 4.0 Hz, 1H, aryl-*H*), 6.44 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.83 (s, 3H, ArOC*H*$_3$), 3.69 (s, 3H, COOC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 (*C*OOCH$_3$), 154.3 (aryl-*C*), 140.3 (aryl-*C*), 132.4 (aryl-*C*), 131.1 (aryl-*C*), 129.3 (aryl-*C*), 128.8 (aryl-*C*), 122.0 (aryl-*C*), 115.1 (aryl-*C*), 106.2 (aryl-*C*), 56.5 (ArO*C*H_3), 52.5 (COO*C*H_3).

HRMS-ESI (m/z): Calcd for [($C_{12}H_{12}N_2O_3$+H)+], 233.0921; found: 233.0925.

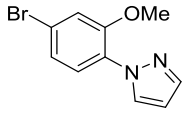


1-(2-bromo-4-methoxyphenyl)-1*H*-pyrazole (18a). 18a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (25.2 mg, 50%).

18a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H, aryl-*H*), 7.69 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.38 (d, *J* = 9.0 Hz, 1H, aryl-*H*), 7.20 (d, *J* = 2.8 Hz, 1H, aryl-*H*), 6.92 (dd, *J* = 8.8,

2.6 Hz, 1H, aryl-*H*), 6.43 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.84 (s, 3H, ArOC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (aryl-*C*), 140.5 (aryl-*C*), 133.2 (aryl-*C*), 131.5 (aryl-*C*), 129.0 (aryl-*C*), 119.9 (aryl-*C*), 118.4 (aryl-*C*), 113.9 (aryl-*C*), 106.2 (aryl-*C*), 55.9 (ArO*C*H$_3$).

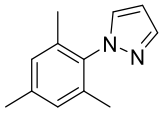
HRMS-ESI (m/z): Calcd for [($C_{10}H_9BrN_2O$+H)+], 252.9971; found: 252.9981.



1-(4-bromo-2-methoxyphenyl)-1*H*-pyrazole (18b). 18b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (16.2 mg, 32%).

18b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 1.8 Hz, 1H, aryl-*H*), 7.63 (d, *J* = 8.3 Hz, 1H, aryl-*H*), 7.23-7.16 (m, 2H, aryl-*H*), 6.43 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.89 (s, 3H, ArOC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6 (aryl-*C*), 140.3 (aryl-*C*), 131.5 (aryl-*C*), 128.9 (aryl-*C*), 126.2 (aryl-*C*), 124.3 (aryl-*C*), 120.8 (aryl-*C*), 115.8 (aryl-*C*), 106.5 (aryl-*C*), 56.3 (ArO*C*H$_3$).

HRMS-ESI (m/z): Calcd for [($C_{10}H_9BrN_2O$+H)+], 252.9971; found: 252.9981.

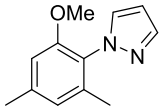


1-mesityl-1*H*-pyrazole (19). 19 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (8:1) to give the title compound as colorless oil (18.5 mg, 50%).

19: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.43 (d, *J* = 2.3 Hz, 1H, aryl-*H*), 6.94 (s, 2H, aryl-*H*), 6.43 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 2.33 (s, 3H, ArC*H*$_3$),

1.97 (s, 6H, ArC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 (aryl-*C*), 138.8 (aryl-*C*), 137.0 (aryl-*C*), 136.0 (aryl-*C*), 130.9 (aryl-*C*), 128.8 (aryl-*C*), 105.8 (aryl-*C*), 21.2 (Ar*C*H$_3$), 17.3 (Ar*C*H$_3$).

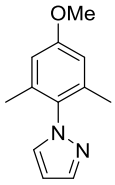
These spectroscopic data correspond to reported data.[1]



1-(2-methoxy-4,6-dimethylphenyl)-1*H*-pyrazole (20a). 20a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (23.2 mg, 57%).

20a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.47 (d, *J* = 2.3 Hz, 1H, aryl-*H*), 6.71 (s, 1H, aryl-*H*), 6.66 (s, 1H, aryl-*H*), 6.42 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 3.72 (s, 3H, ArOC*H*$_3$), 2.37 (s, 6H, ArC*H*$_3$), 2.00 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (aryl-*C*), 140.1 (aryl-*C*), 139.9 (aryl-*C*), 137.5 (aryl-*C*), 132.0 (aryl-*C*), 126.8 (aryl-*C*), 123.2 (aryl-*C*), 110.2 (aryl-*C*), 105.6 (aryl-*C*), 56.1 (ArO*C*H$_3$), 21.8 (Ar*C*H$_3$), 17.3 (Ar*C*H$_3$).

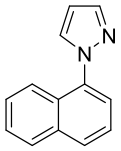
HRMS-ESI (m/z): Calcd for [($C_{12}H_{14}N_2O$+H)+], 203.1179; found: 203.1183.



1-(4-methoxy-2,6-dimethylphenyl)-1*H*-pyrazole (20b). 20b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (8.3 mg, 21%).

2r': ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.42 (d, *J* = 2.3 Hz, 1H, aryl-*H*), 6.65 (s, 2H, aryl-*H*), 6.42 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 3.81 (s, 3H, ArOC*H*$_3$), 1.97 (s, 6H, ArC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (aryl-*C*), 140.1 (aryl-*C*), 137.7 (aryl-*C*), 132.8 (aryl-*C*), 131.2 (aryl-*C*), 113.2 (aryl-*C*), 105.9 (aryl-*C*), 55.5 (ArO*C*H$_3$), 17.7 (Ar*C*H$_3$).

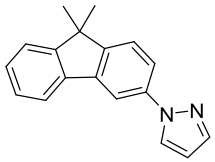
HRMS-ESI (m/z): Calcd for [($C_{12}H_{14}N_2O$+H)+], 203.1179; found: 203.1183.



1-(naphthalen-1-yl)-1*H*-pyrazole (21). 21 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (24.2 mg, 62%).

2s': ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.90 (m, 2H, aryl-*H*), 7.86 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.85-7.81 (m, 1H, aryl-*H*), 7.80 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.58-7.48 (m, 4H, aryl-*H*), 6.55 (t, *J* = 2.1 Hz, 1H, aryl-*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9 (aryl-*C*), 137.5 (aryl-*C*), 134.4 (aryl-*C*), 131.7 (aryl-*C*), 129.3 (aryl-*C*), 129.0 (aryl-*C*), 128.2 (aryl-*C*), 127.3 (aryl-*C*)), 126.7 (aryl-*C*), 125.2 (aryl-*C*), 123.3 (aryl-*C*), 123.3 (aryl-*C*), 106.6 (aryl-*C*).

These spectroscopic data correspond to reported data.[4]

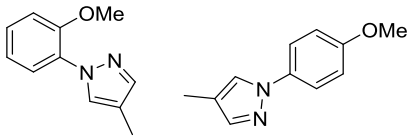


1-(9,9-dimethyl-9*H*-fluoren-3-yl)-1*H*-pyrazole (22). 22 was synthesized following the general procedure. The residue was purified by chromatography on silica gel,

eluting with hexane/ethyl acetate (10:1) to give the title compound as pale yellow oil (31.1 mg, 60%).

2t: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.0 Hz, 1H, aryl-*H*), 7.84 (s, 1H, aryl-*H*), 7.79-7.75 (m, 2H, aryl-*H*), 7.73 (d, *J* = 6.9 Hz, 1H, aryl-*H*), 7.62 (dd, *J* = 8.2, 2.1 Hz, 1H, aryl-*H*), 7.46 (d, *J* = 6.8 Hz, 1H, aryl-*H*), 7.40-7.31 (m, 2H, aryl-*H*), 6.50 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 1.55 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (aryl-C), 153.9 (aryl-C), 141.1 (aryl-C), 139.6 (aryl-C), 138.4 (aryl-C), 137.8 (aryl-C), 127.5 (aryl-C), 127.3 (aryl-C)), 127.1 (aryl-C), 122.8 (aryl-C), 120.8 (aryl-C), 120.1 (aryl-C), 118.2 (aryl-C), 114.4 (aryl-C), 107.7 (aryl-C), 47.3 (*C*(CH_3)$_2$), 27.2 (C(*C*H_3)$_2$).

These spectroscopic data correspond to reported data.[5]



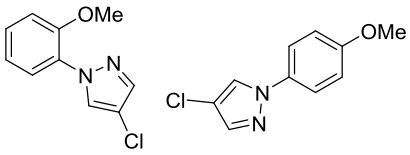
4-chloro-1-(2-methoxyphenyl)-1*H*-pyrazole (23a). 4-chloro-1-(4-methoxyphenyl)-1*H*-pyrazole (23b). 23a and **23b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (15.6 mg, 41%). The *ortho* : *para* ratio of the inseparable mixture was 7:1 as determined by ^{1}H NMR of the isolated product.

23a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H, aryl-*H*), 7.68 (dd, *J* = 7.8, 1.7 Hz, 1H, aryl-*H*), 7.51 (s, 1H, aryl-*H*), 7.27 (td, *J* = 7.9, 1.6 Hz, 1H, aryl-*H*), 7.07-7.00 (m, 2H, aryl-*H*), 3.88 (s, 3H, O*C*H_3), 2.16 (s, 3H, Ar*C*H_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3 (aryl-*C*), 140.9 (aryl-*C*), 130.3 (aryl-*C*), 130.0 (aryl-*C*), 127.8 (aryl-*C*), 125.1 (aryl-*C*), 121.3 (aryl-*C*), 116.7 (aryl-*C*), 112.3 (aryl-*C*), 56.0 (O*C*H_3), 9.1 (Ar*C*H_3).

23b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H, aryl-*H*), 7.54 (d, *J* = 9.1 Hz, 2H, aryl-

H), 7.49 (s, 1H, aryl-*H*), 6.95 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 3.83 (s, 3H, OC*H*$_3$), 2.15 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (aryl-*C*), 141.3 (aryl-*C*), 134.3 (aryl-*C*), 125.6 (aryl-*C*), 120.5 (aryl-*C*), 117.9 (aryl-*C*), 114.6 (aryl-*C*), 55.6 (O*C*H$_3$), 9.0 (Ar*C*H$_3$).

These spectroscopic data correspond to reported data.[1]

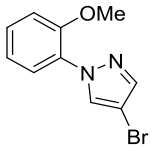


4-chloro-1-(2-methoxyphenyl)-1*H*-pyrazole (24a). 4-chloro-1-(4-methoxyphenyl)-1*H*-pyrazole (24b). 24a and **24b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (24.4 mg, 58%). The *ortho* : *para* ratio of the inseparable mixture was 14:1 as determined by ^{1}H NMR of the isolated product.

24a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H, aryl-*H*), 7.70 (d, *J* = 7.9 Hz, 1H, aryl-*H*), 7.62 (s, 1H, aryl-*H*), 7.31 (t, *J* = 7.8 Hz, 1H, aryl-*H*), 7.09-7.01 (m, 2H, aryl-*H*), 3.89 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0 (aryl-*C*), 138.5 (aryl-*C*), 129.6 (aryl-*C*), 129.3 (aryl-*C*), 128.5 (aryl-*C*), 124.7 (aryl-*C*), 121.2 (aryl-*C*), 112.3 (aryl-*C*), 110.7 (aryl-*C*), 55.9 (O*C*H$_3$).

24b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H, aryl-*H*), 7.62 (s, 1H, aryl-*H*), 7.52 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 6.96 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 3.83 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (aryl-*C*), 139.0 (aryl-*C*), 133.5 (aryl-*C*), 131.6 (aryl-*C*), 124.9 (aryl-*C*), 120.7 (aryl-*C*), 114.6 (aryl-*C*), 55.6 (O*C*H$_3$).

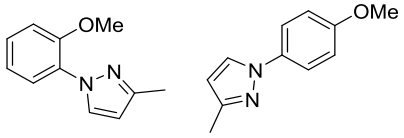
These spectroscopic data correspond to reported data.[6]



4-bromo-1-(2-methoxyphenyl)-1*H*-pyrazole (25). 25 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (22.3 mg, 44%).

25: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H, aryl-*H*), 7.70 (d, *J* = 7.9 Hz, 1H, aryl-*H*), 7.65 (s, 1H, aryl-*H*), 7.31 (t, *J* = 7.8 Hz, 1H, aryl-*H*), 7.09-7.01 (m, 2H, aryl-*H*), 3.89 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1 (aryl-*C*), 140.6 (aryl-*C*), 131.7 (aryl-*C*), 129.3 (aryl-*C*), 128.6 (aryl-*C*), 124.8 (aryl-*C*), 121.3 (aryl-*C*), 112.3 (aryl-*C*), 94.1 (aryl-*C*), 56.0 (O*C*H_3).

These spectroscopic data correspond to reported data.[6]



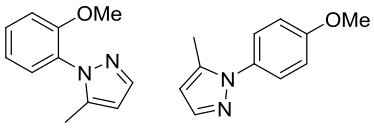
1-(2-methoxyphenyl)-3-methyl-1*H*-pyrazole (26a). 1-(4-methoxyphenyl)-3-methyl-1*H*-pyrazole (26b). 26a and **26b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (14.2 mg, 38%). The *ortho* : *para* ratio of the inseparable mixture was 7:1 as determined by ^{1}H NMR of the isolated product.

26a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 7.70 (d, *J* = 7.7 Hz, 1H, aryl-*H*), 7.30-7.22 (m, 1H, aryl-*H*), 7.08-6.99 (m, 2H, aryl-*H*), 6.21 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 3.86 (s, 3H, OCH_3), 2.38 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3 (aryl-*C*), 149.5 (aryl-*C*), 132.4 (aryl-*C*), 129.9 (aryl-*C*), 127.7 (aryl-*C*),

125.2 (aryl-*C*), 121.3 (aryl-*C*), 112.3 (aryl-*C*), 106.2 (aryl-*C*), 56.0 (O*C*H$_3$), 13.8 (Ar*C*H$_3$).

26b: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (s, 1H, aryl-*H*), 7.54 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.94 (d, *J* = 9.0 Hz, 2H, aryl-*H*), 6.21 (d, *J* = 2.4 Hz, 1H, aryl-*H*), 3.83 (s, 3H, OC*H*$_3$), 2.38 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.0 (aryl-*C*), 150.1 (aryl-*C*), 134.2 (aryl-*C*), 127.6 (aryl-*C*), 120.7 (aryl-*C*), 114.6 (aryl-*C*), 107.1 (aryl-*C*), 55.7 (O*C*H$_3$), 13.8 (Ar*C*H$_3$).

These spectroscopic data correspond to reported data.[1]



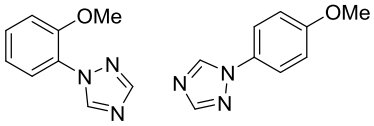
1-(2-methoxyphenyl)-5-methyl-1*H*-pyrazole (26c). 1-(4-methoxyphenyl)-5-methyl-1*H*-pyrazole (26d). 26c and **26d** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (10.0 mg, 27%). The *ortho* : *para* ratio of the inseparable mixture was 1:1 as determined by ^{1}H NMR of the isolated product.

26c: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (s, 1H, aryl-*H*), 7.41 (td, *J* = 8.0, 1.8 Hz, 1H, aryl-*H*), 7.33 (d, *J* = 4.1 Hz, 1H, aryl-*H*), 7.08-7.00 (m, 2H, aryl-*H*), 6.17 (s, 1H, aryl-*H*), 3.79 (s, 3H, OC*H*$_3$), 2.15 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 154.8 (aryl-*C*), 140.8 (aryl-*C*), 139.9 (aryl-*C*), 130.3 (aryl-*C*), 129.2 (aryl-*C*), 128.7 (aryl-*C*), 120.9 (aryl-*C*), 112.2 (aryl-*C*), 105.3 (aryl-*C*), 55.9 (O*C*H$_3$), 11.4 (Ar*C*H$_3$).

26d: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (s, 1H, aryl-*H*), 7.34 (d, *J* = 8.8 Hz, 2H, aryl-*H*), 6.97 (d, *J* = 8.9 Hz, 2H, aryl-*H*), 6.17 (s, 1H, aryl-*H*), 3.85 (s, 3H, ArC*H*$_3$), 2.29 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.1 (aryl-*C*), 139.6 (aryl-*C*), 138.9

(aryl-*C*), 133.1 (aryl-*C*), 126.5 (aryl-*C*), 114.3 (aryl-*C*), 106.4 (aryl-*C*), 55.7 (O*C*H_3) , 12.3 (Ar*C*H_3).

These spectroscopic data correspond to reported data.[1]

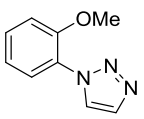


1-(2-methoxyphenyl)-1H-1,2,4-triazole (27a). 1-(4-methoxyphenyl)-1H-1,2,4-triazole (27b). 27a and **27b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as pale yellow oil (15.2 mg, 43%). The *ortho* : *para* ratio of the inseparable mixture was 2:1 as determined by ^{1}H NMR of the isolated product.

27a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, aryl-*H*), 8.06 (d, *J* = 2.0 Hz, 1H, aryl-*H*), 7.35 (t, *J* = 7.8 Hz, 1H, aryl-*H*), 7.08 (t, *J* = 8.2 Hz, 2H, aryl-*H*), 6.99 (d, *J* = 8.5 Hz, 1H, aryl-*H*), 3.90 (s, 2H, O*C*H_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3 (aryl-*C*), 150.9 (aryl-*C*), 144.6 (aryl-*C*), 129.1 (aryl-*C*), 126.4 (aryl-*C*), 124.5 (aryl-*C*), 121.3 (aryl-*C*), 112.2 (aryl-*C*), 56.0 (O*C*H_3).

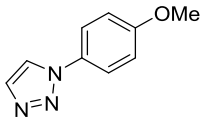
27b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H, aryl-*H*), 8.06 (d, *J* = 2.0 Hz, 1H, aryl-*H*), 7.76 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.55 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 3.84 (s, 3H, O*C*H_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5 (aryl-*C*), 152.4 (aryl-*C*), 140.8 (aryl-*C*), 130.5 (aryl-*C*), 121.9 (aryl-*C*), 114.8 (aryl-*C*), 55.6 (O*C*H_3).

These spectroscopic data correspond to reported data.[1]



1-(2-methoxyphenyl)-1*H*-1,2,3-triazole (28a). 28a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (3:1) to give the title compound as colorless oil (20.5 mg, 59%).

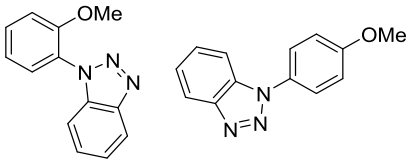
28a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, aryl-*H*), 7.81 (s, 1H, aryl-*H*), 7.78 (dd, *J* = 7.9, 1.6 Hz, 1H, aryl-*H*), 7.42 (td, *J* = 7.9, 1.6 Hz, 1H, aryl-*H*), 7.14-7.05 (m, 2H, aryl-*H*), 3.88 (s, 2H, O*C*H$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3 (aryl-*C*), 133.3 (aryl-*C*), 130.2 (aryl-*C*), 126.4 (aryl-*C*), 125.8 (aryl-*C*), 125.7 (aryl-*C*), 121.3 (aryl-*C*), 112.4 (aryl-*C*), 56.1 (O*C*H$_3$).



1-(4-methoxyphenyl)-1*H*-1,2,3-triazole (28b). 28b were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (3:1) to give the title compound as white solid (5.2 mg, 15%).

28b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H, aryl-*H*), 7.84 (s, 1H, aryl-*H*), 7.64 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 7.03 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 3.87 (s, 3H, O*C*H$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (aryl-*C*), 134.4 (aryl-*C*), 130.7 (aryl-*C*), 122.5 (aryl-*C*), 122.0 (aryl-*C*), 114.9 (aryl-*C*), 55.8 (O*C*H$_3$).

These spectroscopic data correspond to reported data.[1]



1-(2-methoxyphenyl)-1*H*-benzo[d][1,2,3]triazole (29a). 1-(4-methoxyphenyl)-1*H*-benzo[d][1,2,3]triazole (29b). 29a and **29b** were synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with

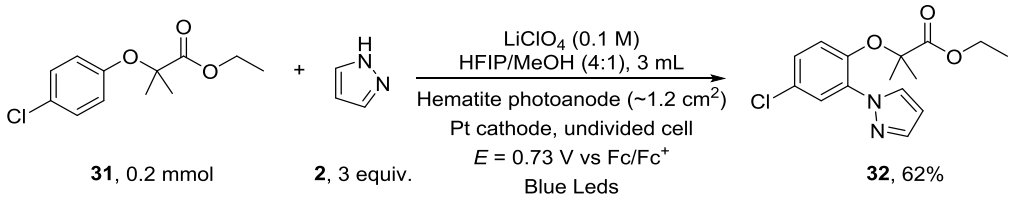
hexane/ethyl acetate (2:1) to give the title compound as pale yellow oil (26.5 mg, 59%). The *ortho* : *para* ratio of the inseparable mixture was 4:1 as determined by ^{1}H NMR of the isolated product.

29a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.54-7.41 (m, 3H, aryl-*H*), 7.37 (t, *J* = 8.6 Hz, 2H, aryl-*H*), 7.16-7.11 (m, 2H, aryl-*H*), 3.77 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7 (aryl-*C*), 145.7 (aryl-*C*), 134.1 (aryl-*C*), 131.1 (aryl-*C*), 128.2 (aryl-*C*), 127.6 (aryl-*C*), 125.3 (aryl-*C*), 123.9 (aryl-*C*), 121.1 (aryl-*C*), 119.9 (aryl-*C*), 112.5 (aryl-*C*), 111.3 (aryl-*C*), 56.0 (O*C*H_3).

29b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.61-7.67 (m, 3H, aryl-*H*), 7.54-7.41 (m, 2H, aryl-*H*), 7.09 (d, *J* = 8.9 Hz, 2H, aryl-*H*), 3.88 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (aryl-*C*), 146.3 (aryl-*C*), 132.7 (aryl-*C*), 130.0 (aryl-*C*), 128.1 (aryl-*C*), 124.6 (aryl-*C*), 124.3 (aryl-*C*), 120.2 (aryl-*C*), 115.0 (aryl-*C*), 110.3 (aryl-*C*), 55.7 (O*C*H_3).

These spectroscopic data correspond to reported data.[1]

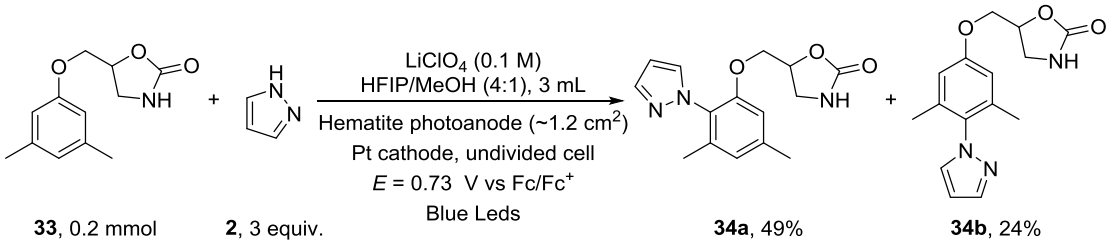
Late-stage Functionalization of Pharmaceuticals



Ethyl 2-(4-chloro-2-(1*H*-pyrazol-1-yl)phenoxy)-2-methylpropanoate (32). 32 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as pale yellow oil (38.2 mg, 62%).

32: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.78 (d, *J* = 2.7 Hz, 1H, aryl-*H*), 7.69 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.15 (dd, *J* = 8.8, 2.7 Hz, 1H, aryl-*H*), 6.95 (d, *J* = 8.9 Hz, 1H, aryl-*H*), 6.41 (t, *J* = 2.2 Hz, 1H, aryl-*H*), 4.22 (q, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_3$), 1.42 (s, 6H, C(C*H*$_3$)$_2$), 1.26 (t, *J* = 7.1 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5 (*C*=O), 145.5 (aryl-*C*), 140.7 (aryl-*C*), 134.2 (aryl-*C*), 131.9 (aryl-*C*), 128.7 (aryl-*C*), 127.2 (aryl-*C*), 125.5 (aryl-*C*), 121.6 (aryl-*C*), 106.8 (aryl-*C*), 81.7 (O*C*(CH$_3$)$_2$), 61.8(O*C*H$_2$CH$_3$), 24.9 (OC(*C*H$_3$)$_2$), 14.2 (OCH$_2$*C*H$_3$).

HRMS-ESI (m/z): Calcd for [($C_{15}H_{17}ClN_2O_3$+H)+], 309.1000; found: 309.1007.



5-((3,5-dimethyl-2-(1*H*-pyrazol-1-yl)phenoxy)methyl)oxazolidin-2-one (34a). 34a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with ethyl acetate to give the title compound as white solid (28.3 mg, 49%).

34a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.9 Hz, 1H, aryl-*H*), 7.48 (d, *J* = 2.3

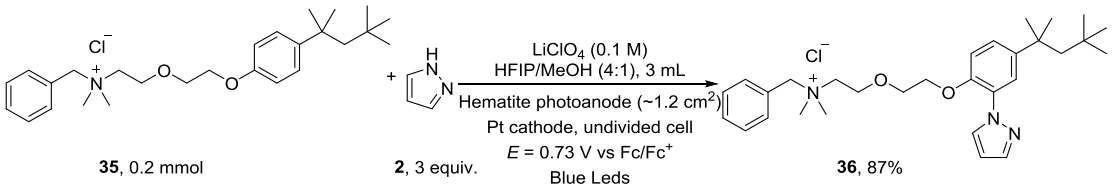
Hz, 1H, aryl-*H*), 6.78 (s, 1H, aryl-*H*), 6.67 (s, 1H, aryl-*H*), 6.42 (s, 1H, aryl-*H*), 5.79 (s, 1H, N*H*), 4.73 (m, 1H, COOC*H*), 4.08 (dd, *J* = 10.3, 4.6 Hz, 1H, ArOCH_2), 3.98 (dd, *J* = 10.3, 3.8 Hz, 1H, ArOCH_2), 3.47 (t, *J* = 8.9 Hz, 1H, CH_2NH), 3.26 (dd, *J* = 8.6, 6.1 Hz, 1H, CH_2NH), 2.36 (s, 3H, ArCH_3), 2.05 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (*C*=O), 153.8 (aryl-*C*), 140.1 (aryl-*C*), 140.0 (aryl-*C*), 137.6 (aryl-*C*), 132.2 (aryl-*C*), 127.5 (aryl-*C*), 124.5 (aryl-*C*), 112.2 (aryl-*C*), 105.8 (aryl-*C*), 74.0 (COO*C*H), 69.1 (ArO*C*H_2), 42.1 (*C*H_2NH), 21.7 (Ar*C*H3), 17.3 (Ar*C*H3).

HRMS-ESI (m/z): Calcd for [($C_{15}H_{17}N_3O_3$+H)+], 288.1343; found: 288.1348.

5-((3,5-dimethyl-4-(1H-pyrazol-1-yl)phenoxy)methyl)oxazolidin-2-one (34b). 34b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, hexane/ethyl acetate (5:1) to give the title compound as white solid (13.7 mg, 24%).

34b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H, aryl-*H*), 7.42 (s, 1H, aryl-*H*), 6.67 (s, 2H, aryl-*H*, aryl-*H*), 6.43 (s, 1H, aryl-*H*), 5.62 (s, 1H, N*H*), 4.97 (m, 1H, COOC*H*), 4.16 (d, *J* = 4.8 Hz, 2H, ArOCH_2), 3.78 (t, *J* = 8.8 Hz, 1H, CH_2NH), 3.61 (t, *J* = 7.4 Hz, 1H, CH_2NH), 1.96 (s, 6H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 (*C*=O), 157.9 (aryl-*C*), 140.1 (aryl-*C*), 137.9 (aryl-*C*), 133.5 (aryl-*C*), 131.1 (aryl-*C*), 113.9 (aryl-*C*), 105.9 (aryl-*C*), 74.1 (COO*C*H), 68.1 (ArO*C*H_2), 42.6 (*C*H_2NH), 16.4 (Ar*C*H3).

HRMS-ESI (m/z): Calcd for [($C_{15}H_{17}N_3O_3$+H)+], 288.1343; found: 288.1346.



Ethyl 2-(4-chloro-2-(1*H*-pyrazol-1-yl)phenoxy)-2-methylpropanoate (36). 36 was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with DCM/MeOH (10:1) to give the title

compound as pale yellow oil (89.8 mg, 87%).

36: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.5 Hz, 1H, aryl-*H*), 7.61 (dd, *J* = 6.1, 2.1 Hz, 2H, aryl-*H*), 7.47-7.35 (m, 5H, aryl-*H*), 7.30-7.25 (m, 1H, aryl-*H*), 6.93 (d, *J* = 8.7 Hz, 1H, aryl-*H*), 6.40 (t, *J* = 2.1 Hz, 1H, aryl-*H*), 4.47 (s, 2H, ArCH_2N), 4.16 (t, *J* = 4.2 Hz, 2H), 3.90 (t, *J* = 4.6 Hz, 2H), 3.83 (t, *J* = 4.2 Hz, 2H), 3.53 (t, *J* = 4.6 Hz, 2H), 2.91 (s, 6H, N(CH_3)$_2$), 1.71 (s, 2H, CH_2C(CH$_3$)$_3$), 1.35 (s, 6H, ArC(CH_3)$_2$), 0.72 (s, 9H, CH$_2$C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0 (aryl-*C*), 144.0 (aryl-*C*), 140.0 (aryl-*C*), 133.3 (aryl-*C*), 131.9 (aryl-*C*), 130.9 (aryl-*C*), 129.3 (aryl-*C*), 129.2 (aryl-*C*), 126.9 (aryl-*C*), 126.0 (aryl-*C*), 123.6 (aryl-*C*), 113.0 (aryl-*C*), 106.5 (aryl-*C*), 69.8, 69.6, 68.3, 65.0, 63.1, 56.8, 50.3, 38.2, 32.4, 31.9, 31.6.

HRMS-ESI (m/z): Calcd for [($C_{30}H_{44}ClN_3O_2$-Cl)+], 478.3428; found: 478.3426.

Supplementary References

1 Romero, N. A., Margrey, K. A., Tay, N. E. & Nicewicz, D. A. Site-selective arene C-H amination via photoredox catalysis. *Science* **349**, 1326-1330 (2015).

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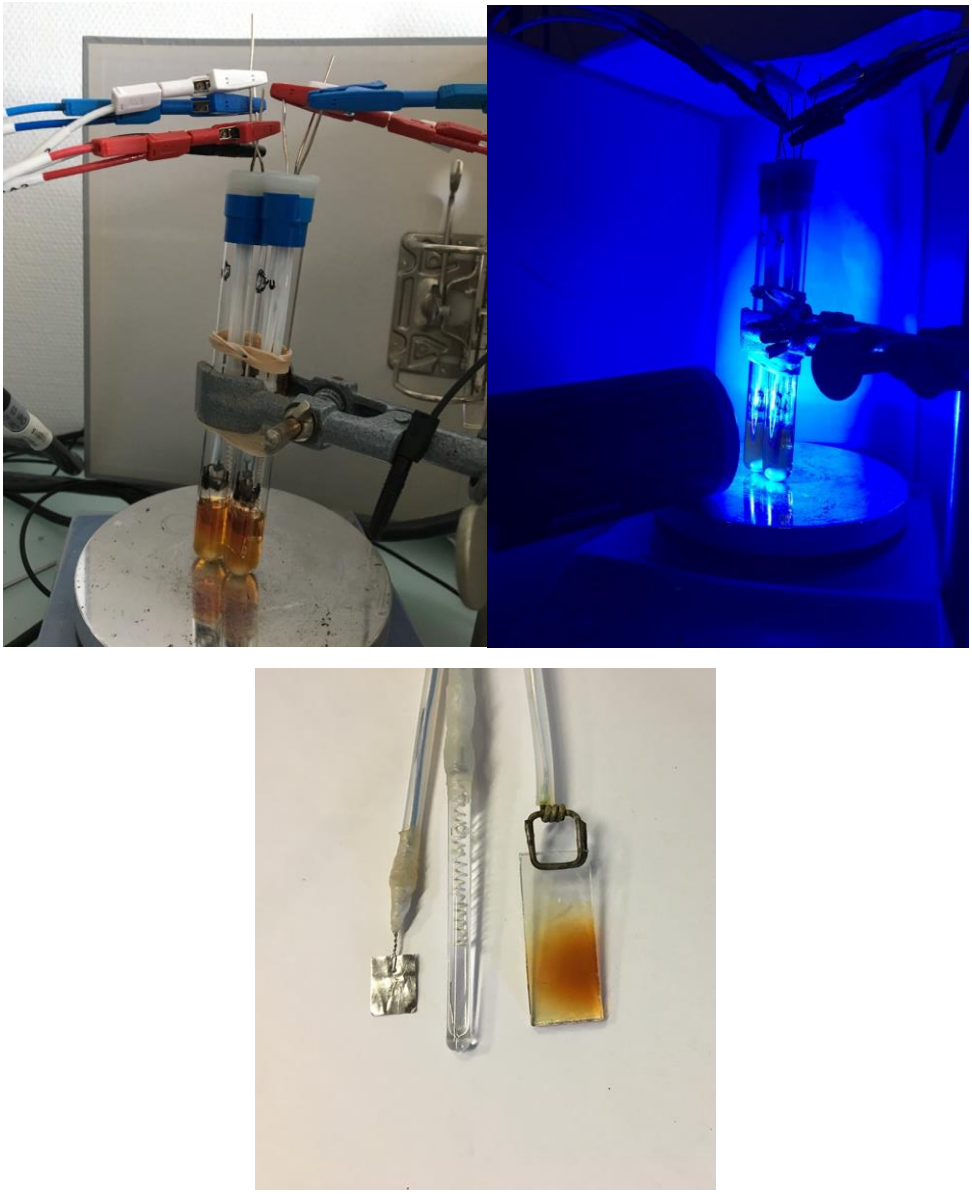
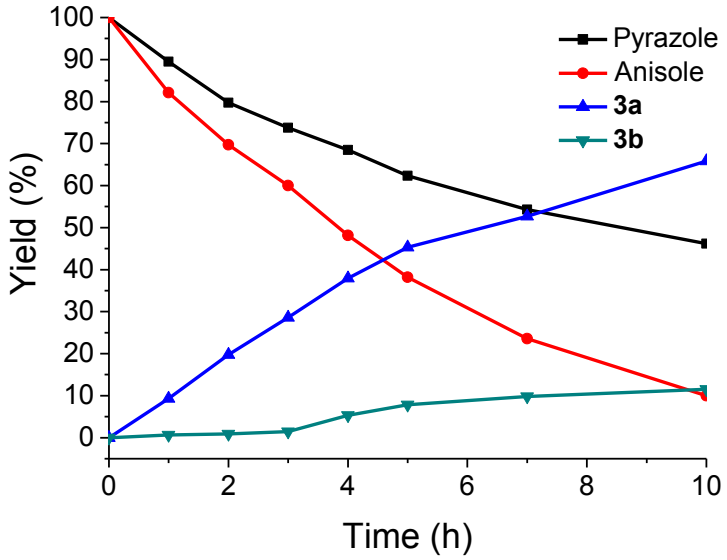
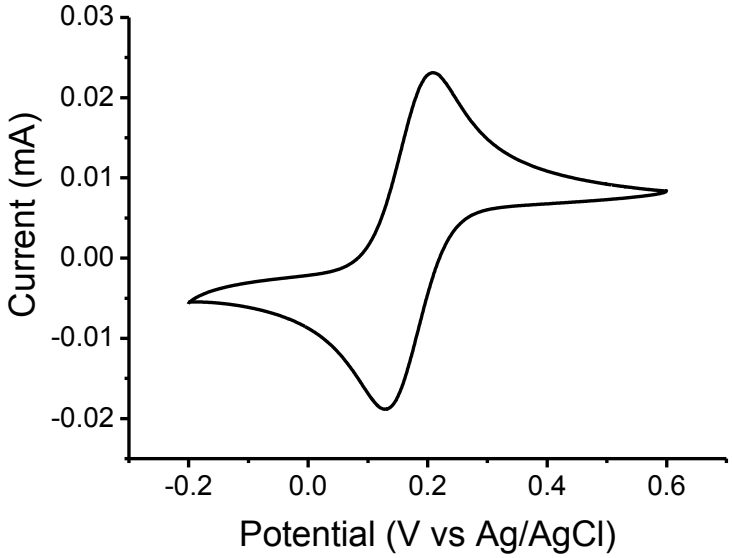
Supplementary Figures



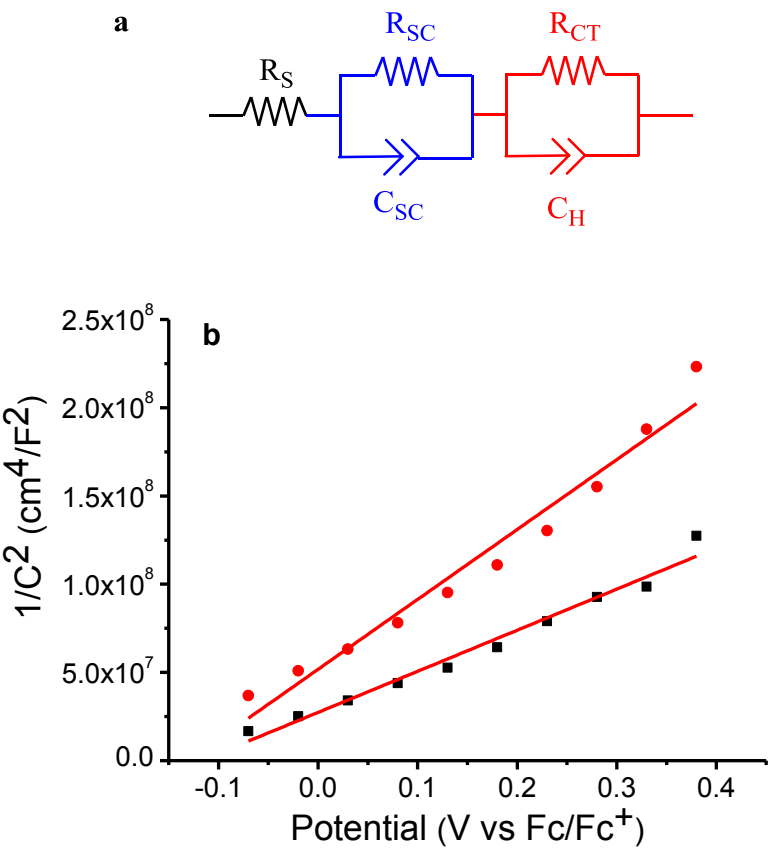
Supplementary Figure 1. Undivided cell for photoelectrochemical oxidation



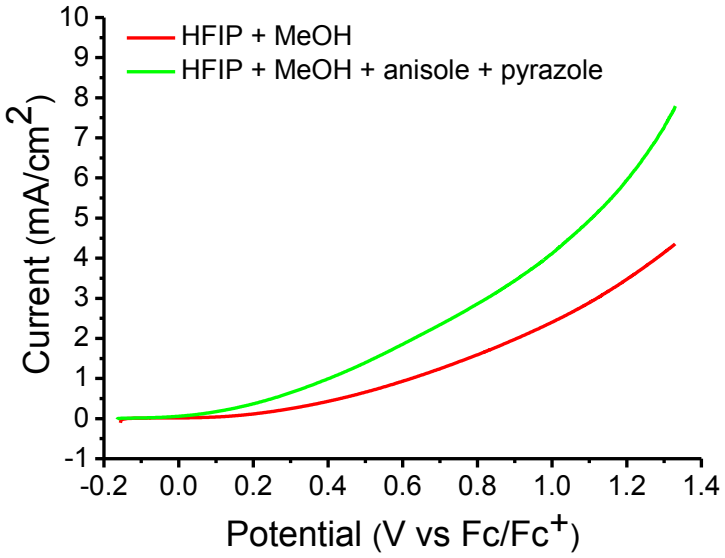
Supplementary Figure 2. Time-dependent concentration profile of reactants and products. Reaction conditions: Anisole (0.2 mmol), Pyrazole (0.4 mmol) in HFIP/MeOH (4:1, 3 mL) containing $LiClO_4$ (0.1 M). Applied potential: E = 0.73 V vs Fc/Fc^+.



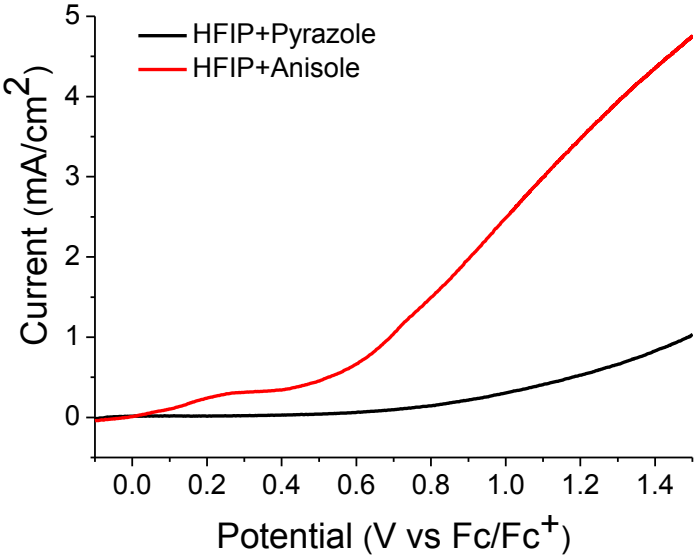
Supplementary Figure 3. CV curve of ferrocene in HFIP/MeOH (3:1) containing $LiClO_4$ (0.1 M). Glassy carbon electrode was used as a working electrode with a Ag/AgCl reference electrode and a Pt counter electrode. Scan rate: 30 mV/s.



Supplementary Figure 4. Electrochemical impedance spectroscopy (EIS) investigation. a. Electronic equivalent circuit representing the photoanode/electrolyte system used for EIS data modeling.[7] R_S represents a circuit series resistance. R_{SC} represent the charge transfer resistance and C_{CS} represent the capacitance of space charge region. R_{CT} represent the semiconductor-electrolyte charge transfer resistance and C_H represent the Helmholtz capacitance. **b**. Mott-Schottky curve of hematite in HFIP/MeOH (4:1) derived from EIS data. Electrochemical impedance spectroscopy (EIS) was conducted on two different hematite samples, and the results are similar.

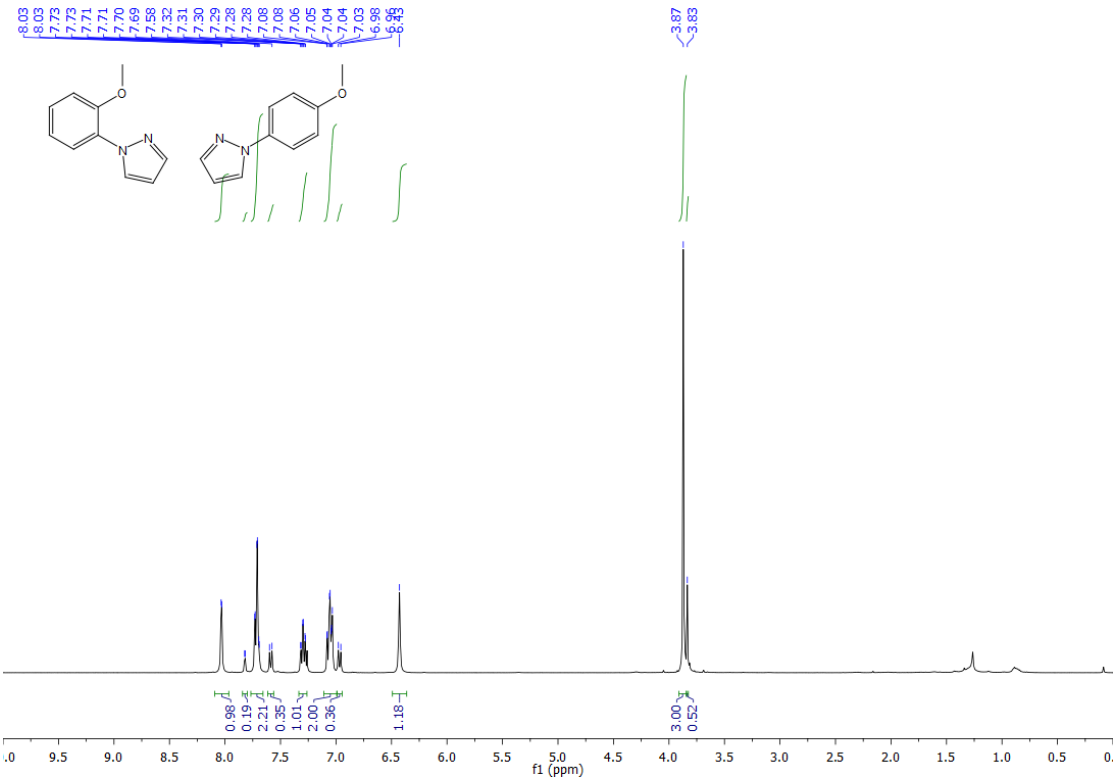


Supplementary Figure 5. LSV curves of PEC oxidation under LED illumination. The electrolyte is 0.3 mmol LiClO4. Photocurrent profiles correspond to the organic solvent alone (HFIP: MeOH = 4:1, 3 mL) (red) and the solvent plus substrates (0.2 mmol anisole and 0.4 mmol pyrazole) (green). Scan rate: 30 mV/s. The oxidation of MeOH appears to occur as a background reaction.

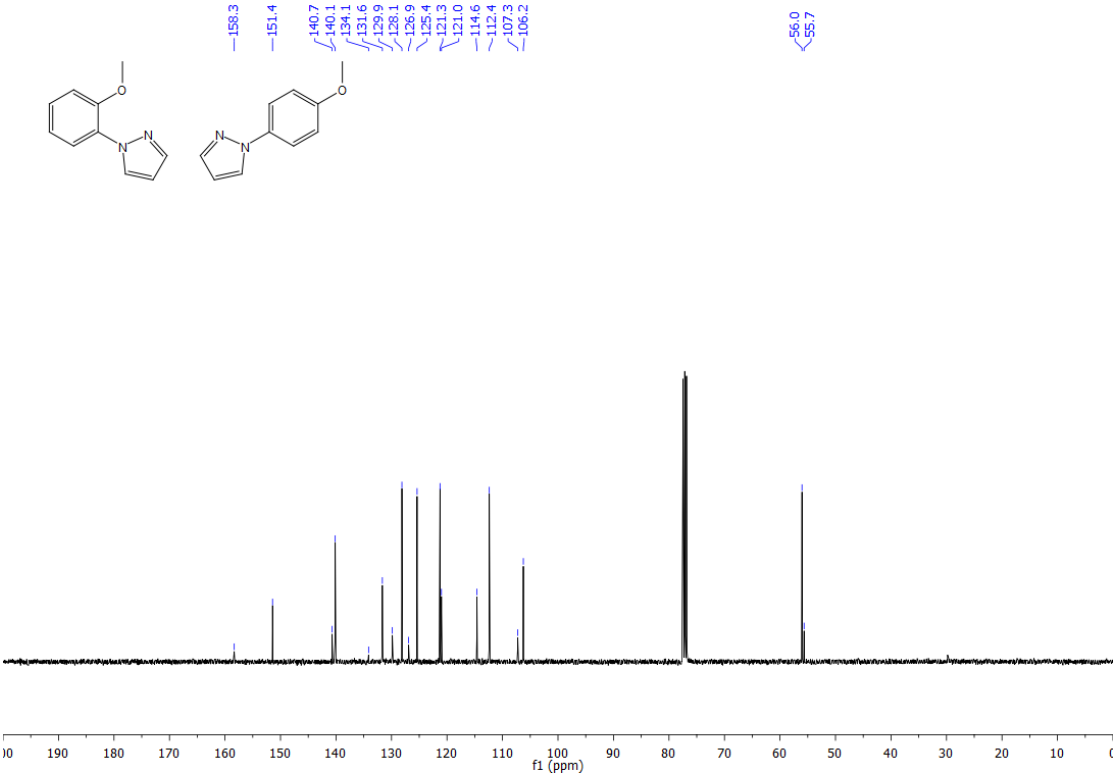


Supplementary Figure 6. LSV curves of PEC oxidation under LED illumination. The electrolyte is 0.3 mmol $TBAPF_6$. Photocurrent profiles correspond to 0.2 mmol anisole in 3 mL HFIP (red) and 0.4 mmol pyrzole in 3 mL HFIP (black). Scan rate: 30 mV/s.

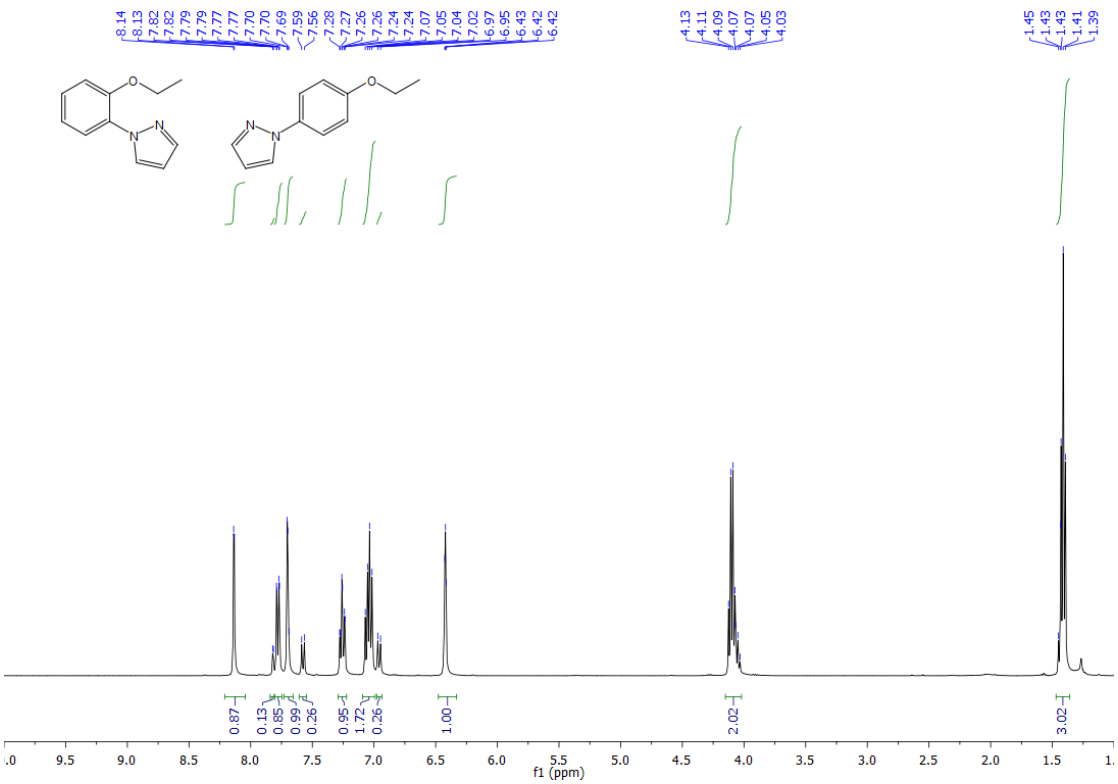
NMR Spectra



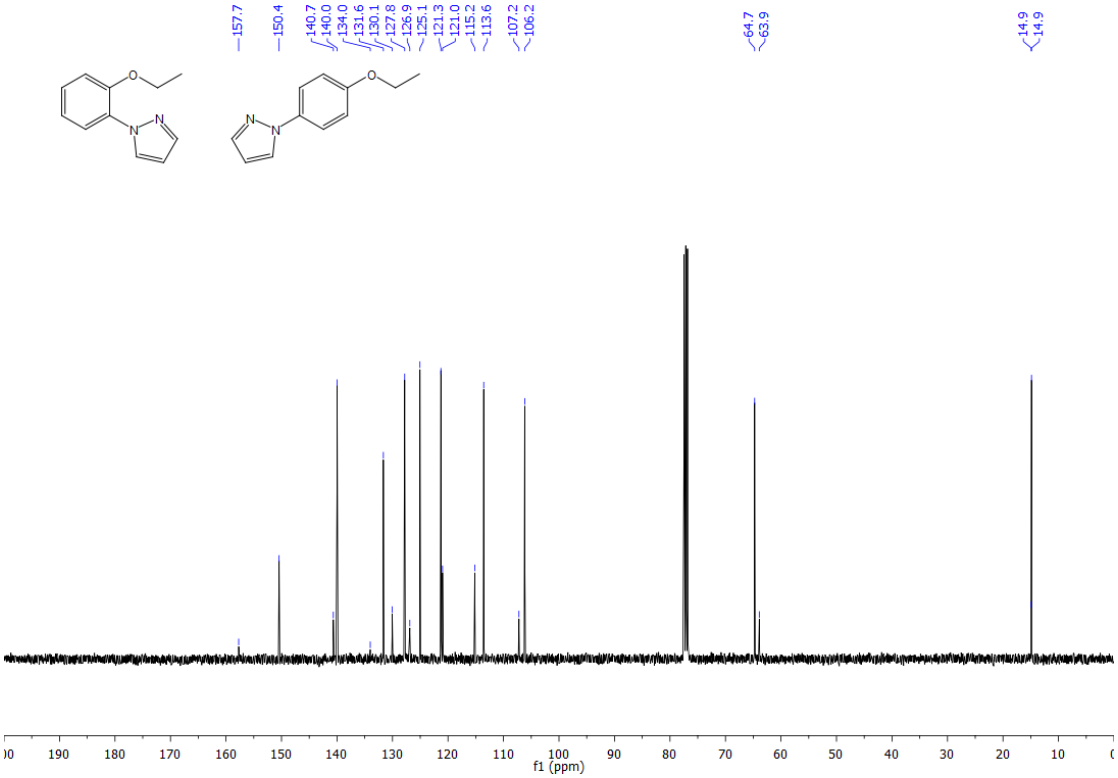
^{1}H NMR (400 MHz, $CDCl_3$) of **3a** and **3b**



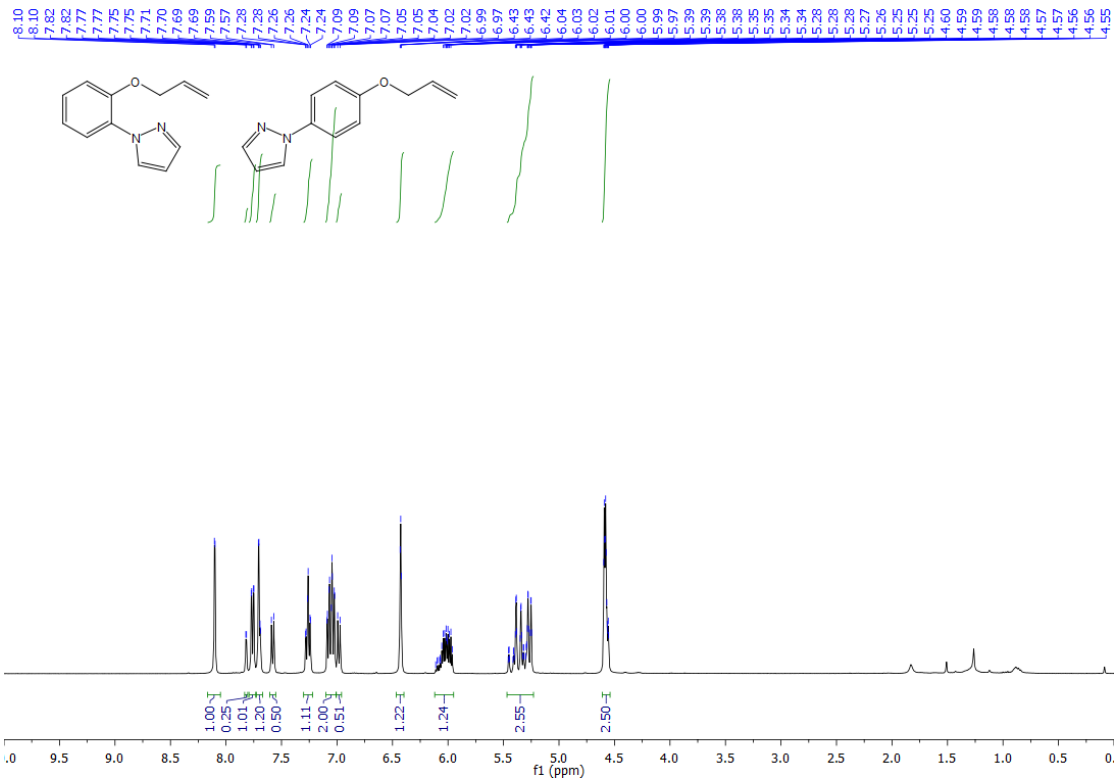
^{13}C NMR (101 MHz, $CDCl_3$) of **3a** and **3b**



^{1}H NMR (400 MHz, $CDCl_3$) of **4a** and **4b**



^{13}C NMR (101 MHz, $CDCl_3$) of **4a** and **4b**



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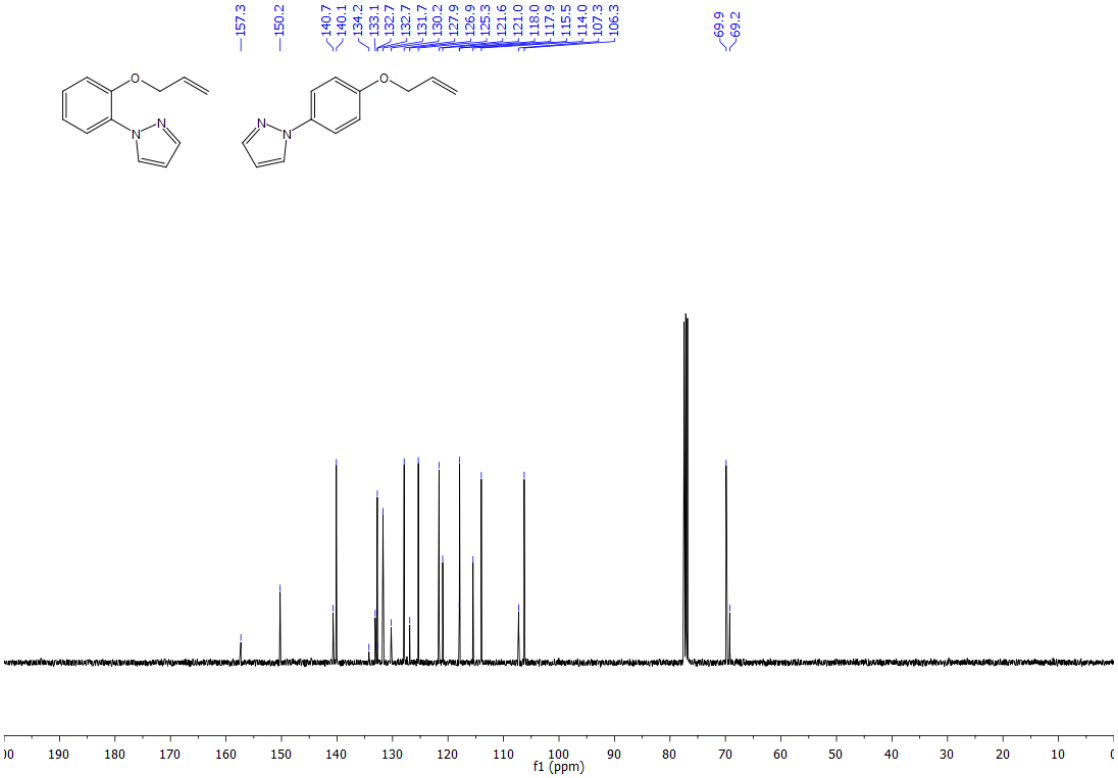
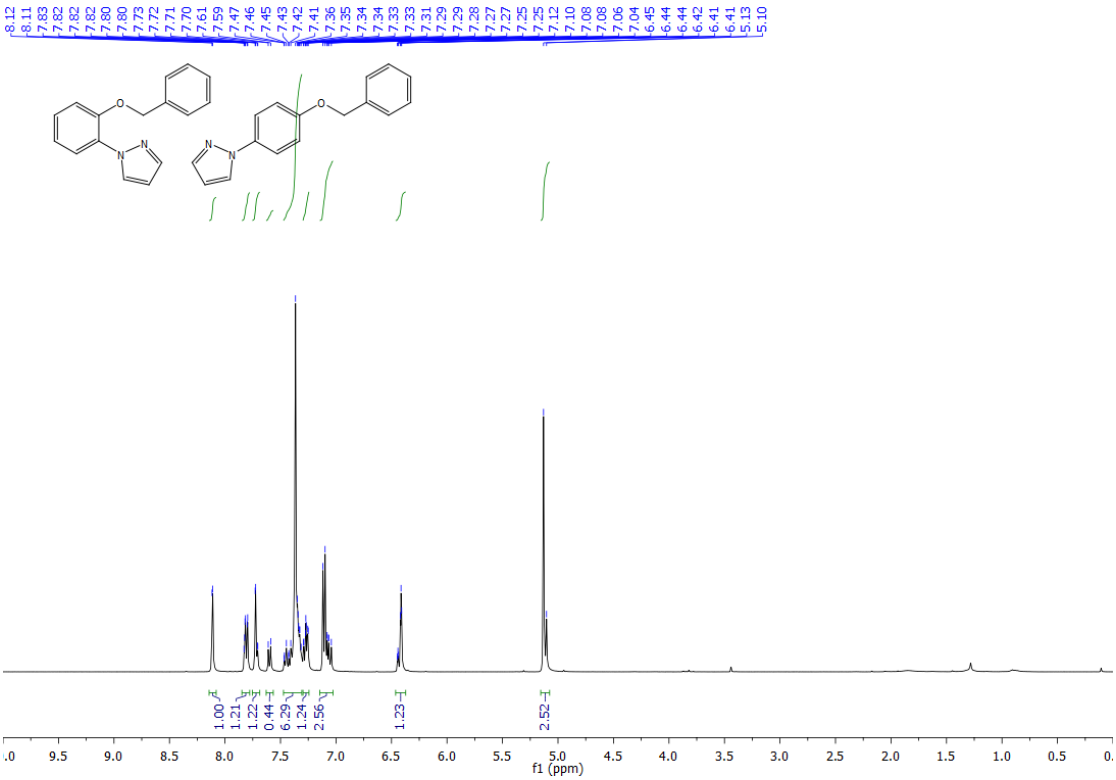
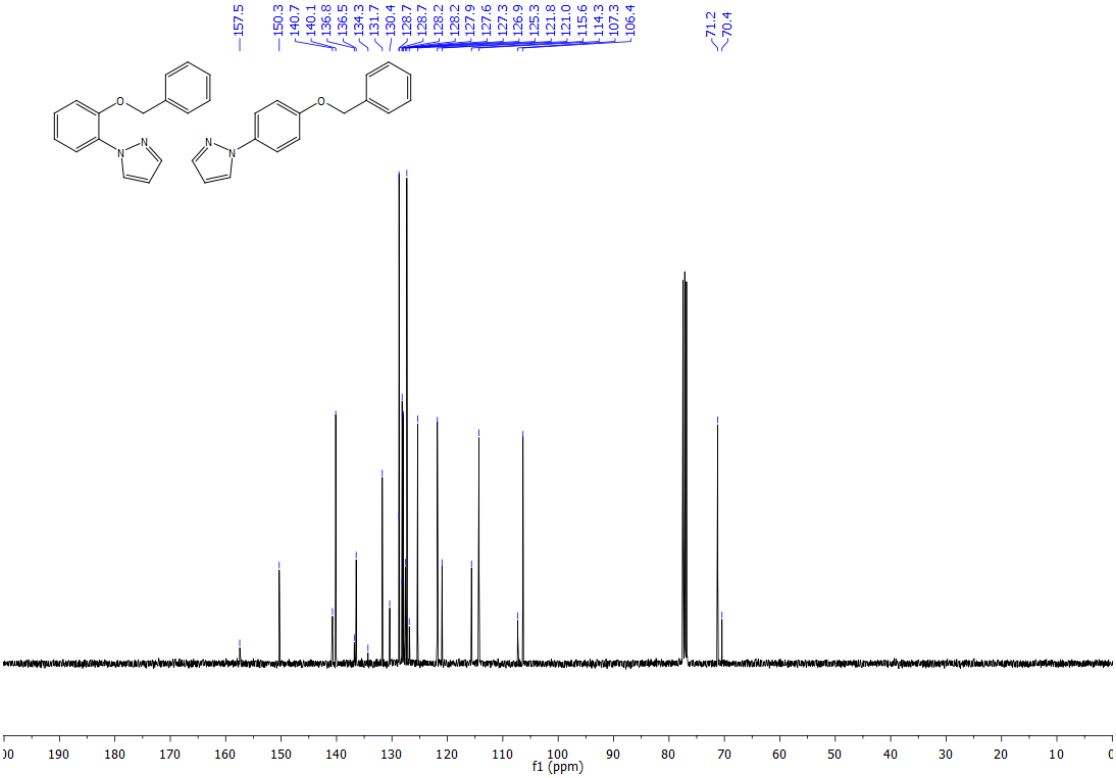


^{13}C NMR (101 MHz, $CDCl_3$) of **5a** and **5b**



^{1}H NMR (400 MHz, $CDCl_3$) of **6a** and **6b**



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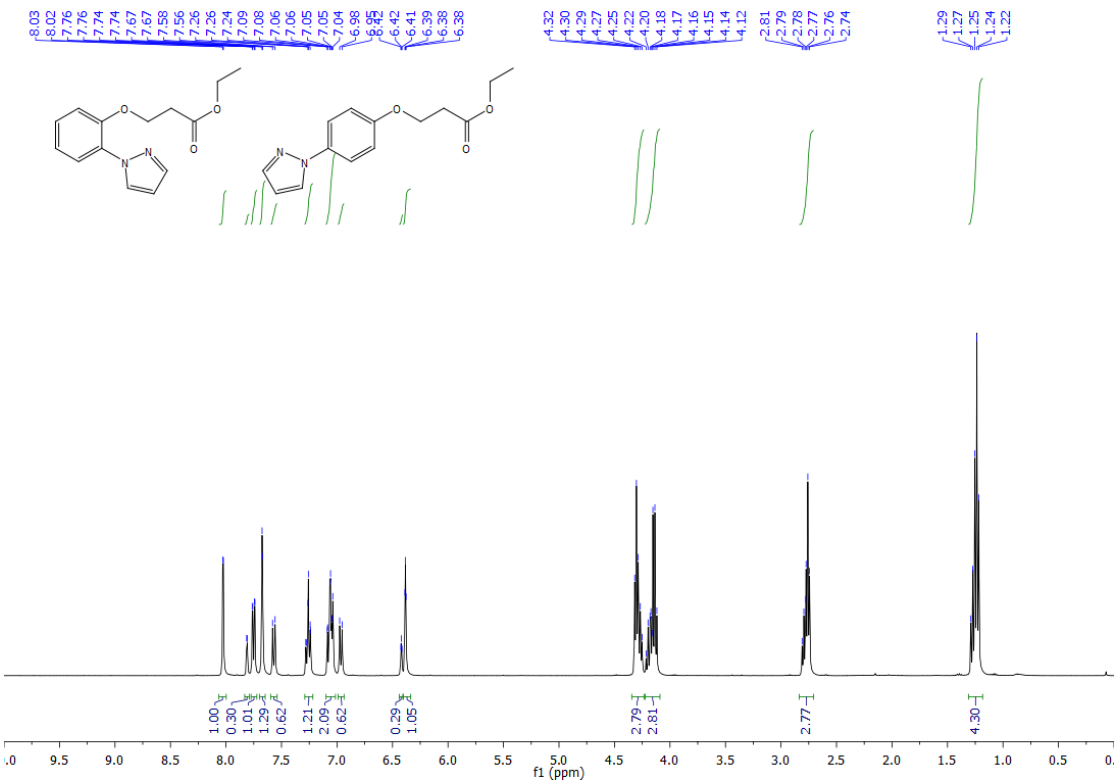

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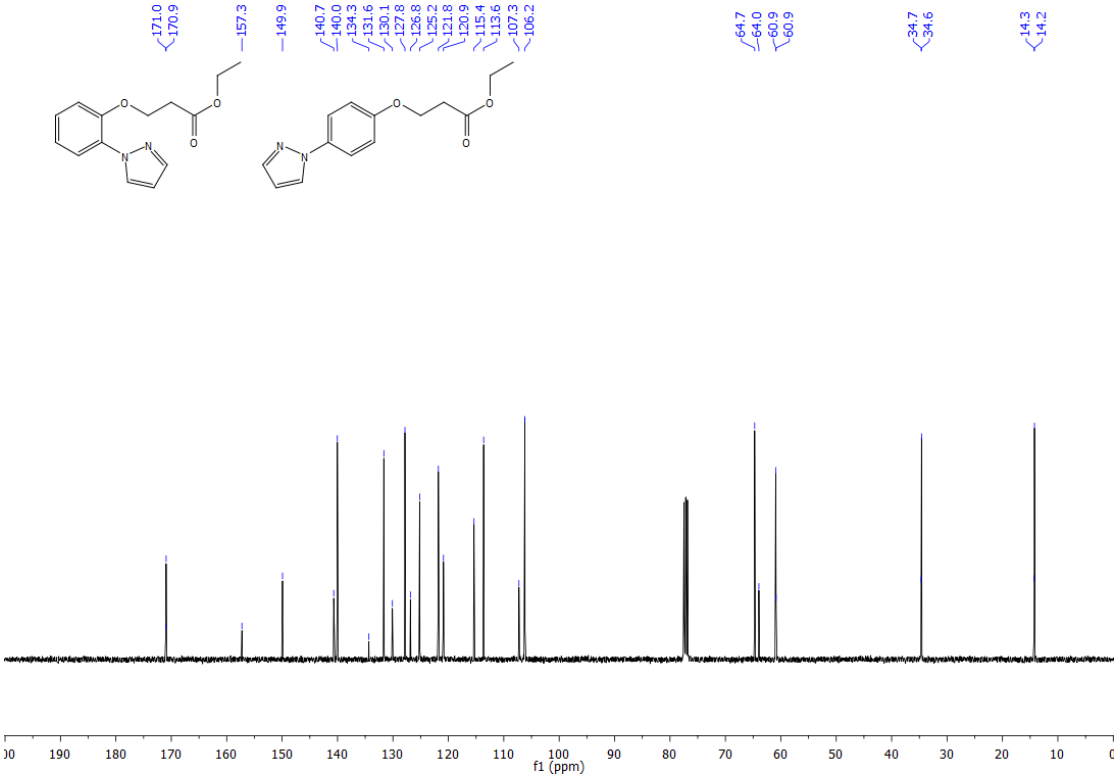

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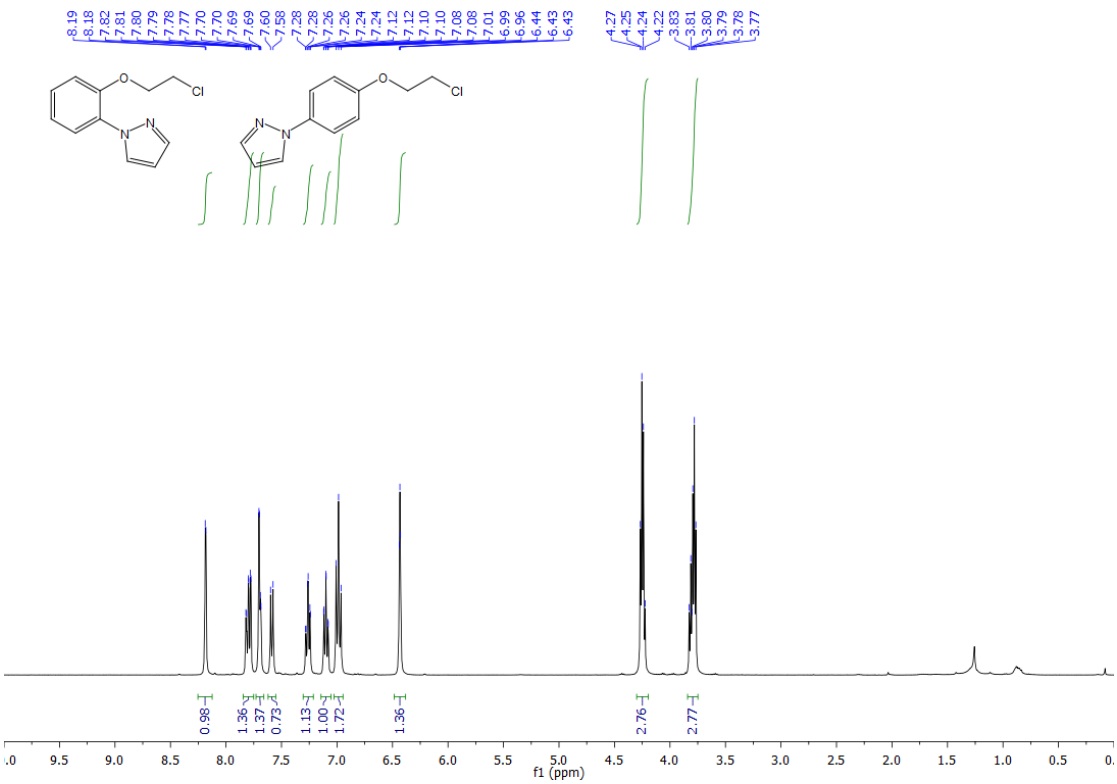

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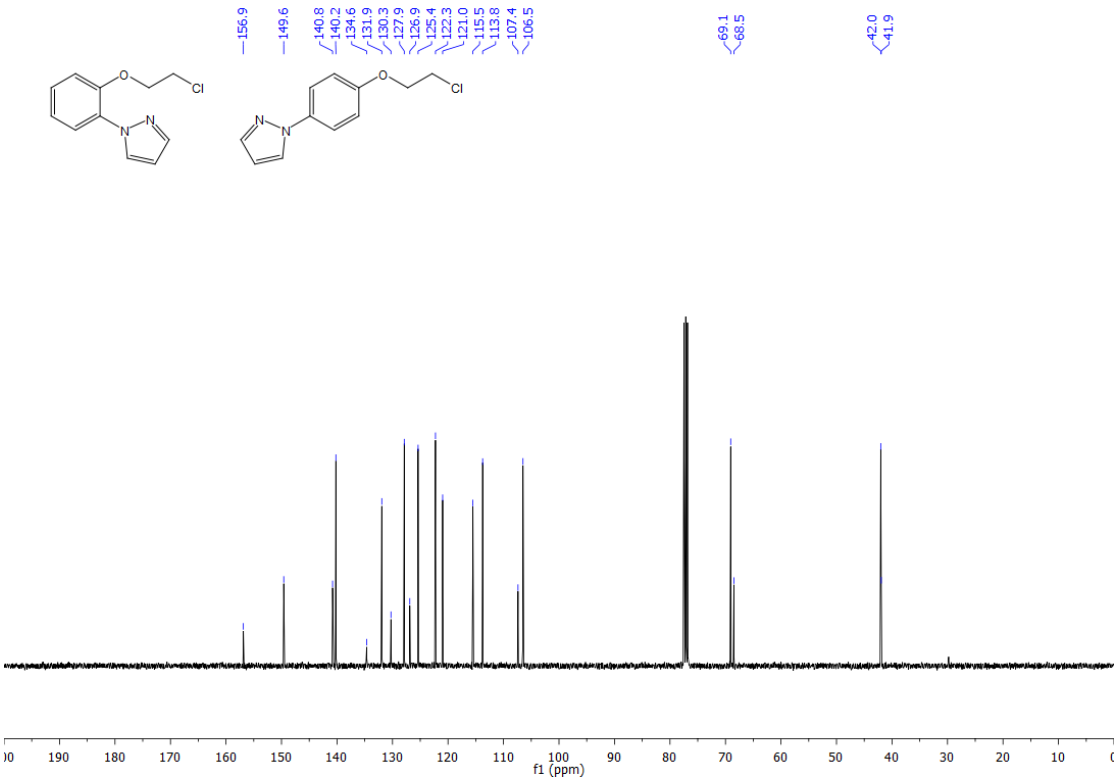
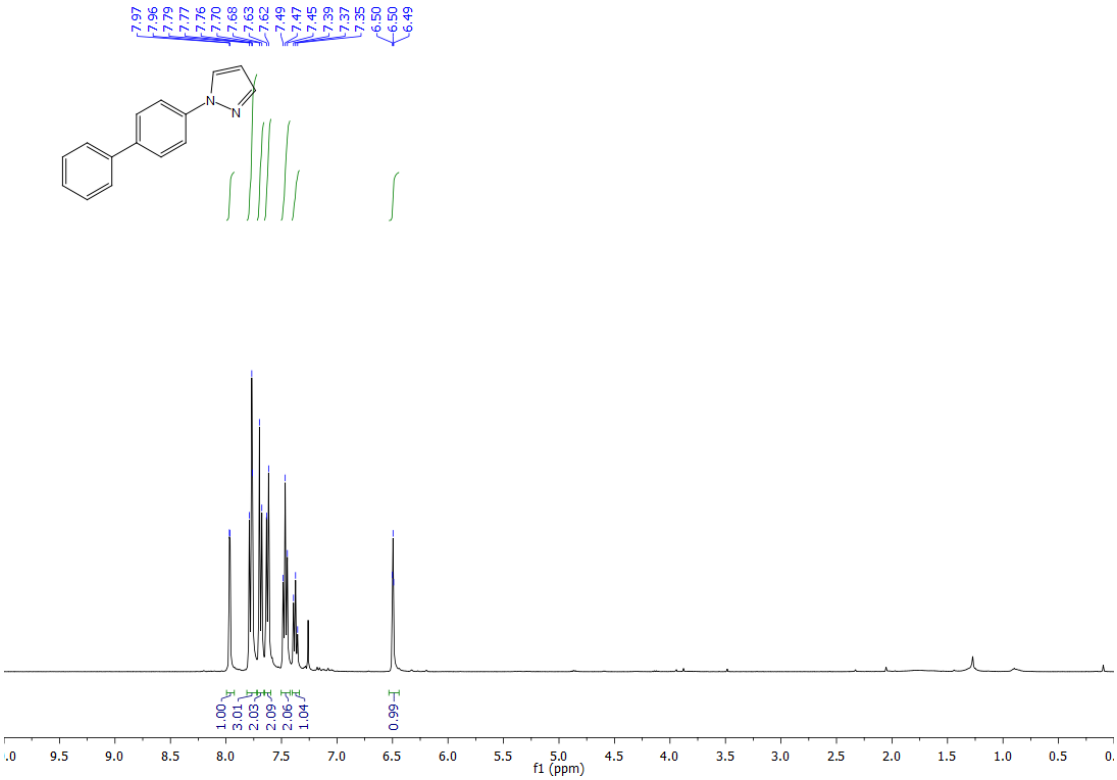
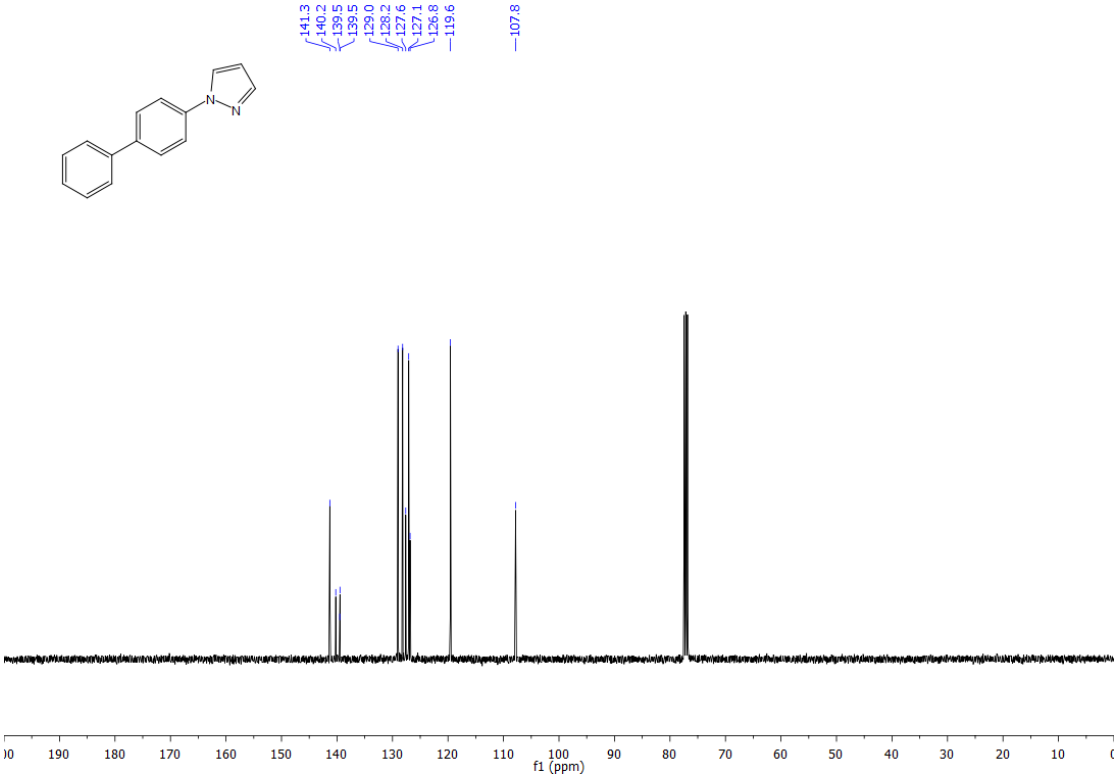


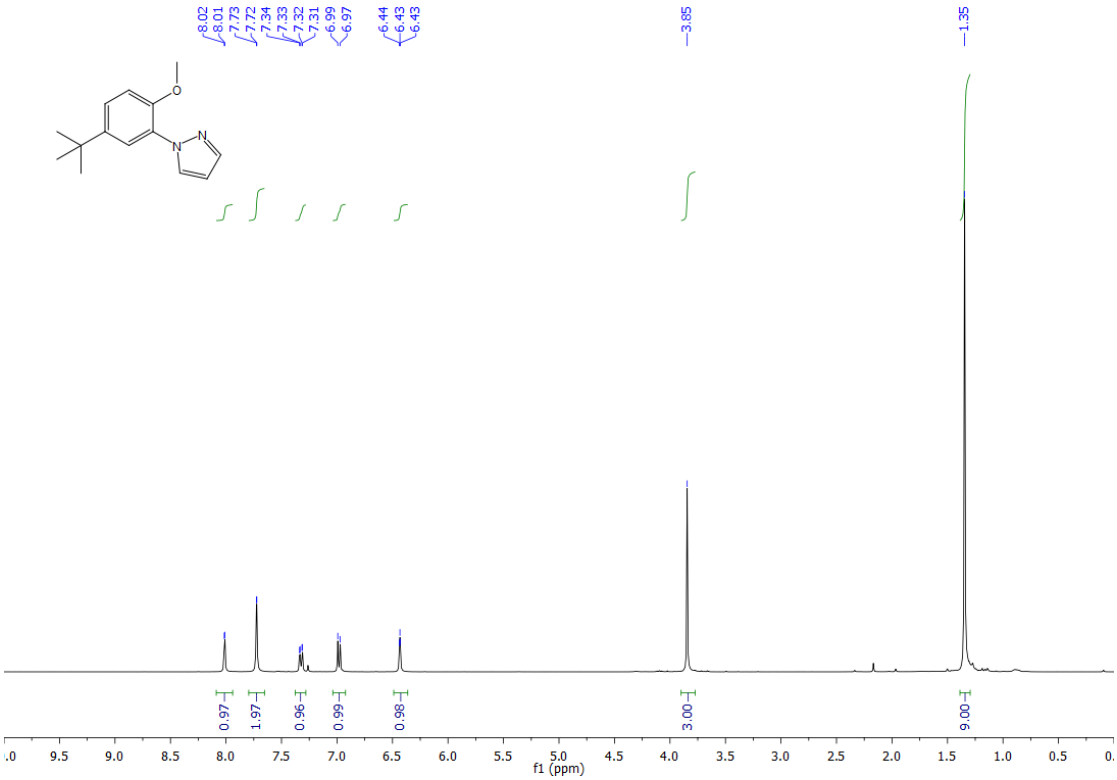
^{13}C NMR (101 MHz, $CDCl_3$) of **8a** and **8b**



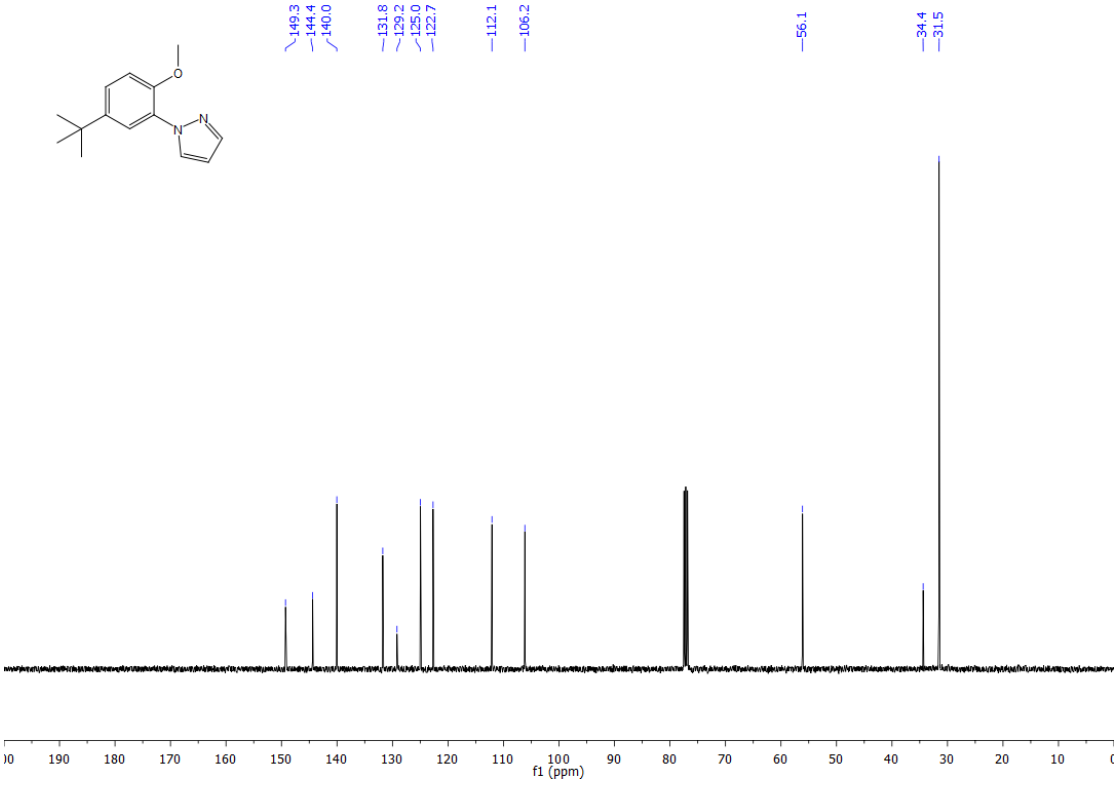
^{1}H NMR (400 MHz, $CDCl_3$) of **9**



^{13}C NMR (101 MHz, $CDCl_3$) of **9**



^{1}H NMR (400 MHz, $CDCl_3$) of **10**



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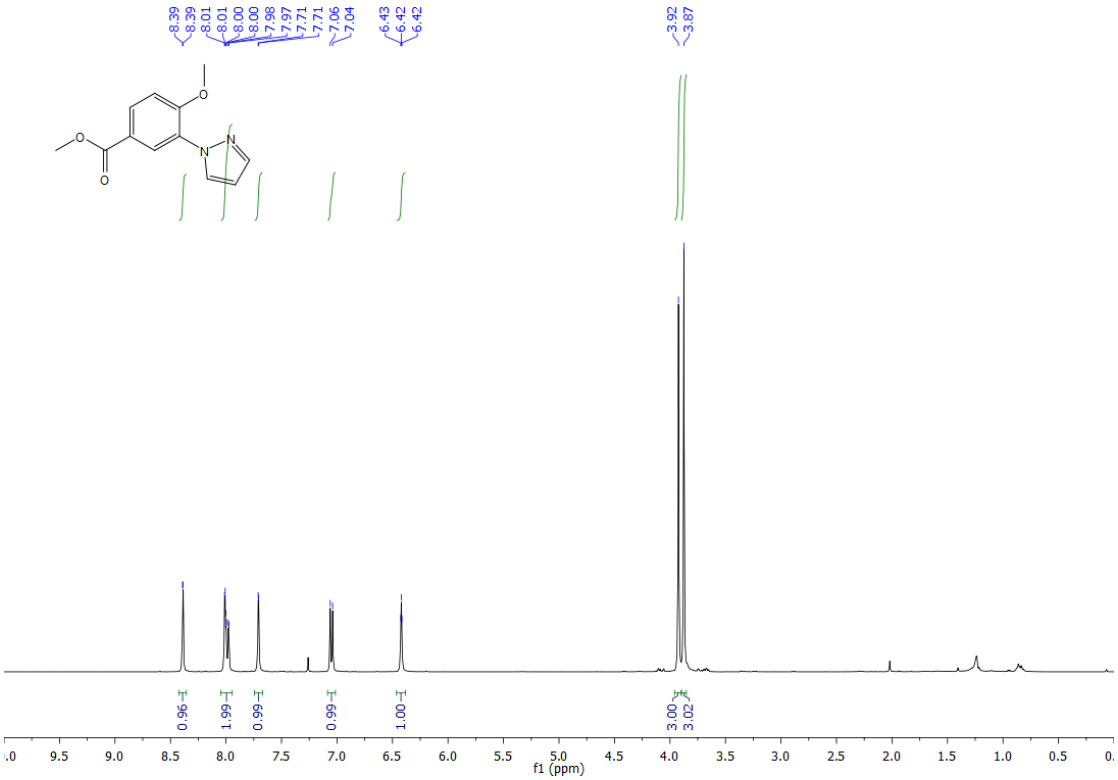

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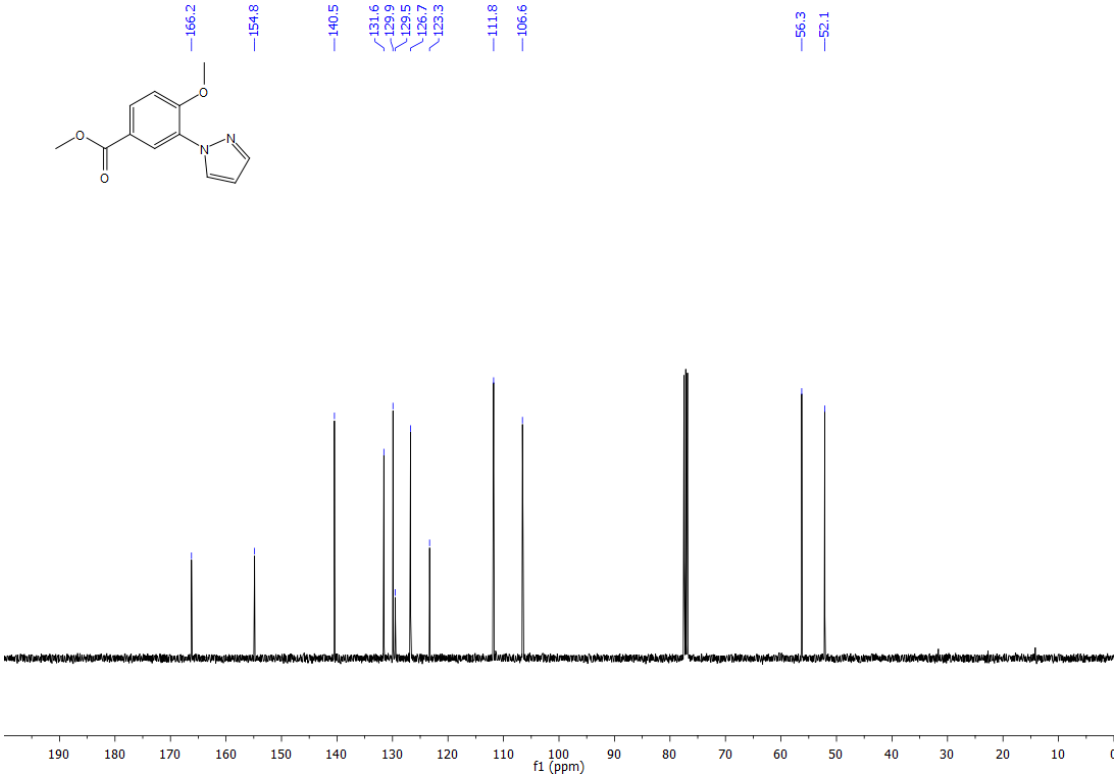

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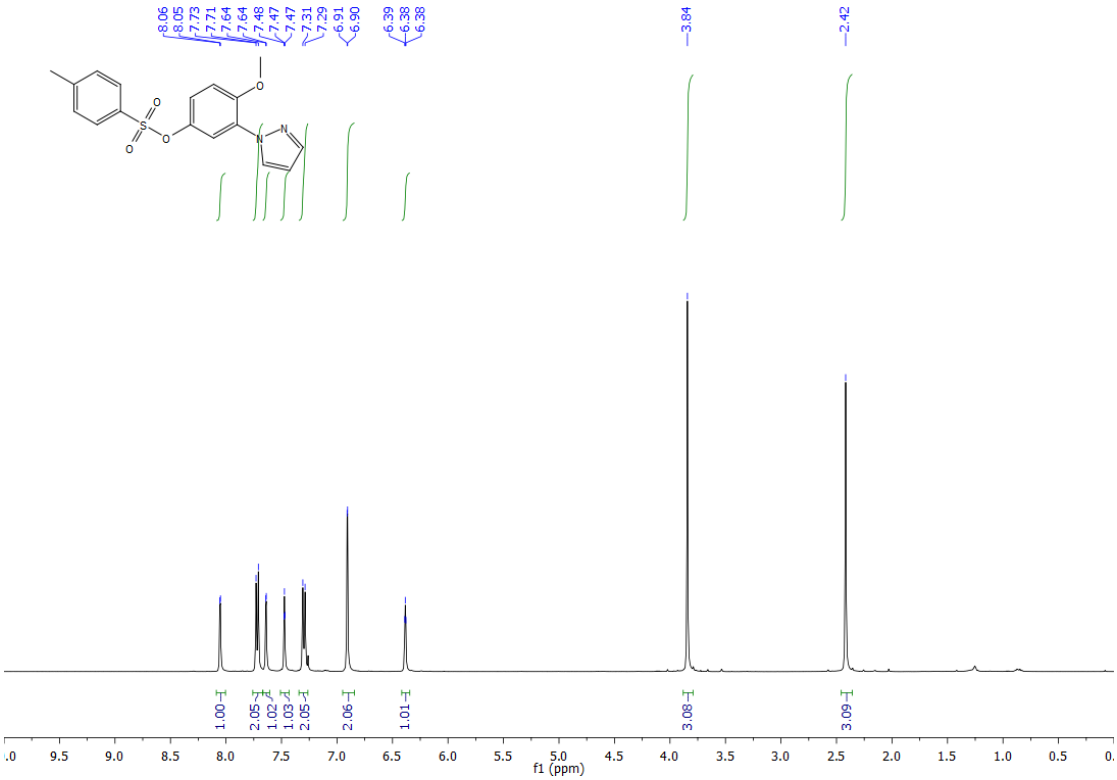

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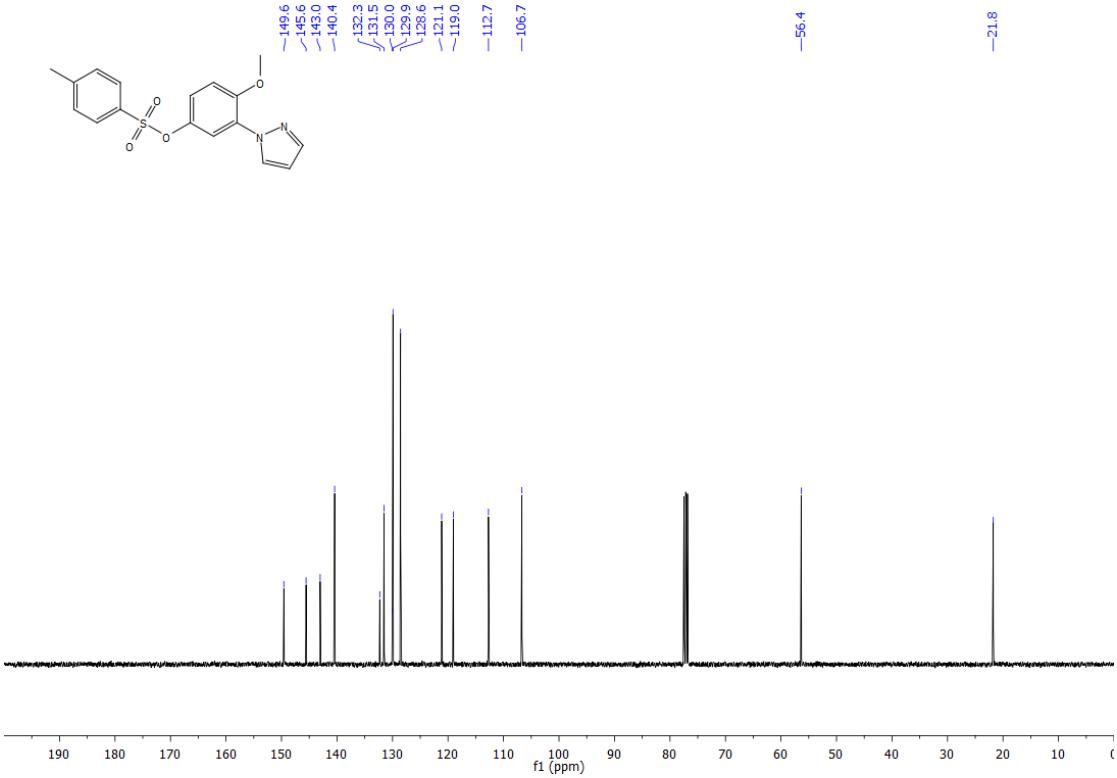

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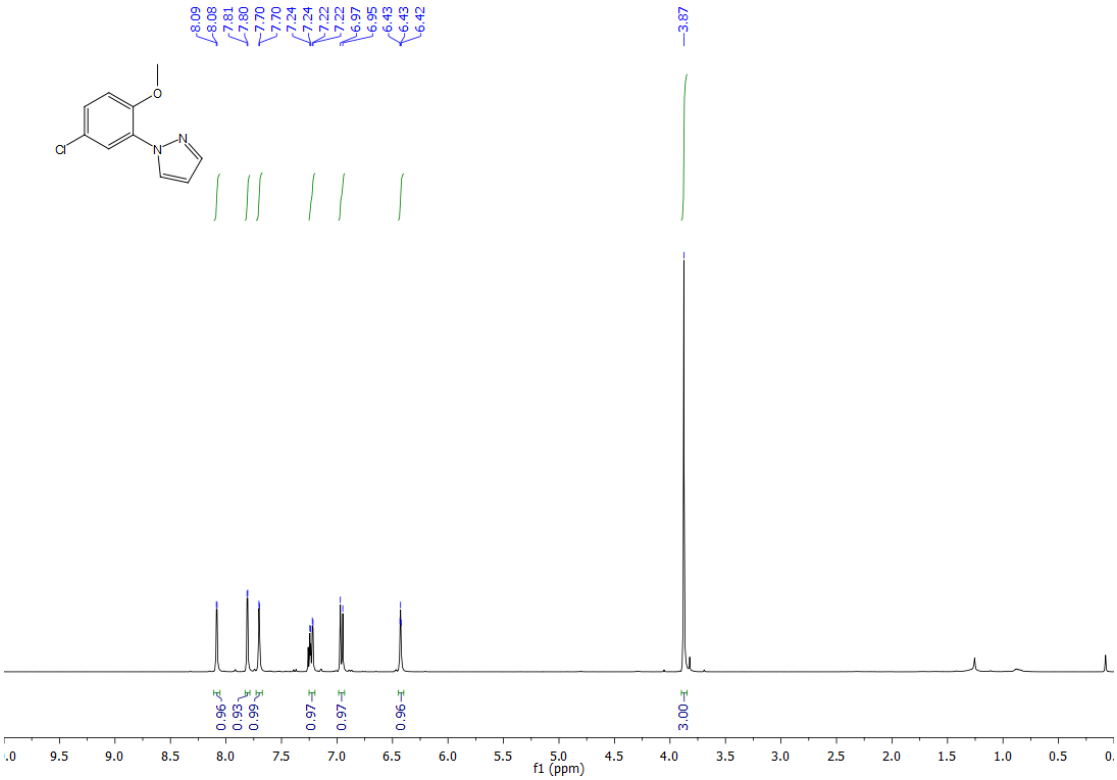

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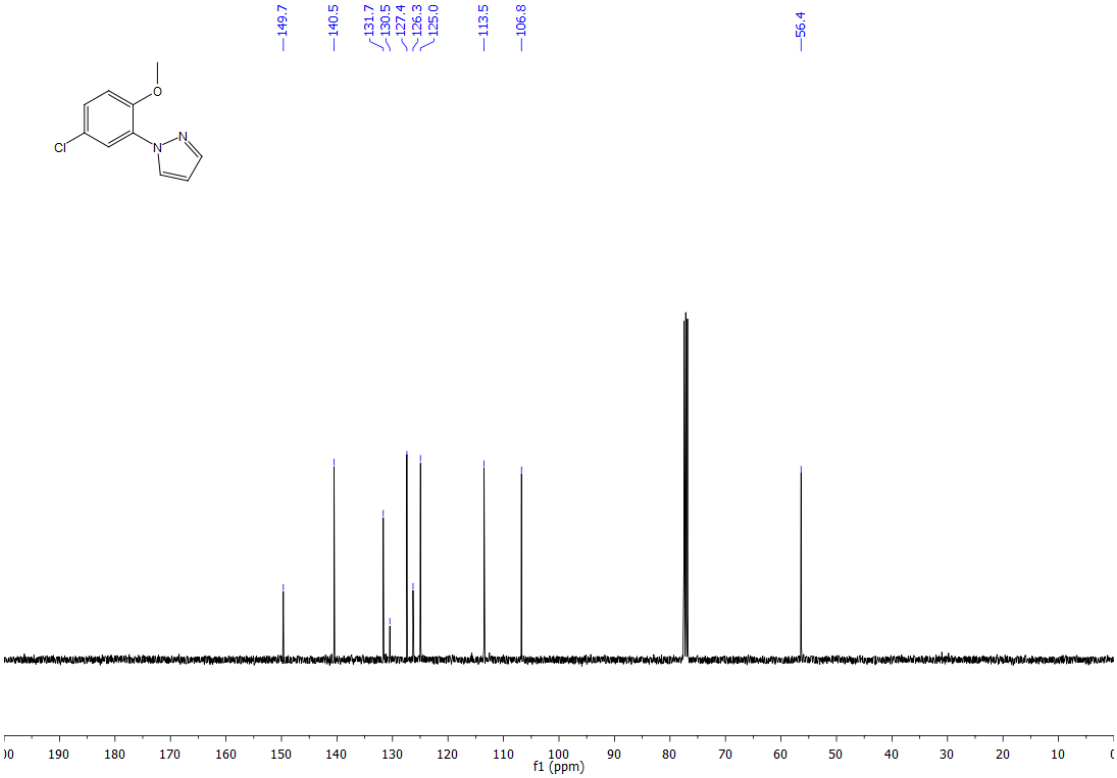

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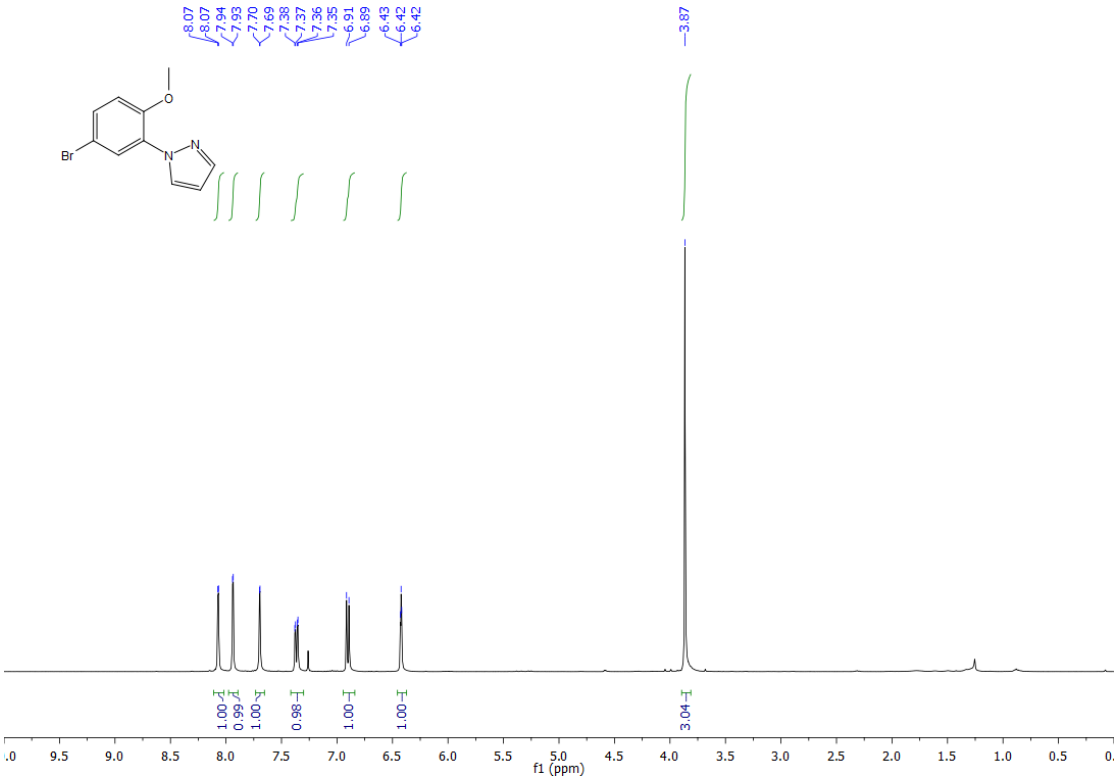
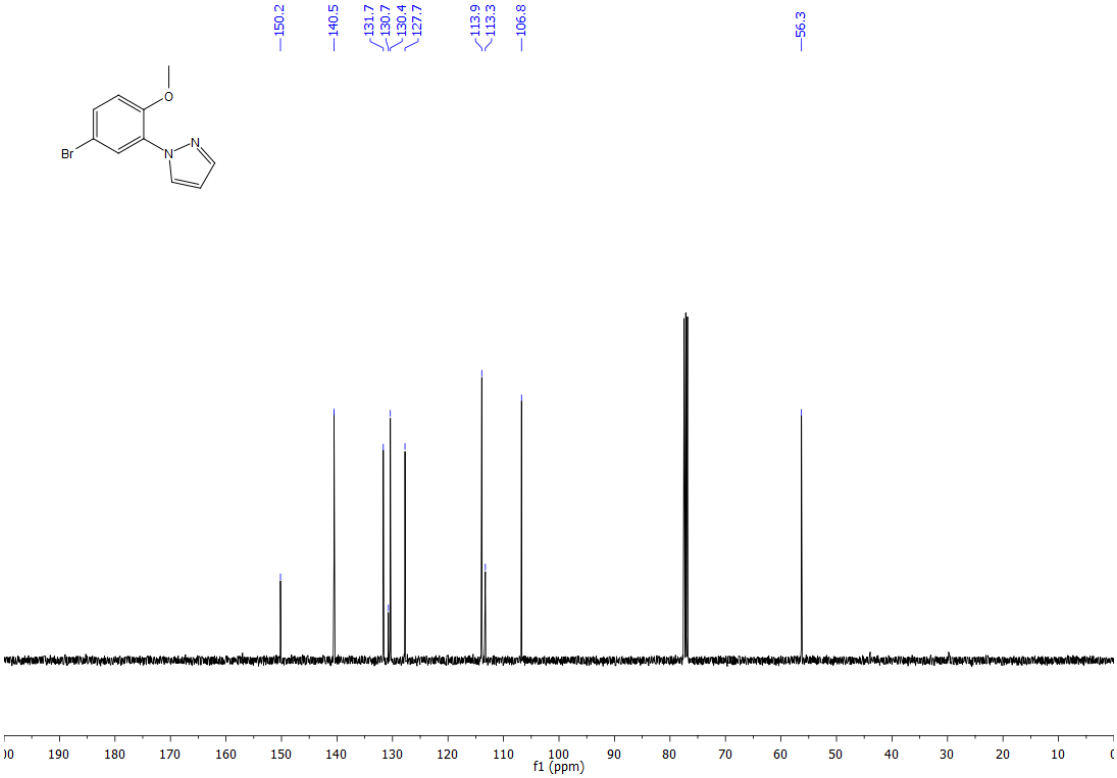


^{1}H NMR (400 MHz, $CDCl_3$) of **14**



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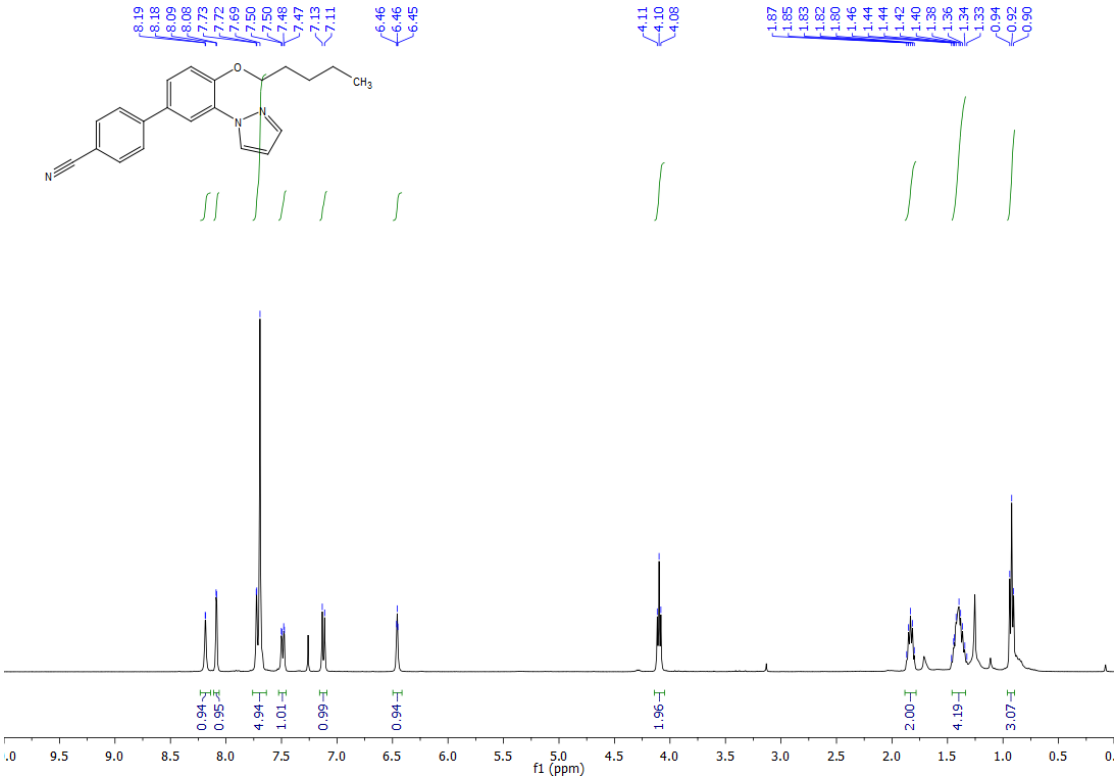

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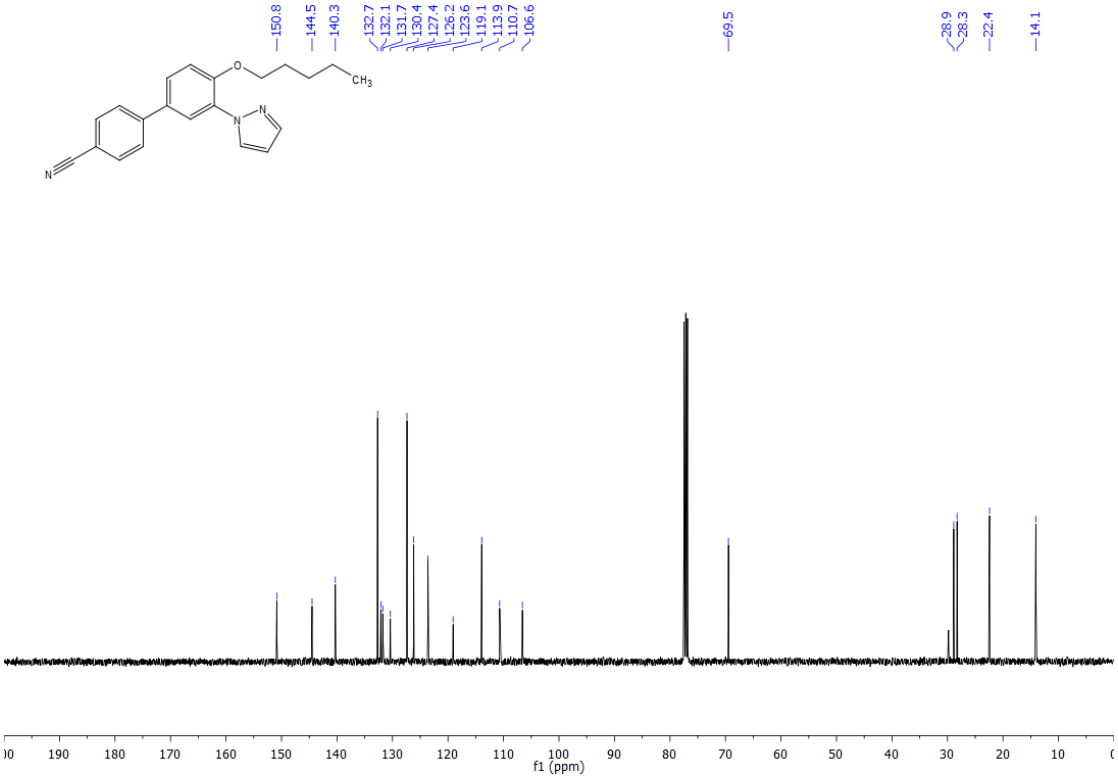

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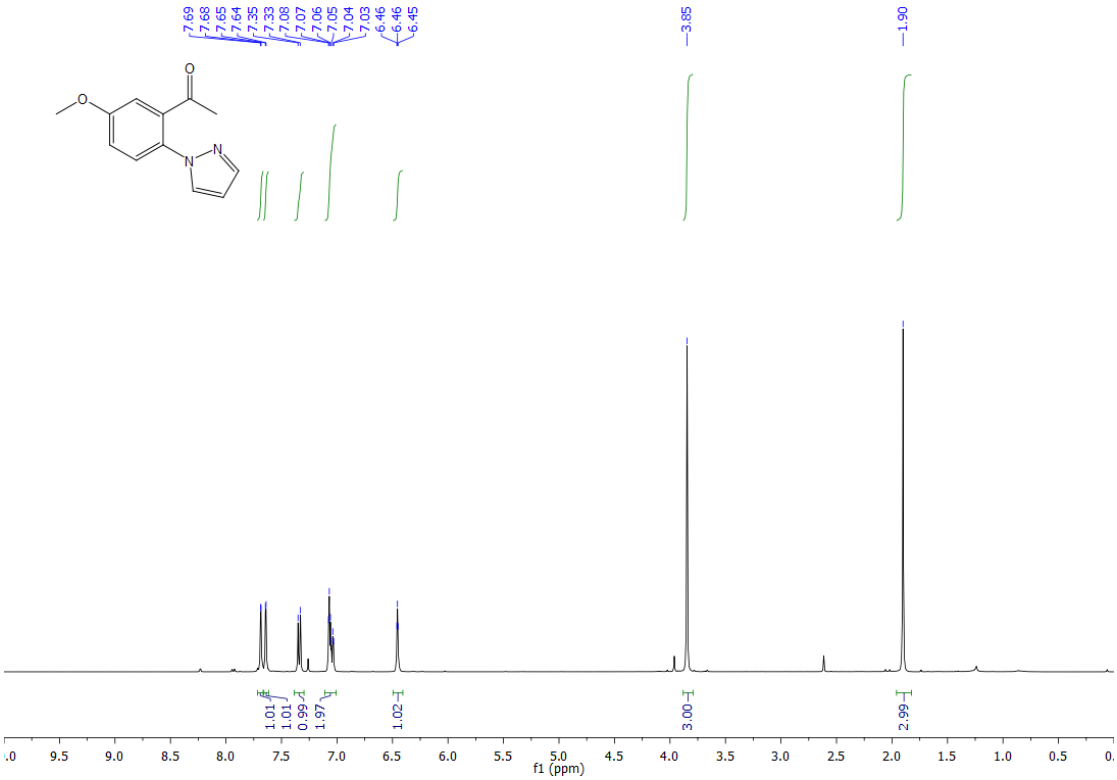

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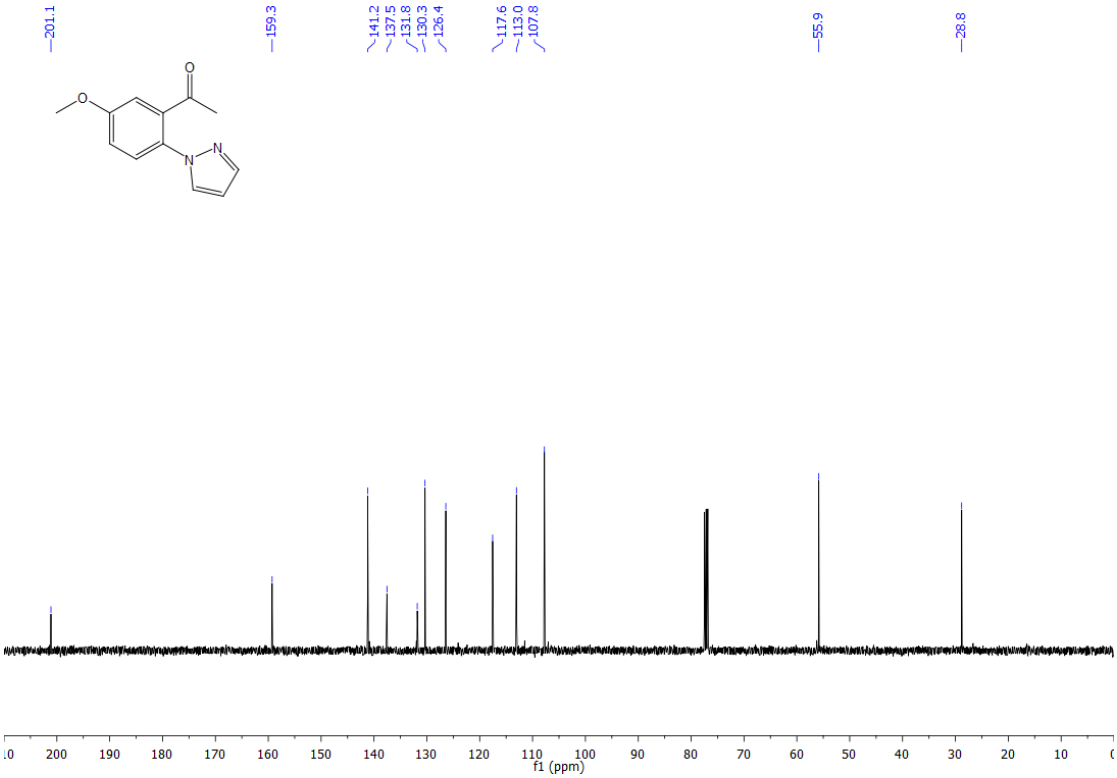

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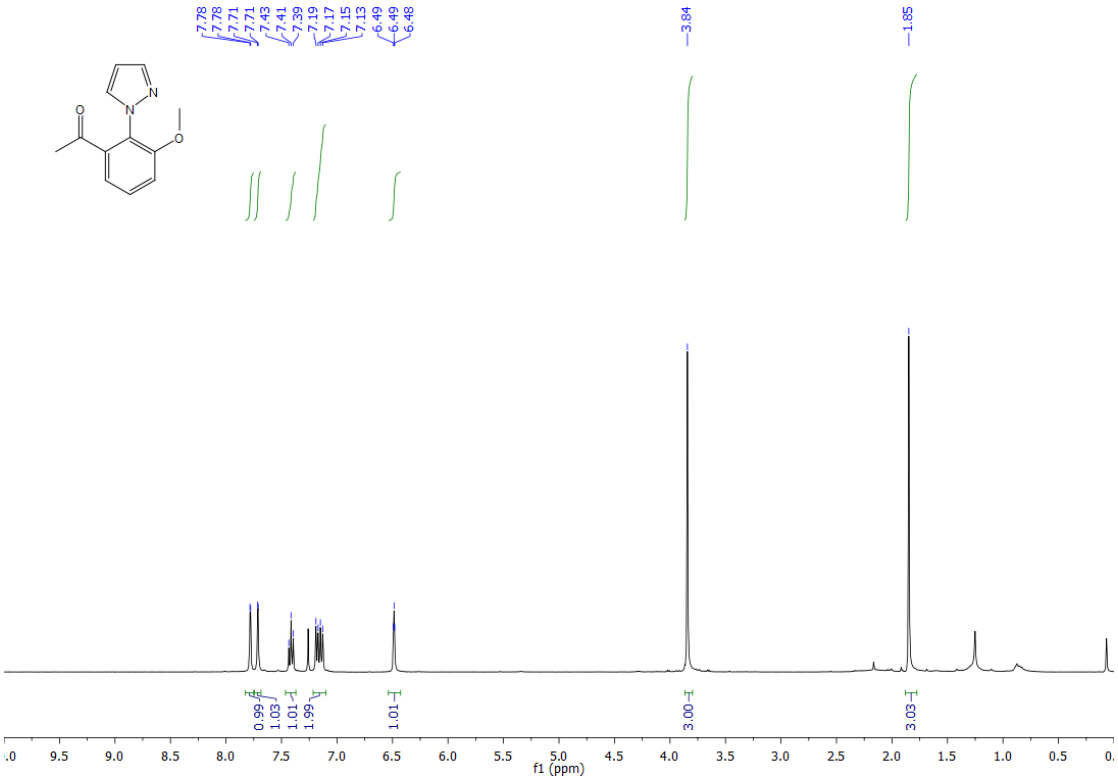

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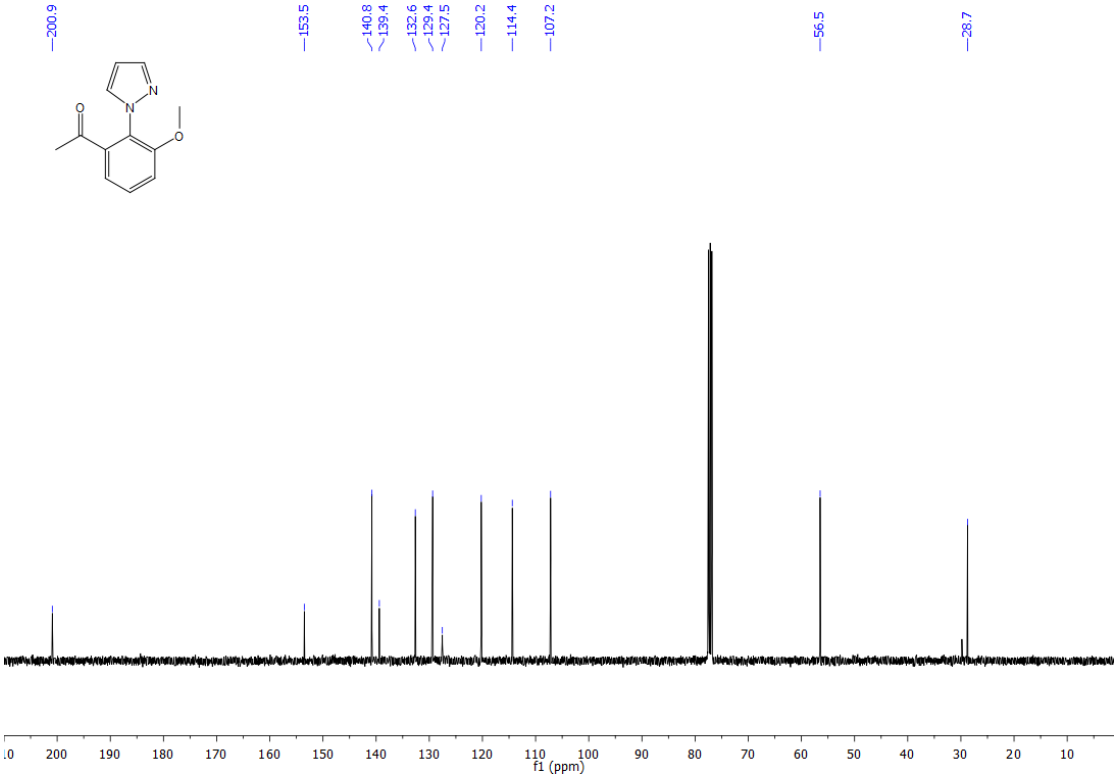

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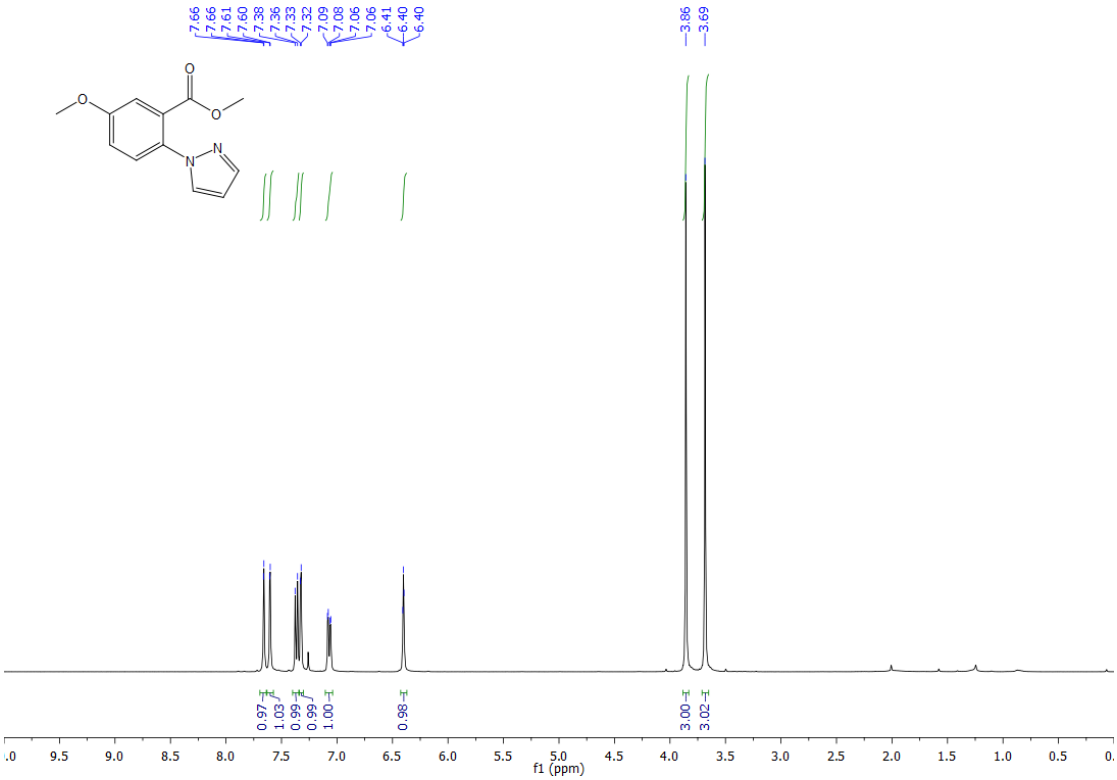

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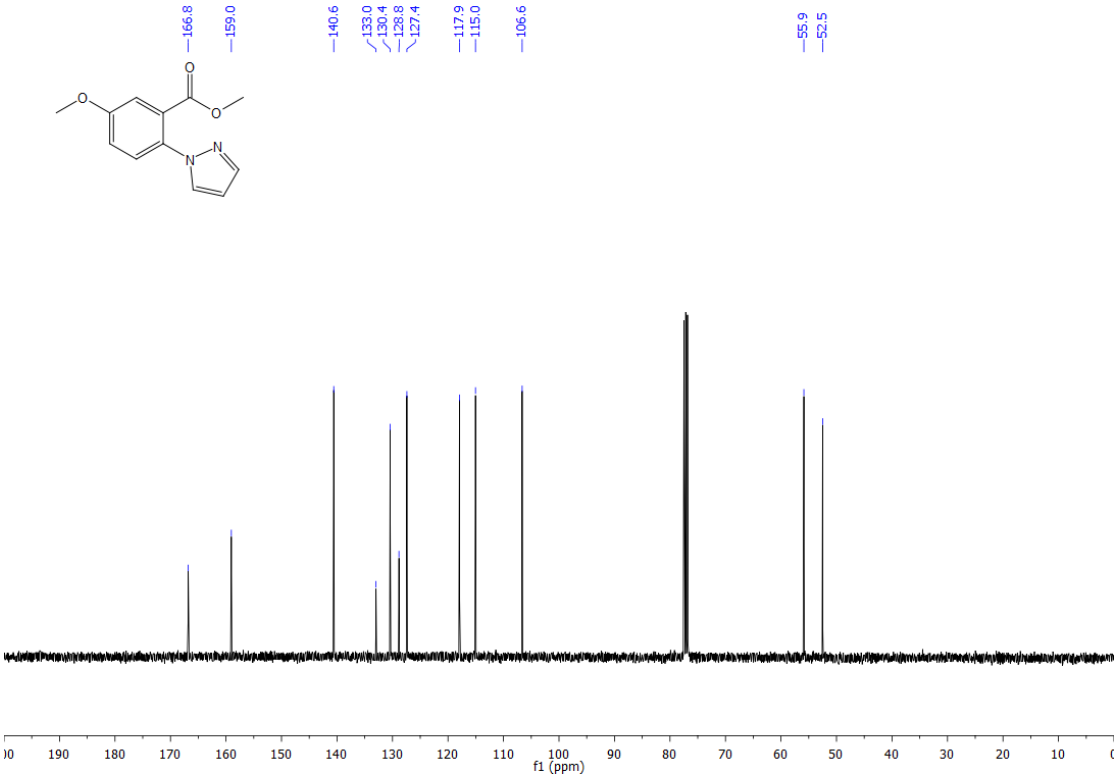

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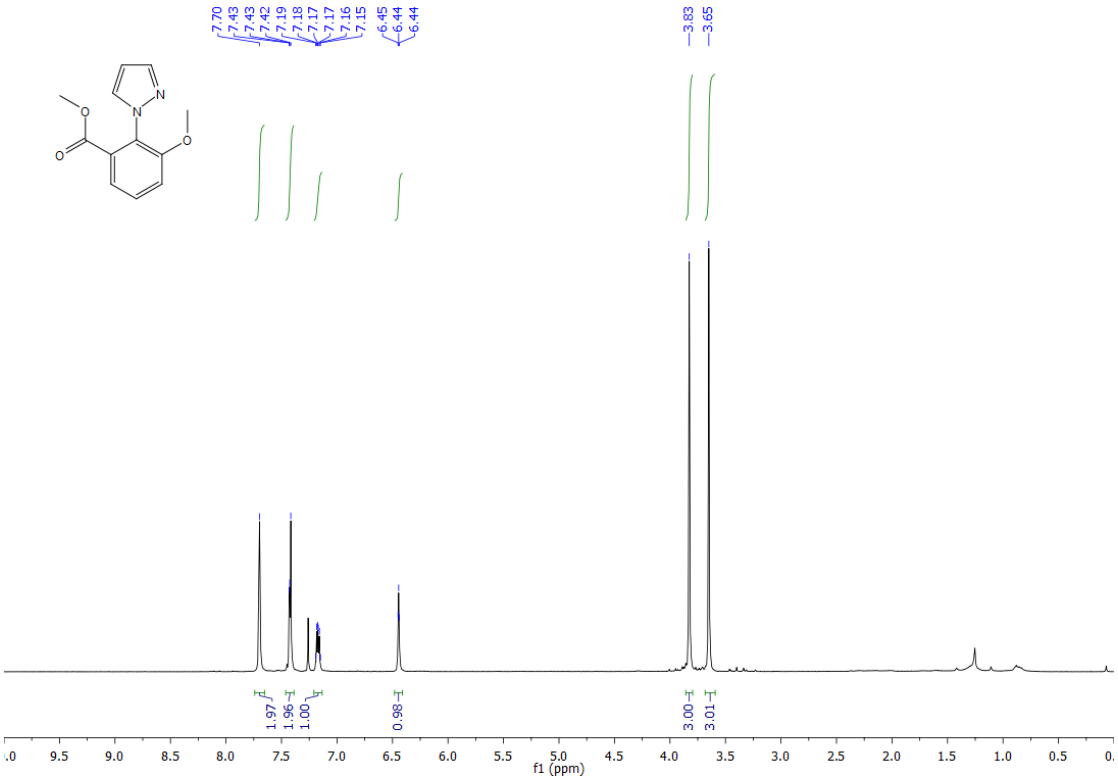

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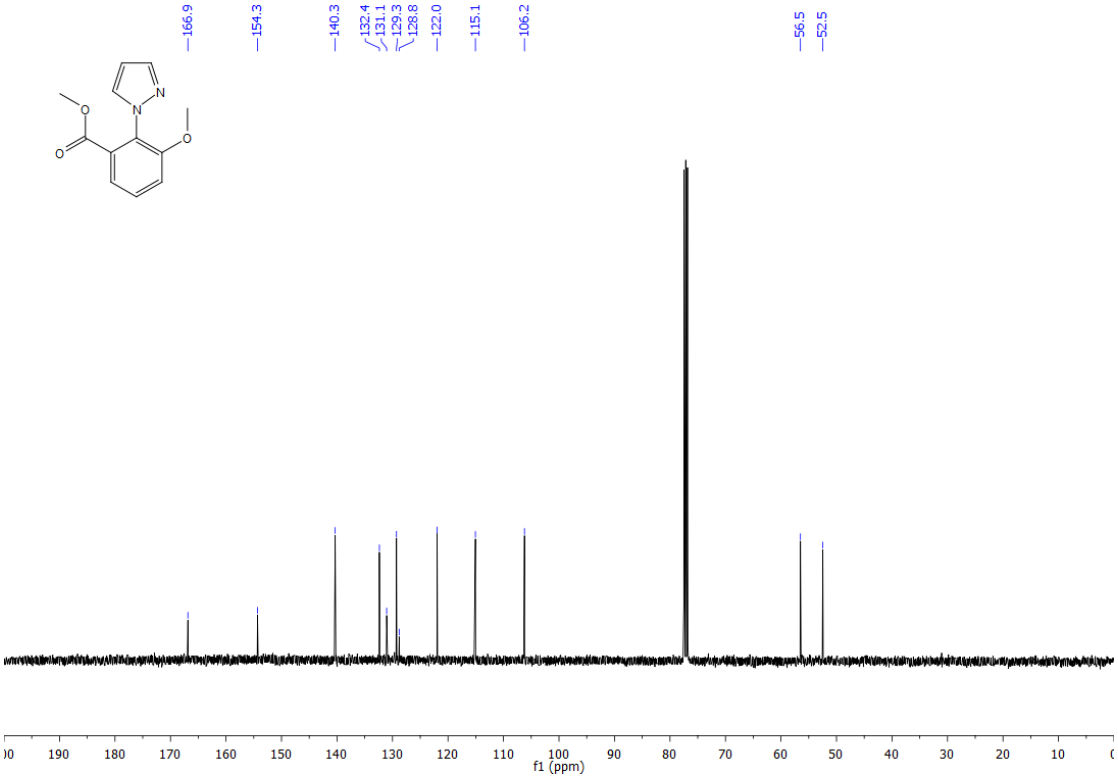
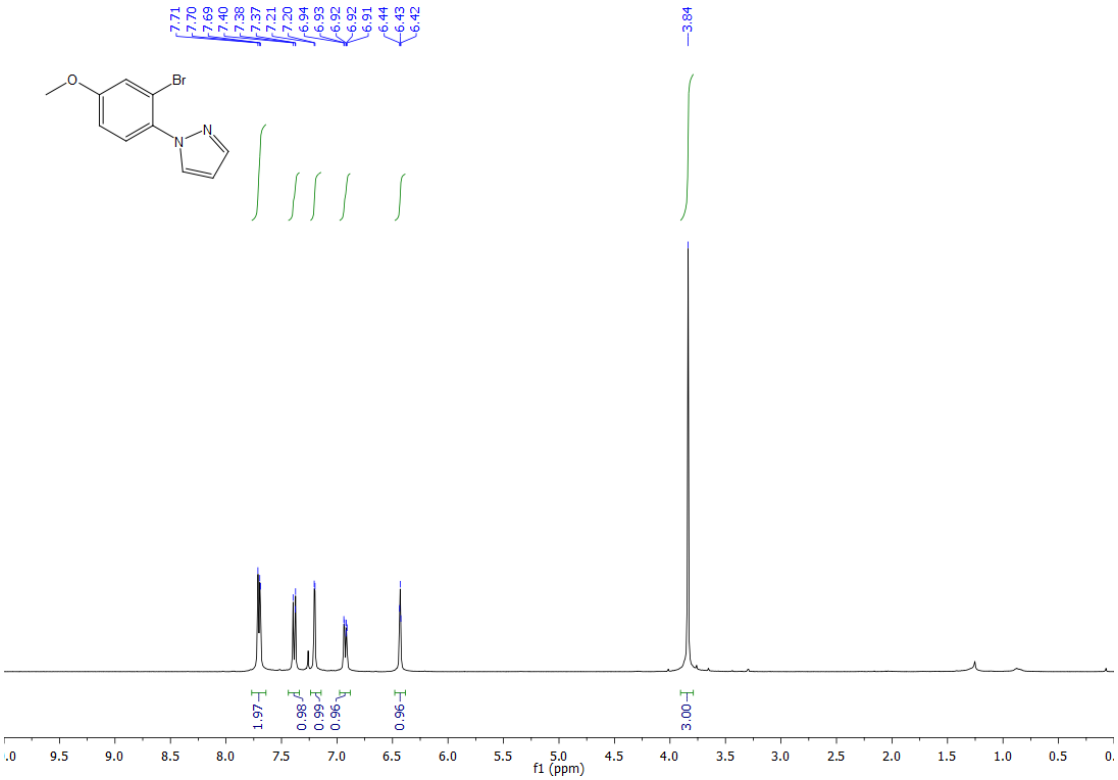


^{13}C NMR (101 MHz, $CDCl_3$) of **17b**



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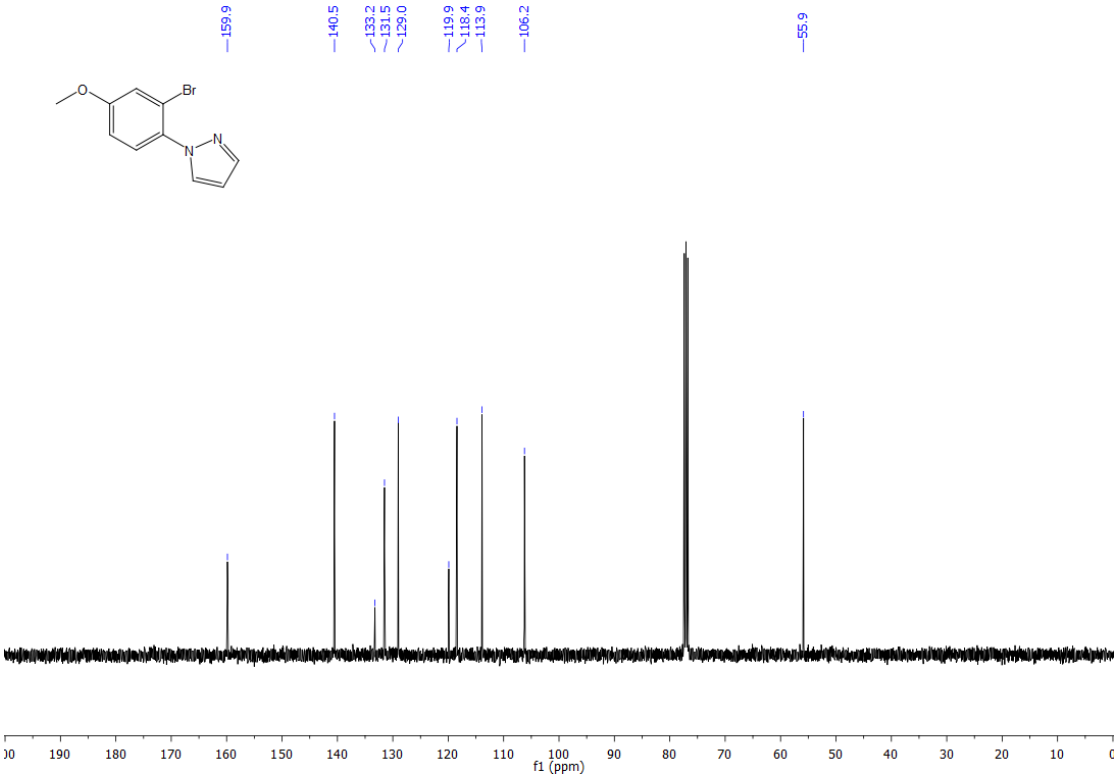
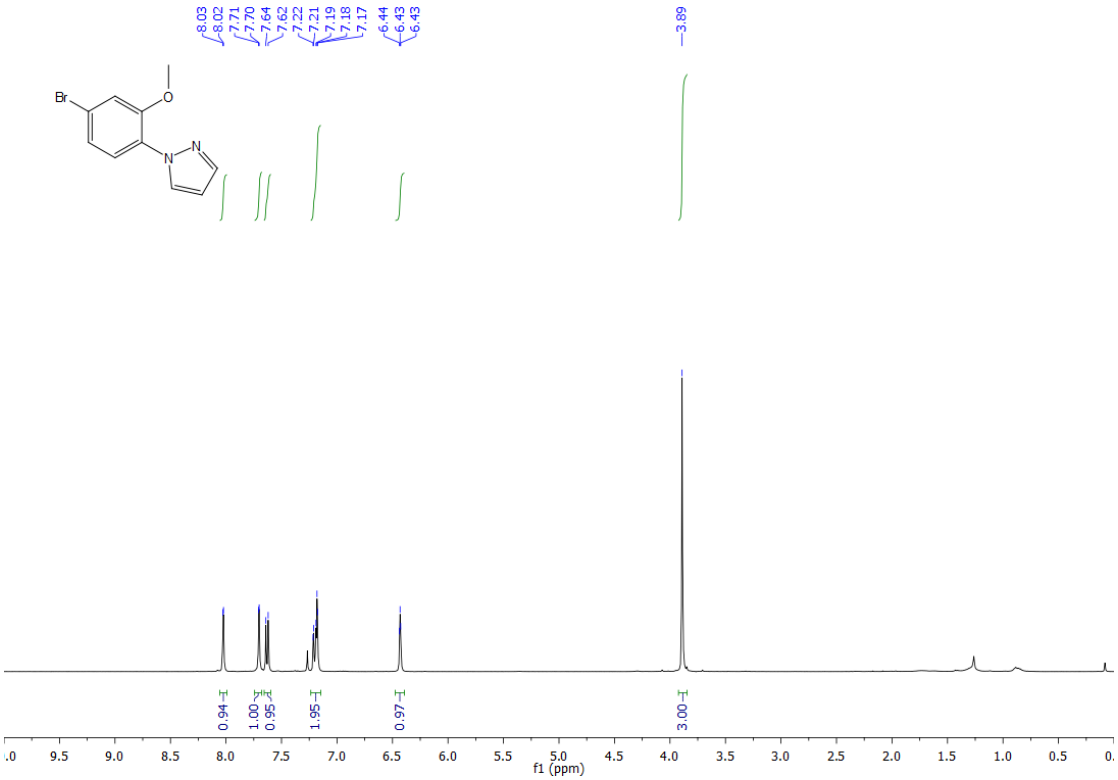
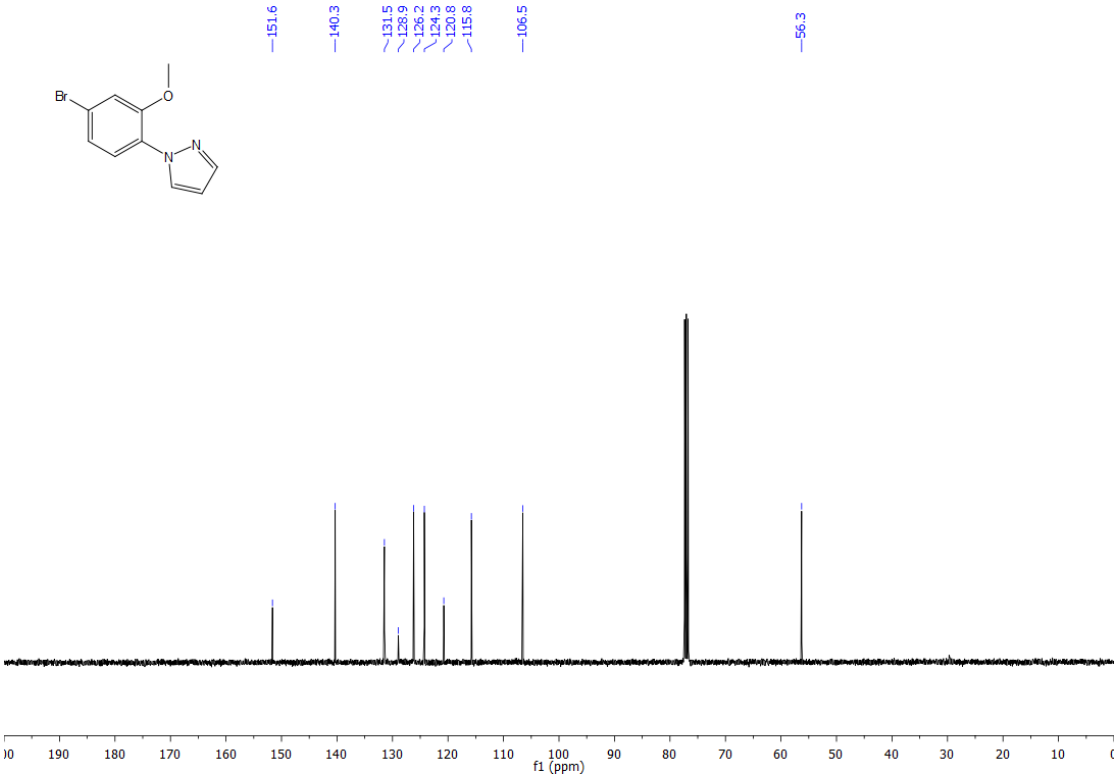


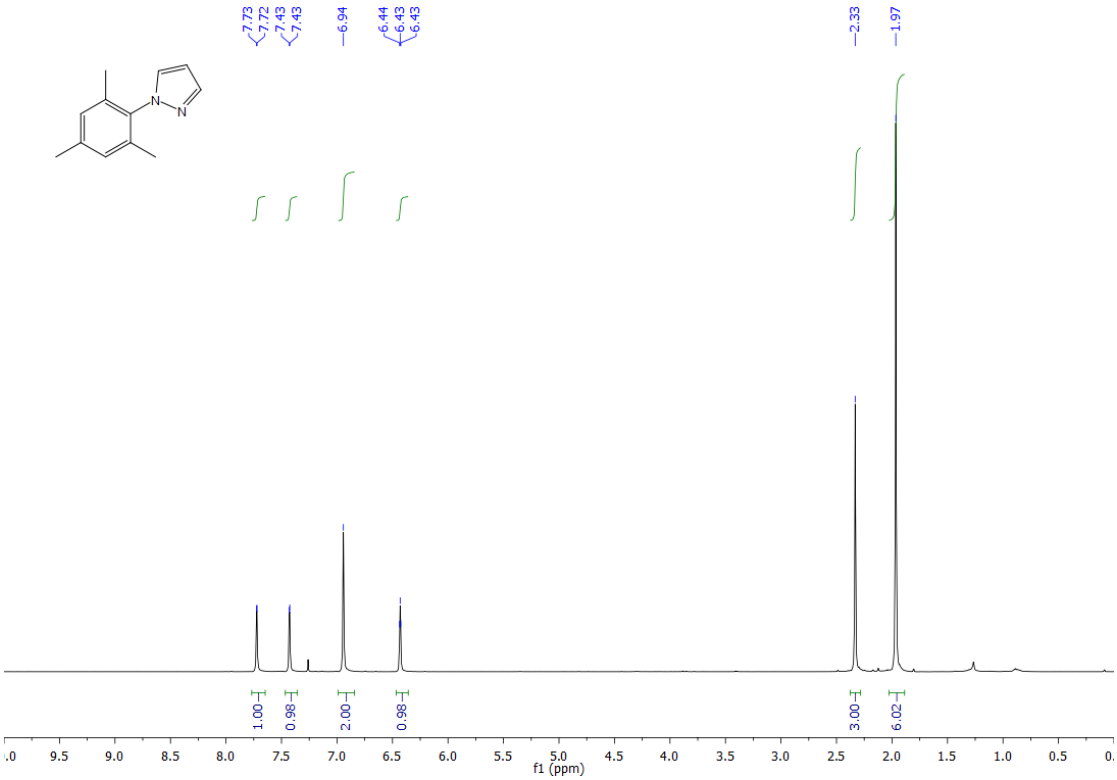
^{13}C NMR (101 MHz, $CDCl_3$) of **18a**



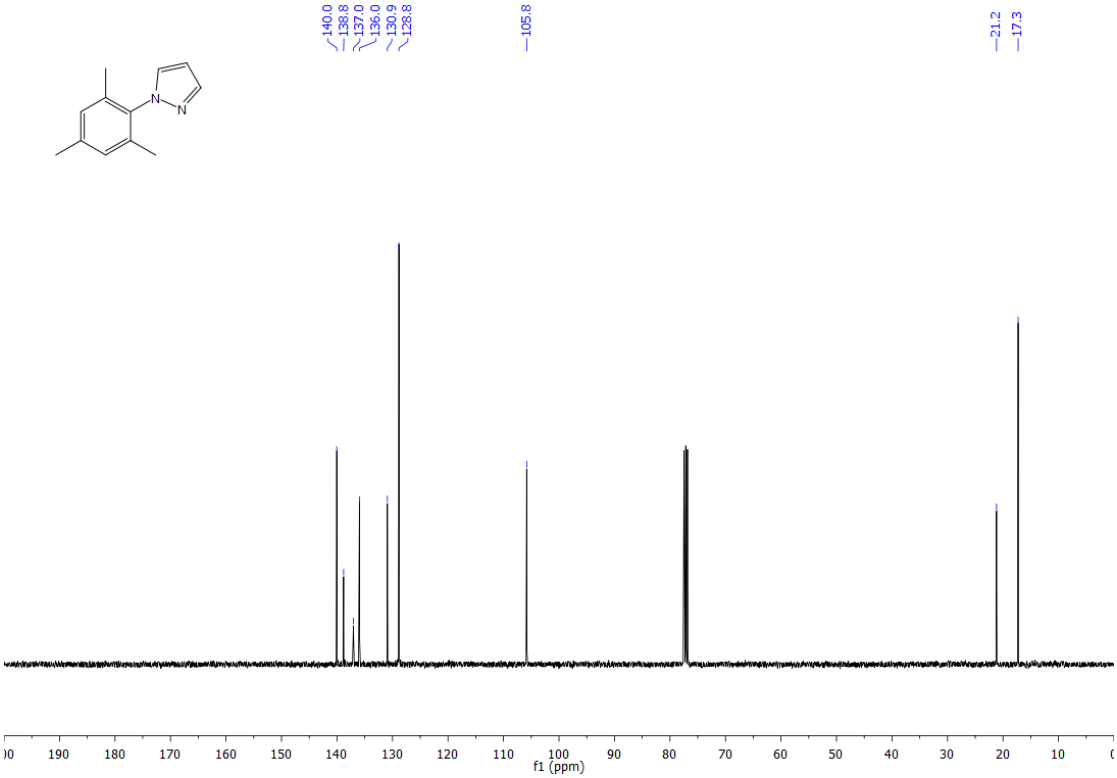
^{1}H NMR (400 MHz, $CDCl_3$) of **18b**



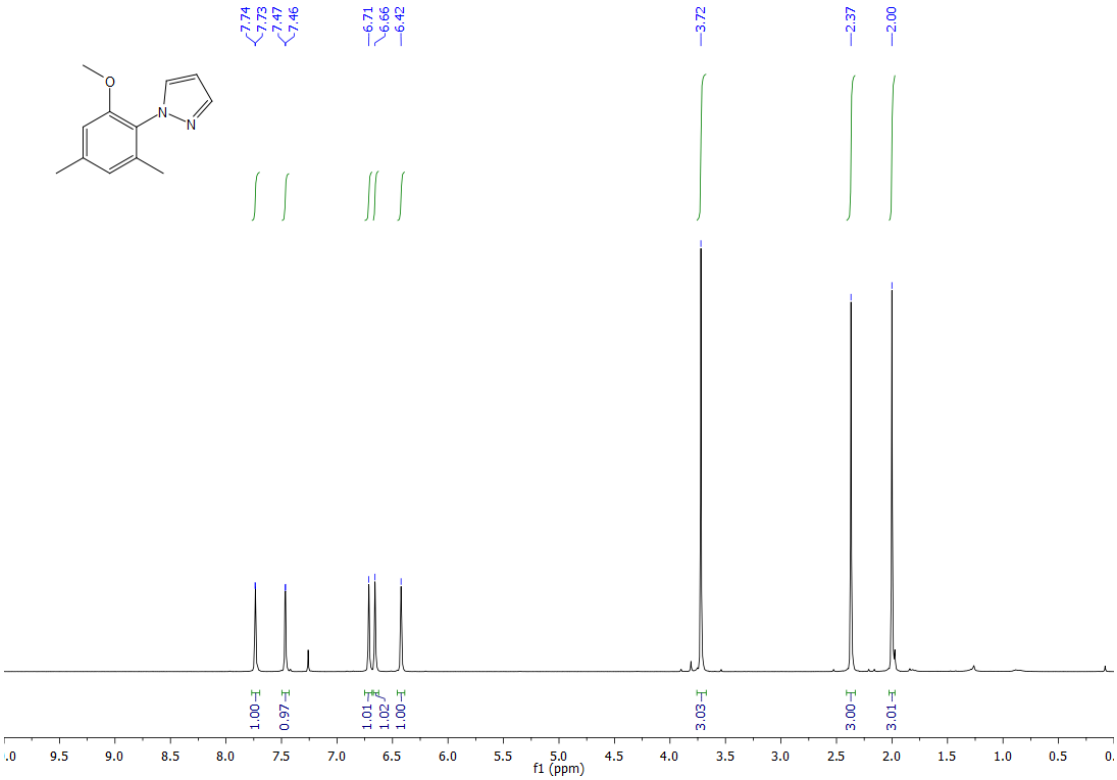
^{13}C NMR (101 MHz, $CDCl_3$) of **18b**



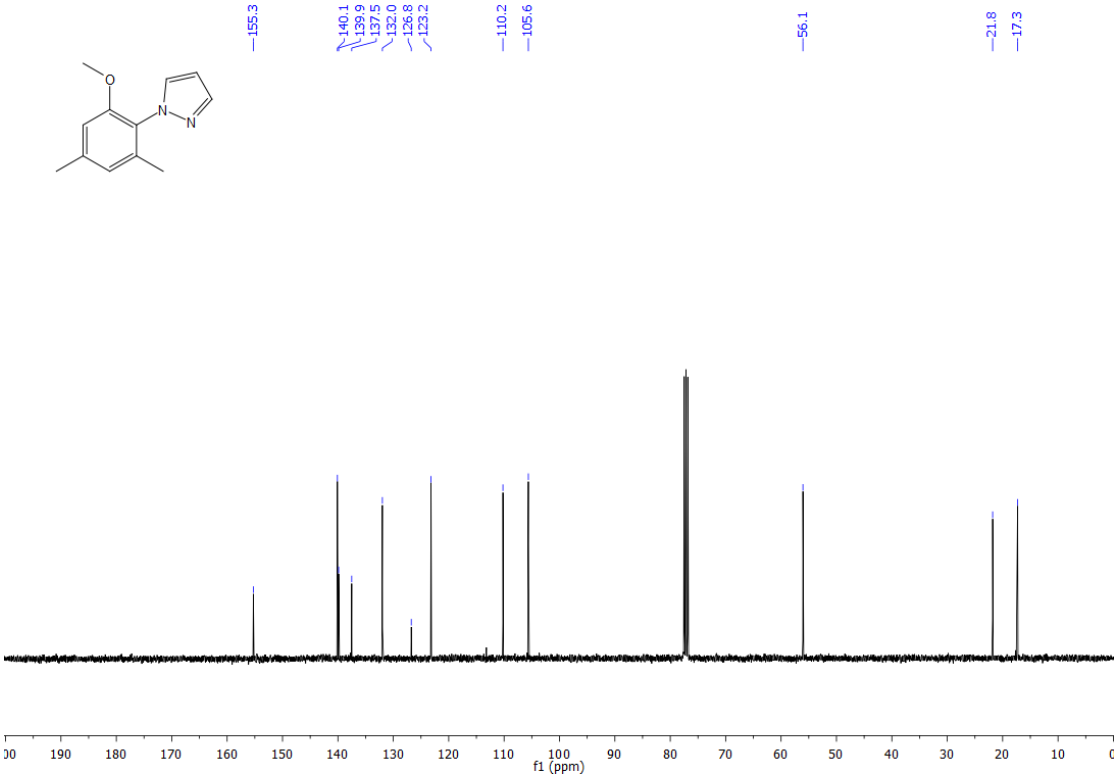
^{1}H NMR (400 MHz, $CDCl_3$) of **19**



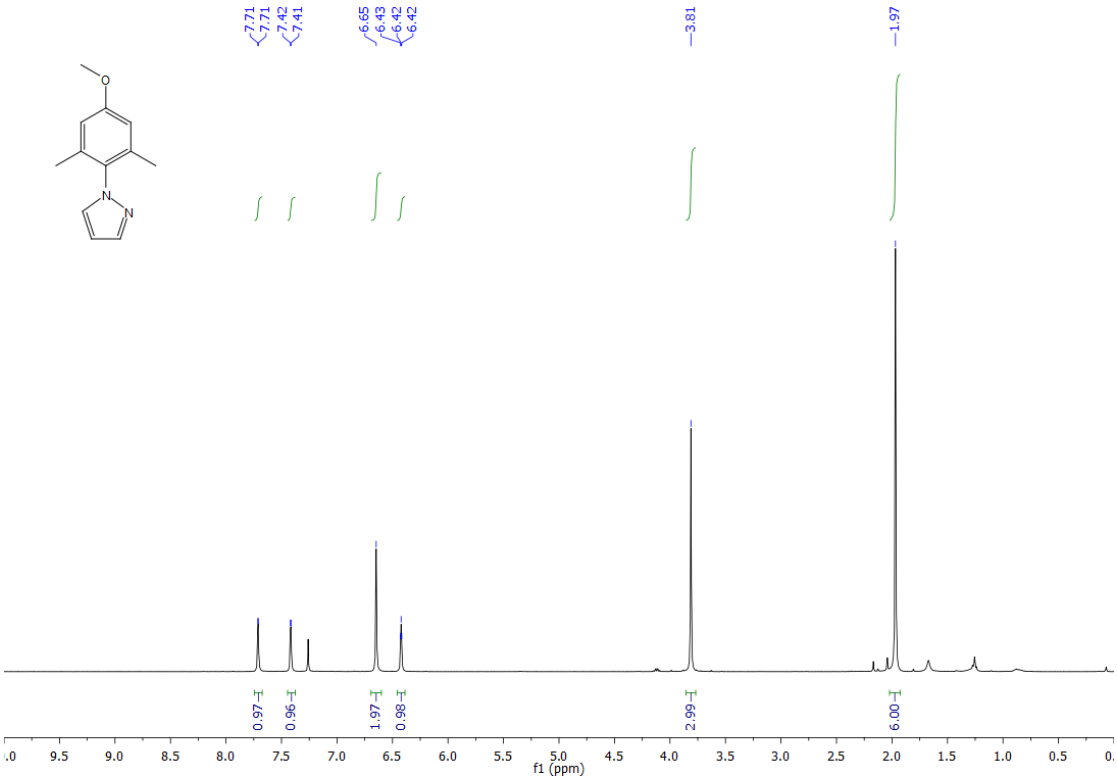
^{13}C NMR (101 MHz, $CDCl_3$) of **19**



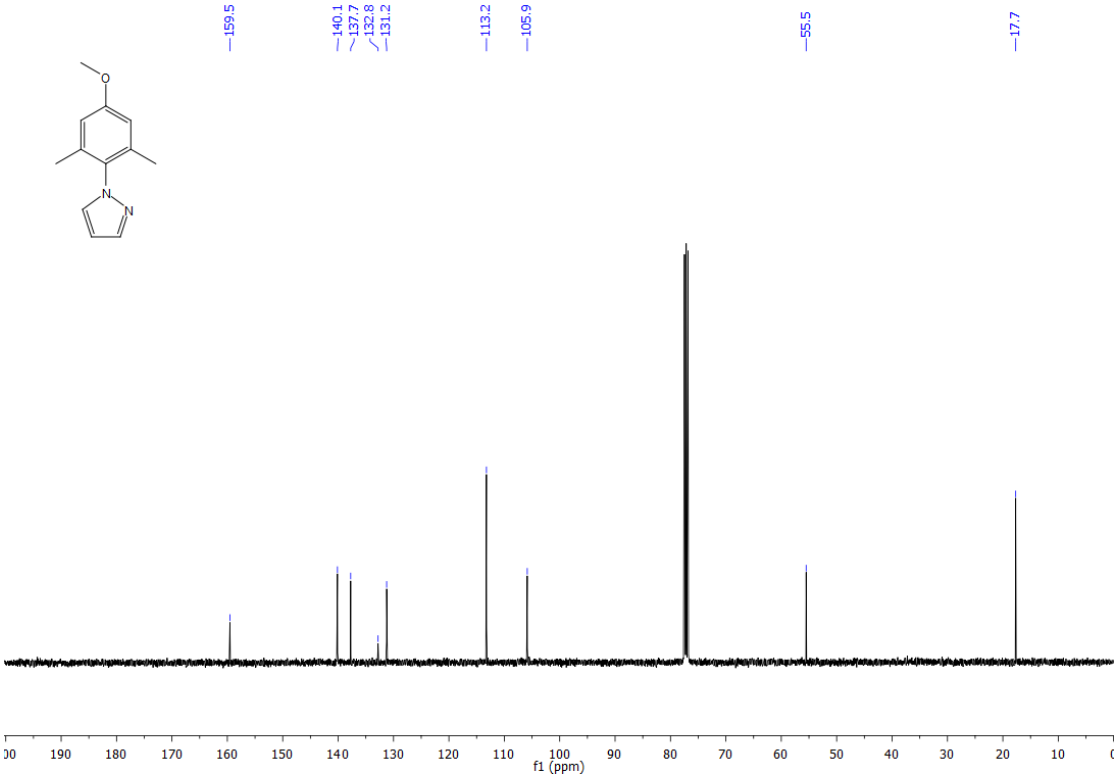
^{1}H NMR (400 MHz, $CDCl_3$) of **20a**



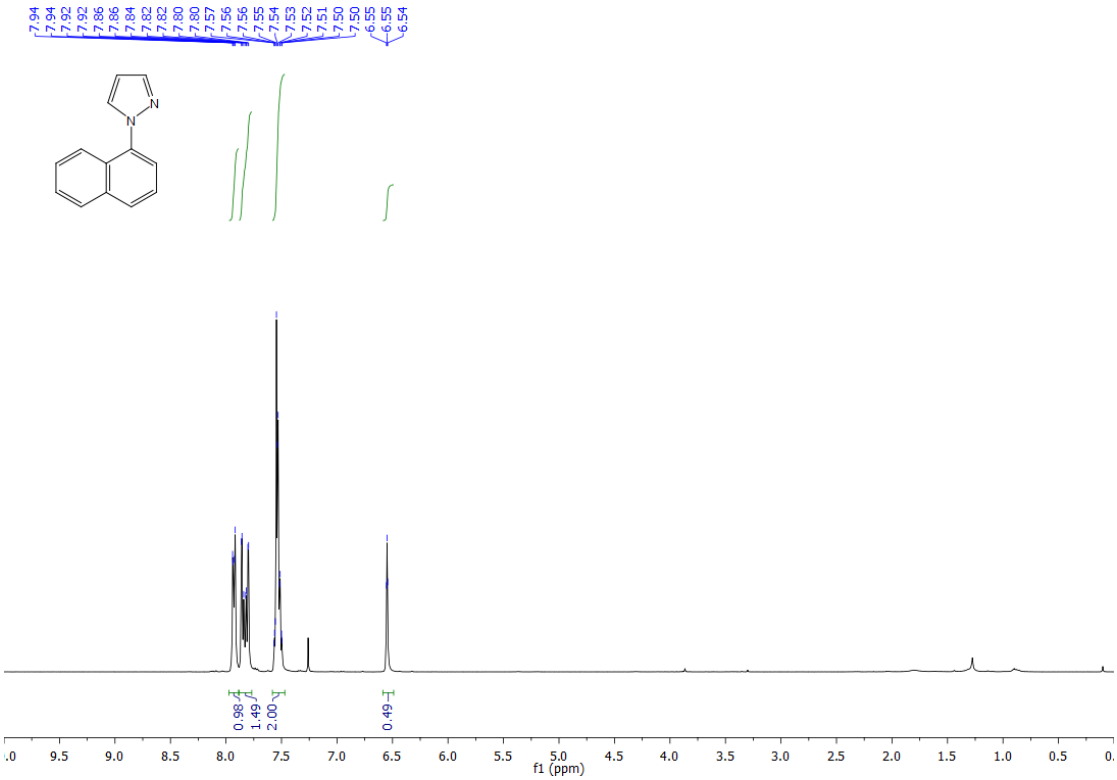
^{13}C NMR (101 MHz, $CDCl_3$) of **20a**



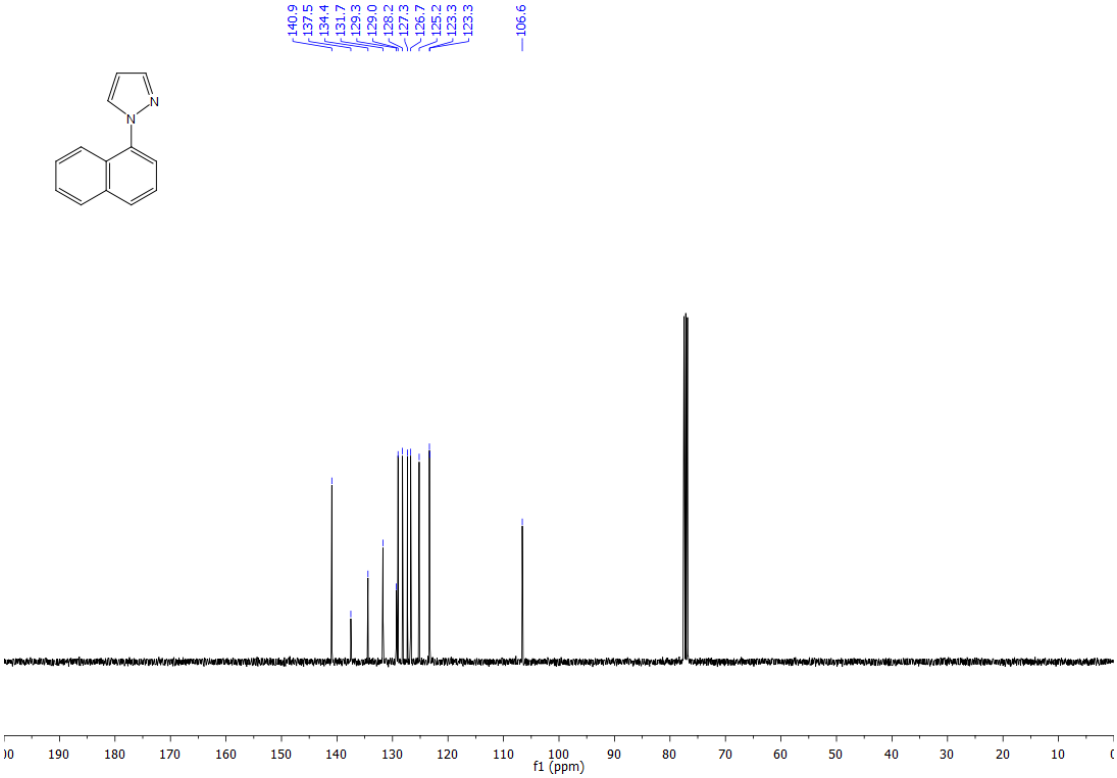
^{1}H NMR (400 MHz, $CDCl_3$) of **20b**



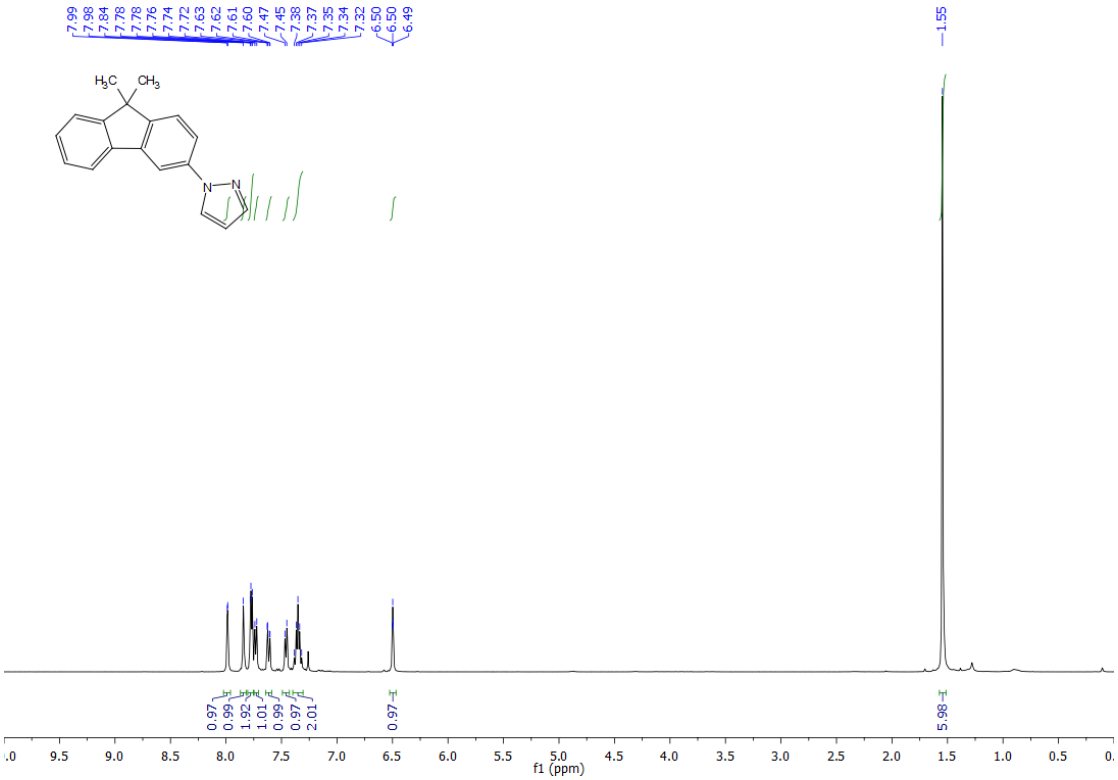
^{13}C NMR (101 MHz, $CDCl_3$) of **20b**



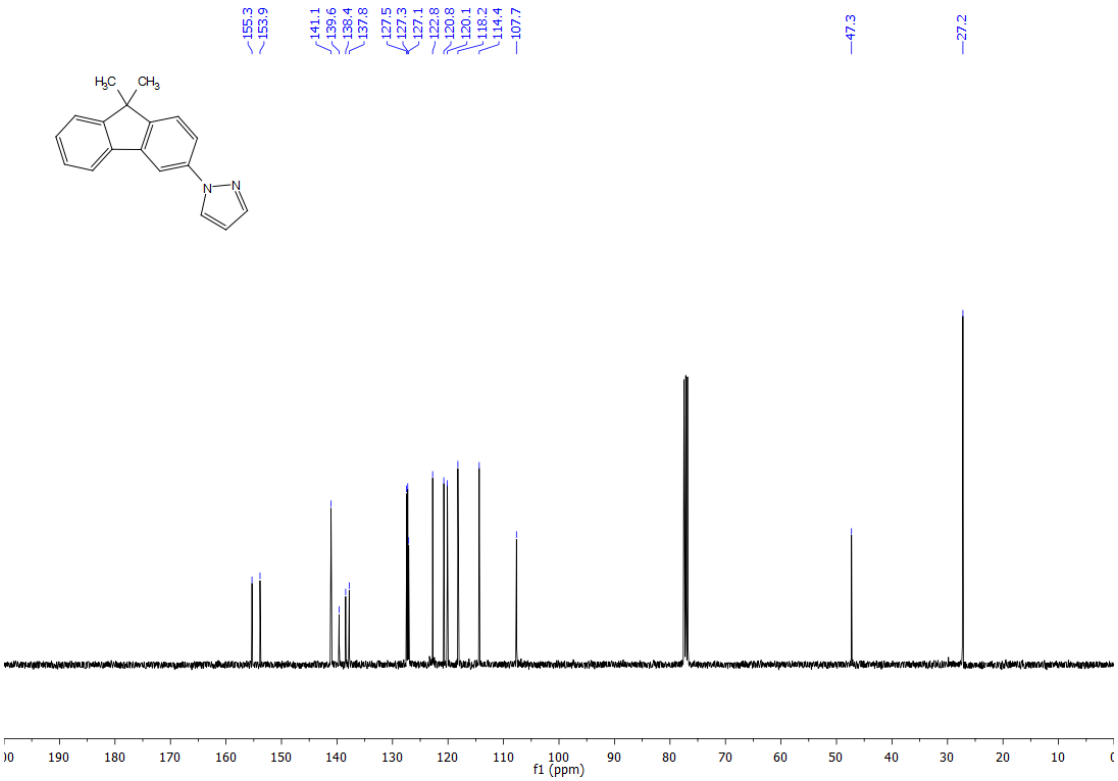
^{1}H NMR (400 MHz, $CDCl_3$) of **21**



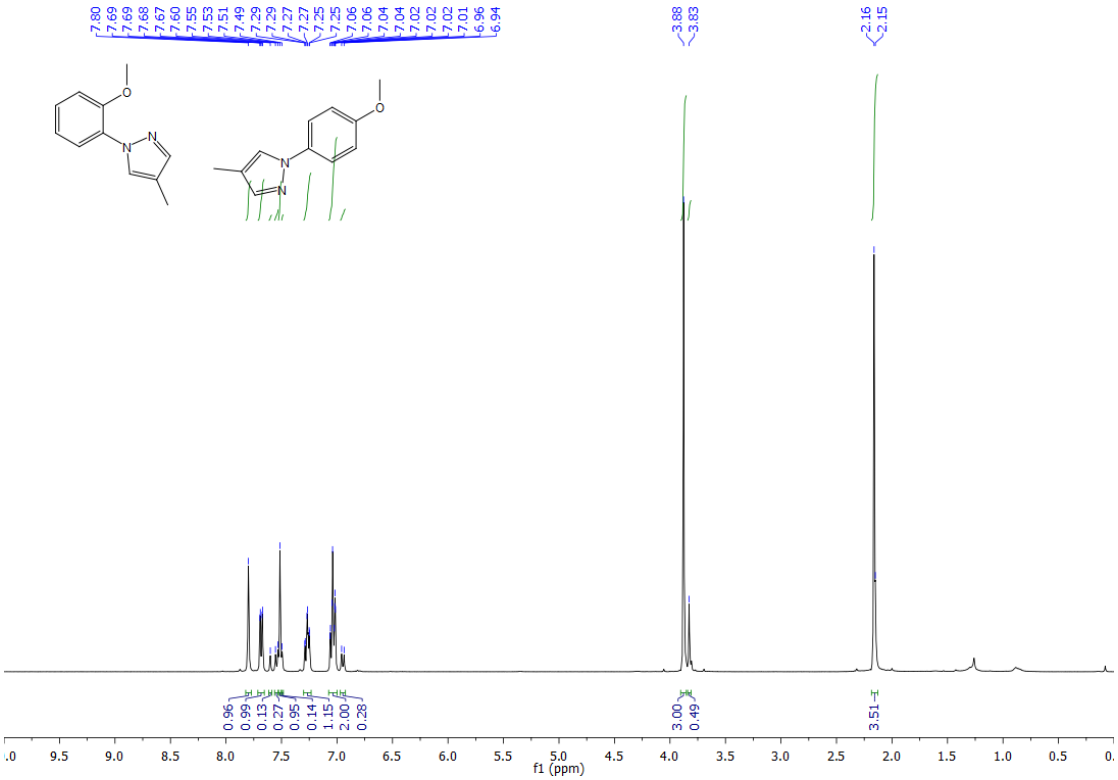
^{13}C NMR (101 MHz, $CDCl_3$) of **21**



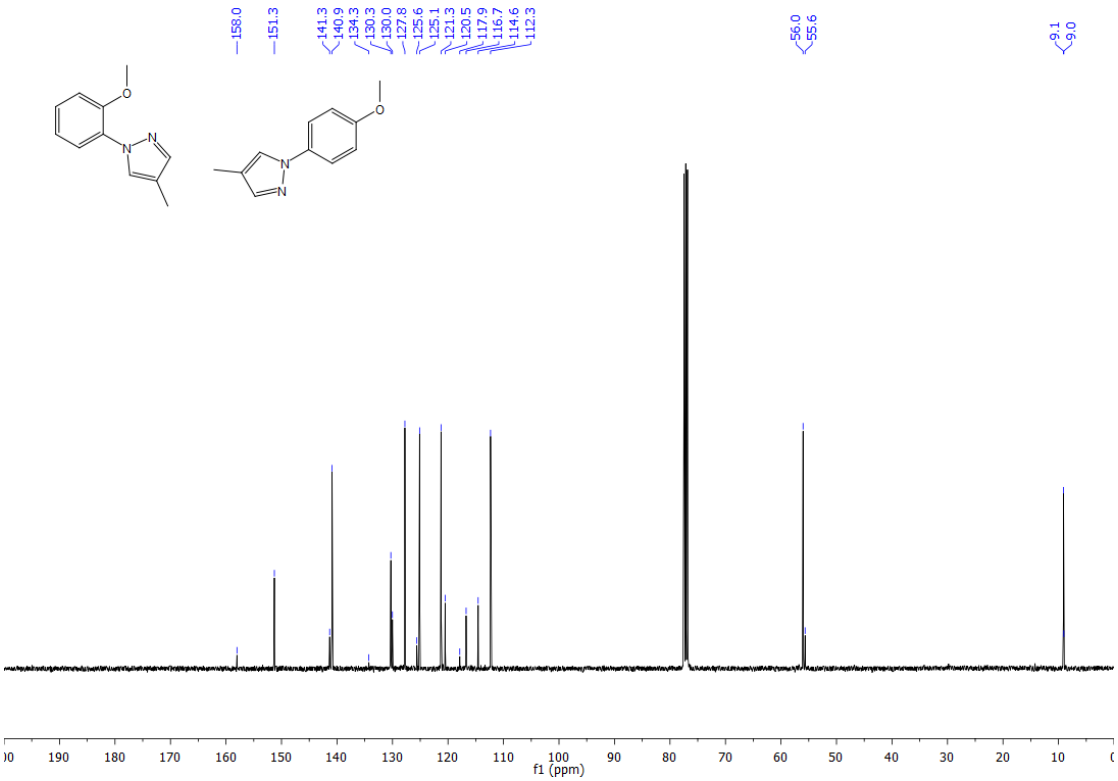
^{1}H NMR (400 MHz, $CDCl_3$) of **22**



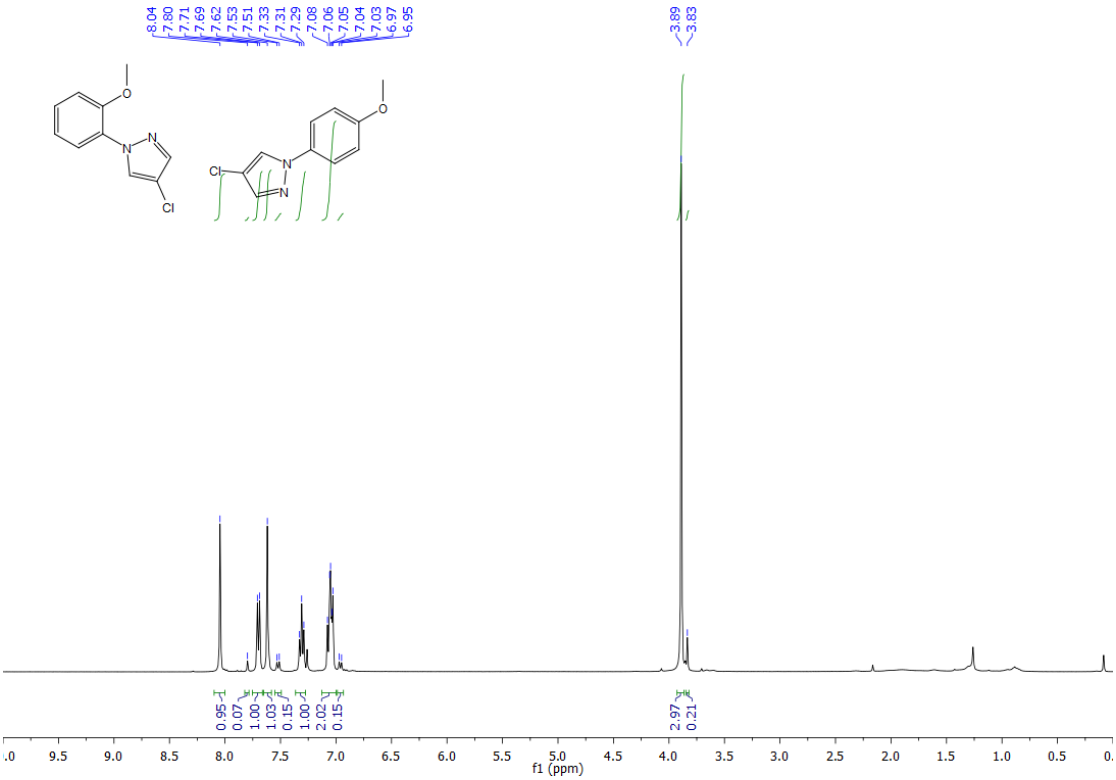
^{13}C NMR (101 MHz, $CDCl_3$) of **22**



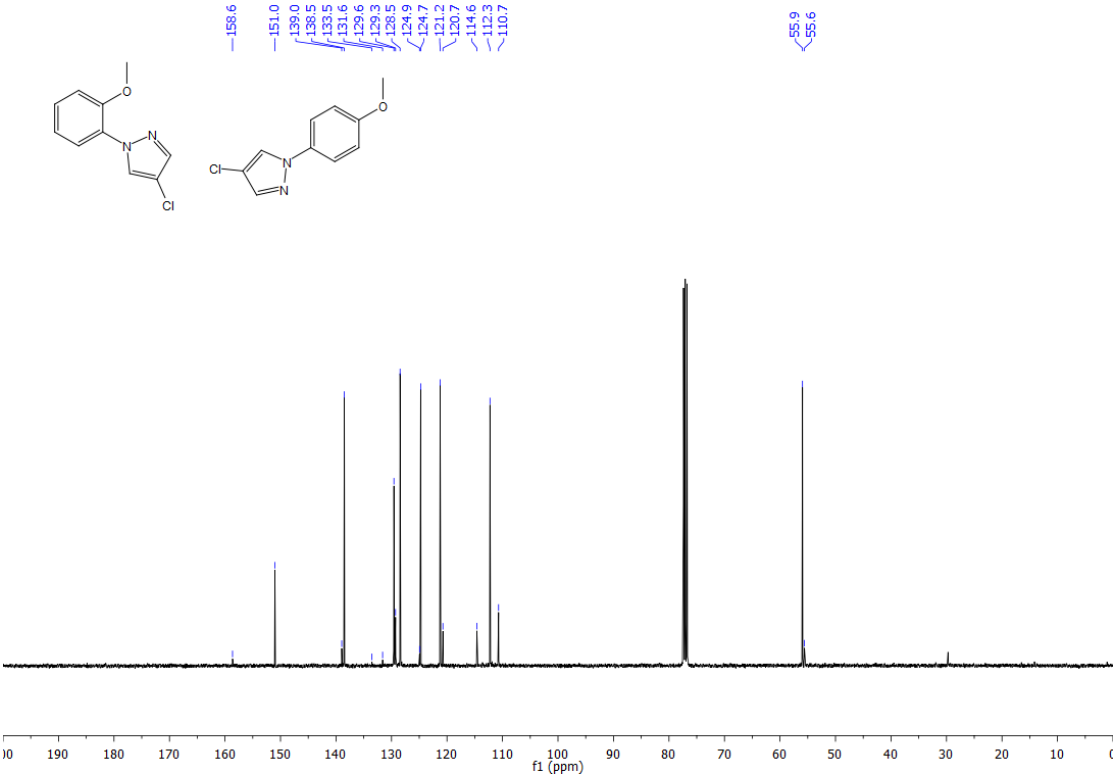
^{1}H NMR (400 MHz, $CDCl_3$) of **23a** and **23b**



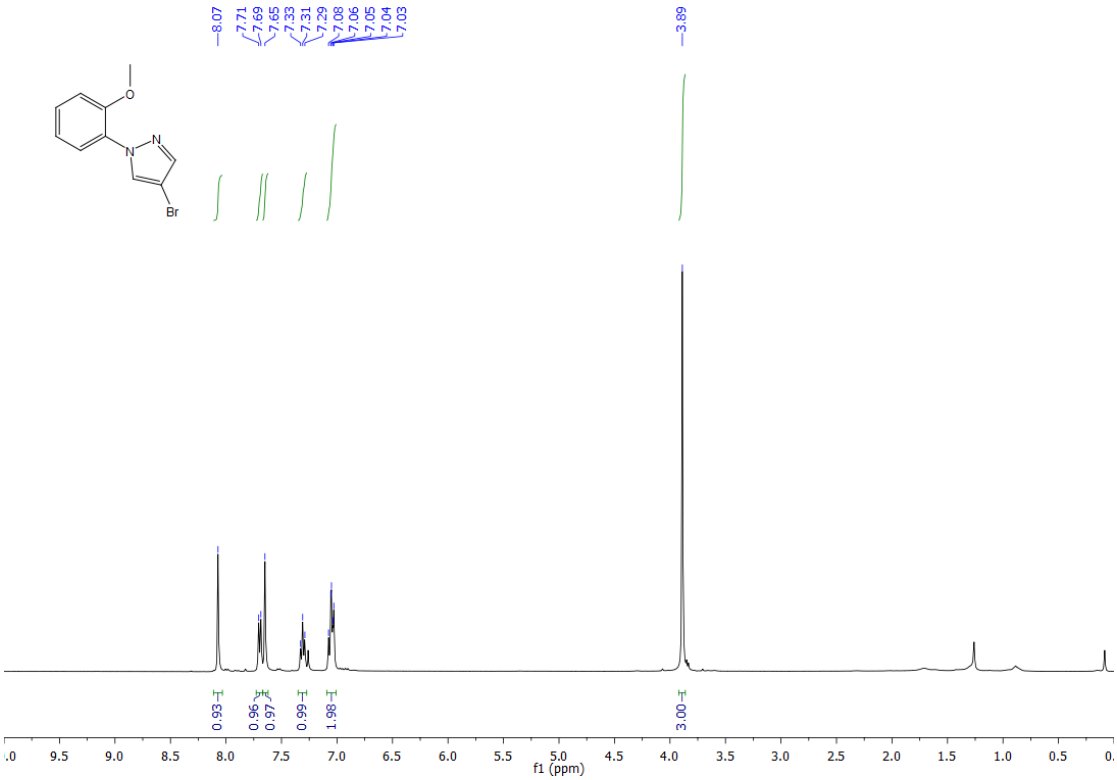
^{13}C NMR (101 MHz, $CDCl_3$) of **23a** and **23b**



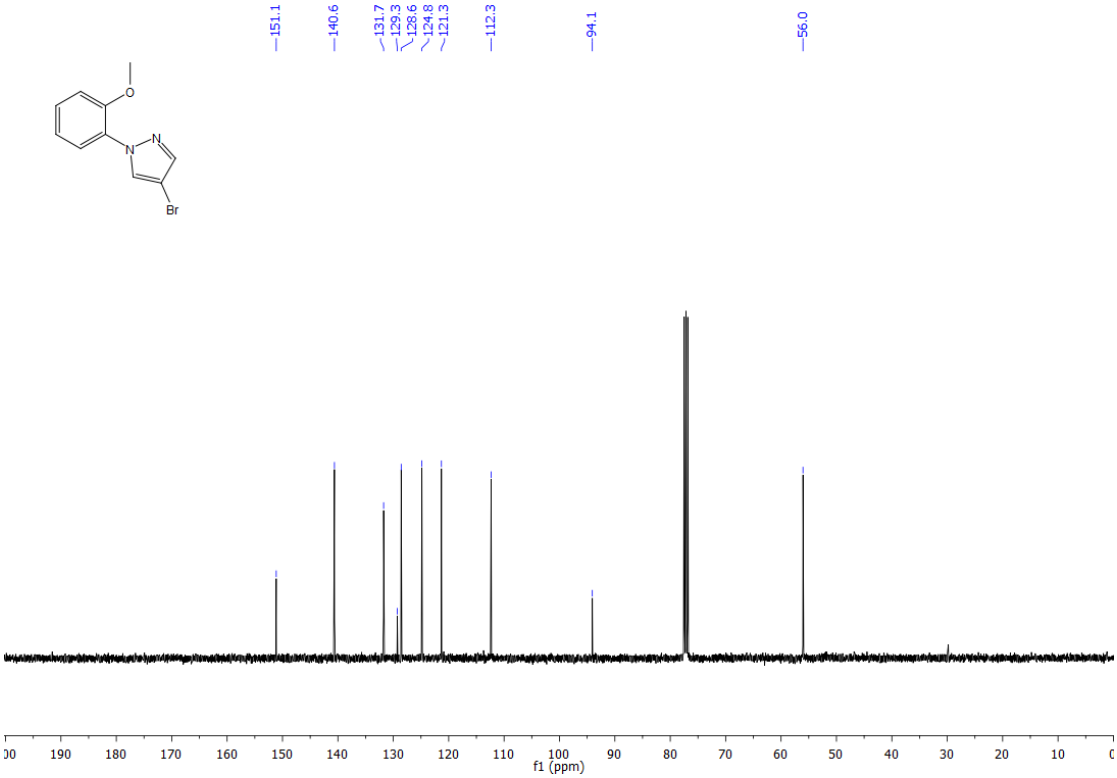
^{1}H NMR (400 MHz, $CDCl_3$) of **24a** and **24b**



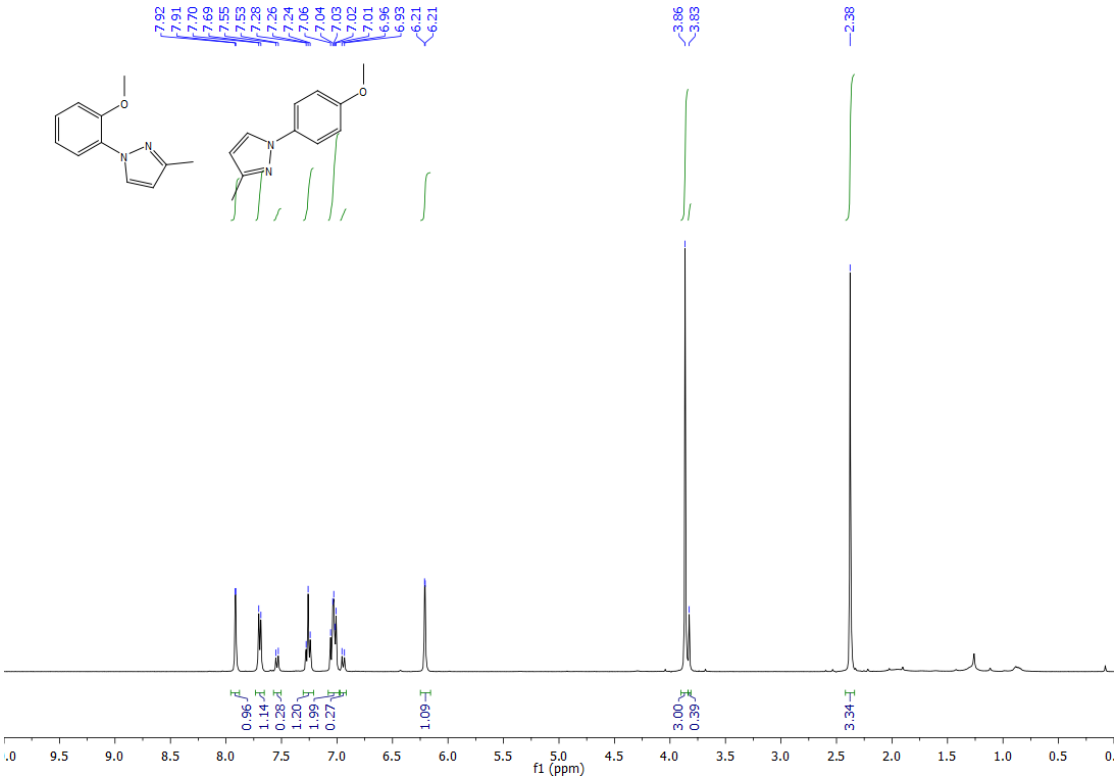
^{13}C NMR (101 MHz, $CDCl_3$) of **24a** and **24b**



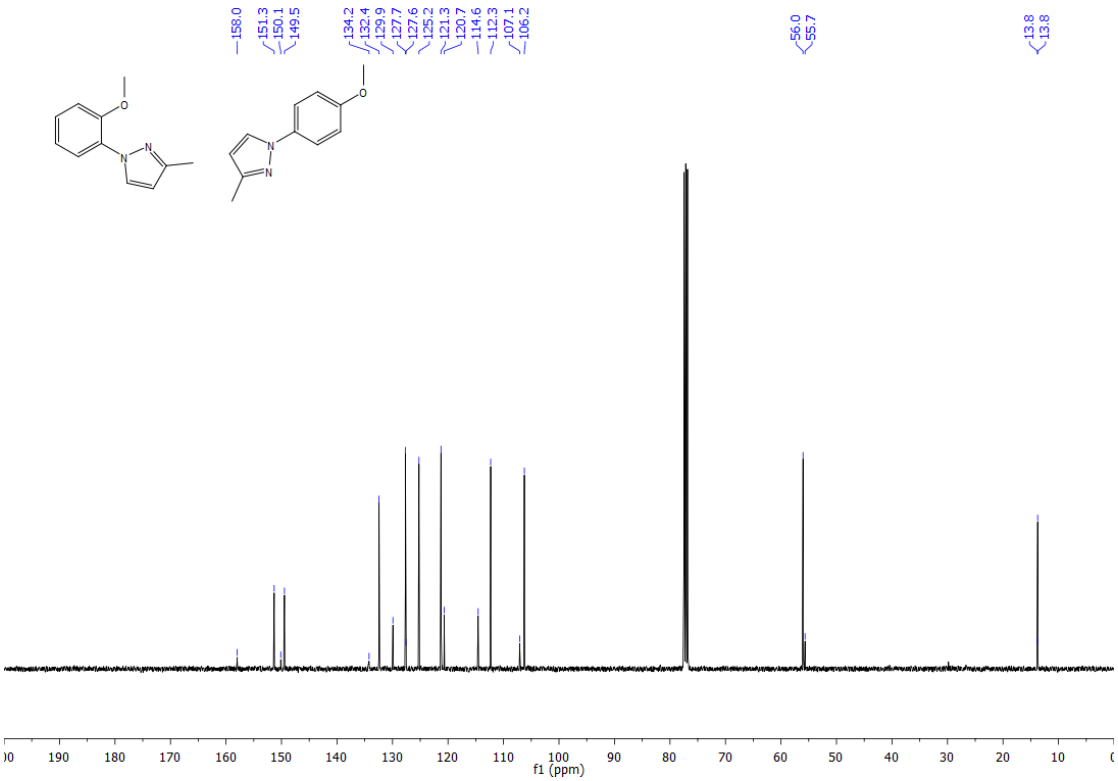
^{1}H NMR (400 MHz, $CDCl_3$) of **25**



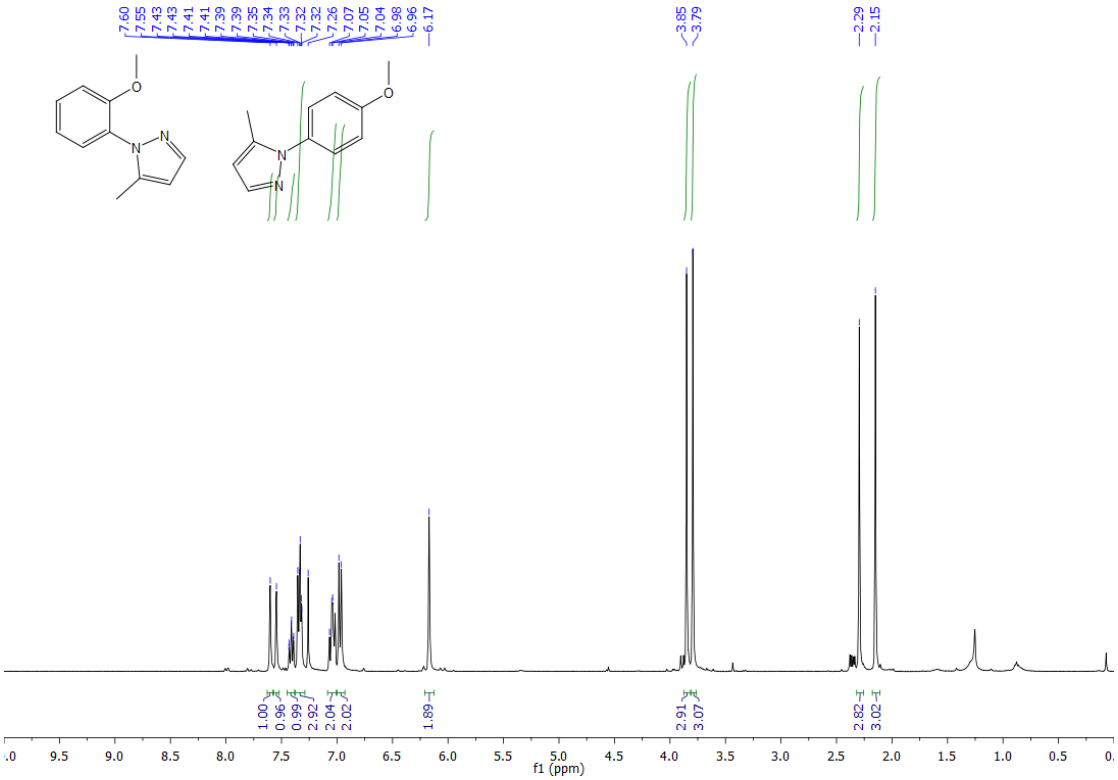
^{13}C NMR (101 MHz, $CDCl_3$) of **25**



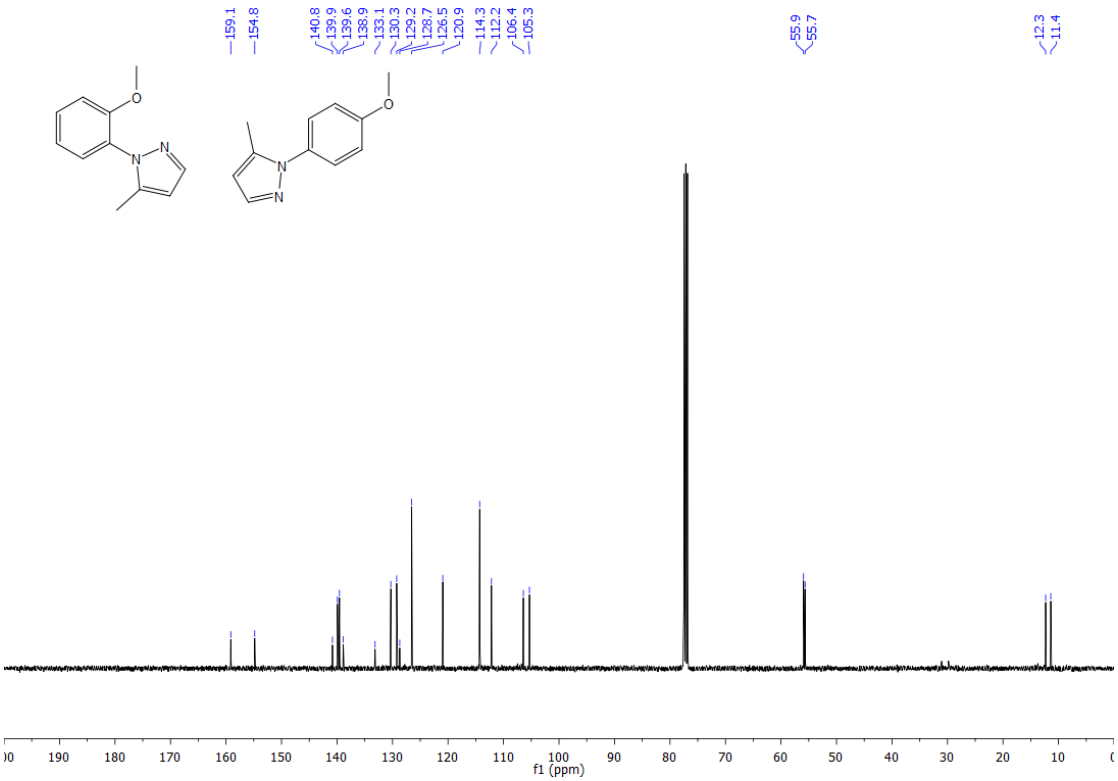
^{1}H NMR (400 MHz, $CDCl_3$) of **26a** and **26b**



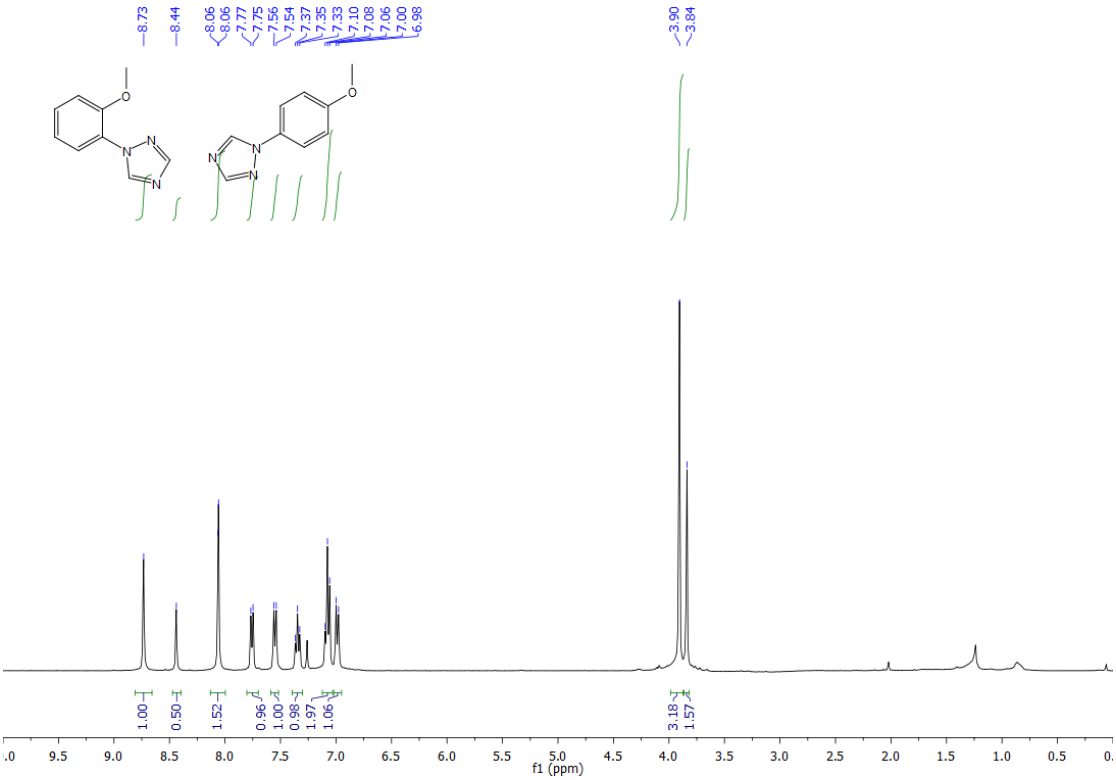
^{13}C NMR (101 MHz, $CDCl_3$) of **26a** and **26b**



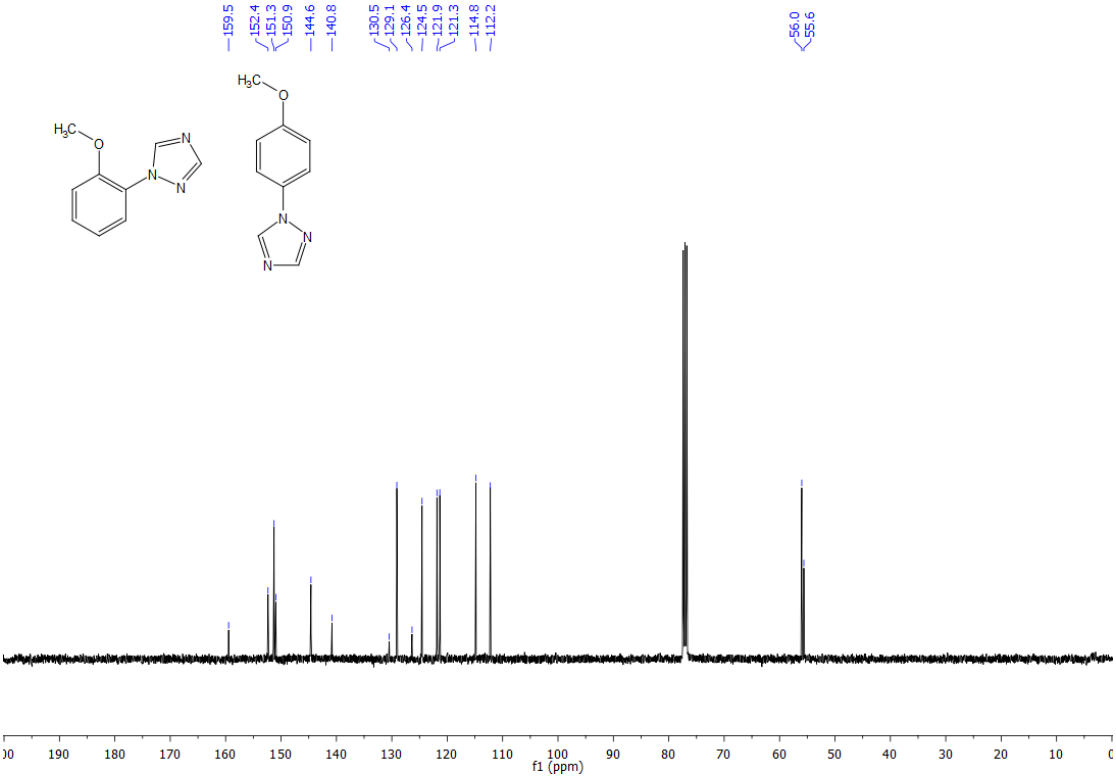
^{1}H NMR (400 MHz, $CDCl_3$) of **26c** and **26d**



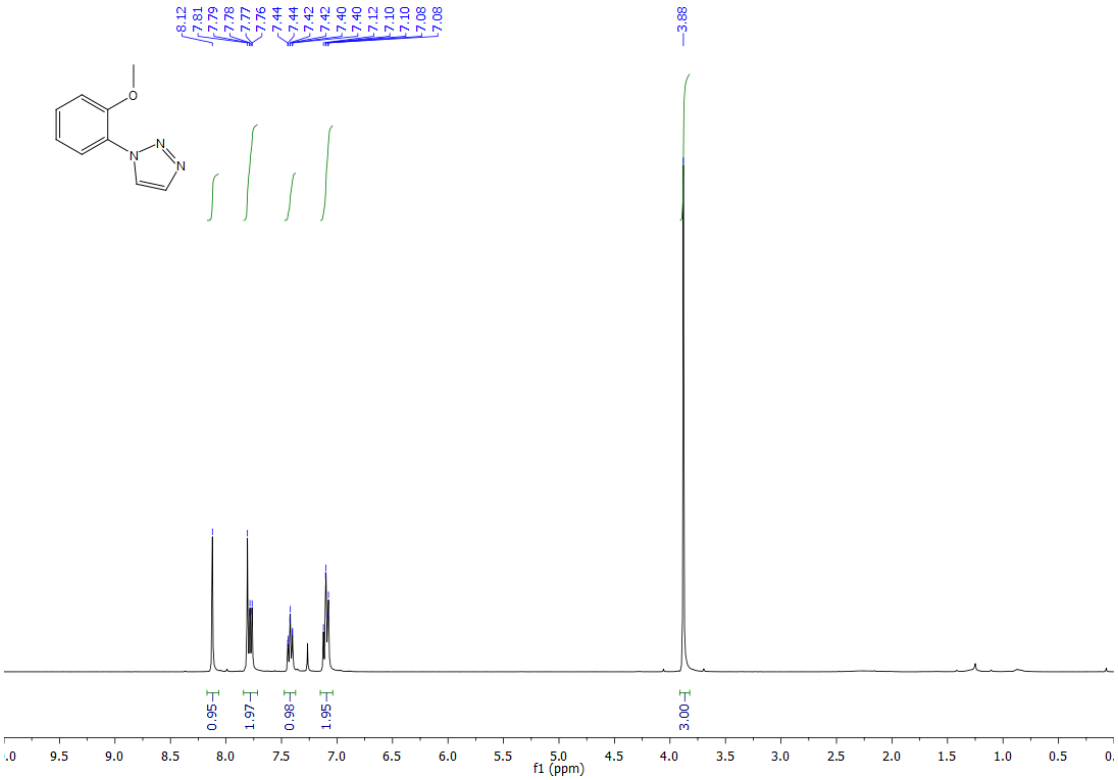
^{13}C NMR (101 MHz, $CDCl_3$) of **26c** and **26d**



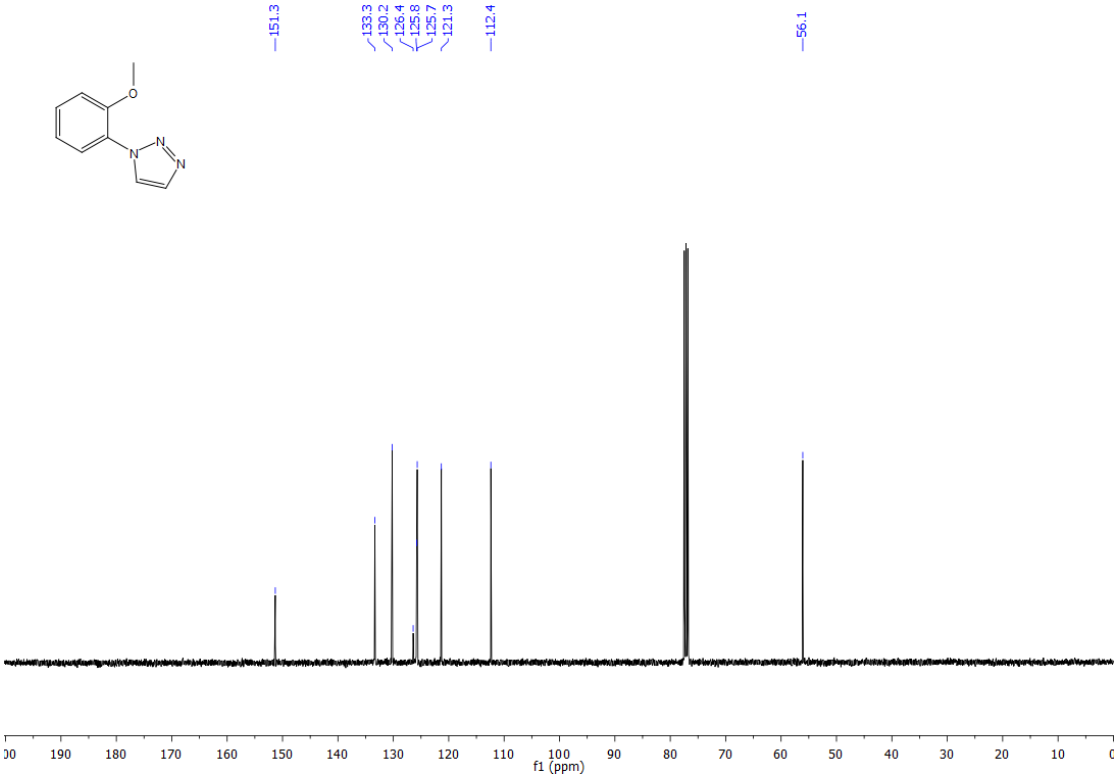
^{1}H NMR (400 MHz, $CDCl_3$) of **27a** and **27b**



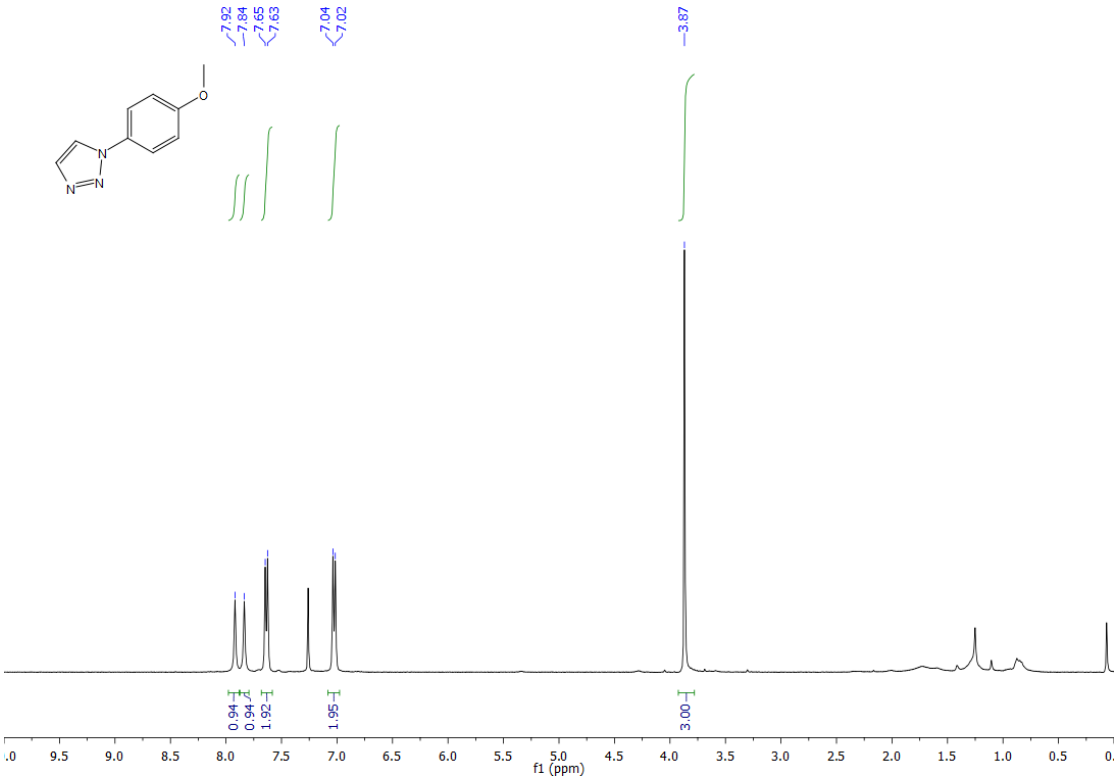
^{13}C NMR (101 MHz, $CDCl_3$) of **27a** and **27b**



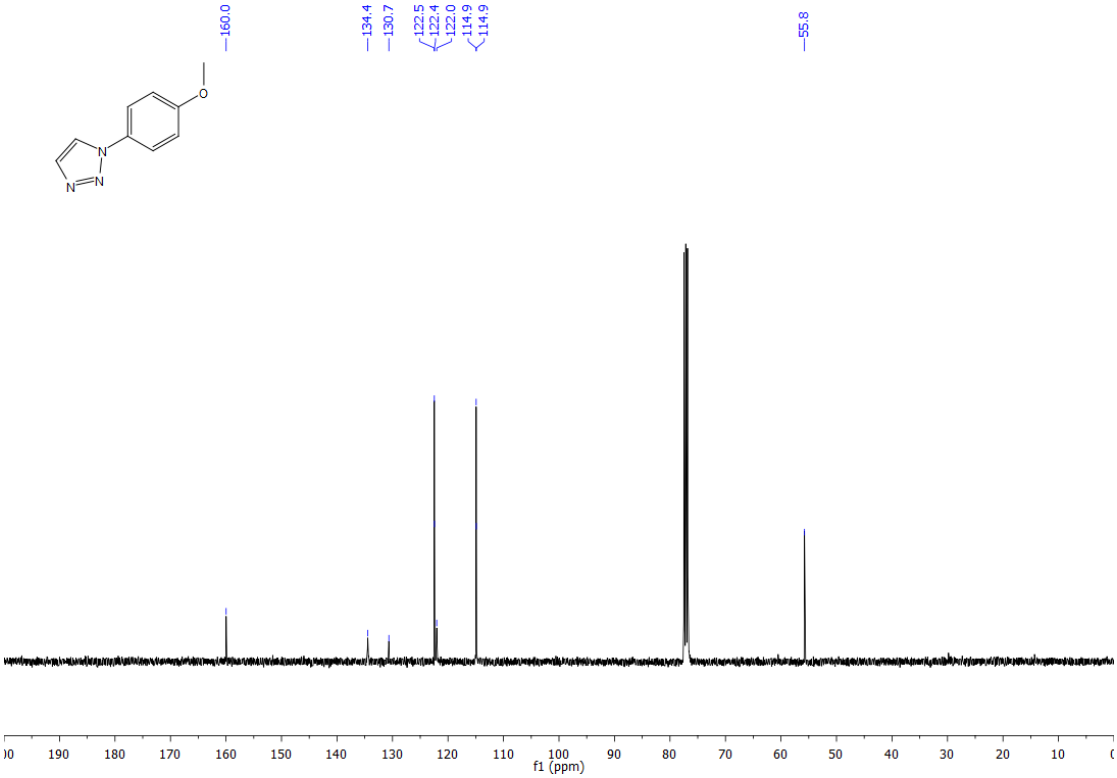
^{1}H NMR (400 MHz, $CDCl_3$) of **28a**



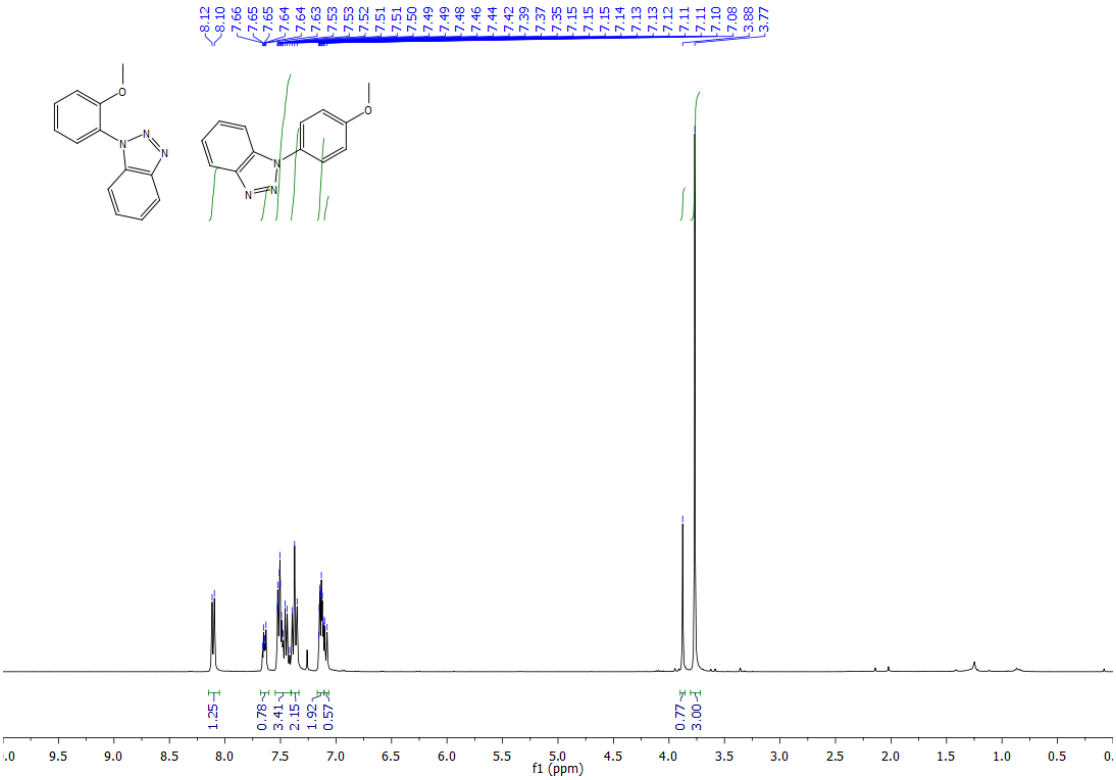
^{13}C NMR (101 MHz, $CDCl_3$) of **28a**



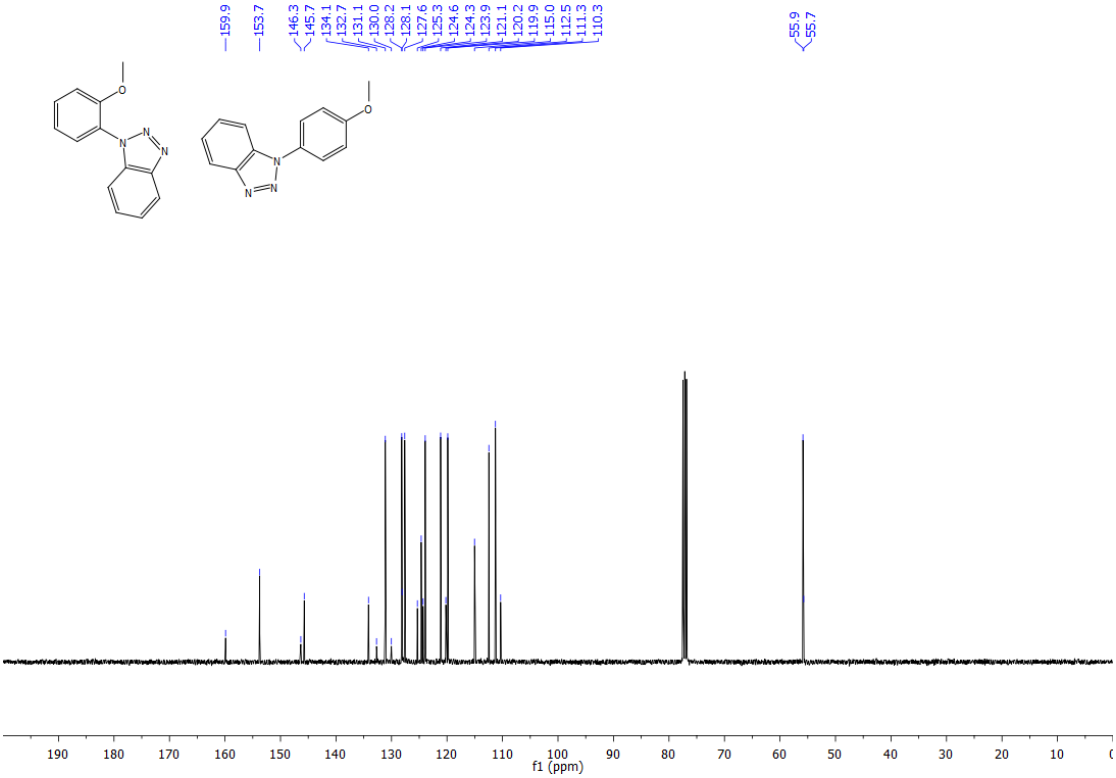
^{1}H NMR (400 MHz, $CDCl_3$) of **28b**



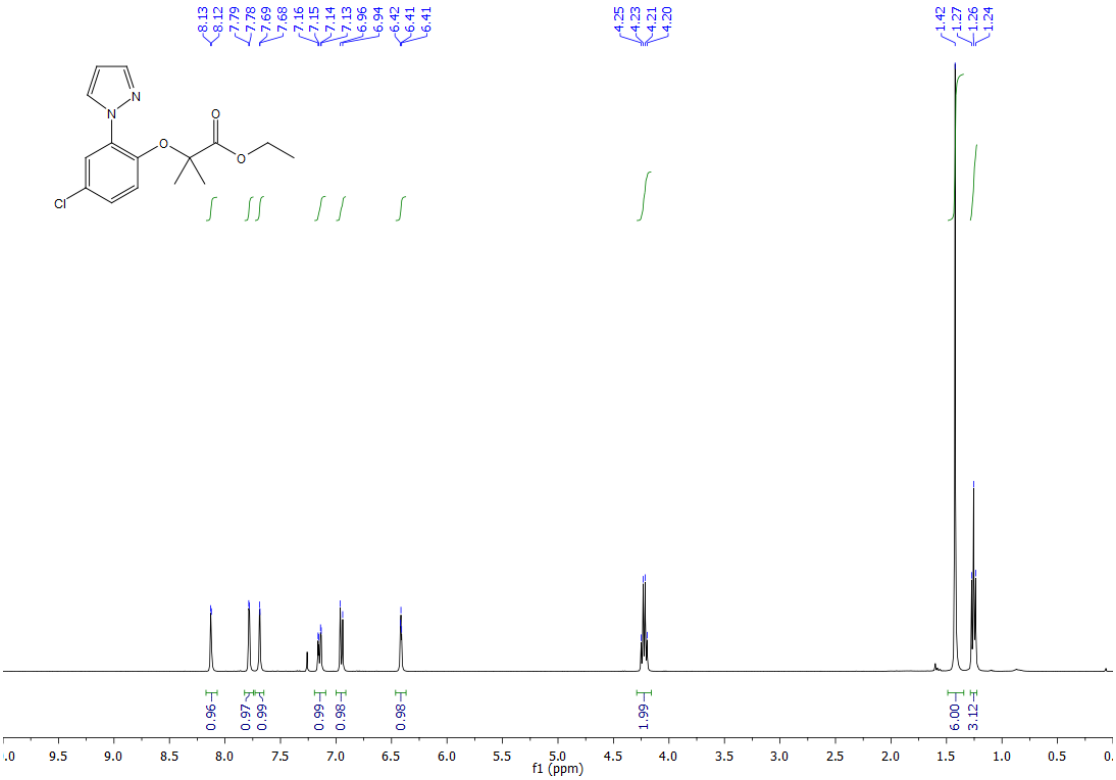
^{13}C NMR (101 MHz, $CDCl_3$) of **28b**



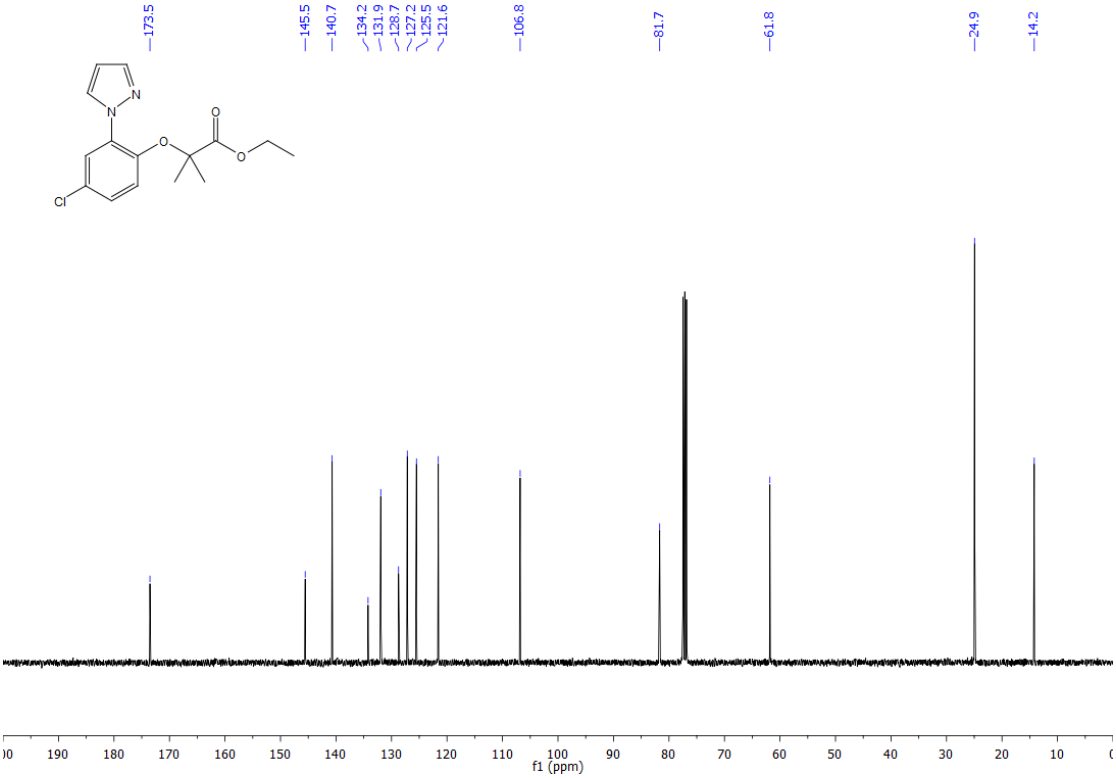
^{1}H NMR (400 MHz, $CDCl_3$) of **29a** and **29b**



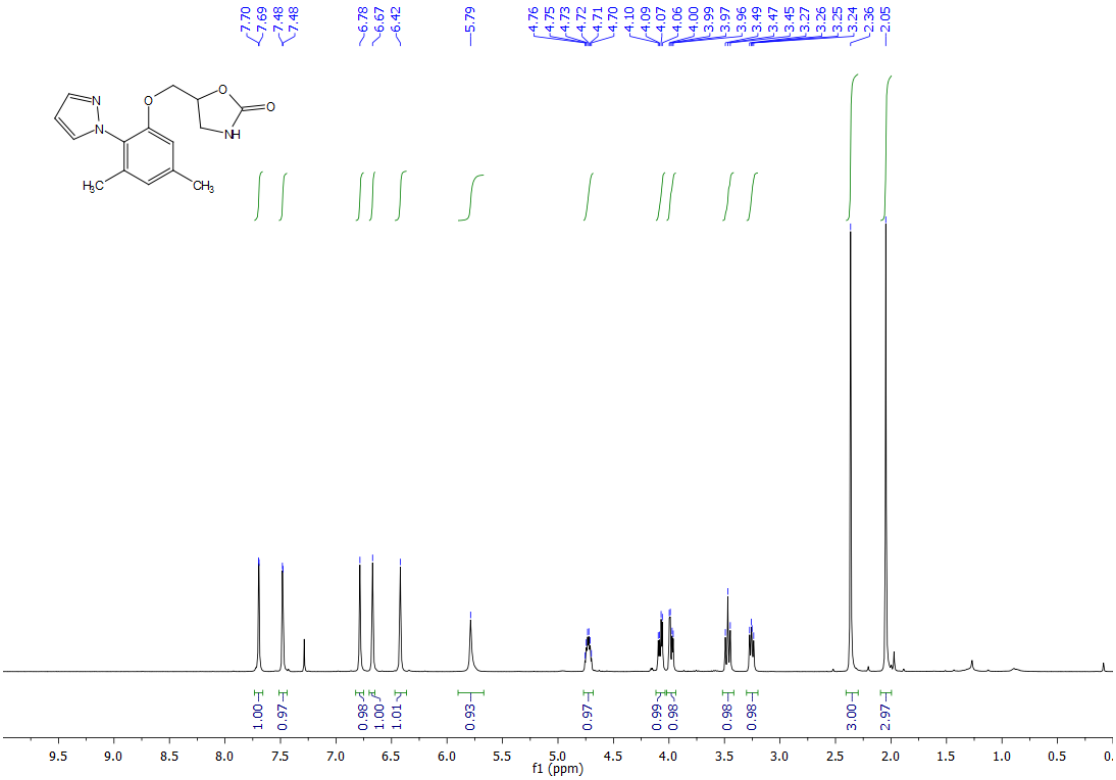
^{13}C NMR (101 MHz, $CDCl_3$) of **29a** and **29b**



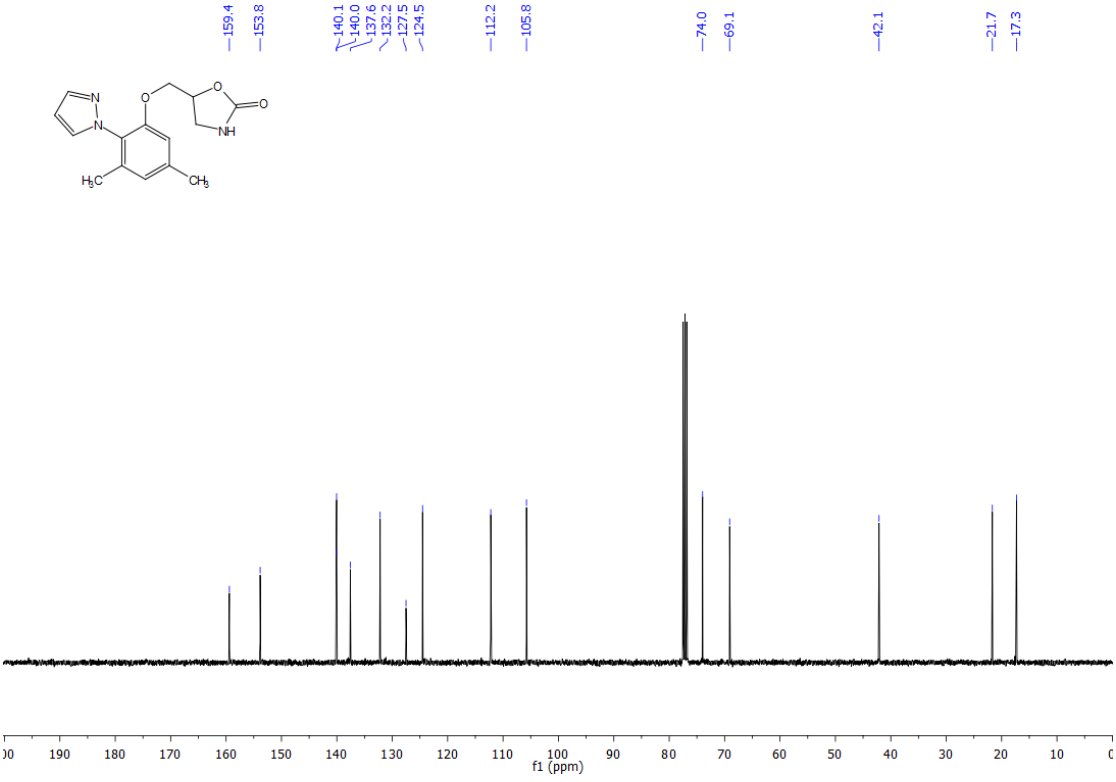
^{1}H NMR (400 MHz, $CDCl_3$) of **32**



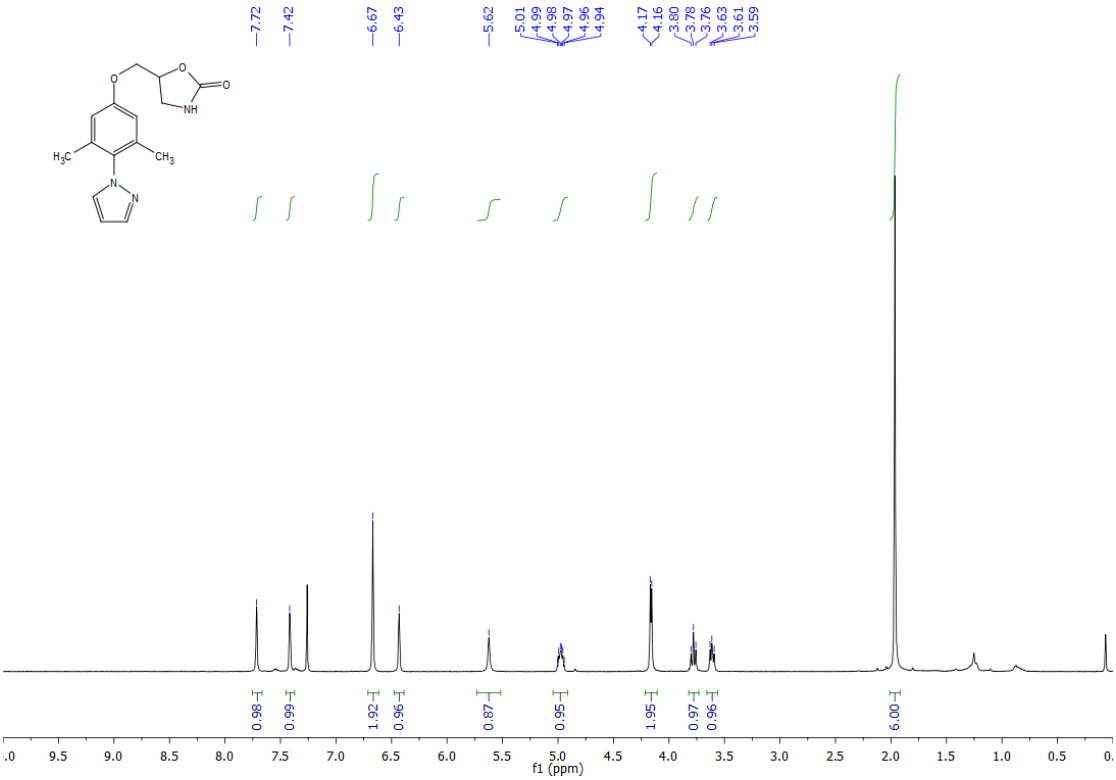
^{13}C NMR (101 MHz, $CDCl_3$) of **32**



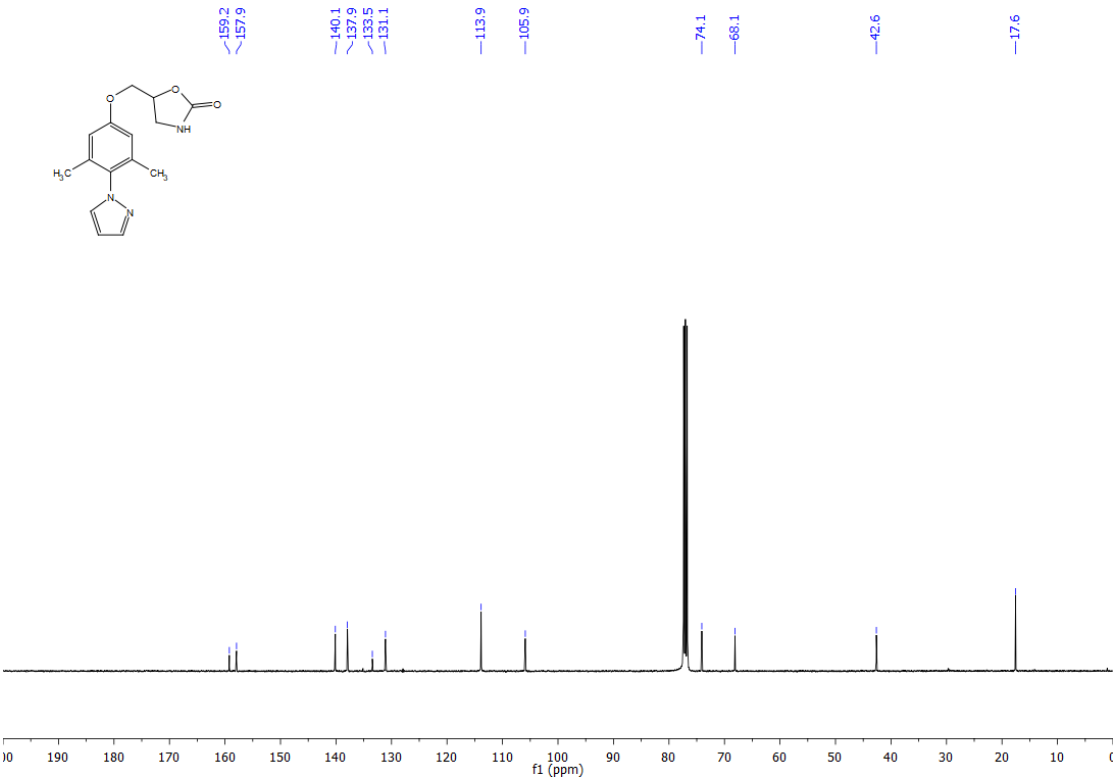
^{1}H NMR (400 MHz, $CDCl_3$) of **34a**



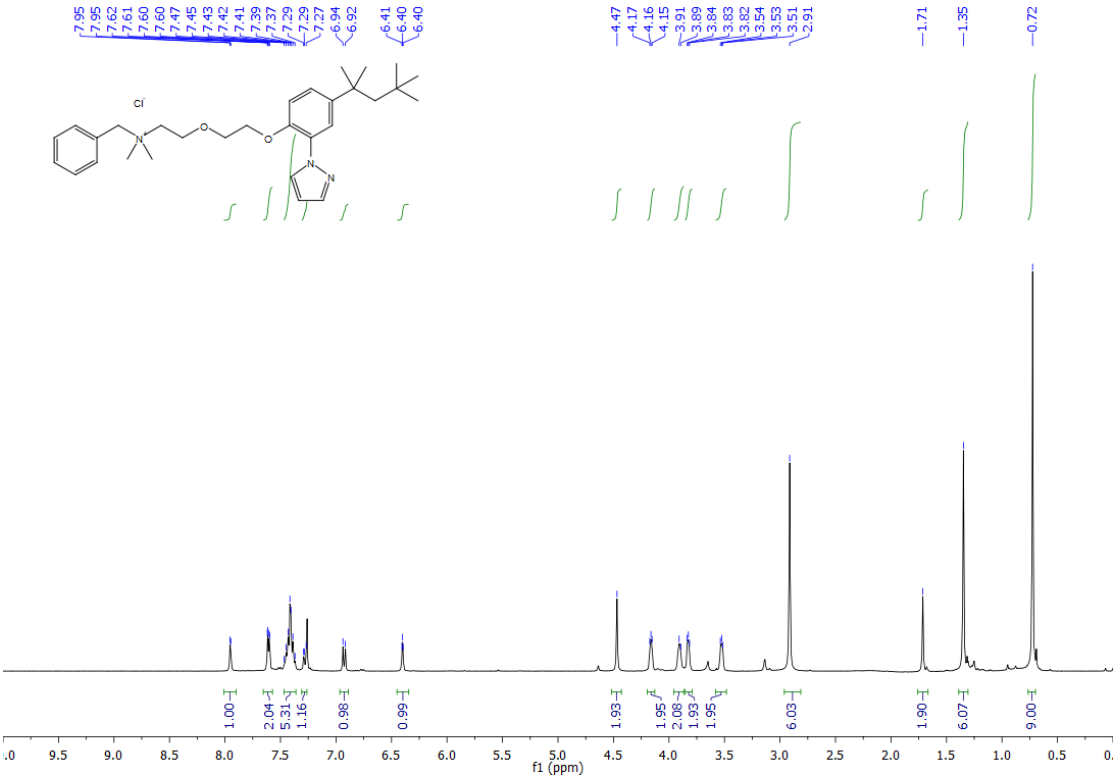
^{13}C NMR (101 MHz, $CDCl_3$) of **34a**



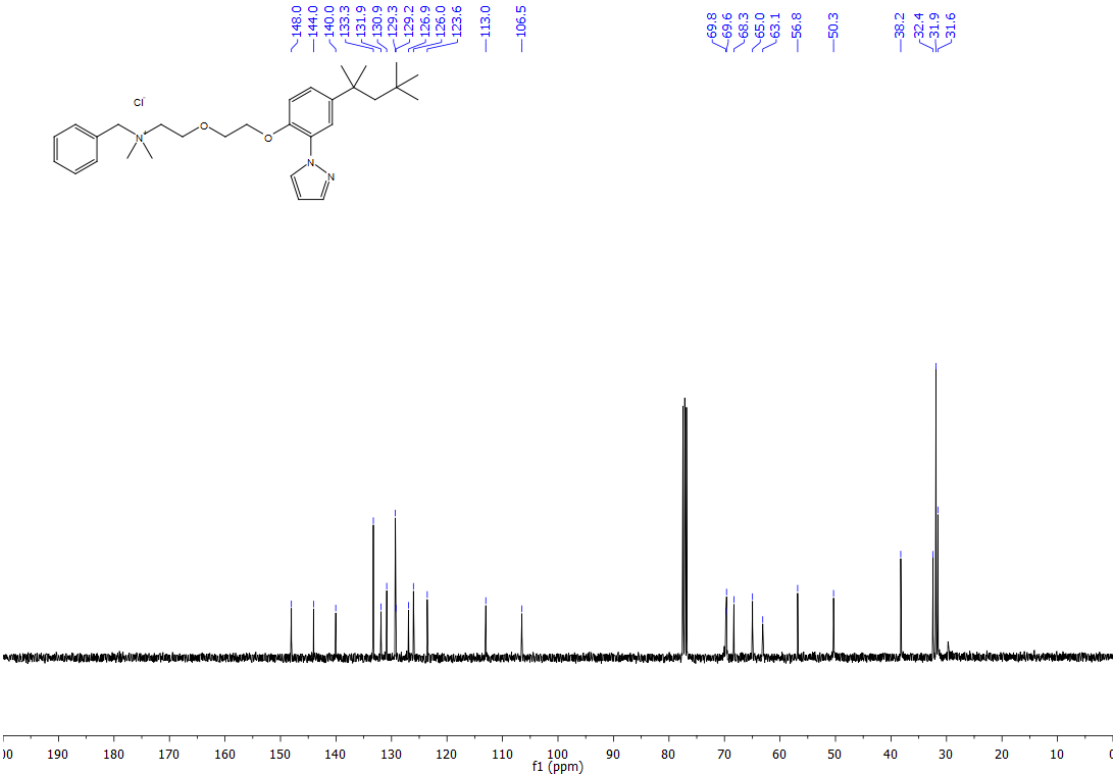
^{1}H NMR (400 MHz, $CDCl_3$) of **34b**



^{13}C NMR (101 MHz, $CDCl_3$) of **34b**



^{1}H NMR (400 MHz, $CDCl_3$) of **36**



^{13}C NMR (101 MHz, $CDCl_3$) of **36**