Supporting Information

Solvent free and Montmorillonite K10 catalysed domino reactions for the synthesis of pyrazoles with alkynylester as a dual synthon

Sesuraj Babiola Annes,[†] Rajendhiran Saritha,[†] Saravanan Subramanian,[‡] Bhaskaran Shankar,[‖] Subburethinam Ramesh*[†]

[†]Department of Chemistry, School of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur 613401, Tamil Nadu, India.

[‡]Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific and Industrial Research (CSIR), G.B. Marg, Bhavnagar - 364 002, Gujarat, India

[‖]Department of Chemistry, Sethu Institute of Technology, Kariapatti-626115, Tamil Nadu, India.

1. General information

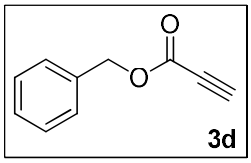
All the reactions were carried out in oven-dried Schlenk reaction tubes. Thin-layer chromatography (TLC) was used to monitor reactions by Merck silica gel 60 F254 pre-coated plates. Silica mesh (230-400) from spectrochem pvt. Ltd., Silica mesh (60-120) from SRL pvt.Ltd. and Hexanes-ethyl acetate mixture was used for compound purification. All reactions were carried out in temperature controlled magnetic stirrers (Heidolph, Ika). ^{1}H and ^{13}C NMR spectrum were recorded on a Bruker 300 MHz and 75 MHz instrument respectively. $CDCl_3$ and DMSO-d_6 solvents were used to take NMR spectrum. Chemical shifts were reported in parts per million and multiplicities are as written as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and dd (doublet of doublet). Coupling constants (*J*) are reported in Hertz. Melting points were recorded on a GUNA CAPILLARY melting point apparatus. High resolution mass Spectrum (HRMS) were recorded on Q-T of Micro mass spectrometer. Solvents used were laboratory grade and procured from PURE CHEM (Dichloromethane, Hexanes) and FINAR (Ethyl acetate). Various phenylhydrazine hydrochloride salts were purchased from Alfa-aesar (**1c**), AVRA synthesis (**1a**,**1b**,**1d-1f**,**1h-1o**), SRL (**1g**). Montmorillonite K10 clay, NBS and Alkynylesters (**3a** and **3b**) from Sigma Aldrich pvt. Ltd, AVRA synthesis and Spectrochem pvt. Ltd. respectively. Single-crystal crystallographic data of 11ab and 12b were collected on a Bruker D8 Quest diffractometer [λ(Mo Kα) = 0.71073 Å]. The structures were solved by direct methods using SHELXS-97 1 and refined using the SHELXL-2018/3 program.[6] All non-hydrogen atoms were refined anisotropically.

2. General procedure for the synthesis of Pyrazole

2.1. Phenylhydrazine preparation from phenylhydrazine hydrochloride salts.

Phenylhydrazine hydrochloride (1 mmol), water (10 mL), NaOH (2 mmol) and dichloromethane (8 ml) were stirred for 10 min. The organic layer was separated and evaporated in rotary evaporator. Phenylhydrazine was obtained in 95% yield (137 mg). The same procedure was followed for the preparation of other phenylhydrazine from respective phenylhydrazine hydrochloride salts.

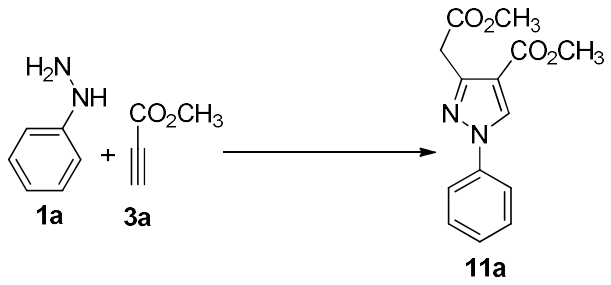
2.2. General procedure for the synthesis of Propiolates



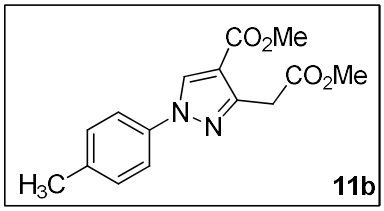
Preparation of 3d: Into the mixture of benzyl bromide (3.5 mmol), NaI (0.35 mmol) and K_2CO_3 (3.86 mmol) in acetone was added propiolic acid (3.5 mmol) and then refluxed for 6 hours. After completion of reaction, the reaction mass was worked up using ethyl acetate and water. The organic layer was separated, dried and concentrated under reduced pressure. The crude was then subjected to silica gel column chromatography and the corresponding propiolate (3d) was obtained in yield 70%. Colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.38 (5H, s), 5.21 (2H, s), 2.89 (1H, s). The spectral data is exactly matching with reported literature spectra.[1] 3c also prepared by same method.

Preparation of 3e and 3f: Propiolic acid (1.4 mmol), benzylalcohol (1.4 mmol), DMAP (0.9 mmol) and DCC (1.4 mmol) were taken in $CHCl_3$. The reaction mass was stirred for 30 mins. After completion of reaction, the reaction mass was filtered and the filtration was dried, concentrated under reduced pressure. The propiolate (3e and 3f) was obtained in 83% yield after column purification.[2]

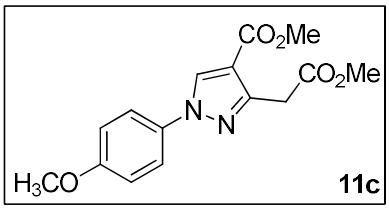
2.3. General procedure for the Synthesis of compound Methyl 3-(2-methoxy-2-oxoethyl)-1-phenyl-1H-pyrazole-4-carboxylate (11a):



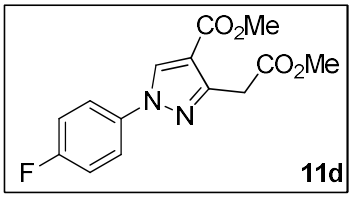
The reaction was carried out in Schlenk tube. Phenylhydrazine (1 mmol), Montmorillonite K10 (200 mol%) were taken and slurry prepared. Propiolate (1 mmol) added dropwise to the slurry. The reaction was conducted in oxygen atmosphere and the temperature was slowly raised to 65 °C. The reaction was monitored by TLC. After completion of reaction, the crude mass was directly transferred to column (silica mesh: 230-400), Hexanes-Ethyl acetate as mobile phase. It afforded the corresponding pyrazole **11a**; Yield = 74% (Wt.: 101 mg). Dark brown Viscous liquid; R_f = 0.26 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.69 (2H, d, *J* = 0.6 Hz), 7.47 (2H, t, *J* = 0.9 Hz), 7.39 – 7.32 (1H, m), 4.03(2H, s), 3.84 (3H, s), 3.74 (3H, s). The spectral data exactly matches with the literature data.[3] The general procedure was followed for the preparation of the compounds **11b – 11z**, **11aa** and **11ab**.



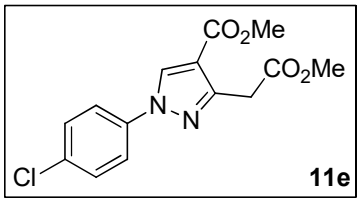
Methyl 3-(2-methoxy-2-oxoethyl)-1-(p-tolyl)-1H-pyrazole-4-carboxylate (11b): Yield = 77% (Wt.: 110 mg); Dark brown liquid; R_f = 0.33 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.34 (1H, s), 7.56 (2H, *J* = 0.9 Hz), 7.29 – 7.25 (2H, m), 4.02 (2H, s), 3.83 (3H, s), 3.74 (3H, s), 2.39 (3H, s). The spectral data exactly matches with the literature data.[3]



Methyl 3-(2-methoxy-2-oxoethyl)-1-(4-methoxyphenyl)-1H-pyrazole-4-carboxylate (11c): Yield = 79% (Wt: 120 mg); Brown semi solid; R_f = 0.27 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.28 (1H, s), 7.57 (2H, d, *J* = 0.9 Hz), 6.96 (2H, d , *J* = 0.3 Hz), 3.73 (3H, s). The spectral data exactly matches with the literature data.[3]

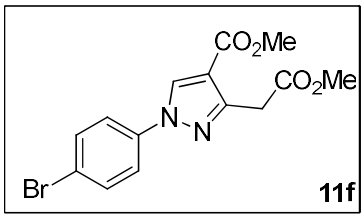


Methyl 1-(4-fluorophenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11d): Yield = 71% (Wt.: 104 mg); Dark yellow solid; mp. = 78-80 °C; R_f = 0.22 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.32 (1H, s), 7.68 – 7.63 (2H, m), 7.19 – 7.13 (2H, m), 4.02 (2H, s), 3.84 (3H, s), 3.74 (3H, s). The spectral data exactly matches with the literature data.[3]

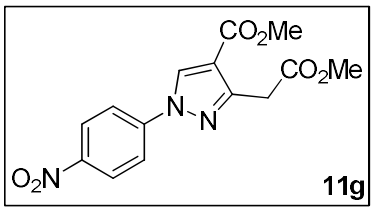


Methyl 1-(4-chlorophenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11e): Yield = 70% (Wt.: 108 mg); Yellow solid; mp. = 98-100 °C; R_f = 0.23 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.36 (1H, s), 7.65 – 7.62 (2H, m),

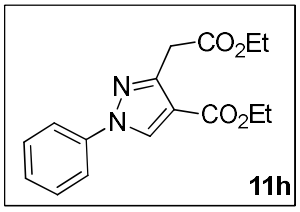
7.45 – 7.42 (2H, m), 4.02 (2H, s), 3.84 (3H, s), 3.74 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.6, 163.1, 149.1, 137.6, 133.0, 131.1, 129.6, 120.5, 141.6, 52.2, 51.5, 33.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}ClN_2O_4$:309.0642; found: 309.0664.



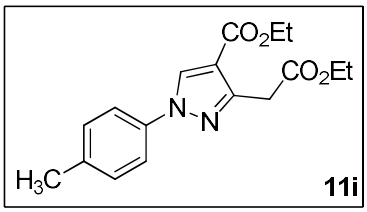
Methyl 1-(4-bromophenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11f): Yield = 68% (Wt.: 120 mg); Pale yellow solid. mp. = 88-90 °C; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.38 (1H, s), 7.76 (1H, s), 7.57 (1H, d, *J* = 0.9 Hz), 7.43 – 7.26 (2H, m), 4.02 (2H, s), 3.84 (3H, s), 3.75 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.6, 163.1, 149.1, 138.1, 132.6, 131.0, 120.8, 114.7, 52.2, 51.5, 33.6. HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}BrN_2O_4$: 253.0132; found: 253.0132



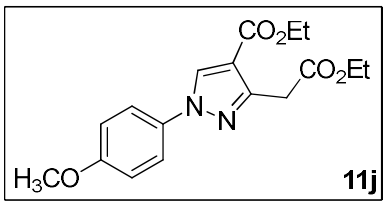
Methyl 3-(2-methoxy-2-oxoethyl)-1-(4-nitrophenyl)-1H-pyrazole-4-carboxylate (11g): Yield = 47% (Wt.: 75 mg); Dark red solid; mp. = 198-200 °C; R_f = 0.19 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.50 (1H, s), 8.39 – 8.34 (2H, m), 7.92 – 7.88 (2H, m), 4.04 (2H, s), 3.86 (3H, s), 3.76 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.3, 162.8, 150.2, 146.2, 143.3, 131.4, 125.4, 119.1, 115.9, 52.3, 51.7, 33.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}N_3O_6$: 320.0875; found: 320.0875.



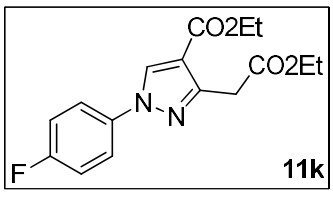
Ethyl 3-(2-ethoxy-2-oxoethyl)-1-phenyl-1H-pyrazole-4-carboxylate (11h): Yield = 73% (Wt.: 110 mg); Yellow solid; mp. = 88-90 °C; R_f = 0.31 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.69 (2H, d, *J* = 0.9 Hz), 7.49 – 7.34 (3H, m), 4.31(2H, q, *J* = 0.9 Hz), 4.19 (2H, d, *J* = 0.6 Hz), 4.01 (2H, s), 1.35 (3H, t, *J* = 0.6 Hz), 1.30 – 1.21 (3H, m). The spectral data exactly matches with the literature data.[3]



Ethyl 3-(2-ethoxy-2-oxoethyl)-1-(p-tolyl)-1H-pyrazole-4-carboxylate (11i): Yield = 77% (Wt.: 121 mg);Brown semi solid; R_f = 0.34 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.35 (1H, s), 7.57 (2H, d, *J* = 0.9 Hz), 7.24 (2H, s), 4.29 (3H, q, *J* = 0.9 Hz), 4.19 (3H, q, *J* = 0.9 Hz), 4.00 (2H, s), 2.39 (3H, s), 1.34 (2H, t, *J* = 0.9 Hz), 1.27 (2H, t, *J* = 0.9 Hz). The spectral data exactly matches with the literature data.[3]

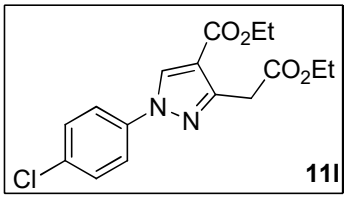


Ethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-methoxyphenyl)-1H-pyrazole-4-carboxylate (11j): Yield = 80% (Wt.: 132 mg); Dark brown liquid; R_f = 0.37 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm)8.29 (1H, s), 7.58 (2H, d, *J* = 0.9 Hz), 6.96 (2H, d, *J* = 0.9 Hz), 4.29 (2H, q, *J* = 0.9 Hz), 4.20 (2H, q, *J* = 0.6 Hz), 4.00 (2H, s), 3.83 (3H, s), 1.34 (3H, t, *J* = 0.6 Hz), 1.27 (3H, *J* = 0.9 Hz). The spectral data exactly matches with the literature data.[3]

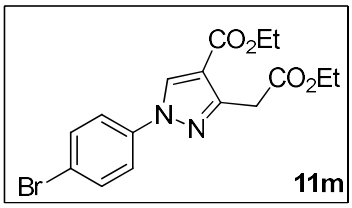


Ethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-fluorophenyl)-1H-pyrazole-4-carboxylate (11k): Yield = 69% (Wt.: 110 mg); Brown solid; mp. = 100-102 °C; R_f = 0.23 (20% of Ethyl acetate in Hexanes); ^{1} NMR (300 MHz, $CDCl_3$, δ ppm) 8.33(1H, s), 7.68 – 7.64 (2H, m), 7.16 (2H, t, *J* = 0.9 Hz), 4.30 (2H, q, *J* = 0.9 Hz), 4.20 (2H, q, *J* = 0.6 Hz); ^{13}C NMR (75

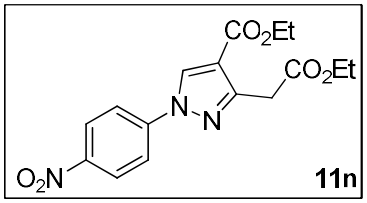
MHz, $CDCl_3$, δ ppm) 170.2, 163.2, 162.8, 159.9, 148.9, 135.5, 131.3, 121.3, 121.2, 116.5, 116.2, 114.9, 61.0, 60.3, 33.9; HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}FN_2O_4$: 321.1273; found: 321.1273.



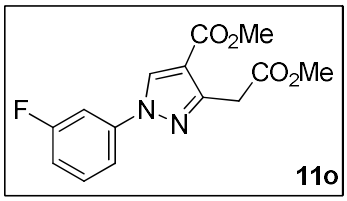
Ethyl 1-(4-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11l): Yield = 71% (Wt.: 119 mg); Brown solid; mp. = 98-100 °C; R_f = 0.25 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.36 (1H, s), 7.67 – 7.62 (2H, m), 7.46 – 7.41 (2H, m), 4.30 (2H, q, *J* = 0.9 Hz), 4.20 (2H, q, *J* = 0.6 Hz), 4.00 (2H, s), 1.35 (3H, t, *J* = 0.6 Hz), 1.28 (3H, t, *J*= 0.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.1, 162.8, 149.1, 137.7, 132.9, 131.1, 129.6, 120.5, 115.1, 61.0, 60.4, 33.9, 14.3, 14.2; HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}ClN_2O_4$: 337.0976; found: 337.0976.



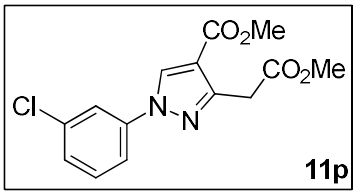
Ethyl 1-(4-bromophenyl)-3-(2-ethoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11m): Yield = 66% (Wt.: 125mg); Brown solid; mp. = 109-111 °C; R_f = 0.25 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.37 (1H, s), 7.59 (4H, s), 4.30 (2H, d, *J* = 0.9 Hz), 4.20 (2H, q, *J* = 0.6 Hz), 4.00 (2H, s), 1.35 (3H, t, *J*= 0.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.1, 162.8, 149.2, 138.2, 132.6, 131.1, 120.8, 116.60, 115.2, 61.0, 60.4, 34.0, 14.3, 14.2. HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}BrN_2O_4$: 381.0443; found:381.0443.



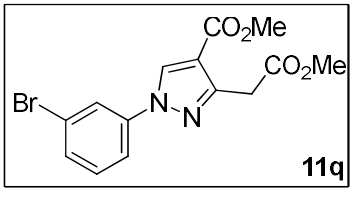
Ethyl 3-(2-ethoxy-2-oxoethyl)-1-(4-nitrophenyl)-1H-pyrazole-4-carboxylate (11n): Yield = 44% (Wt.: 76 mg); Dark red solid; mp. = 198-200 °C; R_f = 0.18 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6, δ ppm) 8.72 (1H, s), 8.36 (2H, d, *J* = 0.9 Hz), 8.00 (2H, d, *J* =0.9 Hz), 4.32 (2H, q, *J* = 0.6 Hz), 4.20 (2H, q, *J* = 0.6 Hz), 4.00 (2H, s), 1.37 (3H, t, *J* = 0.6 Hz), 1.28 (3H, t, *J* = 0.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6, δ ppm) 168.2, 160.9, 148.4, 144.4, 142.0, 131.3, 123.8, 117.8, 114.6, 59.4, 58.9, 32.5, 12.9, 12.8; HRMS (m/z): $[M+NH_4]^+$ calcd. for $C_{16}H_{18}N_3O_6$: 365.1461; found: 365.0557.



Methyl 1-(3-fluorophenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11o): Yield = 65% (Wt.: 94 mg); Yellow solid; mp. = 78-80 °C; R_f = 0.23 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.38 (1H, s), 7.50 – 7.39 (3H, m), 7.07 – 7.01 (1H, m), 4.02 (2H, s), 3.84 (3H, s), 3.75 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.5, 164.8, 163.1, 161.5, 149.1, 140.3, 131.2, 130.8, 114.7, 114.5, 114.1, 107.4, 107.1, 52.2, 51.5, 33.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}FN_2O_4$: 293.0934; found: 293.0934.

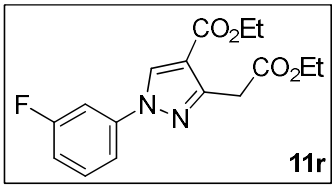


Methyl 1-(3-chlorophenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11p): Yield = 66% (Wt.: 101 mg); Dark Brown solid; mp. = 79-81 °C; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.38 (1H, s), 7.76 (1H, s), 7.75 (1H, d, *J* = 0.9 Hz), 7.43 – 7.30 (2H, m), 4.0 2 (2H, s), 3.84 (3H, s), 3.75 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.5, 163.1, 149.2, 140.0, 136.5, 131.2, 130.2, 127.5, 119.8, 117.2, 114.8, 52.2, 51.5, 33.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}ClN_2O_4$: 309.0642; found: 309.0642.

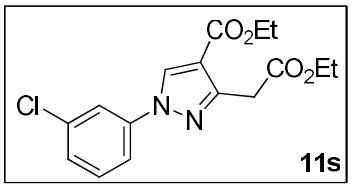


Methyl 1-(3-bromophenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11q): Yield = 62% (Wt.: 109 mg); Yellow

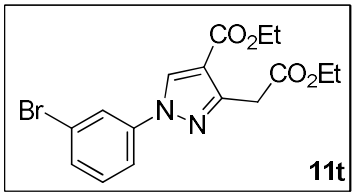
solid; mp. = 110-112 °C; R_f = 0.23 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.37 (1H, s), 7.91 (1H, s), 7.62 (1H, d, *J* = 0.9 Hz), 7.47 (1H, d, *J* = 0.6 Hz), 7.33 (1H, t, *J* = 0.9 Hz), 4.02 (2H, s), 3.84 (3H, s), 3.74 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.5, 163.1, 149.2, 140.1, 131.2, 130.8, 130.4, 123.2, 122.6, 117.7, 114.8, 52.2, 51.5, 33.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{14}BrN_2O_4$: 353.0133; found: 353.0133.



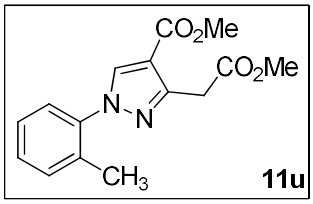
Ethyl 3-(2-ethoxy-2-oxoethyl)-1-(3-fluorophenyl)-1H-pyrazole-4-carboxylate (11r): Yield = 59% (Wt.: 94 mg); Yellow solid; mp. = 78-80 °C; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.51 – 7.40 (3H, m), 7.07 – 7.00 (1H, m), 4.30 (2H, q, *J* = 0.6 Hz), 4.19 (2H, q, *J* = 0.9 Hz), 4.00 (2H, s), 1.35 (3H, t, *J* = 0.6 Hz), 1.28 (3H, t, *J* = 0.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.1, 164.86, 162.7, 161.58, 149.2, 140.4, 131.2, 130.9, 130.8, 115.2, 114.54, 114.50, 114.0, 107.4, 107.0, 61.0, 60.4, 34.0, 14.3, 14.2; HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}FN_2O_4$: 321.1269; found: 321.1269.



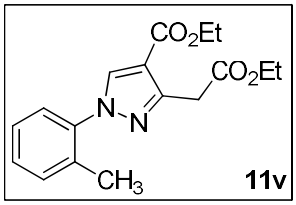
Ethyl 1-(3-chlorophenyl)-3-(2-ethoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11s): Yield = 64% (Wt.: 107 mg); Dark Brown solid; mp. = 76-78 °C; R_f = 0.25 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.76 (1H, t, *J*= 0.3 Hz), 7.60 – 7.56 (1H, m), 7.40 (1H, t, *J* = 0.6 Hz), 7.33 – 7.27 (1H, m), 4.31 (2H, q, *J* = 0.6 Hz), 4.20 (2H, q, *J* = 0.9 Hz), 4.00 (2H, s), 1.35 (3H, t, *J* = 0.6 Hz), 1.28 (3H, t, *J* = 0.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.1, 162.7, 149.3, 140.1, 136.4, 131.2, 130.6, 127.4, 119.7, 117.2, 115.3, 61.0, 60.4, 33.9, 14.3, 14.2; HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}ClN_2O_4$: 337.0950; found: 337.0950.



Ethyl 1-(3-bromophenyl)-3-(2-ethoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (11t): Yield = 63% (Wt.: 120 mg); Dark brown semi solid; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.38 (1H, s), 7.91 (1H, m), 7.61 (1H, d, *J* = 0.9 Hz), 7.45 (1H, d, *J* = 0.6 Hz0, 7.34 – 7.29 (1H, m), 4.30 (2H, q, *J* = 0.6 Hz), 4.22 (2H, q, *J* = 0.9 Hz), 4.00 (2H, s), 1.35 (3H, t, *J* = 0.6 Hz), 1.28 (3H, t, *J* = 0.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.2, 162.7, 149.2, 143.1, 131.2, 130.8, 130.3, 123.2, 122.5, 117.6, 115.2, 61.0, 60.4, 33.9, 14.3, 14.2; HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{18}BrN_2O_4$: 381.0443; found: 381.0443.

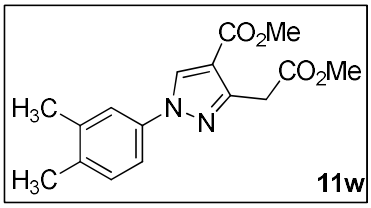


Methyl 3-(2-methoxy-2-oxoethyl)-1-(o-tolyl)-1H-pyrazole-4-carboxylate (11u): Yield = 51% (Wt.: 73 mg); Brown viscous liquid; R_f = 0.35 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.36 – 7.27 (4H, m), 4.02 (2H, s), 3.83 (3H, s), 3.73 (3H, s), 2.26 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.79, 163.55, 148.23, 138.91, 135.12, 135.70, 131.46, 129.16, 126.76, 126.00, 113.27, 52.11, 51.36, 33.55, 17.99, 14.13; HRMS (m/z): $[M+H]^+$ calcd. for $C_{15}H_{17}N_2O_4$: 289.1179; found: 289.1179.

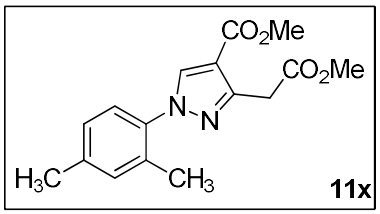


Ethyl 3-(2-ethoxy-2-oxoethyl)-1-(o-tolyl)-1H-pyrazole-4-carboxylate(11v): Yield = 57% (Wt.: 90 mg); Brown viscous liquid; R_f = 0.36 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.07 (1H, s), 7.35 – 7.27 (4H, m), 4.30 (2H, q, *J* = 0.6 Hz), 4.18 (2H, q, *J* = 0.9 Hz), 4.30 (2H, q, *J* = 0.6 Hz), 4.18 (2H, q, *J* = 0.9 Hz), 4.01 (2H, s), 2.26 (3H, s), 1.34 (3H, t, *J* = 0.6 Hz), 1.26 (3H, t, *J* = 0.6 Hz); ^{13}C NMR (75

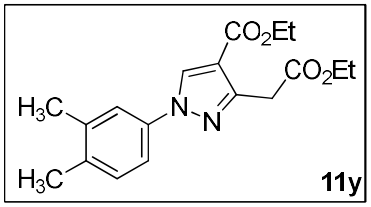
MHz, $CDCl_3$, δ ppm) 170.34, 163.18, 148.2, 138.9, 136.1, 133.7, 131.4, 129.1, 126.7, 126.0, 113.7, 60.9, 60.2, 33.9, 17.9, 14.3, 14.1; HRMS (m/z): $[M+H]^+$ calcd. for $C_{17}H_{21}N_2O_4$: 317.1491; found: 317.1491.



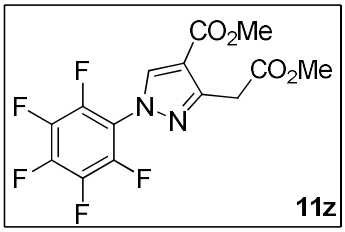
Methyl 1-(3,4-dimethylphenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate(11w): Yield = 70% (Wt.: 105 mg); Brown viscous liquid; R_f = 0.34 (20% of Ethyl acetate in Hexanes); ^1H NMR (300 MHz, $CDCl_3$, δ ppm) 8.33 (1H, s), 7.48 (1H, d, *J* = 0.3 Hz), 7.36 (1H, dd, *J* = 0.9 Hz & 0.6 Hz), 7.19 (1H, d, *J* = 0.9 Hz), 4.02 (2H, s), 3.83 (3H, s), 3.74 (3H, s), 2.32 (3H, s), 2.29 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.79, 163.48, 148.57, 138.13, 137.16, 136.16, 131.19, 130.49, 120.83, 116.82, 113.95, 52.16, 51.38, 33.72, 19.93, 19.37; HRMS (m/z): $[M+H]^+$ calcd. for $C_{16}H_{19}N_2O_4$: 303.1337; found: 303.1337.



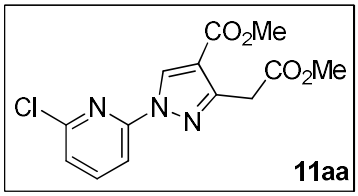
Methyl 1-(2,4-dimethylphenyl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate(11x): Yield = 58% (Wt.: 87 mg); Brown viscous liquid; R_f = 0.35 (20% of Ethyl acetate in Hexanes); ^1H NMR (300 MHz, $CDCl_3$, δ ppm) 8.33 (1H, s), 7.47 (1H, s), 7.38 – 7.34 (1H, m), 7.19 (2H, d, *J* = 0.9 Hz), 4.02 (2H, s), 3.83 (3H, s), 3.74 (3H, s), 2.32 (3H, s), 2.29 (3H, s). The spectral data exactly matches with the literature data.[3]



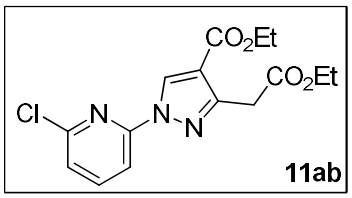
Ethyl 1-(3,4-dimethylphenyl)-3-(2-ethoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate(11y): Yield = 73% (Wt.: 120 mg); Brown solid; mp. = 88-90 °C; R_f = 0.36 (20% of Ethyl acetate in Hexanes); ^1H NMR (300 MHz, $CDCl_3$, δ ppm) 8.34 (1H, s), 7.49 (1H, d, *J* = 0.3 Hz), 7.37 (1H, dd, *J* = 0.9 & 0.6 Hz), 7.20 (1H, d, *J* = 0.9 Hz), 4.30 (2H, q, *J* = 0.6 Hz), 4.20 (2H, q, *J* = 0.6 Hz), 4.00 (1H, s), 2.32 (3H, s), 2.29 (3H, s), 1.35 (3H, t, *J* = 0.6 Hz), 1.27 (3H, t, *J* = 0.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.3, 163.1, 148.5, 138.0, 137.2, 136.0, 131.1, 130.4, 120.7, 116.7, 114.4, 60.9, 60.2, 34.0, 19.9, 19.3, 14.3, 14.2; HRMS (m/z): $[M+H]^+$ calcd. for $C_{18}H_{23}N_2O_4$: 331.1650; found: 331.1650.



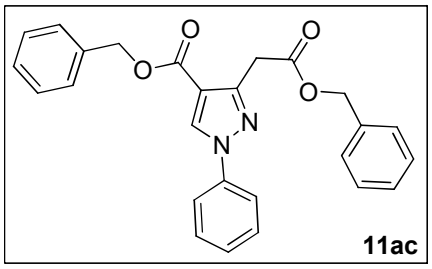
Methyl 3-(2-methoxy-2-oxoethyl)-1-(perfluorophenyl)-1H-pyrazole-4-carboxylate(11z): Yield = 49% (Wt.: 89 mg); Pale yellow solid; mp. = 92-95 °C; R_f = 0.27 (20% of Ethyl acetate in Hexanes); ^1H NMR (300 MHz, $CDCl_3$, δ ppm) 8.14 (1H, s), 4.02 (2H, s), 3.85 (3H, s), 3.74 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.1, 162.6, 190.2, 136.9, 115.2, 52.2, 51.6, 33.4, 29.7; HRMS (m/z): $[M+H]^+$ calcd. for $C_{14}H_{10}F_5N_2O_4$: 365.0557; found: 365.0557.



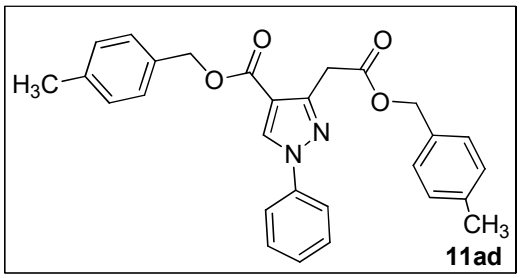
Methyl 1-(6-chloropyridin-2-yl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate(11aa): Yield = 57% (Wt.: 88 mg); Yellow solid; mp. = 103-105 °C; R_f = 0.33 (20% of Ethyl acetate in Hexanes); ^1H NMR (300 MHz, $CDCl_3$, δ ppm) 8.95 (1H, s), 7.92 – 7.83 (2H, m), 7.31 (1H, d, *J* = 0.6 Hz), 4.00 (2H, s), 3.84 (3H, s), 3.73 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 168.81, 161.54, 148.65, 148.30, 140.60, 130.02, 121.44, 113.46, 109.76, 50.75, 50.19, 32.31; HRMS (m/z): $[M+H]^+$ calcd. for $C_{13}H_{13}ClN_2O_4$: 310.0588; found: 310.0588.



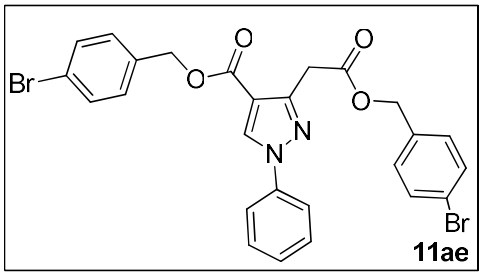
Ethyl 1-(6-chloropyridin-2-yl)-3-(2-ethoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate(11ab): Yield = 60% (Wt.: 101 mg); Yellow solid; mp. = 91-93 °C; R_f = 0.36 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.98 (1H, s), 7.92 – 7.76 (2H, m), 7.28 – 7.25 (1H, m), 4.31 (2H, q, *J* = 0.9 Hz), 4.20 (2H, q, *J* = 0,9 Hz), 4.00 (2H, s), 1.36 (3H, t, *J* = 0.6 Hz), 1.27 (3H, t, *J* = 0.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.0, 162.8, 150.3, 150.2, 149.9, 141.2, 131.7, 122.3, 115.3, 111.0, 61.0, 60.4, 34.0, 14.3, 14.1; HRMS (m/z): $[M+H]^+$ calcd. for $C_{15}H_{17}ClN_3O_4$: 338.0901; found: 338.0901.



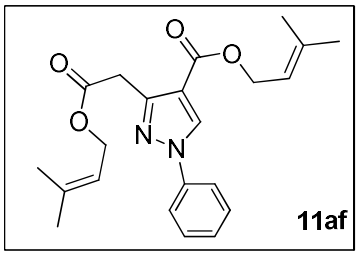
Benzyl 3-(2-(benzyloxy)-2-oxoethyl)-1-phenyl-1H-pyrazole-4-carboxylate (11ac): Yield = 51% (Wt.: 108.74 mg); Yellow viscous liquid; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.66 (2H, d, J = 0.9 Hz), 7.47 – 7.33 (13H, m), 5.23 (2H, s), 5.11 (2H, s), 4.07 (2H, s). The spectral data exactly matches with the literature data.[3]



4-Methylbenzyl 3-(2-((4-methylbenzyl) oxy)-2-oxoethyl)-1-phenyl-1H-pyrazole-4-carboxylate (11ad): Yield = 56% (Wt.: 127.26 mg); Yellow solid. mp. = 89-91 °C; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.38 (1H, s), 7.65 (2H, d, J = 0.9 Hz), 7.45 (2H, t, J = 0.6 Hz), 7.35 – 7.13 (9H, m), 5.19 (2H, s), 5.07 (2H, s), 4.05 (2H, s), 2.35 (3H, s), 2.34 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.0, 162.7, 148.8, 139.1, 138.1, 137.9, 132.9, 132.8, 131.3, 130.0, 129.5, 129.2, 129.1, 128.5, 128.4, 127.4, 119.5, 114.5, 66.6, 66.0, 33.9, 21.2.

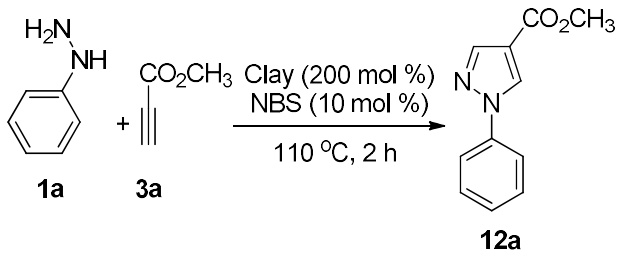


4-Bromobenzyl 3-(2-((4-bromobenzyl) oxy)-2-oxoethyl)-1-phenyl-1H-pyrazole-4-carboxylate (11ae): Yield = 54% (Wt.: 157.74 mg); Yellow solid. mp. = 114-116 °C; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.66 (2H, d, J = 0.6 Hz), 7.51 – 7.44 (5H, m), 7.27 – 7.18 (4H, m), 5.17 (2H, s), 5.06 (2H, s), 4.06 (2H, s),1.59 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 169.8, 162.5, 148.7, 139.0, 134.89, 134.84 131.7, 131.6, 131.3, 130.0, 129.8, 129.6, 127.63, 122.42, 122.2, 119.5, 114.1, 65.8, 65.3, 33.93.

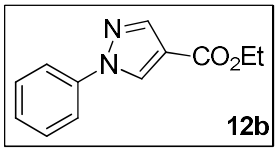


3-Methylbut-2-en-1-yl 3-(2-((3-methylbut-2-en-1-yl) oxy)-2-oxoethyl)-1-phenyl-1H-pyrazole-4-carboxylate (11af): Yield = 52% (Wt.: 47 mg); Yellow viscous liquid; R_f = 0.24 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 7.68 (2H, d, J = 0.6 Hz), 7.46 – 7.43 (2H, m), 7.37 – 7.20 (1H, m),4.74 (2H, d, J = 0.6 Hz), 4.64 (2H, d, J = 0.6 Hz), 4.02 (2H, s), 1 .78 (3H, s), 1.75 (6H, s), 1.70 (3H, s), 1.25 (2H, s). The spectral data exactly matches with the literature data.[3]

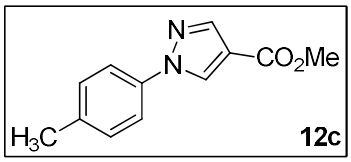
2.4. General procedure for the Synthesis of compound Methyl 1-phenyl-1H-pyrazole-4-carboxylate (12a)



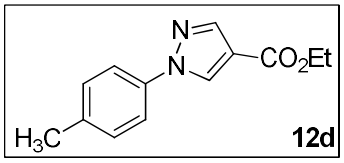
The reaction was carried out in reaction vials. Phenylhydrazine (1 mmol), Montmorillonite K10 (200 mol%) were taken and slurry prepared. NBS (5 mol%) and Propiolate (1 mmol) added dropwise to the slurry. Temperature maintained at 110 ^{o}C. The reaction was monitored by TLC. After completion of reaction, the crude mass was directly transferred to Silica (60-120) column. Hexanes-Ethyl acetate as mobile phase. It afforded the corresponding pyrazole **(12a).** Yield = 72% (Wt.: 71 mg); Brown solid; mp. = 103-105 ^{o}C; R_f = 0.52 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.42 (1H, s), 8.11 (1H, s), 7.71 (2H, d, *J* = 0.9 Hz), 7.49 (2H, t , *J* = 0.9 Hz), 7.37 (1H, t, *J* = 0.6 Hz), 3.88 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 163.28, 142.20, 139.39, 130.10, 129.65, 127.62, 119.63, 51.60; HRMS (m/z): $[M+H]^+$ calcd. for $C_{11}H_{11}N_2O_2$: 203.0742; found: 203.0742. The general procedure was followed for the preparation of the compounds **12a – 12h**.



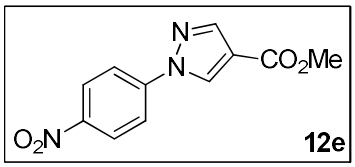
Ethyl 1-phenyl-1H-pyrazole-4-carboxylate(12b): Yield = 71% (Wt.: 76 mg); Dark brown semi solid; R_f = 0.55 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.42 (1H, s), 8.11 (1H, s), 7.71 (2H, d, *J* = 0.6 Hz), 7.49 (2H, t, *J* = 0.9 Hz), 7.39 – 7.34 (1H, m), 4.33 (2H, q, *J* = 0.9 Hz), 1.38 (3H, t, *J* = 0.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.8, 142.2, 139.4, 130.0, 129.6, 127.5, 119.6, 116.9, 60.4, 14.4; HRMS (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}N_2O_2$: 217.0982; found: 217.0977.



Methyl 1-(p-tolyl)-1H-pyrazole-4-carboxylate(12c): Yield = 75% (Wt.: 81 mg); Brown solid; mp. = 98-100 ^{o}C; R_f = 0.51 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.37 (1H, s), 8.09 (1H, s), 7.58 (2H, d, *J* = 0.9 Hz), 7.28 (2H, d, *J* = 0.9 Hz), 3.87 (3H, s), 2.40 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm)163.3, 141.9, 137.5, 137.1, 130.1, 129.9, 119.5, 116.2, 51.5, 20.9; HRMS (m/z): $[M+H]^+$ calcd. for $C_{12}H_{13}N_2O_2$: 217.0977; found: 217.0977.

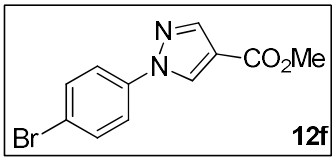


Ethyl 1-(p-tolyl)-1H-pyrazole-4-carboxylate(12d): Yield = 76% (Wt.: 87 mg); Brown solid; mp = 68-70 ^{o}C; R_f = 0.53 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.37 (1H, s), 8.09 (1H, s), 7.58 (2H, d, *J* = 0.6 Hz), 7.29 (2H, d, *J* = 0.9 Hz), 4.34 (2H, q, *J* = 0.6 Hz), 2.40 (3H, s), 1.38 (3H, t, *J* = 0.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.9, 142.0, 137.5, 137.2, 130.1, 129.9, 119.5, 116.7, 60.4, 29.7, 21.0, 14.4; HRMS (m/z): $[M+H]^+$ calcd. for $C_{13}H_{15}N_2O_2$: 231.1134; found: 231.1134.

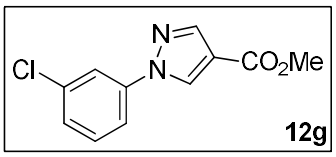


Methyl 1-(4-nitrophenyl)-1H-pyrazole-4-carboxylate(12e): Yield = 49% (Wt.: 60 mg); Brown solid; mp. = 188-190 ^{o}C; R_f = 0.46 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.54 (1H, s), 8.39 (2H, d, *J* = 0.9 Hz), 8.16 (1H, s), 7.93 (2H, d, *J* = 0.9 Hz), 3.90 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.6, 146.3, 143.5,

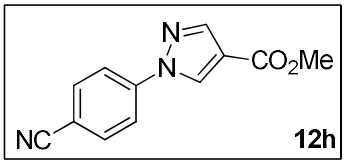
143.3, 130.3, 125.4, 119.3, 118.0, 51.8; HRMS (m/z): $[M+H]^+$ calcd. for $C_{11}H_{10}N_3O_2$: 248.0666; found: 248.0671.



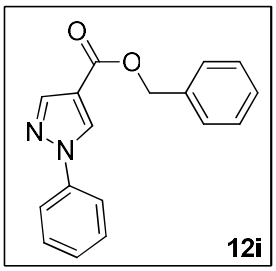
Methyl 1-(4-bromophenyl)-1H-pyrazole-4-carboxylate(12f): Yield = 65% (Wt.: 91 mg); Brown solid; mp. = 128-130 °C; R_f = 0.51 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.39 (1H, s), 8.09 (1H, s), 7.60 (4H, s), 3.87 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 103.0, 142.4, 138.3, 132.7, 129.9, 121.0, 121.0, 116,9, 51.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{11}H_{10}BrN_2O_2$: 280.9922; found: 280.9926



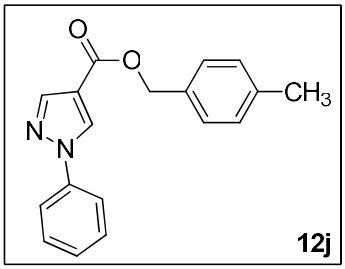
Methyl 1-(3-chlorophenyl)-1H-pyrazole-4-carboxylate(12g): Yield = 63% (Wt.: 74 mg); Yellow solid; mp. = 114-116 °C; R_f = 0.53 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.41 (1H, s), 8.10 (1H, s), 7.77 (1H, s), 7.59 (1H, d, *J* = 0.9 Hz), 7.44 – 7.32 (2H, m), 3.88 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm 163.0, 142.4, 140.2, 136.5, 130.6, 130.1, 127.6, 119.9, 117.4, 117.0, 51.6; HRMS (m/z): $[M+H]^+$ calcd. for $C_{11}H_{10}ClN_2O_2$: 237.0425; found: 237.0431



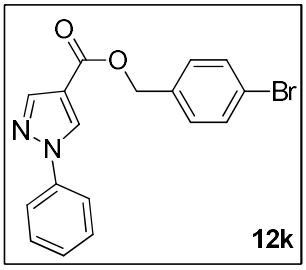
Methyl 1-(4-cyanophenyl)-1H-pyrazole-4-carboxylate(12h): Yield = 55% (Wt.: 62 mg); Yellow solid; mp. = 188-190 °C; R_f = 0.52 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.49 (1H, s), 8.14 (1H, s), 7.84 (4H, q, *J* = 1.5 Hz), 3.89 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.7, 143.1, 142.1, 138.8, 130.1, 119.5, 118.0, 117.8, 111.0, 51.8; HRMS (m/z): $[M+H]^+$ calcd. for $C_{12}H_{10}N_3O_2$: 228.0769; found: 228.0773.



Benzyl 1-phenyl-1H-pyrazole-4-carboxylate (12i): Yield = 51% (Wt.: 70 mg); Pale yellow solid; mp. = 80-82 °C; R_f = (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.43 (1H, s), 8.13(1H, s), 7.70 (2H, d, J = 0.9 Hz), 7.51 - 7.33 (8H, m), 5.33 (2H, s)); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.,142.3, 140.2, 139.2, 135.9, 130.2, 129.6, 128.6, 128.3, 127.6, 119.6, 116.5, 66.2. HRMS (m/z): $[M+H]^+$ calcd. for $C_{17}H_{14}N_2O_2$: 279.1134; found: 279.1122



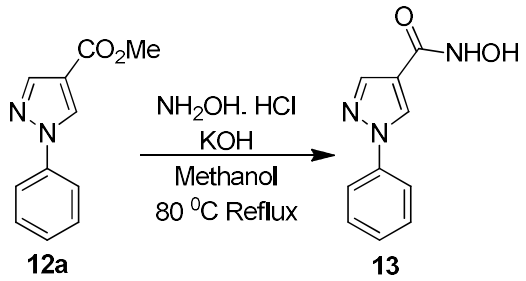
4-Methylbenzyl 1-phenyl-1H-pyrazole-4-carboxylate (12j): Yield = 49% (Wt.: 71 mg); Yellow solid; mp. = 92-94 °C; R_f = (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.41 (1H, s), 8.12 (1H, s), 7.69 (2H, d, J = 0.6 Hz), 7.48 (2H, t, J = 0.6 Hz), 7.34 (3H, d, J = 0.6 Hz),7.21 (2H, d, J = 0.9 Hz), 5.29 (2H, s), 2.37 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.71, 142.32, 139.38, 138.23, 132.97, 130.18, 129.62,129.31, 128.52, 127.60, 119.65, 116.62, 66.19, 21.24



4-Bromobenzyl 1-phenyl-1H-pyrazole-4-carboxylate (12k): Yield = 52% (Wt.: 40 mg); Yellow solid; mp. = 95-97 °C; R_f = (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.42 (1H, s), 8.12 (1H, s), 7.70 (2H, d, J = 0.9 Hz), 7.50 (4h, dd, J = 1.8 Hz & 0.9 Hz), 7.35 (3H, dd, J = 1.8 Hz & 0.9 Hz), 5.27 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 162.48, 142.28, 139.33, 135.02, 131.80, 130.23, 130.00, 129.64,

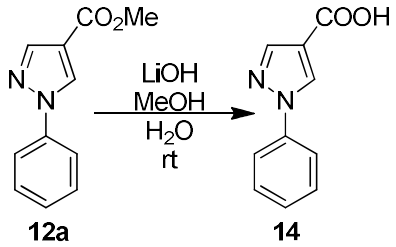
127.70, 122.40, 119.68, 116.29, 65.40.

2.5. Synthesis of compound N-hydroxy-1-phenyl-1H-pyrazole-4-carboxamide (13)



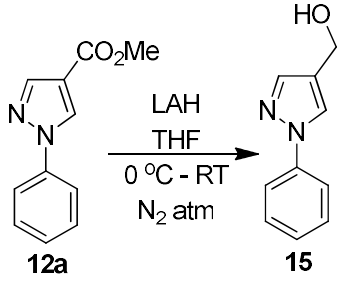
Pyrazole (1 mmol), $NH_4OH.HCl$ (8 mmol), KOH (8 mmol) were purged with Nitrogen gas. Dried methanol (3 mL) was added and refluxed for 3 h. After cooling, Acetic acid and Ethyl acetate was added and Organic layer was dried. The compound (13) was obtained 77% yield (Wt.: 156mg); Brown solid; mp. = 88-90 ^{o}C; R_f = 0.25 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 9.07 (1H, s), 8.14 (1H, s), 7.98 (2H, d, *J* = 0.9 Hz), 7.59 (2H, t, *J* = 0.9 Hz), 7.43 (1H, t, *J* = 0.9 Hz); The spectral data exactly matches with the literature data.[4]

2.6. Synthesis of 1-phenyl-1H-pyrazole-4-carboxylic acid (14)



Pyrazole (1 mmol) was dissolved in 2 mL of dry THF and 0.5 mL of water. LiOH (2 mmol) added to the reaction mass. After completion of reaction, the crude mass was quenched with 10% HCl. Extracted in Ethyl acetate and was evaporated. Hexane wash gives the corresponding acid (93%) yield (Wt.: 174mg); Pale brown solid; mp. = 178-180 ^{o}C; R_f = 0.16 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6, δ ppm) 8.46 (1H, s), 8.08 (1H, s), 7.73 (2H, d, *J* = 0.9 Hz), 7.52 – 7.45 (2H, m), 7.38 – 7.34 (1H, m); The spectral data exactly matches with the literature data.[4]

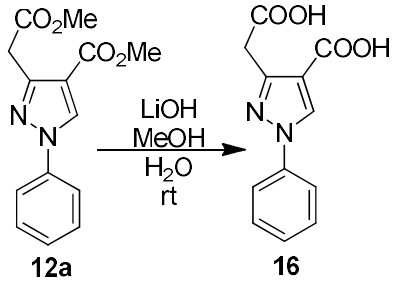
2.7. Synthesis of (1-phenyl-1H-pyrazol-4-yl) methanol (15)



Pyrazole (1 mmol) was dissolved in 10 mL of dry THF and cooled to 0 ^{o}C. Lithium aluminium hydride (3 mmol) added by portions. The reaction was maintained in Nitrogen atmosphere to reach room temperature. After completion of reaction the crude mass quenched with saturated Ammonium Chloride-Ethyl acetate. The organic layer was evaporated and dried. It provided the corresponding

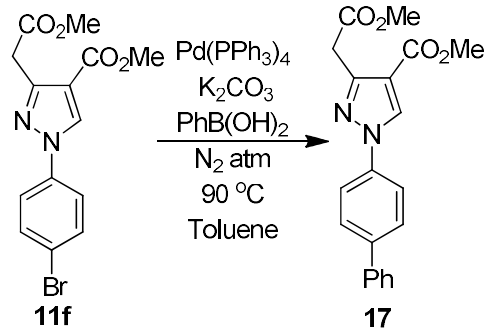
alcohol (74%) yield (Wt.: 128 mg); Brown solid; mp. = 46-48 °C; R_f = 0.35 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.90 (1H, s), 7.68 – 7.62 (3H, m), 7.43 (2H, t, *J* = 0.9 Hz), 7.30 – 7.25 (1H, m), 4.64 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 140.3, 139.9, 129.4, 126.6, 125.8, 123.6, 119.1, 55.8; HRMS (m/z): $[M+H]^+$ calcd. for $C_{10}H_{10}N_2O$: 175.0827; found: 175.0827.

2.8. Synthesis of 3-(carboxymethyl)-1-phenyl-1H-pyrazole-4-carboxylic acid (16)



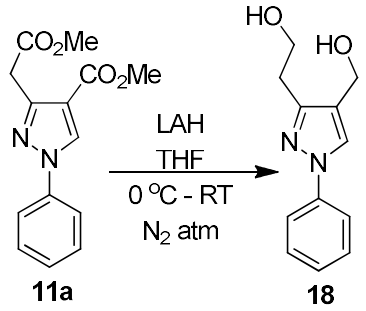
Pyrazole (1 mmol) was dissolved in 5 mL of dry THF and 1 mL of water. LiOH (2 mmol) added to the reaction mass. After completion of reaction, the crude mass was quenched with 10% HCl. Extracted in ethyl acetate and was evaporated. Hexane wash gives the corresponding acid (88%) yield (Wt.: 216 mg); Brown liquid; R_f = 0.11 (20% of ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6, δ ppm) 8.45 (1H, s), 7.71 (2H, d, *J* = 0.6 Hz), 7.51 – 7.44 (2H, m), 7.36 – 7.31 (1H, m), 3.99 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO. d_6, δ ppm) 171.4, 163.9, 148.6, 138.5, 130.7, 128.8, 126.5, 118.5, 114.6, 33.0; HRMS (m/z): $[M+H]^+$ calcd. for $C_{12}H_{10}N_2O_4$: 247.0674; found: 247.0674.

2.9. Synthesis of compound Methyl 1-([1,1'-biphenyl]-4-yl)-3-(2-methoxy-2-oxoethyl)-1H-pyrazole-4-carboxylate (17)



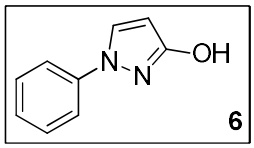
Halogen substituted Pyrazole (1 mmol) was dissolved in 10 mL of toluene. $Pd(PPh_3)_4$ (0.1 mmol), K_2CO_3 (3 mmol), $PhB(OH)_2$ (3 mmol) added and allowed to reflux for 2 h in Nitrogen atmosphere. After cooling, the mixture was filtered by celite and washed with DCM. Organic layer was evaporated and again washed with Hexanes, provided the compound (**17**) (82%) yield (Wt.: 286 mg); Yellow solid; mp. = 118-120 °C; R_f = 0.31 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 8.41 (1H, s), 7.71 (4H, q, *J* = 1.5 Hz), 7.60 (2H, d, *J* = 0,6 Hz), 7.46 (2H, t, *J* = 0.6 Hz), 7.37 (1H, t, *J* = 0.6 Hz), 4.04 (2H, s), 3.84 (3H, s), 3.75 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm) 170.7, 163.3, 148.9, 140.4, 139.8, 138.3, 131.1, 128.9, 128.1, 127.7, 127.0, 119.7, 114.4, 52.1, 51.4, 33.7; HRMS (m/z): [M] calcd. for $C_{11}H_{10}N_3O_2$: 350.1267; found: 350.0023.

2.10. Synthesis of 2-(4-(hydroxymethyl)-1-phenyl-1H-pyrazol-3-yl)ethanol (18)



Pyrazole (1 mmol) was dissolved in 10 mL of dry THF and cooled to 0 °C. Lithium aluminium hydride (3 mmol) added by portions. The reaction was maintained in Nitrogen atmosphere to reach room temperature. After completion of reaction the crude mass quenched with saturated Ammonium Chloride-Ethyl acetate. The organic layer was evaporated and dried. It provided the corresponding diol (78%) yield (Wt.: 170 mg); Brown viscous liquid; R_f = 0.37 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.84 (1H, s), 7.60 (2H, d, *J* = 0.6 Hz), 7.42 (2H, t, *J* = 0.9 Hz), 7.28 – 7.23 (1H, m), 4.54 (2H, s), 3.93 (2H, t, *J* = 0.6 Hz), 2.95 (2H, t, *J* = 0.6 Hz); The spectral data exactly matches with the literature data.[3]

3. Synthesis of 3-OH substituted Pyrazole (6)



1-phenyl-1H-pyrazol-3-ol (6): Yield = 80%; Brown solid; mp. = 156-158 °C; R_f = 0.32 (20% of Ethyl acetate in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 7.67 (1H, d, *J* = 0.3 Hz), 7.53 – 7.43 (5H, m), 5.91 (1H, Broad s); The spectral data exactly matches with the literature data.[5]

4. Recycle of Clay-K10

Phenylhydrazine (1 mmol), Montmorillonite K10 (200 mol% - 300mg) were taken and slurry prepared. Propiolate (1 mmol) was added dropwise to the slurry. The reaction was conducted in oxygen atmosphere and the temperature was slowly raised to 65 °C. The reaction was monitored by TLC. After completion of reaction, ethanol or DCM was added into the reaction mass at room temperature. The slurry was filtered after 15 min. The residue was washed with ethanol and the air dried clay was used for the next cycle. The recycle experiment was followed for all the consecutive cycles. During the process, clay weight was noted after each cycle. Weight loss of 8-12 mg of the clay was observed in each cycle such as 293mg, 287mg, 281mg and 276mg respectively.

Similarly, Phenylhydrazine (1 mmol), Montmorillonite K10 (200 mol% - 300mg) were taken and slurry prepared. NBS (5 mol%) and propiolate (1 mmol) added dropwise to the slurry. Temperature maintained at 110 °C. After completion of reaction, ethanol or DCM was added into the reaction mass at room temperature. The slurry was filtered after 15 min. The residue was washed with ethanol and was air dried. The recycle experiment was followed for all the consecutive cycles. The dried clay was then reused with addition of 10 mol% of NBS for the consecutive reactions and clay weight was noted after each cycle. Weight loss of 5-10 mg of the clay was observed and weight of the recovered clay was 293 mg, 290 mg, 285 mg and 279 mg in each cycle respectively.

5. References:

1) Chahdoura, F.; Lassauque, N.; Bourissou, D.; Amgoune, A. *Org. Chem. Front.* **2016**, 3, 856-860.

2) Mercedes, A.; Hermenegildo, G.; Sara, I.; Miguel, A. M.; Jaime, P. *Tetrahedron*. **1987**, 43, 143-148.

3) Thombal, R. S.; Le, Y. R. *Org. Lett.* **2018**, *20*, 4681-4685.

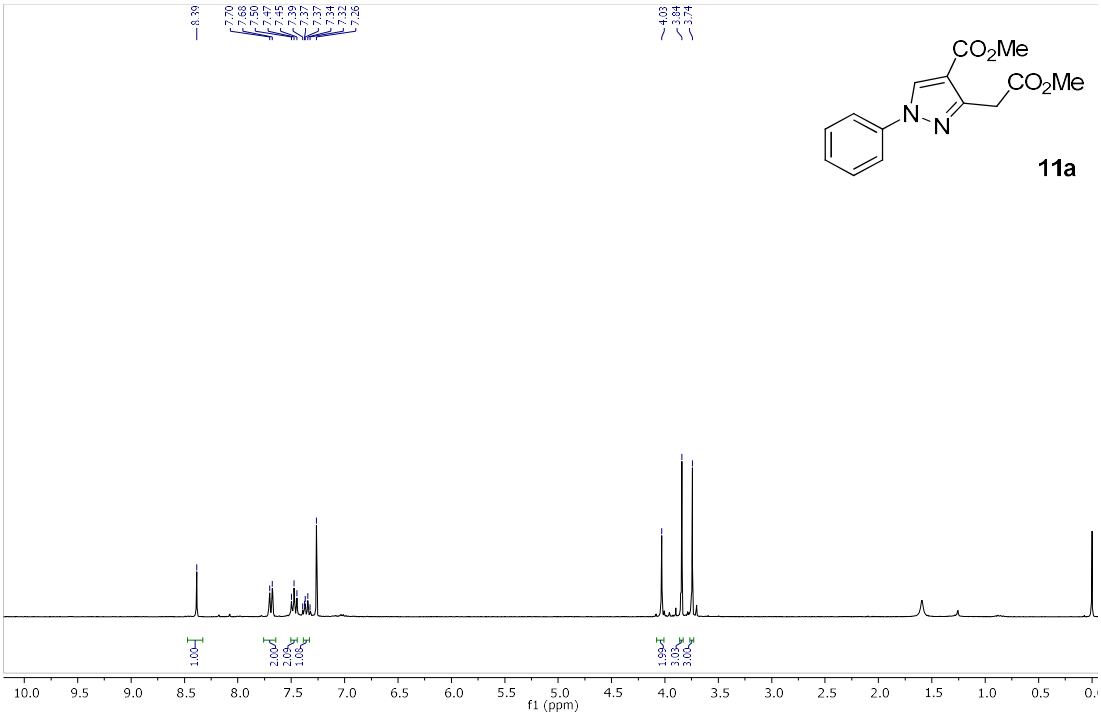
4) Barros, T. G.; Williamson, J. S.; Antunes, O. A. C.; Muri, E. M. F. *Lett. Drug. Des. Discov.* **2009**, *6*, 186-192.

5) Liu, Y.; He, G.; Chen, K.; Jin, Y.; Li, Y.; Zhu, H. *Eur. J. Org. Chem.* **2011**, *27*, 5323-5330.

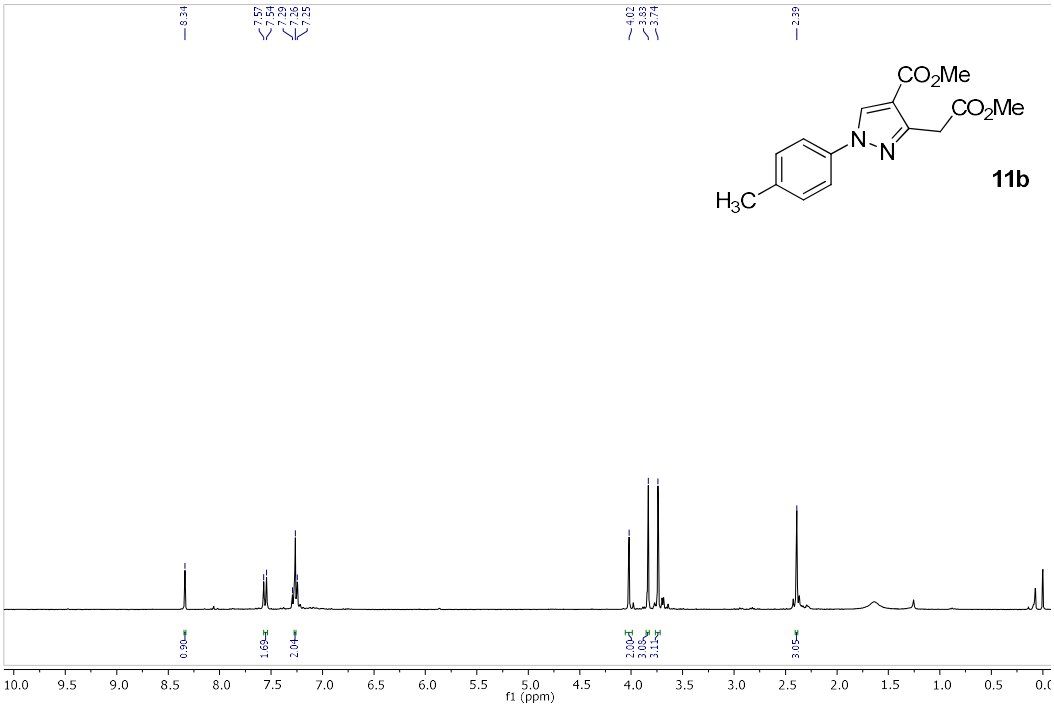
6) (a) G. M. Sheldrick, *Program for Crystal Structure Solution. SHELXS-97*, University of Göttingen, Göttingen, Germany, 1997; (b) G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr., Sect. A: Found. Crystallogr*., 2008, **64**, 112; (c) G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, **71**, 3.

6. ^{1}H and ^{13}C spectra for all compounds:

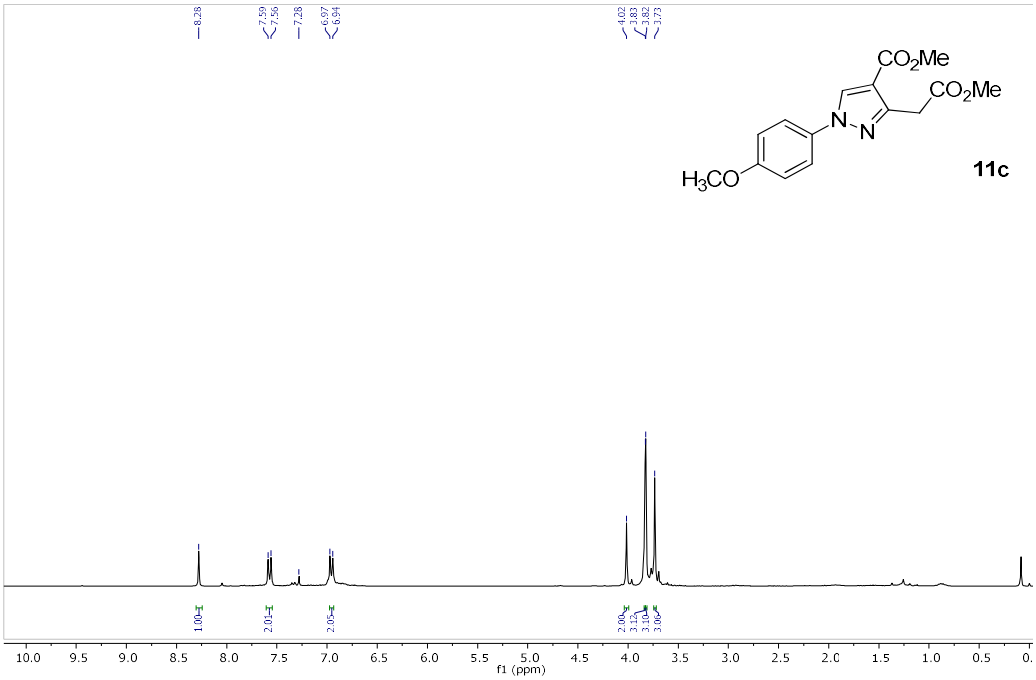
^{1}H Spectrum for 11a



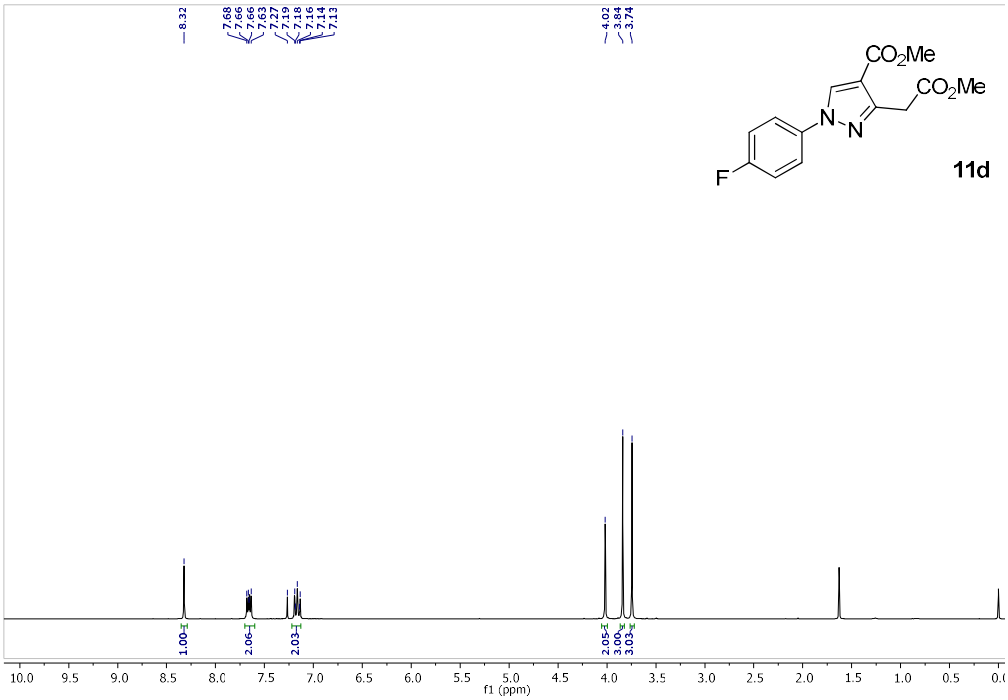
^{1}H Spectrum for 11b



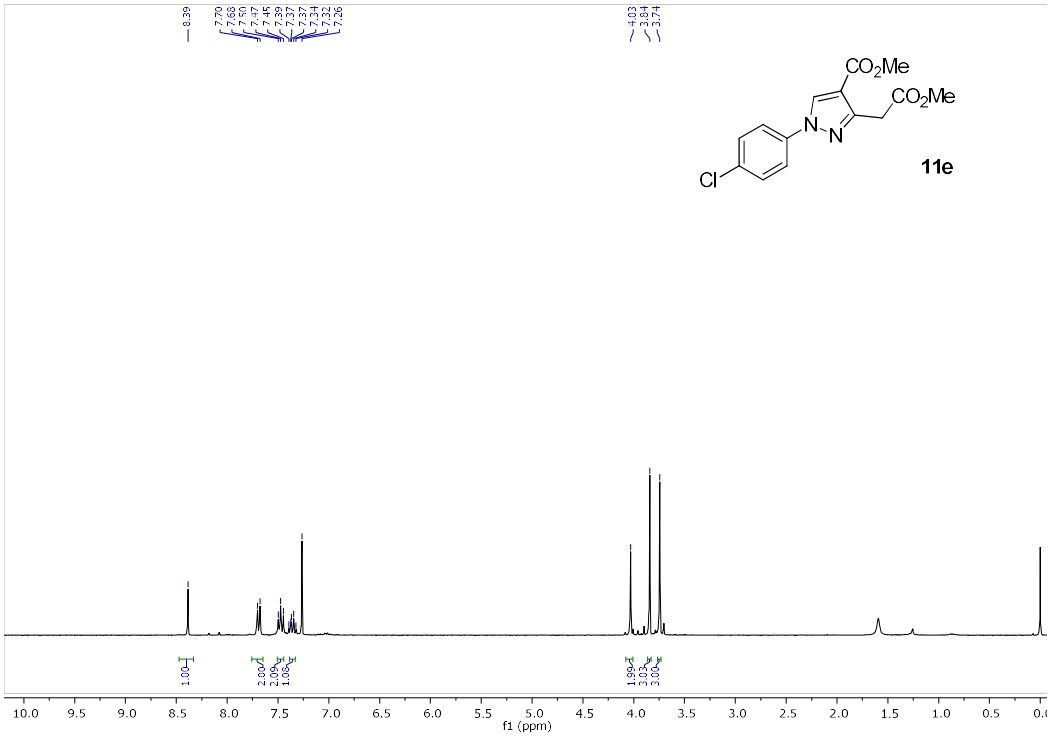
^{1}H Spectrum for 11c



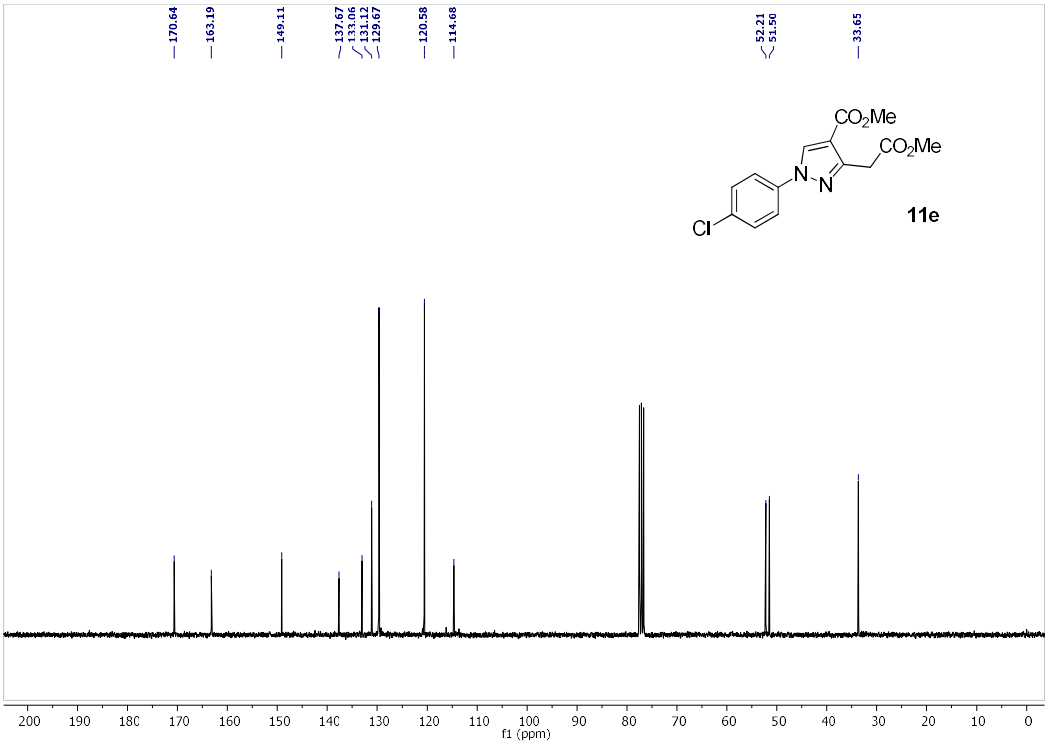
^{1}H Spectrum for 11d



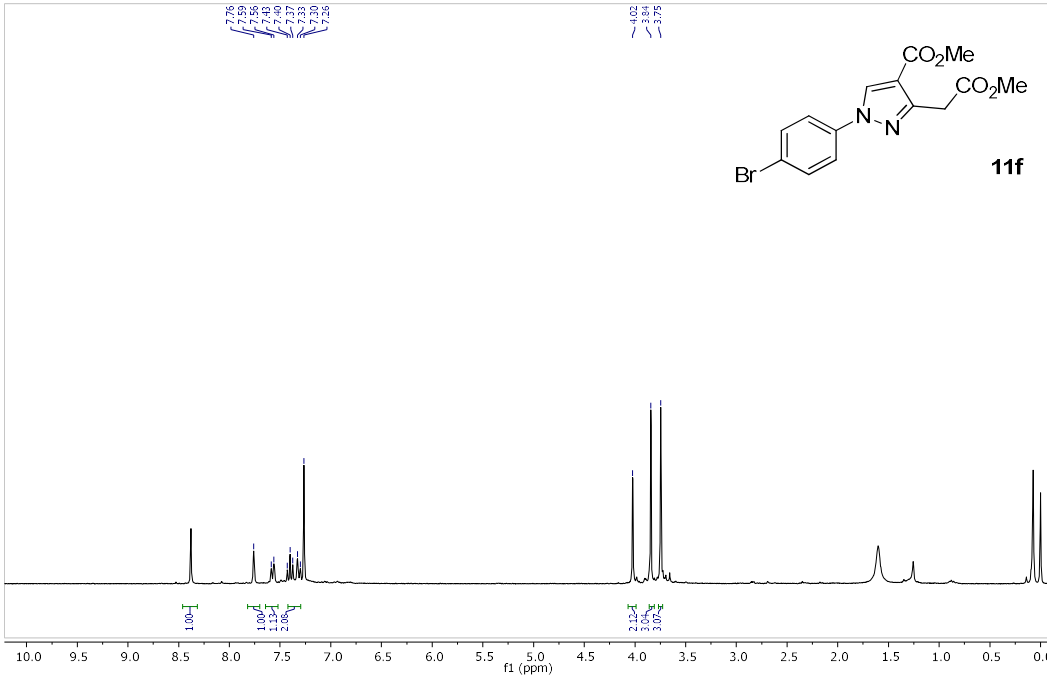
^{1}H Spectrum for 11e



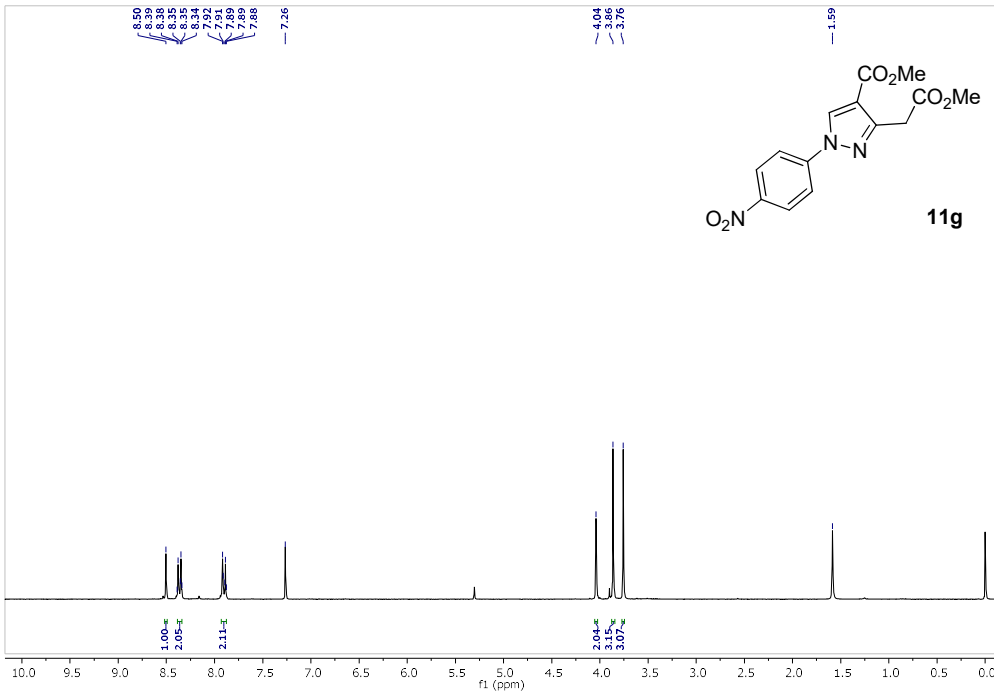
^{13}C Spectrum for 11e



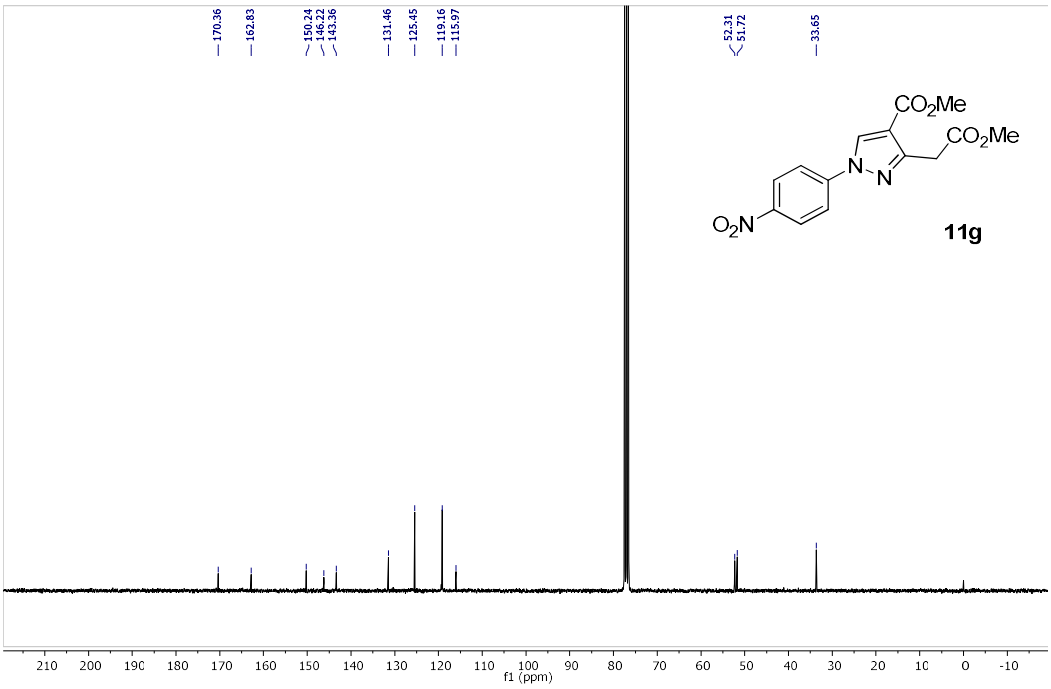
^{1}H Spectrum for 11f



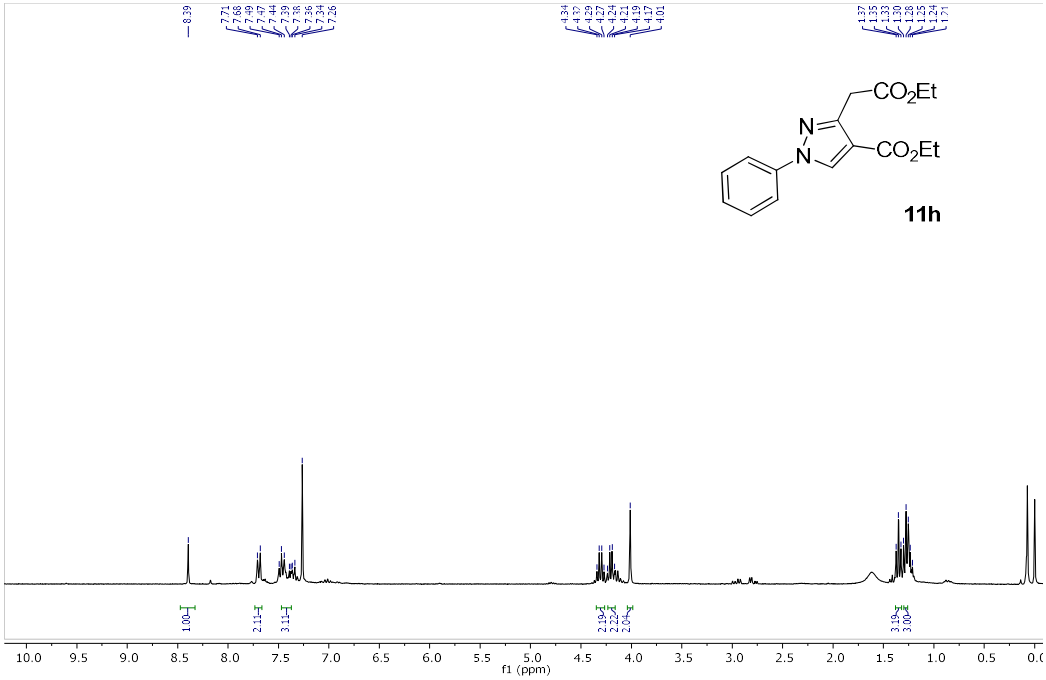
^{1}H Spectrum for 11g



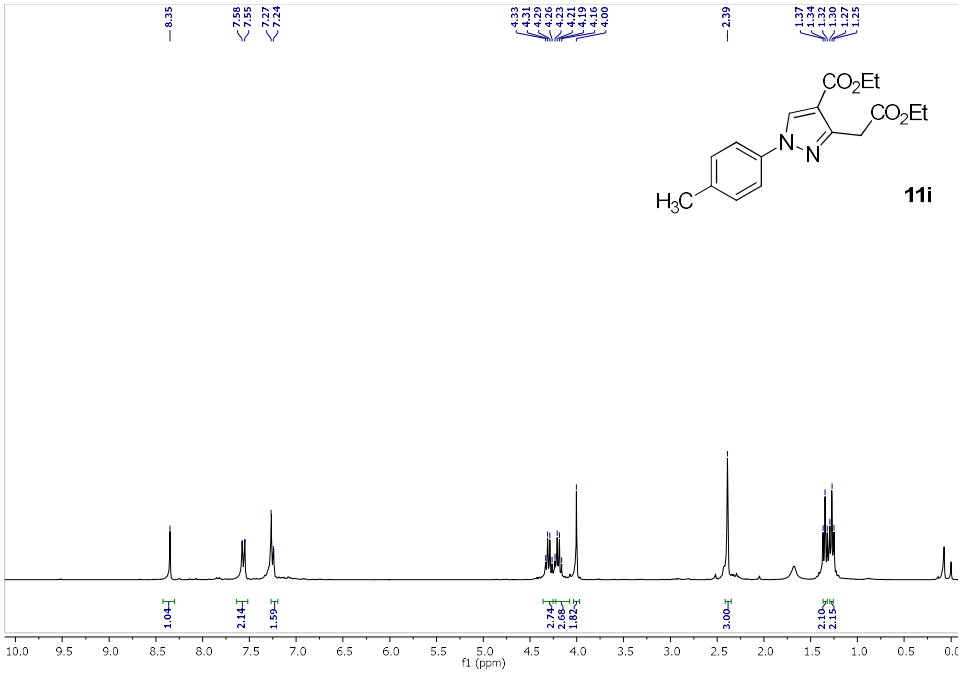
^{13}C Spectrum for 11g



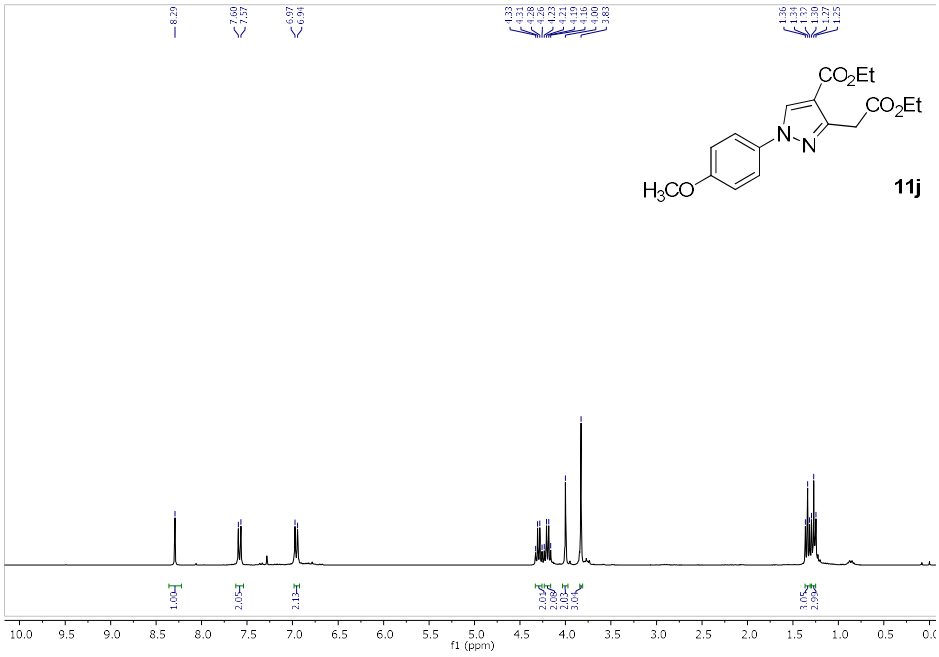
^{1}H Spectrum for 11h



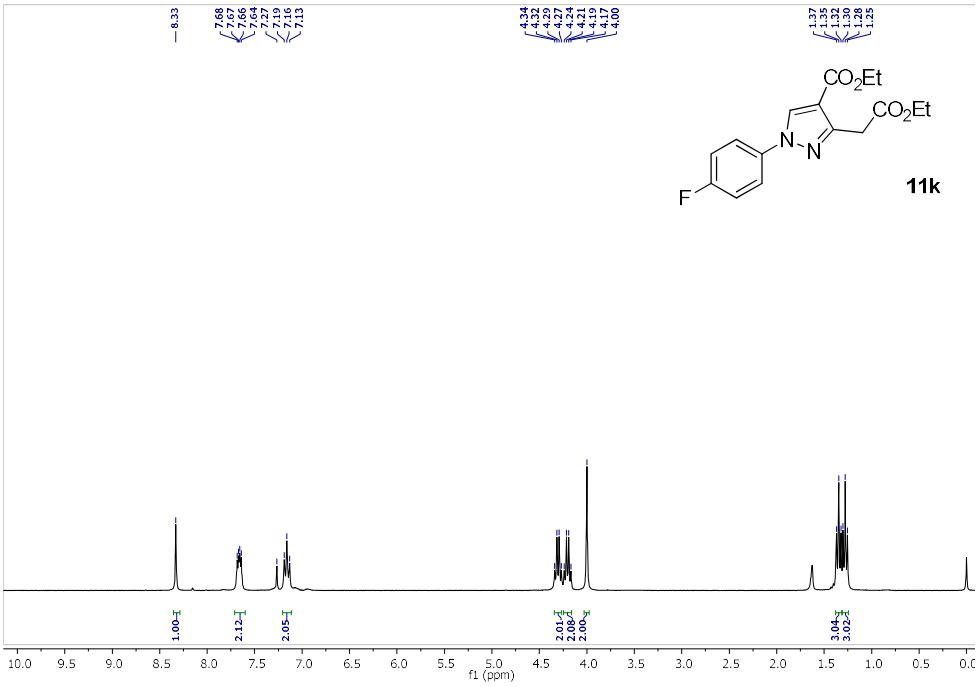
^{1}H Spectrum for 11i



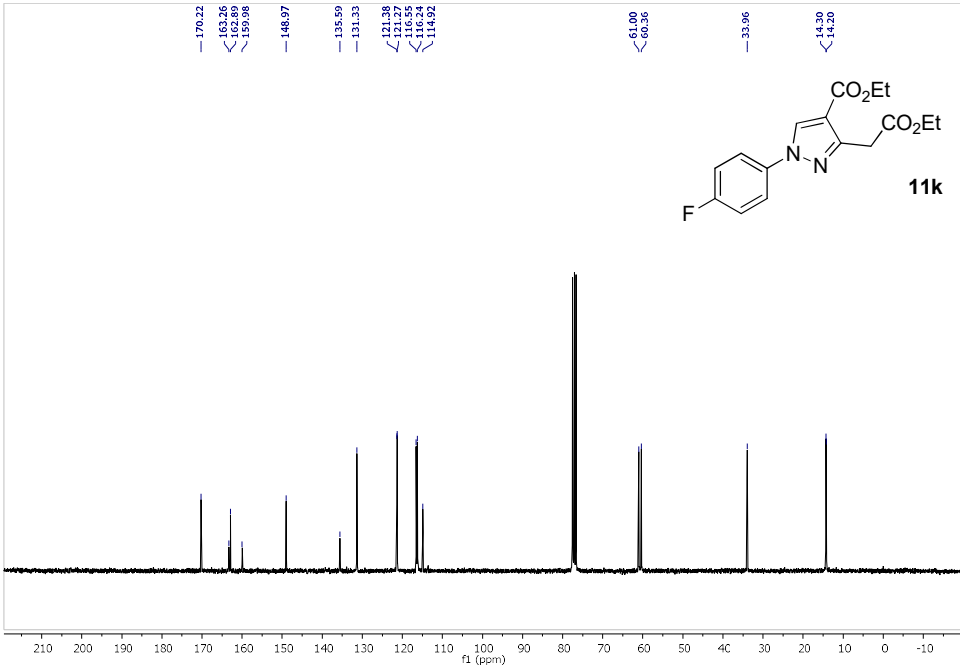
^{1}H Spectrum for 11j



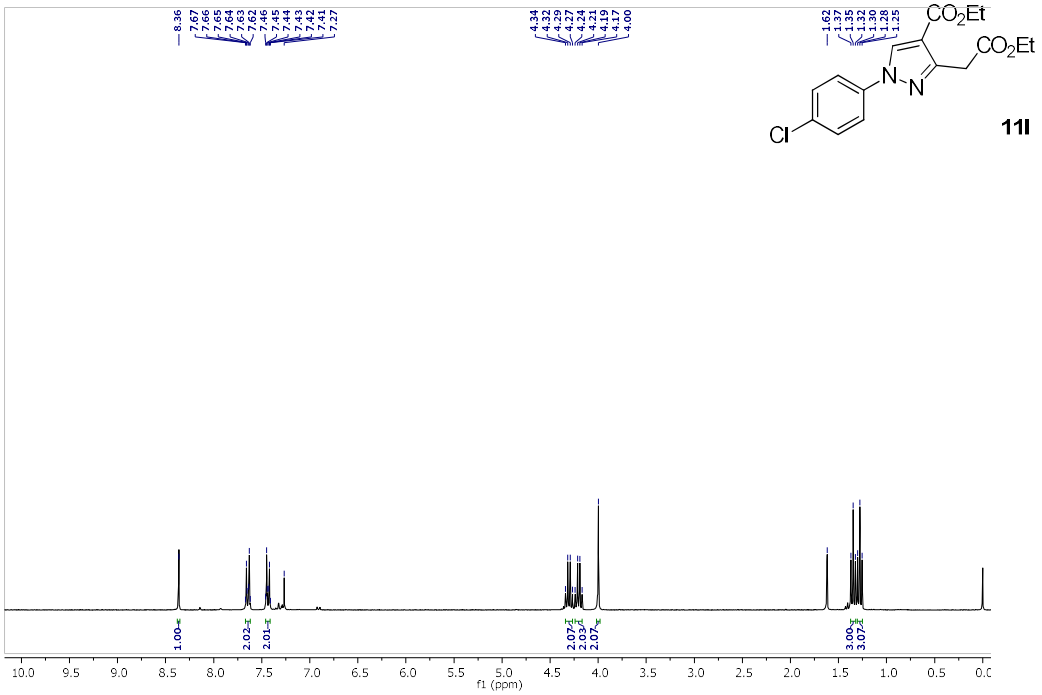
^{1}H Spectrum for 11k



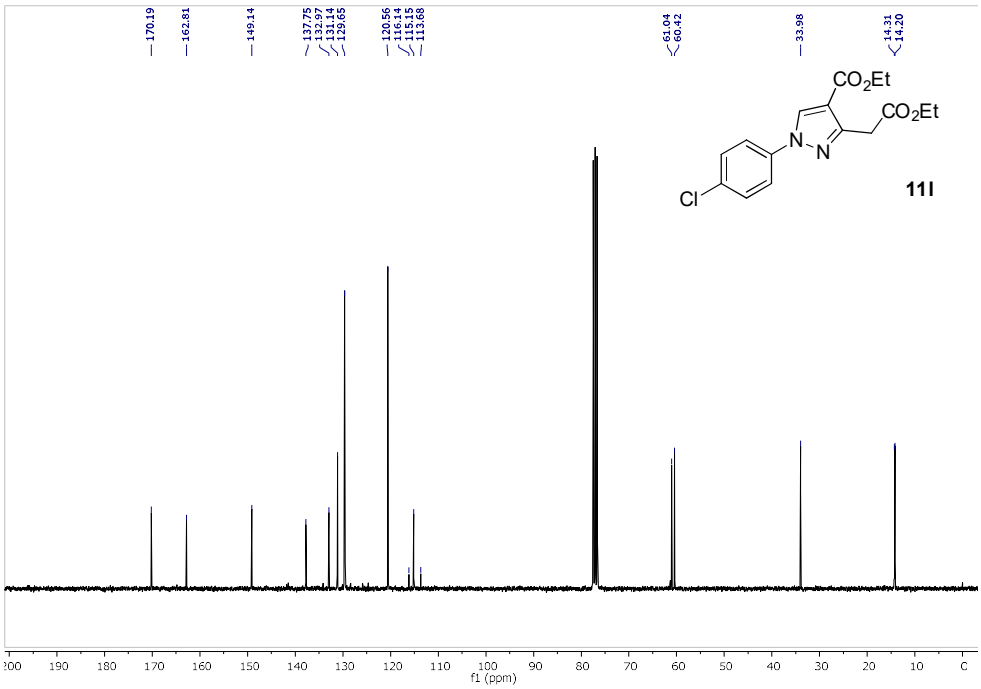
^{13}C Spectrum for 11k



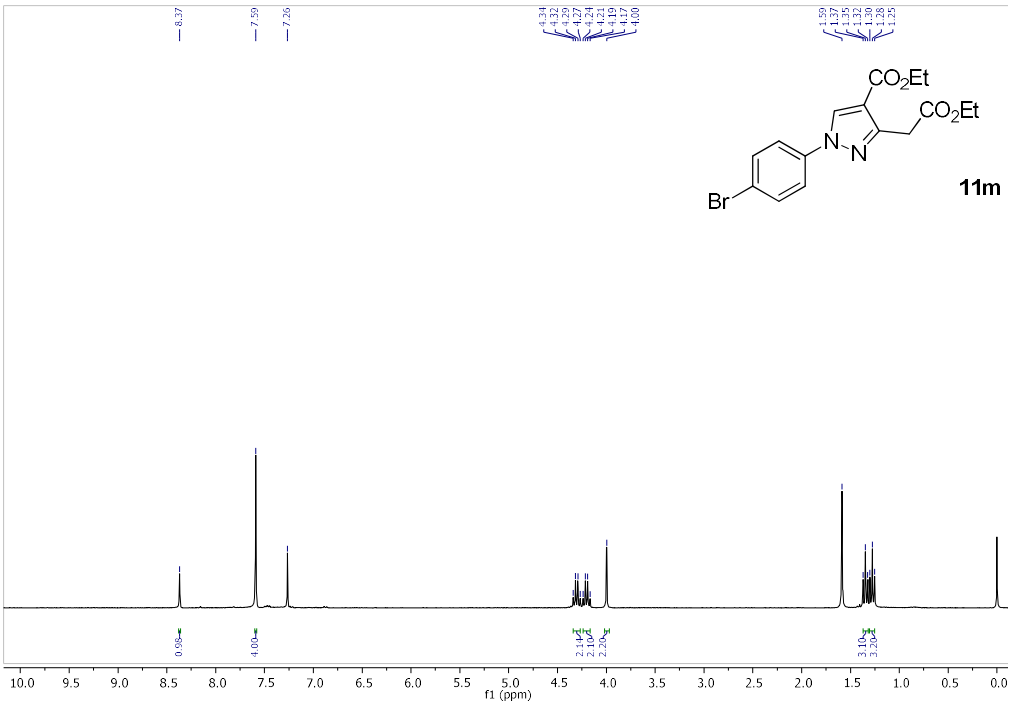
^{1}H Spectrum for 11l



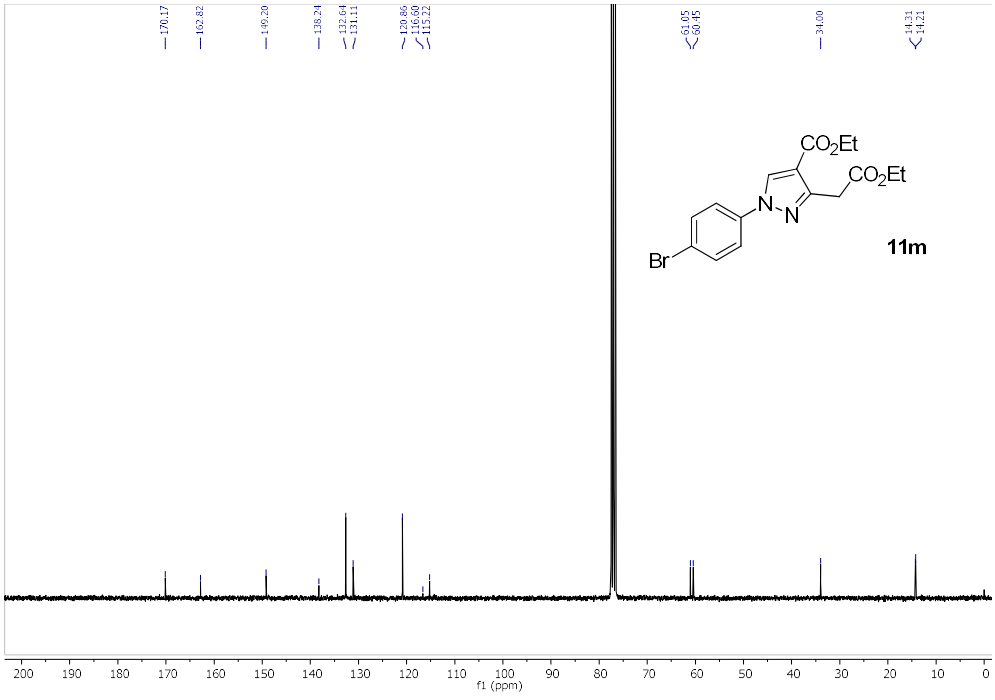
^{13}C Spectrum for 11l



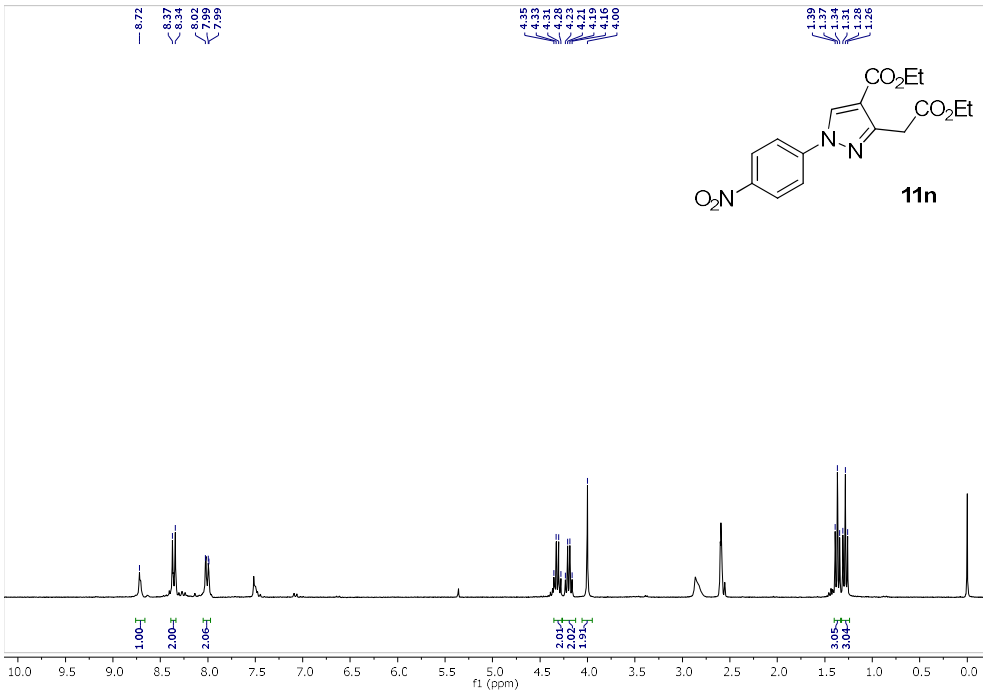
^{1}H Spectrum for 11m



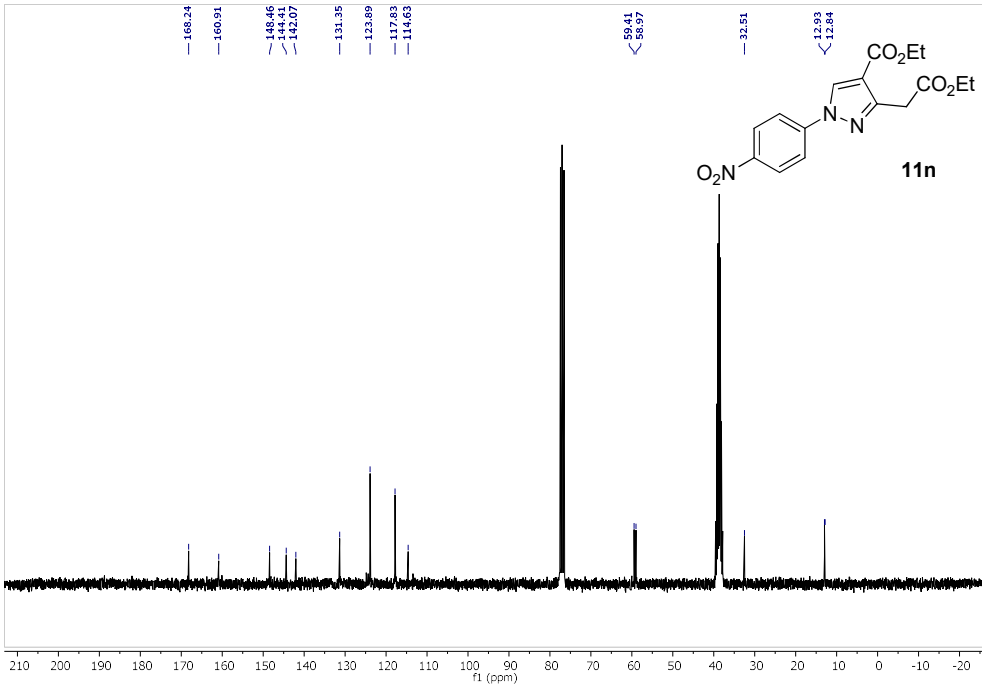
^{13}C Spectrum for 11m



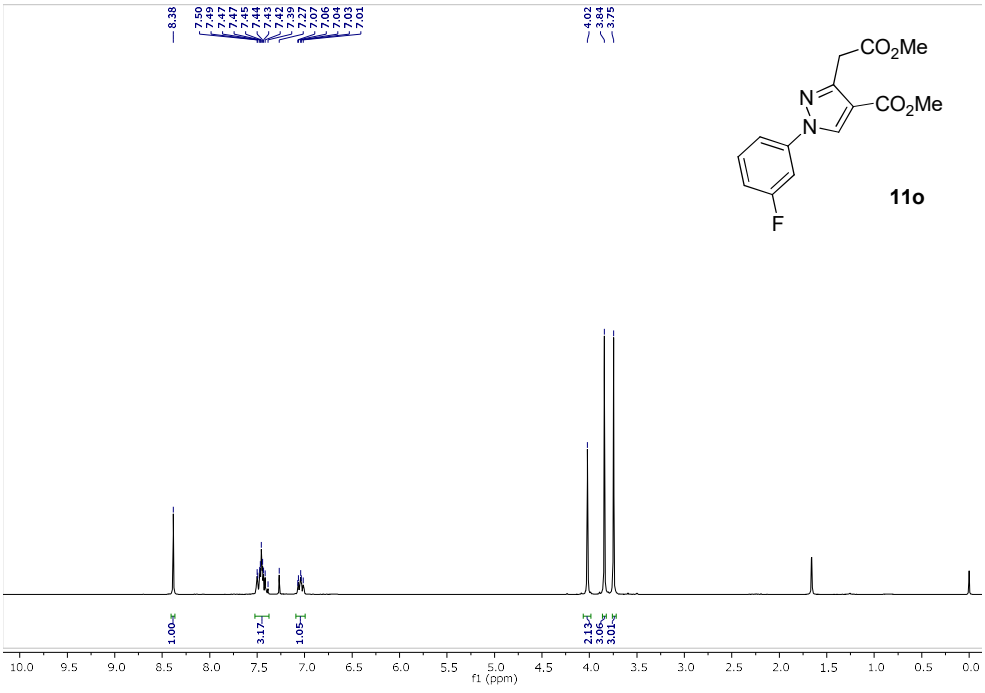
^{1}H Spectrum for 11n



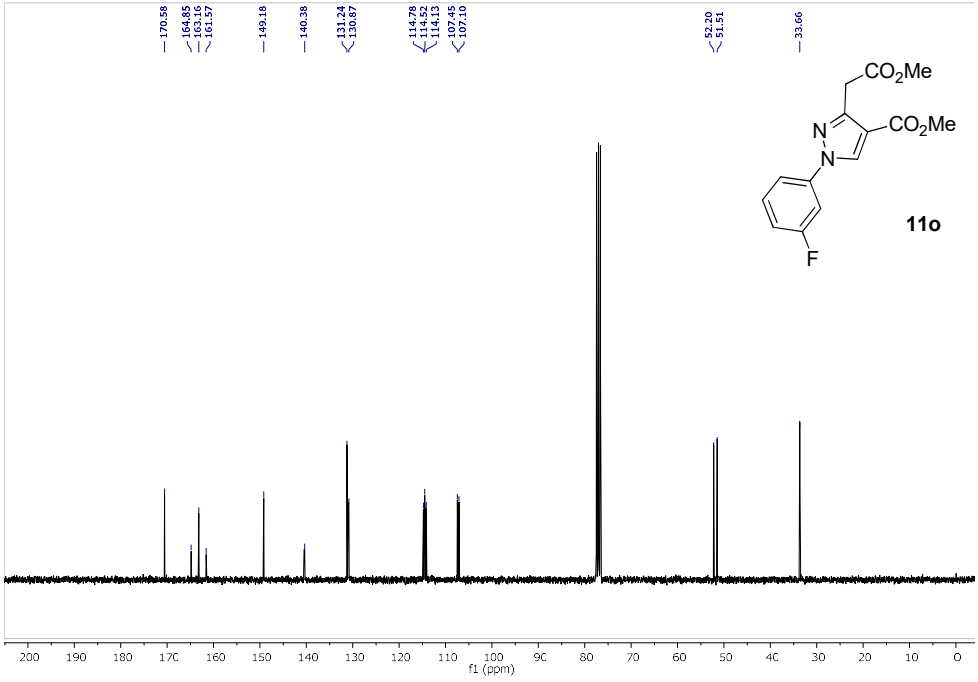
^{13}C Spectrum for 11n



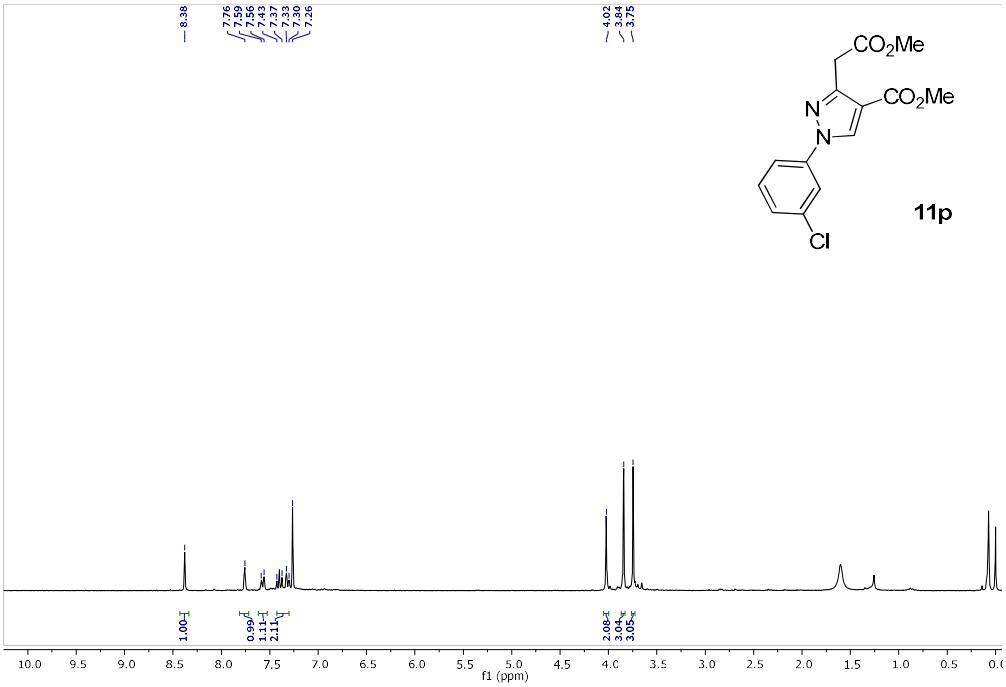
^{1}H Spectrum for 11o



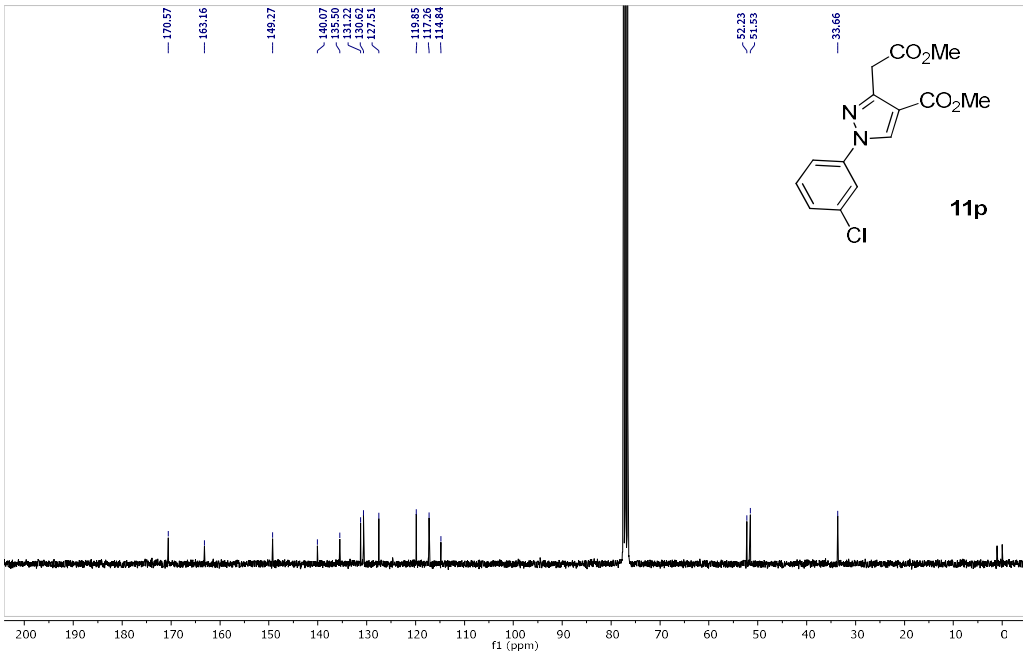
^{13}C Spectrum for 11o



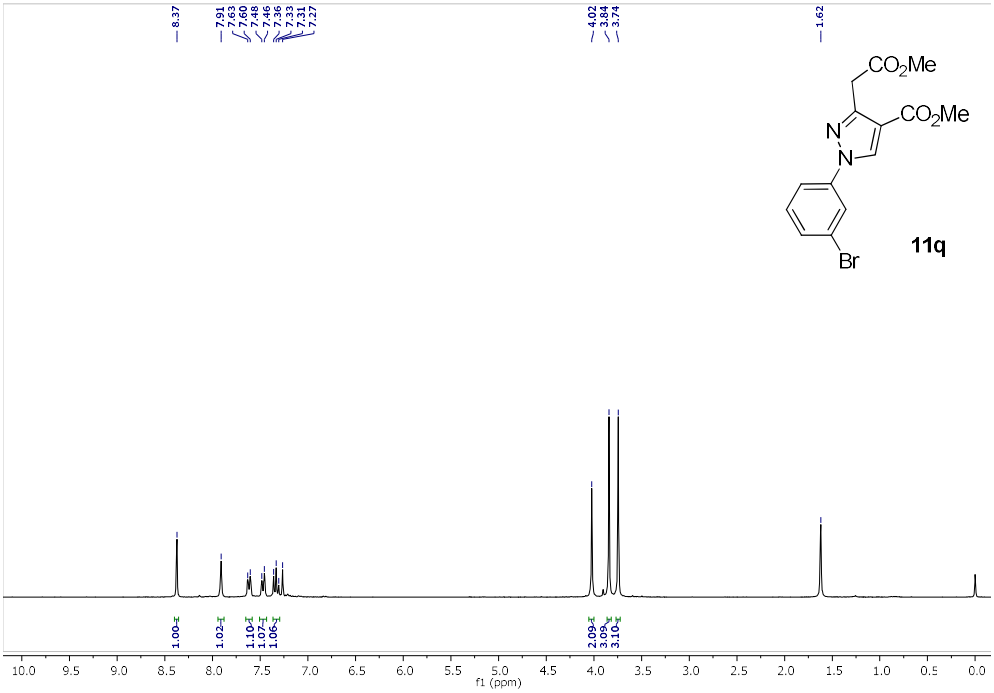
^{1}H Spectrum for 11p



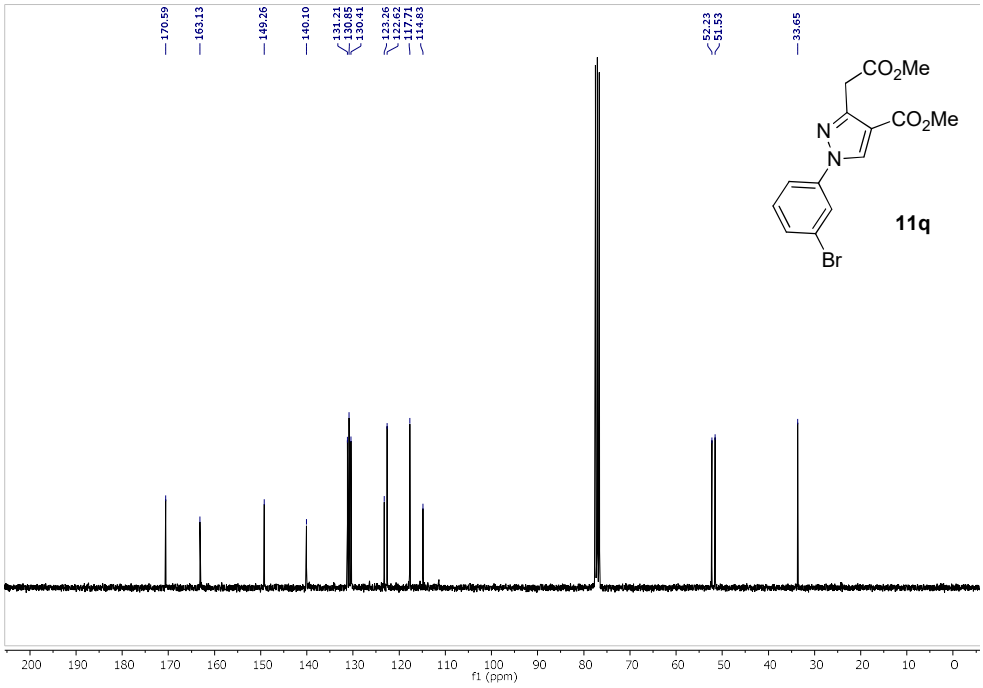
^{1}H Spectrum for 11p



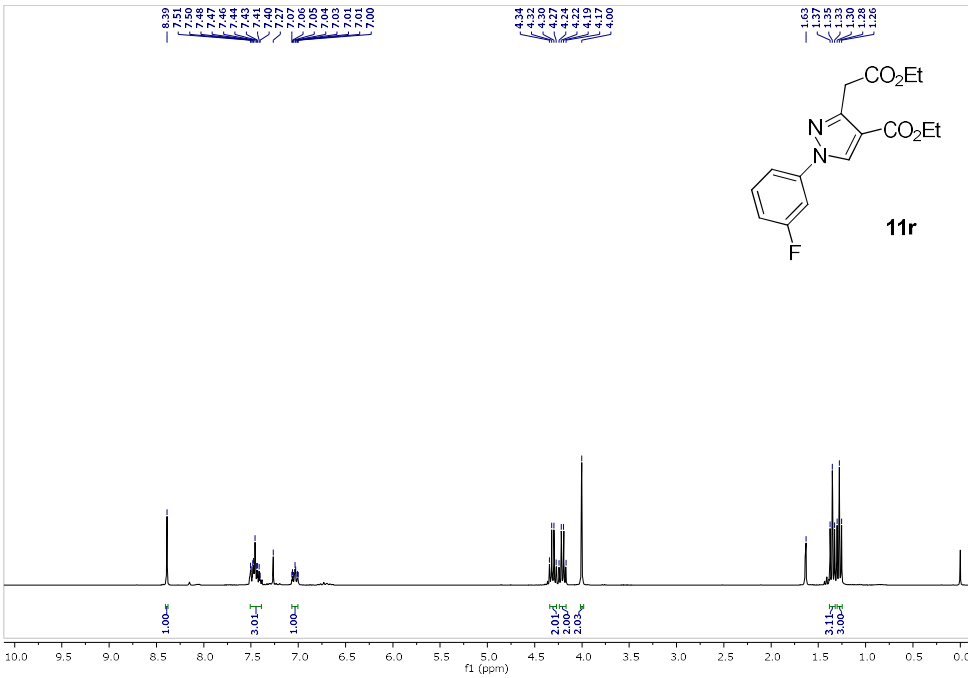
^{1}H Spectrum for 11q



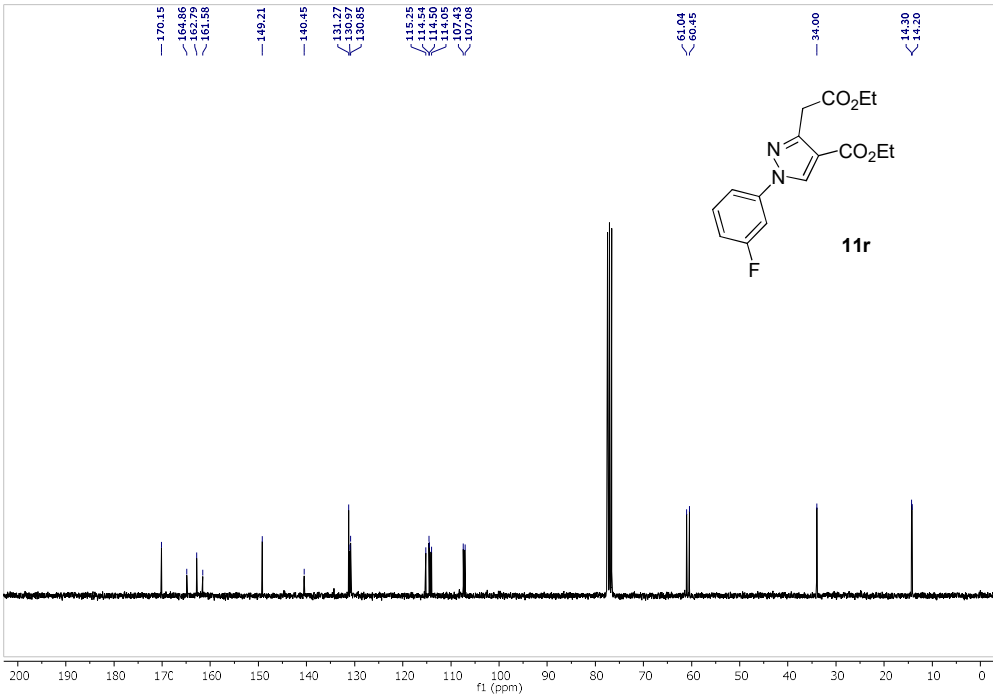
^{13}C Spectrum for



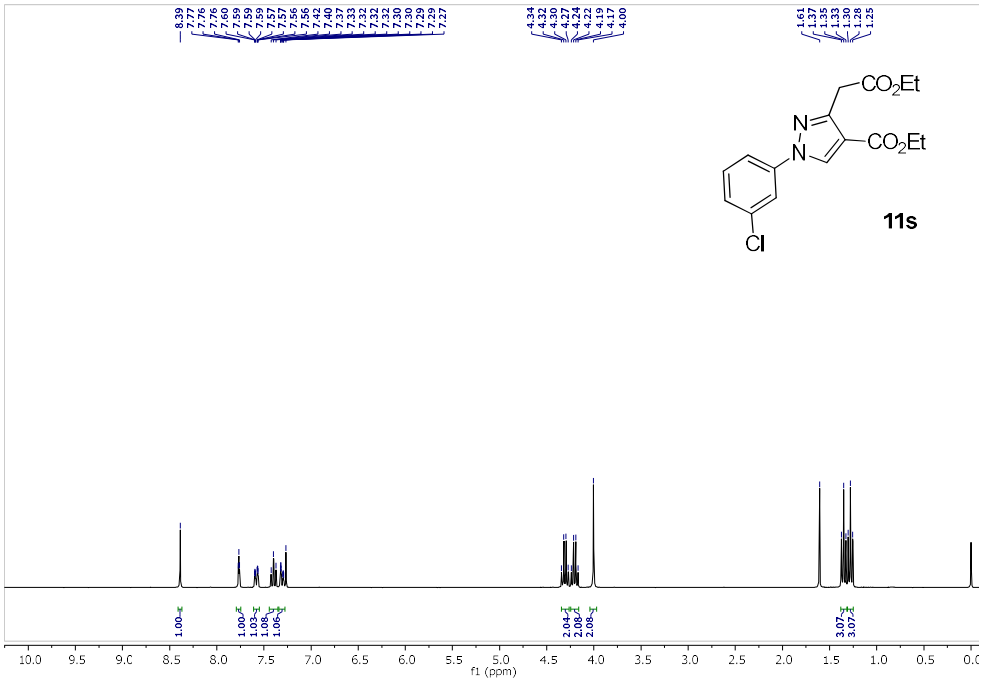
^{1}H Spectrum for 11r



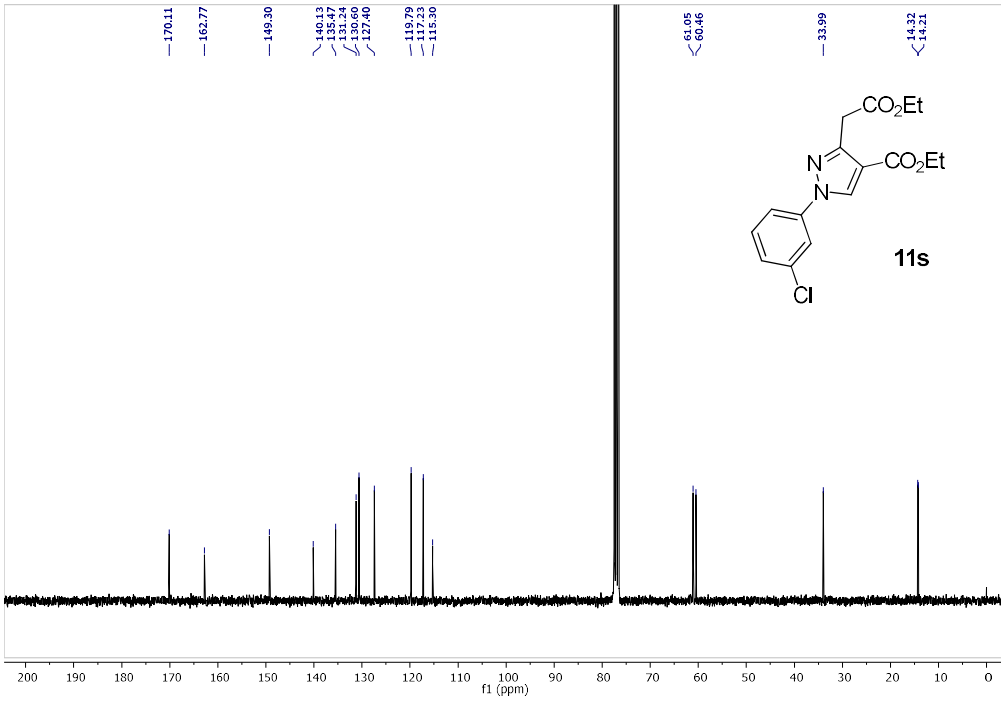
^{13}C Spectrum for 11r



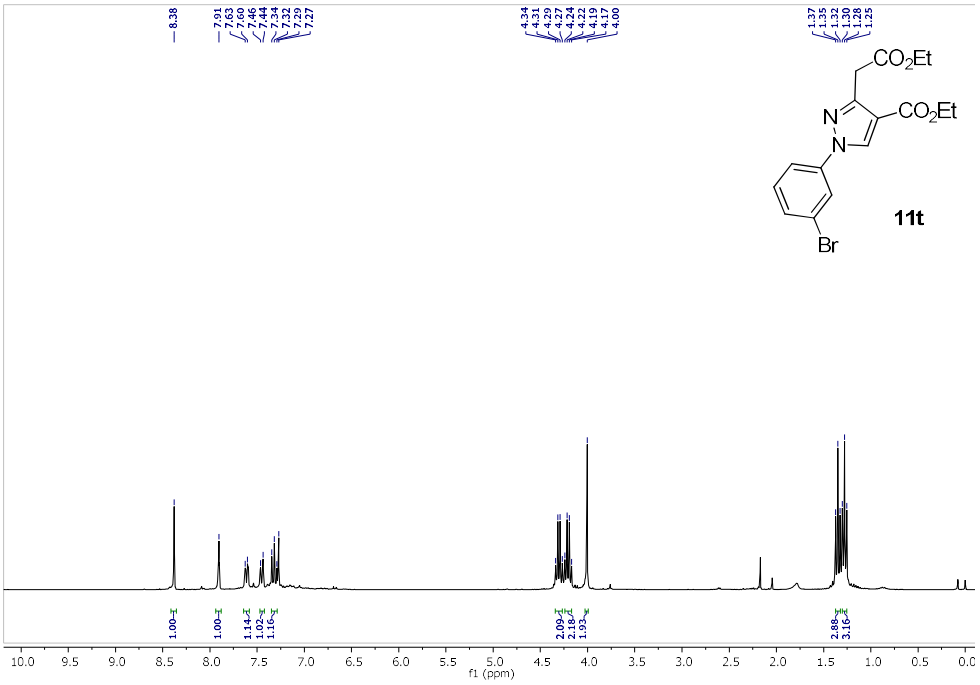
^{1}H Spectrum for 11s



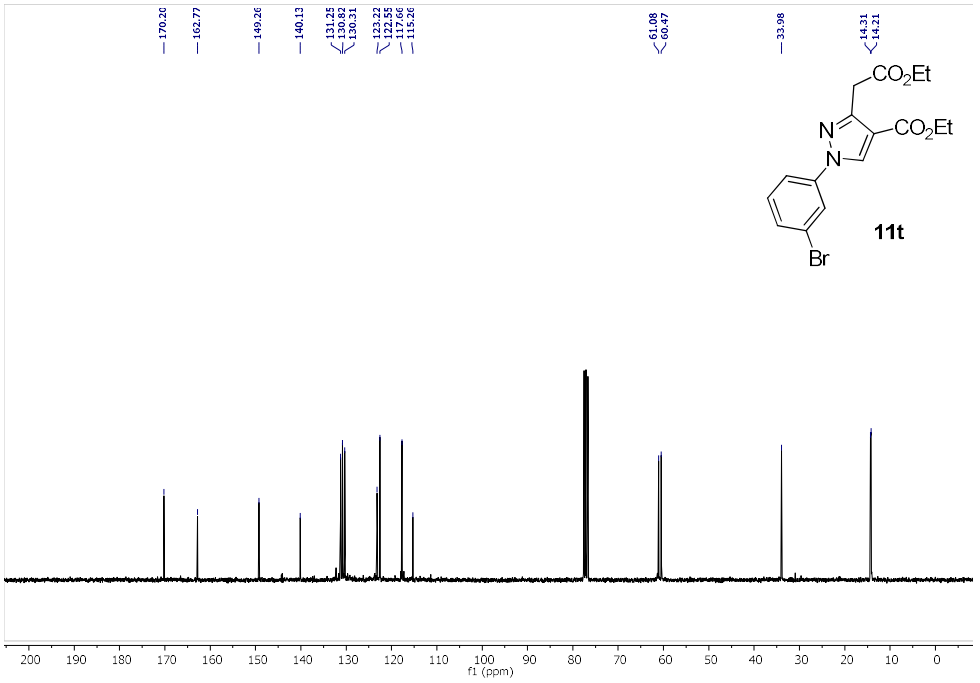
^{13}C Spectrum for 11s



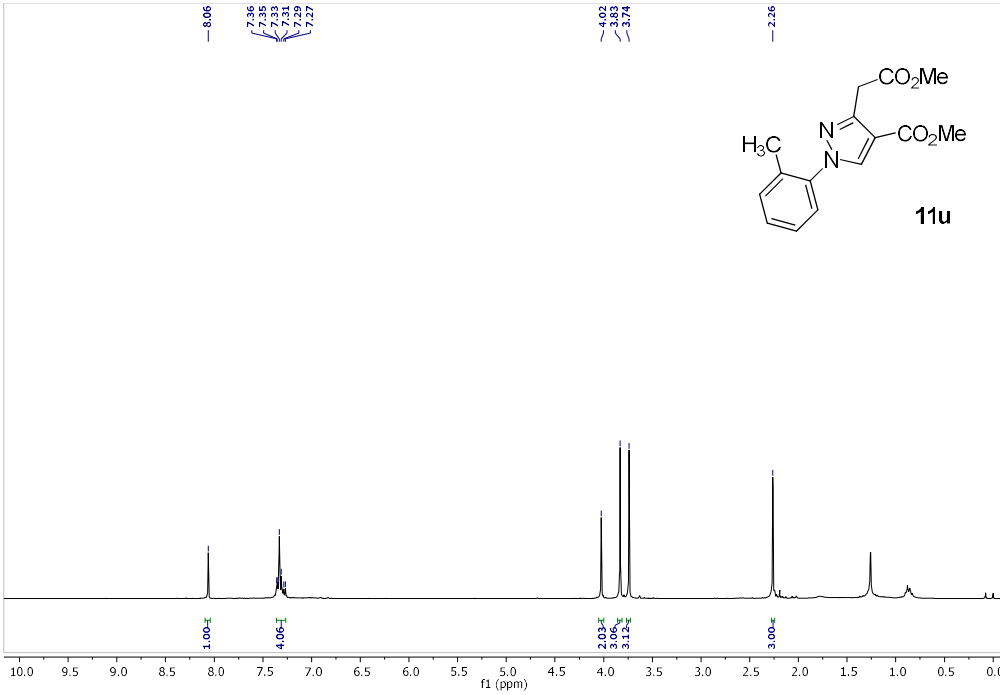
^{1}H Spectrum for 11t



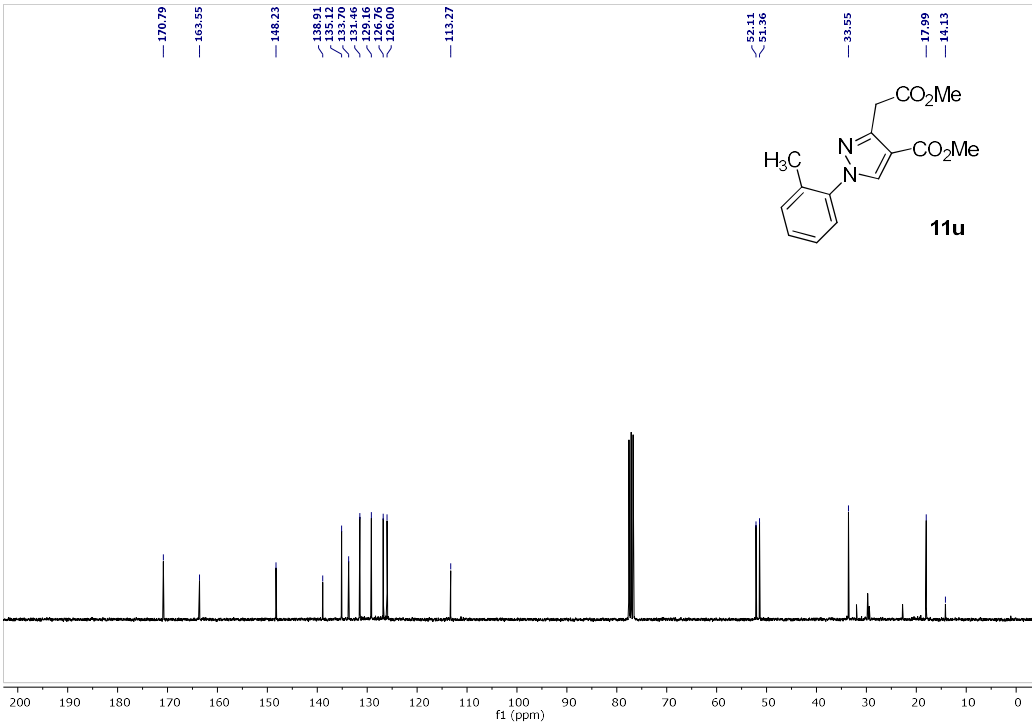
^{13}C Spectrum for 11t



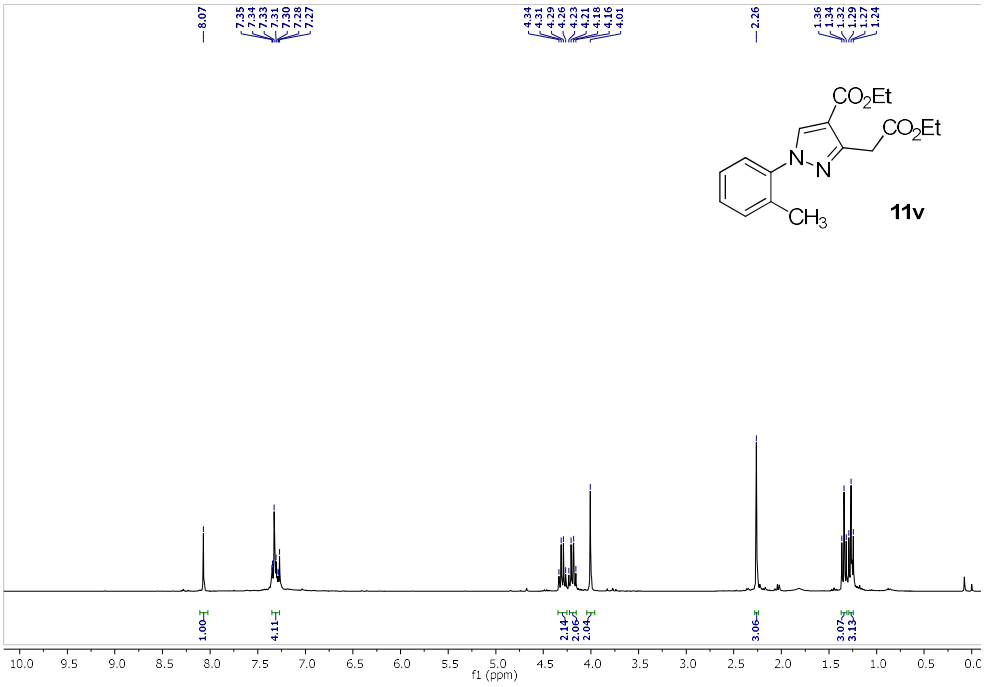
^{1}H Spectrum for 11u



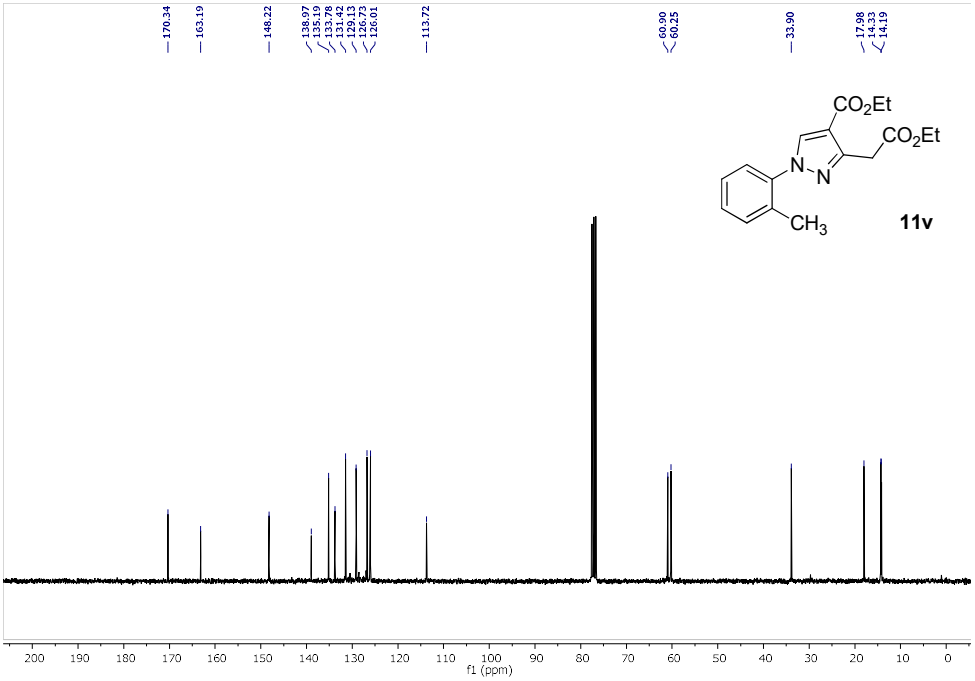
^{13}C Spectrum for 11u



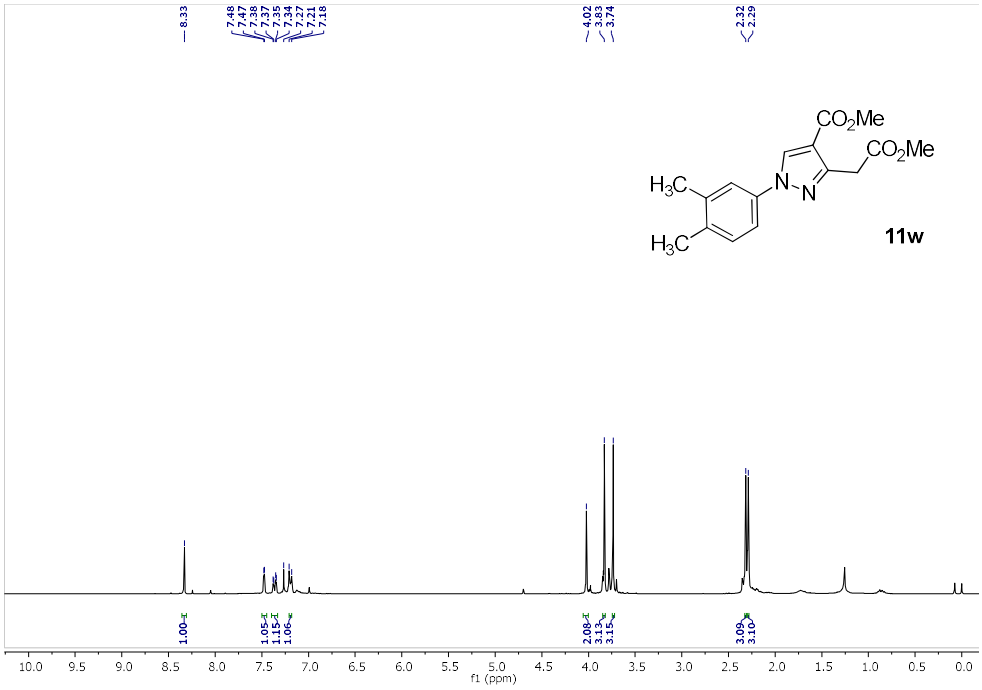
^{1}H Spectrum for 11v



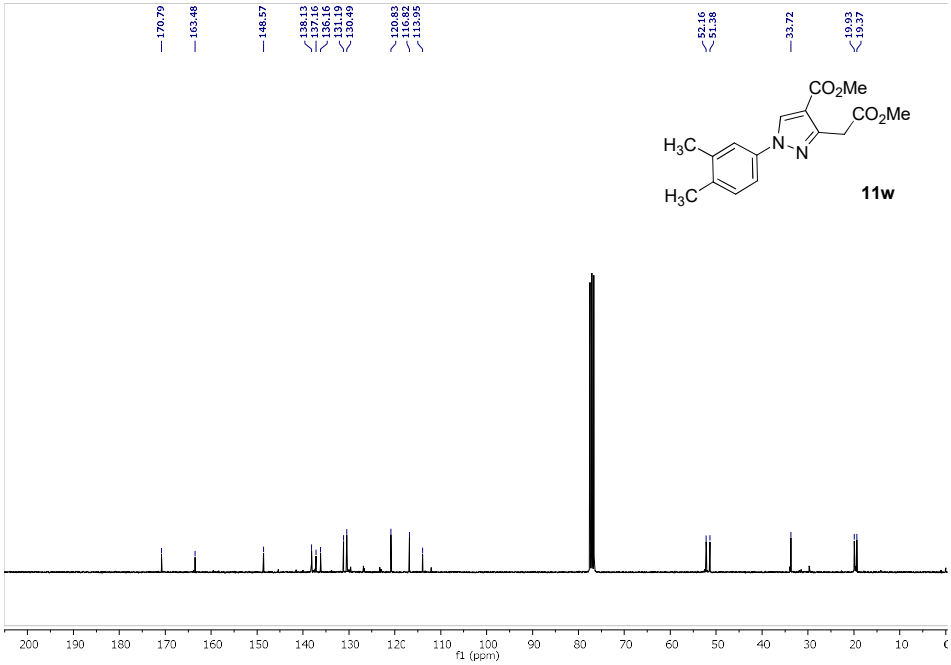
^{13}C Spectrum for 11v



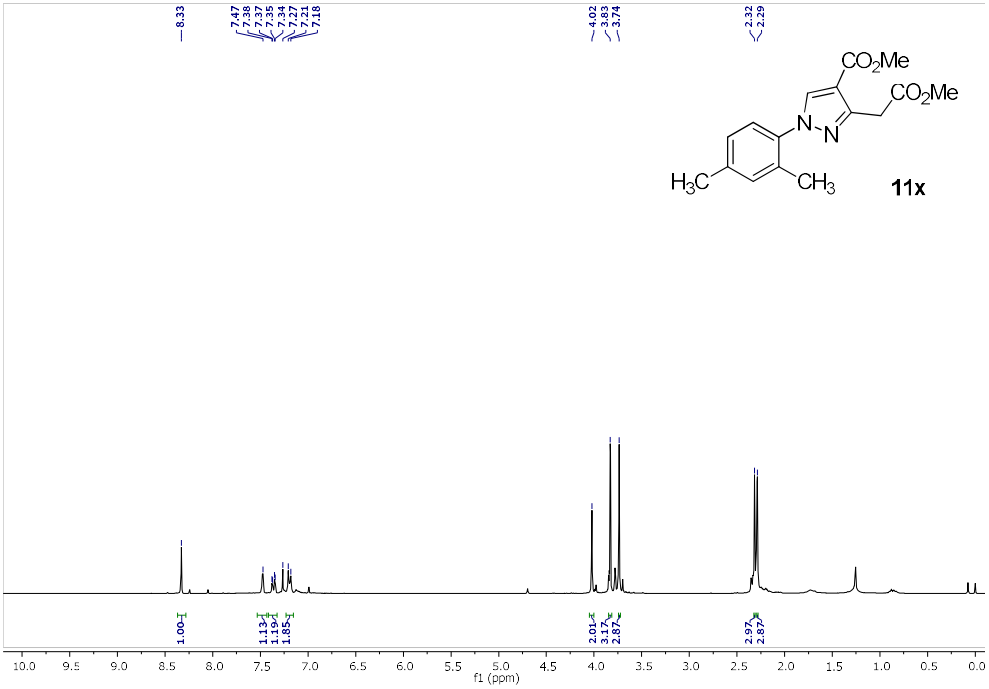
^{1}H Spectrum for 11w



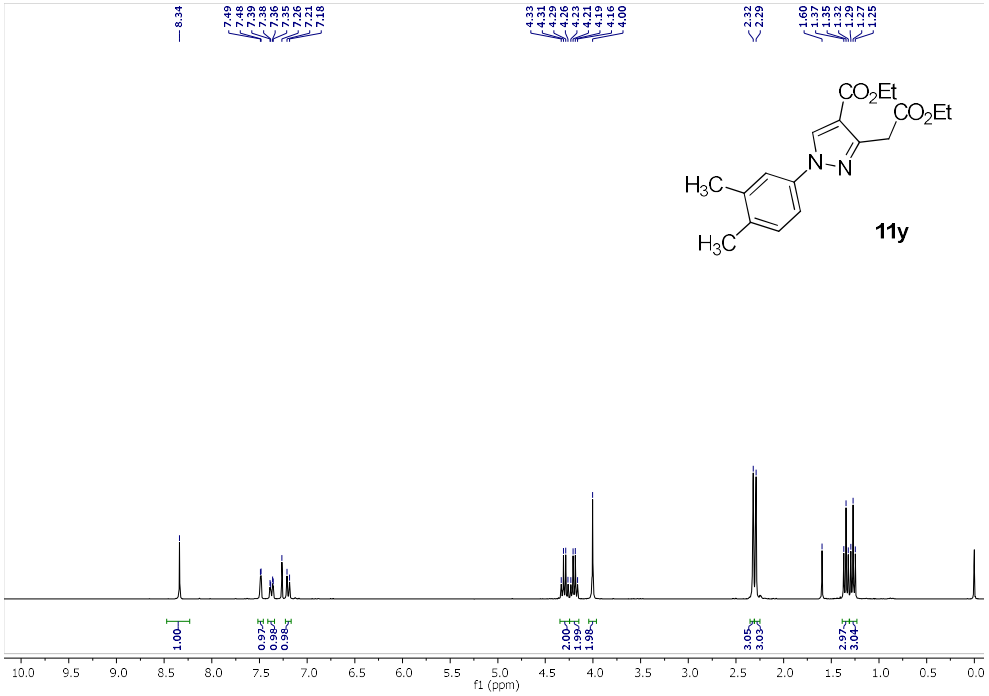
^{13}C Spectrum for 11w



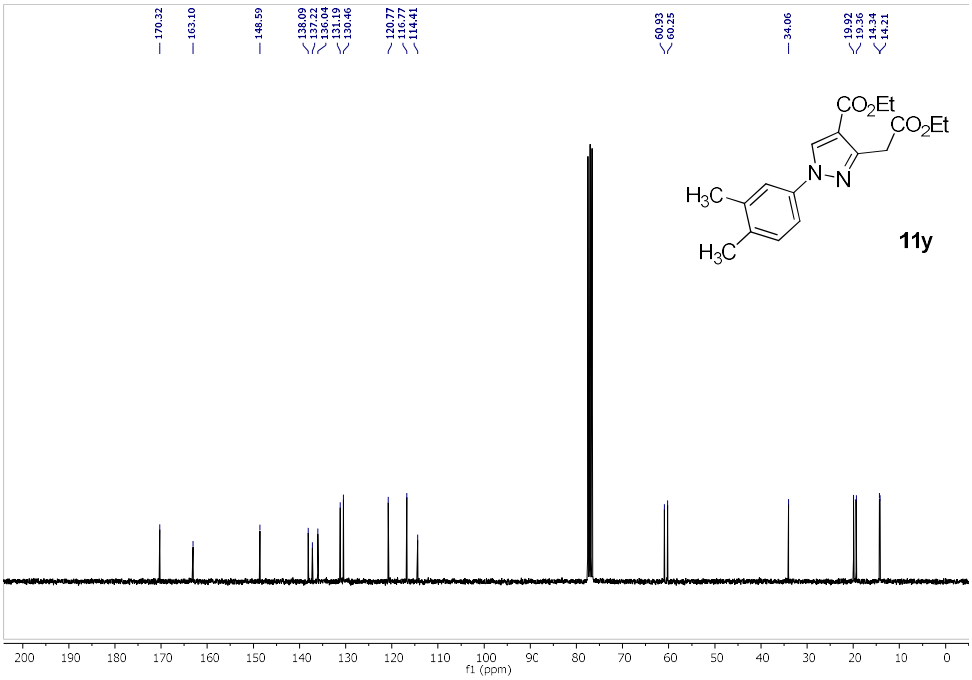
^{1}H Spectrum for 11x



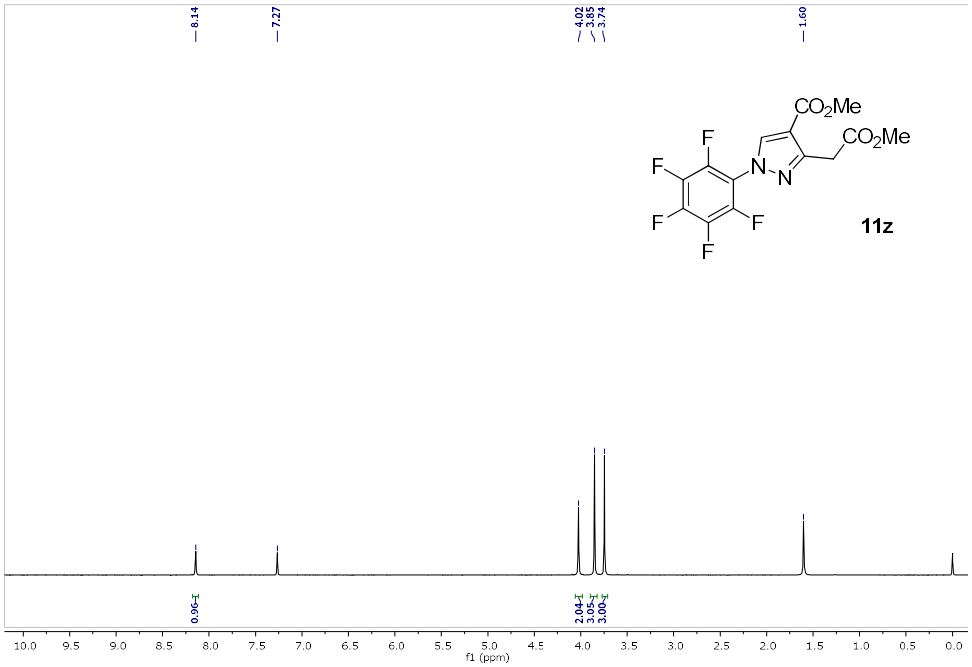
^{1}H Spectrum for 11y



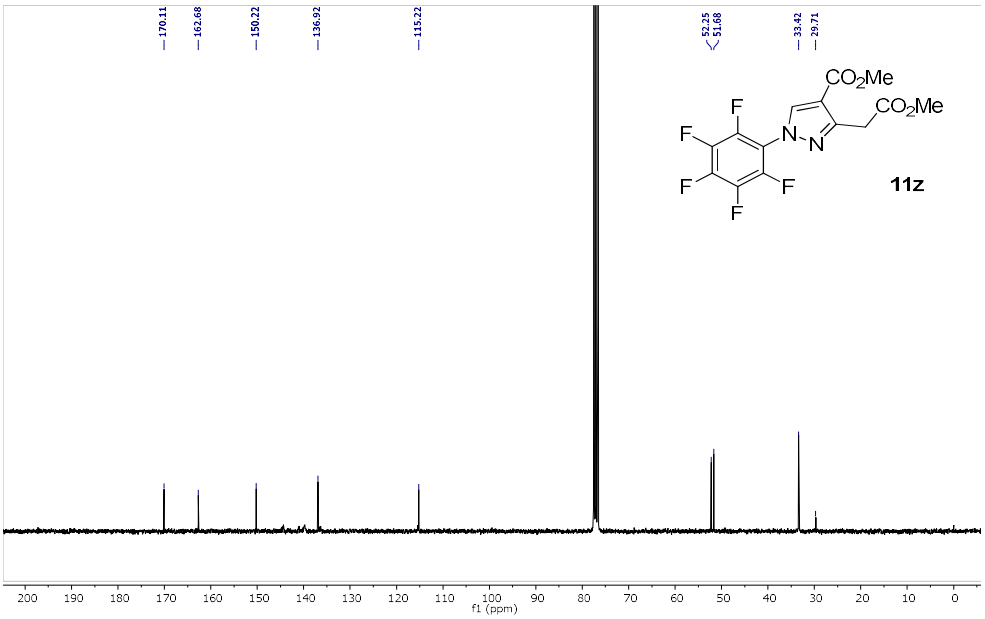
^{13}C Spectrum for 11y



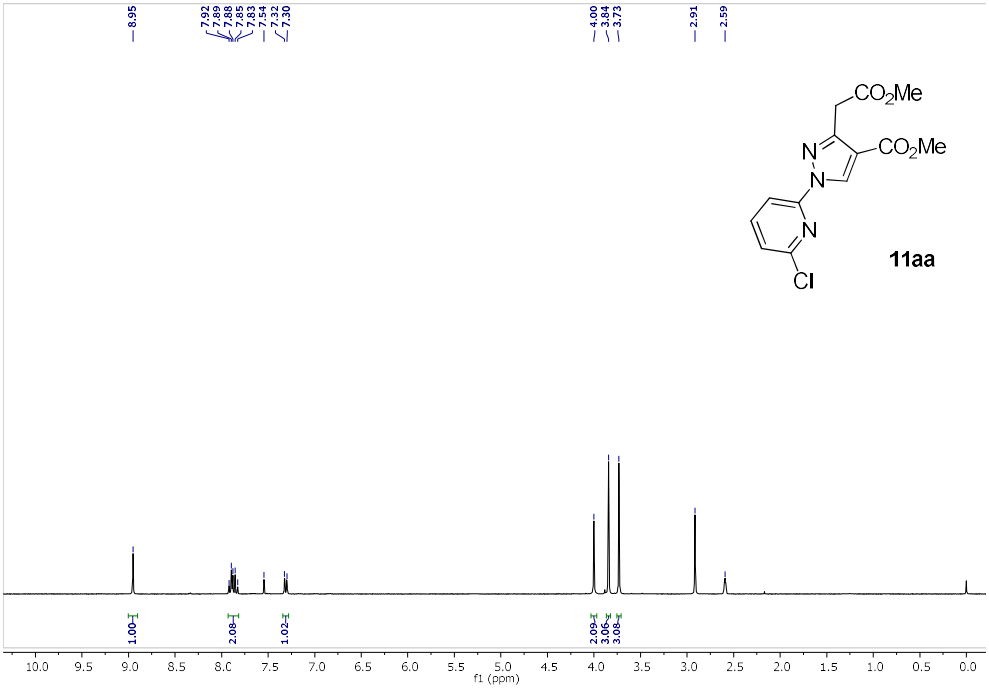
^{1}H Spectrum for 11z



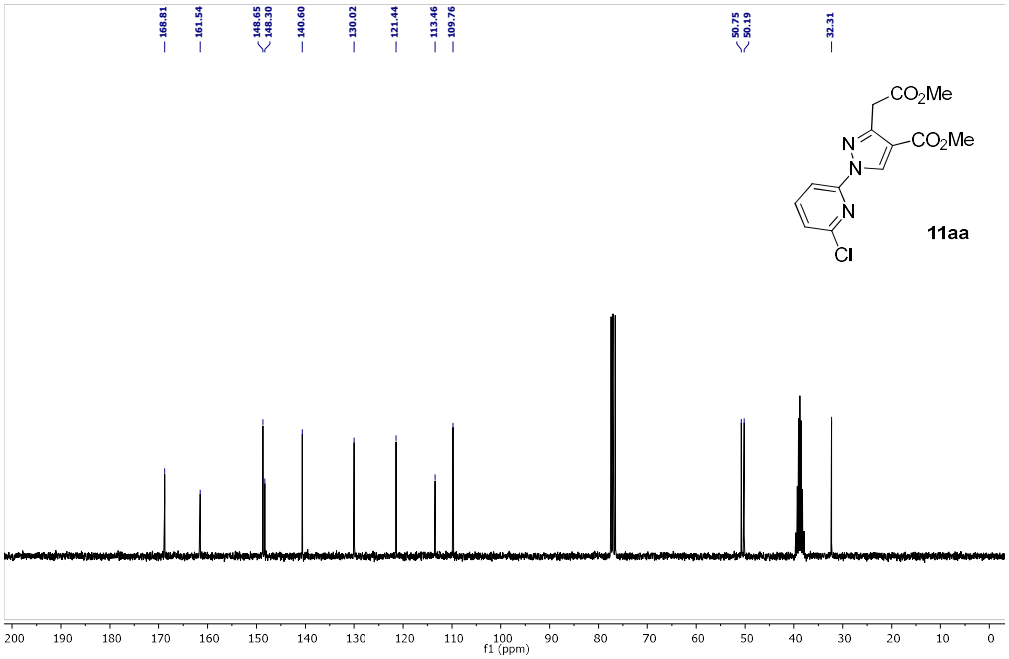
^{13}C Spectrum for 11z



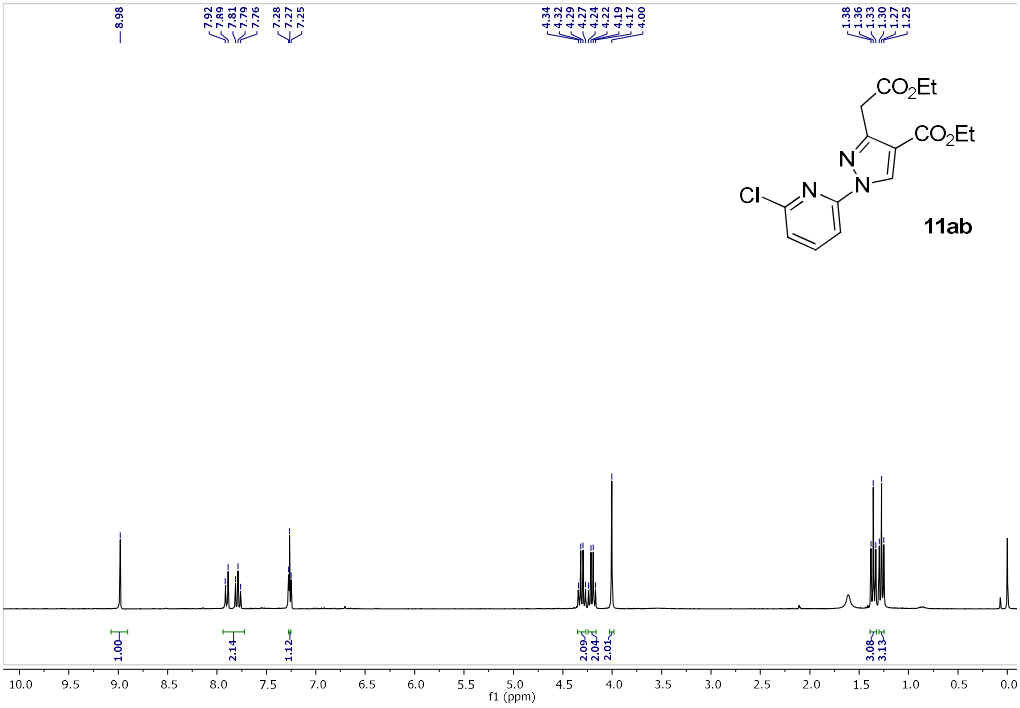
^{1}H Spectrum for 11aa



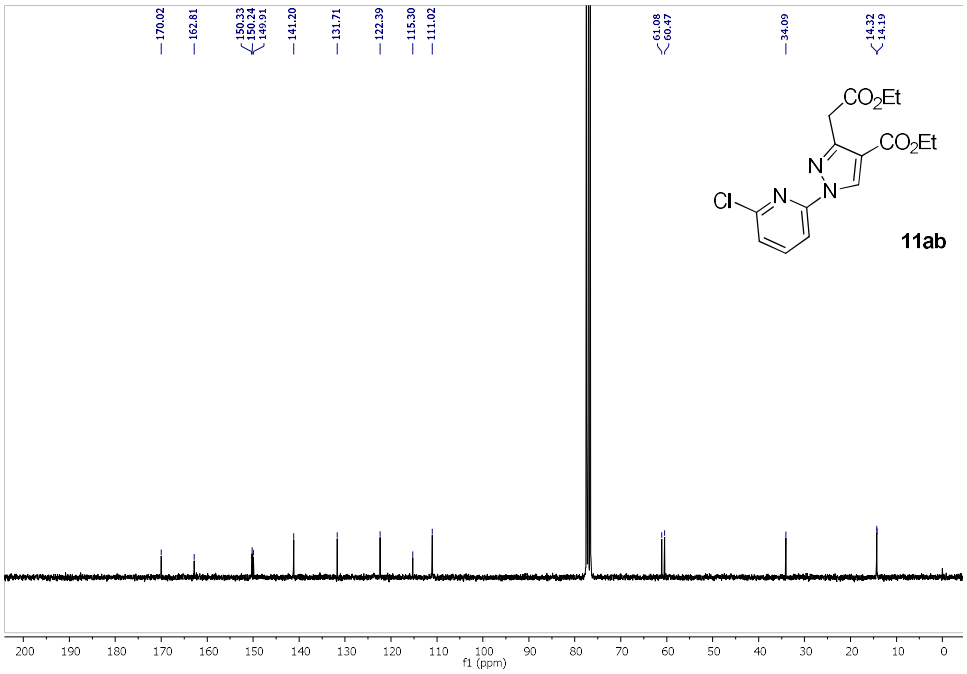
^{13}C Spectrum for 11aa



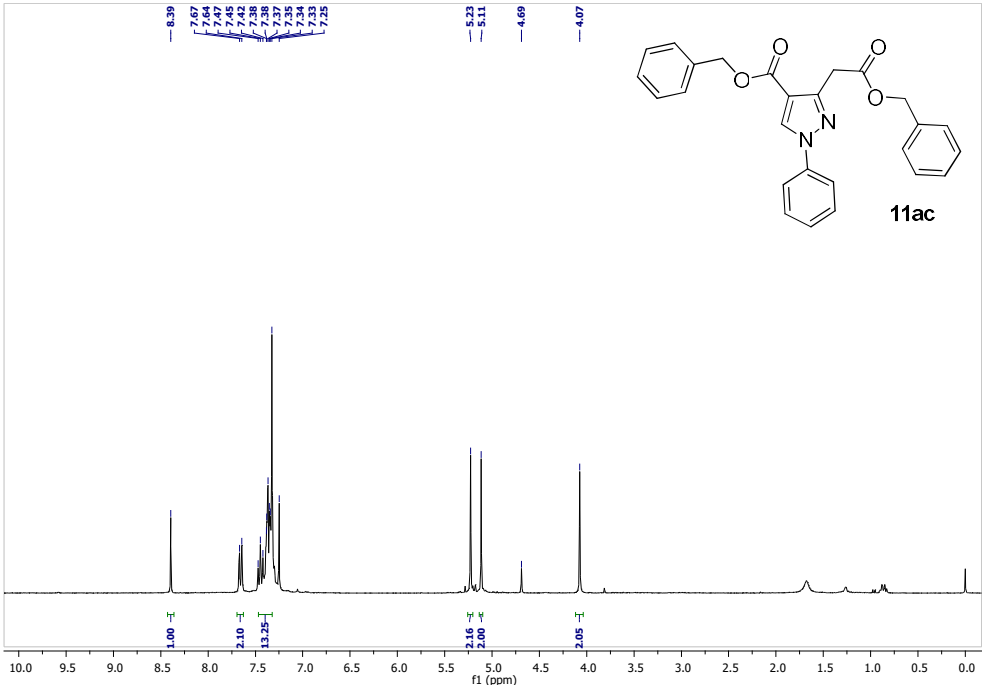
^{1}H Spectrum for 11ab



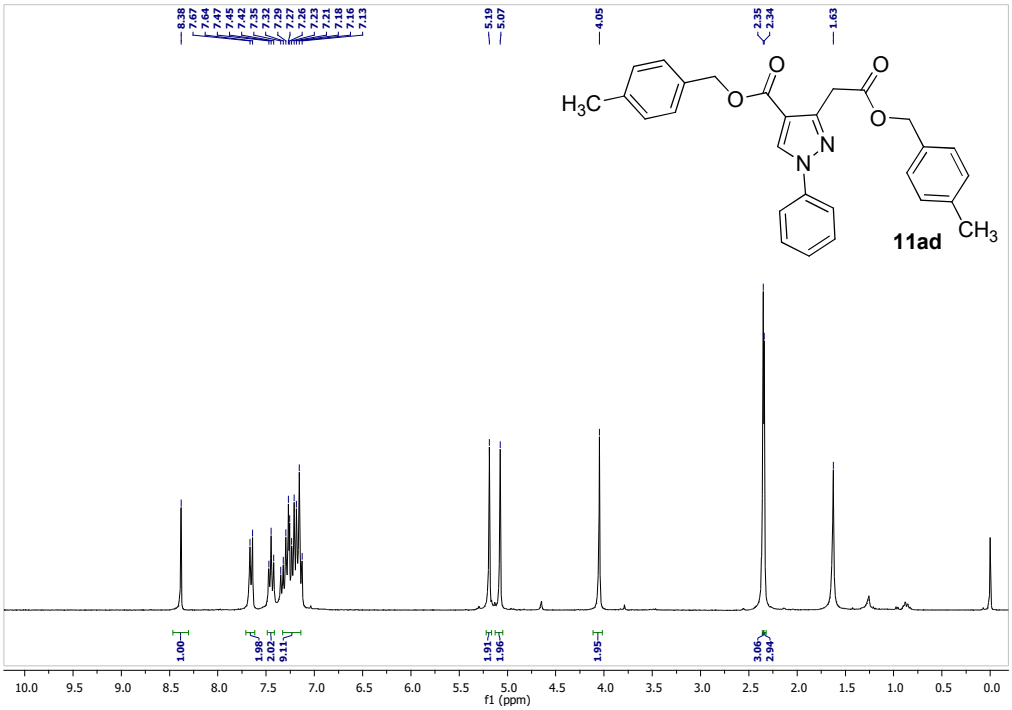
^{13}C Spectrum for 11ab



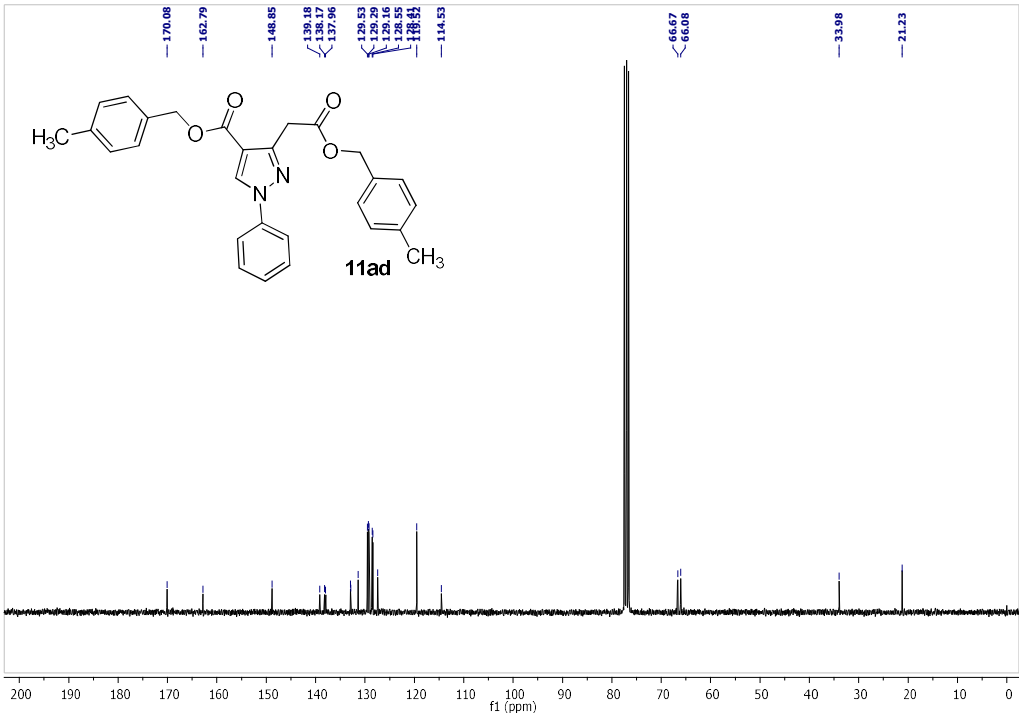
^{1}H Spectrum for 11ac



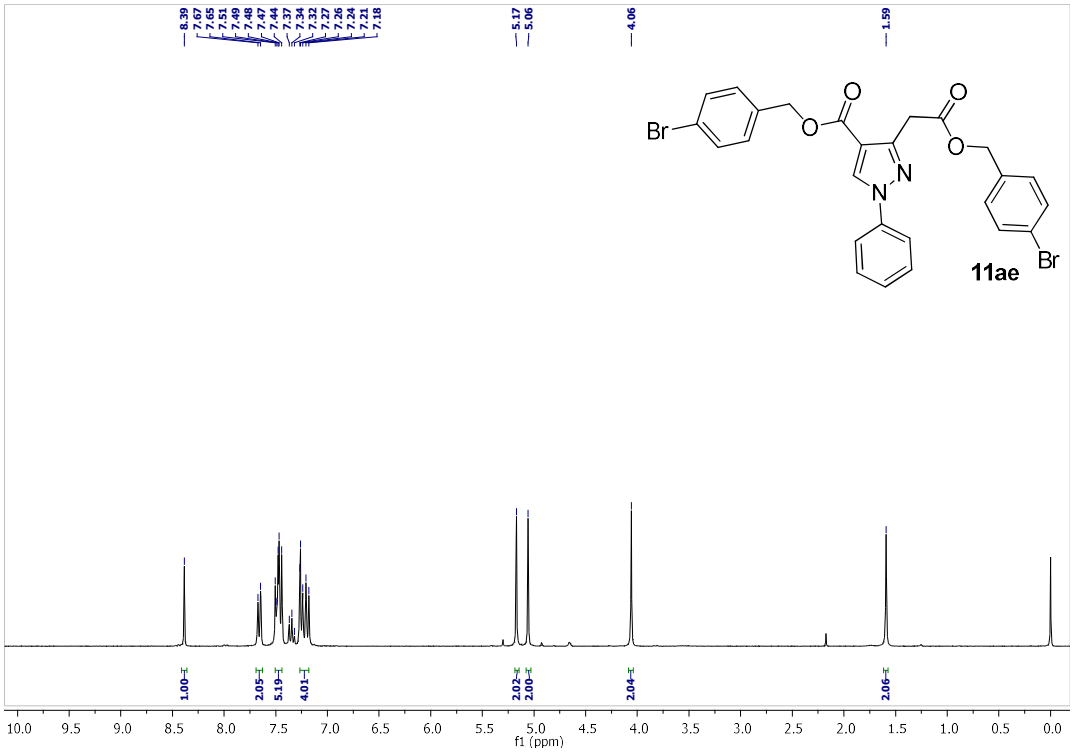
^{1}H Spectrum for 11ad



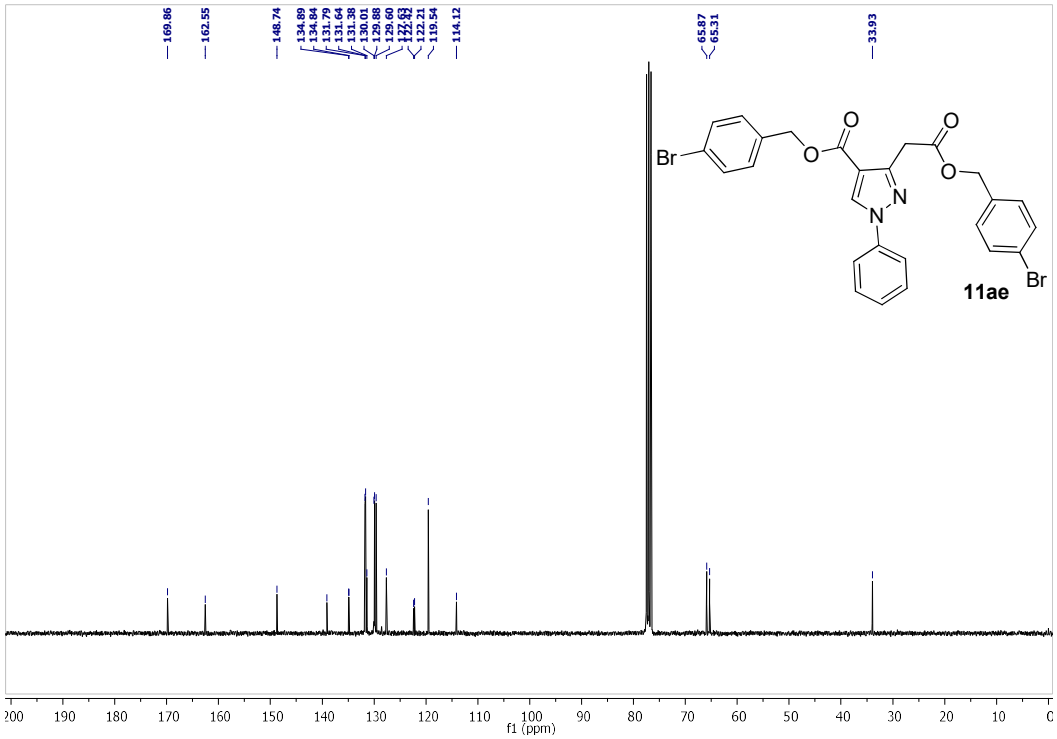
^{13}C Spectrum for 11ad



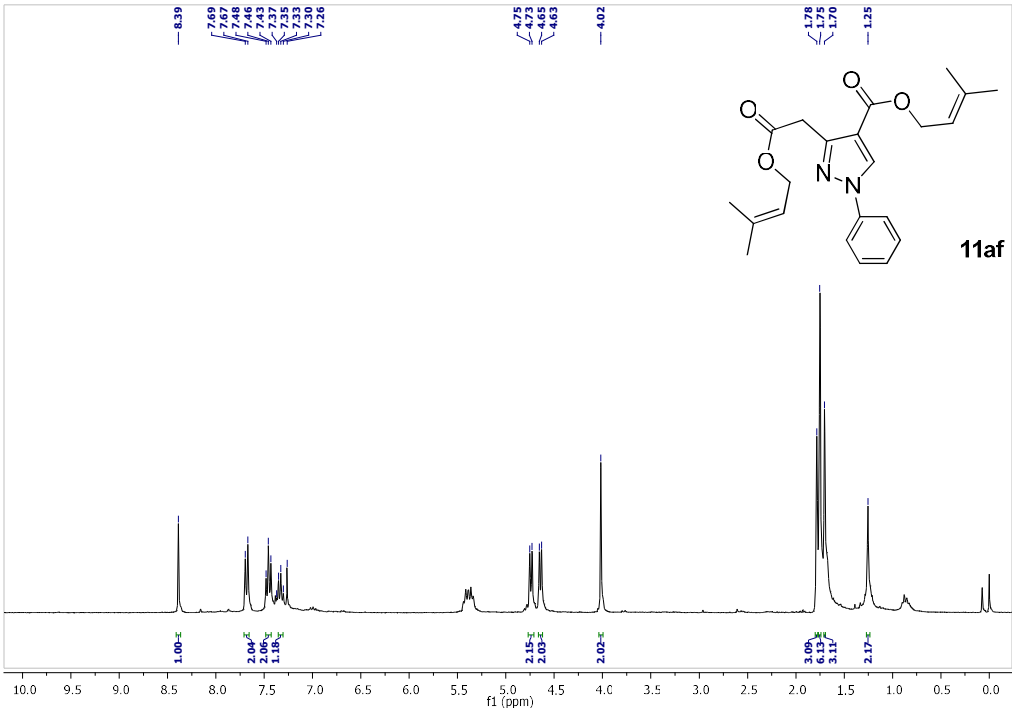
^{1}H Spectrum for 11ae



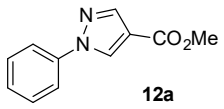
^{13}C Spectrum for 11ae



^{1}H Spectrum for 11af

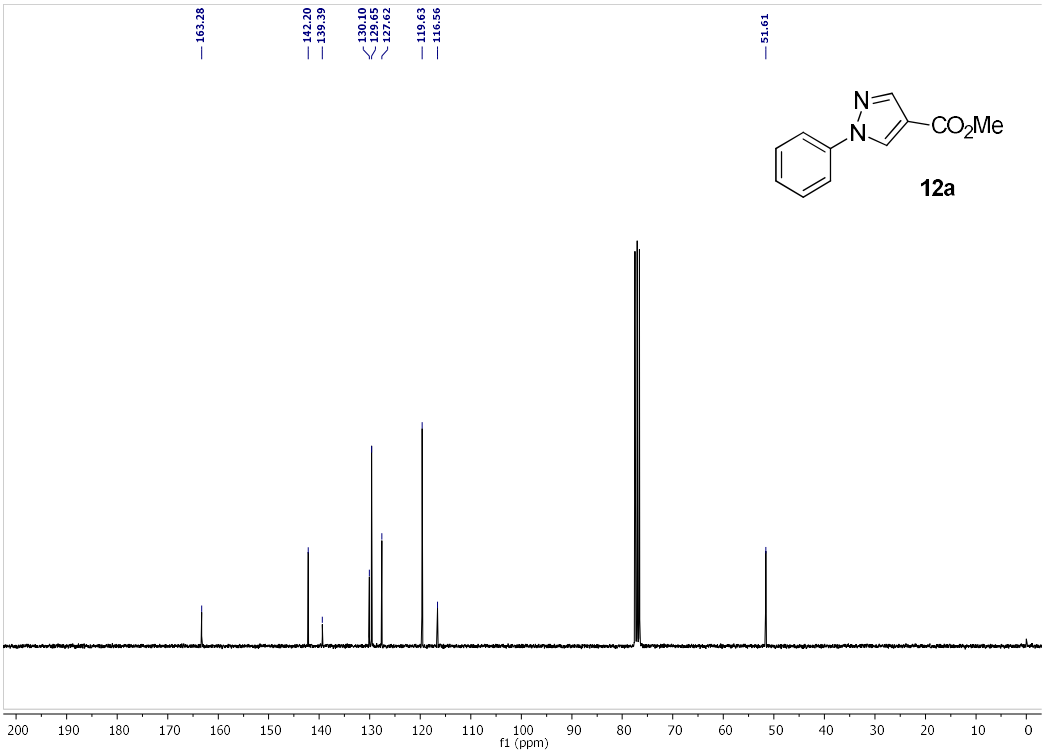


^{1}H Spectrum for 12a

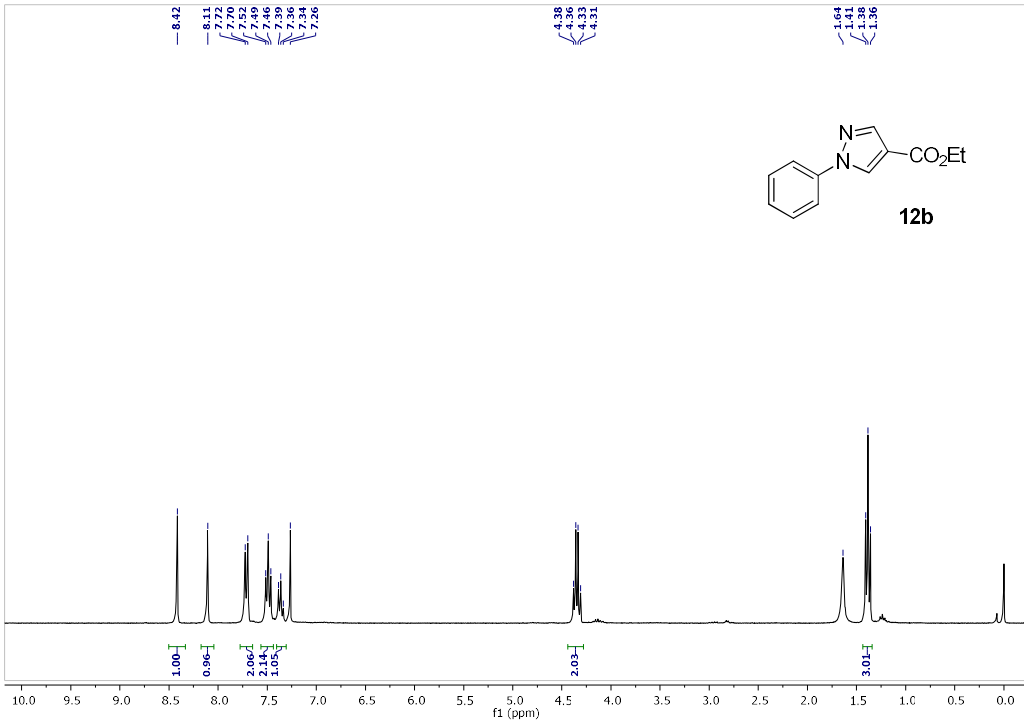


12a

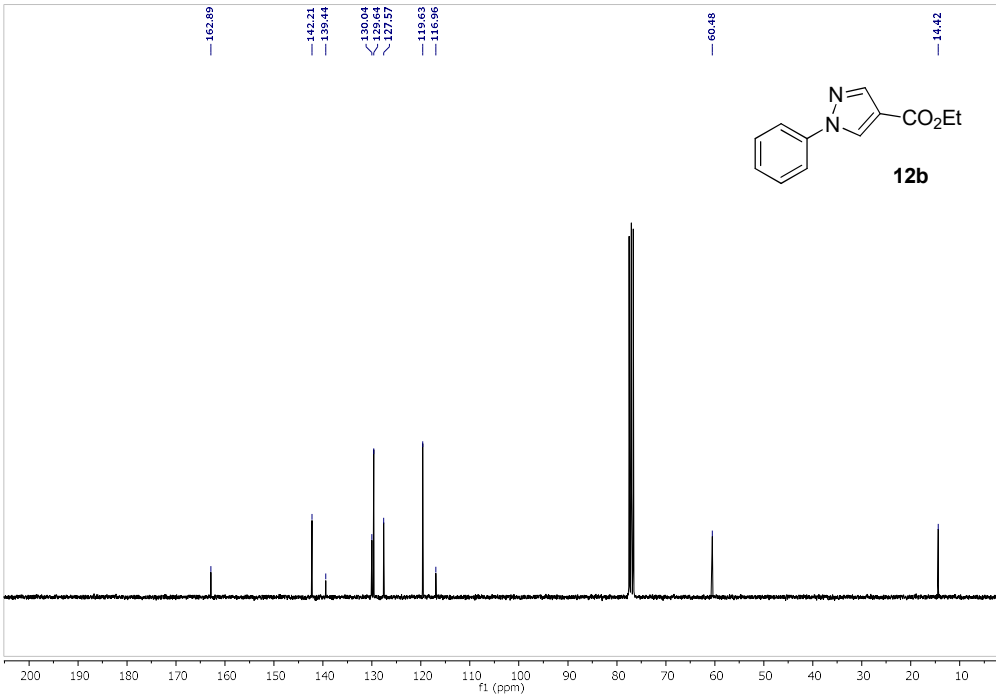
^{13}C Spectrum for 12a



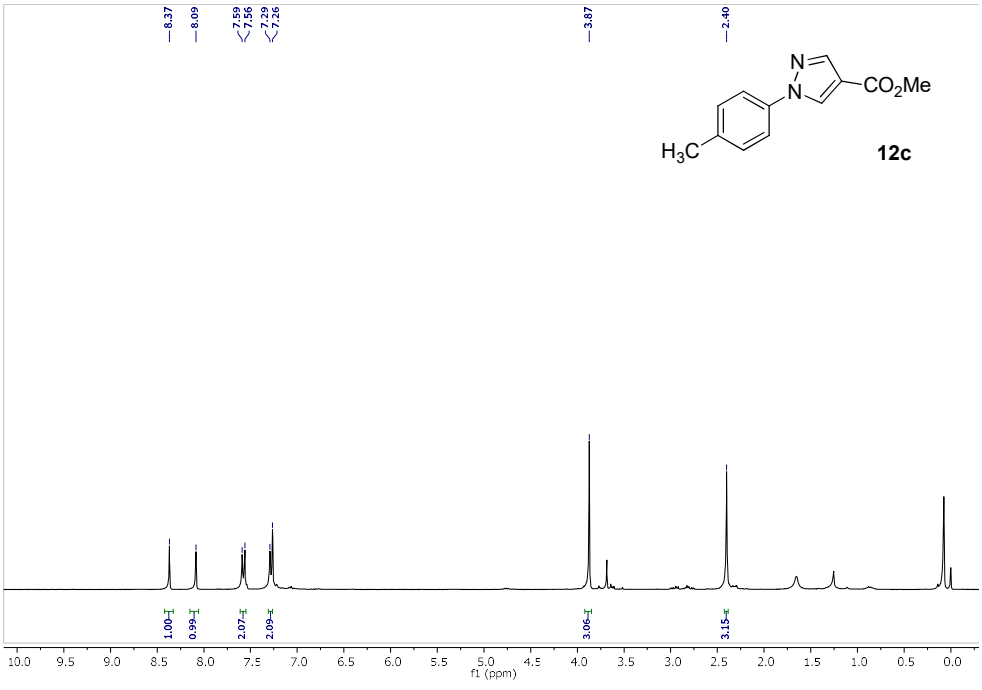
^{1}H Spectrum for 12b



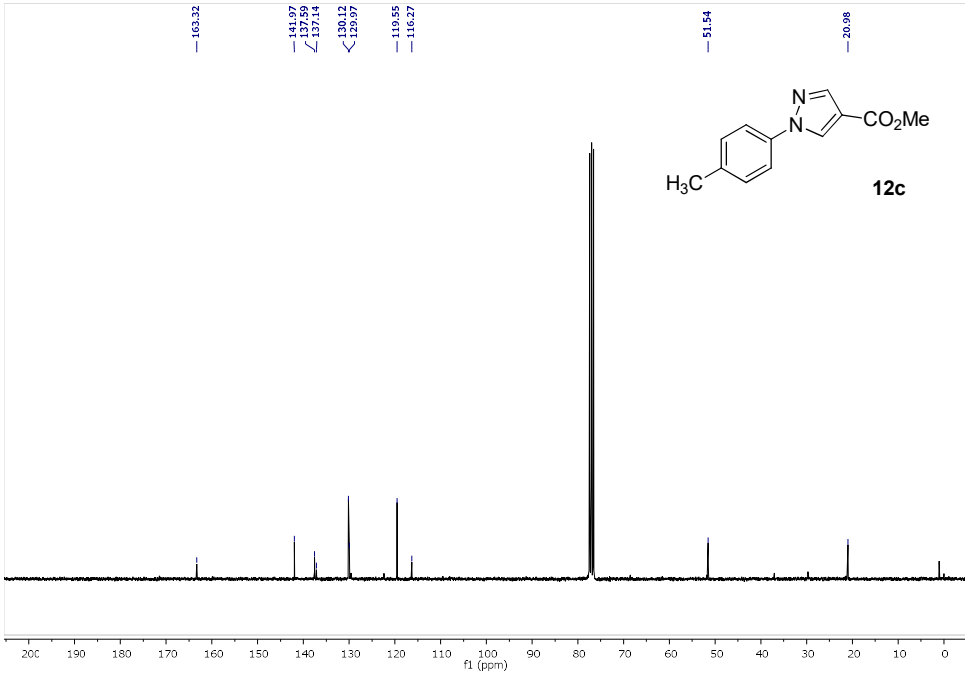
^{13}C Spectrum for 12b



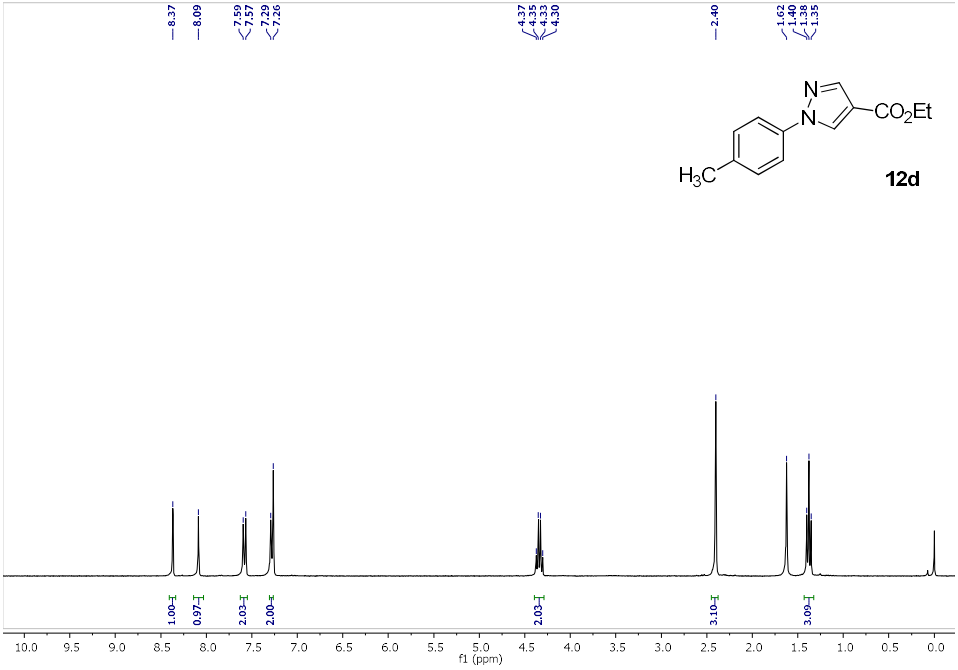
^{1}H Spectrum for 12c



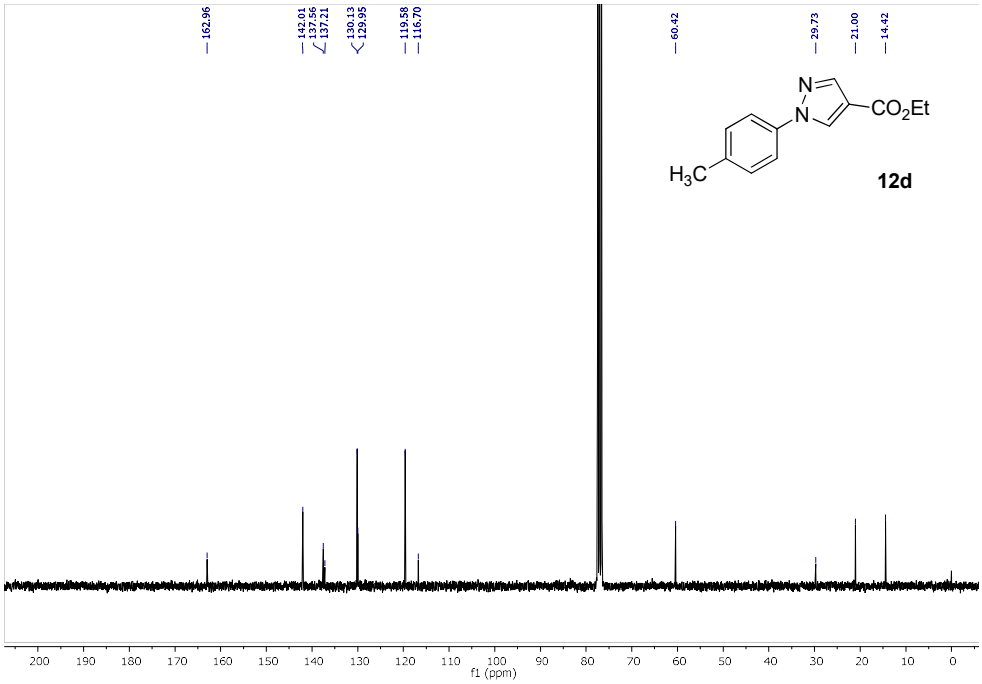
^{13}C Spectrum for 12c



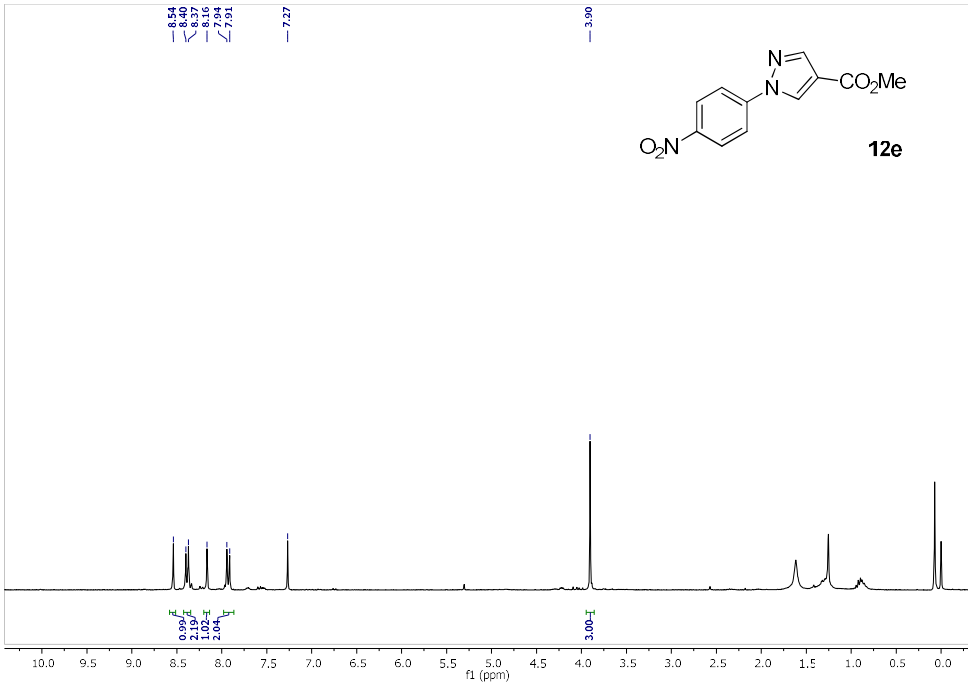
^{1}H Spectrum for 12d



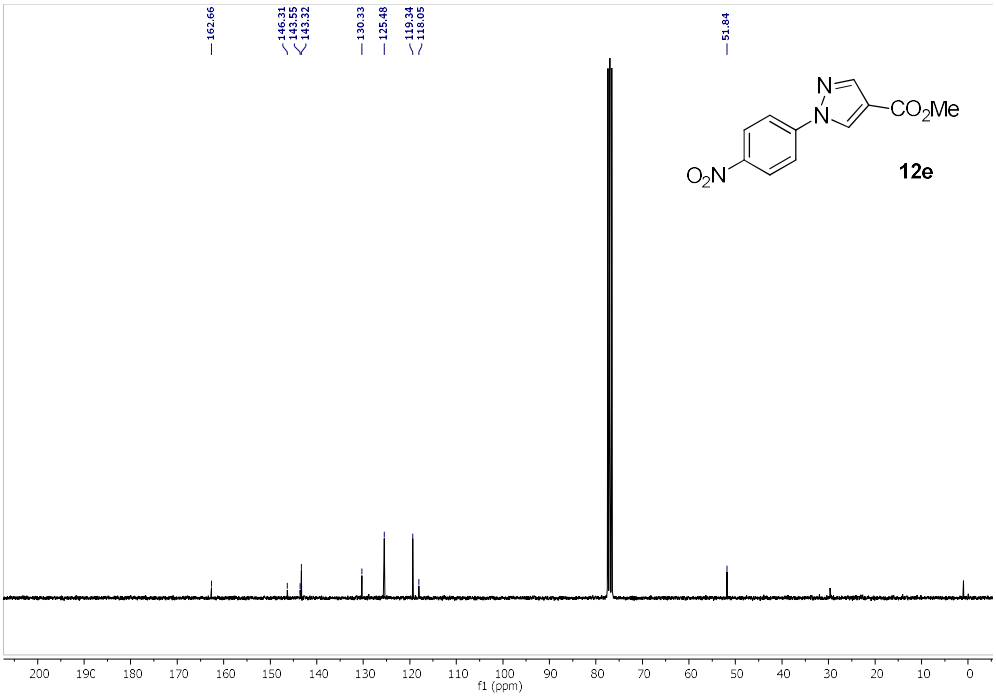
^{13}C Spectrum for 12d



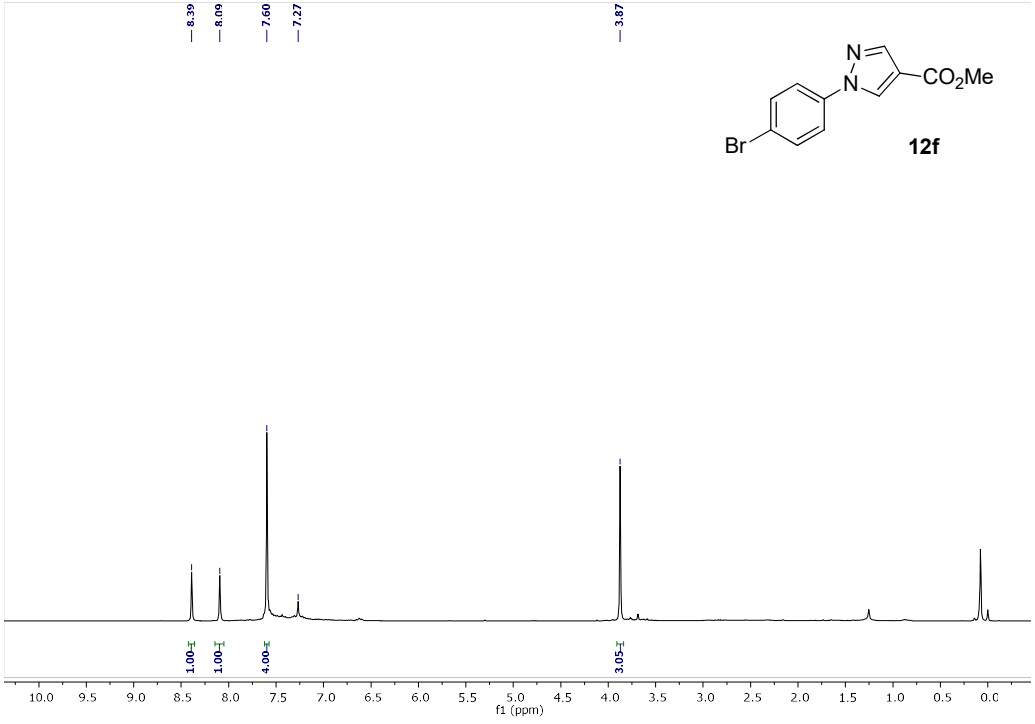
^{1}H Spectrum for 12e



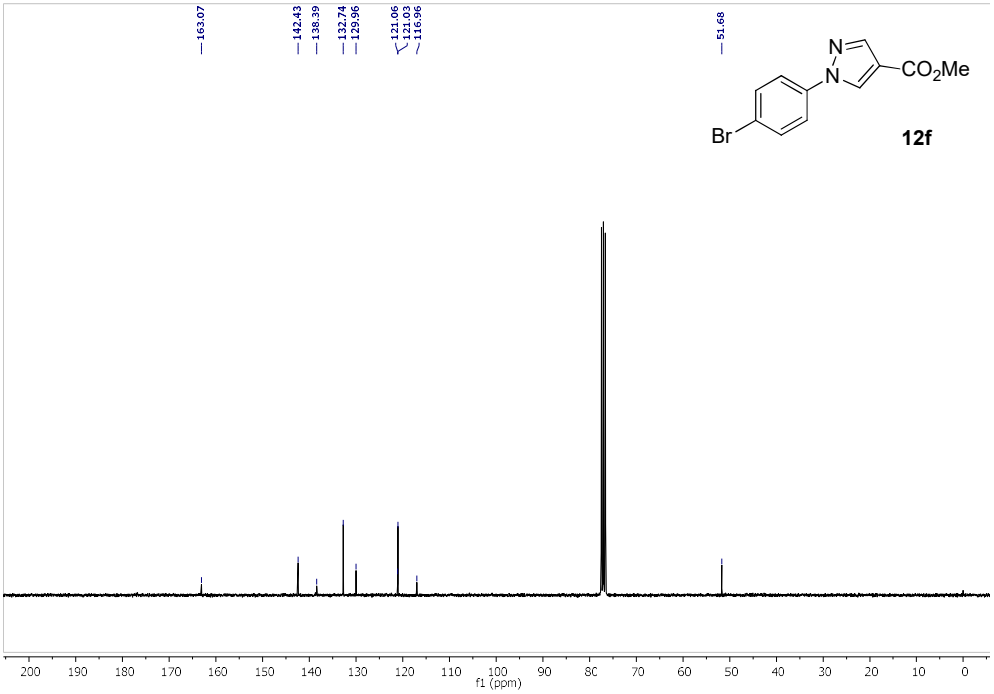
^{13}C Spectrum for 12e



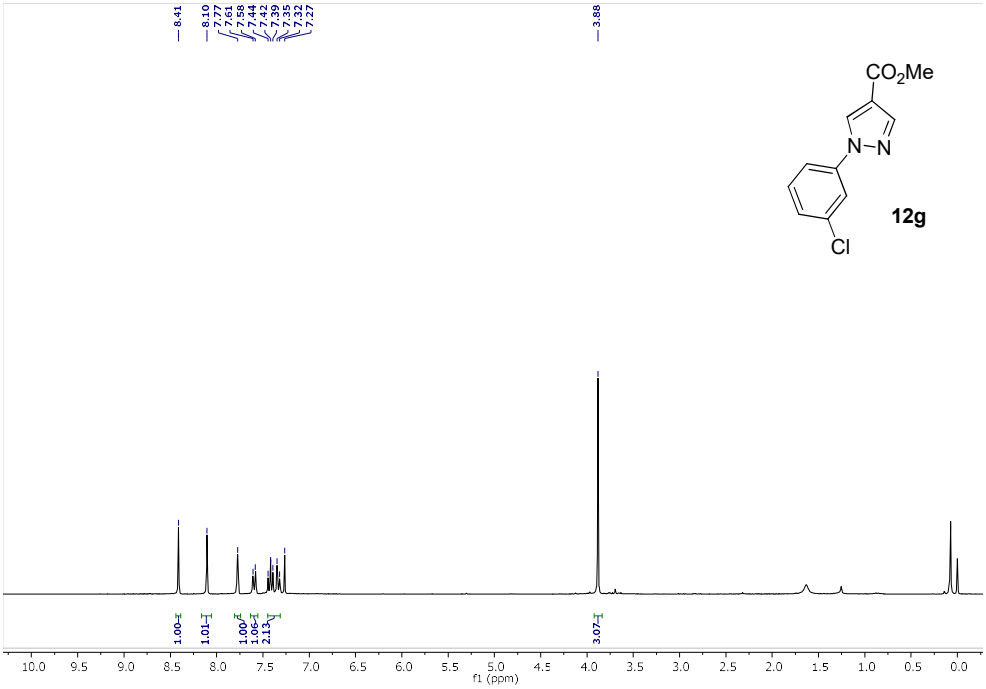
^{1}H Spectrum for 12f



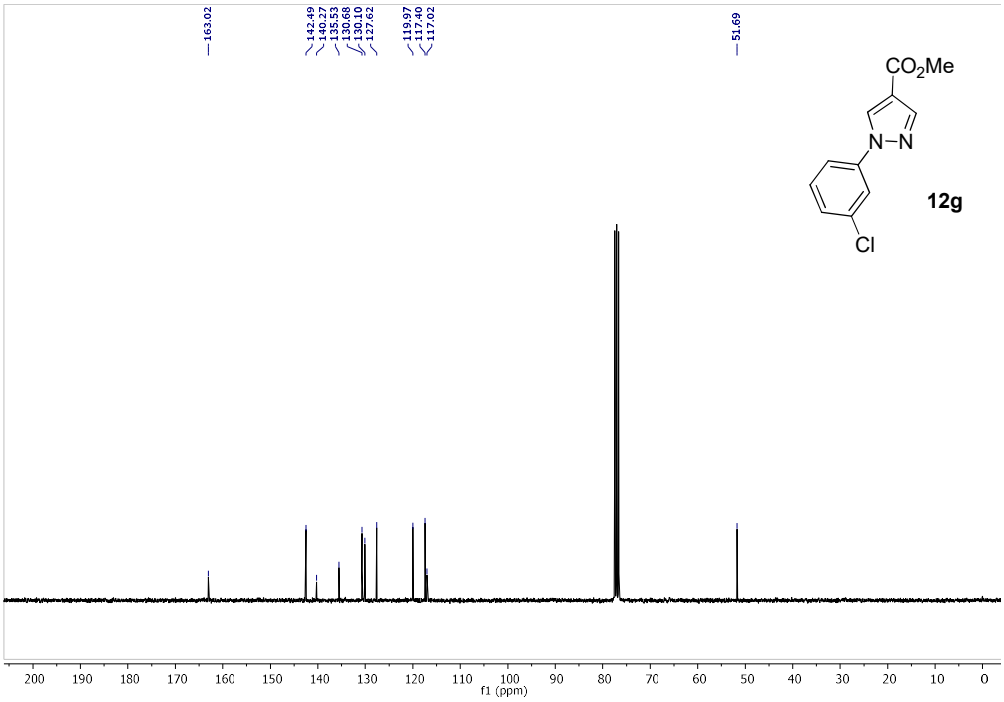
^{13}C Spectrum for 12f



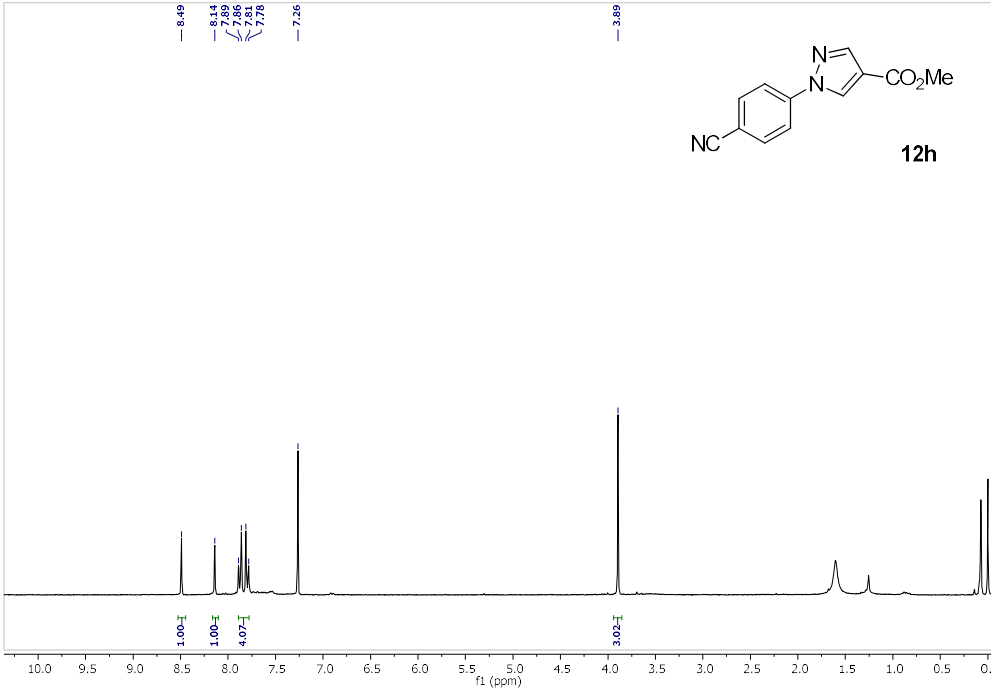
^{1}H Spectrum for 12g



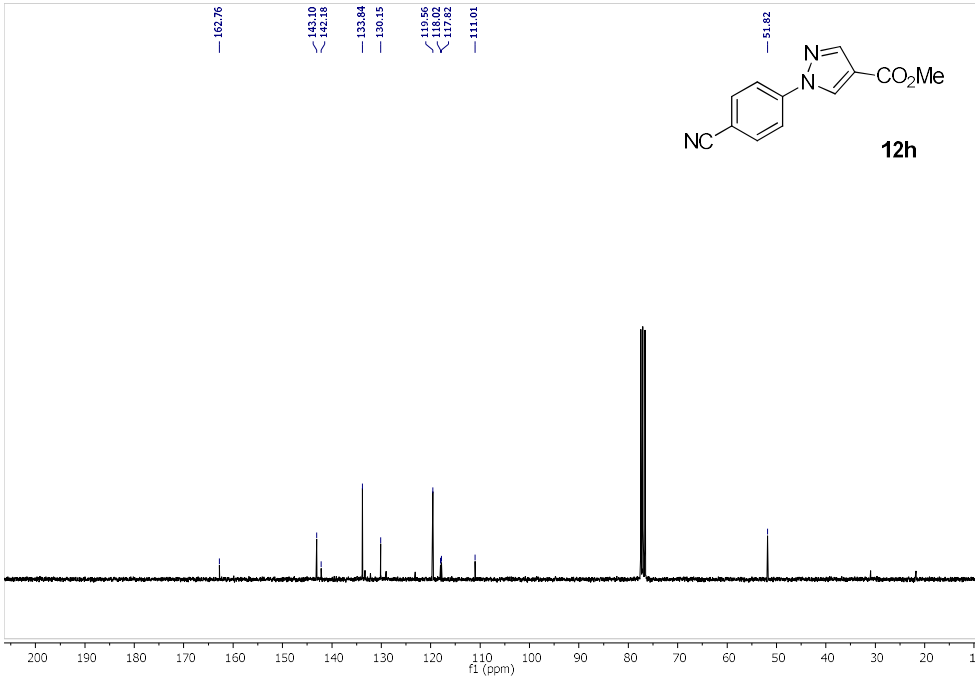
^{13}C Spectrum for 12g



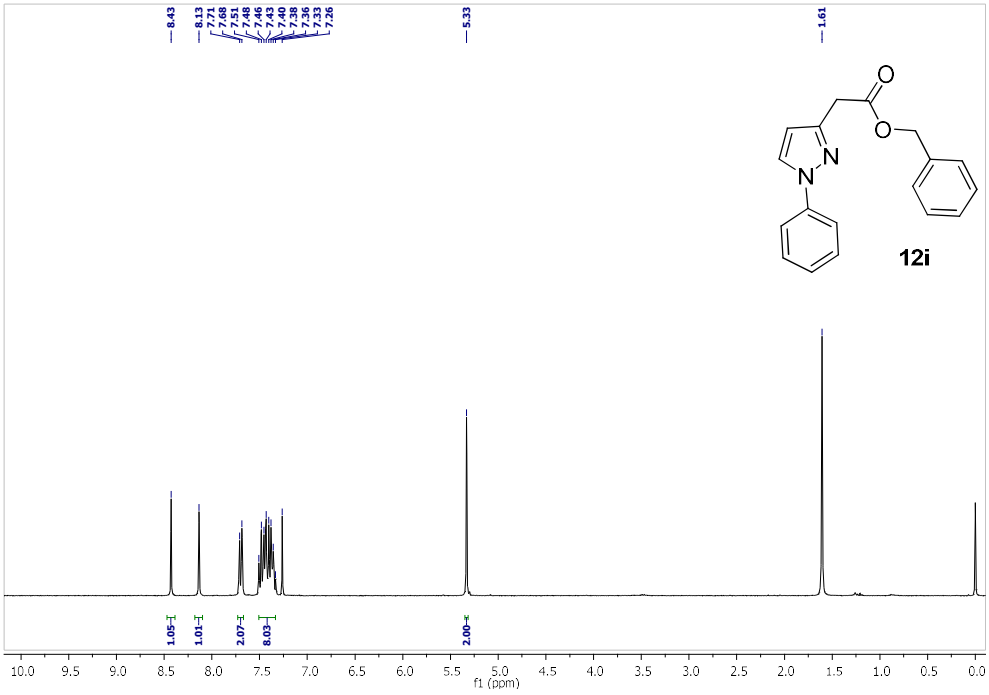
^{1}H Spectrum for 12h



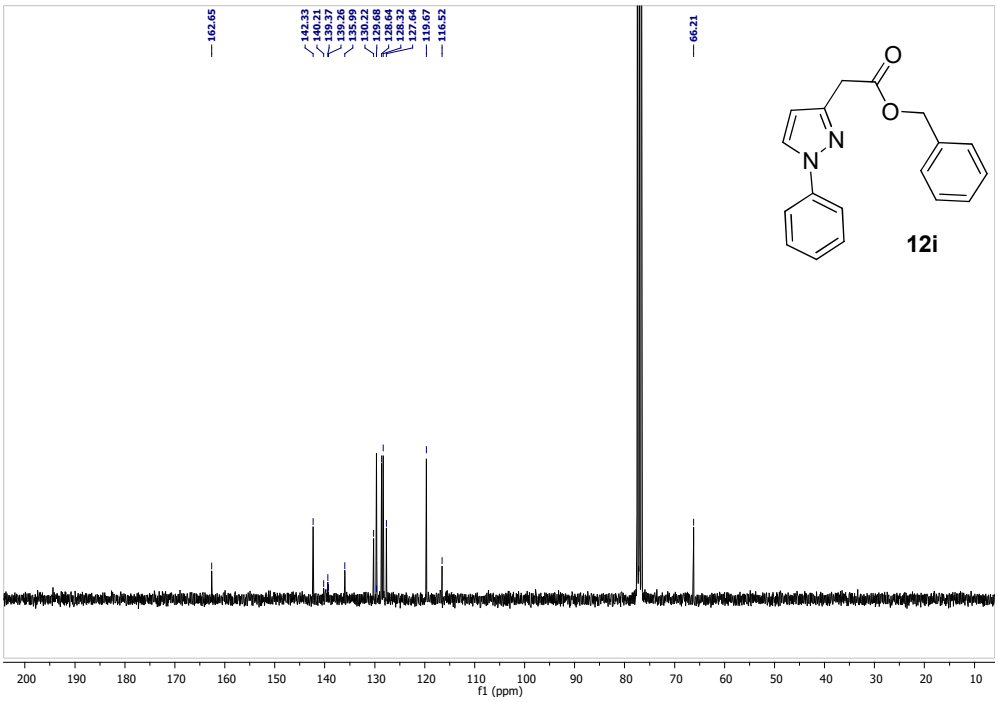
^{13}C Spectrum for 12h



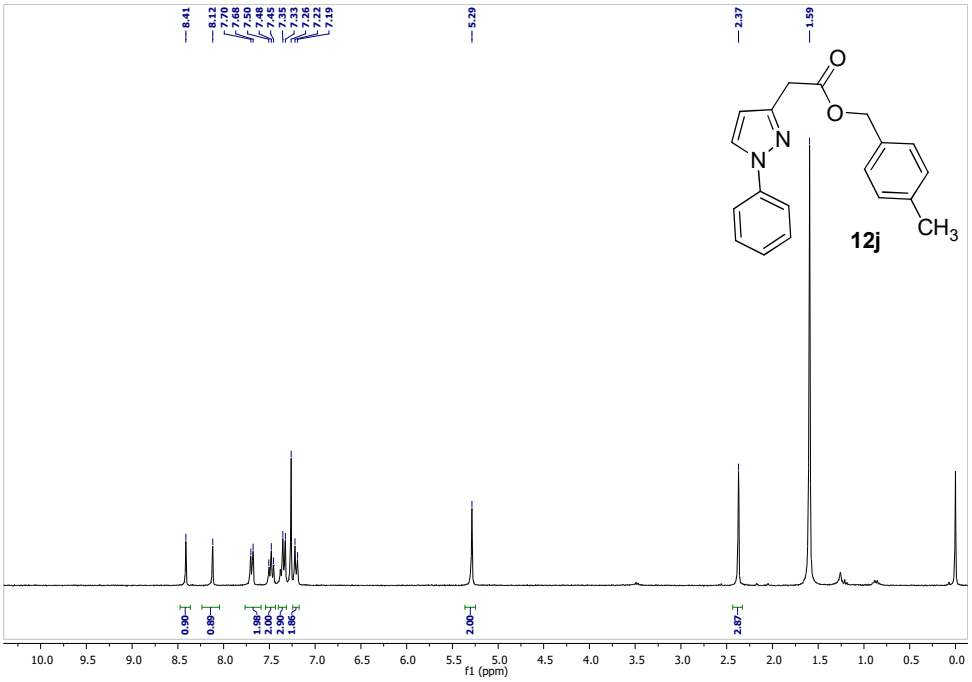
^{1}H Spectrum for 12i



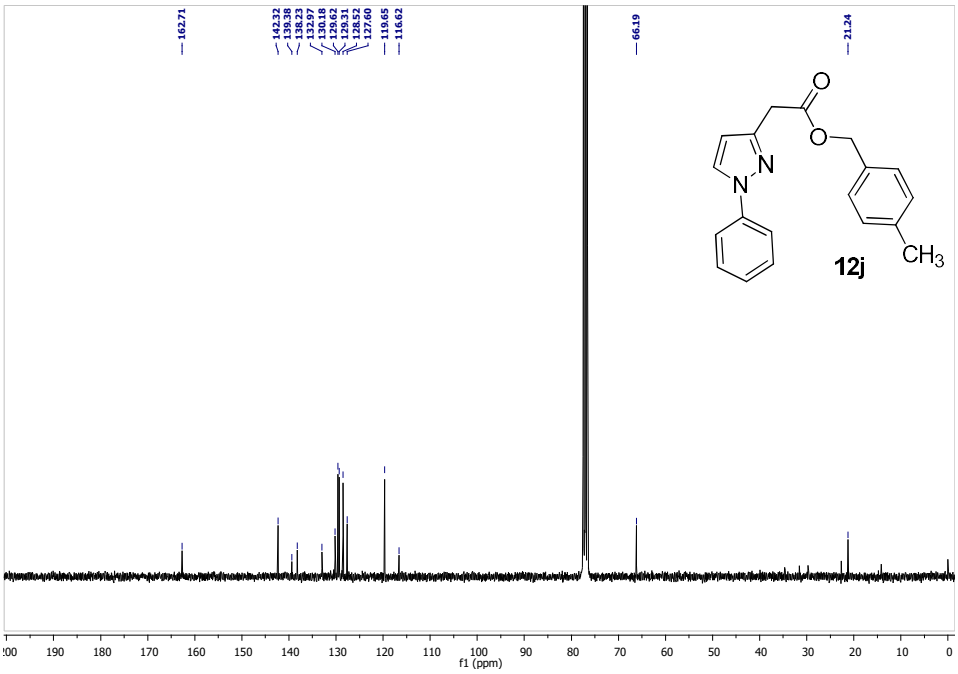
^{13}C Spectrum for 12i



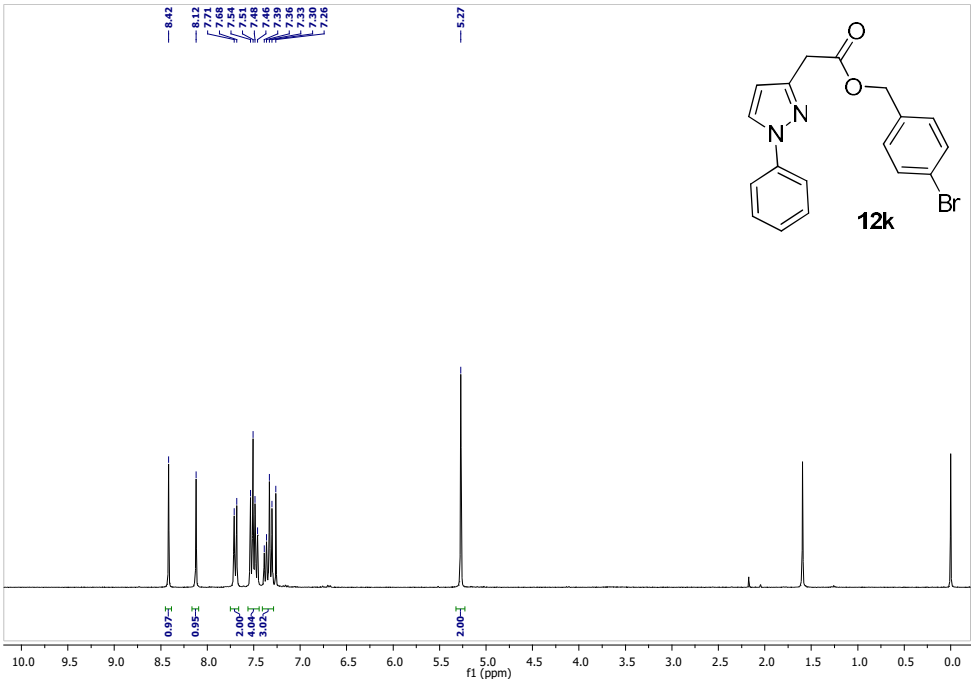
^{1}H Spectrum for 12j



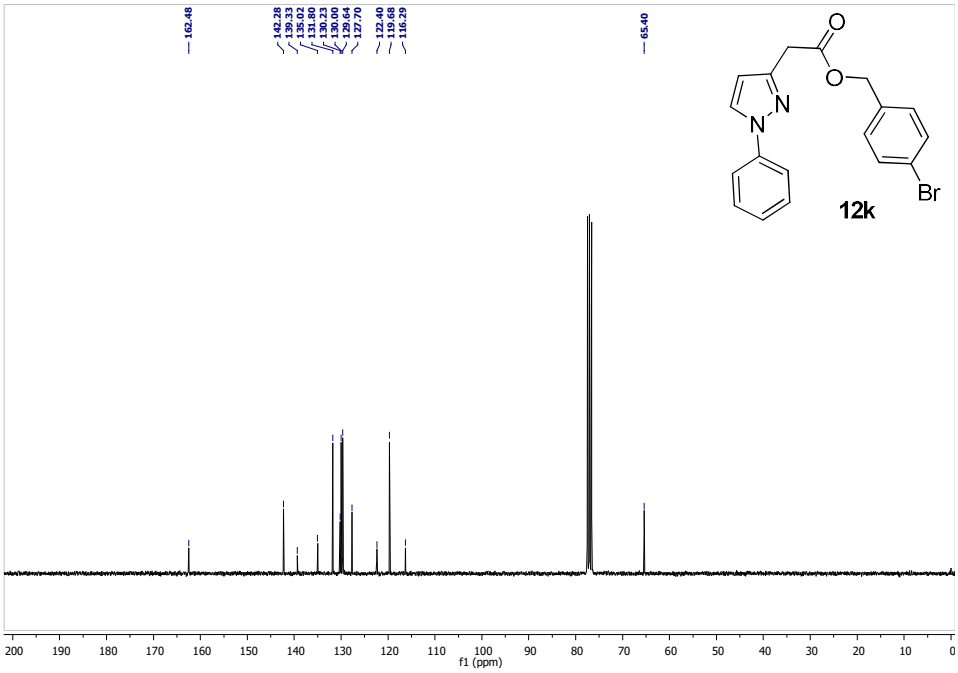
^{13}C Spectrum for 12j



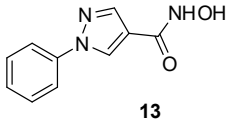
^{1}H Spectrum for 12k



^{13}C Spectrum for 12k

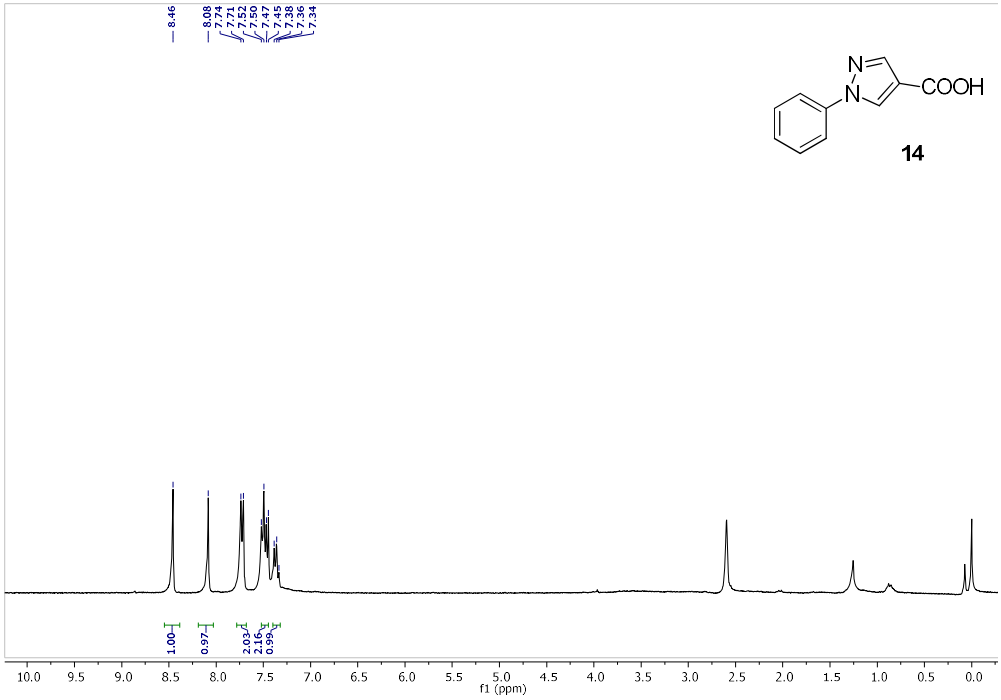


^{1}H Spectrum for 13

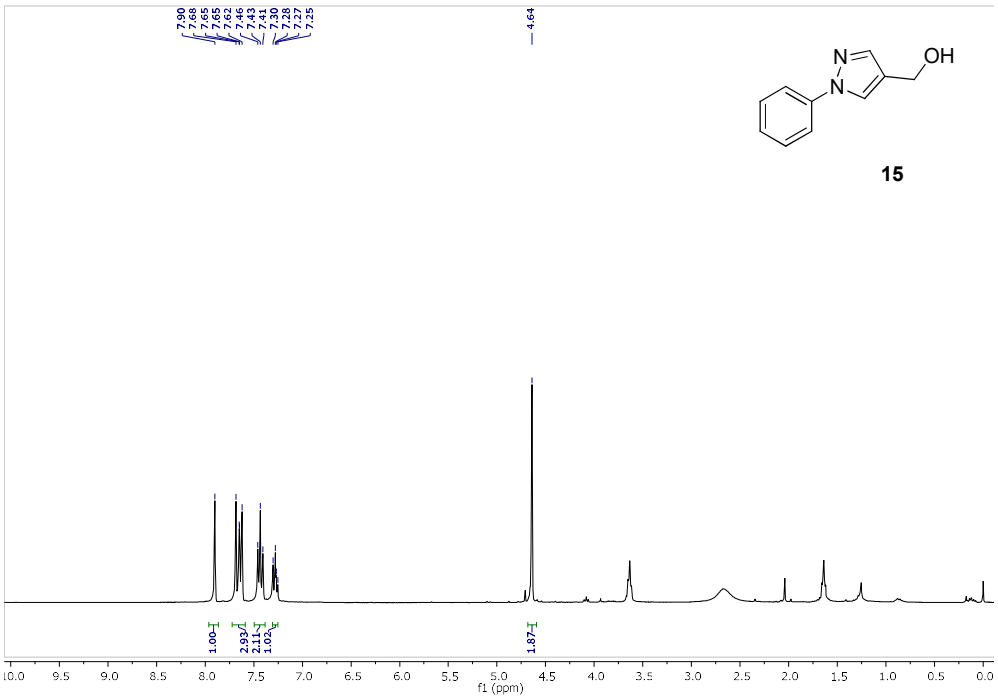


13

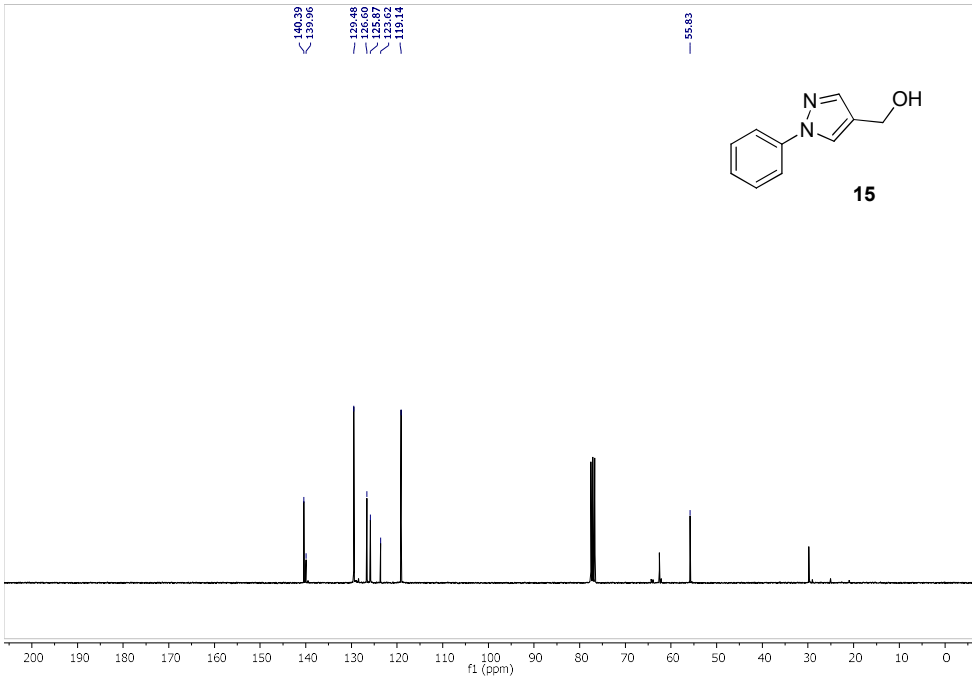
^{1}H Spectrum for 14



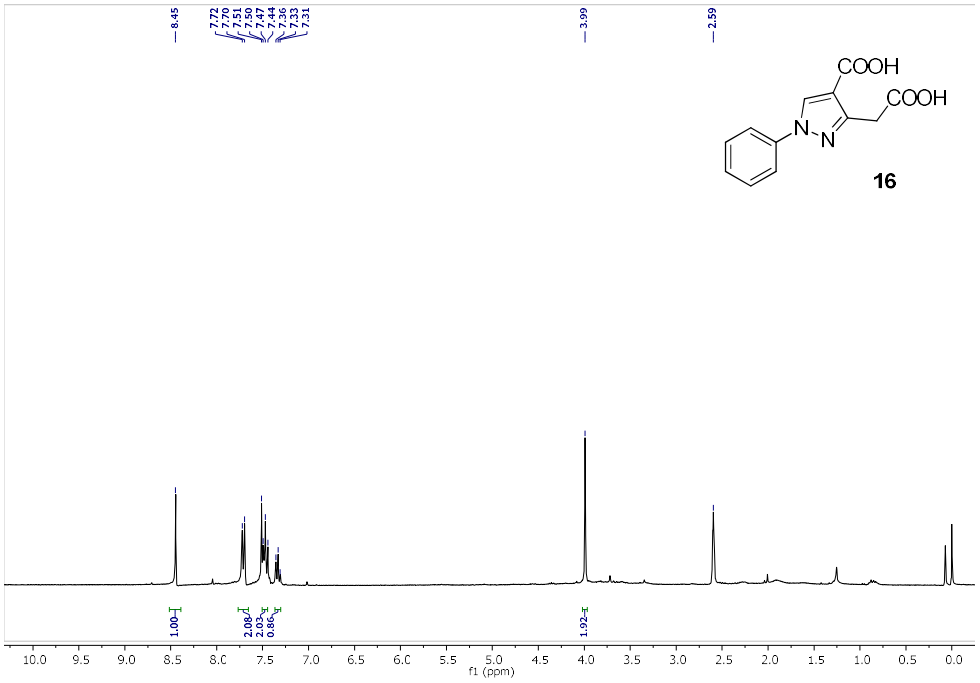
^{1}H Spectrum for 15



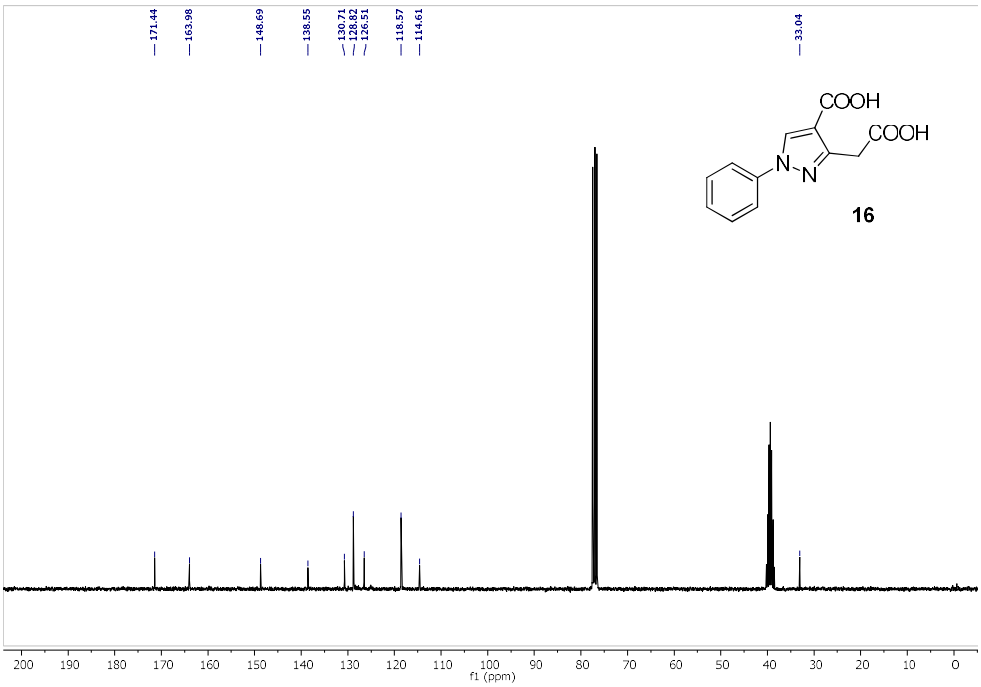
^{13}C Spectrum for 15



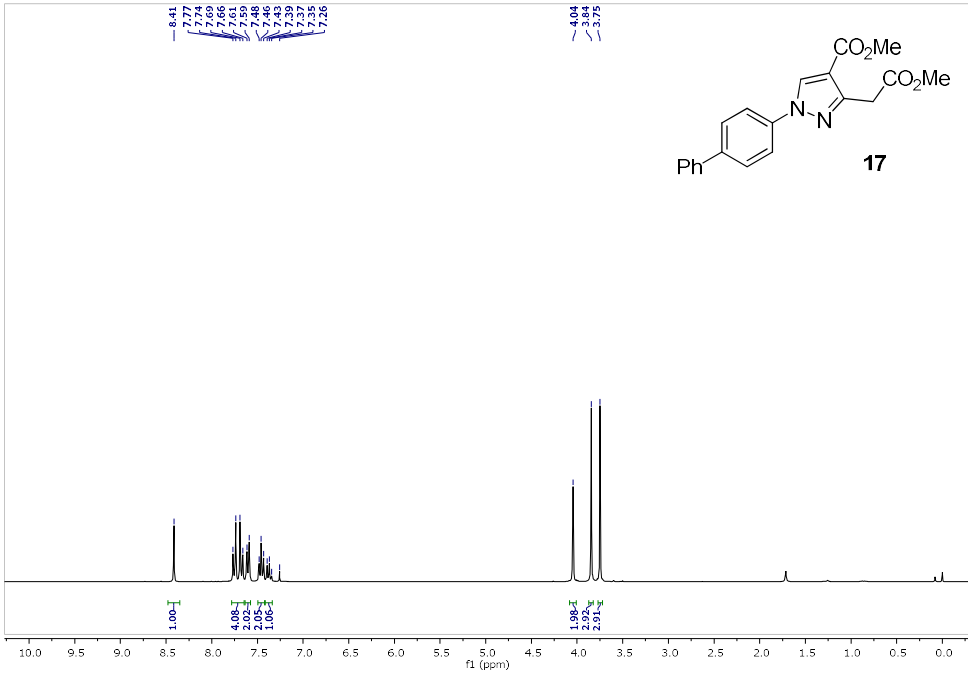
^{1}H Spectrum for 16



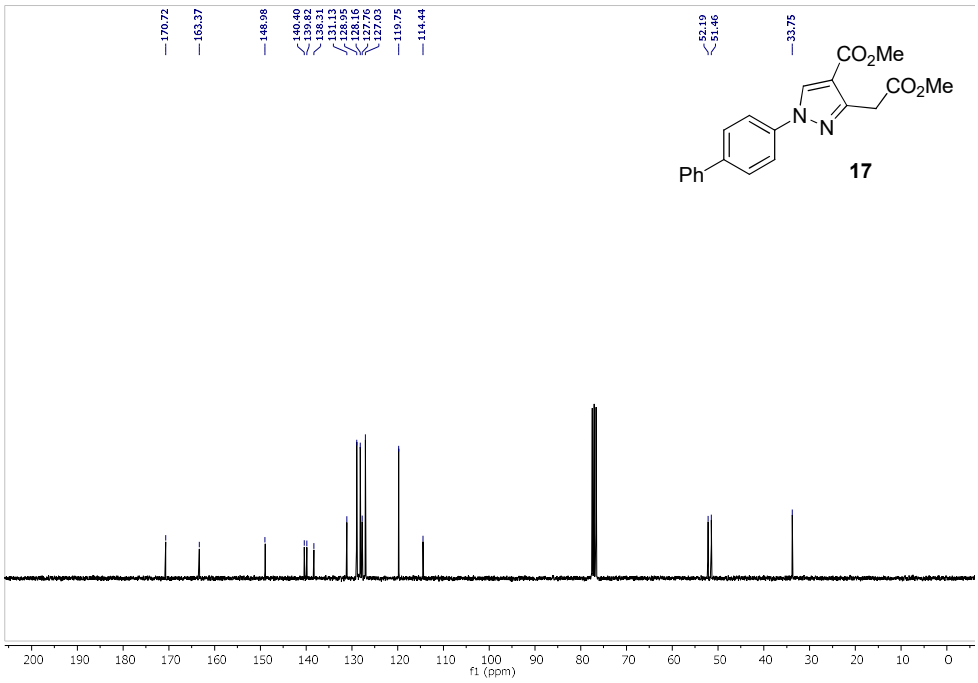
^{13}C Spectrum for 16



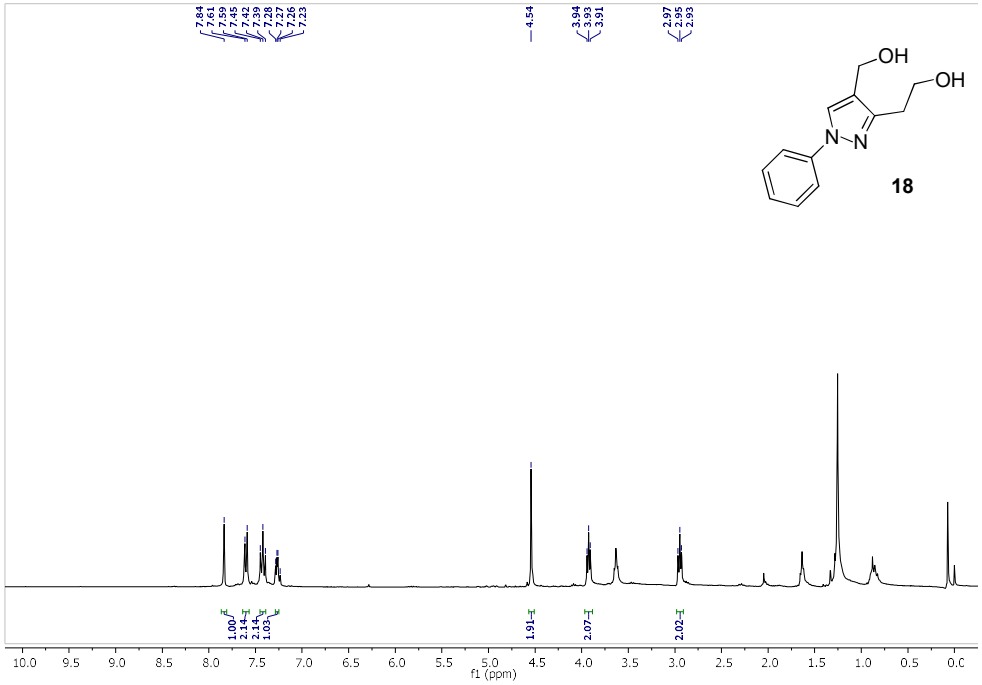
^{1}H Spectrum for 17



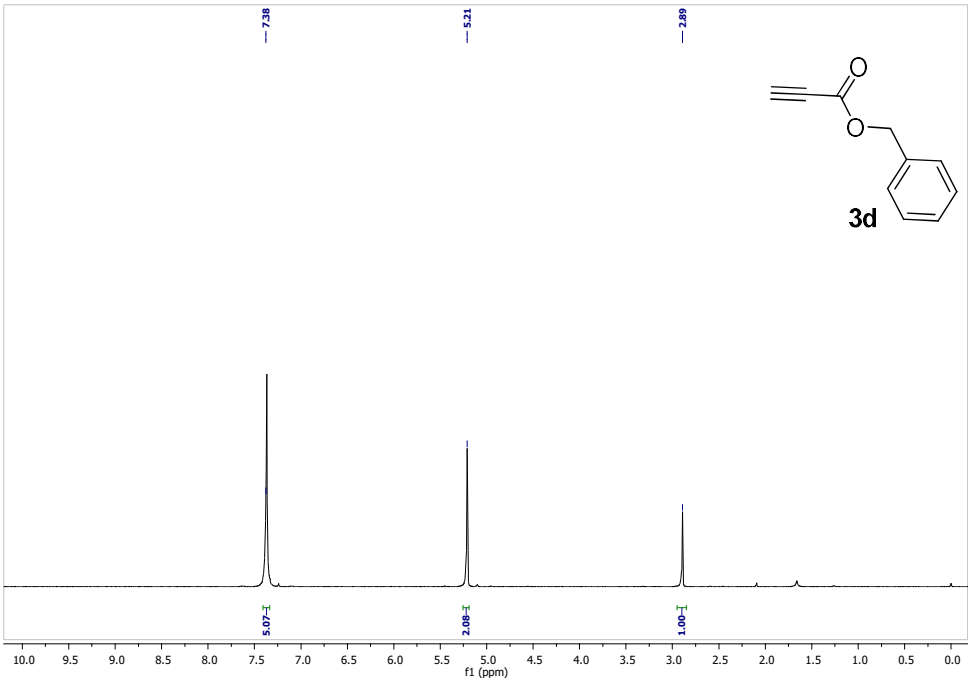
^{13}C Spectrum for 17



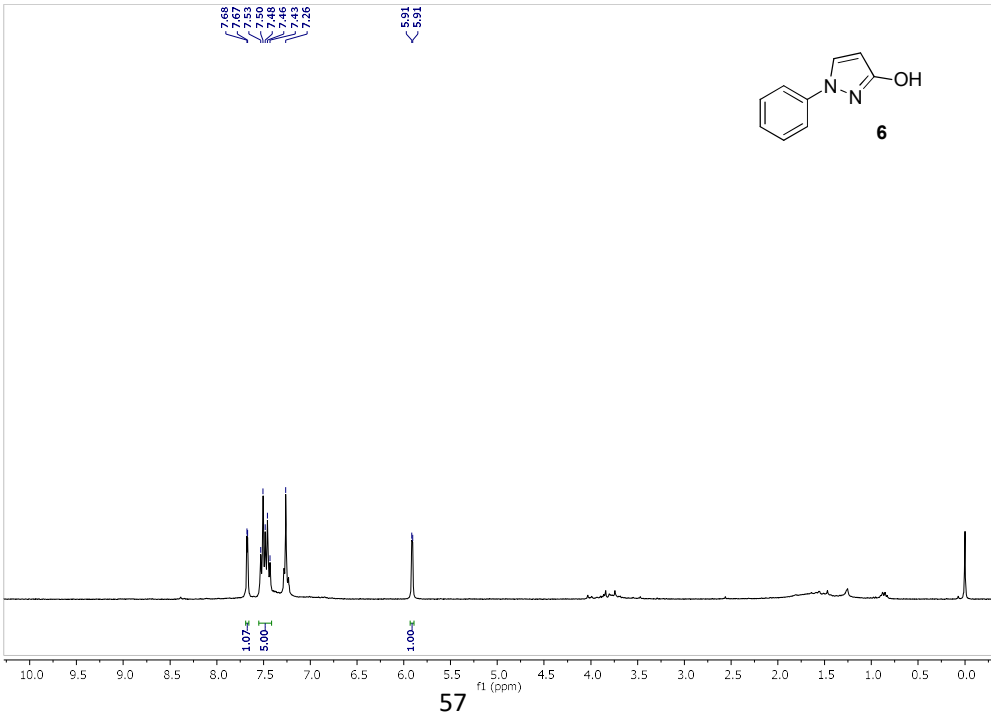
^{1}H Spectrum for 18



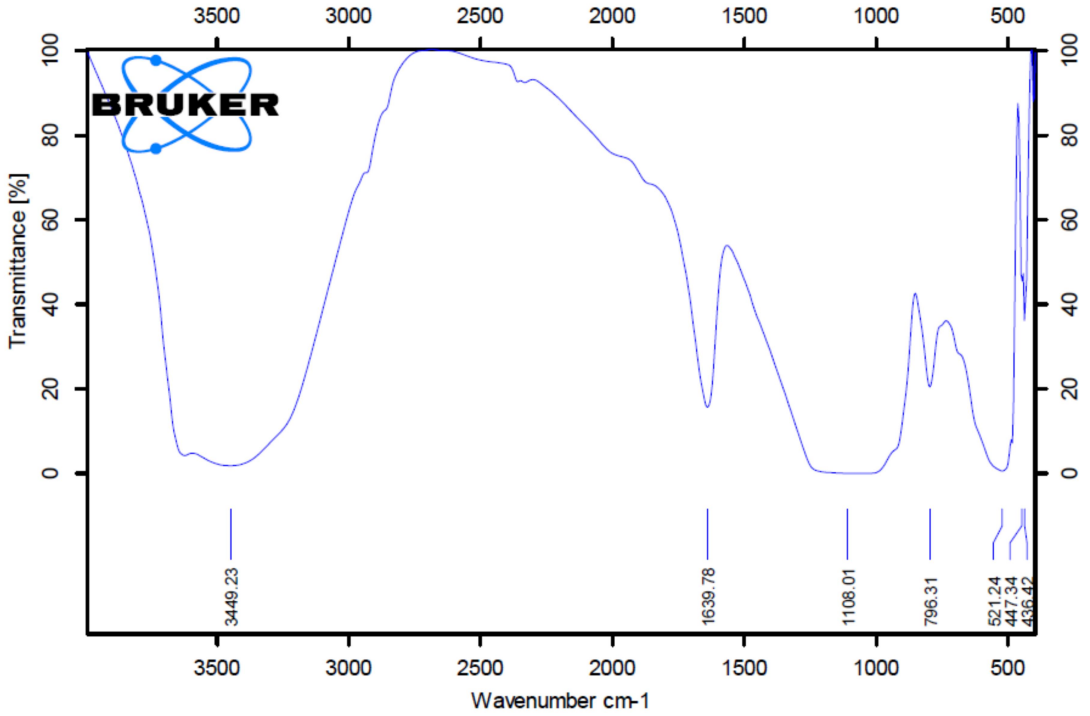
^{1}H Spectrum for Benzyl propiolate (3d)



^{1}H Spectrum for 6



7.1. IR Spectrum of Fresh Clay



7.2. IR Spectrum of Reused Clay