• Supplementary Information

Visible-light-mediated multi-component carbene transfer reactions of α-diazoesters to construct multisubstituted pyrazoles and 1,3-dicarbonyl derivatives

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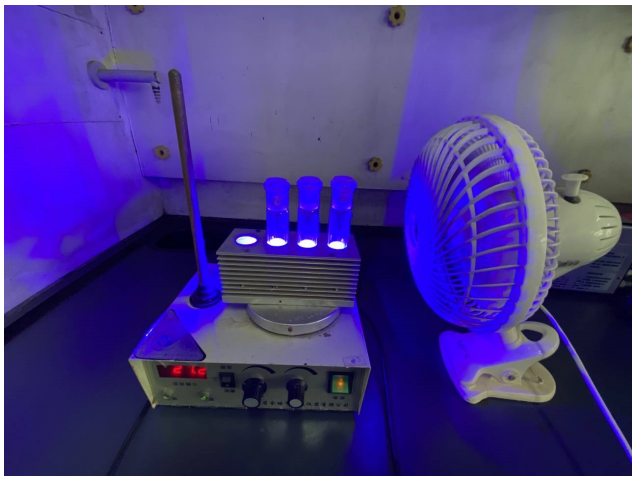
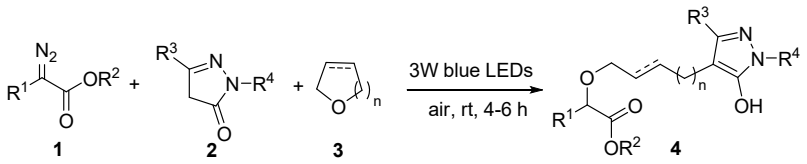
1.General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Bidepharm and Energy Chemical Company and used as received without further purification unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker Avance III spectrometer with TMS as internal standard (500 MHz ^{1}H, 125 MHz ^{13}C or 400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.

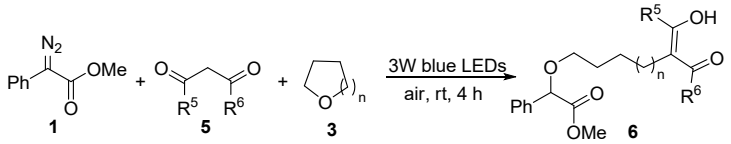


Picture of reaction setup

2. General procedure for the synthesis of multisubstituted pyrazoles and 1,3-dicarbonyl derivatives.

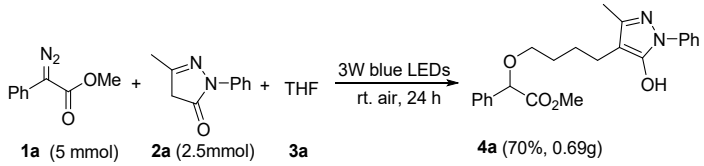


To a mixture of α-diazoester **1** (0.2 mmol) and pyrazolone **2** (0.1 mmol) was added cyclic ether **3** (2 mL). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 4-6 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired multi-substituted pyrazole **4**.



To a mixture of α-diazoester **1** (0.2 mmol),1,3-dicarbonyl compound **5** (0.1 mmol) was added cyclic ether **3** (2 mL). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 4 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired substituted 1,3-dicarbonyl derivative **6**.

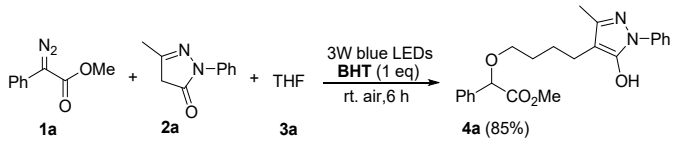
Experimental procedure for model reaction (2.5 mmol).



In a tube (25 mL), to a mixture of methyl phenyldiazoacetate **1a** (5 mmol, 0.88 g)

and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **2a** (2.5 mmol, 0.435 g) was added THF **3a** (8 mL). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 24 h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **4a** in 70% yield (0.69 g).

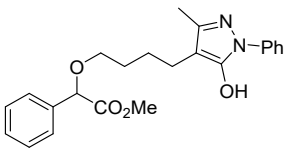
3. The addition of BHT in the model reaction system.



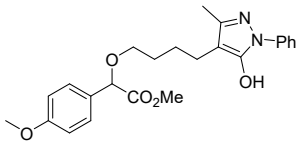
1a **2a** **3a** **4a** (85%)

To a mixture of methyl phenyldiazoacetate **1a** (0.2 mmol, 35.2 mg) and 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **2a** (0.1 mmol, 17.4 mg) and BHT (0.1 mmol, 22 mg) was added THF (AR, 2 mL). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 4 h. After completion of the reaction, the solution was concentrated in vacuum, the desired product **4a** was isolated in 85% (33.5 mg) yield.

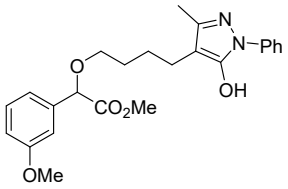
4.Characterization data of products 4a- 4z'', 6a-6j



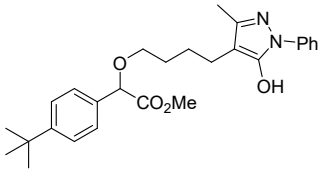
methyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate (4a). Compound **4a** was obtained in 91% yield (36.3 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.9 Hz, 2H), 7.43 - 7.42 (m, 2H), 7.39 - 7.33 (m, 5H), 7.21 (t, J = 7.4 Hz, 1H), 5.46 (s, 1H), 4.84 (s, 1H), 4.12 - 4.09 (m, 2H), 3.70 (s, 3H), 3.60 - 3.57 (m, 1H), 3.51 - 3.46 (m, 1H), 2.26 (s, 3H), 1.96 - 1.90 (m, 2H), 1.82 - 1.77 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 154.9, 148.7, 138.9, 136.5, 128.8, 128.7, 128.6, 127.1, 125.7, 121.7, 86.3, 81.1, 71.8, 69.2, 52.2, 26.1, 25.9, 14.6; ESI HRMS: calculated for $C_{23}H_{27}N_2O_4$ $[M+H]^+$ 395.1971, found 395.1995.



methyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-(4-methoxyphenyl)acetate (4b). Compound **4b** was obtained in 95% yield (40.2 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 - 7.26 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.01 - 6.98 (m, 2H), 6.88 - 6.86 (m, 1H), 5.46 (s, 1H), 4.82 (s, 1H), 4.12 - 4.09 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.59 - 3.55 (m, 1H), 3.51 - 3.48 (m, 1H), 2.26 (s, 3H), 1.95 - 1.92 (m, 2H), 1.83 - 1.78 (m, 2H).^{13}CNMR (125 MHz, $CDCl_3$) δ 171.2, 159.8, 154.9, 148.7, 138.9, 138.0, 129.6, 128.7, 125.7, 121.7, 119.5, 114.4, 112.5, 86.3, 81.0, 71.8, 69.2, 55.3, 52.3, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{24}H_{29}N_2O_5$ $[M+H]^+$ 425.2076, found 425.2077.

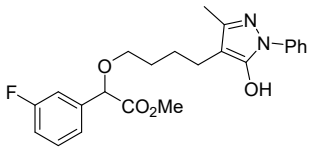


methyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-(3-methoxyphenyl)acetate (4c). Compound **4c** was obtained in 84% yield (35.7 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.66 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 - 7.26 (m, 1H), 7.22 - 7.19 (m, 1H), 7.01 - 6.98 (m, 2H), 6.88 - 6.86 (m, 1H), 5.46 (s, 1H), 4.81 (s, 1H), 4.12 - 4.09 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 3.58 - 3.55 (m, 1H), 3.51 - 3.48 (m, 1H), 2.26 (s, 3H), 1.95 - 1.90 (m, 2H), 1.82 - 1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 159.8, 154.9, 148.7, 138.9, 138.0, 129.7, 128.8, 125.7, 121.7, 119.5, 114.4, 112.5, 86.3, 81.0, 71.8, 69.2, 55.3, 52.3, 26.0, 25.9, 14.6. ESI HRMS: calculated for $C_{24}H_{29}N_2O_5$ $[M+H]^+$ 425.2076, found 425.2085.

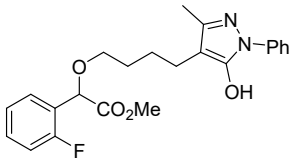


Methyl 2-(4-(tert-butyl)phenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)acetate (4d). Compound **4d** was obtained in 90% yield (40.5 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7

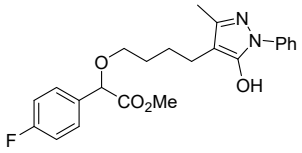
0 (d, *J* = 8.5 Hz, 2H), 7.42 - 7.36 (m, 7H), 5.49 (s, 1H), 4.85 (s, 1H), 4.15 - 4.11 (m, 2H), 3.73 (s, 3H), 3.61 - 3.57 (m, 1H), 3.54 - 3.50 (m, 1H), 2.29 (s, 3H), 1.98 - 1.93 (m, 2H), 1.84 - 1.80 (m, 2H), 1.33 (s, 9H). ^{13}C NMR (1 01 MHz, $CDCl_3$) δ 171.5, 154.9, 151.7, 148.7, 138.9, 133.4, 128.8, 126.9, 125. 7, 125.6, 121.7, 86.3, 80.9, 71.8, 69.1, 52.2, 34.6, 31.3, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{27}H_{35}N_2O_4$ $[M+H]^+$ 451.2597, found 451.2597.



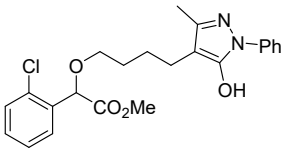
methyl 2-(3-fluorophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)b utoxy)acetate (4e). Compound **4e** was obtained in 81% yield (33.4 mg) accord ing to the general procedure for 4h (eluent ratio for column chromatography: p etroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.34 - 7.29 (m, 1H), 7.23 - 7.15 (m, 3H), 7.04 - 7.00 (m, 1H), 5.47 (s, 1H), 4.83 (s, 1H), 4.13 - 4.10 (m, 2H), 3.71 (s, 3H), 3.62 - 3.58 (m, 1H), 3.51 - 3.47 (m, 1H), 2.26 (s, 3H), 1.95 - 1.91 (m, 2H), 1.83 - 1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 16 2.9(d, *J* = 245.3 Hz), 154.9, 148.7, 138.9 (d, *J* = 7.2 Hz), 138.9, 130.2 (d, *J* = 8.1 Hz), 128.8, 125.7, 122.7 (d, *J* = 3.0 Hz), 121.7, 115.6 (d, *J* = 21.0 Hz), 114.1(d, *J* = 22.4 Hz), 86.3, 80.4, 71.7, 69.4, 52.4, 26.0, 25.9, 14.6. ESI HR MS: calculated for $C_{23}H_{26}FN_2O_4$ $[M+H]^+$ 413.1877, found 413.1879.



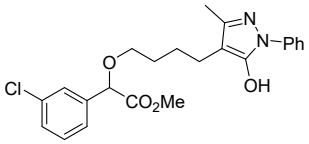
methyl 2-(2-fluorophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)b utoxy)acetate (4f). Compound **4f** was obtained in 81% yield (33.4 mg) accordi ng to the general procedure for 4h (eluent ratio for column chromatography: p etroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.47 - 7.43 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.34 - 7.30 (m, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 9.4 Hz, 1H), 5.45 (s, 1H), 5.20 (s, 1H), 4.11 - 4.08 (m, 2H), 3.72 (s, 3H), 3.66 - 3.62 (m, 1H), 3.53 - 3.48 (m, 1H), 2.26 (s, 3H), 1.93 - 1.89 (m, 2H), 1.81 - 1.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 160.4(d, *J* =246.6 Hz), 1 54.9, 148.7, 138.9, 130.4 (d, *J* = 8.2 Hz), 128.7, 128.6 (d, *J* = 3.3 Hz) 125.7, 124.5 (d, *J* = 3.5 Hz), 124.0 (d, *J* = 14.1 Hz), 121.7, 115.6(d, *J* = 21.6 Hz), 86.3, 74.0 (d, *J* = 3.1 Hz), 71.7, 69.5, 52.4, 26.0, 25.8, 14.6. ESI HRMS: calc ulated for $C_{23}H_{26}FN_2O_4$ $[M+H]^+$ 413.1877, found 413.1879.



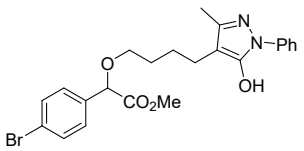
methyl 2-(4-fluorophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)acetate (4g). Compound **4g** was obtained in 78% yield (32.3 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 - 7.67 (m, 2H), 7.41 - 7.36 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.05 - 7.02 (m, 2H), 5.46 (s, 1H), 4.81 (s, 1H), 4.12 - 4.09 (m, 2H), 3.70 (s, 3H), 3.59 - 3.56 (m, 1H), 3.49 - 3.46 (m, 1H), 2.26 (s, 3H), 1.94 - 1.91 (m, 2H), 1.81 - 1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 162.9 (d, *J* = 245.9 Hz), 154.9, 148.8, 138.8, 132.4 (d, *J* = 3.2 Hz), 128.9 (d, *J* = 8.2 Hz), 128.8, 125.7, 121.7, 115.6 (d, *J* = 21.5 Hz), 86.3, 80.3, 71.7, 69.3, 52.3, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{23}H_{26}FN_2O_4$ $[M+H]^+$ 413.1877, found 413.1879.



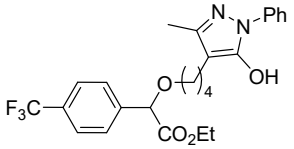
methyl 2-(2-chlorophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)acetate (4h). Compound **4h** was obtained in 84% yield (36.1 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.53 - 7.50 (m, 1H), 7.42 - 7.38 (m, 3H), 7.31 - 7.28 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 5.48 (s, 1H), 5.37 (s, 1H), 4.12 (t, *J* = 6.3 Hz, 2H), 3.74 (s, 3H), 3.71 - 3.65 (m, 1H), 3.57 - 3.51 (m, 1H), 2.29 (s, 3H), 1.96 - 1.91 (m, 2H), 1.85 - 1.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.9, 148.7, 138.9, 134.6, 133.7, 129.9, 129.6, 128.8, 128.7, 127.3, 125.7, 121.7, 86.3, 77.2, 71.7, 69.6, 52.4, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{23}H_{26}ClN_2O_4$ $[M+H]^+$ 429.1581, found 429.1589.



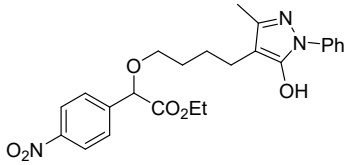
methyl 2-(3-chlorophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)acetate (4i). Compound **4i** was obtained in 59% yield (25.3 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.46 (s, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.32 - 7.29 (m, 4H), 5.49 (s, 1H), 4.83 (s, 1H), 4.15 - 4.12 (m, 2H), 3.74 (s, 3H), 3.65 - 3.59 (m, 1H), 3.54 - 3.48 (m, 1H), 2.29 (s, 3H), 1.98 - 1.95 (m, 2H), 1.85 - 1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.9, 148.8, 138.9, 138.5, 134.6, 129.9, 128.9, 128.8, 127.2, 125.7, 125.2, 121.7, 86.3, 80.4, 71.7, 69.5, 52.4, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{23}H_{26}ClN_2O_4$ $[M+H]^+$ 429.1581, found 429.1592.



methyl 2-(4-bromophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl) butoxy)acetate (4j). Compound **4j** was obtained in 88% yield (41.6 mg) accor ding to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.67 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.46 (s, 1H), 4.79 (s, 1H), 4.12 - 4. 09 (m, 2H), 3.70 (s, 3H), 3.61 - 3.57 (m, 1H), 3.49 - 3.45 (m, 1H), 2.26 (s, 3H), 1.94 - 1.90 (m, 2H), 1.82 - 1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 154.9, 148.7, 138.9, 135.6, 131.8, 128.8, 125.7, 122.8, 121.7, 86.3, 80.4 , 71.7, 69.4, 52.4, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{23}H_{26}BrN_2O_4$ [M+H]$^+$ 473.1076, found 473.1071.

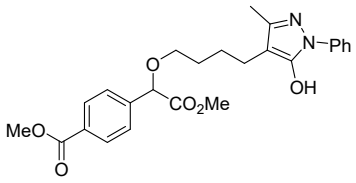


Ethyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-(4-(trifluor omethyl)phenyl)acetate (4k). Compound **4k** was obtained in 87% yield (40.2 mg) according to the general procedure for 4h (eluent ratio for column chroma tography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2 H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 5.49 (s, 1H), 4.90 (s, 1H), 4.22 - 4.13 (m, 4H), 3.69 - 3.64 (m, 1H), 3.55 - 3.50 (m, 1H), 2.29 (s, 3H), 2.01 - 1.94 (m, 2H), 1.88 - 1.81 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 154.9, 148.8, 140.5, 138.8, 130.8 (d, *J* = 3 7.6 Hz), 128.8, 127.3, 125.7, 125.5 (q, *J* = 3.8 Hz), 121.7, 86.3, 80.5, 71.7, 6 9.5, 61.5, 26.1, 25.9, 14.6, 14.1. ESI HRMS: calculated for $C_{25}H_{28}F_3N_2O_4$ [M+ H]$^+$ 477.2001, found 477.1996.

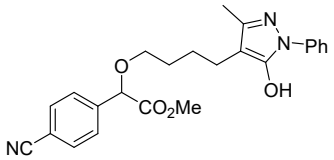


ethyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-(4-nitrophe nyl)acetate (4l). Compound **4l** was obtained in 58% yield (26.1 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petrol eum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 5.49 (s, 1H), 4.94 (s, 1H), 4.22 - 4.14 (m, 4H), 3.72 - 3.67 (m, 1H), 3.57 - 3.52 (m, 1H), 2.29 (s, 3H), 2.00 - 1.95 (m, 2H), 1.89 - 1.84 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100

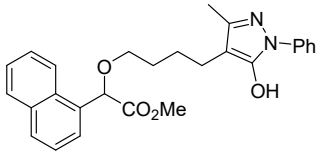
MHz, $CDCl_3$) δ 169.8, 154.8, 148.8, 148.0, 143.6, 138.9, 128.8, 127.7, 125.7, 123.7, 121.7, 86.3, 80.2, 71.7, 69.8, 61.8, 26.1, 25.9, 14.6, 14.1. ESI HRMS: c alculated for $C_{24}H_{28}N_3O_6$ $[M+H]^+$ 454.1978, found 454.1997.



methyl 3-(1-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-methoxy-2-oxoethyl)benzoate (4m). Compound **4m** was obtained in 48% yield (22.2 mg) according to the general procedure for 4h (eluent ratio for column chroma tography: petroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.68 - 7.67 (m, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.46 (s, 1H), 4.89 (s, 1H), 4.13 - 4.10 (m, 2H), 3.91 (s, 3H), 3.70 (s, 3H), 3.64 - 3.60 (m, 1H), 3.51 - 3.47 (m, 1H), 2.26 (s, 3H), 1.96 - 1.91 (m, 2H), 1.84 - 1.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 166.7, 154.9, 148.7, 141.4, 138.8, 130.5, 129.9, 128.8, 127.0, 125.7, 121.7, 86.3, 80.7, 71.7, 69.5, 52.4, 52.2, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{25}H_{29}N_2O_6$ $[M+H]^+$ 453.2026, found 453.2024.

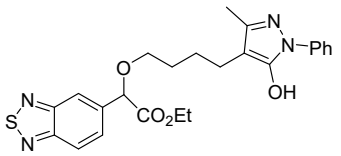


methyl 2-(4-cyanophenyl)-2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)acetate (4n). Compound **4n** was obtained in 56% yield (23.3 mg) according to the general procedure for 6h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.63 (m, 4H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.47 (s, 1H), 4.88 (s, 1H), 4.12 (t, *J* = 6.3 Hz, 2H), 3.71 (s, 3H), 3.66 - 3.62 (m, 1H), 3.52 - 3.48 (m, 1H), 2.27 (s, 3H), 1.97 - 1.92 (m, 2H), 1.85 - 1.81 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 154.8, 148.8, 141.6, 138.8, 132.4, 128.8, 127.6, 125.8, 121.7, 118.5, 112.6, 86.3, 80.3, 71.6, 69.8, 52.6, 26.1, 25.8, 14.6. ESI HRMS: calculated for $C_{24}H_{26}N_3O_4$ $[M+H]^+$ 420.1923, found 420.1928.

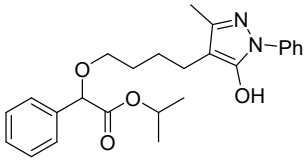


methyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-(naphthalen-1-yl)acetate (4o). Compound **4o** was obtained in 59% yield (26.8 mg) according to the general procedure for 6h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (

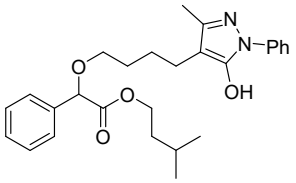
d, *J* = 8.2 Hz, 1H), 7.85 (t, *J* = 9.4 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.52 - 7.44 (m, 3H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 5.45 (s, 1H), 5.38 (s, 1H), 4.06 - 4.01 (m, 2H), 3.68 - 3.64 (m, 4H), 3.53 - 3.49 (m, 1H), 2.25 (s, 3H), 1.93 - 1.87 (m, 2H), 1.82 - 1.75 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 154.9, 148.7, 138.9, 134.0, 13 2.4, 131.0, 129.5, 128.7, 126.7, 126.6, 126.0, 125.7, 125.3, 124.1, 121.7, 86.3, 79.8, 71.7, 69.2, 52.3, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{27}H_{29}N_2O_4$ $[M+H]^+$ 445.2127, found 445.2126.



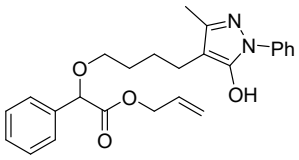
ethyl 2-(1,3-dihydrobenzo[c][1,2,5]thiadiazol-5-yl)-2-(4-(5-hydroxy-3-methyl-1-p henyl-1H-pyrazol-4-yl)butoxy)acetate (4p). Compound **4p** was obtained in 69% yield (32.5 mg) according to the general procedure for 4h (eluent ratio for col umn chromatography: petroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 0.5 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.72 - 7.6 7 (m, 3H), 7.40 - 7.36 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.47 (s, 1H), 5.00 (s, 1H), 4.24 - 4.16 (m, 2H), 4.14 - 4.12 (m, 2H), 3.71 - 3.67 (m, 1H), 3.59 - 3.54 (m, 1H), 2.26 (s, 3H), 2.00 - 1.95 (m, 2H), 1.88 - 1.82 (m, 2H), 1.24 - 1.21 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 154.8, 154.8, 154.6, 14 8.7, 138.8, 138.4, 128.7, 128.3, 125.7, 121.7, 119.9, 86.3, 80.7, 71.7, 69.6, 61. 6, 26.1, 25.9, 14.6, 14.1. ESI HRMS: calculated for $C_{24}H_{27}N_4O_4S$ $[M+H]^+$ 467. 1753, found 467.1748.



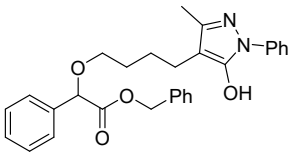
isopropyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-phenyl acetate (4q). Compound **4q** was obtained in 85% yield (35.9 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleu m ether/EtOAc=6/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.36 - 7.28 (m, 6H), 7.25 (s, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 5.3 8 (s, 1H), 4.97 - 4.94 (m, 1H), 4.72 (s, 1H), 4.04 (t, *J* = 6.1 Hz, 2H), 3.53 - 3.51 (m, 1H), 3.45 - 3.42 (m, 1H), 2.19 (s, 3H), 1.89 - 1.85 (m, 2H), 1.74 - 1.71 (m, 2H), 1.16 - 1.15 (m, 3H), 1.04 - 1.03 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.9, 148.7, 138.9, 136.7, 128.8, 128.5, 127.0, 125.7, 121.7, 86.3, 81.2, 71.8, 69.1, 68.8, 26.1, 26.0, 21.8, 21.5, 14.6. ESI HRMS: calculate d for $C_{25}H_{31}N_2O_4$ $[M+H]^+$ 423.2284, found 423.2289.



isopentyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate (4r). Compound **4r** was obtained in 74% yield (33.1 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=7/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.36 - 7.27 (m, 6H), 7.25 - 7.23 (m, 1H), 7.13 (t, *J* = 7.1 Hz, 1H), 5.38 (s, 1H), 4.75 (s, 1H), 4.07 - 4.02 (m, 4H), 3.55 - 3.50 (m, 1H), 3.44 - 3.39 (m, 1H), 2.19 (s, 3H), 1.88 - 1.83 (m, 2H), 1.76 - 1.71 (m, 2H), 1.50 - 1.43 (m, 1H), 1.40 - 1.35 (m, 2H), 0.78 - 0.74 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 154.9, 148.7, 138.9, 136.7, 128.8, 128.6, 128.6, 127.1, 125.7, 121.7, 86.3, 81.2, 71.8, 69.1, 63.9, 37.2, 26.1, 25.9, 25.0, 22.4, 22.3, 14.6. ESI HRMS: calculated for $C_{27}H_{35}N_2O_4$ $[M+H]^+$ 451.2597, found 451.2596.

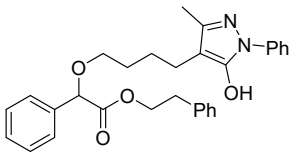


allyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate (4s). Compound **4s** was obtained in 90% yield (37.9 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.47 - 7.46 (m, 2H), 7.42 - 7.37 (m, 5H), 7.24 (t, *J* = 7.4 Hz, 1H), 5.91 - 5.81 (m, 1H), 5.49 (s, 1H), 5.23 - 5.18 (m, 2H), 4.89 (s, 1H), 4.64 - 4.62 (m, 2H), 4.15 - 4.12 (m, 2H), 3.64 - 3.61 (m, 1H), 3.55 - 3.50 (m, 1H), 2.29 (s, 3H), 1.99 - 1.93 (m, 2H), 1.86 - 1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 154.9, 148.7, 138.9, 136.5, 131.6, 128.8, 128.7, 128.6, 127.2, 125.7, 121.7, 118.4, 86.3, 81.1, 71.8, 69.2, 65.6, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{25}H_{29}N_2O_4$ $[M+H]^+$ 421.2127, found 421.2129.

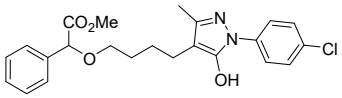


benzyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate (4t). Compound **4t** was obtained in 82% yield (38.6 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.46 - 7.31 (m, 10H), 7.25 - 7.22 (m, 3H), 5.48 (s, 1H), 5.17 (q, *J* = 11.0 Hz, 2H), 4.92 (s, 1H), 4.12 (t, *J* = 6.2 Hz, 2H), 3.65 - 3.59 (m, 1H), 3.55 - 3.50 (m, 1H), 2.30 (s, 3H), 1.97 - 1.92 (m, 2H), 1.85 - 1.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.9, 148.7, 138.9, 136.5, 135.5, 128.8,

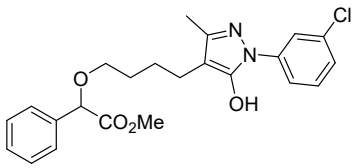
128.7, 128.6, 128.5, 128.3, 128.0, 127.2, 125.7, 121.7, 86.3, 81.1, 71.8, 69.2, 6 6.8, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{29}H_{31}N_2O_4$ $[M+H]^+$ 471.2284, found 471.2292.



phenethyl 2-(4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)butoxy)-2-phenyl acetate (4u). Compound **4u** was obtained in 92% yield (49.5 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleu m ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.43 - 7.36 (m, 8H), 7.26 - 7.24 (m, 3H), 7.11 - 7.10 (m, 2H), 5.49 (s, 1H), 4.83 (s, 1H), 4.39 - 4.34 (m, 2H), 4.13 (t, *J* = 5.9 Hz, 2H), 3.5 8 - 3.54 (m, 1H), 3.50 - 3.45 (m, 1H), 2.90 (t, *J* = 6.6 Hz, 2H), 2.30 (s, 3H), 1.96 - 1.91 (m, 2H), 1.84 - 1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1 70.8, 154.9, 148.7, 138.9, 137.5, 136.5, 128.9, 128.8, 128.6, 128.6, 128.5, 127. 1, 126.6, 125.7, 121.7, 86.3, 81.1, 71.8, 69.1, 65.5, 34.9, 26.1, 25.9, 14.6. ESI HRMS: calculated for $C_{30}H_{33}N_2O_4$ $[M+H]^+$ 485.2440, found 485.2443.

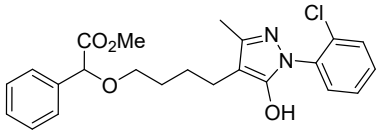


methyl 2-(4-(1-(4-chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate(4v). Compound **4v** was obtained in 86% yield (36.6 mg) accordi ng to the general procedure for 4h (eluent ratio for column chromatography: p etroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 - 7.66 (m, 2H), 7.46 - 7.44 (m, 2H), 7.38 - 7.35 (m, 5H), 5.48 (s, 1H), 4.87 (s, 1H), 4.13 (t, *J* = 6.2 Hz, 2H), 3.73 (s, 3H), 3.64 - 3.59 (m, 1H), 3.54 - 3.49 (m, 1H), 2.27 (s, 3H), 1.98 - 1.93 (m, 2H), 1.85 - 1.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 154.9, 149.1, 137.5, 136.5, 131.0, 128.8, 128.8, 12 8.7, 127.1, 122.6, 86.5, 81.1, 71.9, 69.2, 52.3, 26.1, 25.9, 14.6. ESI HRMS: ca lculated for $C_{23}H_{26}ClN_2O_4$ $[M+H]^+$ 429.1581, found 429.1583.

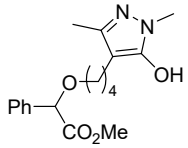


methyl 2-(4-(1-(3-chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate(4w). Compound **4w** was obtained in 96% yield (41.0 mg) accor ding to the general procedure for 6h (eluent ratio for column chromatography: petroleum ether/EtOAc=5/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (t, *J* = 2.0 Hz, 1H), 7.63 - 7.61 (m, 1H), 7.44 - 7.42 (m, 2H), 7.37 - 7.33 (m, 3H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.18 - 7.16 (m, 1H), 5.45 (s, 1H), 4.86 (s, 1H),

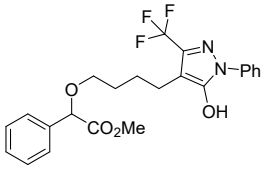
4.14 - 4.11 (m, 2H), 3.70 (s, 3H), 3.63 - 3.58 (m, 1H), 3.53 - 3.48 (m, 1H), 2.25 (s, 3H), 1.97 - 1.93 (m, 2H), 1.84 - 1.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 155.1, 149.3, 139.9, 136.5, 134.4, 129.8, 128.7, 128.6, 127.1, 125.5, 121.5, 119.2, 86.7, 81.1, 72.0, 69.2, 52.2, 26.0, 25.9, 14.6. ESI HRMS: calculated for $C_{23}H_{26}ClN_2O_4$ $[M+H]^+$ 429.1581, found 429.1589.



methyl 2-(4-(1-(2-chlorophenyl)-5-hydroxy-3-methyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate(4x). Compound **4x** was obtained in 73% yield (31.3 mg) accordi ng to the general procedure for 6h (eluent ratio for column chromatography: p etroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 - 7.45 (m, 1H), 7.41 - 7.40 (m, 3H), 7.36 - 7.31 (m, 5H), 5.44 (s, 1H), 4.81 (s, 1H), 4.08 - 4.05 (m, 2H), 3.69 (s, 3H), 3.53 - 3.50 (m, 1H), 3.44 - 3.40 (m, 1H), 2.27 (s, 3H), 1.84 - 1.80 (m, 2H), 1.72 - 1.69 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 155.8, 149.4, 136.5, 136.0, 132.2, 130.0, 129.7, 129.6, 128.7, 128.6, 127.3, 127.1, 85.0, 81.0, 71.7, 69.2, 52.2, 25.9, 25.8, 14.7. ESI HRMS: calculated for $C_{23}H_{26}ClN_2O_4$ $[M+H]^+$ 429.1581, found 429.1615.

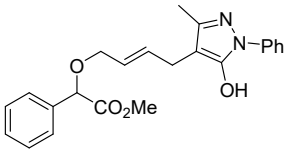


methyl 2-(4-(5-hydroxy-1,3-dimethyl-1H-pyrazol-4-yl)butoxy)-2-phenylacetate(4 y). Compound **4y** was obtained in 84% yield (27.8 mg) according to the gener al procedure for 4h (eluent ratio for column chromatography: petroleum ether/E tOAc=2/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 - 7.43 (m, 2H), 7. 38 - 7.34 (m, 3H), 5.27 (s, 1H), 4.87 (s, 1H), 4.03 - 4.00 (m, 2H), 3.71 (s, 3 H), 3.62 - 3.58 (m, 1H), 3.54 (s, 3H), 3.52 - 3.48 (m, 1H), 2.17 (s, 3H), 1.91 - 1.87 (m, 2H), 1.82 - 1.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 1 54.8, 146.8, 136.5, 128.7, 128.7, 127.1, 84.3, 81.1, 71.2, 69.3, 52.3, 33.2, 26.0, 25.9, 14.4. ESI HRMS: calculated for $C_{18}H_{25}N_2O_4$ $[M+H]^+$ 333.1814, found 33 3.1803.

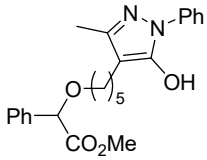


methyl 2-(4-(5-hydroxy-1-phenyl-3-(trifluoromethyl)-1H-pyrazol-4-yl)butoxy)-2-phenylacetate (4z). Compound **4z** was obtained in 92% yield (41.1 mg) accord ing to the general procedure for 6h (eluent ratio for column chromatography: p etroleum ether/EtOAc=7/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 -

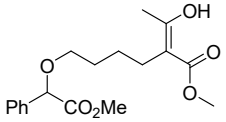
7.67 (m, 2H), 7.45 - 7.40 (m, 4H), 7.37 - 7.32 (m, 4H), 5.91 (s, 1H), 4.84 (s, 1H), 4.21 - 4.17 (m, 2H), 3.70 (s, 3H), 3.61 - 3.57 (m, 1H), 3.51 - 3.47 (m, 1H), 1.98 - 1.94 (m, 2H), 1.82 - 1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 154.8, 141.8 (d, *J* = 38.2 Hz), 137.9, 136.4, 129.0, 128.8, 128.7, 127.4, 127.1, 122.7, 84.6, 81.1, 72.5, 69.1, 52.3, 29.7, 25.9. ESI HRMS: calculated for $C_{23}H_{24}F_3N_2O_4$ $[M+H]^+$ 449.1688, found 449.1652.



methyl (E)-2-((4-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)but-2-en-1-yl)oxy)-2-phenylacetate（4z'）. Compound **4z'** was obtained in 41% yield (16.1 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=6/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 - 7.66 (m, 2H), 7.43 - 7.39 (m, 4H), 7.37 - 7.35 (m, 3H), 7.23 (t, *J* = 7.4 Hz, 1H), 5.89 - 5.84 (m, 2H), 5.45 (s, 1H), 4.90 (s, 1H), 4.66 - 4.63 (m, 2H), 4.19 - 4.16 (m, 1H), 4.13 - 4.09 (m, 1H), 3.70 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 154.4, 148.7, 138.7, 136.0, 129.4, 128.9, 128.8, 128.8, 127.9, 127.3, 125.9, 121.9, 86.8, 80.3, 67.9, 65.1, 52.4, 14.6. ESI HRMS: calculated for $C_{23}H_{25}N_2O_4$ $[M+H]^+$ 393.1814, found 393.1824.

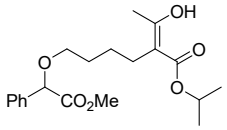


methyl 2-((5-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)pentyl)oxy)-2-phenylacetate(4z''). Compound **4z''** was obtained in 23% yield (18.0 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (500 MHz, CDCl3) δ 7.69 - 7.67 (m, 2H), 7.44 - 7.43 (m, 2H), 7.38 - 7.37 (m, 2H), 7.35 - 7.32 (m, 3H), 7.22 - 7.19 (m, 1H), 5.46 (s, 1H), 4.85 (s, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.70 (s, 3H), 3.57 - 3.52 (m, 1H), 3.46 - 3.42 (m, 1H), 2.27 (s, 3H), 1.85 - 1.79 (m, 2H), 1.73 - 1.68 (m, 2H), 1.58 - 1.53 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 154.9, 148.7, 138.9, 136.6, 128.7, 128.7, 128.6, 127.1, 125.7, 121.7, 86.3, 81.1, 71.9, 69.6, 52.2, 29.2, 28.7, 22.6, 14.6. ESI HRMS: calculated for $C_{24}H_{29}N_2O_4$ $[M+H]^+$ 409.2127, found 409.2121.

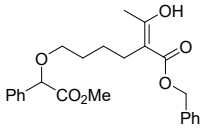


(Z)-methyl2-(1-hydroxyethylidene)-6-(2-methoxy-2-oxo-1-phenylethoxy)hexanoate (6a), Compound **6a** was obtained in 71% yield (23.8 mg) according to the general procedure for 4h (eluent ratio for column chromatography:

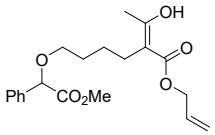
petroleum ether/EtOAc=8/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.38 – 7.33 (m, 3H), 4.99 (s, 1H), 4.87 (s, 1H), 3.79 – 3.76 (m, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 3.60 – 3.56 (m, 1H), 3.50 – 3.46 (m, 1H), 2.27 (s, 3H), 1.85 – 1.80 (m, 2H), 1.79 – 1.75 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 171.4, 168.5, 136.5, 128.7, 128.6, 127.1, 90.7, 81.1, 69.3, 67.8, 52.3, 50.7, 26.2, 25.5, 19.1. ESI HRMS: calculated for $C_{18}H_{25}O_6$ $[M+H]^+$ 377.1651, found 377.1657.



(Z)-isopropyl 2-(1-hydroxyethylidene)-6-(2-methoxy-2-oxo-1-phenylethoxy)hexanoate (6b), Compound **6b** was obtained in 83% yield (30.3 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=8/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.37 – 7.33 (m, 3H), 5.05 – 5.00 (m, 1H), 4.95 (s, 1H), 4.87 (s, 1H), 3.78 – 3.75 (m, 2H), 3.71 (s, 3H), 3.60 – 3.57 (m, 1H), 3.50 – 3.47 (m, 1H), 2.27 (s, 3H), 1.84 – 1.80 (m, 2H), 1.78 – 1.74 (m, 2H), 1.25 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 171.4, 167.6, 136.5, 128.7, 128.6, 127.1, 91.7, 81.1, 69.3, 67.7, 66.2, 52.3, 26.2, 25.5, 22.1, 19.1. ESI HRMS: calculated for $C_{20}H_{29}O_6$ $[M+H]^+$ 365.1964, found 365.1969.

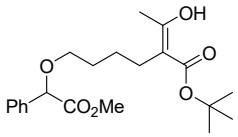


(Z)-benzyl 2-(1-hydroxyethylidene)-6-(2-methoxy-2-oxo-1-phenylethoxy)hexanoate (6c), Compound **6c** was obtained in 70% yield (28.9 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=8/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H), 7.37 – 7.29 (m, 8H), 5.12 (s, 2H), 5.05 (s, 1H), 4.86 (s, 1H), 3.79 – 3.75 (m, 2H), 3.70 (s, 3H), 3.59 – 3.55 (m, 1H), 3.49 – 3.45 (m, 1H), 2.29 (s, 3H), 1.84 – 1.80 (m, 2H), 1.78 – 1.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 171.4, 167.8, 136.8, 136.5, 128.7, 128.6, 128.5, 128.2, 128.0, 127.1, 90.9, 81.1, 69.3, 67.9, 65.3, 52.3, 26.1, 25.5, 19.2. ESI HRMS: calculated for $C_{24}H_{29}O_6$ $[M+H]^+$ 413.1964, found 413.1971.

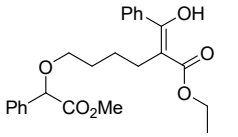


(Z)-allyl 2-(1-hydroxyethylidene)-6-(2-methoxy-2-oxo-1-phenylethoxy)hexanoate (6d), Compound **6d** was obtained in 89% yield (32.1 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=8/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H),

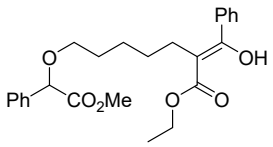
7.38 – 7.33 (m, 3H), 5.99 – 5.91 (m, 1H), 5.34 – 5.30 (m, 1H), 5.23 – 5.21 (m, 1H), 5.02 (s, 1H), 4.87 (s, 1H), 4.59 (d, *J* = 5.7 Hz, 2H), 3.80 – 3.76 (m, 2H), 3.71 (s, 3H), 3.60 – 3.56 (m, 1H), 3.50 – 3.46 (m, 1H), 2.28 (s, 3H), 1.84 – 1.75 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 171.4, 167.6, 136.5, 133.0, 128.7, 128.6, 127.1, 117.6, 90.8, 81.1, 69.3, 67.9, 64.2, 52.3, 26.2, 25.5, 19.1. ESI HRMS: calculated for $C_{20}H_{27}O_6$ $[M+H]^+$ 363.1808, found 363.1813.



(Z)-tert-butyl 2-(1-hydroxyethylidene)-6-(2-methoxy-2-oxo-1-phenylethoxy)hexanoate (6e), Compound **6e** was obtained in 47% yield (17.7 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=10/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.37 – 7.33 (m, 3H), 4.91 (s, 1H), 4.87 (s, 1H), 3.76 – 3.73 (m, 2H), 3.71 (s, 3H), 3.58 – 3.56 (m, 1H), 3.48 – 3.45 (m, 1H), 2.23 (s, 3H), 1.82 – 1.74 (m, 4H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 171.3, 167.6, 136.5, 128.7, 128.6, 127.1, 92.9, 81.1, 79.0, 69.3, 67.6, 52.3, 28.4, 26.2, 25.5, 18.9. ESI HRMS: calculated for $C_{21}H_{31}O_6$ $[M+H]^+$ 379.2121, found 379.2128.

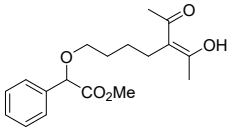


(Z)-ethyl 2-(hydroxy(phenyl)methylene)-6-(2-methoxy-2-oxo-1-phenylethoxy)hexanoate (6f), Compound **6f** was obtained in 87% yield (35.8 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=8/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.43 – 7.41 (m, 3H), 7.39 – 7.36 (m, 3H), 7.35 – 7.33 (m, 2H), 5.52 (s, 1H), 4.87 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.01 – 3.98 (m, 2H), 3.69 (s, 3H), 3.60 – 3.57 (m, 1H), 3.51 – 3.48 (m, 1H), 1.87 – 1.82 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 167.8, 165.3, 136.6, 135.3, 130.2, 128.6, 128.6, 128.6, 127.4, 127.1, 100.7, 81.0, 72.6, 69.4, 59.7, 52.2, 26.8, 26.0, 14.4. ESI HRMS: calculated for $C_{24}H_{29}O_6$ $[M+H]^+$ 413.1964, found 413.1967.

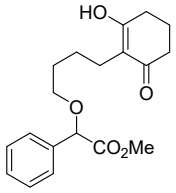


(Z)-ethyl 2-(hydroxy(phenyl)methylene)-7-(2-methoxy-2-oxo-1-phenylethoxy)heptanoate (6g), Compound **6g** was obtained in 53% yield (22.6 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petrol

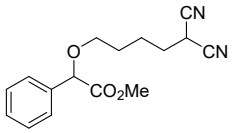
eum ether/EtOAc=8/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.44 – 7.41 (m, 3H), 7.40 – 7.36 (m, 3H), 7.35 – 7.33 (m, 2H), 5.53 (s, 1H), 4.86 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.70 (s, 3H), 3.56 – 3.53 (m, 1H), 3.46 – 3.43 (m, 1H), 1.78 – 1.74 (m, 2H), 1.72 – 1.68 (m, 2H), 1.54 – 1.50 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 167.8, 165.4, 136.7, 135.3, 130.2, 128.6, 128.6, 128.6, 127.4, 127.1, 100.6, 81.1, 72.8, 69.7, 59.7, 52.2, 29.8, 29.3, 22.4, 14.4. ESI HRMS: calculated for $C_{25}H_{31}O_6$ $[M+H]^+$ 427.2121, found 427.2128.



methyl (Z)-2-((5-acetyl-6-hydroxyhept-5-en-1-yl)oxy)-2-phenylacetate (6h), Compound **6h** was obtained in 95% yield (30.3 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=4/1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.35 (m, 3H), 5.44 (s, 1H), 4.87 (s, 1H), 3.83 – 3.78 (m, 2H), 3.71 (s, 3H), 3.61 – 3.58 (m, 1H), 3.51 – 3.48 (m, 1H), 2.26 (s, 3H), 2.14 (s, 3H), 1.86 – 1.82 (m, 2H), 1.80 – 1.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 172.2, 171.4, 136.5, 128.7, 128.6, 127.1, 99.8, 81.1, 69.3, 67.8, 52.2, 31.9, 26.1, 25.6, 19.8. ESI HRMS: calculated for $C_{18}H_{25}O_5$ $[M+H]^+$ 321.1702, found 321.1709.



methyl 2-(4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)butoxy)-2-phenylacetate (6i), Compound **6i** was obtained in 94% yield (31.2 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=2/1). classless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.38 – 7.33 (m, 3H), 5.34 (s, 1H), 4.87 (s, 1H), 3.86 (t, *J* = 6.3 Hz, 2H), 3.71 (s, 3H), 3.60 – 3.56 (m, 1H), 3.50 – 3.46 (m, 1H), 2.38 (t, *J* = 6.3 Hz, 2H), 2.34 (t, *J* = 6.6 Hz, 2H), 1.99 – 1.94 (m, 2H), 1.87 – 1.84 (m, 2H), 1.80 – 1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 178.0, 171.3, 136.5, 128.7, 128.7, 127.1, 102.8, 81.1, 69.2, 68.2, 52.3, 36.7, 29.0, 26.1, 25.4, 21.2. ESI HRMS: calculated for $C_{19}H_{25}O_5$ $[M+H]^+$ 333.1702, found 333.1707.



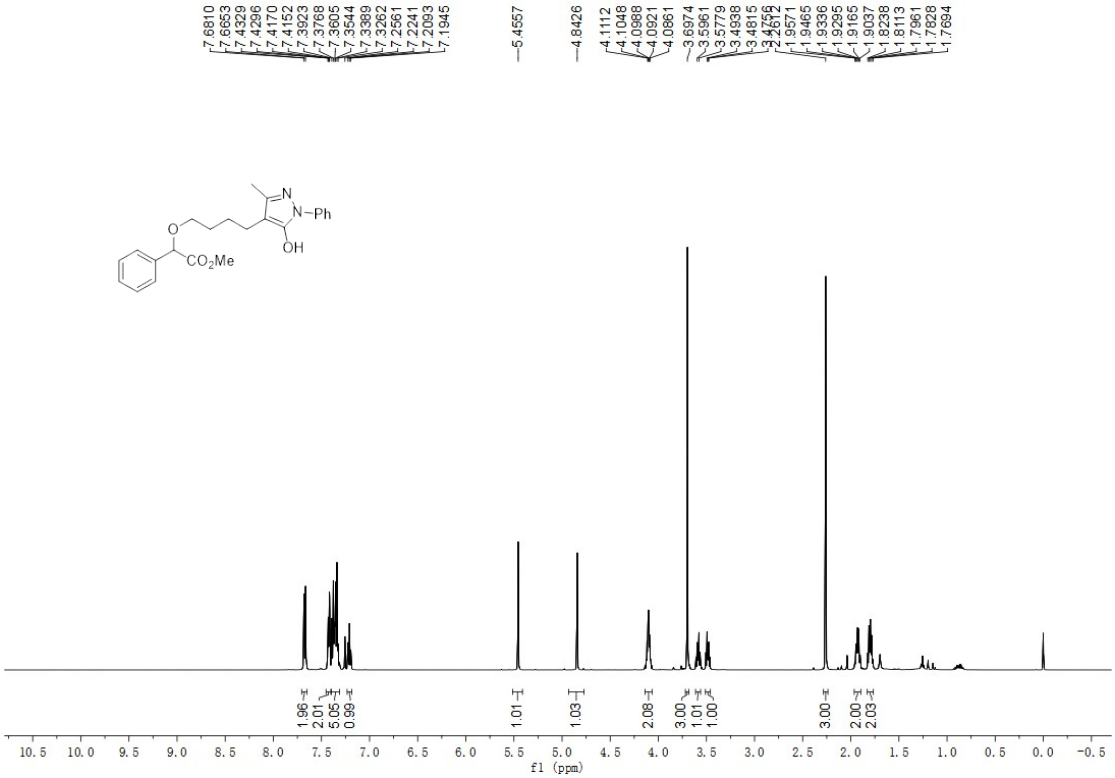
methyl 2-((5,5-dicyanopentyl)oxy)-2-phenylacetate (6j), Compound **6j** was obtained in 64% yield (18.3 mg) according to the general procedure for 4h (eluent ratio for column chromatography: petroleum ether/EtOAc=3/1). Yellow oil. ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.40 – 7.36 (m, 3H), 4.84 (s, 1H), 3.88 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.59 – 3.56 (m, 1H), 3.51 – 3.48 (m, 1H), 2.15 – 2.10 (m, 2H), 1.79 – 1.73 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 136.2, 128.9, 128.8, 127.2, 112.7, 112.7, 81.3, 69.0, 52.3, 30.5, 28.0, 23.8, 22.4. ESI HRMS: calculated for $C_{16}H_{19}N_2O_3$ $[M+H]^+$ 287.1396, found 287.1403.

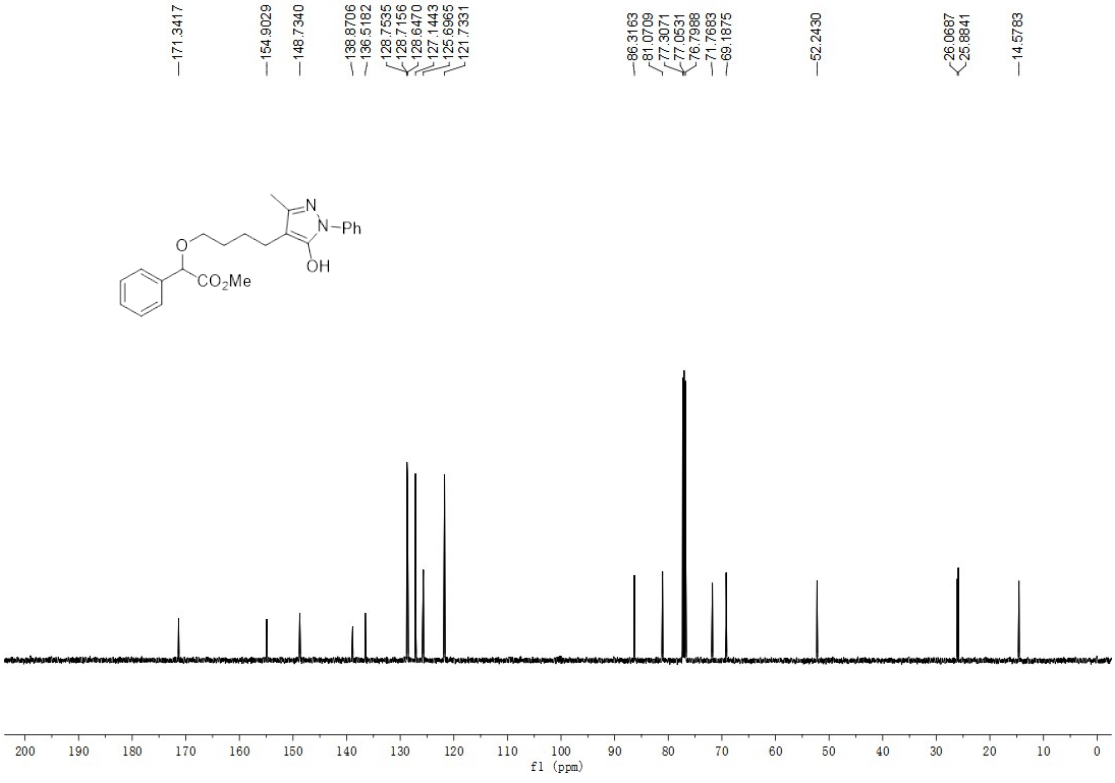
5 Copies of NMR spectra for products

5.1Copies of NMR spectra for 4a−4z''

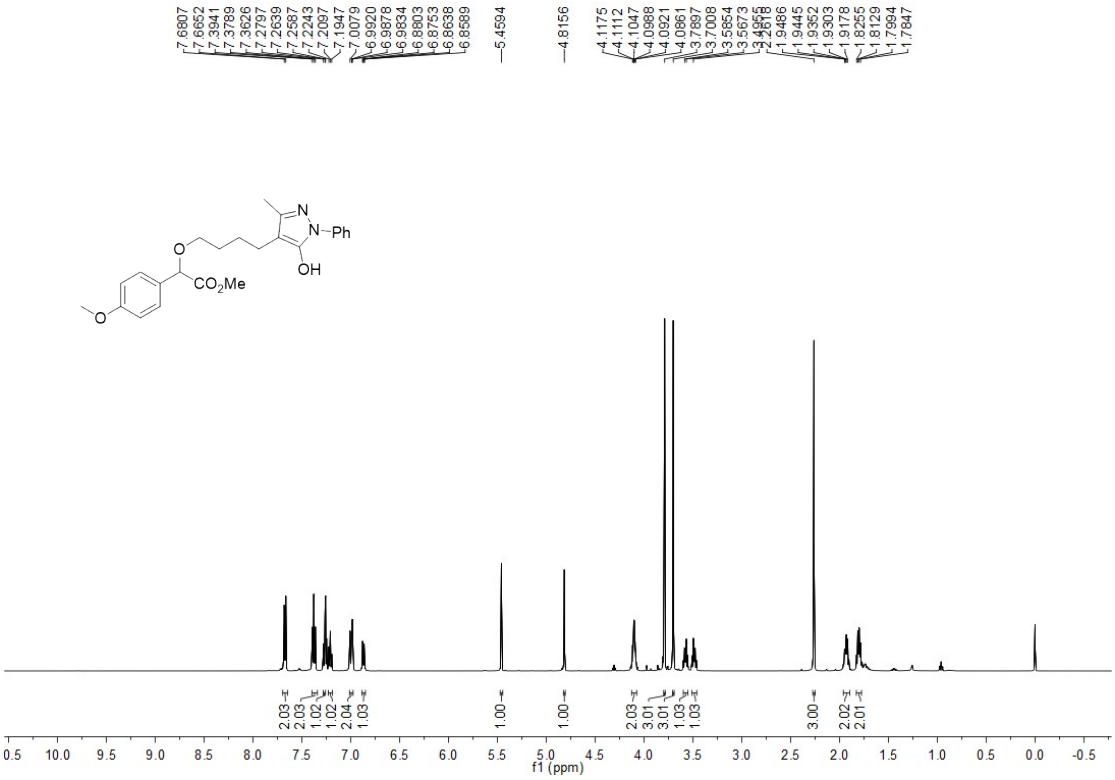
4a ^{1}H NMR (500 MHz, $CDCl_3$)



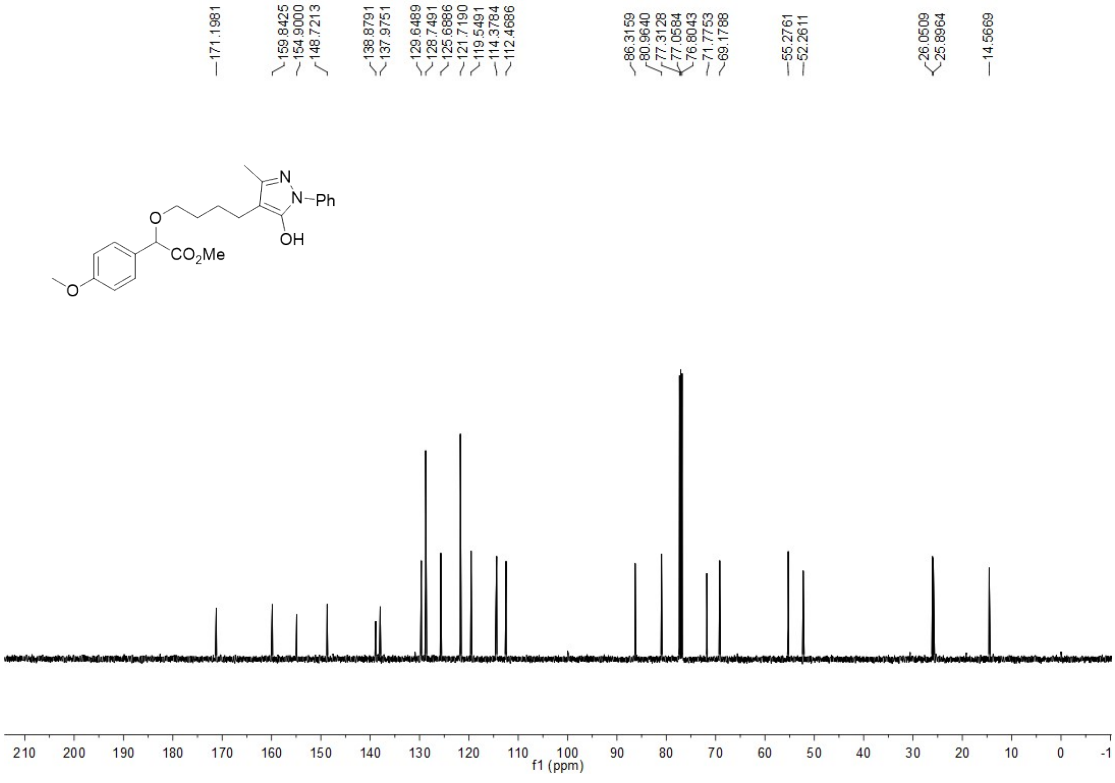
4a ^{13}C NMR (125MHz, $CDCl_3$)



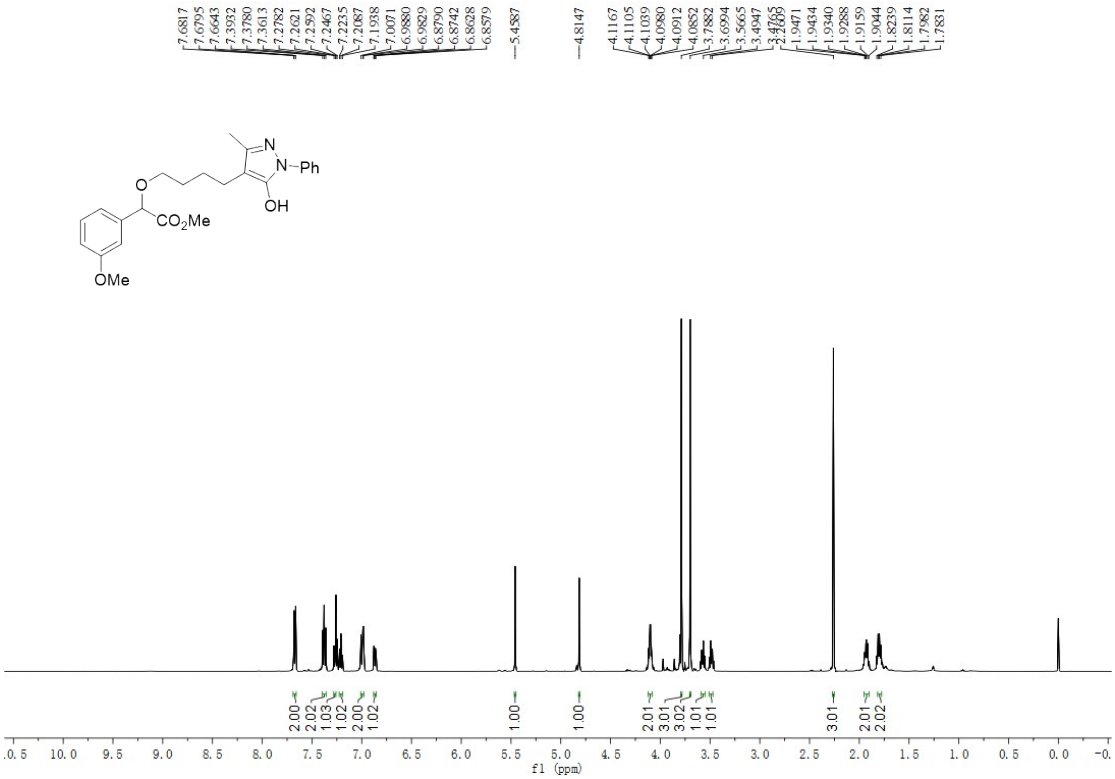
4b ^{1}H NMR (500 MHz, $CDCl_3$)



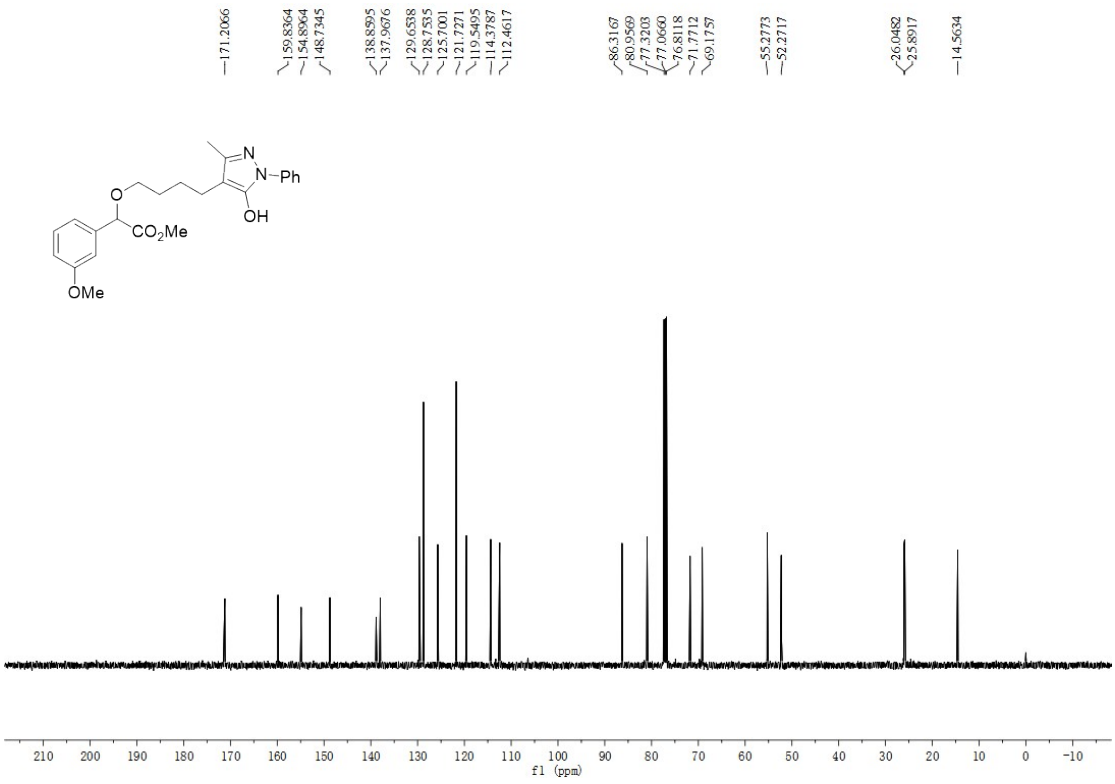
4b ^{13}C NMR (125 MHz, $CDCl_3$)



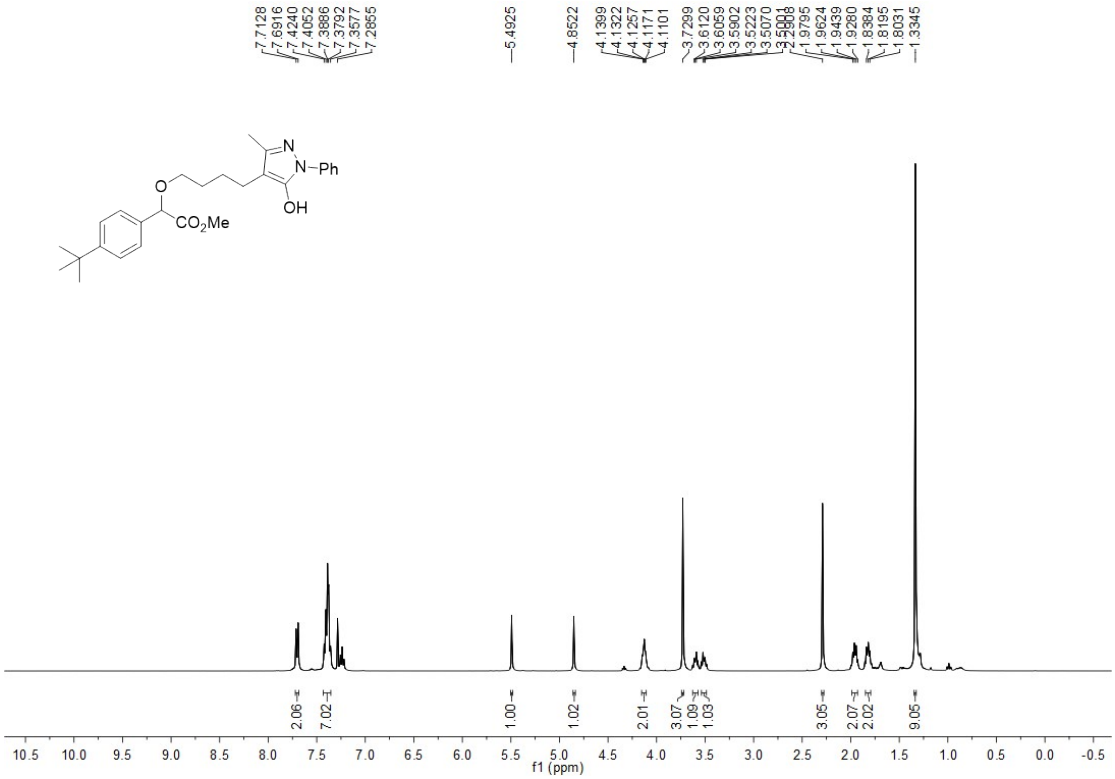
4c NMR (500 MHz, $CDCl_3$)



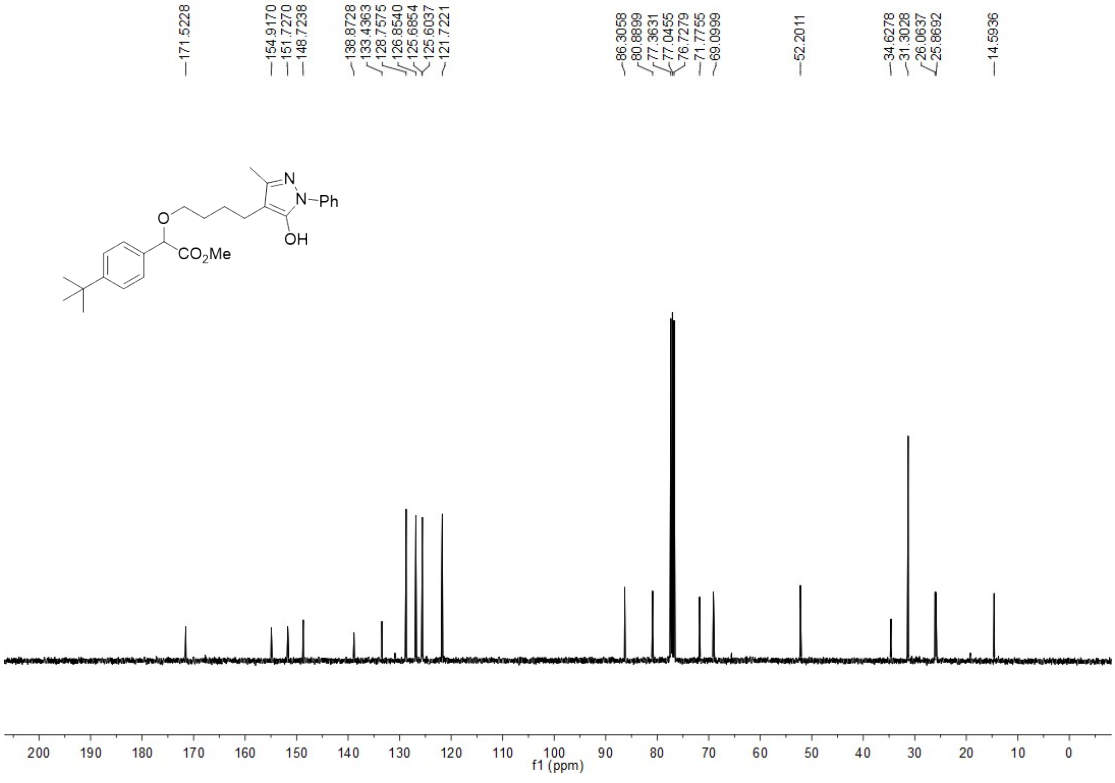
4c ^{13}C NMR (125 MHz, $CDCl_3$)



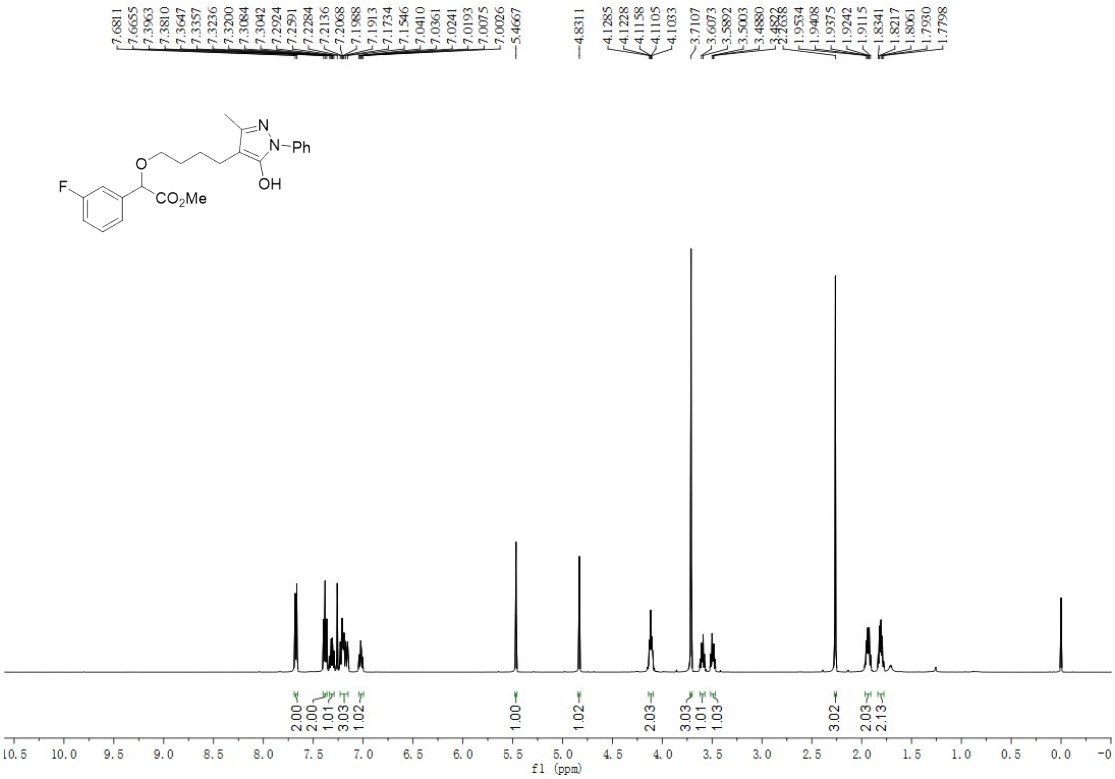
4d ^{1}H NMR (400 MHz, $CDCl_3$)



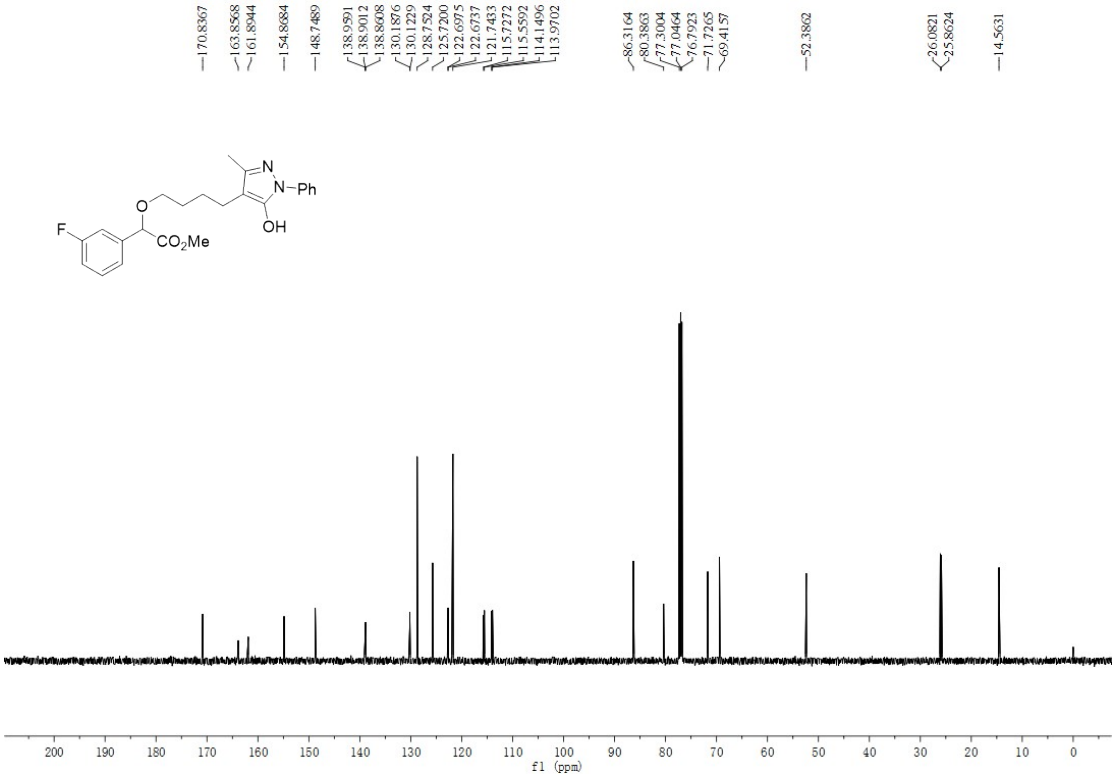
4d ^{13}C NMR (101 MHz, $CDCl_3$)



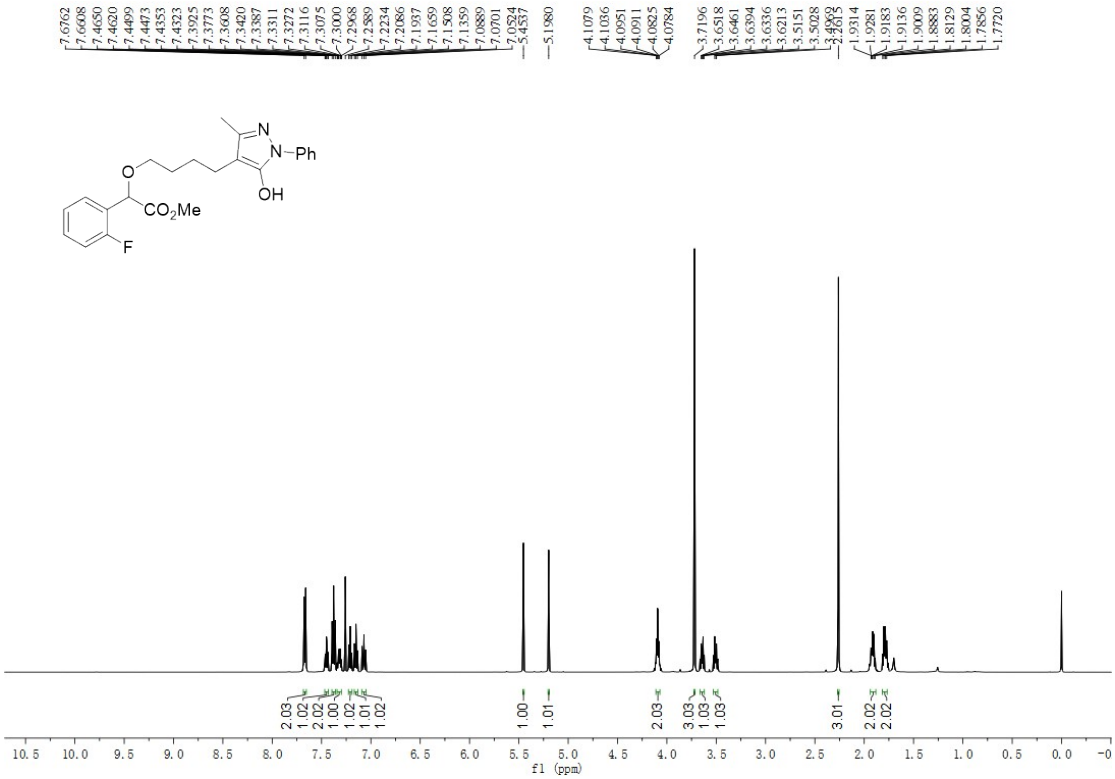
4e ^{1}H NMR (500 MHz, $CDCl_3$)



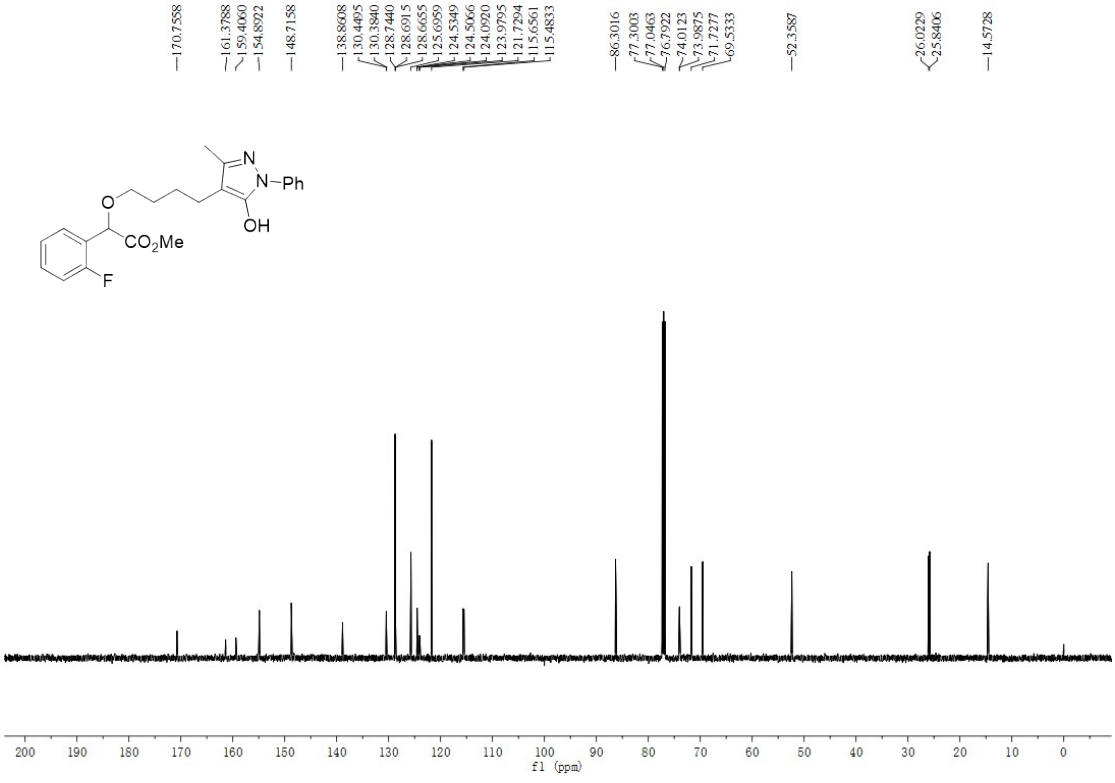
4e ^{13}C NMR (125 MHz, $CDCl_3$)



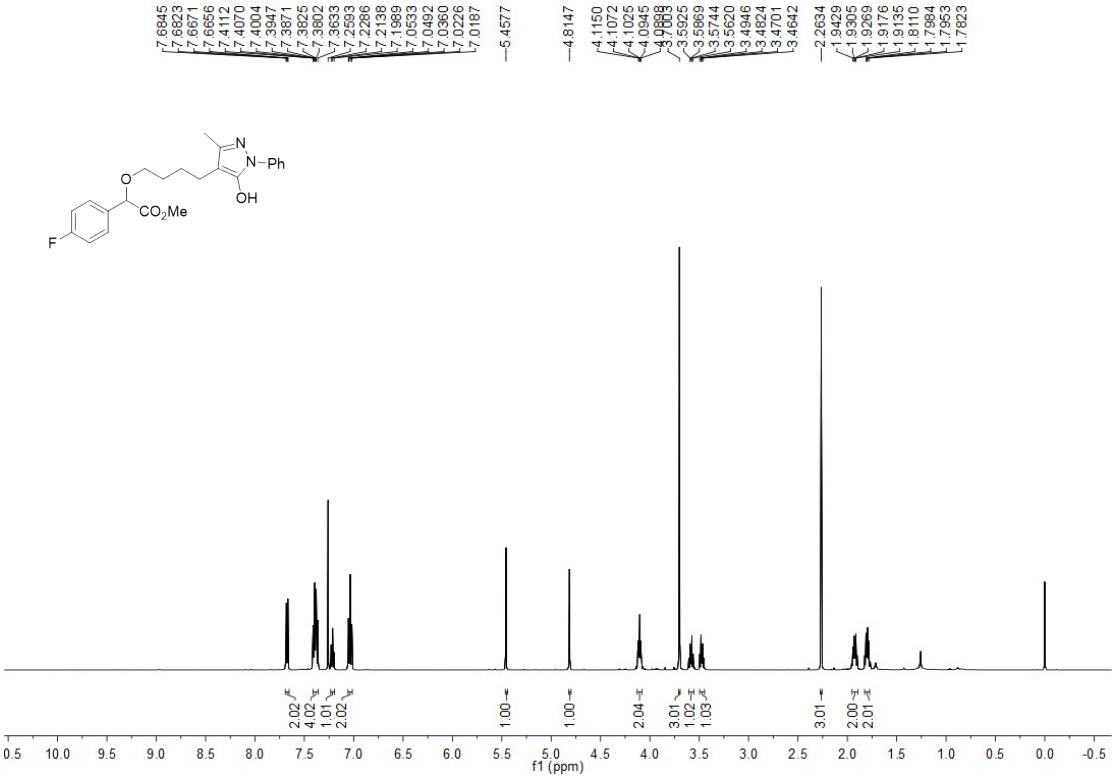
4f ^{1}H NMR (500 MHz, $CDCl_3$)



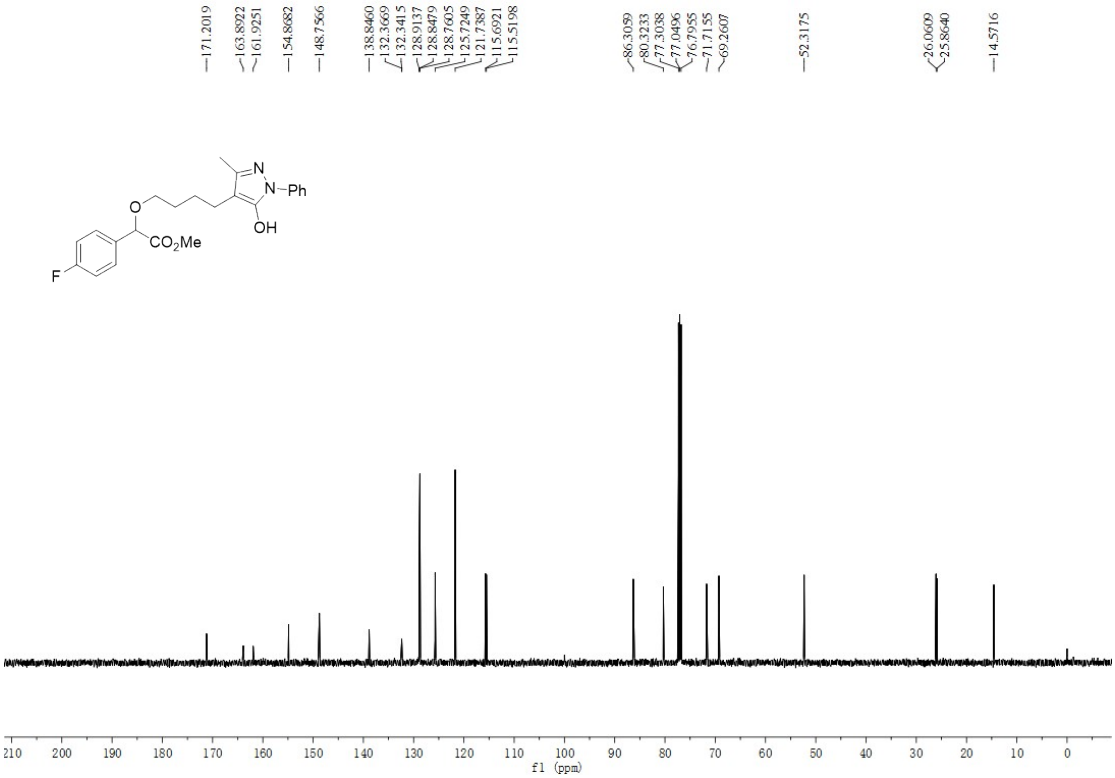
4f ^{13}C NMR (125 MHz, $CDCl_3$)



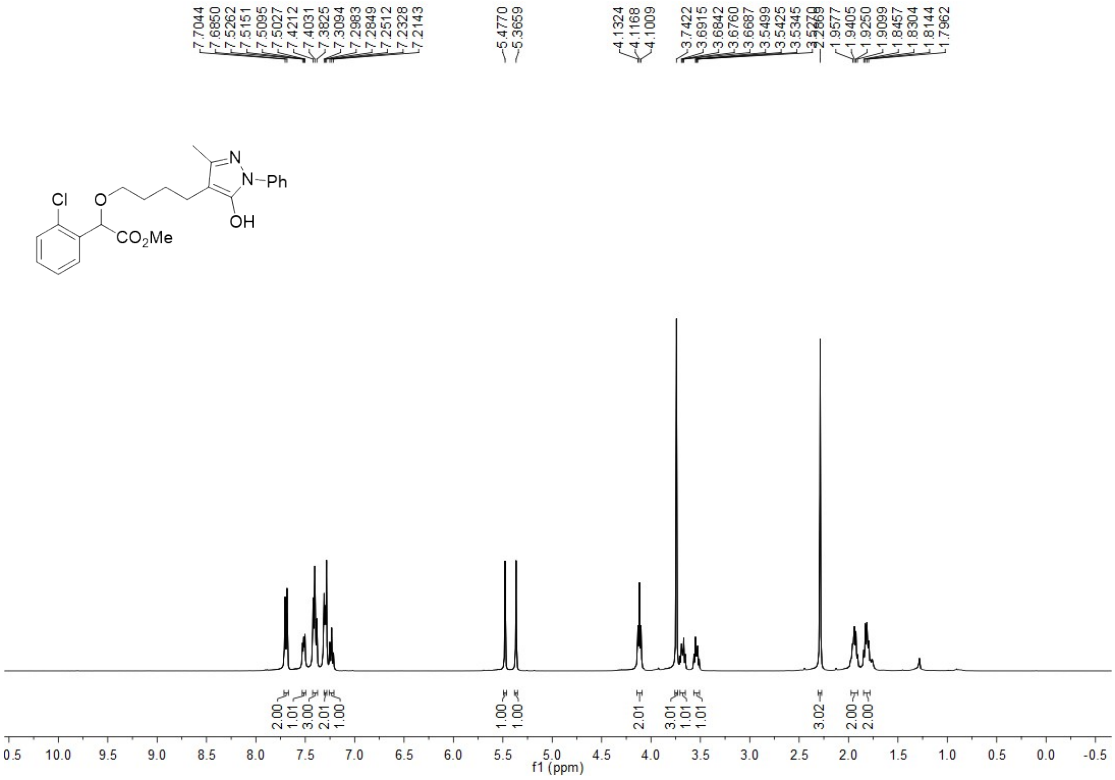
4g ^{1}H NMR (500 MHz, $CDCl_3$)



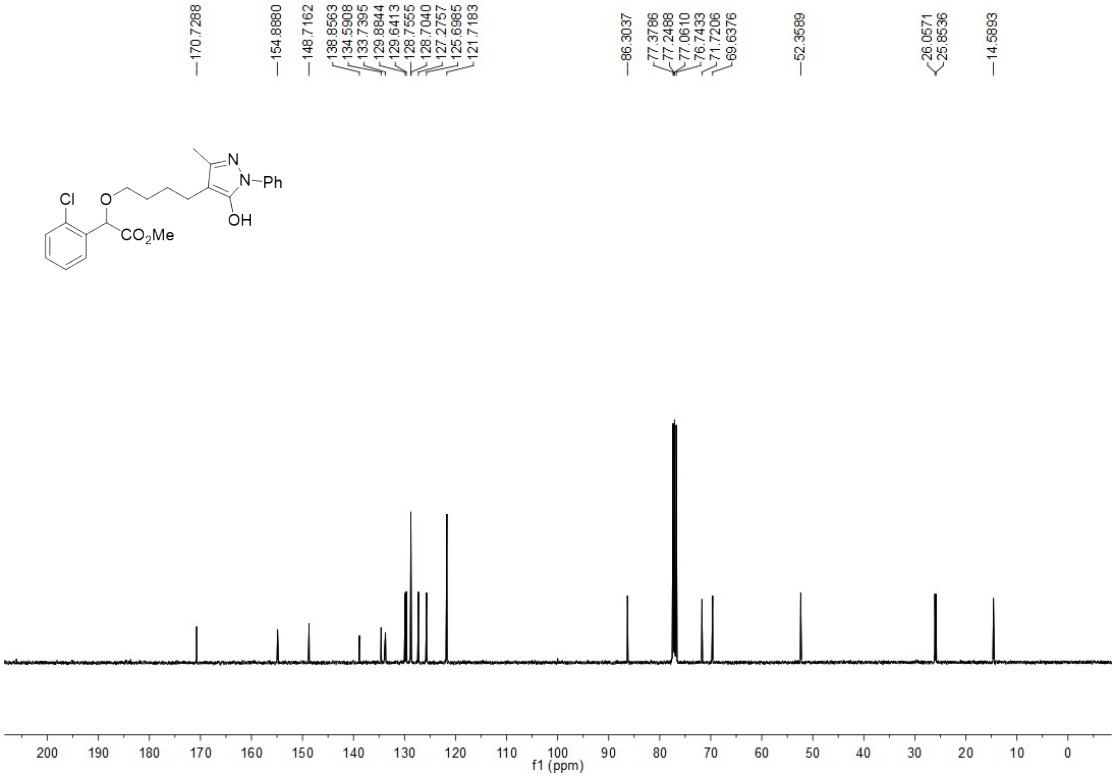
4g ^{13}C NMR (125 MHz, $CDCl_3$)



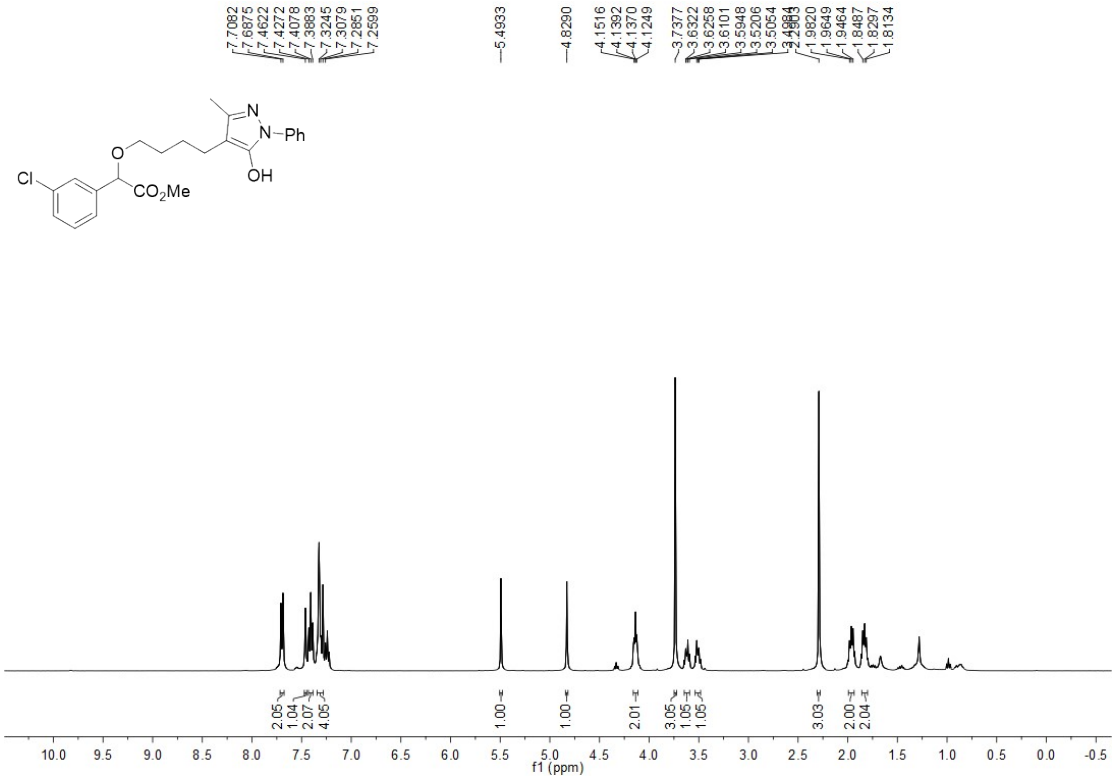
4h ^{1}H NMR (400 MHz, $CDCl_3$)



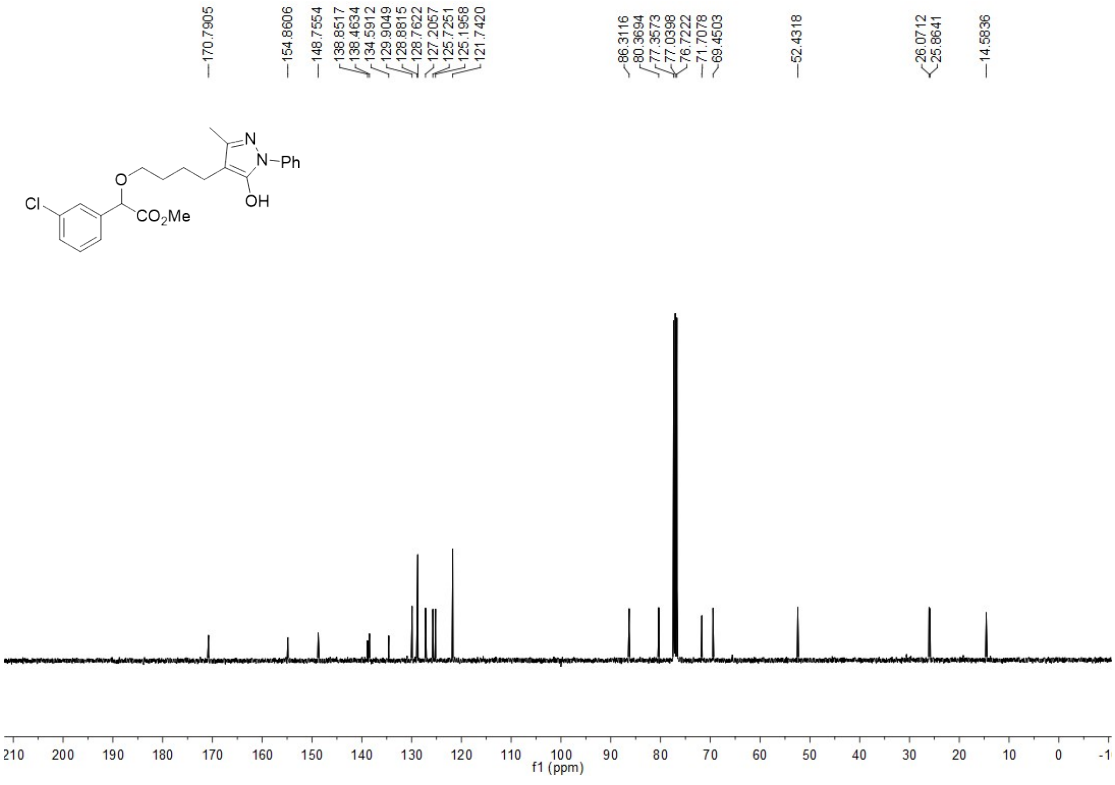
4h ^{13}C NMR (100 MHz, $CDCl_3$)



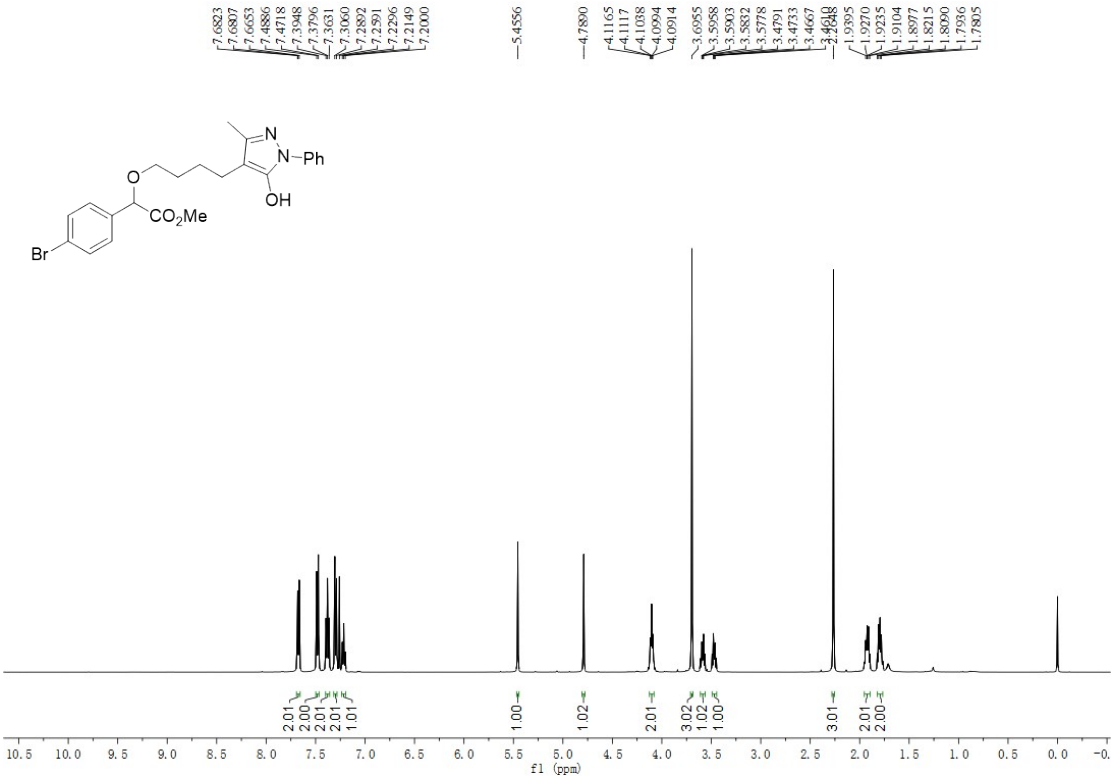
4i ^{1}H NMR (400 MHz, $CDCl_3$)



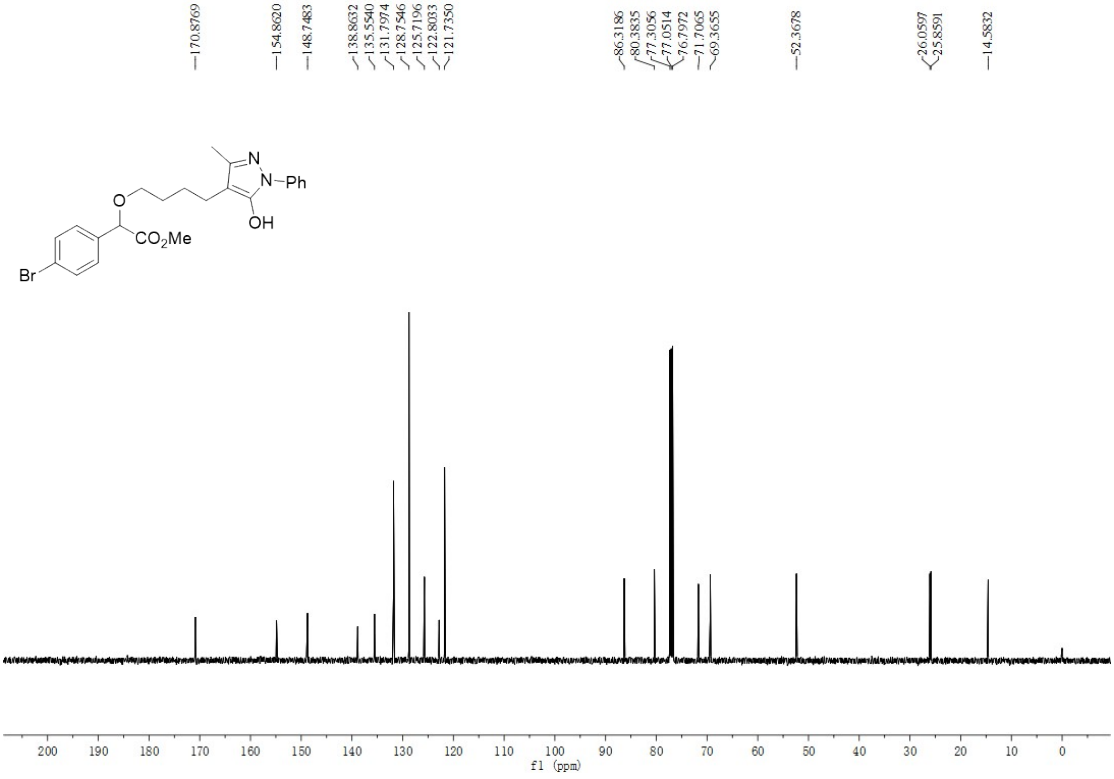
4i ^{13}C NMR (100 MHz, $CDCl_3$)



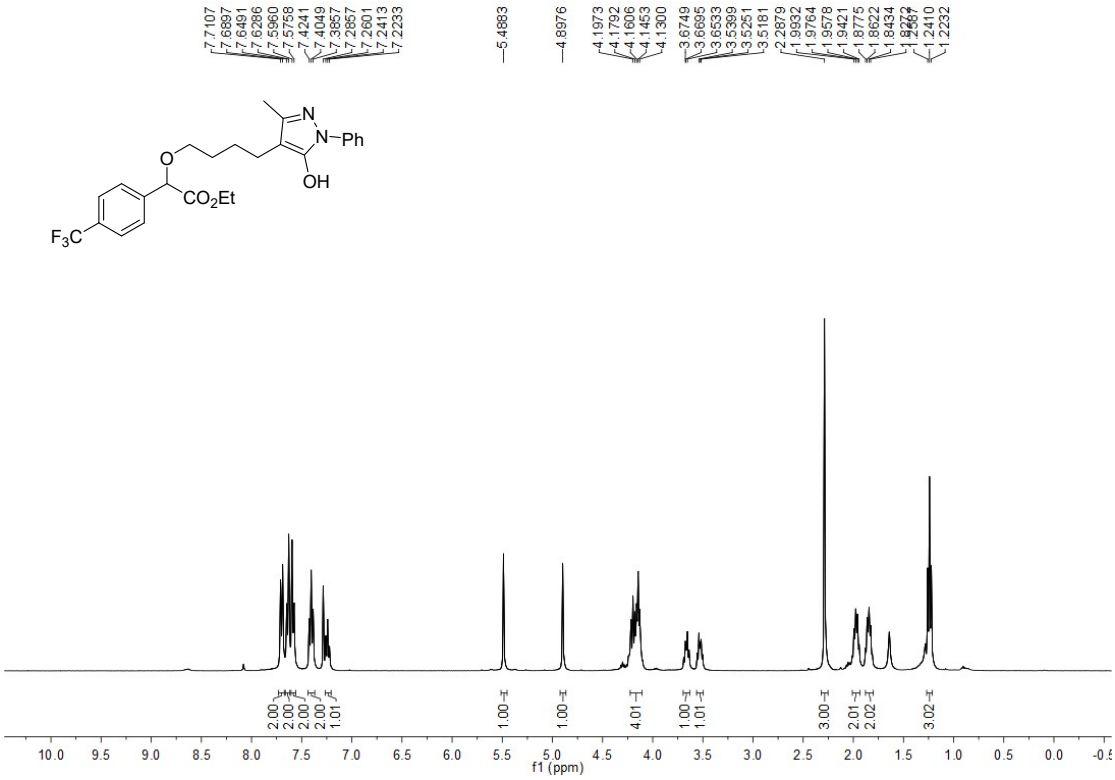
4j ^{1}H NMR (500 MHz, $CDCl_3$)



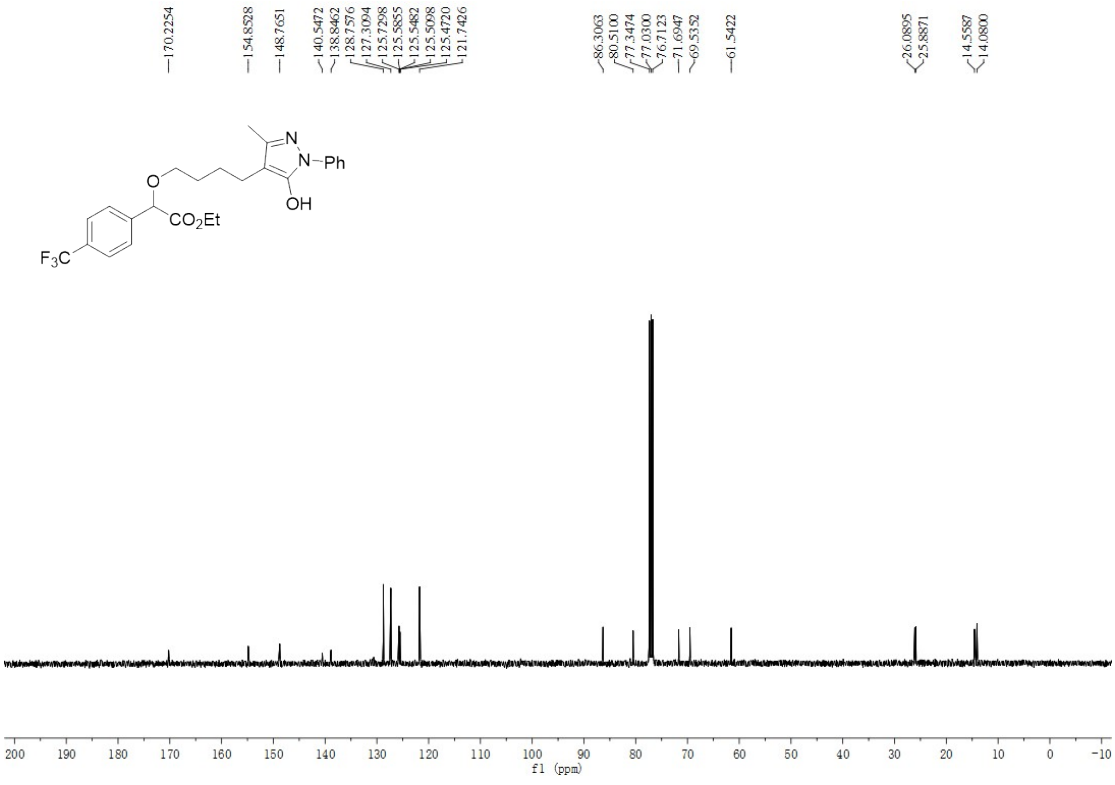
4j ^{13}C NMR (125 MHz, $CDCl_3$)



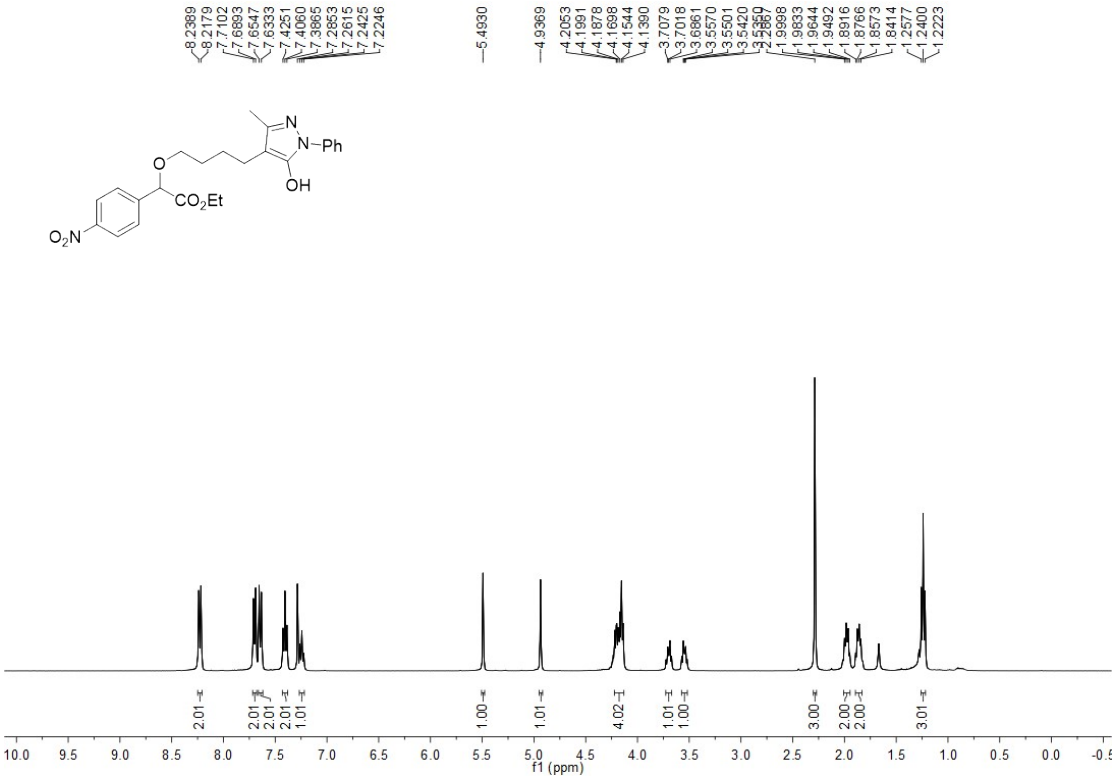
4k ^{1}H NMR (400 MHz, $CDCl_3$)



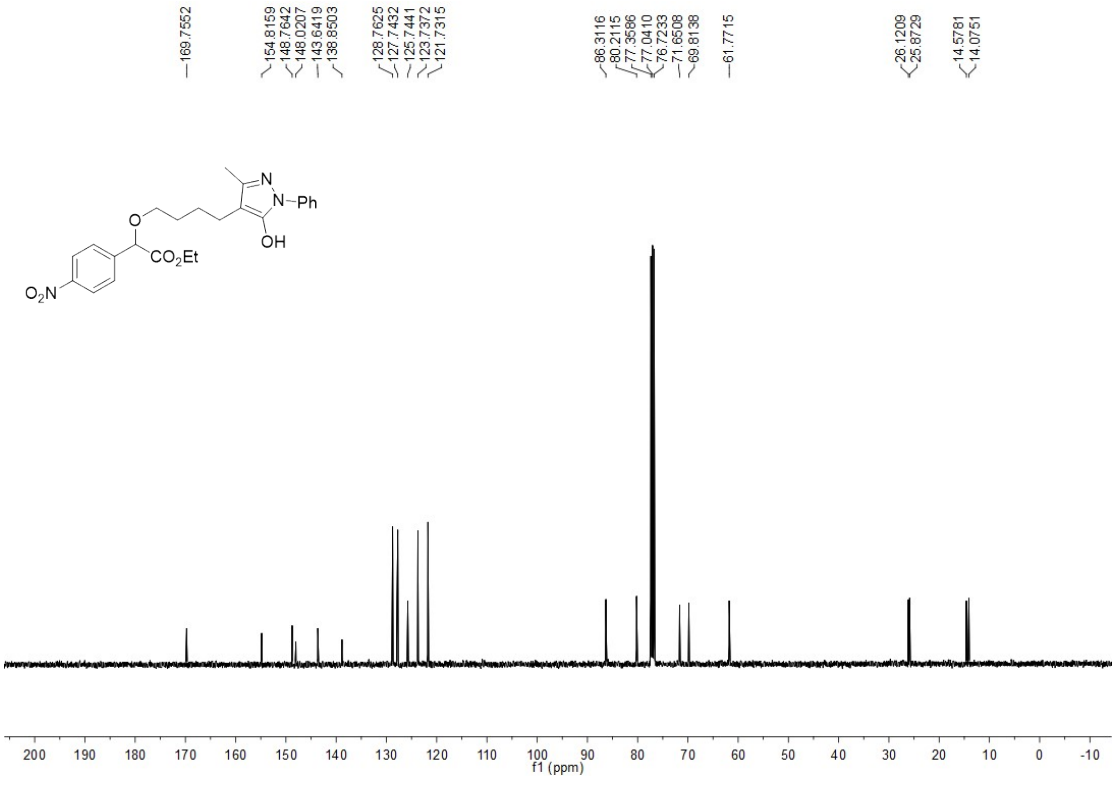
4k ^{13}C NMR (100 MHz, $CDCl_3$)



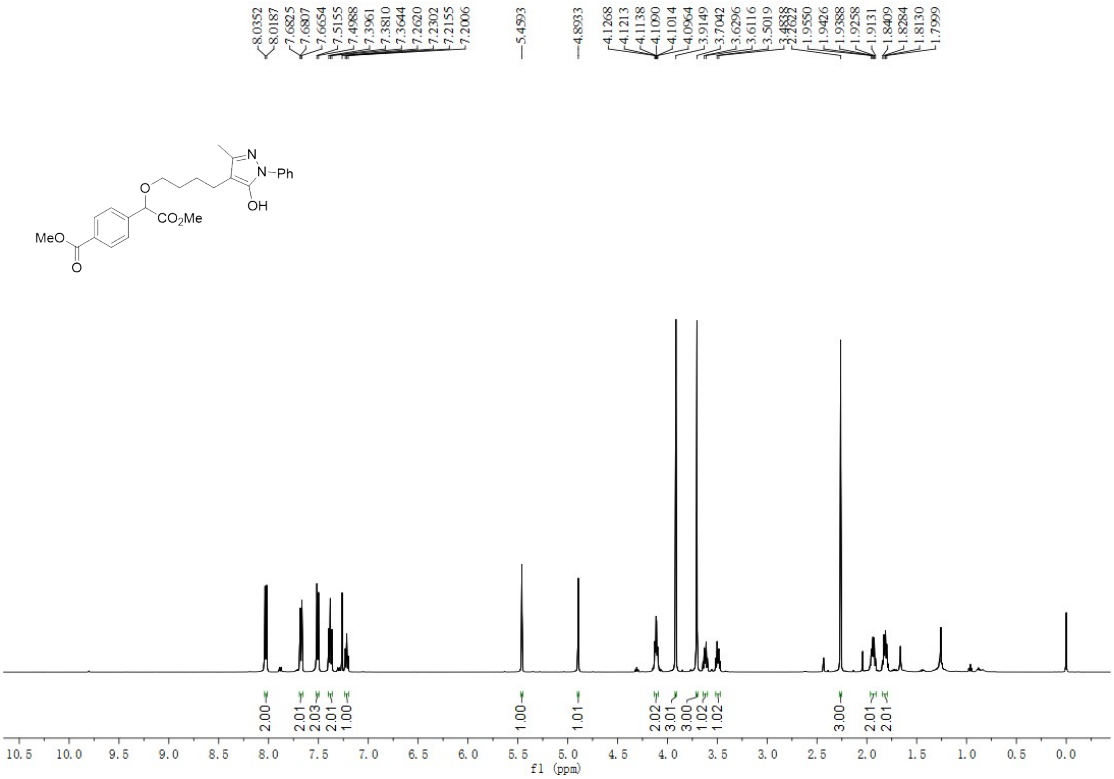
4l ^{1}H NMR (400 MHz, $CDCl_3$)



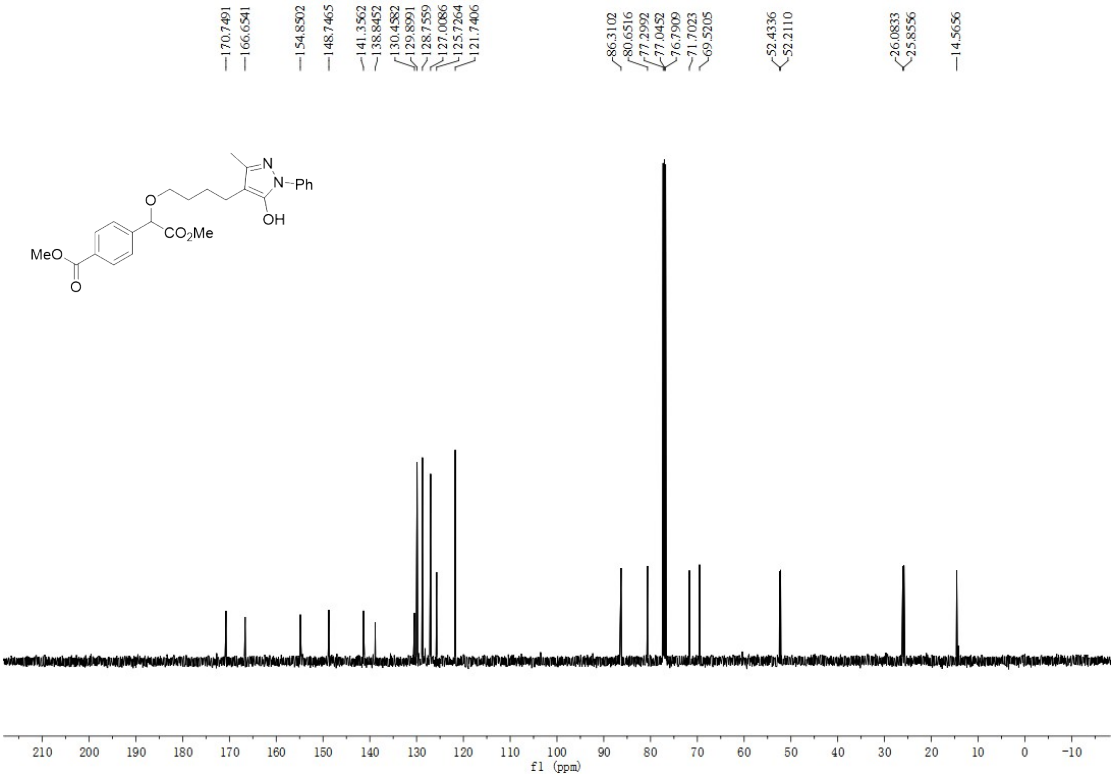
4l ^{13}C NMR (100 MHz, $CDCl_3$)



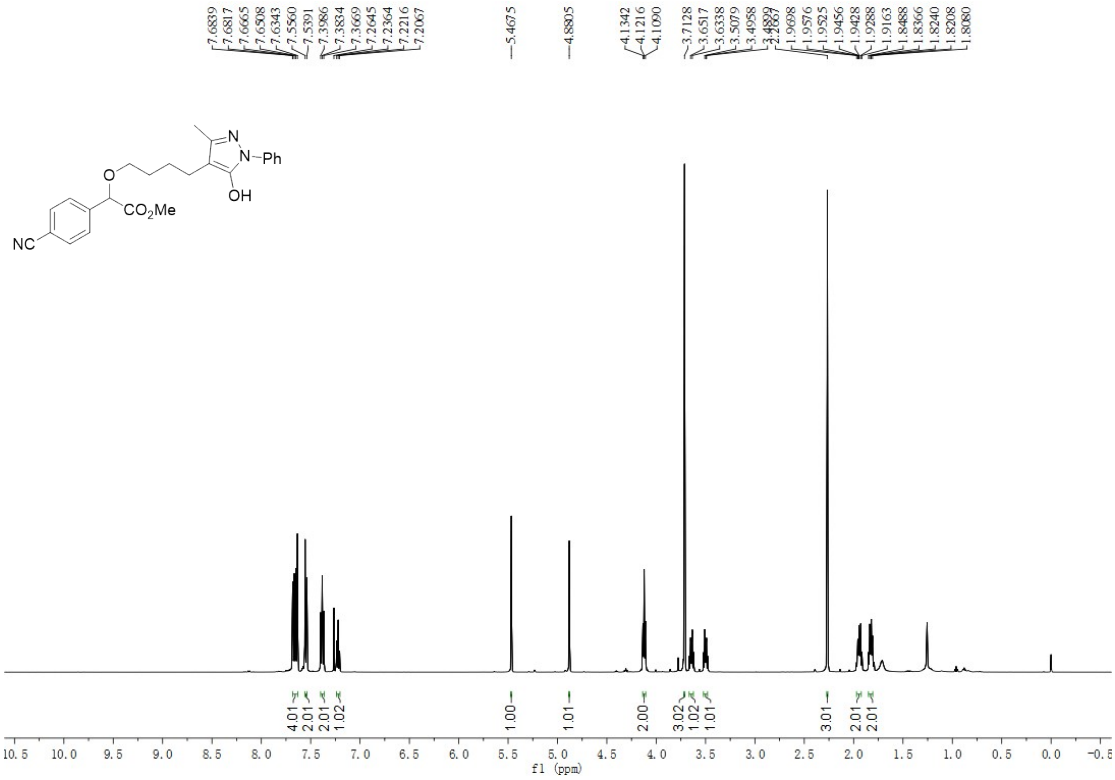
4m ^{1}H NMR (500 MHz, $CDCl_3$)



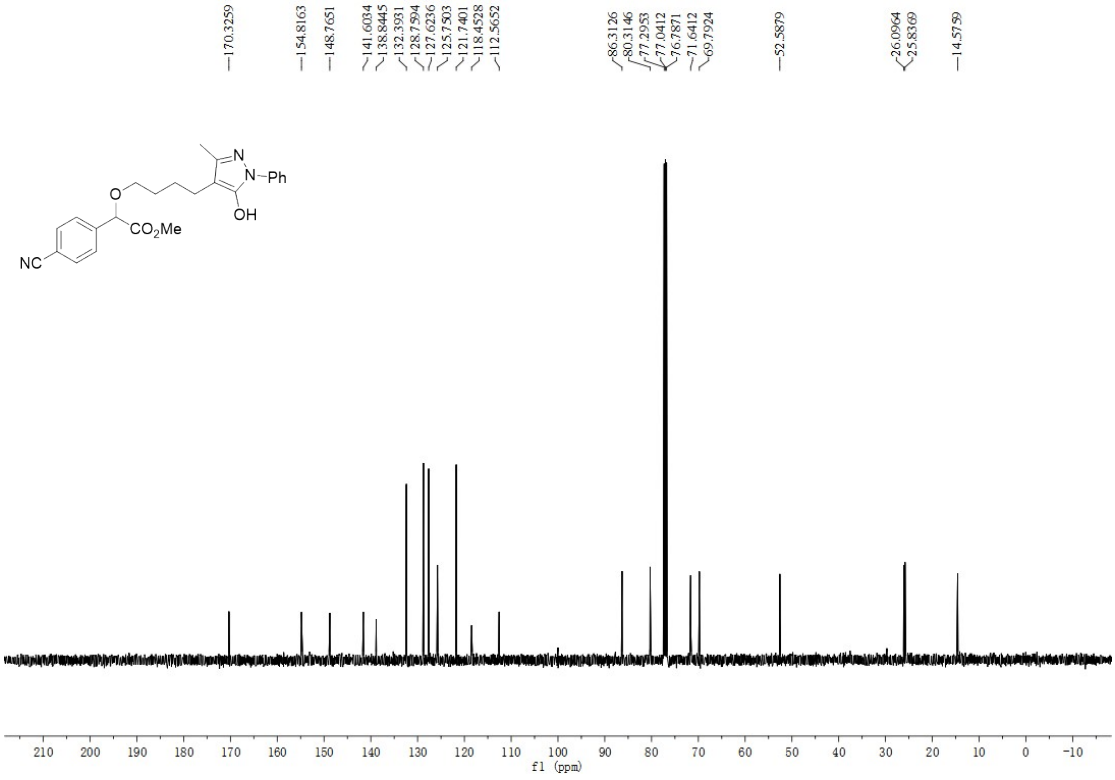
4m ^{13}C NMR (125 MHz, $CDCl_3$)



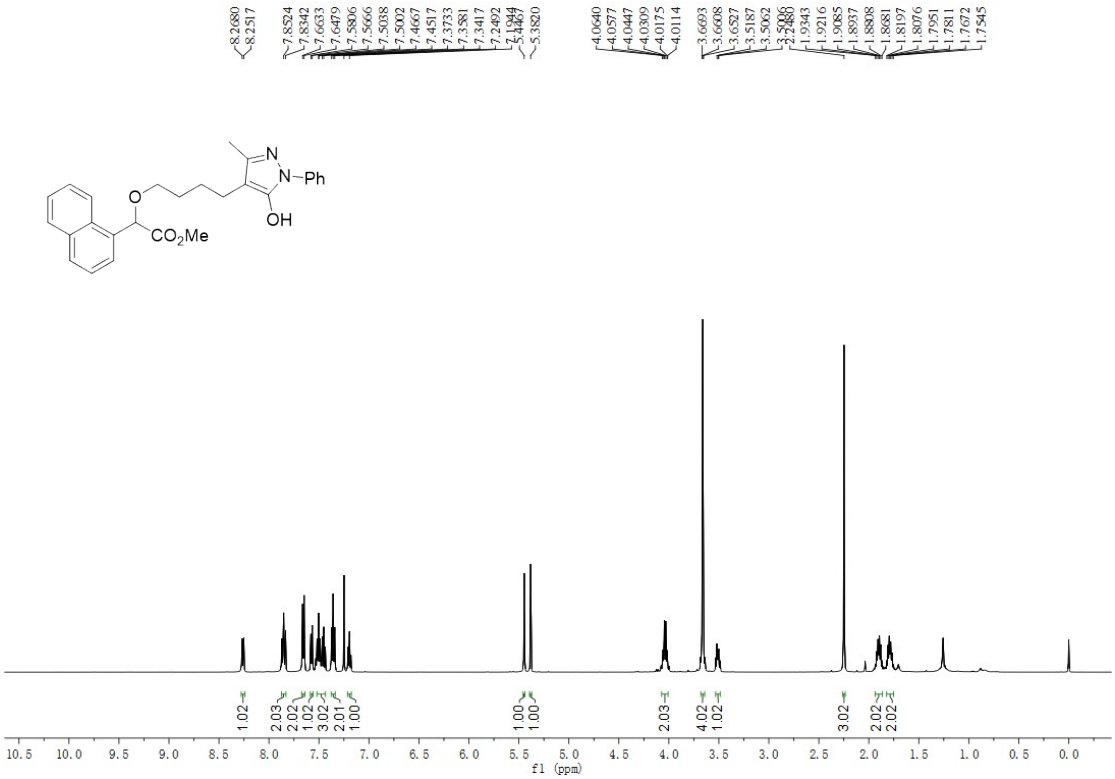
4n ^{1}H NMR (500 MHz, $CDCl_3$)



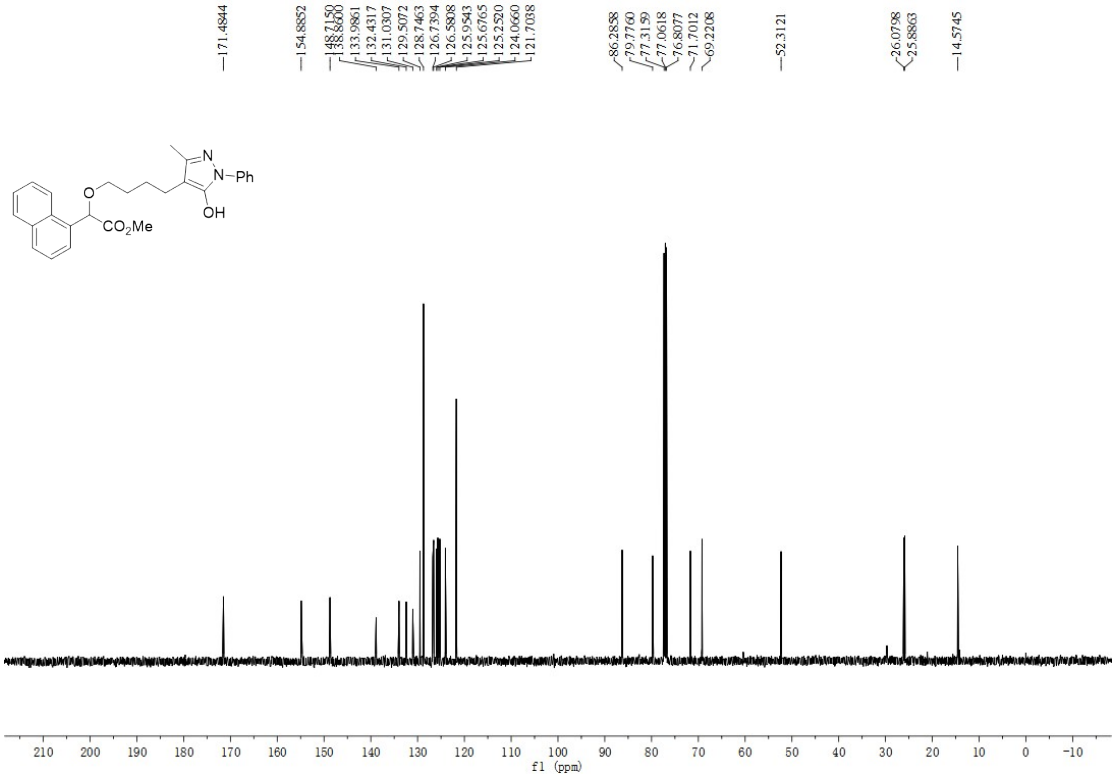
4n ^{13}C NMR (125 MHz, $CDCl_3$)



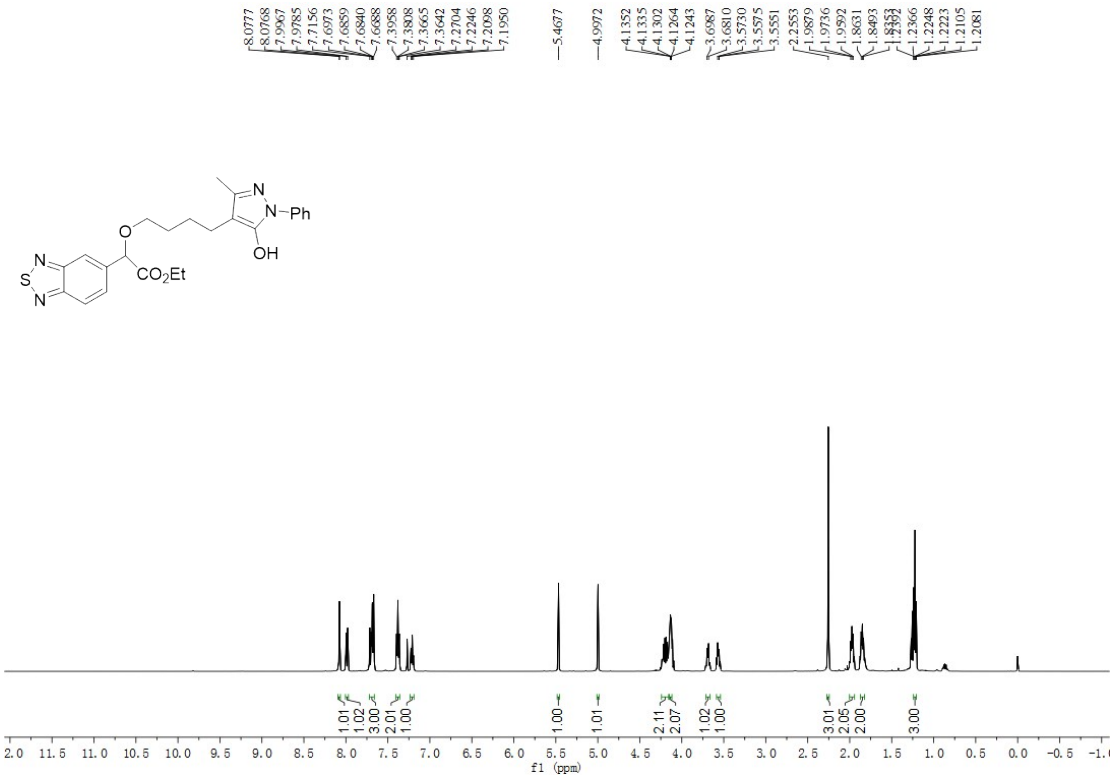
4o ^{1}H NMR (500 MHz, $CDCl_3$)



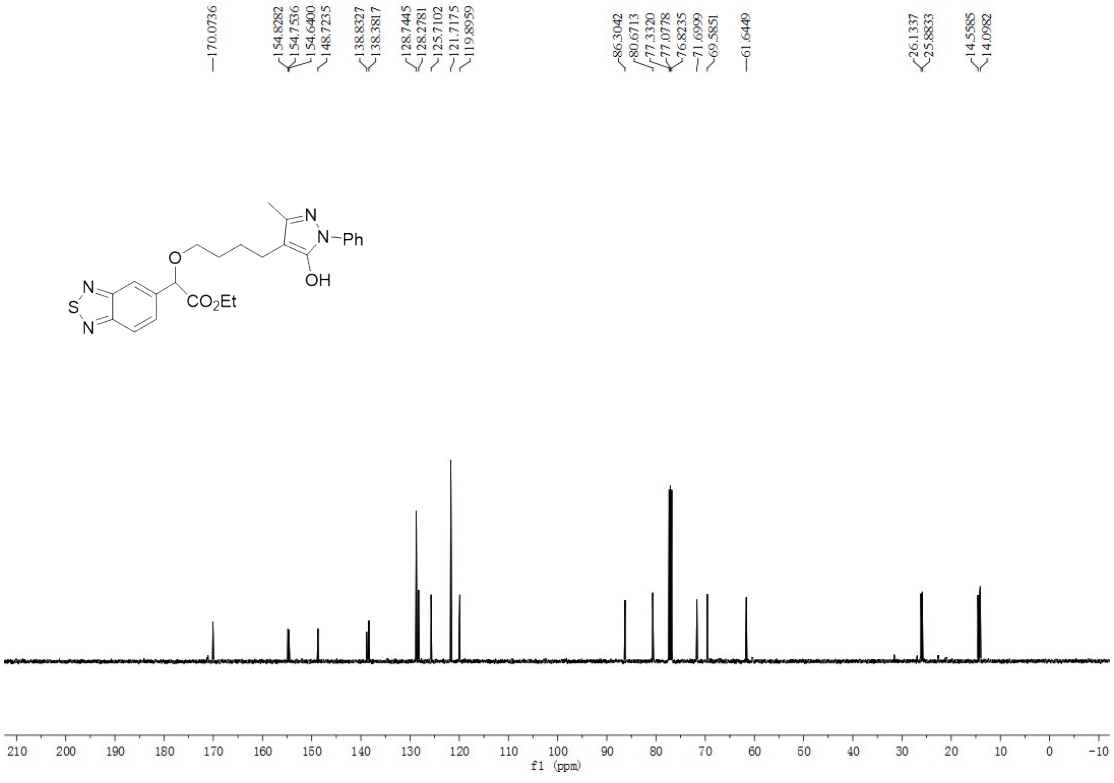
4o ^{13}C NMR (125 MHz, $CDCl_3$)



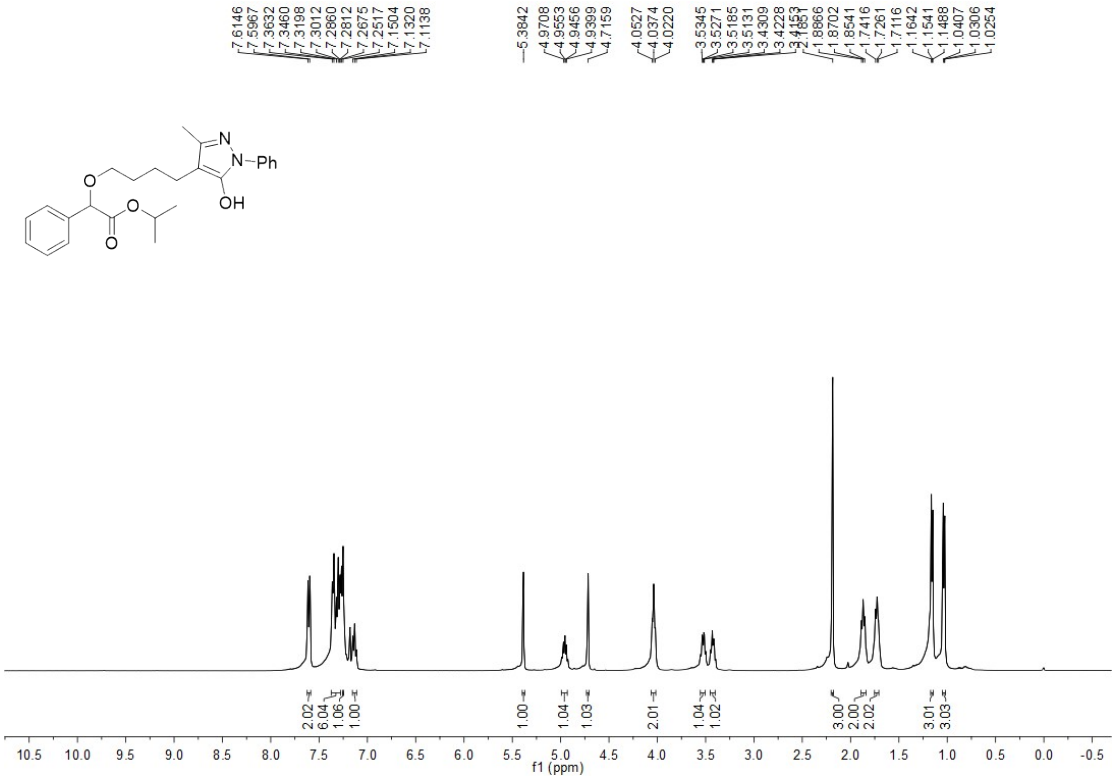
4p ^{1}H NMR (500 MHz, $CDCl_3$)



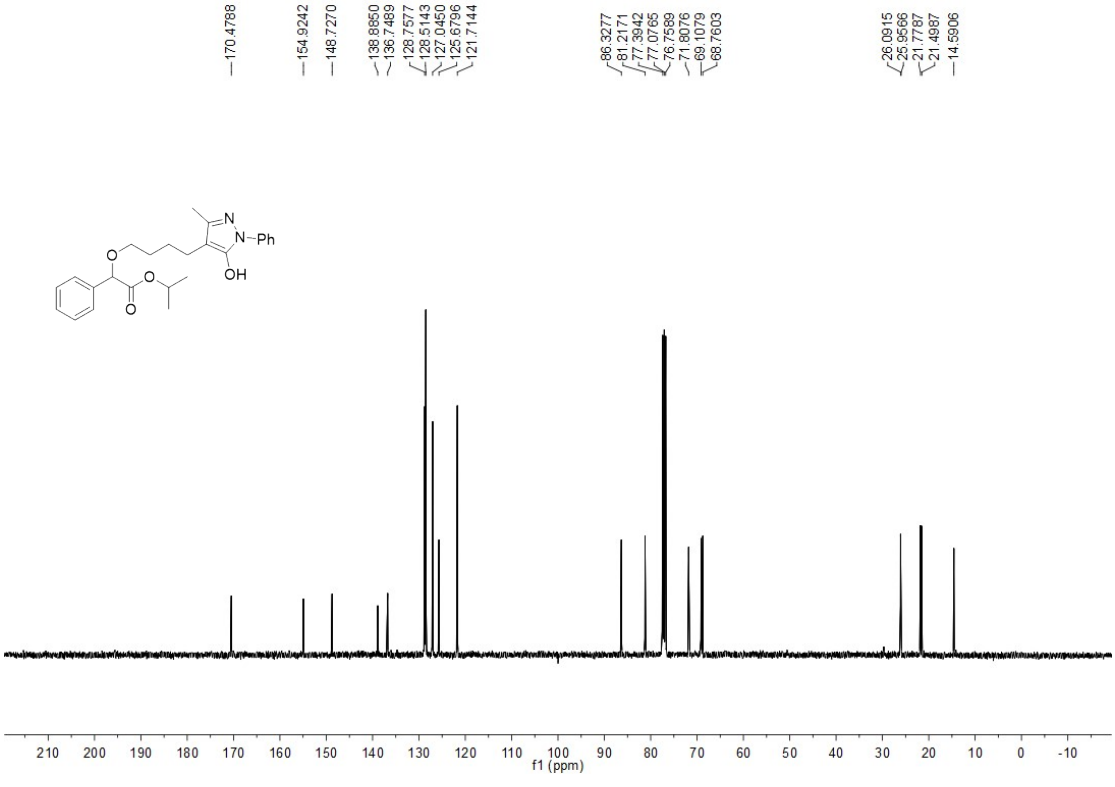
4p ^{13}C NMR (125 MHz, $CDCl_3$)



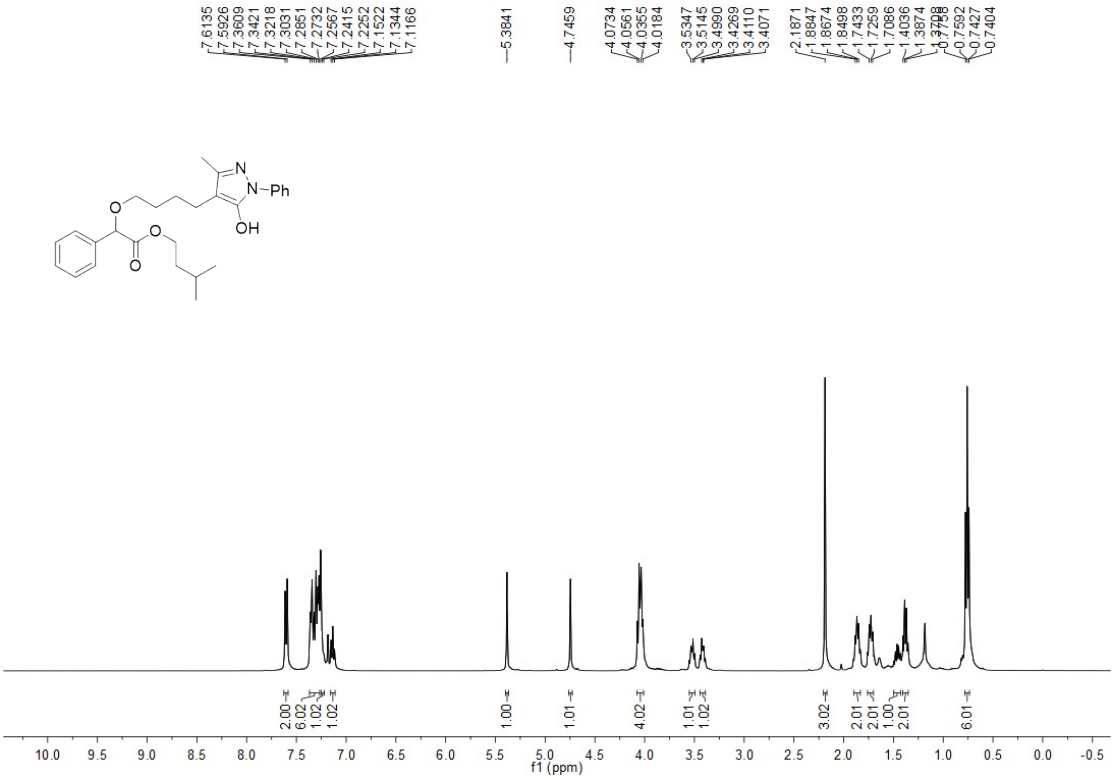
4q ^{1}H NMR (400 MHz, $CDCl_3$)



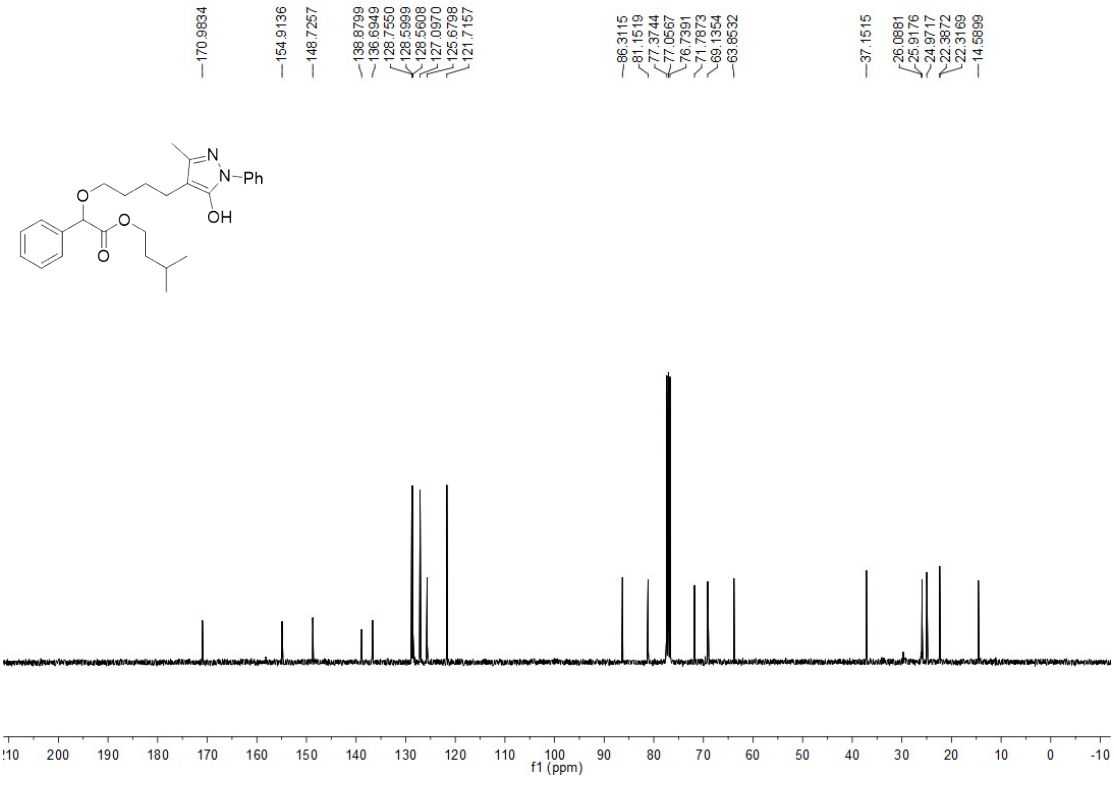
4q ^{13}C NMR (100 MHz, $CDCl_3$)



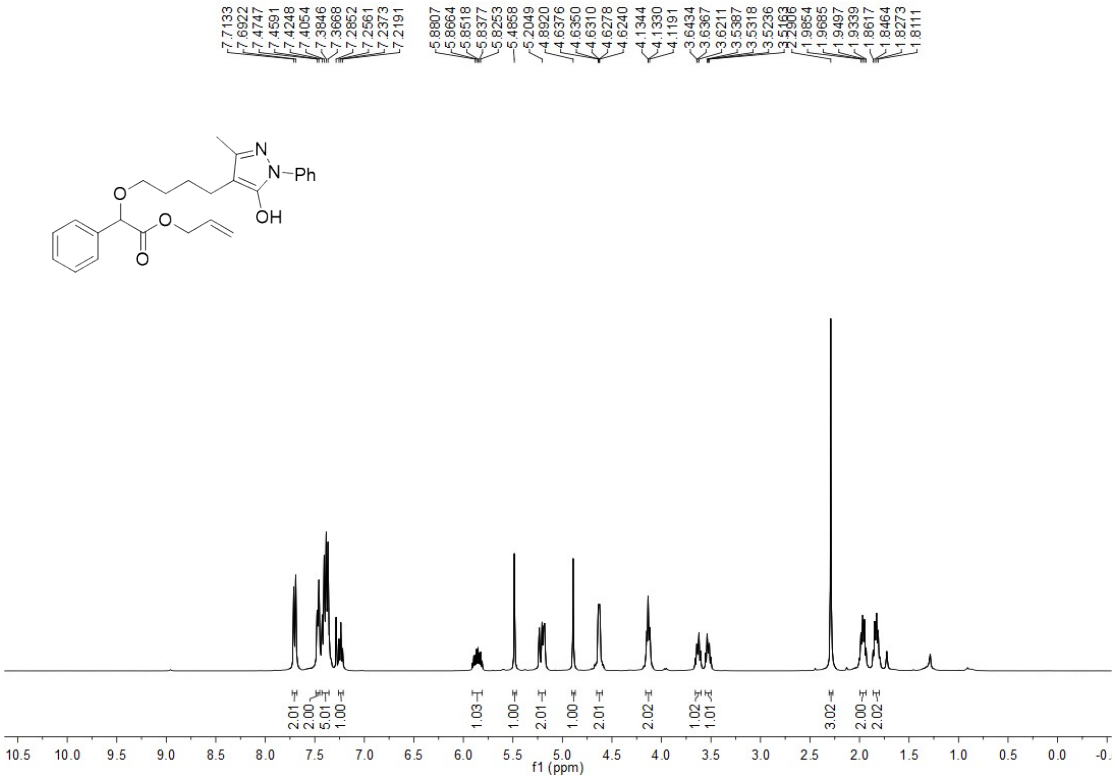
4r ^{1}H NMR (400 MHz, $CDCl_3$)



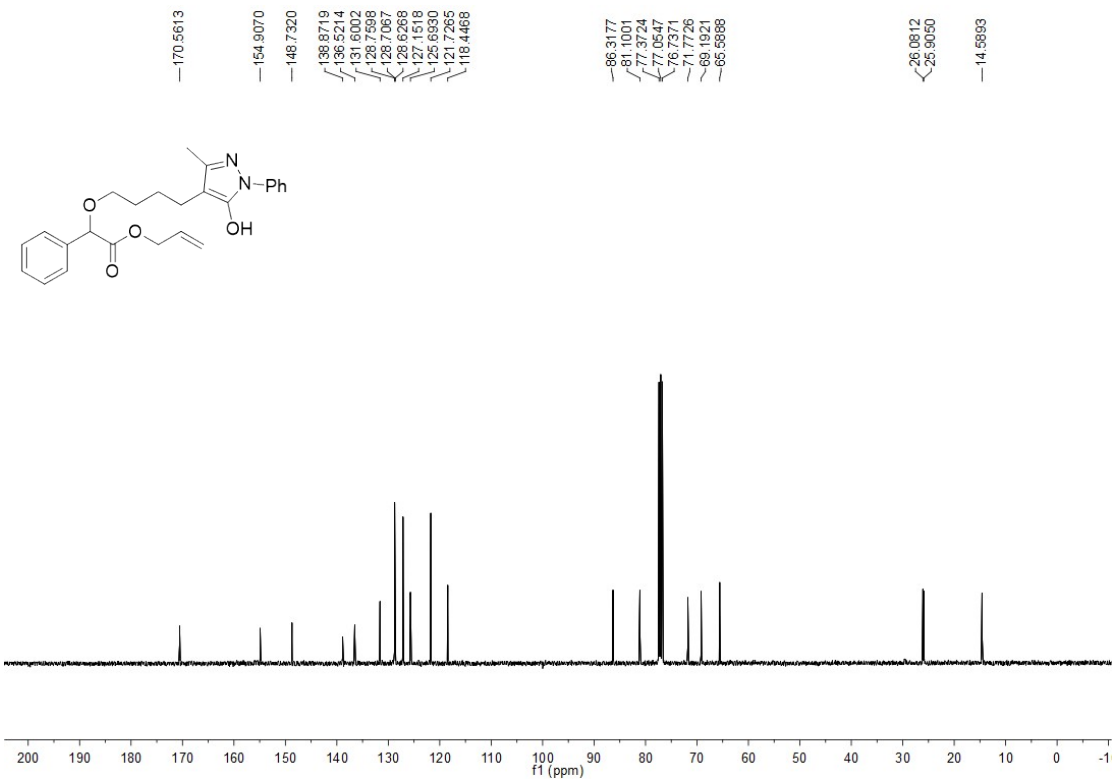
4r ^{13}C NMR (100 MHz, $CDCl_3$)



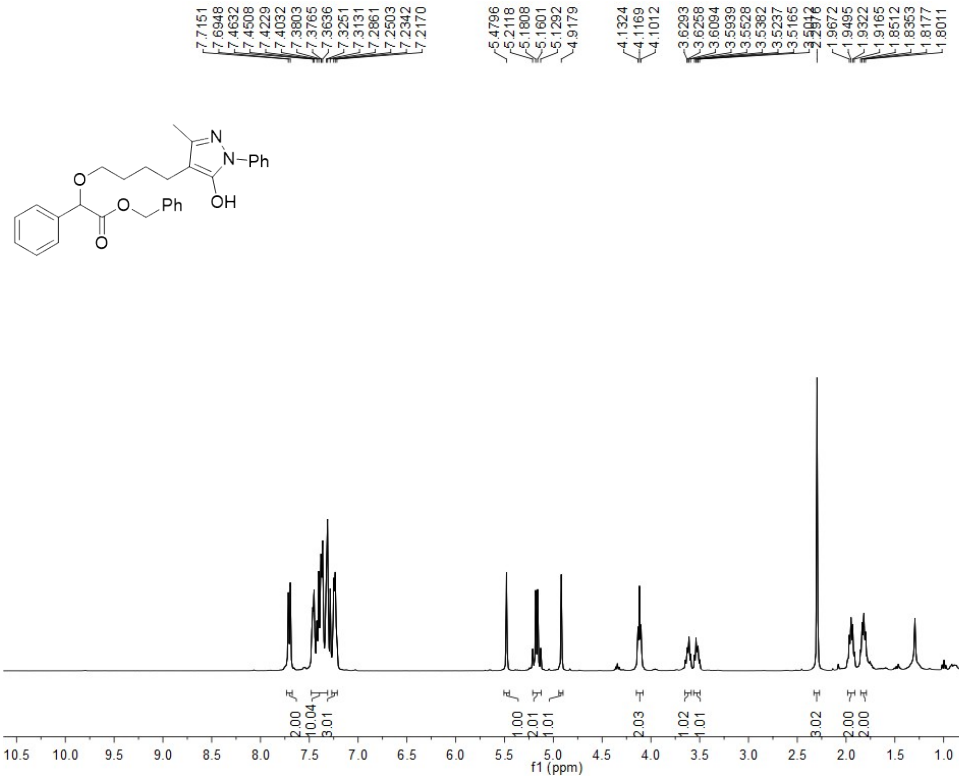
4s ^{1}H NMR (400 MHz, $CDCl_3$)



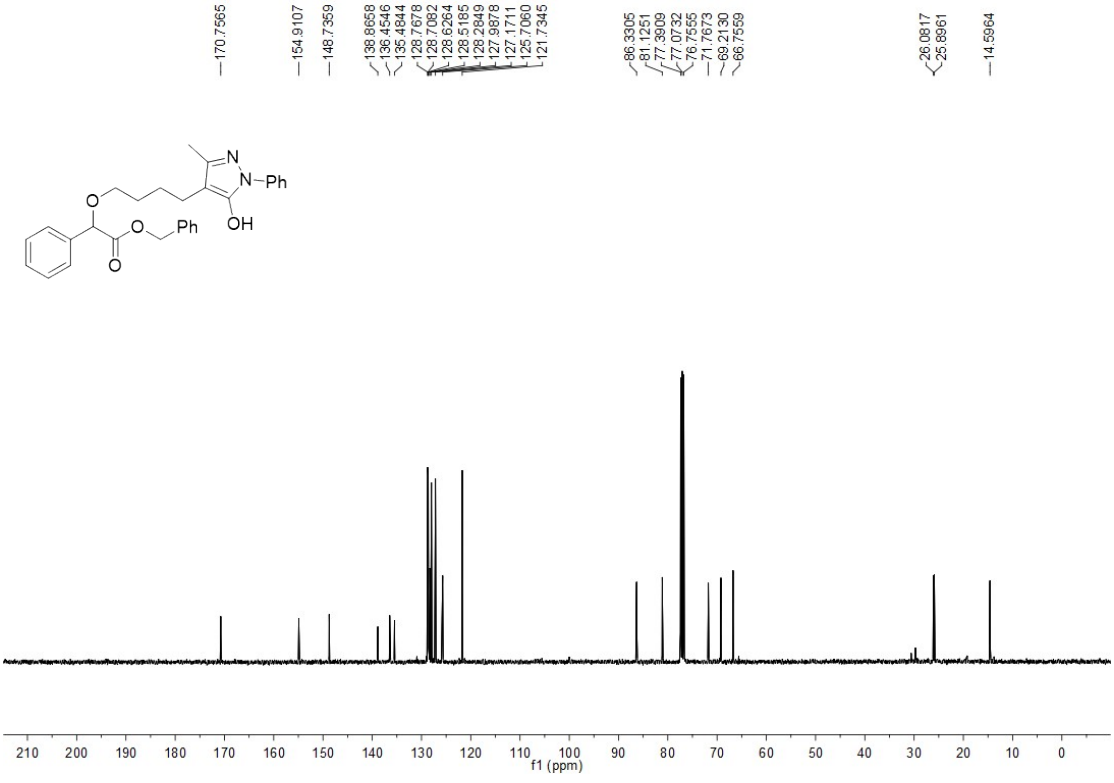
4s ^{13}C NMR (100 MHz, $CDCl_3$)



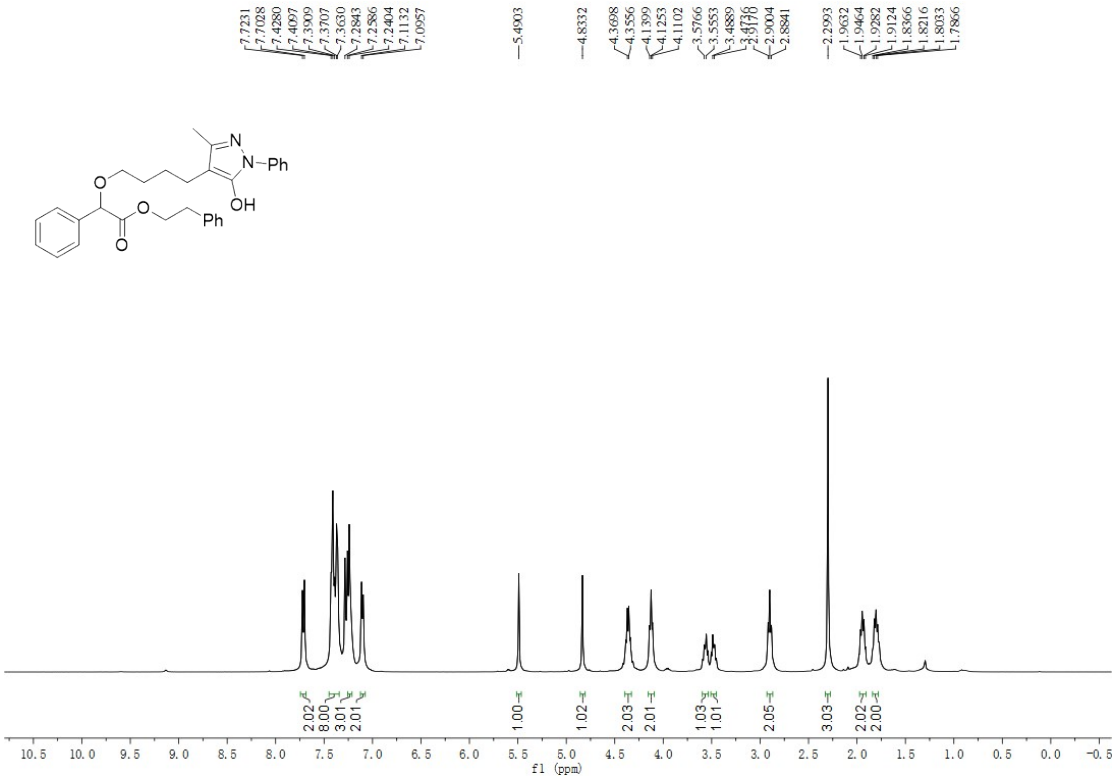
4t ^{1}H NMR (400 MHz, $CDCl_3$)



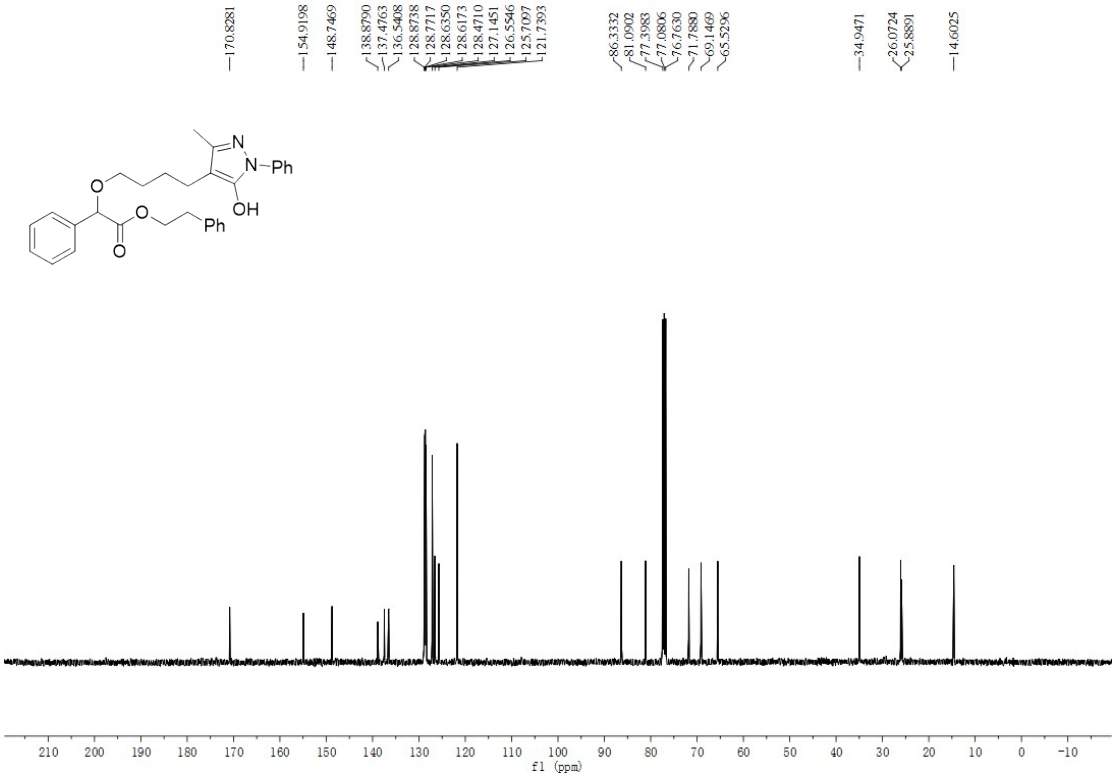
4t ^{13}C NMR (100 MHz, $CDCl_3$)



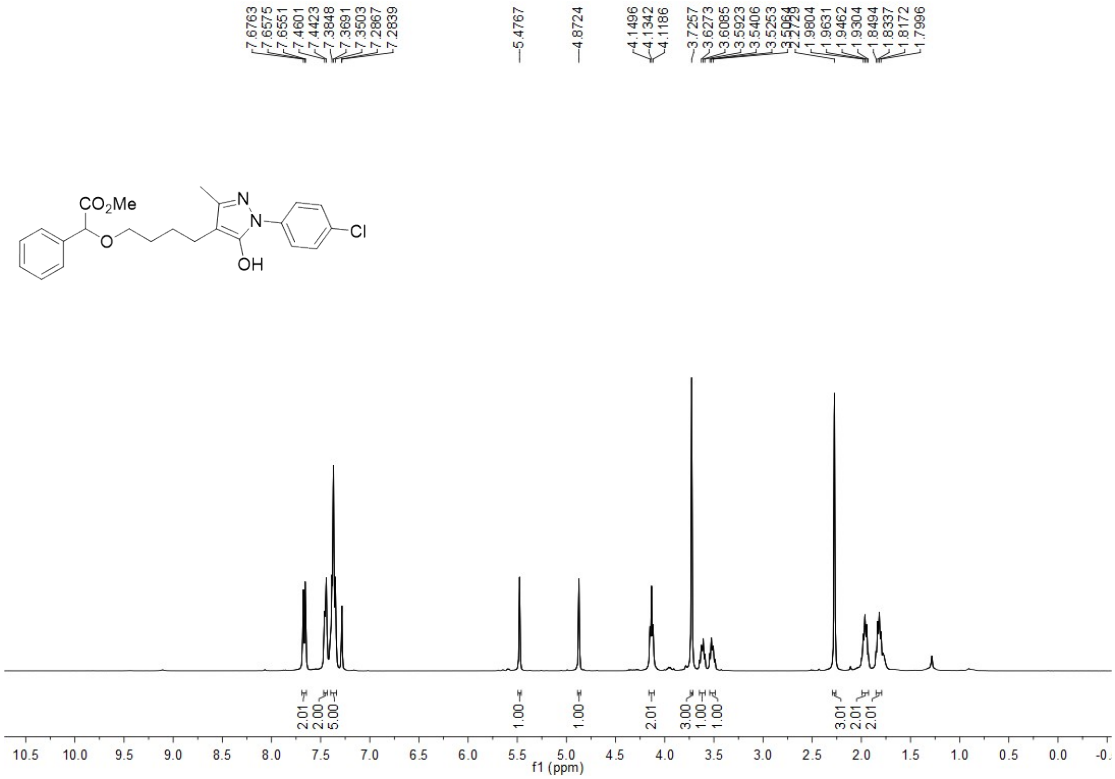
4u ^{1}H NMR (400 MHz, $CDCl_3$)



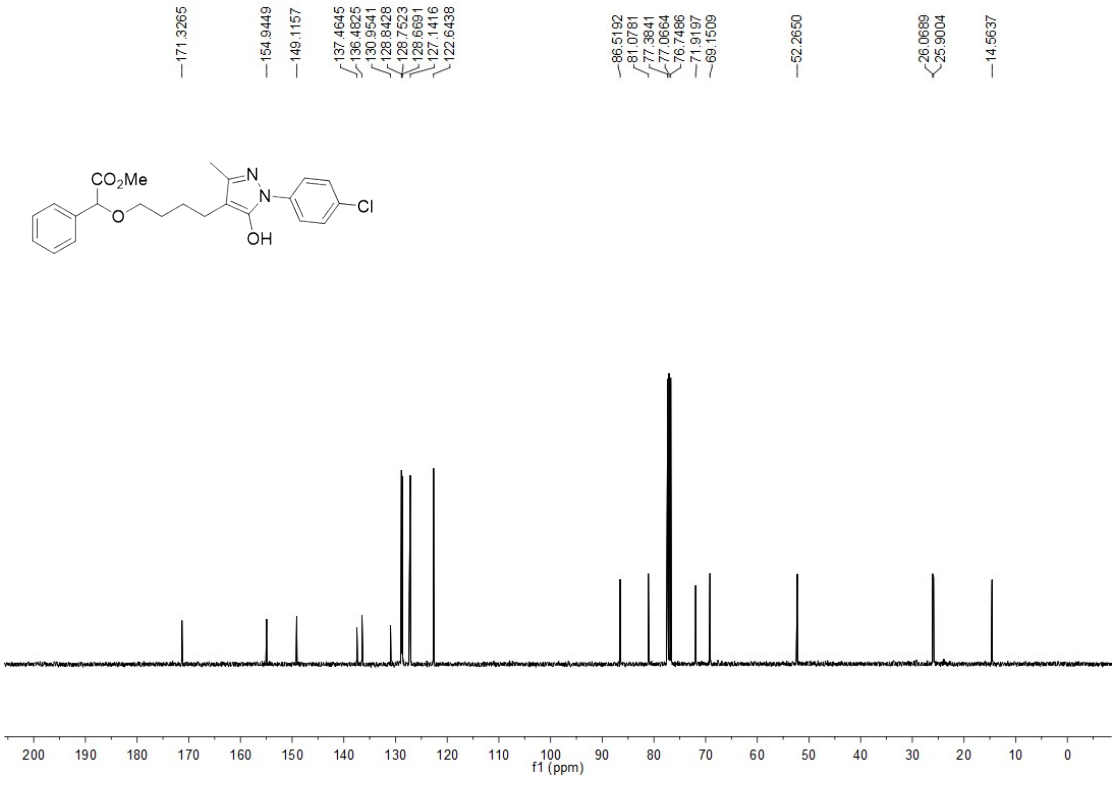
4u ^{13}C NMR (100 MHz, $CDCl_3$)



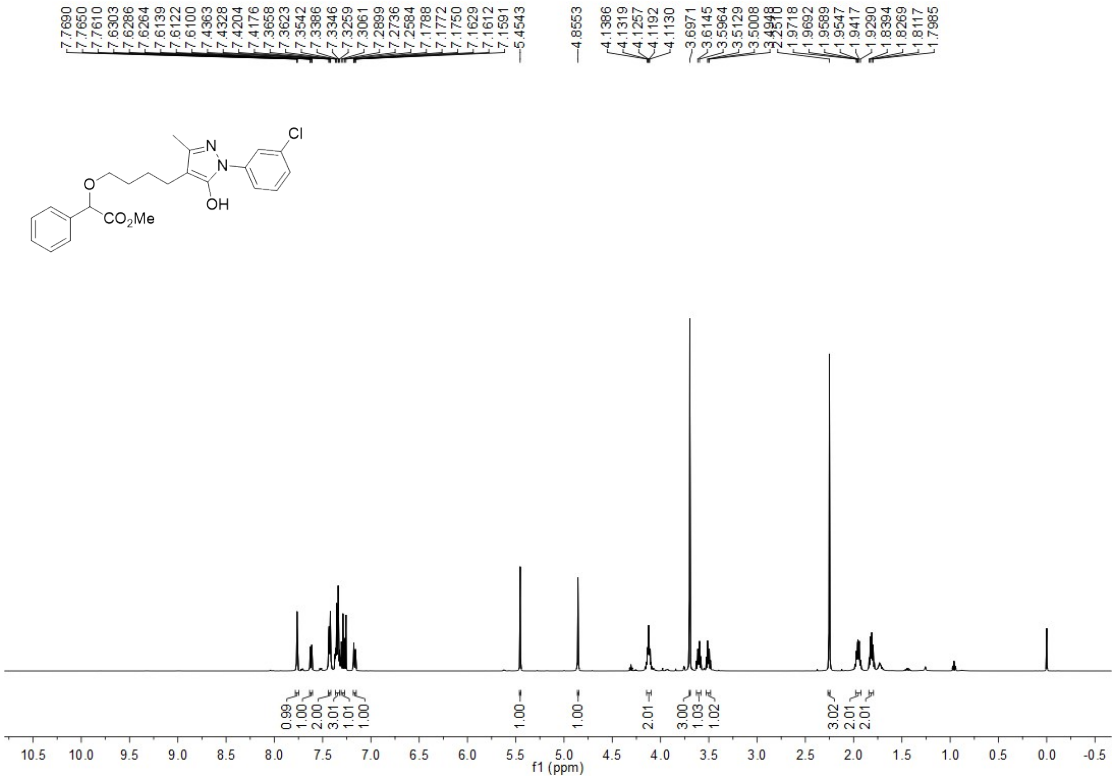
4v ^{1}H NMR (400 MHz, $CDCl_3$)



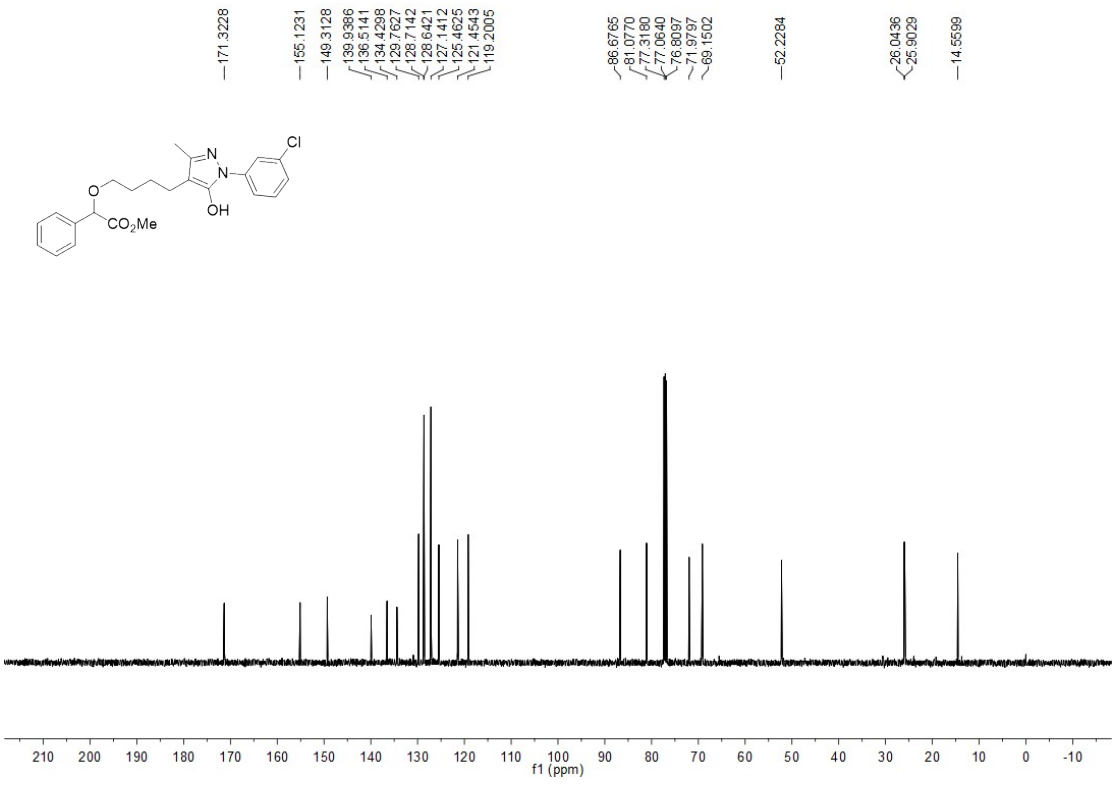
4v ^{13}C NMR (100 MHz, $CDCl_3$)



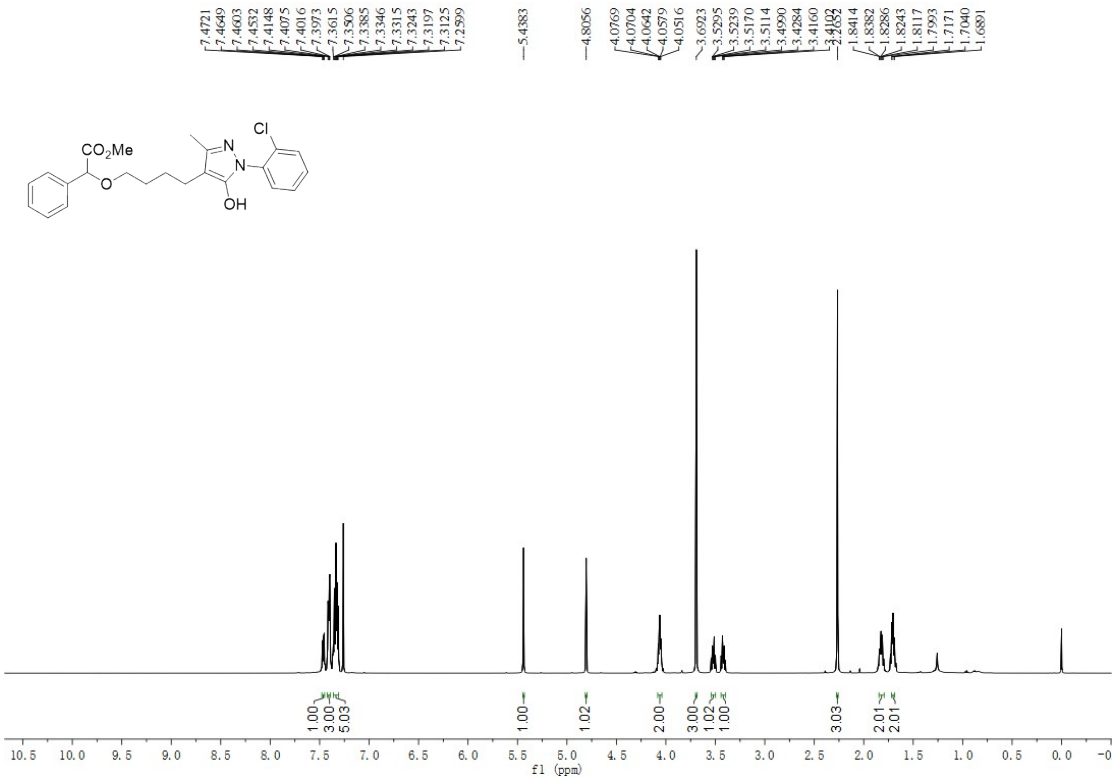
4w ^{1}H NMR (500 MHz, $CDCl_3$)



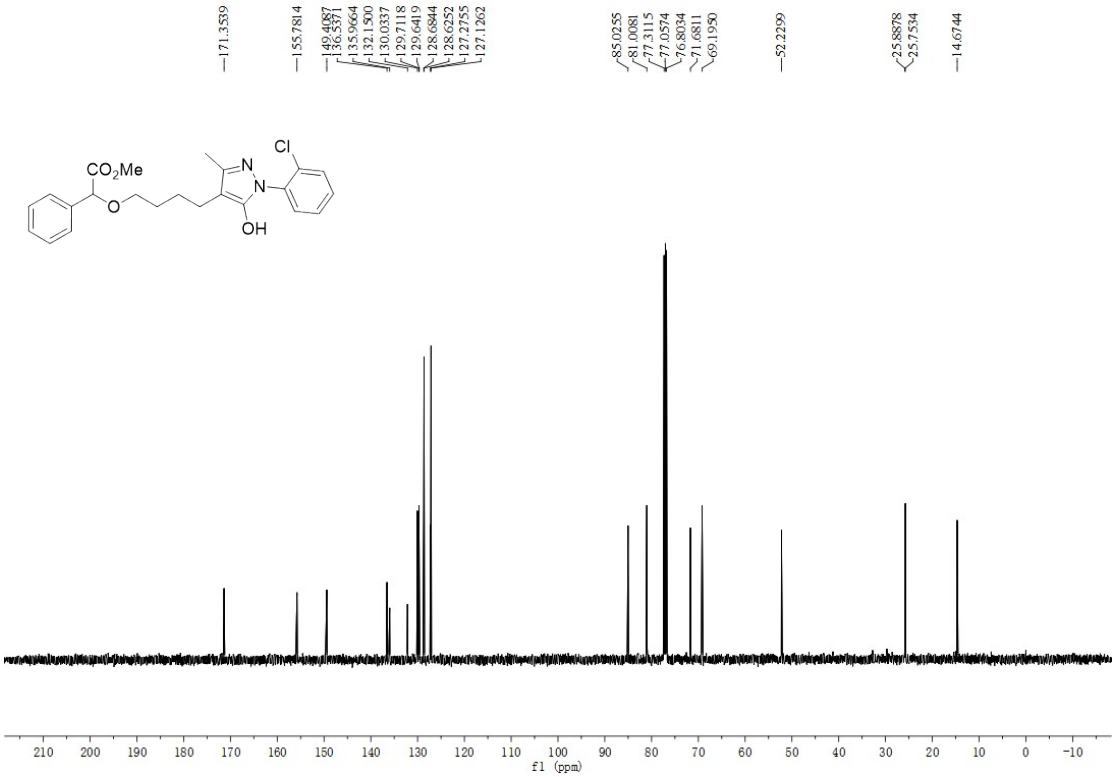
4w ^{13}C NMR (125 MHz, $CDCl_3$)



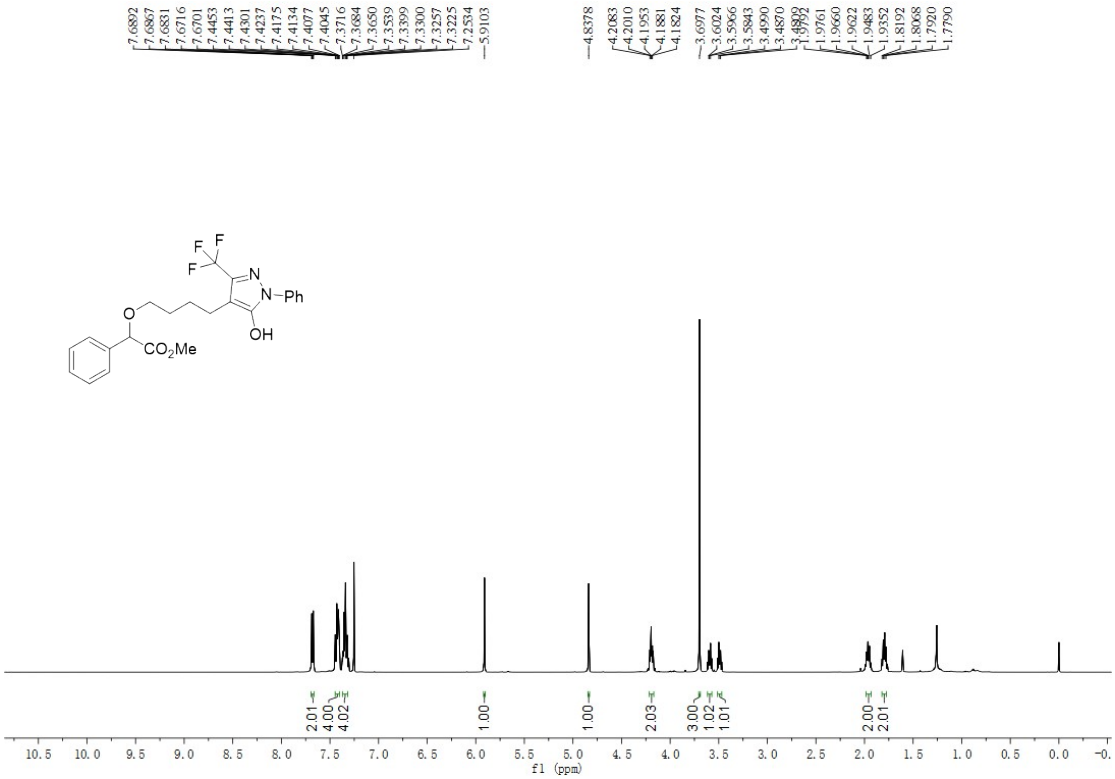
4x ^{1}H NMR (500 MHz, $CDCl_3$)



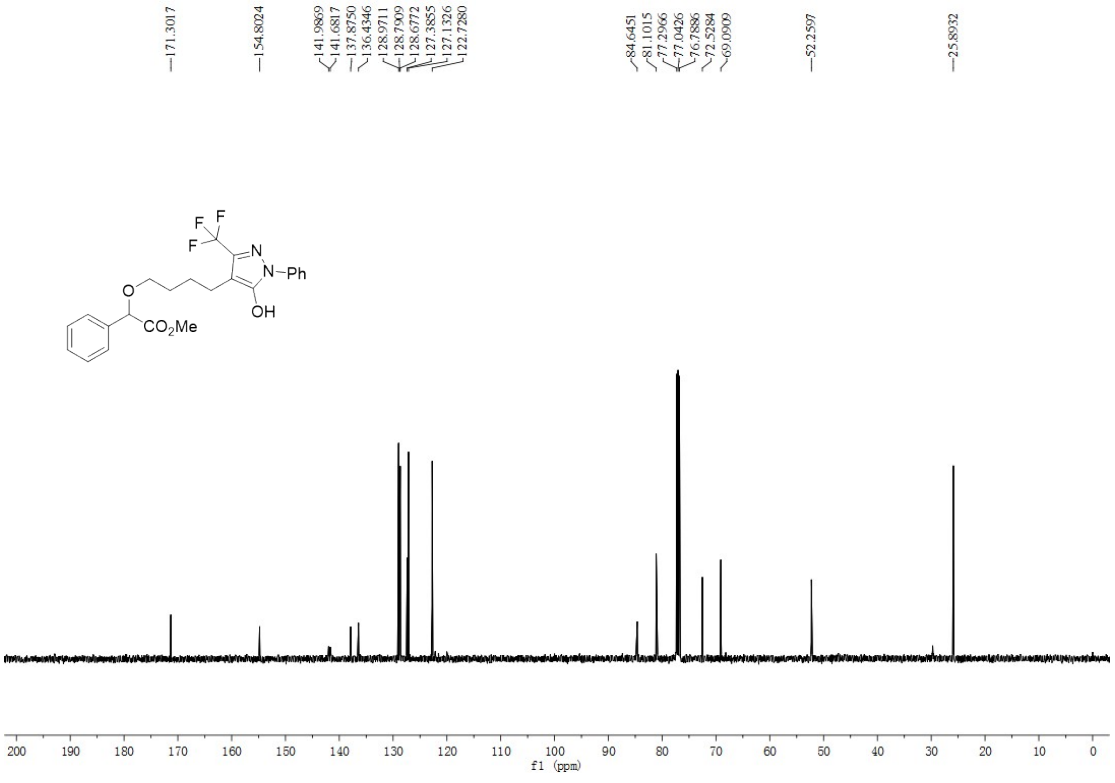
4x ^{13}C NMR (125 MHz, $CDCl_3$)



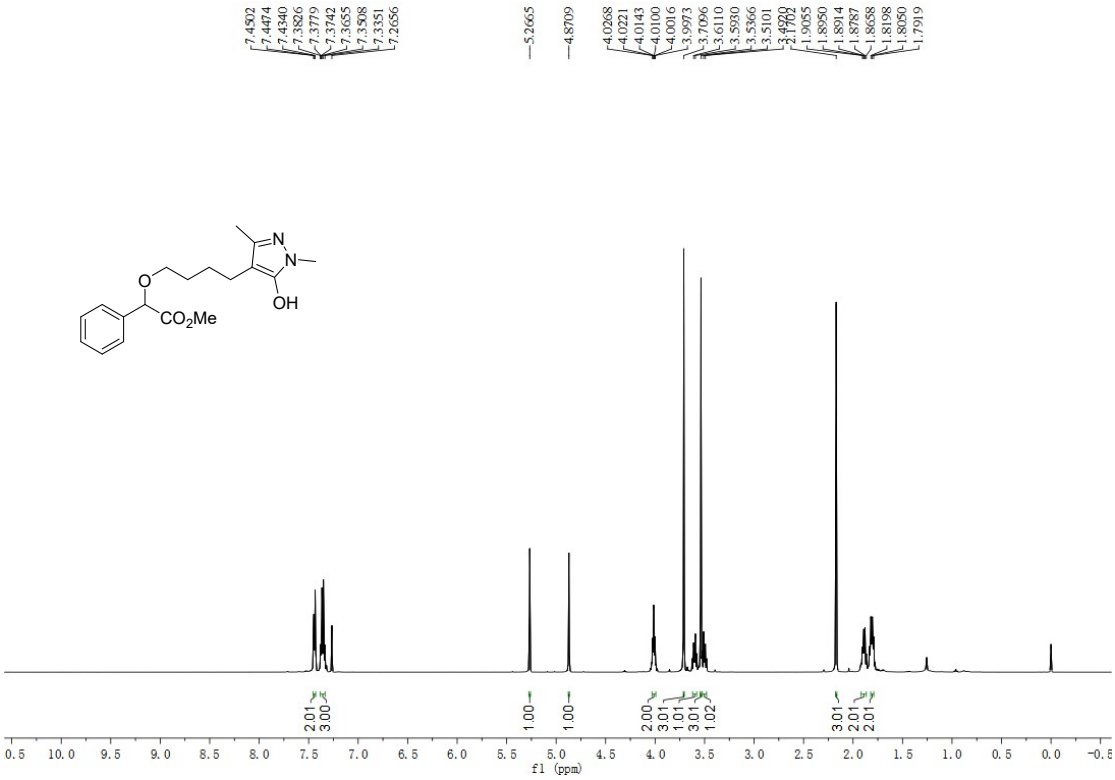
4y ^{1}H NMR (500 MHz, $CDCl_3$)



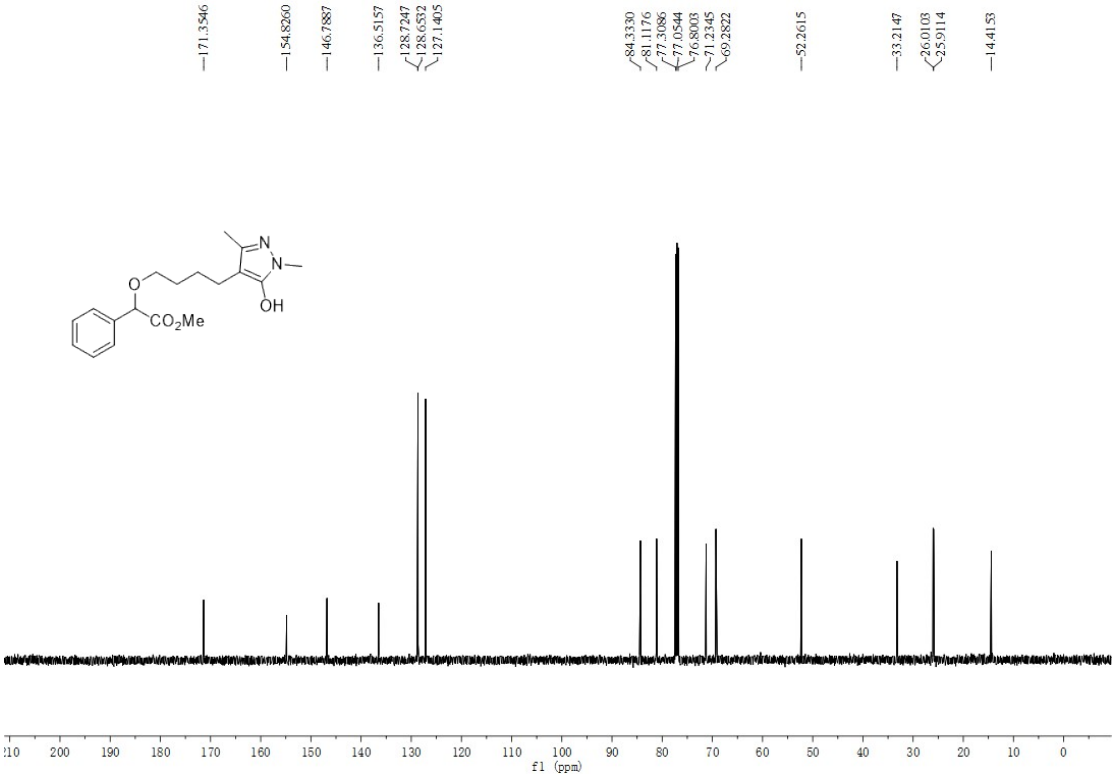
4y ^{13}C NMR (125 MHz, $CDCl_3$)



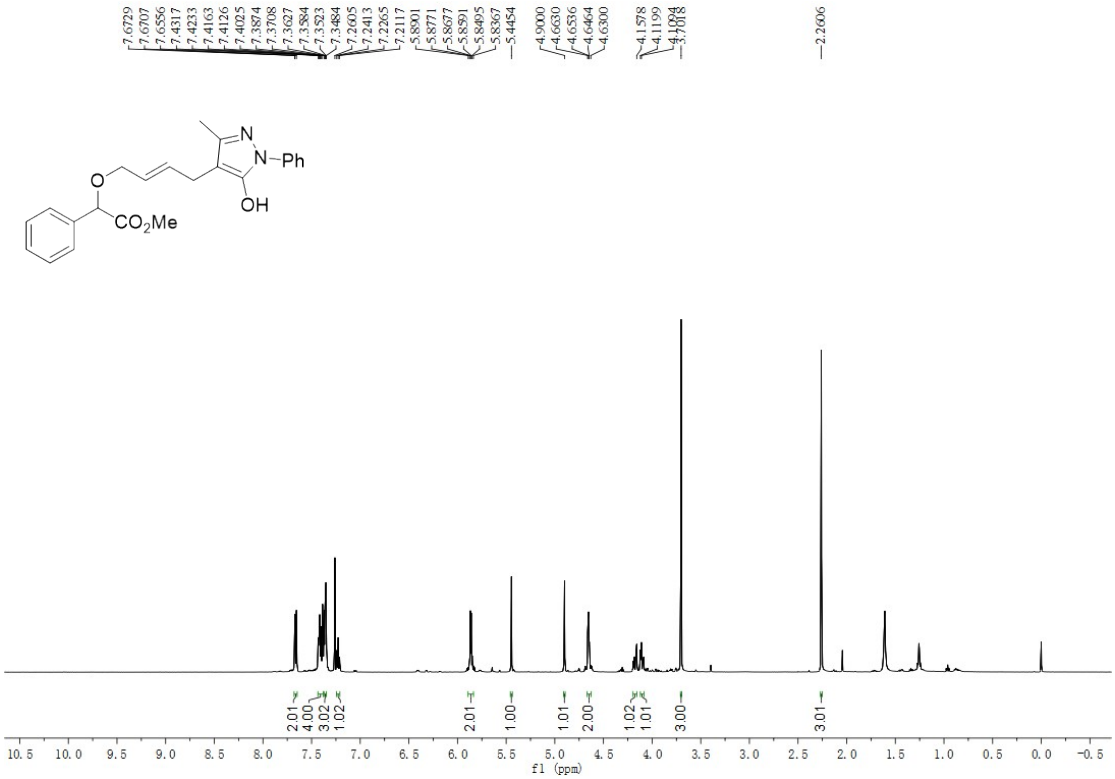
4z ^{1}H NMR (500 MHz, $CDCl_3$)



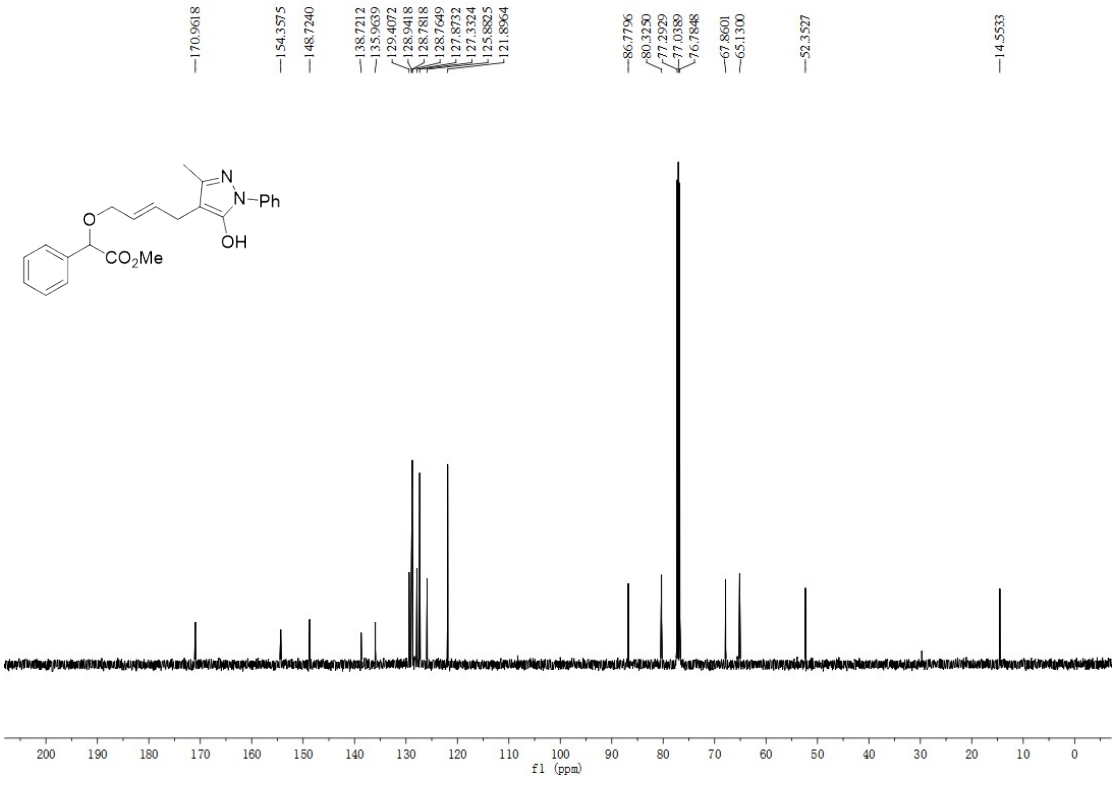
4z ^{13}C NMR (125 MHz, $CDCl_3$)



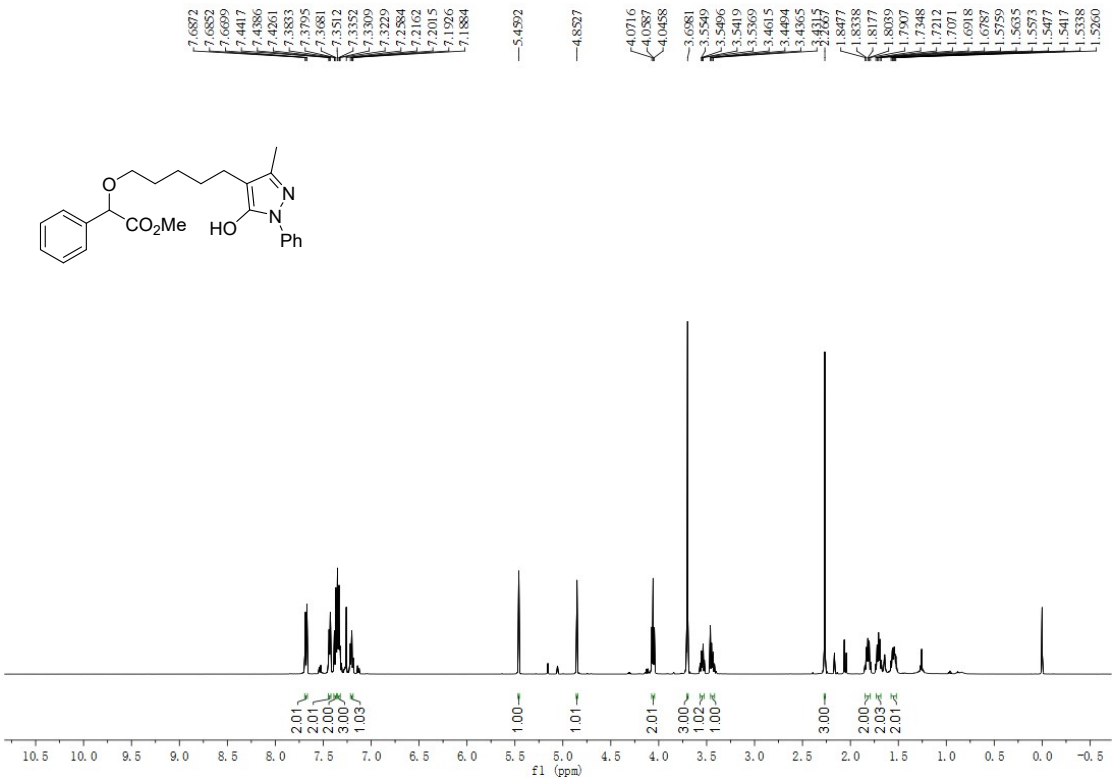
4z' ^{1}H NMR (500 MHz, $CDCl_3$)



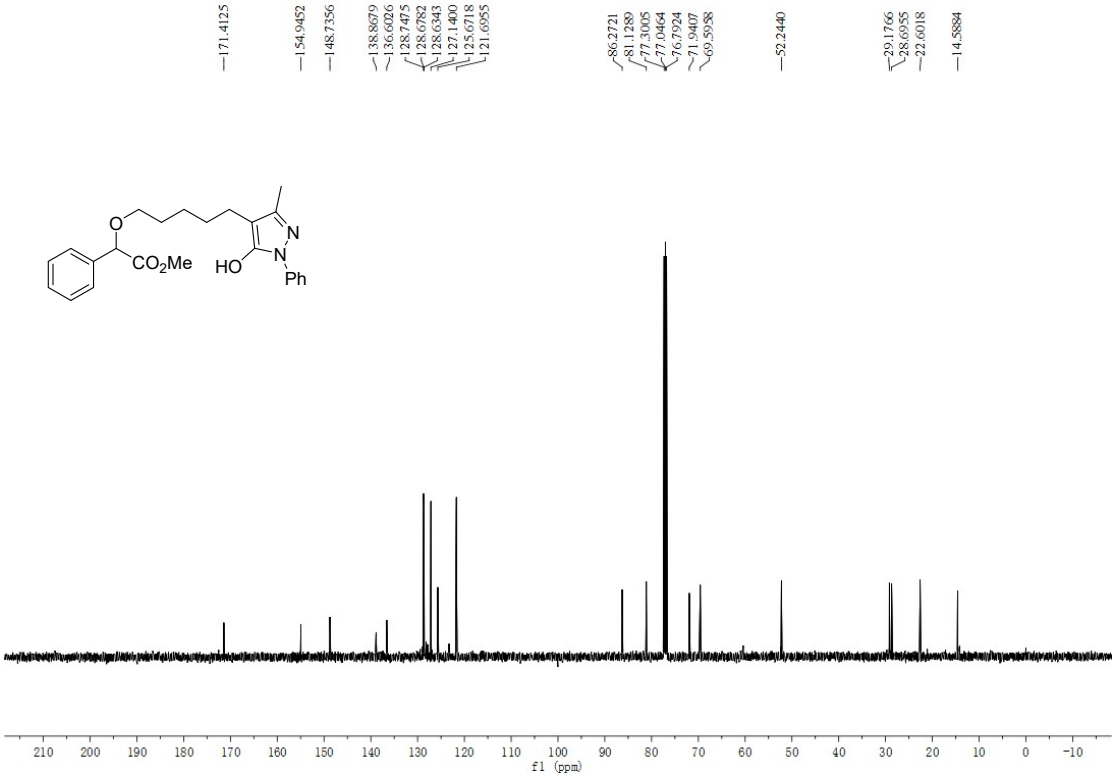
4z' ^{13}C NMR (125 MHz, $CDCl_3$)



4z'' ^{1}H NMR (500 MHz, $CDCl_3$)

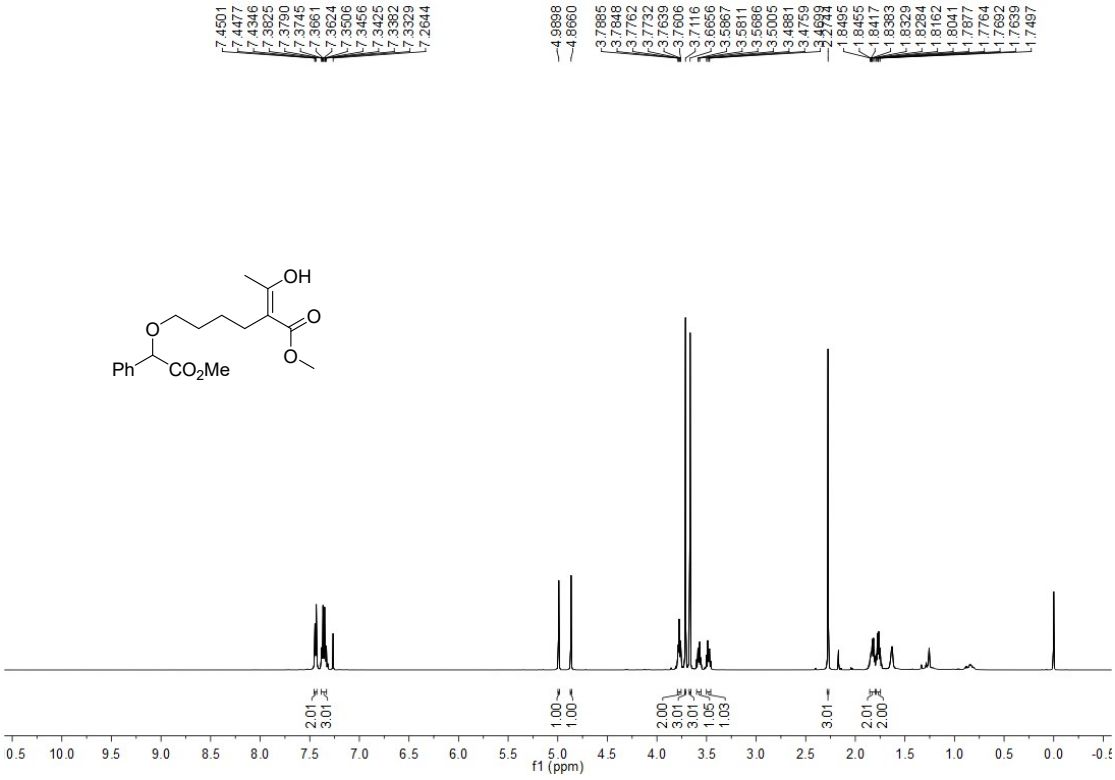


4z'' ^{13}C NMR (125 MHz, $CDCl_3$)

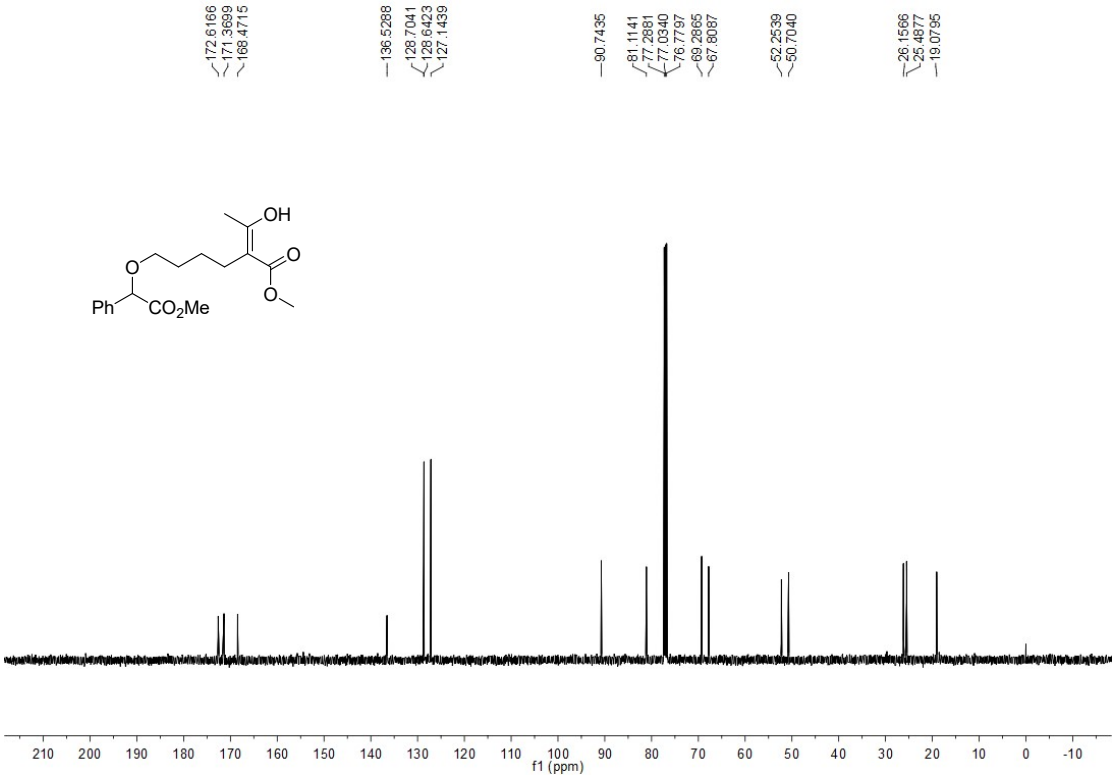


5.2 Copies of NMR spectra for 6a−6j

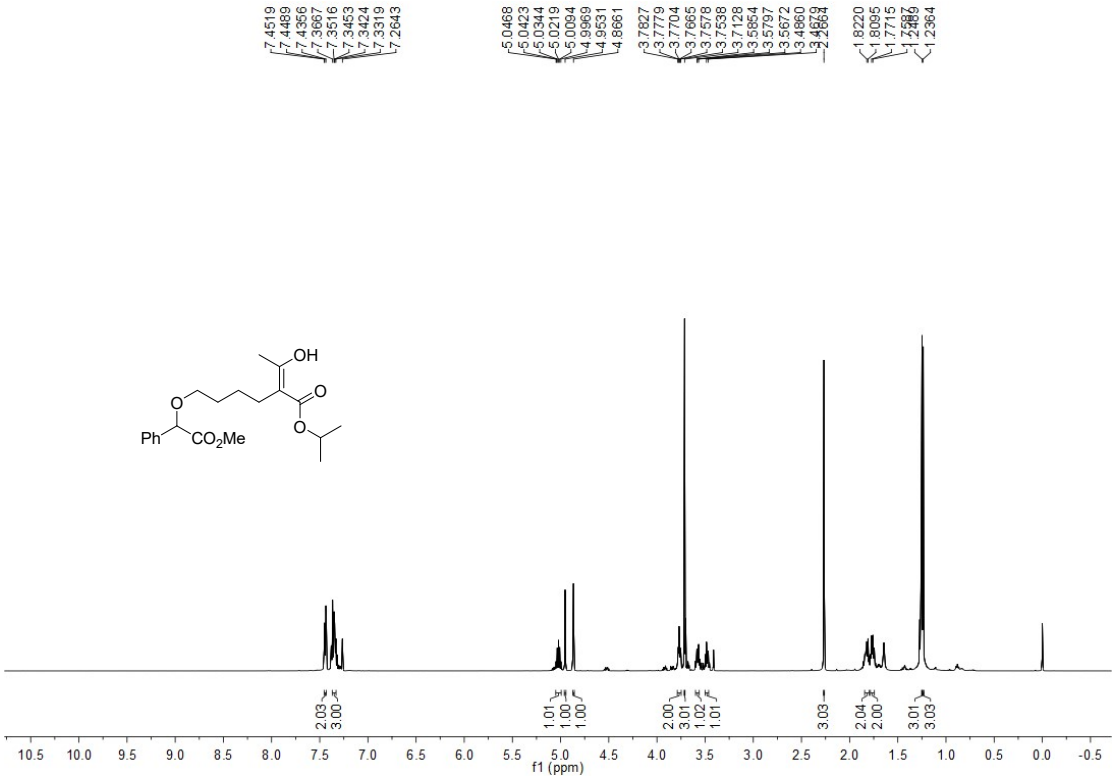
6a ^{1}H NMR (500 MHz, $CDCl_3$)



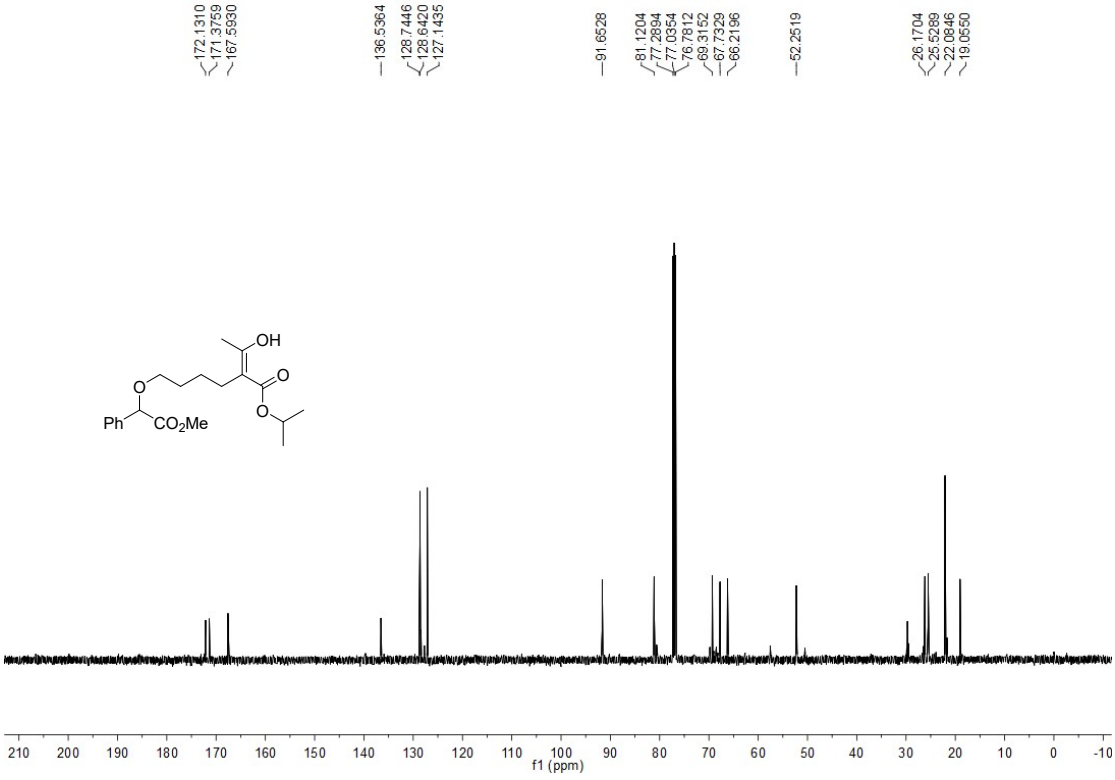
6a ^{13}C NMR (125 MHz, $CDCl_3$)



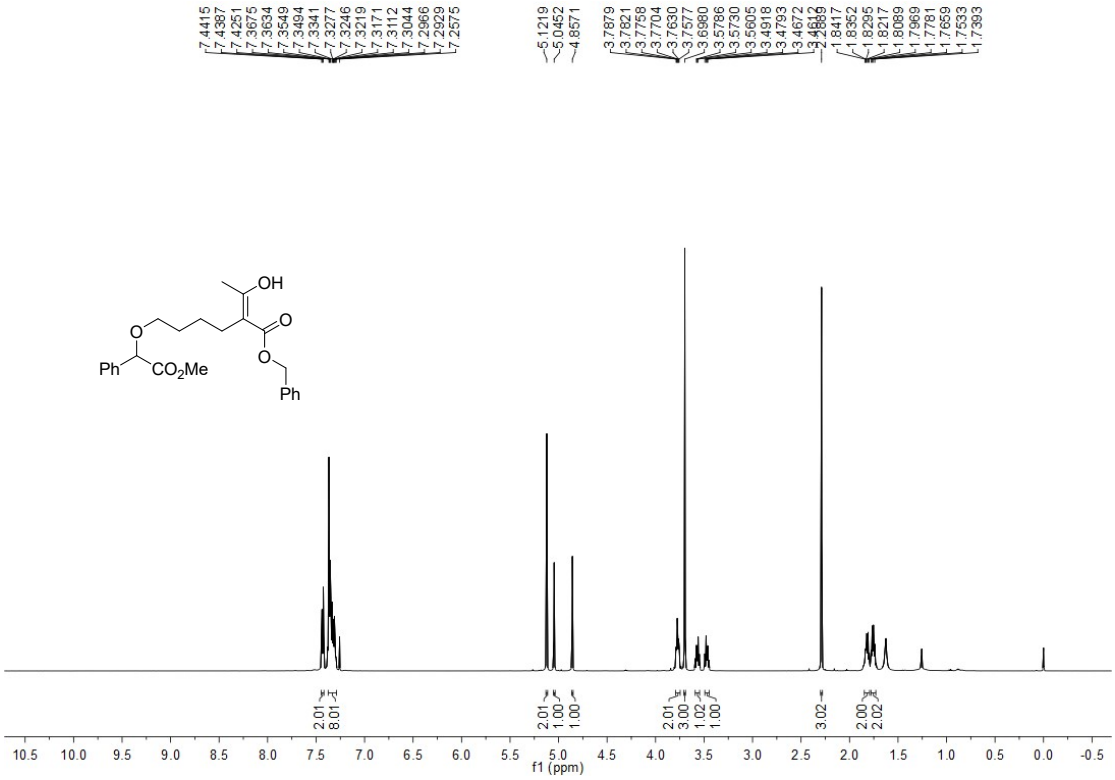
6b ^{1}H NMR (500 MHz, $CDCl_3$)



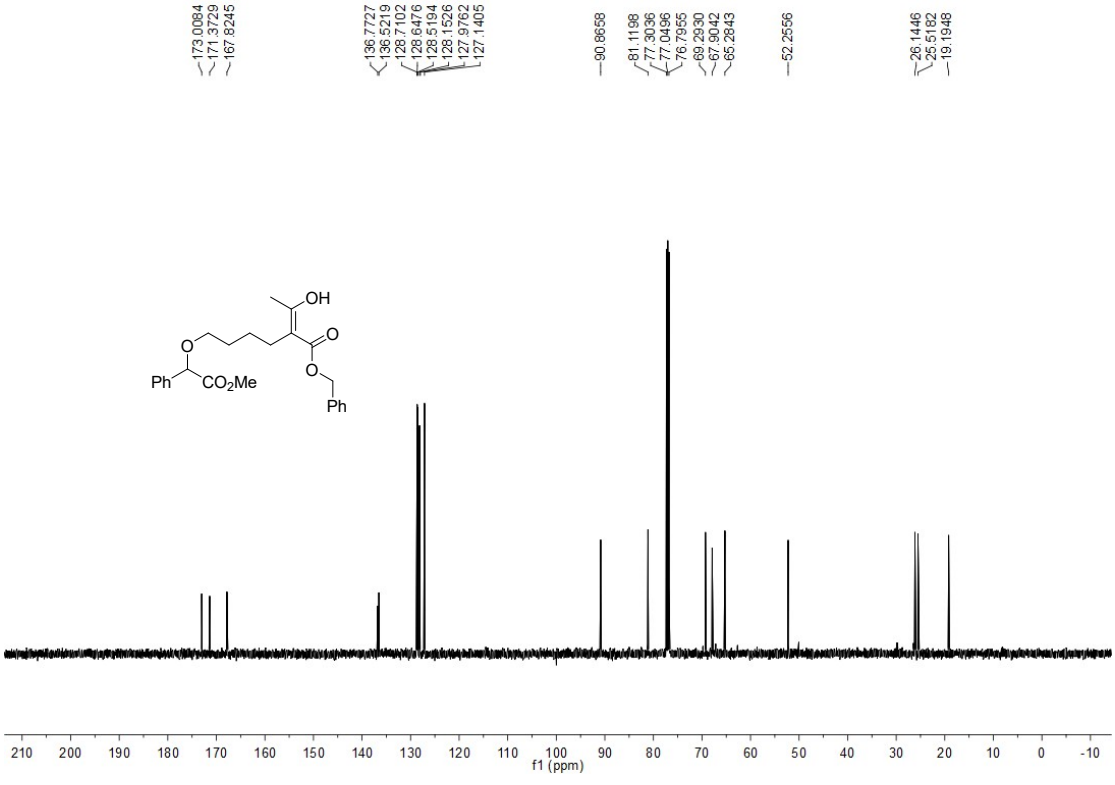
6b ^{13}C NMR (125 MHz, $CDCl_3$)



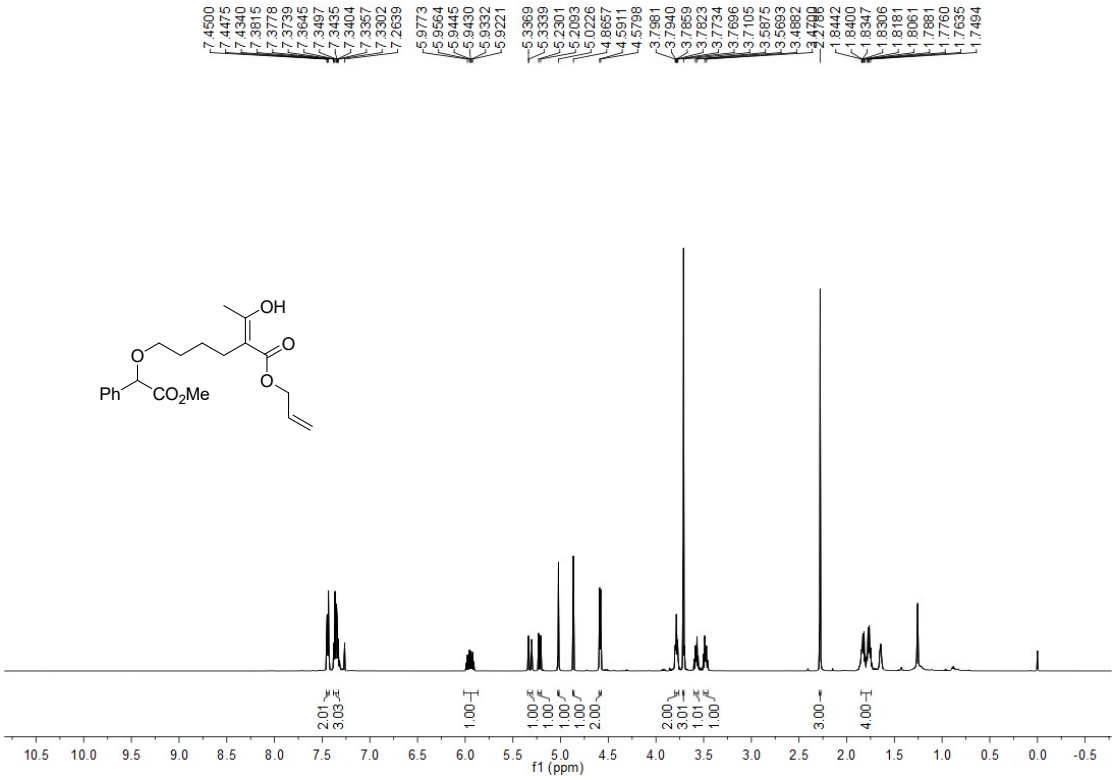
6c ^{1}H NMR (500 MHz, $CDCl_3$)



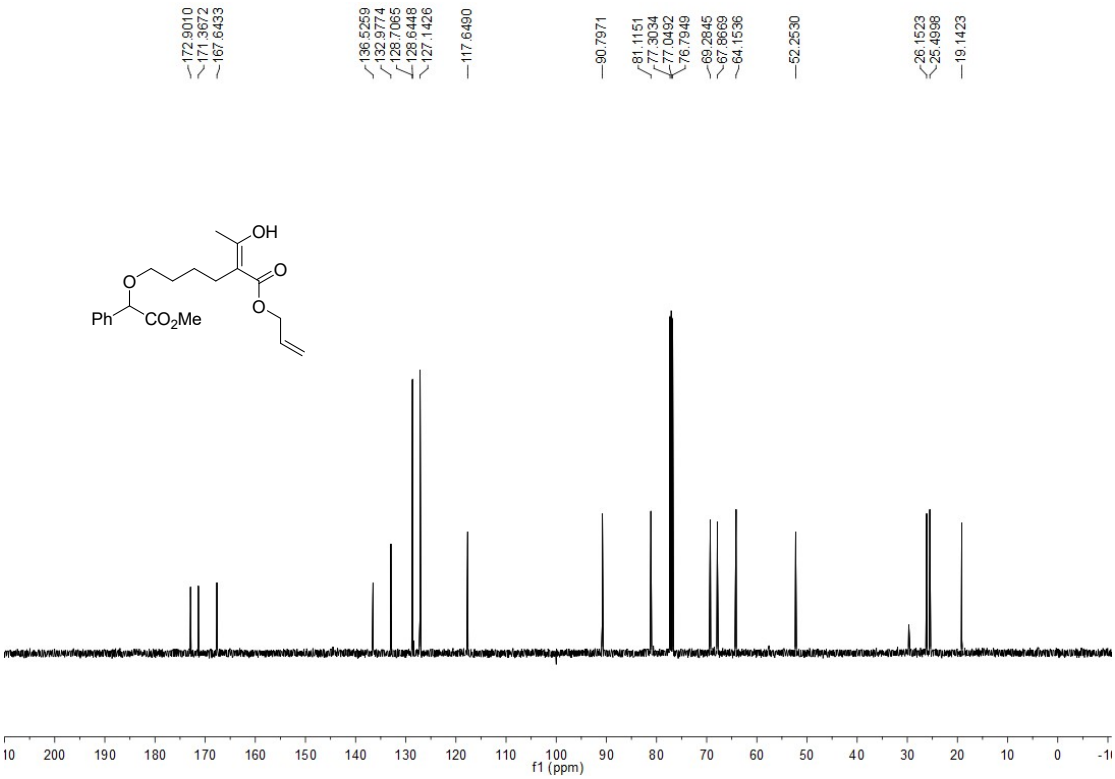
6c ^{13}C NMR (125 MHz, $CDCl_3$)



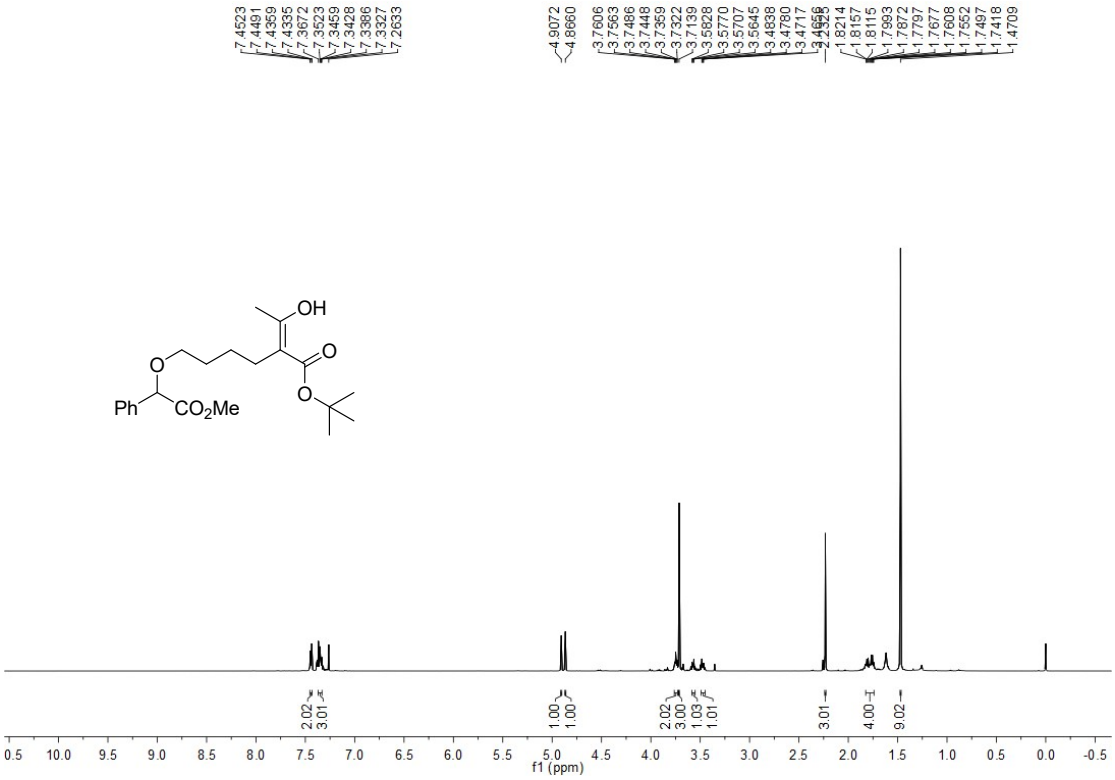
6d ^{1}H NMR (500 MHz, $CDCl_3$)



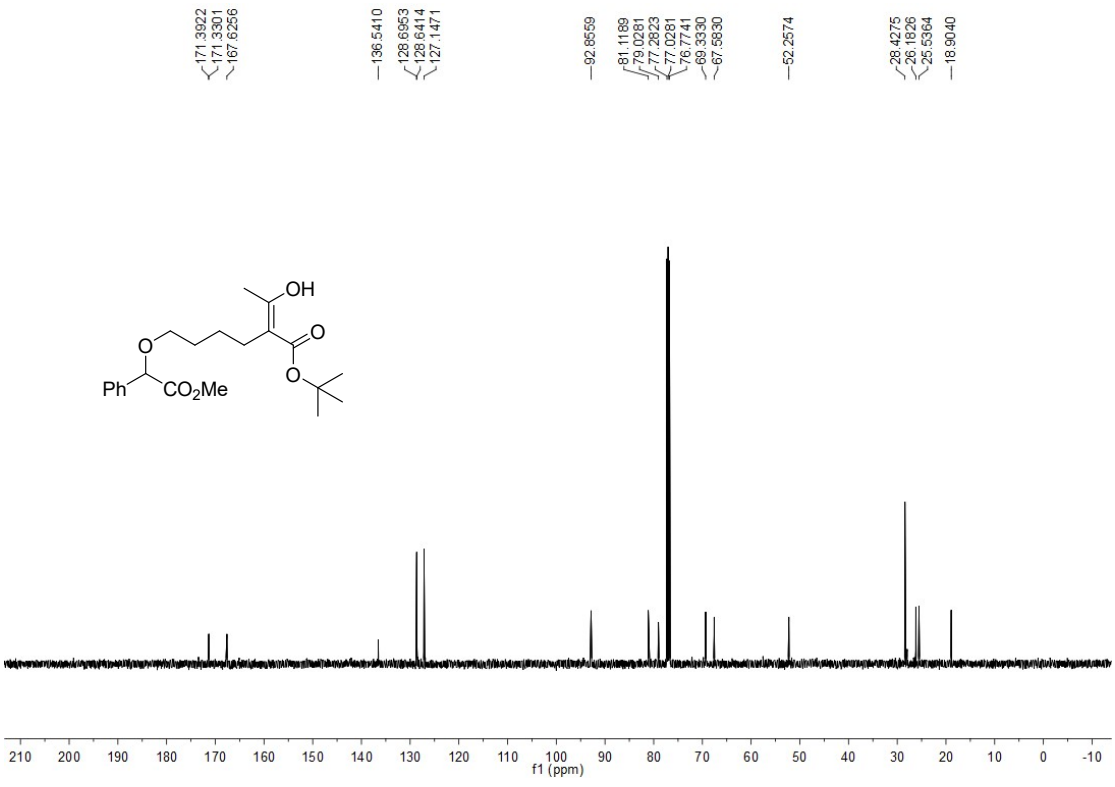
6d ^{13}C NMR (125 MHz, $CDCl_3$)



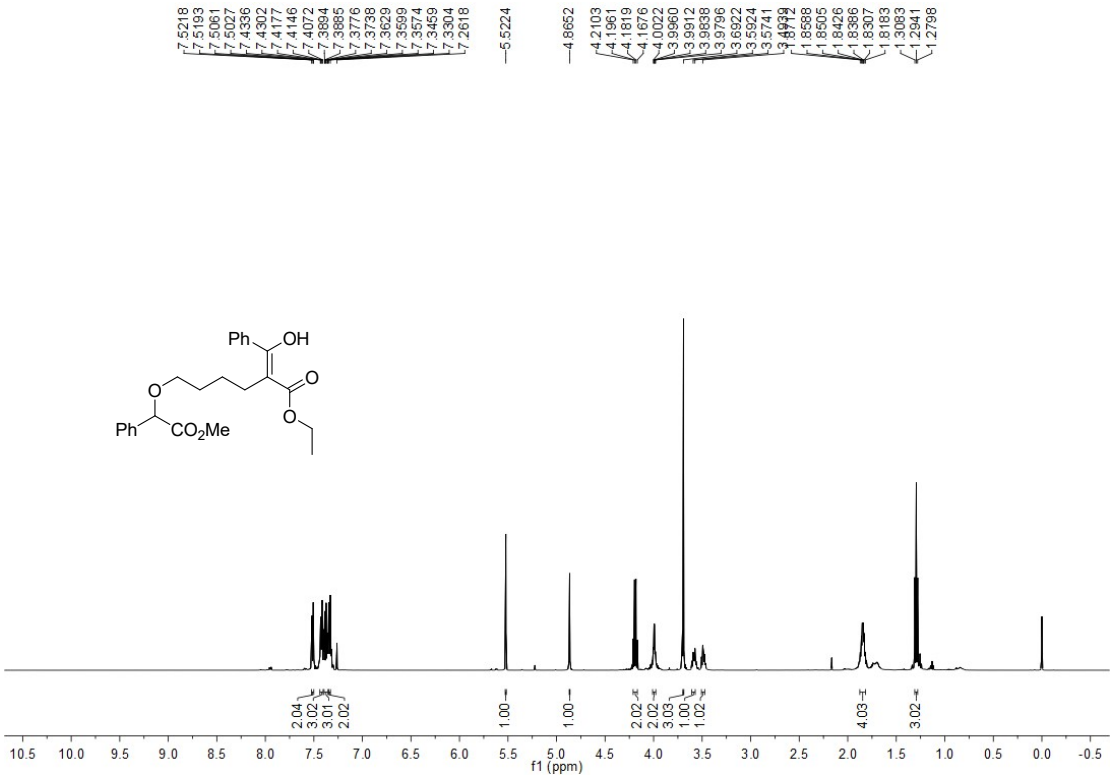
6e ^{1}H NMR (500 MHz, $CDCl_3$)



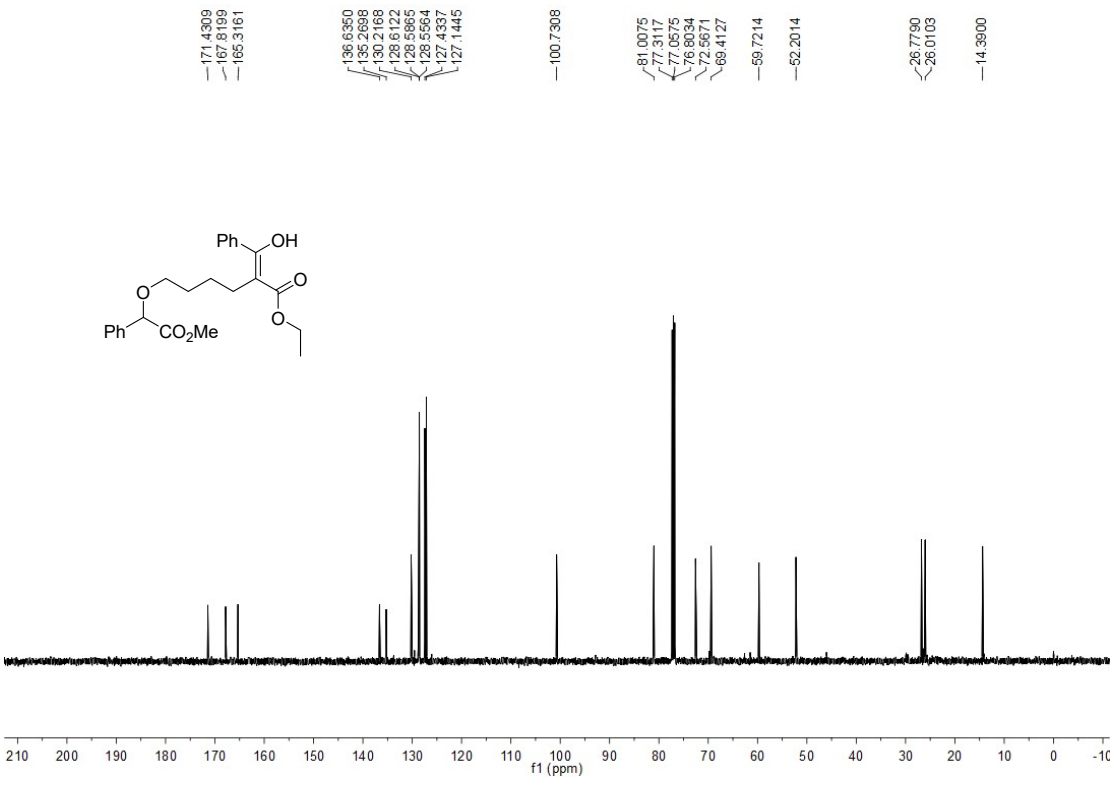
6e ^{13}C NMR (125 MHz, $CDCl_3$)



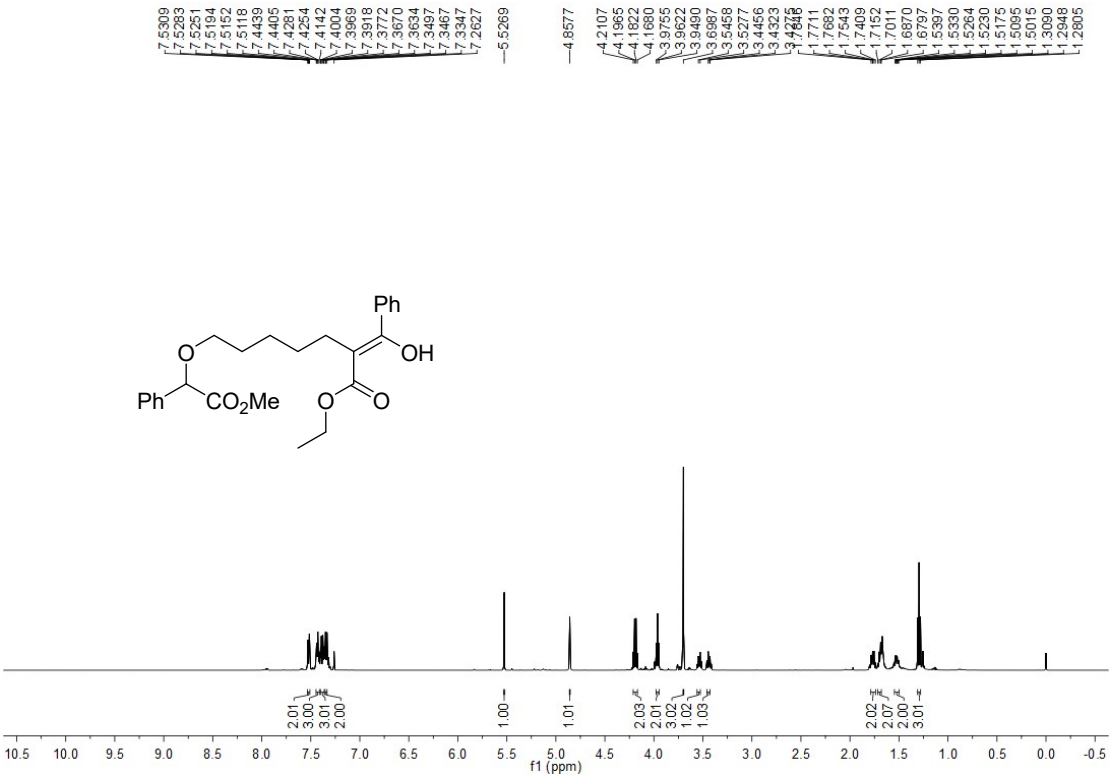
6f ^{1}H NMR (500 MHz, $CDCl_3$)



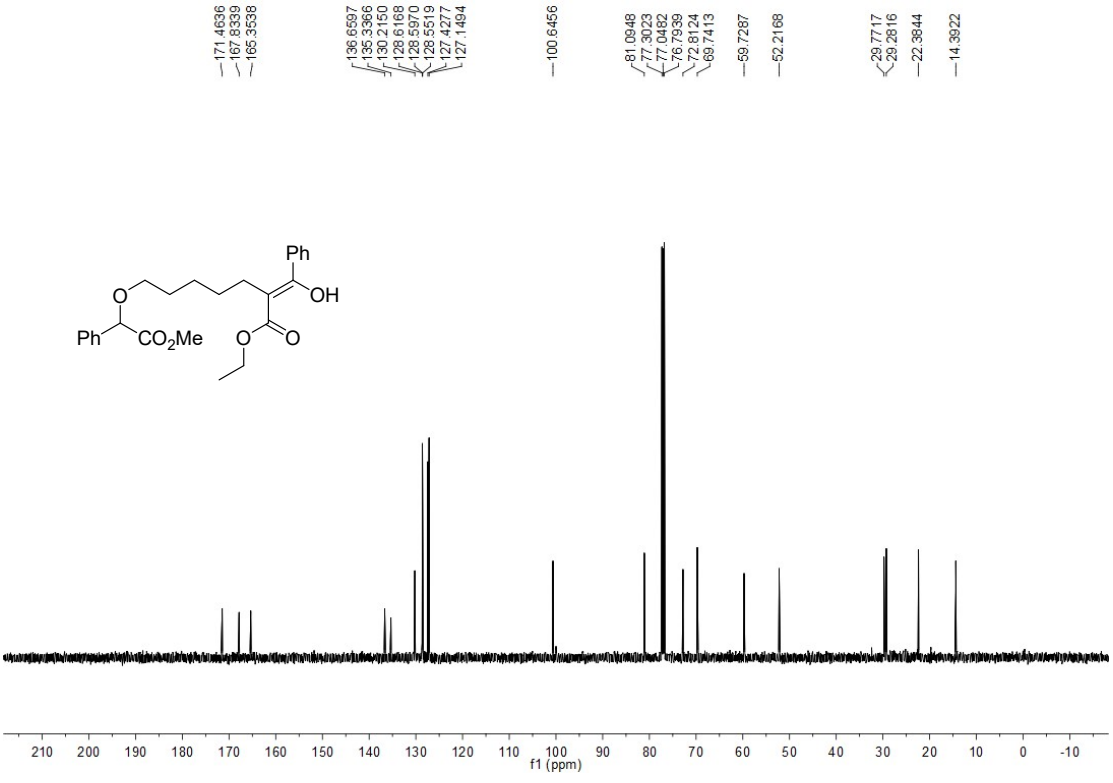
6f ^{13}C NMR (125 MHz, $CDCl_3$)



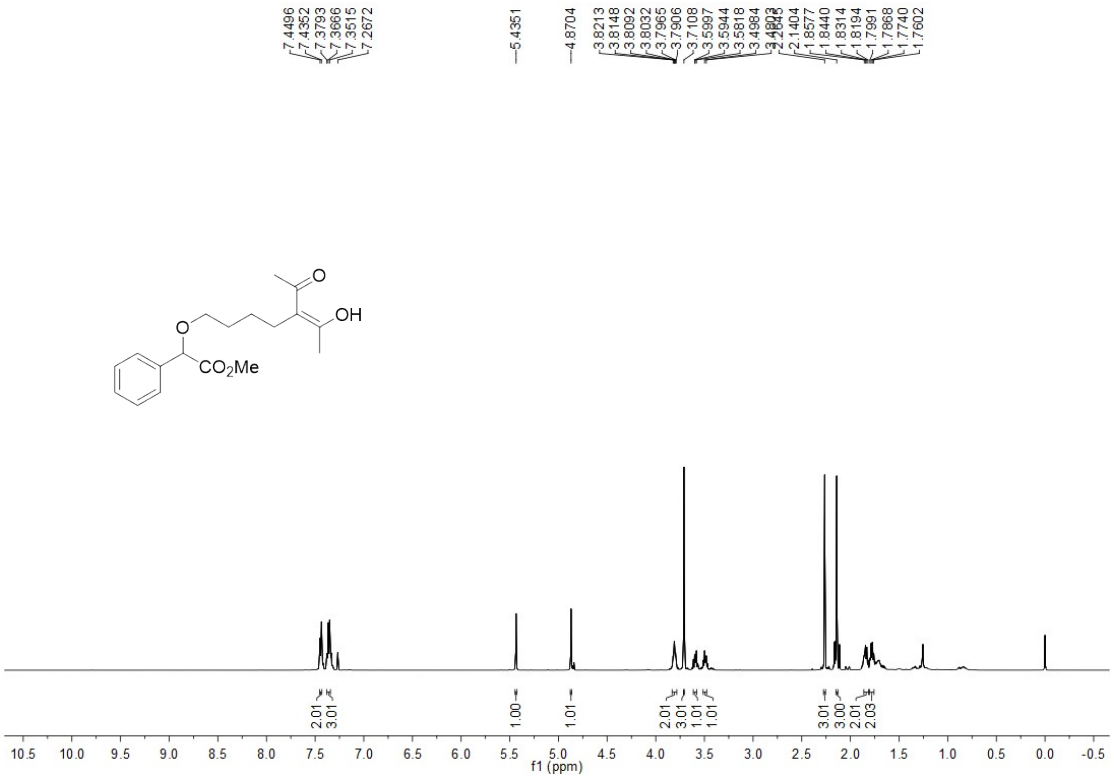
6g ^{1}H NMR (500 MHz, $CDCl_3$)



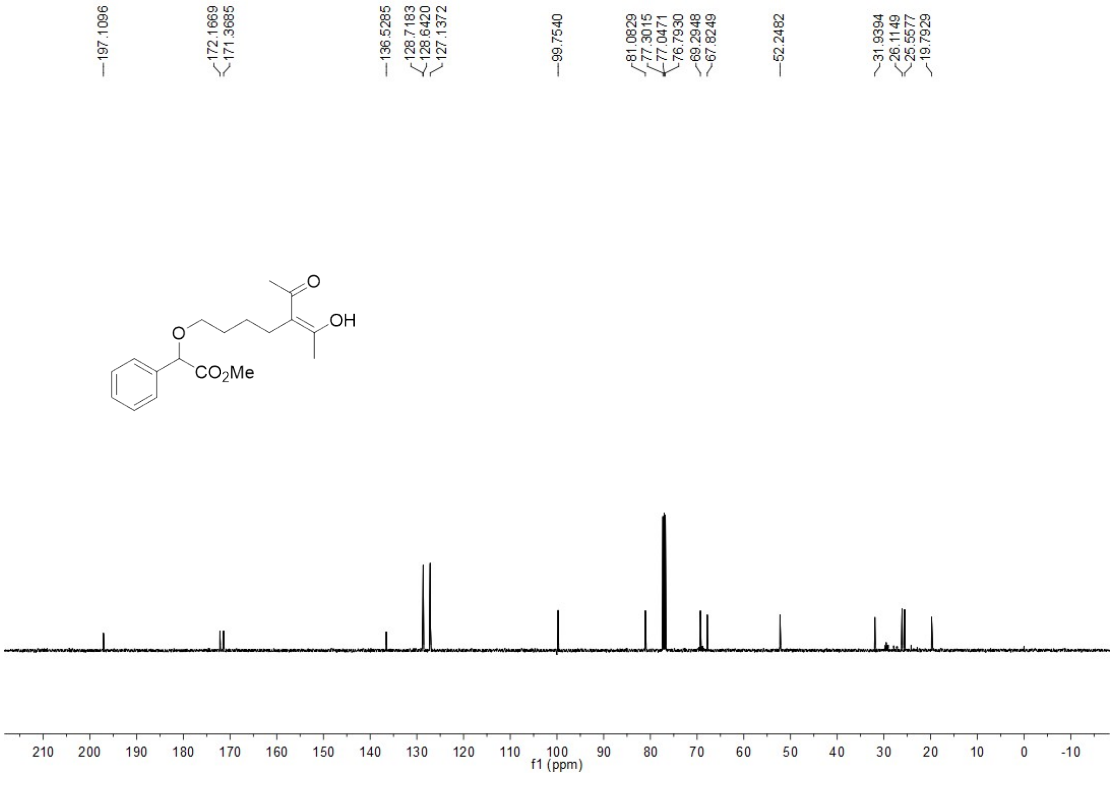
6g ^{13}C NMR (125 MHz, $CDCl_3$)



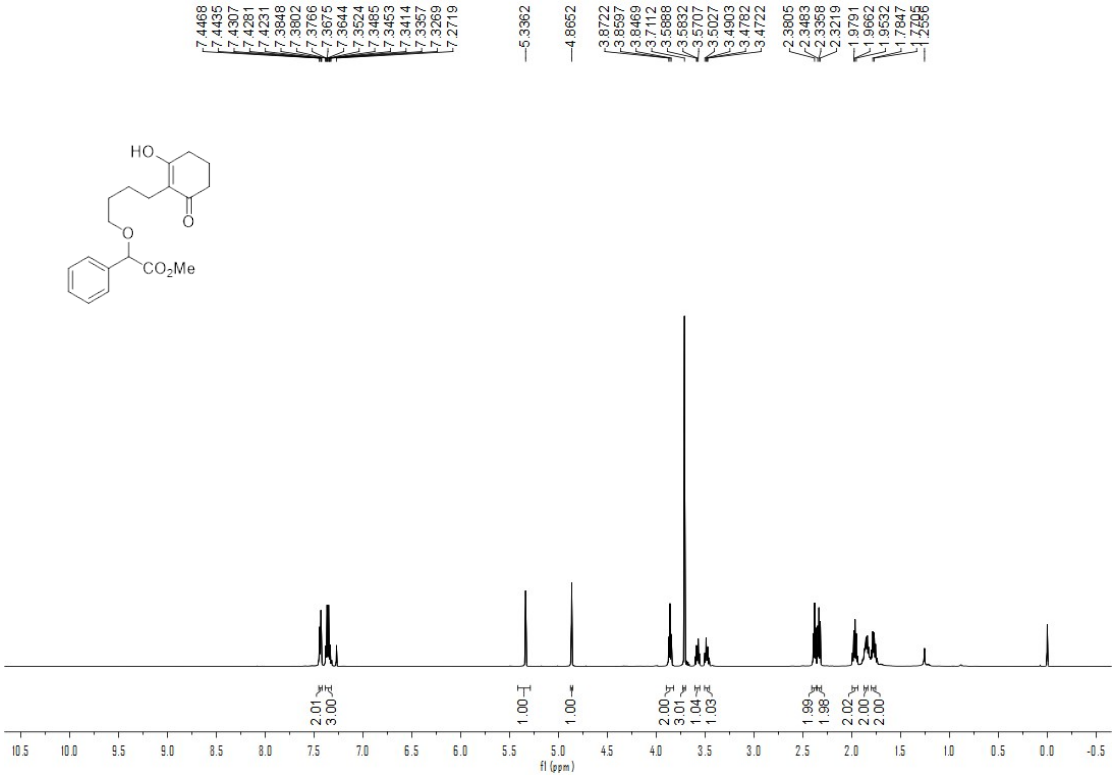
6h ^{1}H NMR (500 MHz, $CDCl_3$)



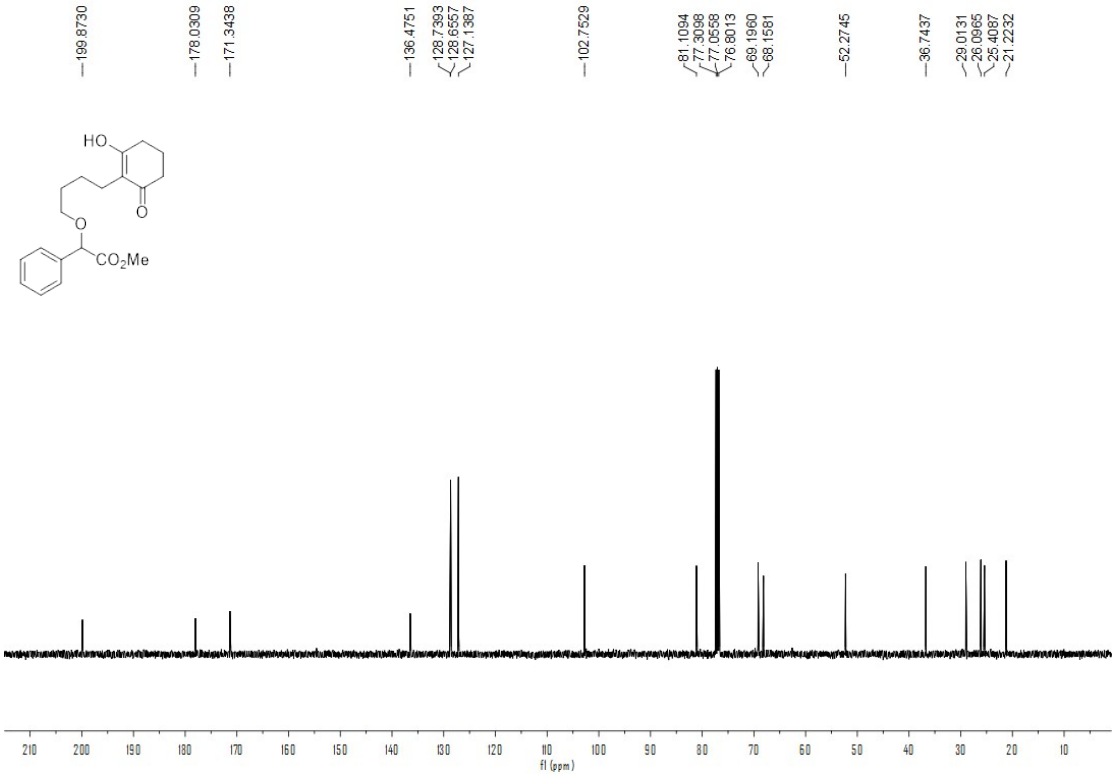
6h ^{13}C NMR (125 MHz, $CDCl_3$)



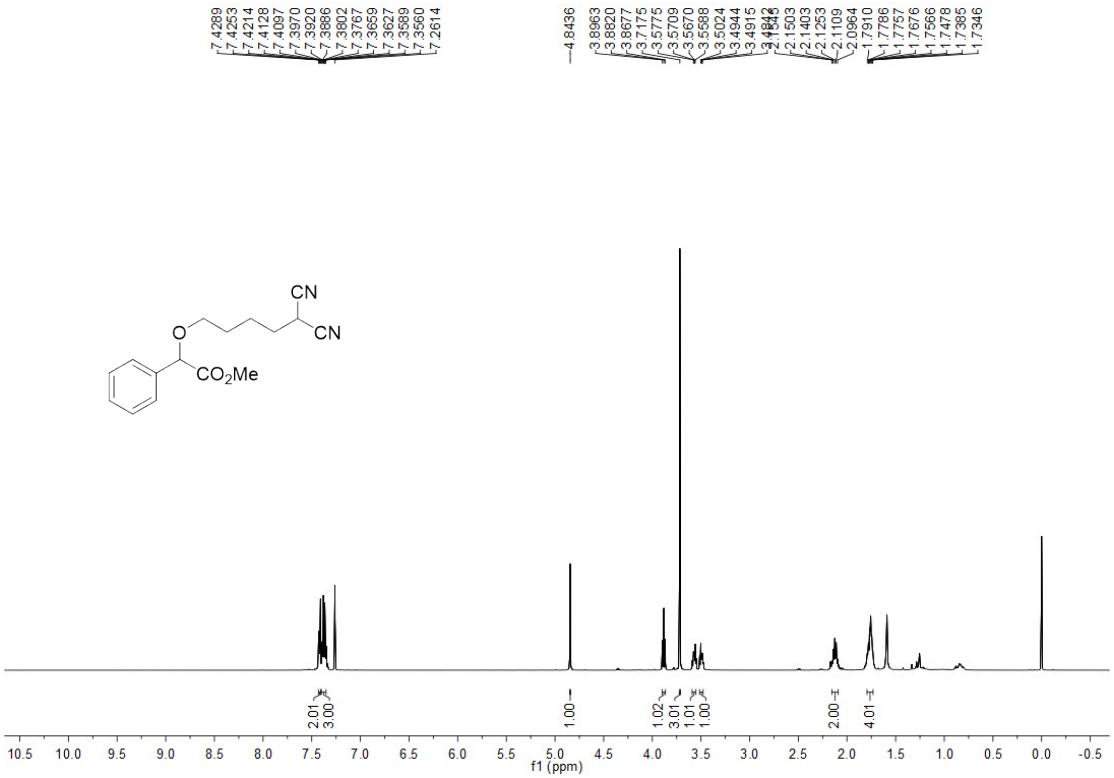
6i ^{1}H NMR (500 MHz, $CDCl_3$)



6i ^{13}C NMR (125 MHz, $CDCl_3$)



6k ^{1}H NMR (500 MHz, $CDCl_3$)



6i ^{13}C NMR (125 MHz, $CDCl_3$)