Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Diazenylation of active methyne compounds via arylazo sulfones†

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General Information

All glassware was oven dried at 100 ºC for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Purification of reaction products was carried out by flash chromatography on silica gel (200~300 mesh). ^{1}H NMR spectra were recorded at 500 or 400 MHz, ^{13}C NMR spectra were recorded at 125 or 100 MHz, and in $CDCl_3$ or DMSO-d_6 (containing 0.03% TMS) solutions with Bruker Advance III spectrometers. ^{1}H NMR spectra were recorded with Me_4Si (δ = 0.00), $CDCl_3$ (δ = 7.26) or DMSO-d_6 (δ = 2.50) as the internal reference, and ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.16) or DMSO-d_6 (δ = 39.52) as the internal reference. High-resolution mass spectra were obtained using a Bruker Maxis Impact mass spectrometer with a TOF (for ESI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers with molybdenum cathodes.

All the starting materials **1**, **2** and **4** could be obtained from commercial sources or synthesized according to literature methods (>95% purity).[1-7] β-Keto ester **1**,[1,2] arylazo sulfones **2**,[3] cyclic 1,3-ketoester **4a**,[4] **4b**,[5] **4c**,[5] **4d**,[6] **4e**[4] and **4f**[7] were easily prepared according to the references, and their analytical data were consistent with that previously reported.

X-ray crystal structure of 3c

The displacement ellipsoids are drawn at the 50% probability level. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the mixed solution of THF/petroleum ether (1/10, v/v). Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the number CCDC 2325997 (**3c**) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

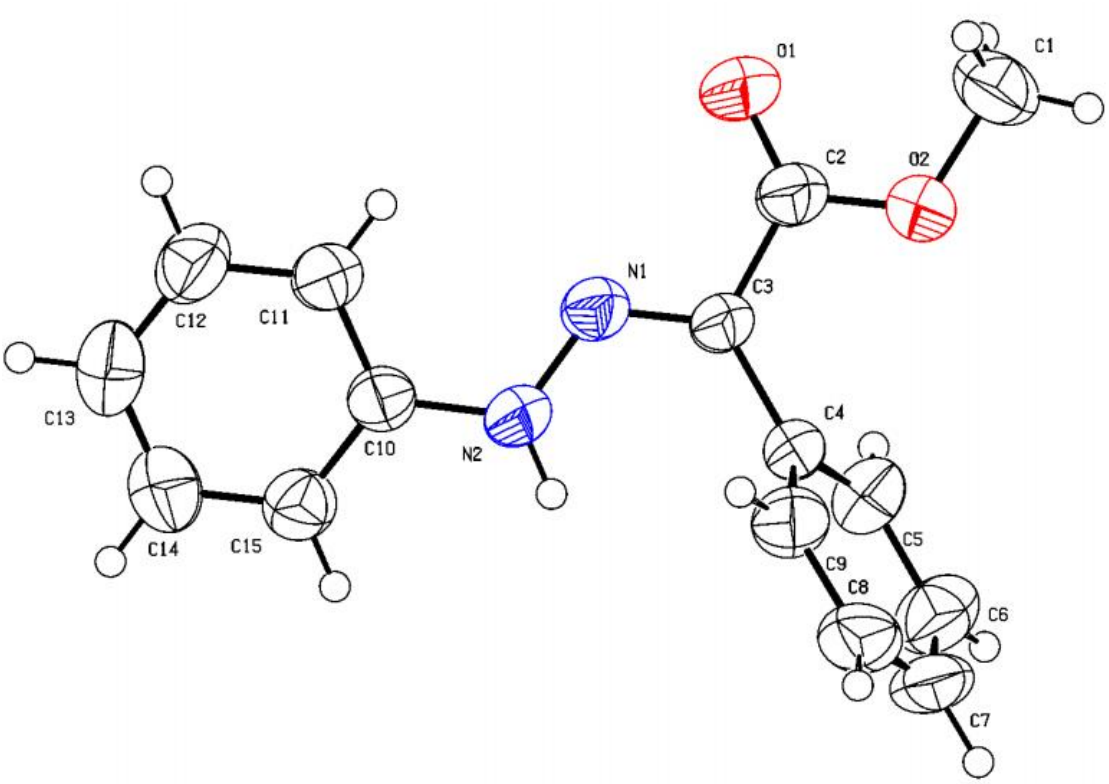
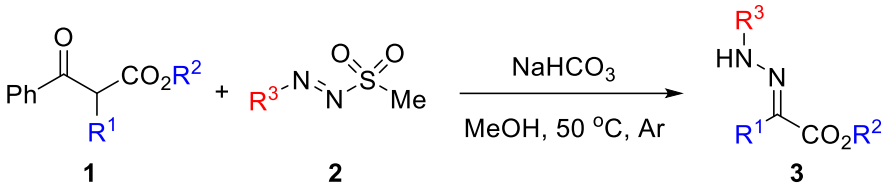


Figure S1. X-ray ORTEP illustration of methyl (E)-2-phenyl-2-(2-phenylhydrazono)acetate (**3c**) (50% probability ellipsoids)

Table S1. Crystal data and structure refinement for **3c**.

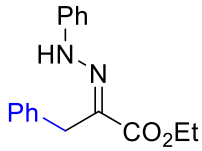
Identification code	240117_zyl1_0m	
Empirical formula	C15 H14 N2 O2	
Formula weight	254.28	
Temperature	273 K	
Wavelength	0.71076 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 15.000(2) Å	α= 90 °
	b = 9.0818(13) Å	β= 90 °
	c = 19.698(3) Å	γ = 90 °
Volume	2683.5(6) $Å^3$	
Z	8	
Density (calculated)	1.259 mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	1072	
Theta range for data collection	2.474 to 19.729 °	
Index ranges	-18<=h<=16, -11<=k<=10, -24<=l<=24	
Reflections collected	20275	
Independent reflections	2749 [R(int) = 0.1411]	
Completeness to theta = 25.242 °	100 %	
Max. and min. transmission	1.00 and 1.00	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2749 / 0 / 173	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1411	
R indices (all data)	R1 = 0.1849, wR2 = 0.1911	
Largest diff. peak and hole	0.239 and -0.277 $e.Å^{-3}$	

General procedure for the synthesis of 3



In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), $NaHCO_3$ (42.0 mg, 0.5 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under Ar, MeOH (4 mL) was added, and the mixture was stirred in the 50 °C oil bath for 4-14 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The pure product was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 7:1-20:1).

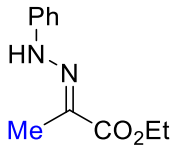
Detail descriptions for products 3



3a

Ethyl (E)-3-phenyl-2-(2-phenylhydrazineylidene)propanoate (3a)[8]

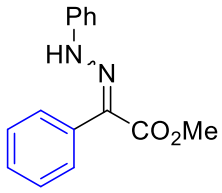
Compound **3a** was prepared in 92% yield (52 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 20/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.26-7.23 (m, 2H), 7.18-7.15 (m, 5H), 6.98 (d, J = 8.0 Hz, 2H), 6.88-6.85 (m, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.95 (s, 2H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 143.1, 135.2, 133.9, 129.4, 128.1, 127.2, 122.3, 114.1, 61.5, 31.2, 14.5. Analytical data for **3a** was consistent with that previously reported.[8]



3b

Ethyl (E)-2-(2-phenylhydrazineylidene)propanoate (3b)[9]

Compound **3b** was prepared in 80% yield (33 mg) according to the general procedure; R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 118-119 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.31-7.28 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.98-6.95 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.11 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 143.4, 132.6, 129.4, 122.1, 114.2, 61.3, 14.4, 10.4. Analytical data for **3b** was consistent with that previously reported.[9]

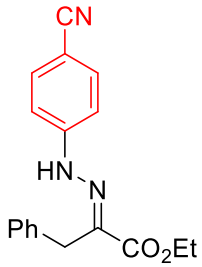


3c

Methyl 2-phenyl-2-(2-phenylhydrazineylidene)acetate (3c)[10]

Compound **3c** was prepared in 96% yield (49 mg, Z:E = 1.7:1) according to the general procedure. E isomer was prepared in 36% yield (18 mg); R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 107-108 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.57-7.54 (m, 2H), 7.51-7.48 (m, 1H), 7.35-7.34 (m, 2H), 7.29-7.26 (m, 2H), 7.14-7.12 (m, 2H), 6.98-6.95 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 142.7, 134.4, 129.9, 129.8, 129.7, 129.5, 129.2, 122.5, 114.3, 52.5. The analytical data was consistent with that previously reported.[10] Z isomer was prepared in 60% yield (31 mg); R_f = 0.2 (petroleum ether); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.41 (s, 1H), 7.67-7.65 (m, 2H), 7.41-7.38 (m, 2H), 7.36-7.29 (m, 5H), 7.03-7.00 (m, 1H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.3, 143.3, 136.6, 129.5, 128.8, 128.0, 127.8,

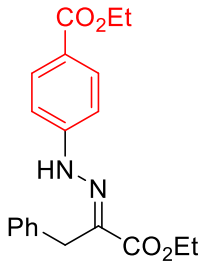
127.8, 122.7, 114.4, 51.8; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{15}H_{14}N_2NaO_2$ 277.0947, Found 277.0952.



3d

Ethyl (E)-2-(2-(4-cyanophenyl)hydrazineylidene)-3-phenylpropanoate (3d)[11]

Compound **3d** was prepared in 74% yield (45 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.48 (d, J = 8.8 Hz, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 3H), 7.07 (d, J = 8.7 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 4.02 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.0, 146.5, 137.4, 134.6, 133.7, 129.6, 128.1, 127.6, 119.5, 114.3, 104.7, 61.9, 31.6, 14.4. Analytical data for **3d** was consistent with that previously reported.[11]

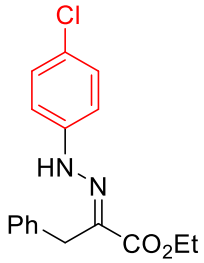


3e

Ethyl (E)-4-(2-(1-ethoxy-1-oxo-3-phenylpropan-2-ylidene)hydrazineyl)benzoate (3e)

Compound **3e** was prepared in 79% yield (56 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.93 (d, J = 8.7 Hz, 2H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 3H), 7.06 (d, J = 8.8 Hz, 2H), 4.35 (q, J = 6.9 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.03 (s, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 165.3,

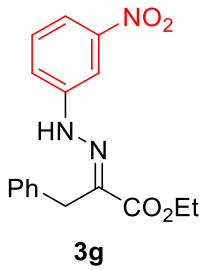
146.7, 136.2, 134.8, 131.4, 129.5, 128.1, 127.4, 124.1, 113.5, 61.8, 60.8, 31.4, 14.5, 14.4; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{20}H_{22}N_2NaO_4$ 377.1472, Found 377.1478.



3f

Ethyl (E)-2-(2-(4-chlorophenyl)hydrazineylidene)-3-phenylpropanoate (3f)[12]

Compound **3f** was prepared in 78% yield (49 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 3H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 141.8, 135.0, 134.7, 129.4, 129.3, 128.1, 127.4, 127.1, 115.3, 61.6, 31.3, 14.5. Analytical data for **3f** was consistent with that previously reported.[12]

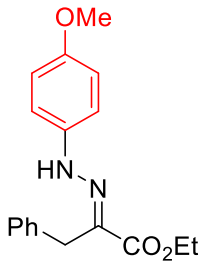


3g

Ethyl (E)-2-(2-(3-nitrophenyl)hydrazineylidene)-3-phenylpropanoate (3g)

Compound **3g** was prepared in 49% yield (32 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.14 (d, *J* = 9.2 Hz, 2H), 7.37-7.34 (m, 2H), 7.30-7.24 (m, 3H), 7.09 (d, *J* = 9.2 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.07 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9, 148.2, 142.3, 138.4, 134.5, 129.7, 128.1, 127.7,

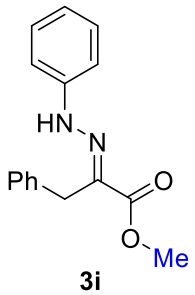
125.9, 113.6, 62.0, 31.7, 14.4; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{17}H_{17}N_3NaO_4$ 350.1111, Found 350.1107.



3h

Ethyl (E)-2-(2-(4-methoxyphenyl)hydrazineylidene)-3-phenylpropanoate (3h)[11]

Compound **3h** was prepared in 58% yield (36 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow oil; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.15 (s, 1H), 7.30-7.27 (m, 2H), 7.22-7.19 (m, 5H), 6.90-6.88 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.99 (s, 2H), 3.71 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.9, 154.2, 137.9, 136.8, 131.8, 128.4, 128.1, 126.1, 114.9, 114.5, 60.1, 55.2, 30.0, 14.2. Analytical data for **3h** was consistent with that previously reported.[11]



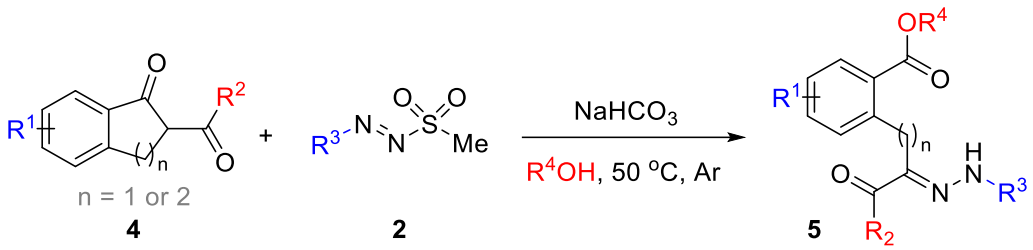
3i

Methyl (E)-3-phenyl-2-(2-phenylhydrazineylidene)propanoate (3i)[13]

Compound **3i** was prepared in 88% yield (47 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 81-83 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 5H), 7.05 (d, J = 7.7 Hz, 2H), 6.96-6.93 (m, 1H), 4.04 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$):

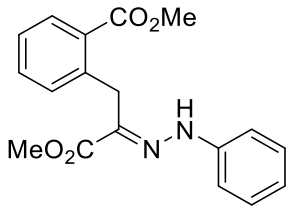
δ 166.1, 143.0, 135.1, 133.7, 129.4, 129.4, 128.1, 127.3, 122.5, 114.2, 52.6, 31.3. Analytical data for **3i** was consistent with that previously reported.[13]

General procedure for the synthesis of 5



In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **4** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), $NaHCO_3$ (42.0 mg, 0.5 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, alcoholic solvent (4 mL) was added, and the mixture was stirred in the 50 °C oil bath for 2-48 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The pure product **5** was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 7:1-20:1).

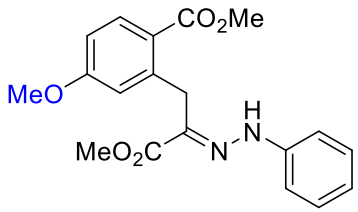
Detail descriptions for products 5



5a

Methyl (E)-2-(3-methoxy-3-oxo-2-(2-phenylhydrazineylidene)propyl)benzoate (5a)

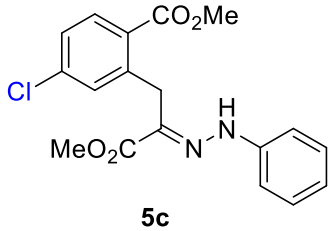
Compound **5a** was prepared in 90% yield (59 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 20/1); Yellow solid; mp 89-91 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.86-7.84 (m, 1H), 7.57-7.55 (m, 1H), 7.48-7.45 (m, 1H), 7,31-7.22 (m, 5H), 6.96-6.92 (m, 1H), 4.34 (s, 2H), 4.07 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 167.3, 143.7, 138.1, 133.0, 132.5, 131.4, 130.3, 129.3, 128.9, 126.9, 121.9, 114.1, 53.1, 52.7, 27.4; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_4$ 349.1159, Found 349.1162.



5b

Methyl (E)-4-methoxy-2-(3-methoxy-3-oxo-2-(2-phenylhydrazineylidene)propyl)-benzoate (5b)

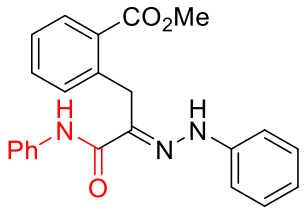
Compound **5b** was prepared in 56% yield (40 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow solid; mp 157-159 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.59 (s, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.29-7.22 (m, 4H), 7.13 (s, 1H), 6.95-6.92 (m, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 4.38 (s, 2H), 4.03 (s, 3H), 3.96 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 167.4, 163.2, 143.8, 141.1, 132.7, 132.4, 129.3, 121.8, 120.9, 116.2, 114.1, 113.0, 55.5, 52.7, 52.6, 27.6; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2NaO_5$ 379.1264, Found 379.1268.



5c

Methyl (E)-4-chloro-2-(3-methoxy-3-oxo-2-(2-phenylhydrazineylidene)propyl)-benzoate (5c)

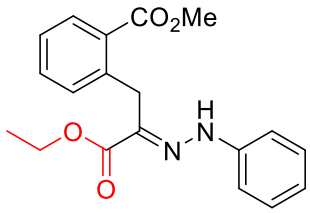
Compound **5c** was prepared in 76% yield (55 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 122-123 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.42, (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.29-7.26 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.96-6.93 (m, 1H), 4.32 (s, 2H), 4.06 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 167.1, 143.6, 140.2, 139.4, 131.7, 131.6, 131.4, 129.3, 127.3, 127.2, 122.1, 114.2, 53.2, 52.7, 27.2; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{17}ClN_2NaO_4$ 383.0769, Found 383.0772.



5d

Methyl (E)-2-(3-oxo-3-(phenylamino)-2-(2-phenylhydrazineylidene)propyl)benzoate (5d)

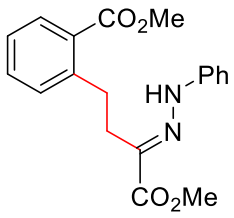
Compound **5d** was prepared in 93% yield (72 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 122-123 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.57 (s, 1H), 9.10 (s, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.47-7.39 (m, 3H), 7.32-7.27 (m, 3H), 7.19-7.14 (m, 3H), 6.96-6.93 (m, 1H), 4.41 (s, 2H), 4.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 163.7, 143.7, 138.3, 138.0, 135.8, 133.0, 131.9, 130.3, 129.4, 129.2, 128.9, 126.7, 123.8, 121.6, 119.6, 113.6, 53.1, 25.3; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{23}H_{21}N_3NaO_3$ 410.1475, Found 410.1481.



5e

Methyl (E)-2-(3-ethoxy-3-oxo-2-(2-phenylhydrazineylidene)propyl)benzoate (5e)

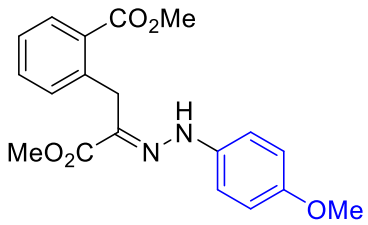
Compound **5e** was prepared in 85% yield (58 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid, mp 134-135 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.42 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.43-7.40 (m, 1H), 7.26-7.18 (m, 5H), 6.90-6.88 (m, 1H), 4.39 (q, J = 6.8 Hz, 2H), 4.29 (s, 2H), 4.02 (s, 3H), 1.42 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 166.8, 143.8, 138.1, 132.9, 132.7, 131.3, 130.3, 129..2, 128.9, 126.8, 121.7, 114.1, 61.5, 53.1, 27.3, 14.5; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2NaO_4$ 363.1315, Found 363.1315.



5f

Methyl (E)-2-(4-methoxy-4-oxo-3-(2-phenylhydrazineylidene)butyl)benzoate (5f)

Compound **5f** was prepared in 90% yield (61 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 79-80 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.54-7.51 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.35-7.32 (m, 3H), 6.98-6.96 (m, 1H), 4.03 (s, 3H), 3.90 (s, 3H), 3.05 (q, *J* = 5.7 Hz, 2H), 2.91 (q, *J* = 5.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5, 166.1, 144.1, 143.7, 133.9, 133.4, 132.1, 131.3, 129.3, 128.0, 126.9, 121.6, 114.0, 52.6, 52.3, 30.8, 28.3; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2NaO_4$ 363.1315, Found 363.1319.

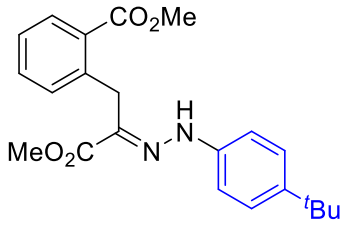


5g

Methyl (E)-2-(3-methoxy-2-(2-(4-methoxyphenyl)hydrazineylidene)-3-oxopropyl)-benzoate (5g)

Compound **5g** was prepared in 95% yield (68 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 115-117 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.39 (s, 1H), 7.84-7.82 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.46-7.43 (m, 1H), 7.29-7.28 (m, 1H), 7.17-7.15 (m, 2H), 6.84-6.82 (m, 2H), 4.30 (s, 2H), 4.04 (s, 3H), 3.95 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 167.4, 155.1, 138.2, 137.7, 132.9, 131.3, 131.3, 130.3, 129.0, 126.8, 115.2, 114.6, 55.7, 53.0,

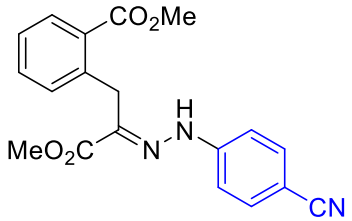
52.6, 27.3; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2NaO_5$ 379.1264, Found 379.1268.



5h

Methyl (E)-2-(2-(2-(4-(tert-butyl)phenyl)hydrazineylidene)-3-methoxy-3-oxopropyl)-benzoate (5h)

Compound **5h** was prepared in 86% yield (66 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.40 (s, 1H), 7.84-7.83 (m, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.46-7.43 (m, 1H), 7.30-7.26 (m, 3H), 7.16 (d, *J* = 8.7 Hz, 2H), 4.33 (s, 2H), 4.06 (s, 3H), 3.96 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 167.3, 144.8, 141.3, 138.2, 132.9, 131.9, 131.2, 130.3, 128.9, 126.8, 126.0, 113.8, 53.0, 52.6, 34.3, 31.5, 27.3; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{22}H_{26}N_2NaO_4$ 405.1785, Found 405.1791.

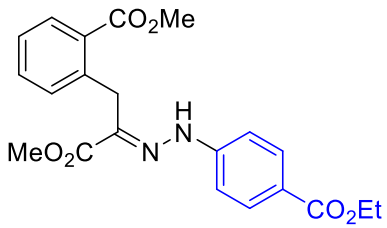


5i

Methyl (E)-2-(2-(2-(4-cyanophenyl)hydrazineylidene)-3-methoxy-3-oxopropyl)-benzoate (5i)

Compound **5i** was prepared in 68% yield (48 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 169-170 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.01 (s, 1H), 7.87-7.85 (m, 1H), 7.57-7.53 (m, 3H), 7.51-7.48 (m, 1H), 7.34-7.31 (m, 1H), 7.29-7.26 (m, 2H), 4.32 (s, 2H), 4.09 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 166.8, 147.3, 137.2, 135.7, 133.6, 133.2, 131.4,

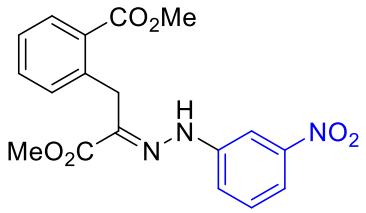
130.5, 128.8, 127.1, 119.8, 114.2, 103.9, 53.3, 52.9, 27.6; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{19}H_{17}N_3NaO_4$ 374.1111, Found 374.1116.



5j

Methyl (E)-2-(2-(2-(4-(ethoxycarbonyl)phenyl)hydrazineylidene)-3-methoxy-3-oxopropyl)benzoate (5j)

Compound **5j** was prepared in 88% yield (70 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 148-150 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.80 (s, 1H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.46-7.44 (m, 1H), 7.30-7.27 (m, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 4.32 (q, *J* = 7.3 Hz, 4H), 4.05 (s, 3H), 3.96 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 167.0, 166.6, 147.5, 137.6, 134.7, 133.1, 131.4, 131.2, 130.5, 128.8, 127.0, 123.5, 113.4, 60.6, 53.2, 52.8, 27.5, 14.5; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{21}H_{22}N_2NaO_6$ 421.1370, Found 421.1375.

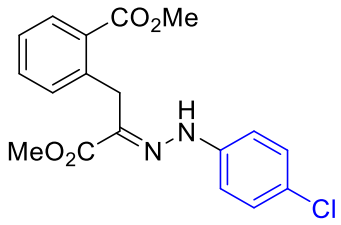


5k

Methyl (E)-2-(3-methoxy-2-(2-(3-nitrophenyl)hydrazineylidene)-3-oxopropyl)-benzoate (5k)

Compound **5k** was prepared in 62% yield (46 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 150-151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.96 (s, 1H), 7.99 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.48-7.45 (m, 1H), 7.39-

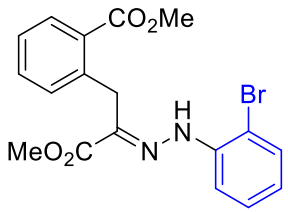
7.35 (m, 1H), 7.31-7.28 (m, 1H), 4.31 (s, 2H), 4.08 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 167.0, 149.3, 145.0, 137.4, 134.9, 133.2, 131.5, 130.5, 130.0, 128.8, 127.1, 119.7, 116.1, 108.9, 53.4, 52.9, 27.6; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{17}N_3NaO_6$ 394.1010, Found 394.1014.



5l

Methyl (E)-2-(2-(2-(4-chlorophenyl)hydrazineylidene)-3-methoxy-3-oxopropyl)-benzoate (5l)

Compound **5l** was prepared in 86% yield (62 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 143-145 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.58 (s, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.29-7.26 (m, 1H), 7.20-7.18 (m, 2H), 7.14-7.12 (m, 2H), 4.28 (s, 2H), 4.04 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 167.2, 142.5, 137.8, 133.1, 133.0, 131.4, 130.4, 129.2, 128.9, 127.0, 126.6, 115.3, 53.2, 52.7, 27.4; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{17}ClN_2NaO_4$ 383.0769, Found 383.0771.

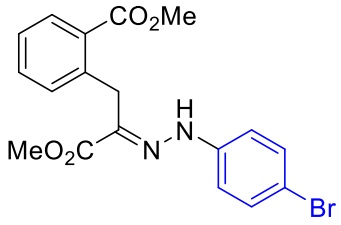


5m

methyl (E)-2-(2-(2-(2-bromophenyl)hydrazineylidene)-3-methoxy-3-oxopropyl)-benzoate (5m)

Compound **5m** was prepared in 90% yield (73 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.46-7.43 (m, 1H),

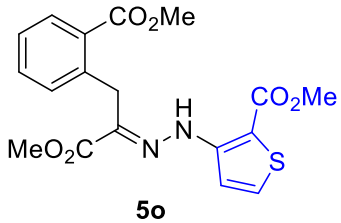
7.37-7.32 (m, 2H), 7.29-7.26 (m, 2H), 6.82-6.79 (m, 1H), 4.54 (s, 2H), 3.95 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 166.1, 140.4, 136.4, 136.1, 133.0, 132.4, 131.4, 129.5, 129.5, 128.6, 127.2, 123.0, 116.3, 108.8, 52.7, 52.4, 29.5; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{17}BrN_2NaO_4$ 427.0264, Found 427.0270.



5n

methyl (E)-2-(2-(2-(4-bromophenyl)hydrazineylidene)-3-methoxy-3-oxopropyl)-benzoate (5n)

Compound **5n** was prepared in 97% yield (79 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 138-140 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.59 (s, 1H), 7.83-7.81 (m ,1H), 7.53 (d, J = 7.6 Hz, 1H), 7.46-7.43 (m, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.29-7.26 (m, 1H), 7.09-7.07 (m, 2H), 4.28 (s, 2H), 4.04 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9, 167.1, 142.9, 137.7, 133.2, 133.0, 132.0, 131.4, 130.3, 128.9, 126.9, 115.7, 113.9, 53.1, 52.7, 27.4; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{17}BrN_2NaO_4$ 427.0264, Found 427.0269.

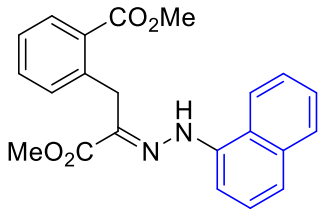


5o

Methyl (E)-3-(2-(1-methoxy-3-(2-(methoxycarbonyl)phenyl)-1-oxopropan-2-ylidene)hydrazineyl)thiophene-2-carboxylate (5o)

Compound **5o** was prepared in 58% yield (45 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 119-120 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.39 (s, 1H), 7.93-7.91 (m, 1H), 7.46-7.43 (m, 1H), 7.33-7.27

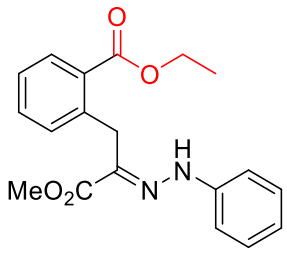
(m, 3H), 6.96 (d, J = 5.5 Hz, 1H), 4.29 (s, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.2, 164.1, 163.0, 150.9, 139.5, 131.9, 131.7, 131.3, 130.5, 130.4, 126.5, 118.2, 103.9, 52.2, 52.0, 52.0, 37.2; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{18}H_{18}N_2NaO_6S$ 413.0778, Found 413.0783.



5p

Methyl (E)-2-(3-methoxy-2-(2-(naphthalen-1-yl)hydrazineylidene)-3-oxopropyl)-benzoate (5p)

Compound **5p** was prepared in 56% yield (42 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.00 (s, 1H), 7.92 (d, J = 7.8 Hz, 2H), 7.83-7.81 (m, 1H), 7.51-7.44 (m, 4H), 7.40-7.30 (m, 4H), 4.36 (s, 2H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4, 164.5, 140.0, 138.4, 134.2, 131.9, 131.2, 130.6, 130.5, 129.0, 128.7, 126.5, 126.4, 126.0, 125.7, 122.2, 121.7, 119.9, 108.4, 52.1, 51.9, 37.0; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{22}H_{20}N_2NaO_4$ 399.1315, Found 399.1321.

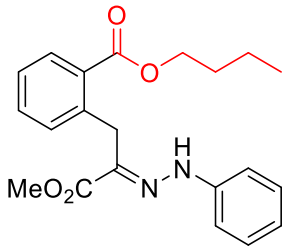


5q

Ethyl (E)-2-(3-methoxy-3-oxo-2-(2-phenylhydrazineylidene)propyl)benzoate (5q)

Compound **5q** was prepared in 92% yield (63 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 93-95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.52 (s, 1H), 7.82-7.80 (m, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.42-

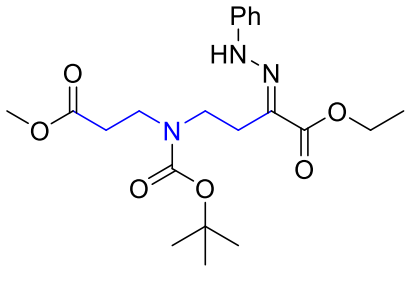
7.39 (m, 1H), 7.24-7.17 (m, 5H), 6.90-6.87 (m, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.29 (s, 2H), 3.92 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 167.3, 143.7, 137.9, 132.8, 132.4, 131.3, 130.2, 129.2, 129.2, 126.7, 121.8, 114.1, 62.1, 52.6, 27.3, 14.3; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{19}H_{20}N_2NaO_4$ 363.1315, Found 363.1318.



5r

Butyl (E)-2-(3-methoxy-3-oxo-2-(2-phenylhydrazineylidene)propyl)benzoate (5r)

Compound **5r** was prepared in 72% yield (53 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.54 (s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.43-7.39 (m, 1H), 7.24-7.17 (m, 5H), 6.90-6.87 (m, 1H), 4.43 (t, J = 6.6 Hz, 2H), 4.29 (s, 2H), 3.92 (s, 3H), 1.83-1.78 (m, 2H), 1.55-1.48 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 167.4, 143.8, 138.1, 132.8, 132.5, 131.4, 130.2, 129.3, 129.2, 126.8, 121.8, 114.1, 66.0, 52.7, 30.8, 27.4, 19.4, 13.9; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{21}H_{24}N_2NaO_4$ 391.1628, Found 391.1633.

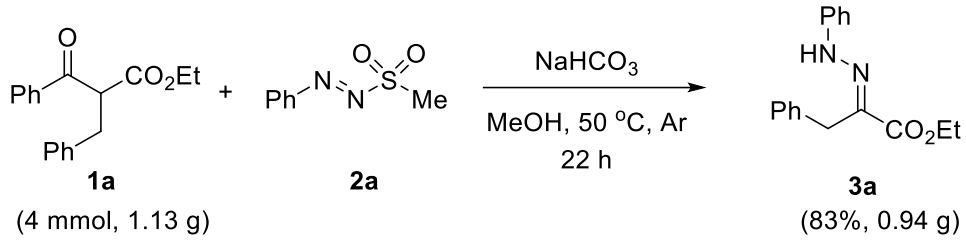


5'

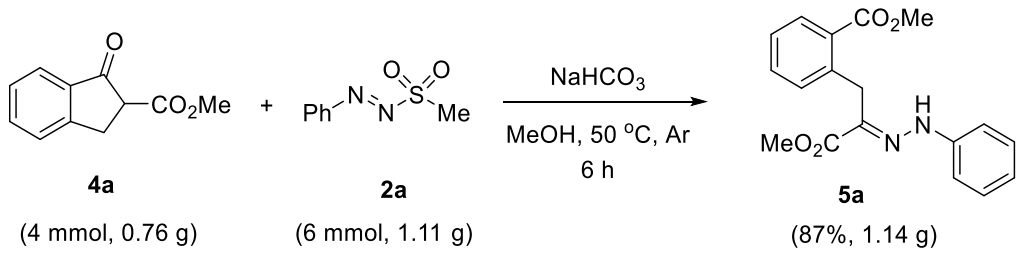
Ethyl (E)-4-((tert-butoxycarbonyl)(3-methoxy-3-oxopropyl)amino)-2-(2-phenylhydrazineylidene)butanoate (5')

Compound **5'** was prepared in 58% yield (49 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.46 (s, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30-7.27 (m, 2H), 6.95-6.92 (m, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 3.56 (t, *J* = 6.9 Hz, 2H), 3.23 (t, *J* = 7.7 Hz, 2H), 2.87 (t, *J* = 8.1 Hz, 2H), 2.57 (t, *J* = 6.7 Hz, 2H), 1.53 (s, 9H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.9, 165.7, 156.6, 144.2, 131.1, 129.2, 121.7, 114.1, 81.3, 61.2, 52.0, 45.3, 44.5, 34.3, 28.6, 25.3, 14.5; HRMS (ESI) m/z $[M+Na]^+$ Calcd for $C_{21}H_{31}N_3NaO_6$ 444.2105, Found 444.2109.

Scale-up Reaction:



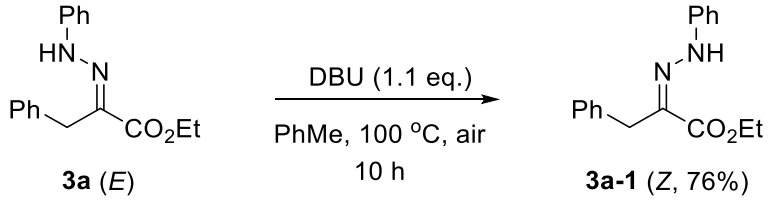
In an oven-dried Schlenk tube (50 mL) equipped with a stir bar, **1a** (1.13 g, 4 mmol, 1.0 equiv), **2a** (1.11 g, 6 mmol, 1.5 equiv), $NaHCO_3$ (0.84 g, 10 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, MeOH (30 mL) was added, and the mixture was stirred in the 50 °C oil bath for 22 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The pure product **3a** (83%, 0.94 g) was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1).



In an oven-dried Schlenk tube (50 mL) equipped with a stir bar, **4a** (0.76 g, 4 mmol, 1.0 equiv), **2a** (1.11 g, 6 mmol, 1.5 equiv), $NaHCO_3$ (0.84 g, 10 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, MeOH (30 mL) was added, and the mixture was stirred in the 50 °C oil bath for 6 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The pure product **5a** (87%, 1.14 g) was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1).

Control Experiments:

(a)



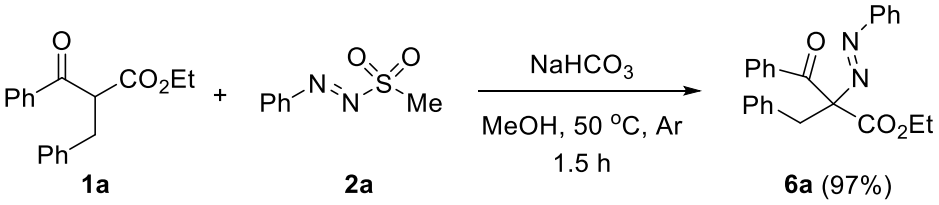
3a (*E*) **3a-1** (*Z*, 76%)

In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **3a** (56.5 mg, 0.2 mmol, 1.0 equiv), toluene (4 mL) and DBU (32.9 uL, 0.22 mmol, 1.1 equiv) were added. Then, the vessel was stirred in the 100 °C oil bath for 10 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The pure product **3a-1** was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1).

Ethyl (Z)-3-phenyl-2-(2-phenylhydrazineylidene)propanoate (3a-1)[11]

Compound **3a-1** was prepared in 76% yield (43 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 100/1); Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.96 (s, 1H), 7.32-7.24 (m, 8H), 7.21-7.18 (m, 1H), 6.96-6.92 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.78 (s, 2H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.7, 143.3, 138.8, 129.3, 128.7, 128.3, 128.0, 126.2, 121.8, 113.6, 60.6, 13.8. Analytical data for **3a-1** was consistent with that previously reported.[11]

(b)



1a **2a** **6a** (97%)

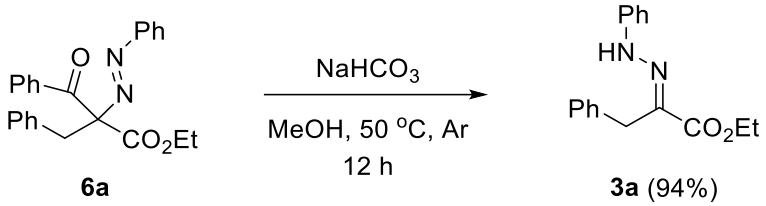
In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **1a** (56.5 mg, 0.2 mmol, 1.0 equiv), **2a** (55.3 mg, 0.3 mmol, 1.5 equiv), $NaHCO_3$ (42.0 mg, 0.5 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, MeOH (4 mL) was added, and the mixture was stirred in the 50 °C oil bath for 1.5 hours. After the reaction finished as monitored with TLC, the

resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The **6a** (97%, 75 mg) was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 15:1).

Ethyl (E)-2-benzyl-3-oxo-3-phenyl-2-(phenyldiazenyl)propanoate (6a)

Compound **6a** was prepared in 97% yield (75 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 20/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.70 (m, 4H), 7.46-7.42 (m, 4H), 7.36-7.33 (m, 2H), 7.21-7.19 (m, 3H), 7.15-7.13 (m, 2H), 4.17-4.04 (m, 2H), 3.80 (d, *J* = 14.0 Hz, 1H), 3.66 (d, *J* = 14.0 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 169.6, 151.9, 135.3, 134.8, 132.9, 131.8, 130.7, 129.7, 129.2, 128.5, 128.2, 127.1, 122.8, 89.0, 61.7, 42.7, 13.8.

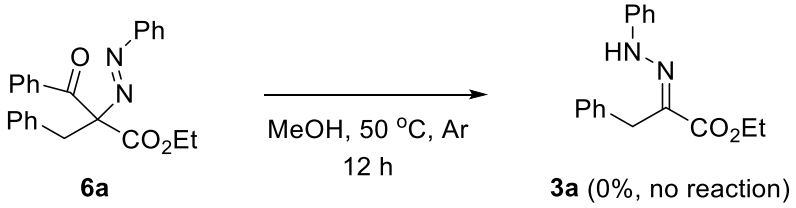
(c)



6a **3a** (94%)

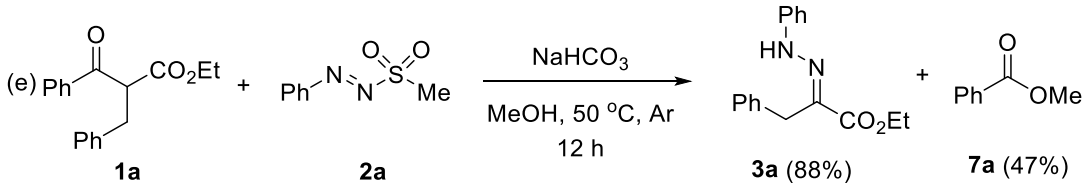
In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **6a** (77.3 mg, 0.2 mmol, 1.0 equiv), $NaHCO_3$ (42.0 mg, 0.5 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, MeOH (4 mL) was added, and the mixture was stirred in the 50 °C oil bath for 12 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The **3a** (94%, 53 mg) was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 25:1).

(d)

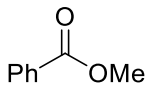


6a **3a** (0%, no reaction)

In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **6a** (77.3 mg, 0.2 mmol, 1.0 equiv) was added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, MeOH (4 mL) was added, and the mixture was stirred in a 50 °C oil bath for 12 hours. After the reaction was monitored by TLC, no reaction was observed.



In an oven-dried Schlenk tube (25 mL) equipped with a stir bar, **1a** (56.5 mg, 0.2 mmol, 1.0 equiv), **2a** (55.3 mg, 0.3 mmol, 1.5 equiv), $NaHCO_3$ (42.0 mg, 0.5 mmol, 2.5 equiv) were added. Then, the vessel was evacuated and refilled with argon (Ar) for three times. Under argon, MeOH (4 mL) was added, and the mixture was stirred in a 50 °C oil bath for 12 hours. After the reaction finished as monitored with TLC, the resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly. The **7a** (47%, 13 mg) was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 40:1), and **3a** (88%, 45 mg) was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 15:1).



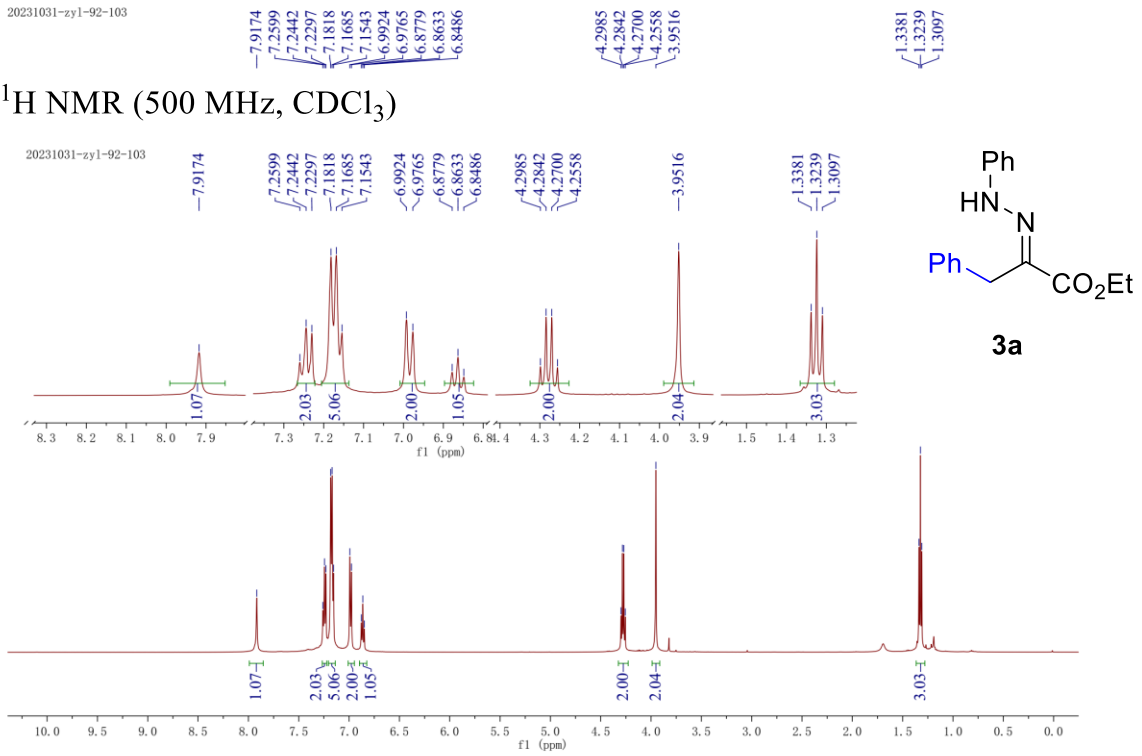
7a

Methyl benzoate (7a)[14]

Compound **7a** was prepared in 47% yield (13 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 60/1); Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H), 7.57-7.54 (m, 1H), 7.45-7.42 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2, 133.0, 130.3, 129.7, 128.5, 52.2. Analytical data for **7a** was consistent with that previously reported.[14]

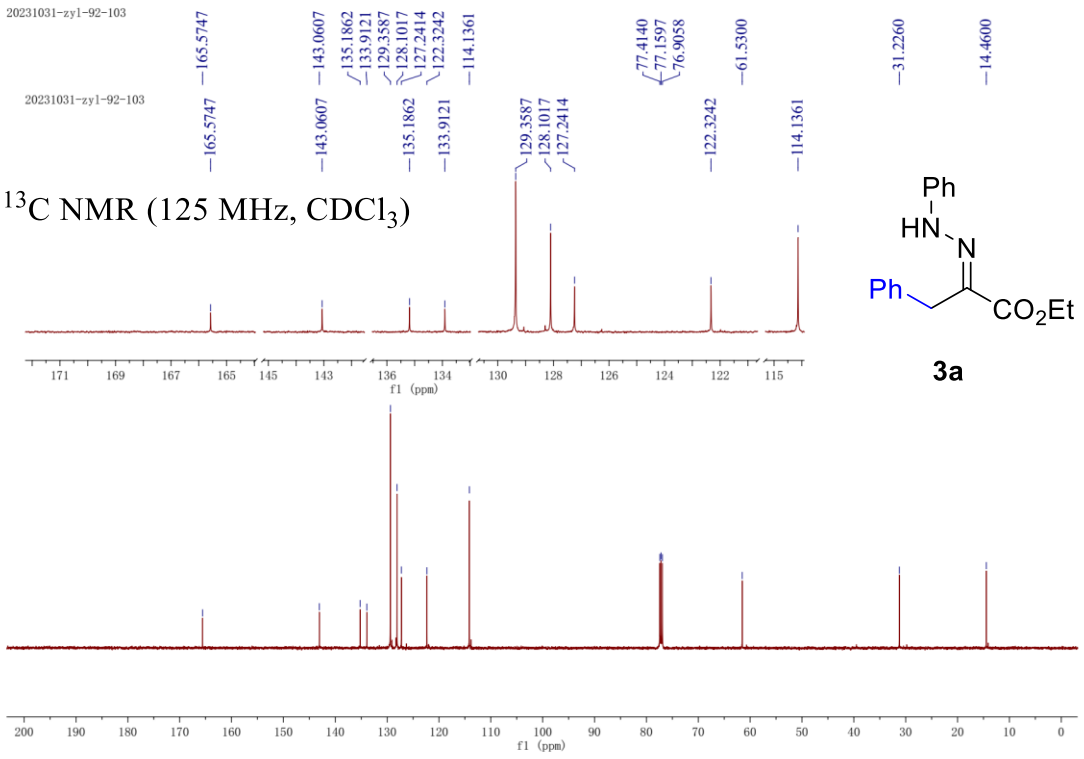
NMR spectra of compounds 3

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



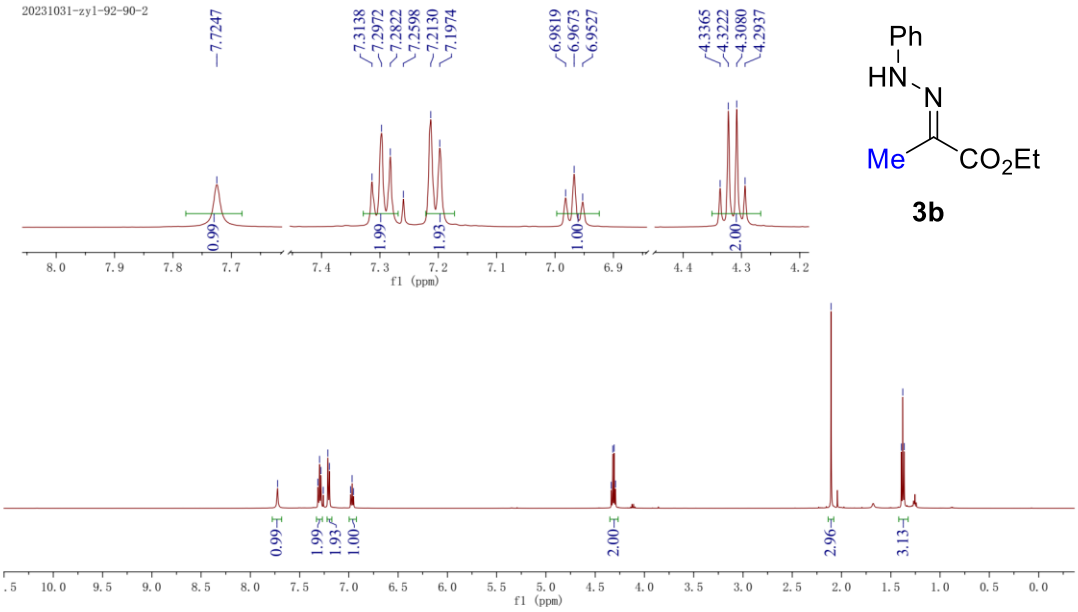
3a

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



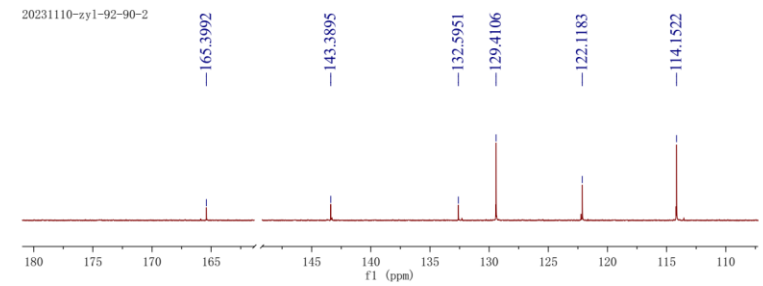
3a

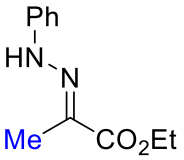
^{1}H NMR (500 MHz, $CDCl_3$)



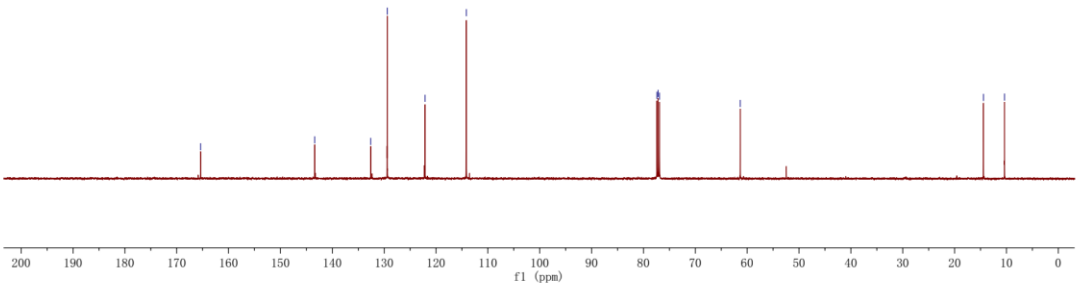
3b

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

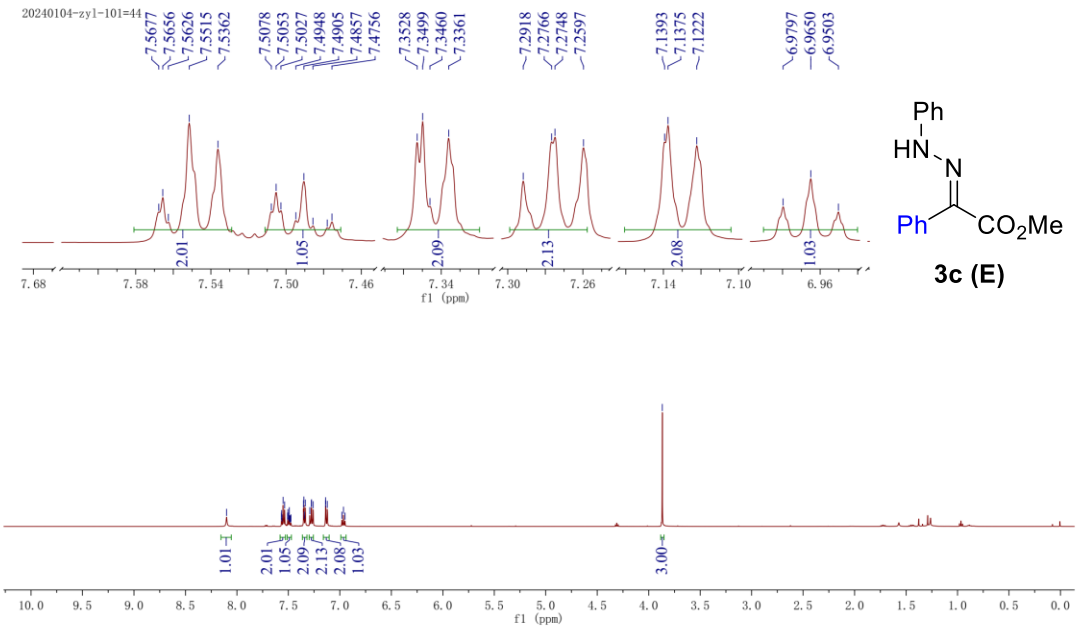


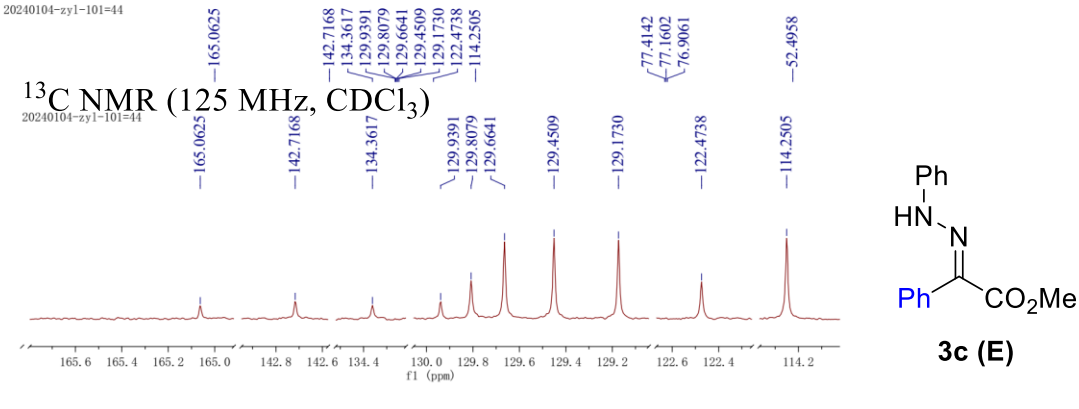


3b

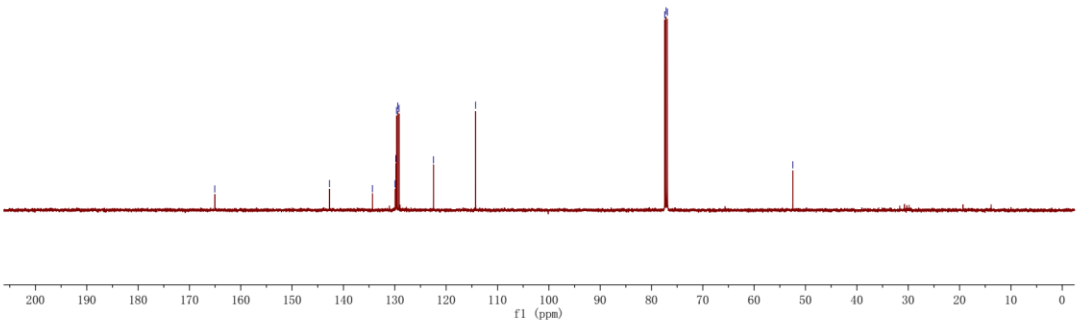


^{1}H NMR (500 MHz, $CDCl_3$)

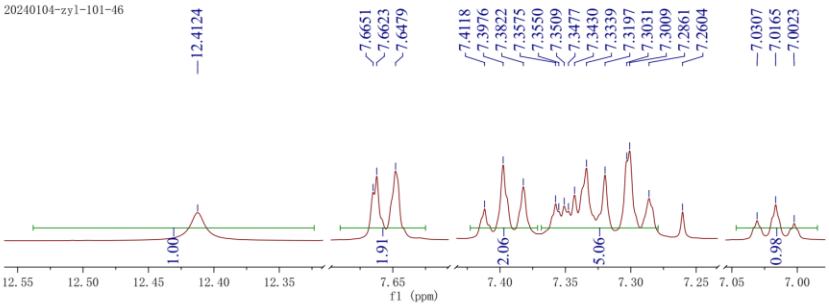


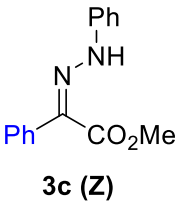


^{13}C NMR (125 MHz, $CDCl_3$)

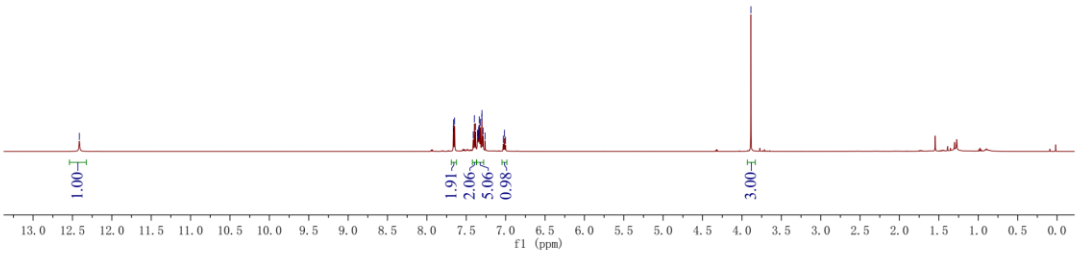


^{1}H NMR (500 MHz, $CDCl_3$)

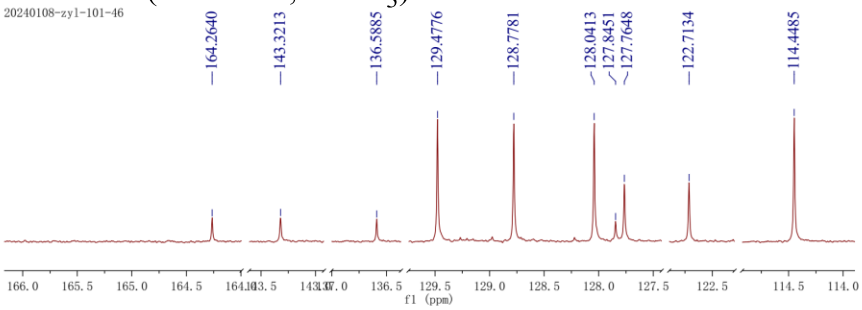


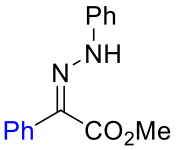


3c (Z)



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





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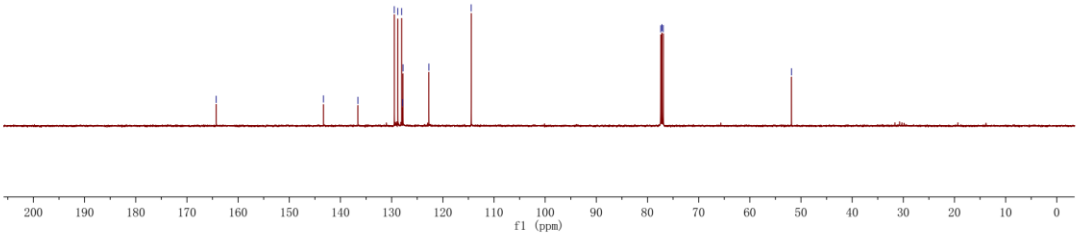

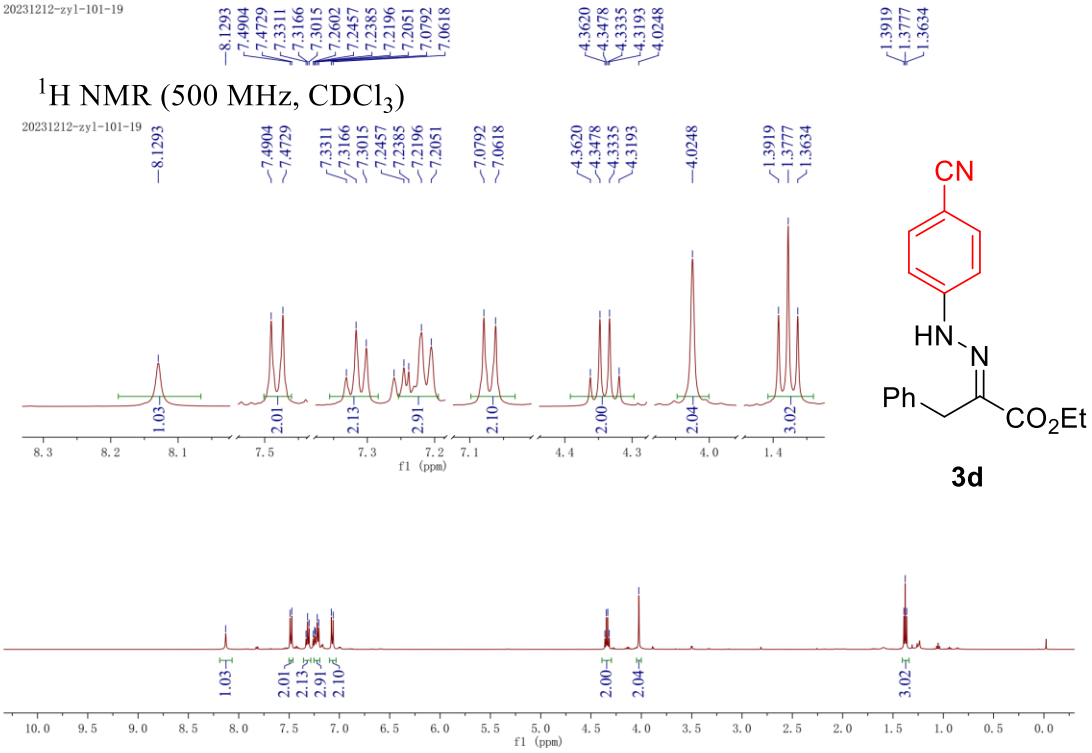
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7.3311
7.3166
7.3015
7.2602
7.2457
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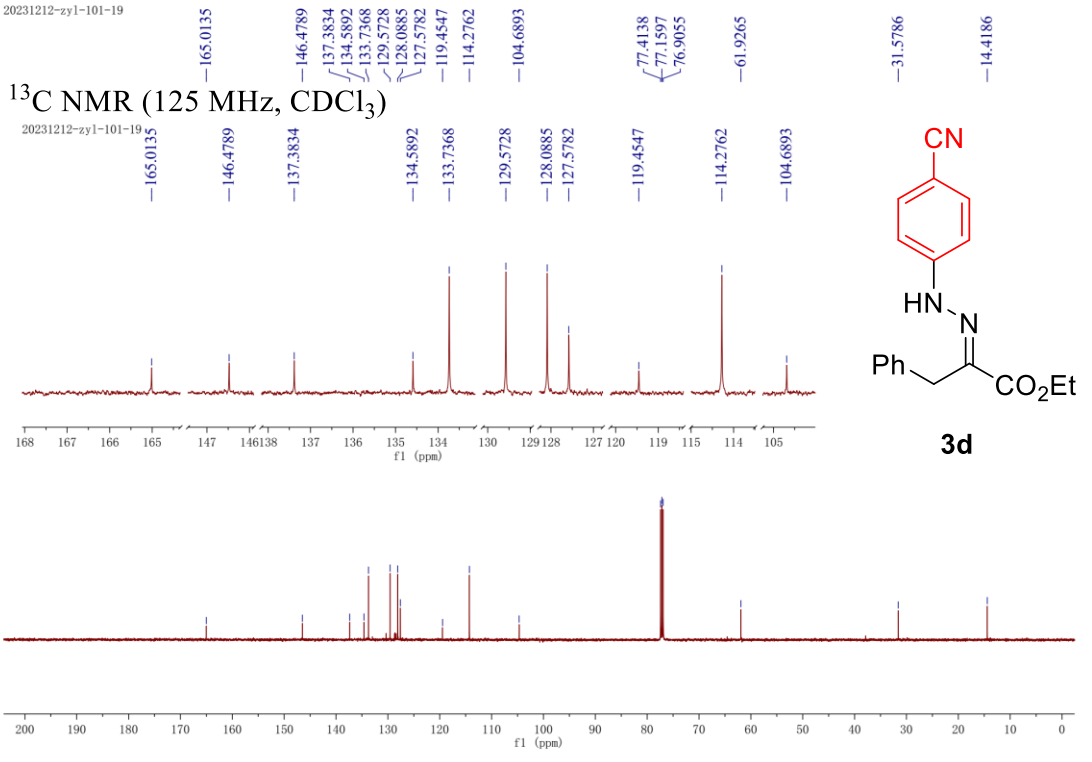
7.2196
7.2051
7.0792
7.0618
4.3620
4.3478
4.3335
4.3193
4.0248
1.3919
1.3777
1.3634
1H NMR (500 MHz, CDCl3)
1.03
2.01
2.13
2.91
2.10
2.00
2.04
3.02
f1 (ppm)
CN
HN
N
Ph
CO2Et
3d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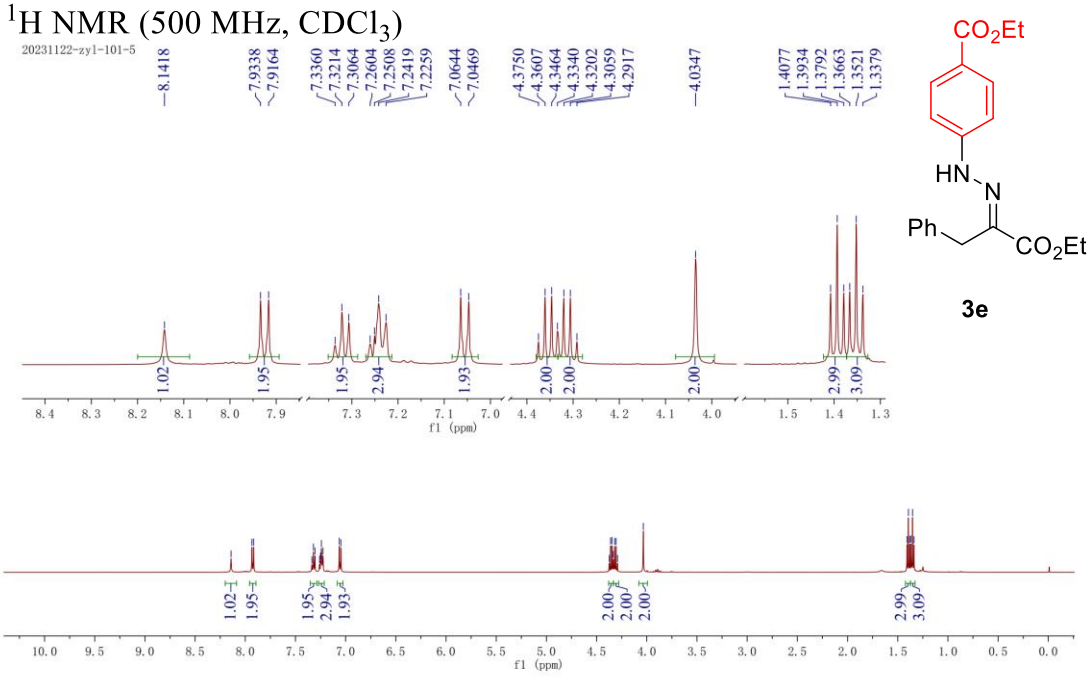
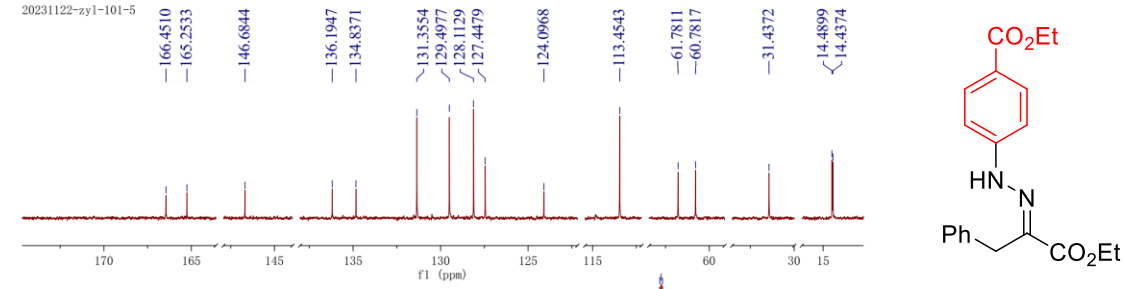
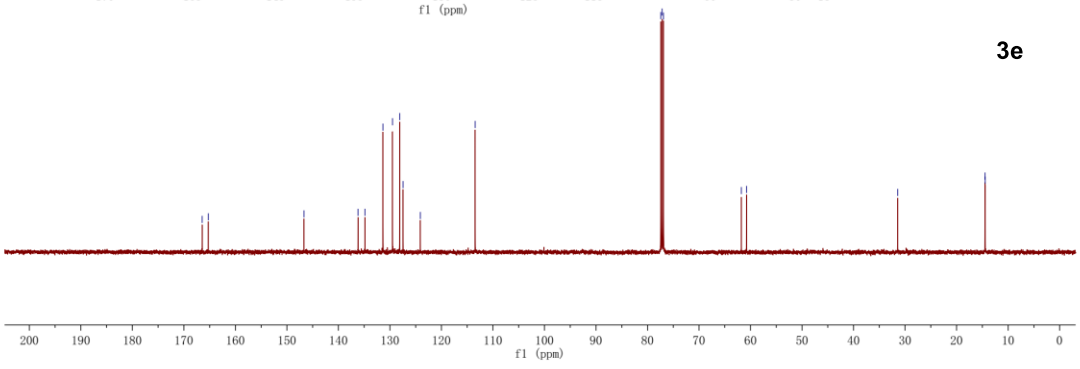
77.4138
77.1597
76.9055
61.9265
31.5786
14.4186
13C NMR (125 MHz, CDCl3)
f1 (ppm)
CN
HN
N
Ph
CO2Et
3d

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

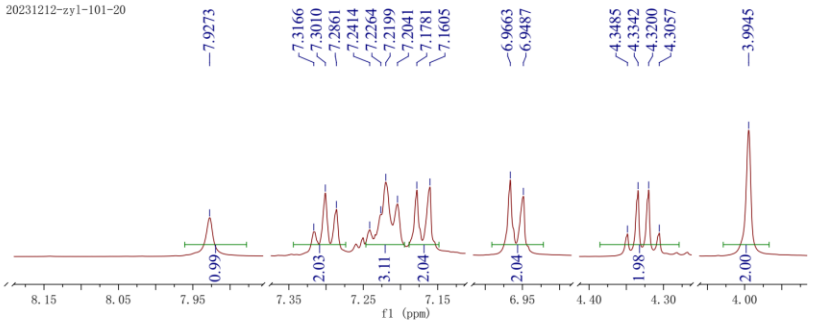


^{13}C NMR (125 MHz, $CDCl_3$)

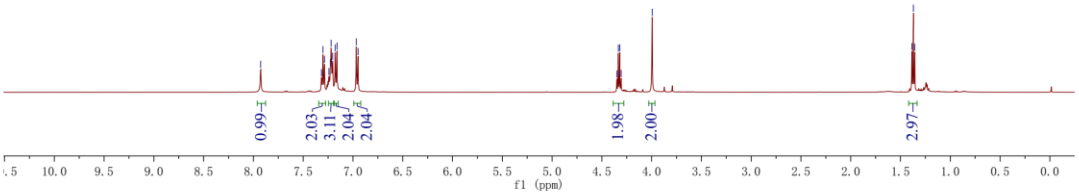


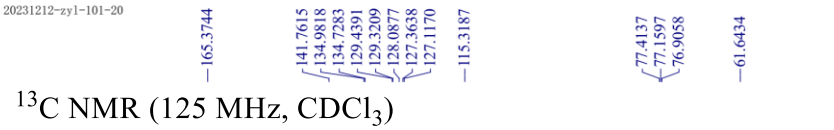


^{1}H NMR (500 MHz, $CDCl_3$)

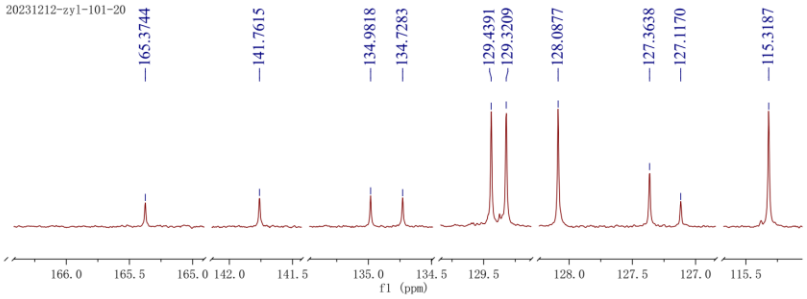


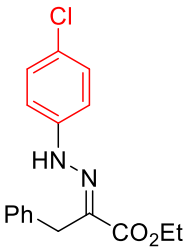
3f



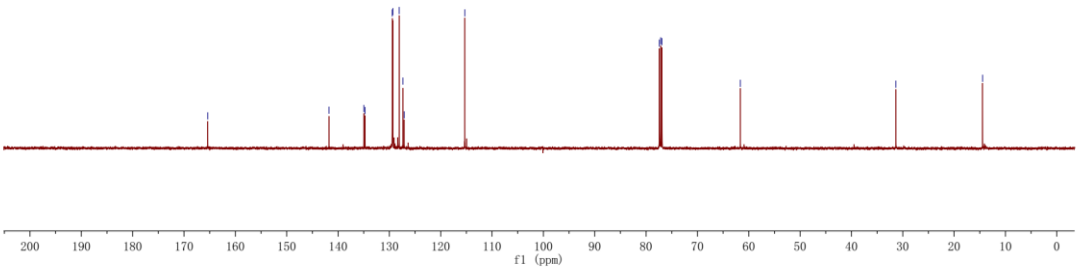


^{13}C NMR (125 MHz, $CDCl_3$)





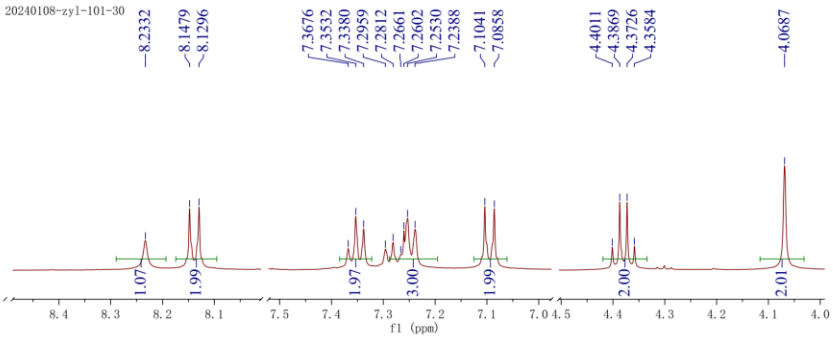
3f

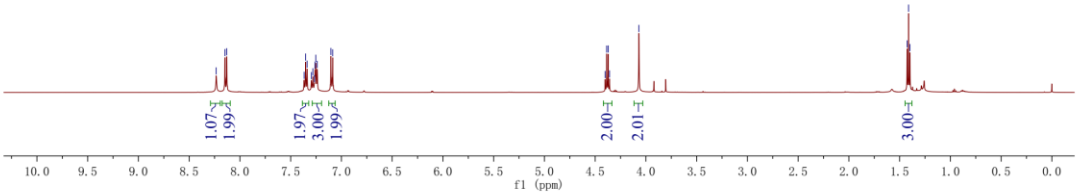


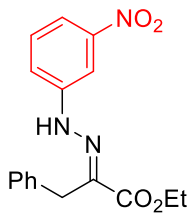
20240108-zyl-101-30

8.2332, 8.1479, 8.1296, 7.3676, 7.3532, 7.3380, 7.2959, 7.2812, 7.2661, 7.2602, 7.2530, 7.2388, 7.1041, 7.0858, 4.4011, 4.3869, 4.3726, 4.3584, 4.0687, 1.4265, 1.4123, 1.3980

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





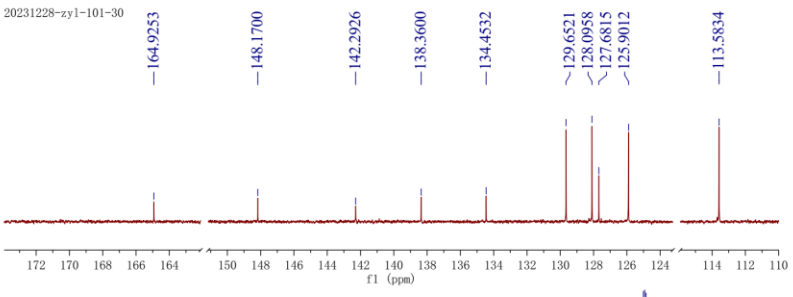


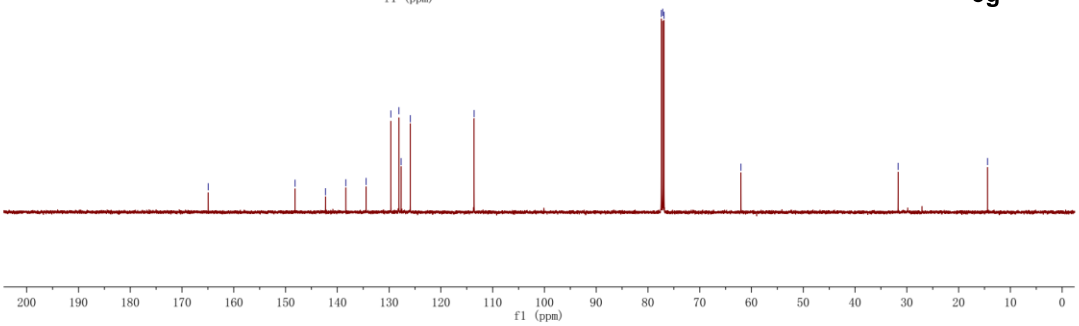
3g

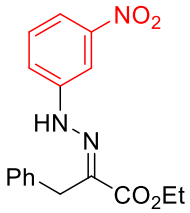
20231228-zyl-101-30

164.9253, 148.1700, 142.2926, 138.3600, 134.4532, 129.6521, 128.0958, 127.6815, 125.9012, 113.5834, 77.4138, 77.1597, 76.9056, 62.0355, 31.6888, 14.4202

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

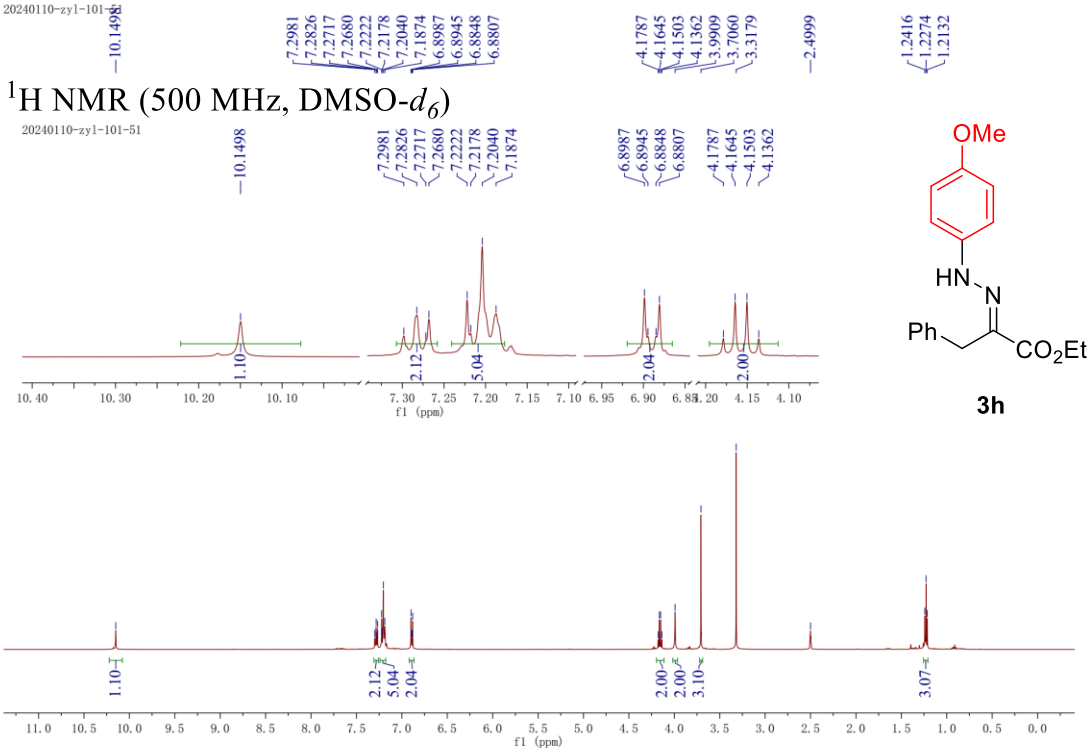




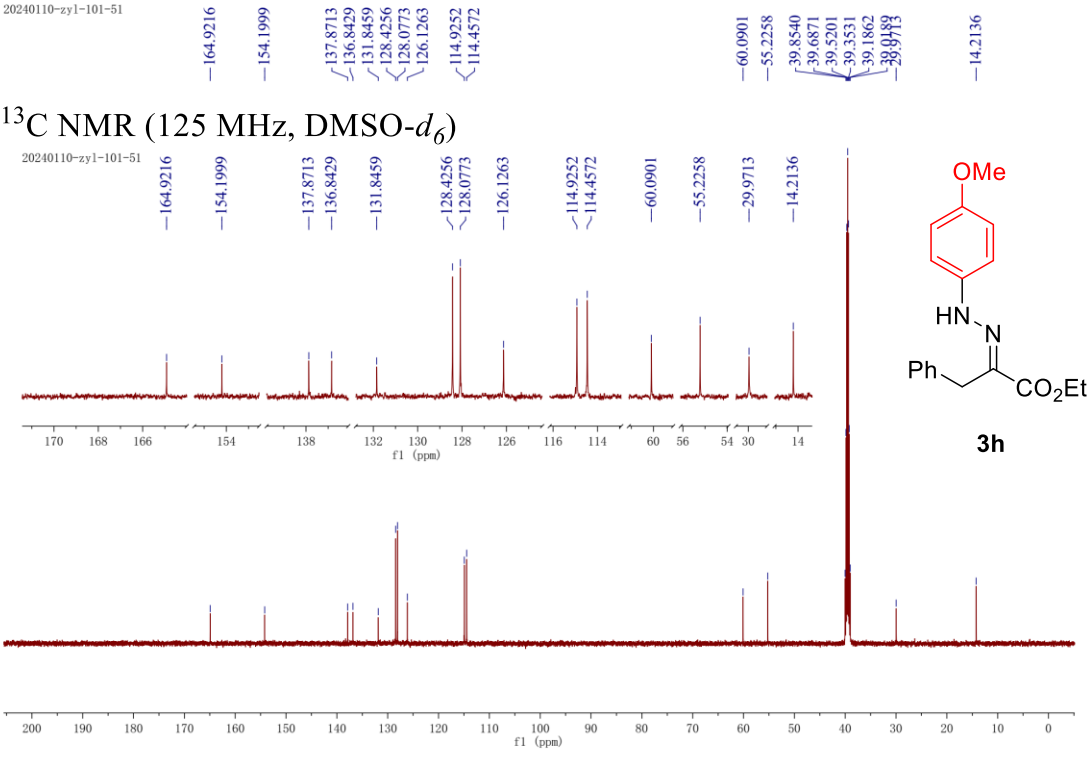


3g

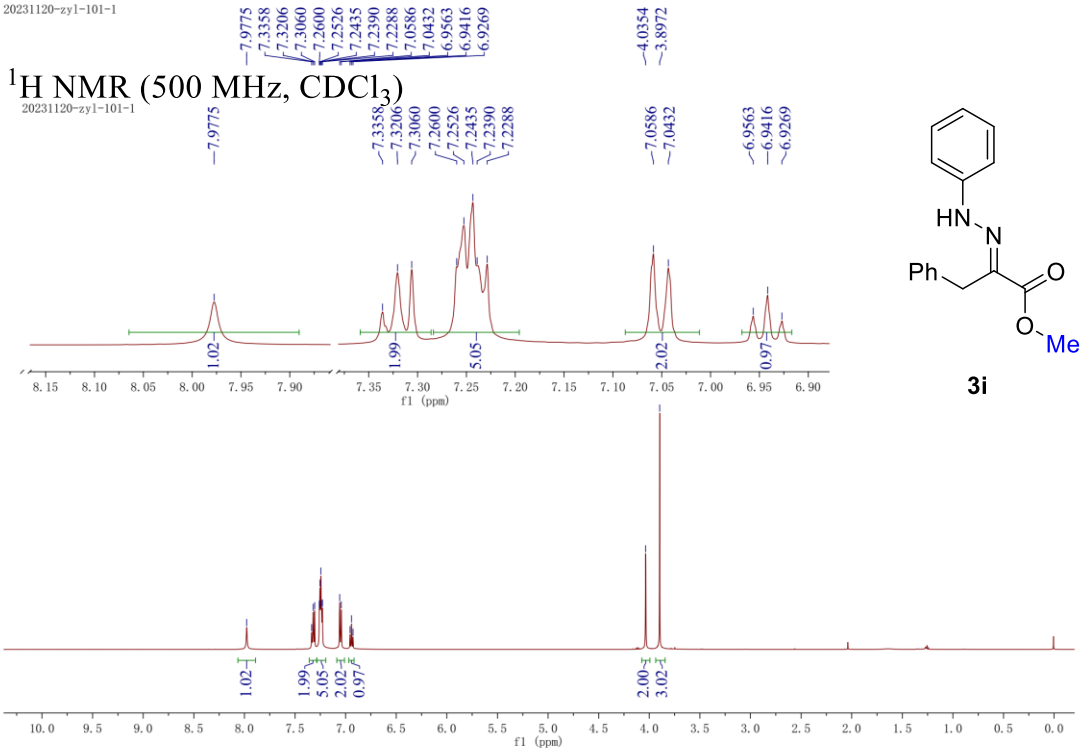
^{1}H NMR (500 MHz, DMSO-d_6)



^{13}C NMR (125 MHz, DMSO-d_6)

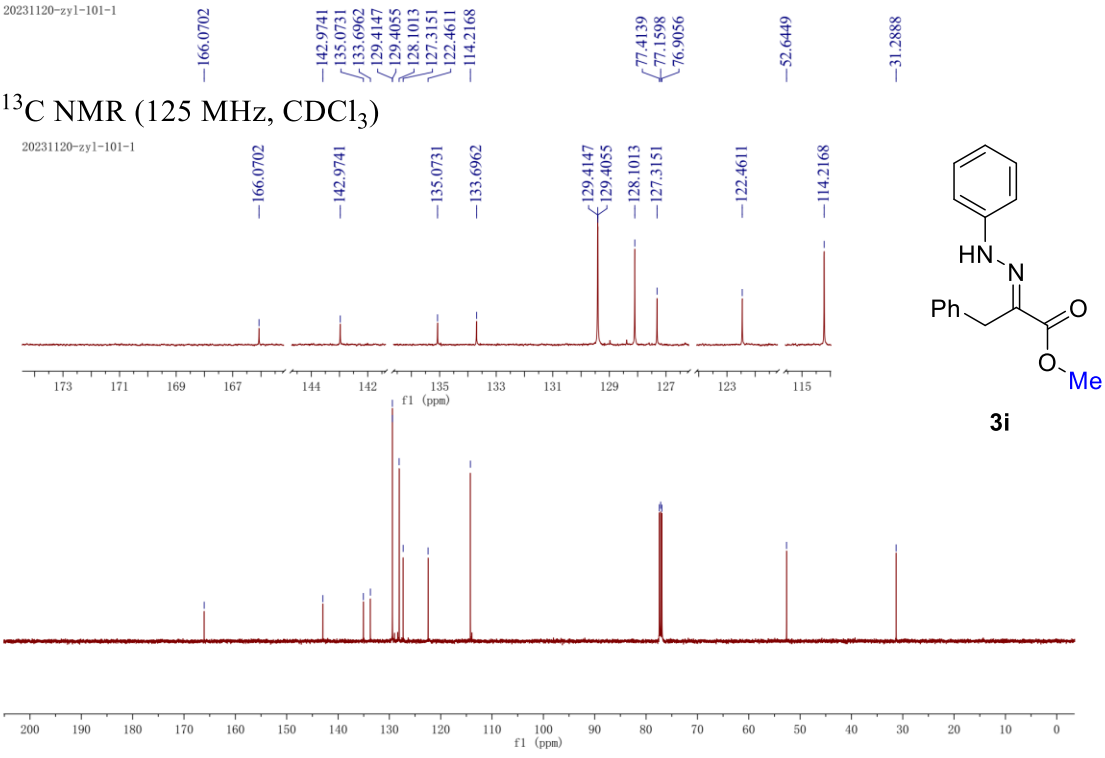


^{1}H NMR (500 MHz, $CDCl_3$)



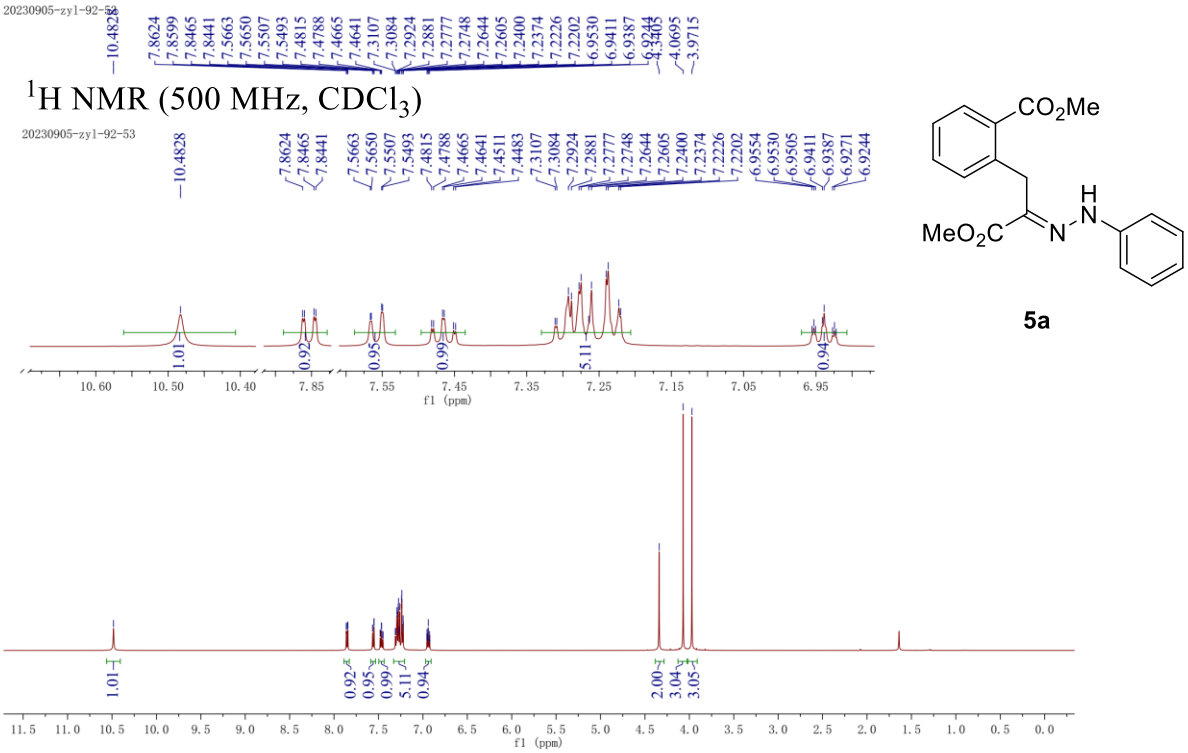
3i

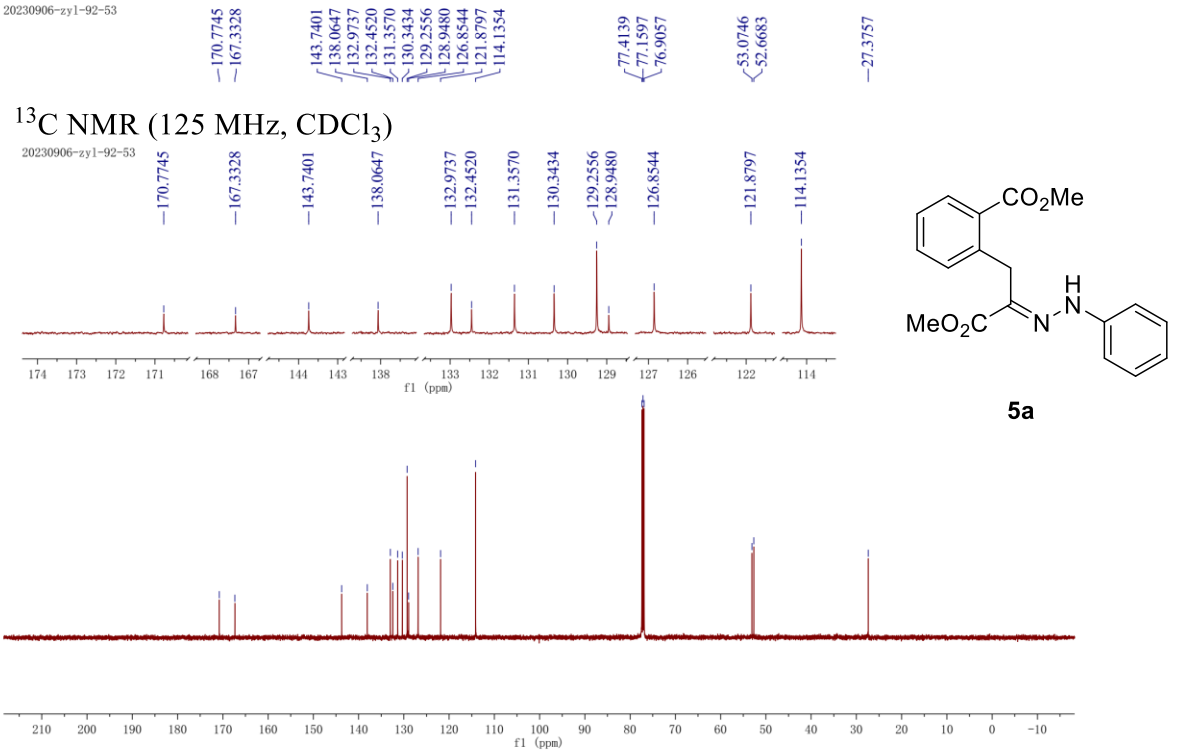
^{13}C NMR (125 MHz, $CDCl_3$)

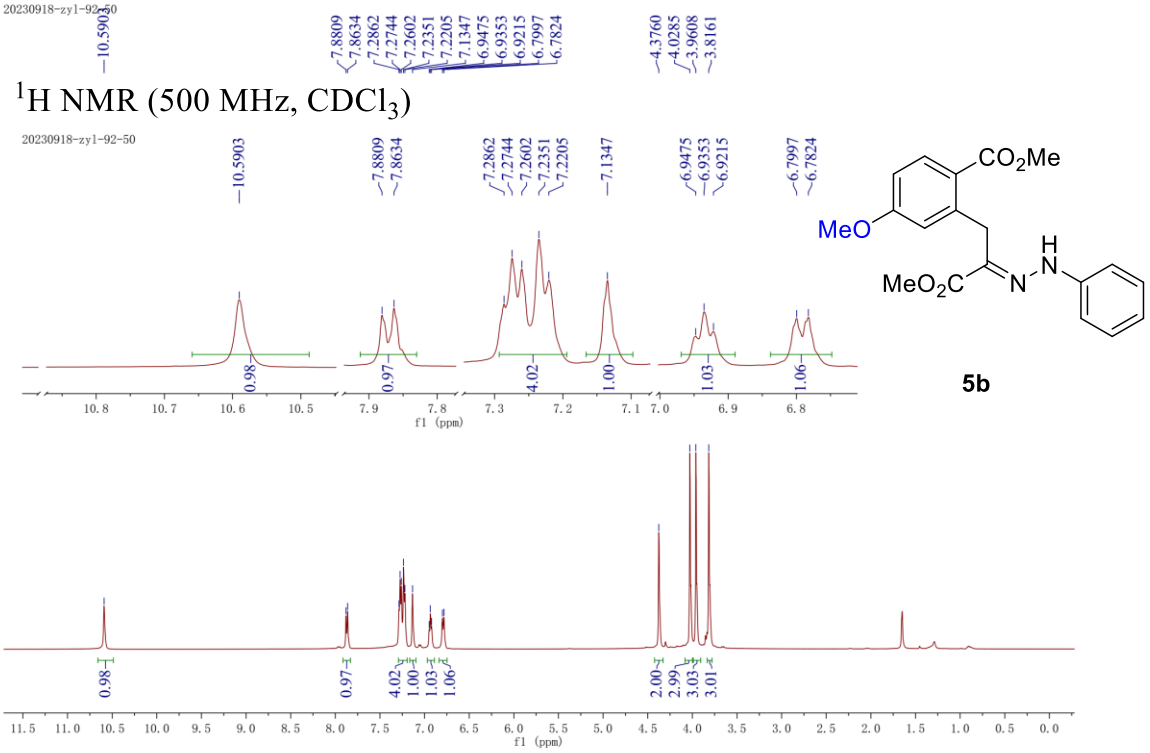


3i

NMR spectra of compounds 5

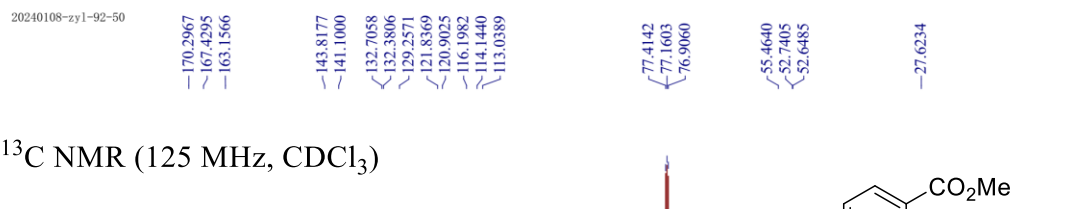






^{1}H NMR (500 MHz, $CDCl_3$)

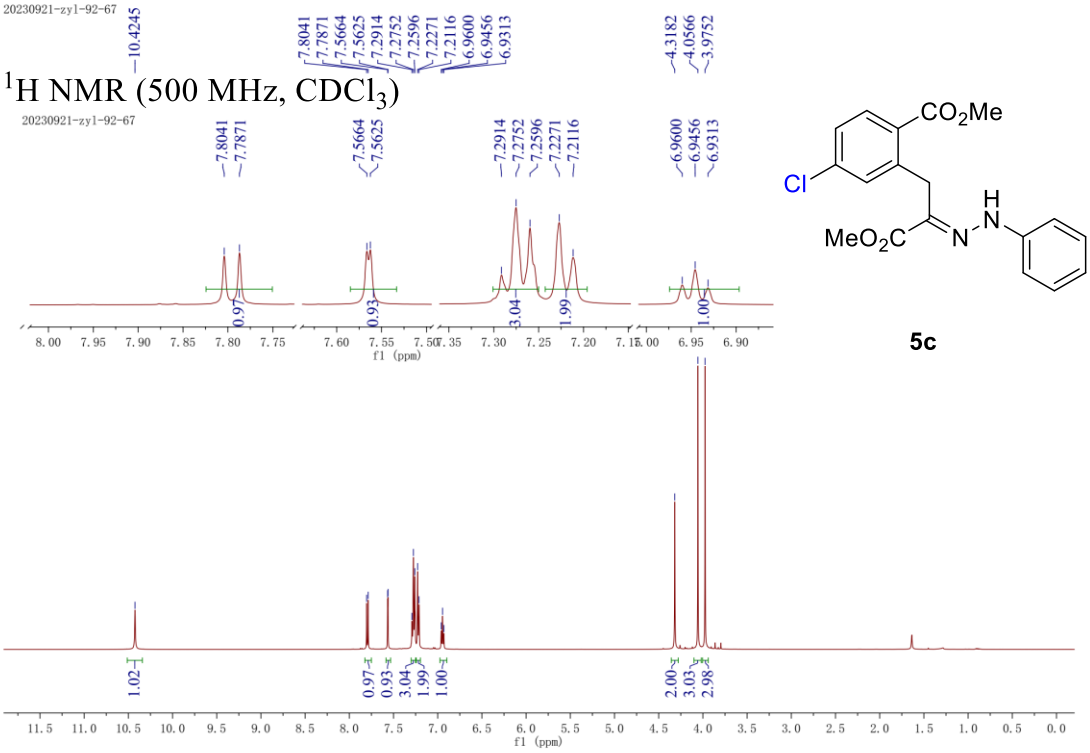
5b



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

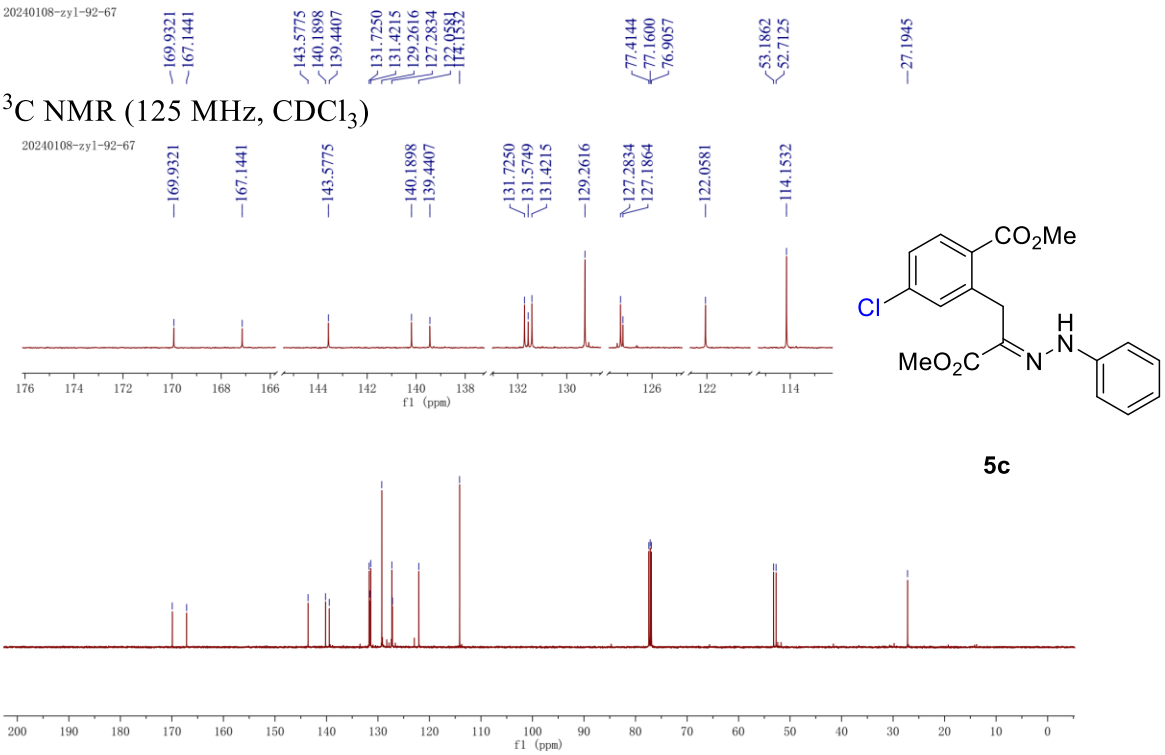
5b

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



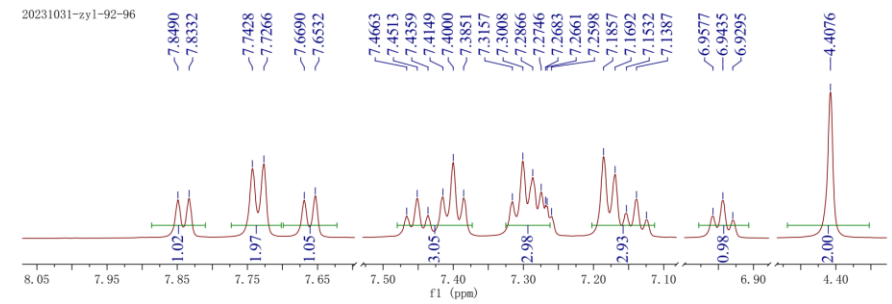
5c

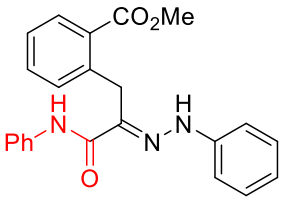
^{13}C NMR (125 MHz, $CDCl_3$)



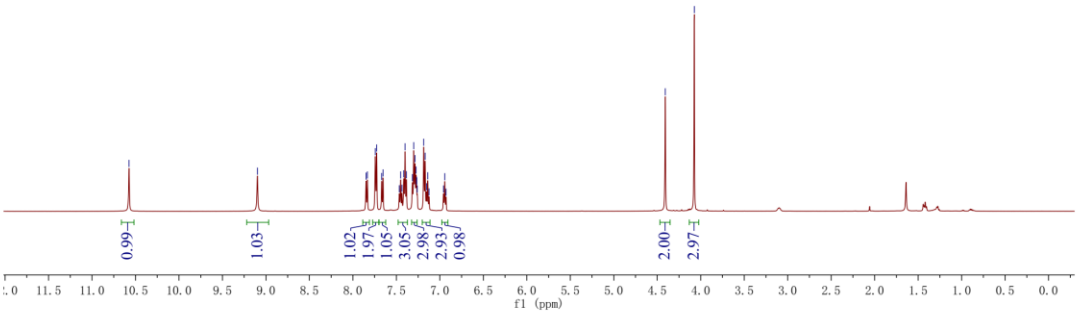
5c

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

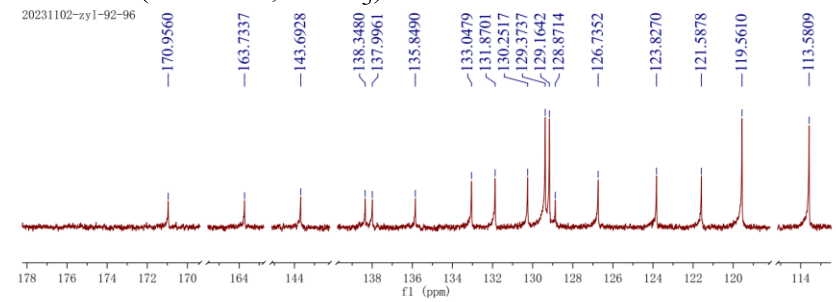


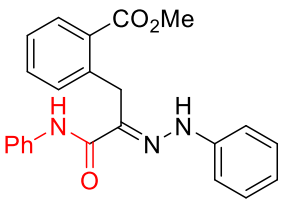


5d

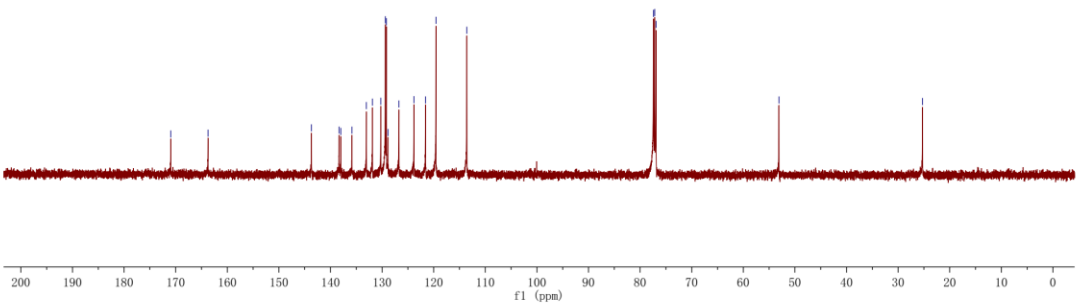


^{13}C NMR (125 MHz, $CDCl_3$)

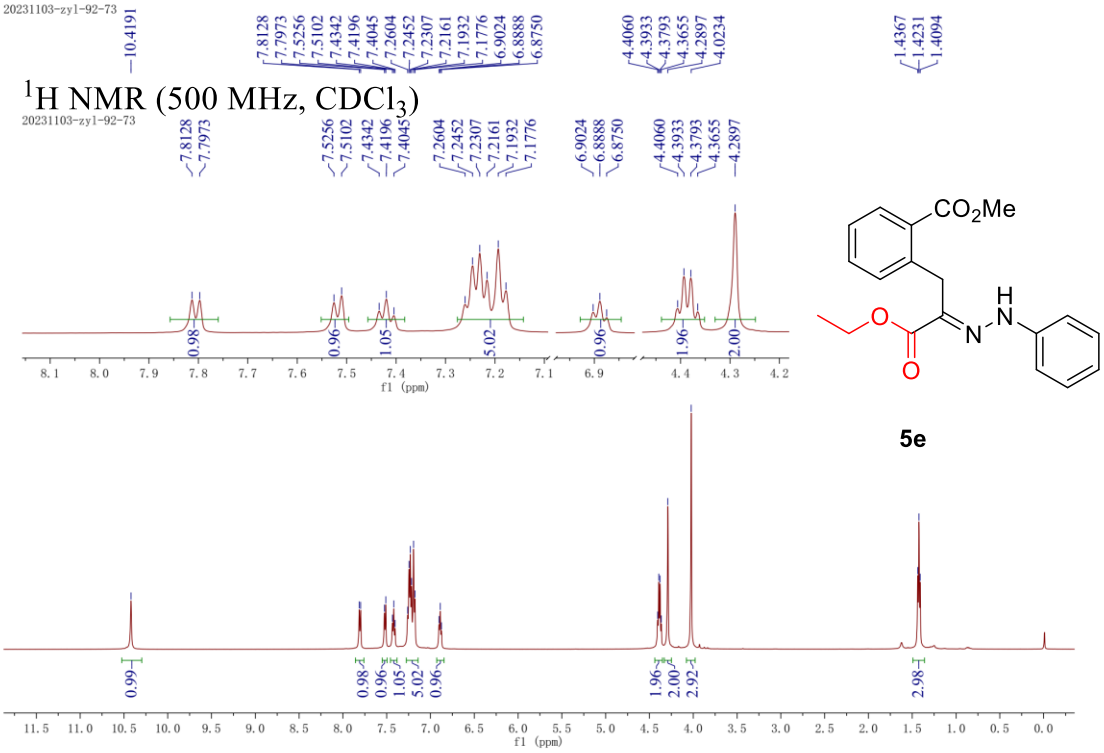




5d

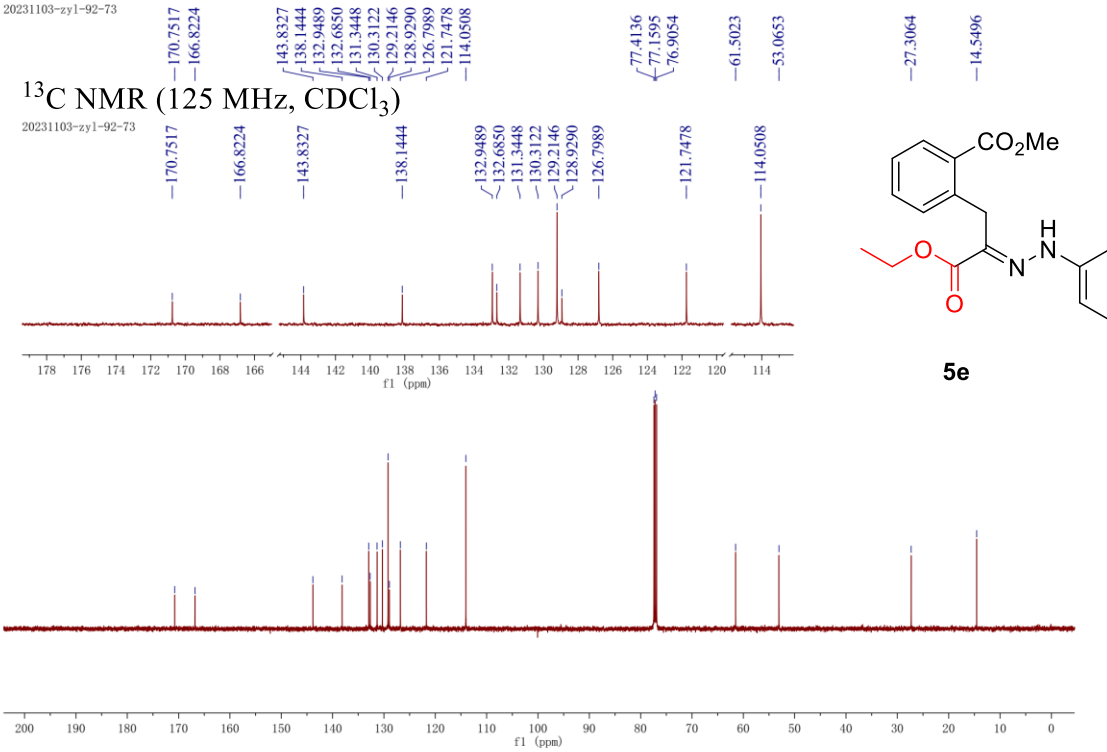


^{1}H NMR (500 MHz, $CDCl_3$)



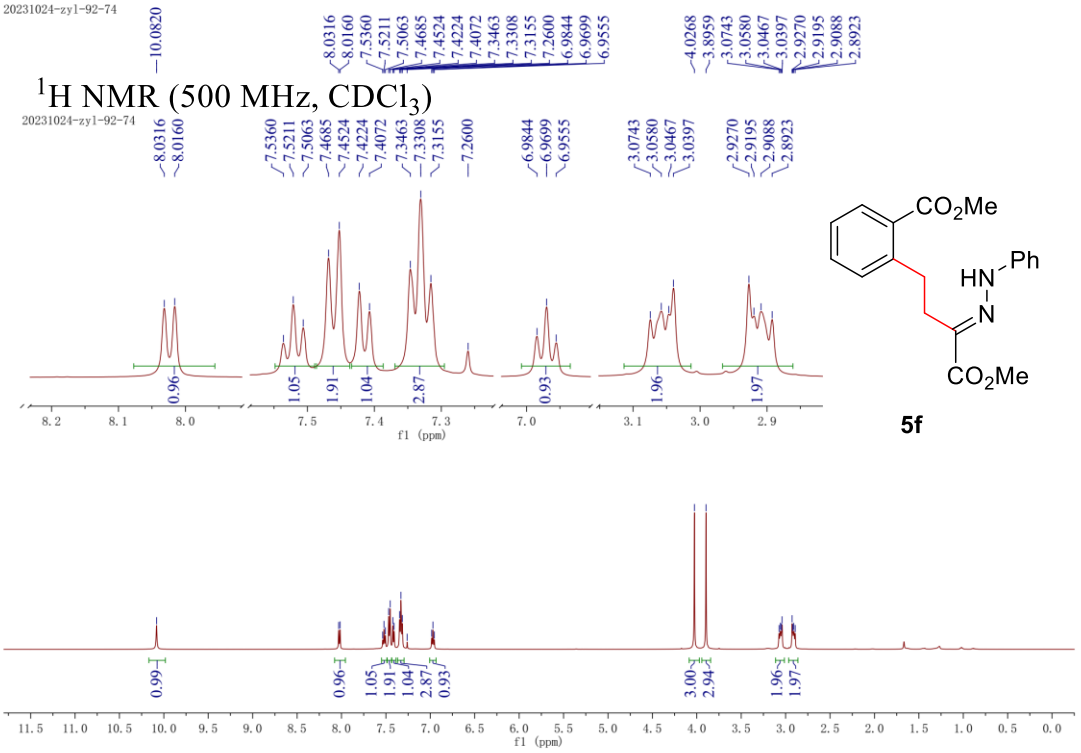
5e

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



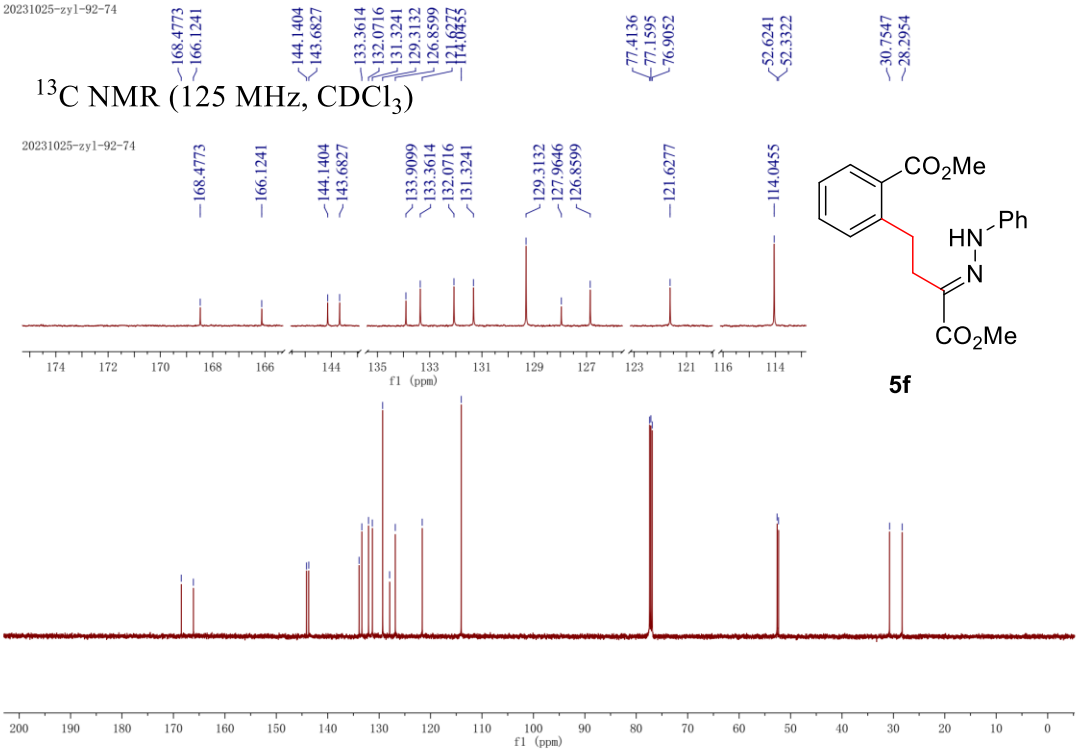
5e

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



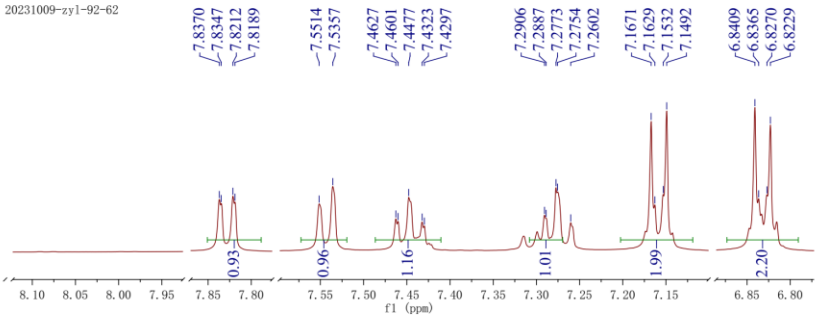
5f

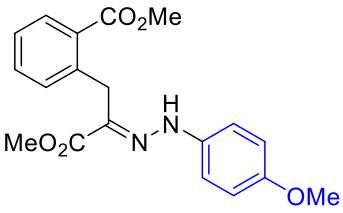
^{13}C NMR (125 MHz, $CDCl_3$)



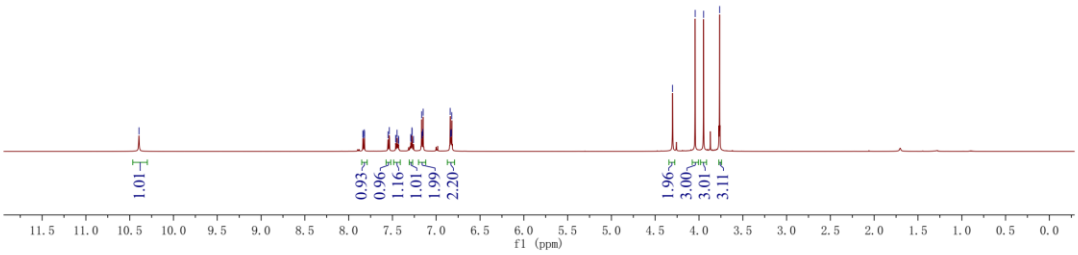
5f

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

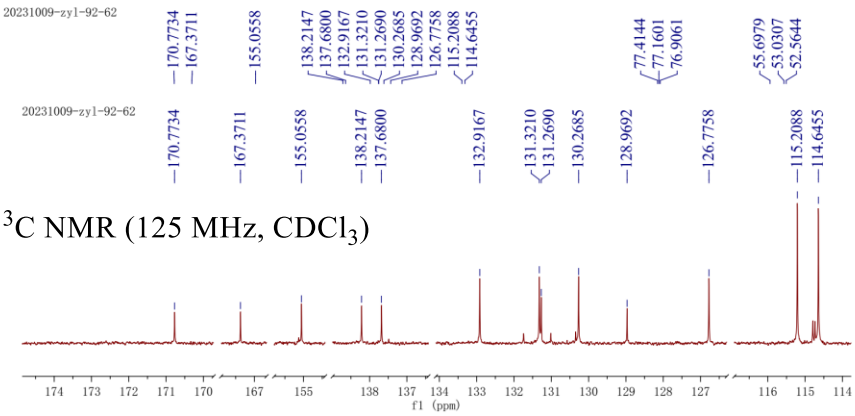


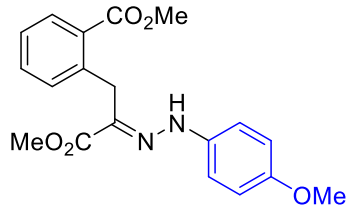


5g

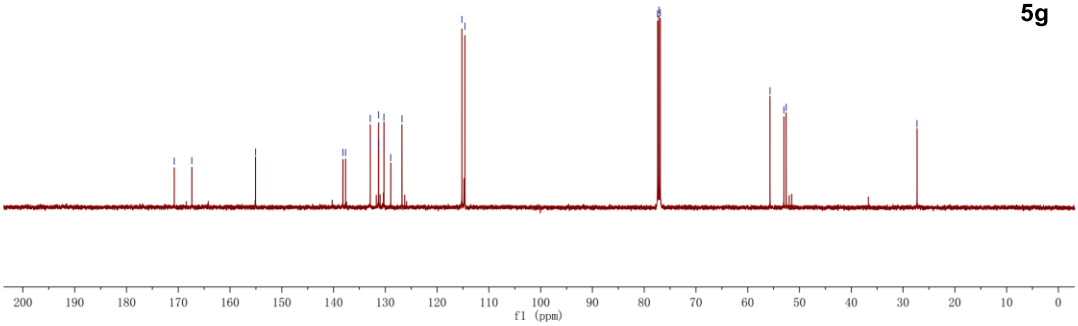


^{13}C NMR (125 MHz, $CDCl_3$)

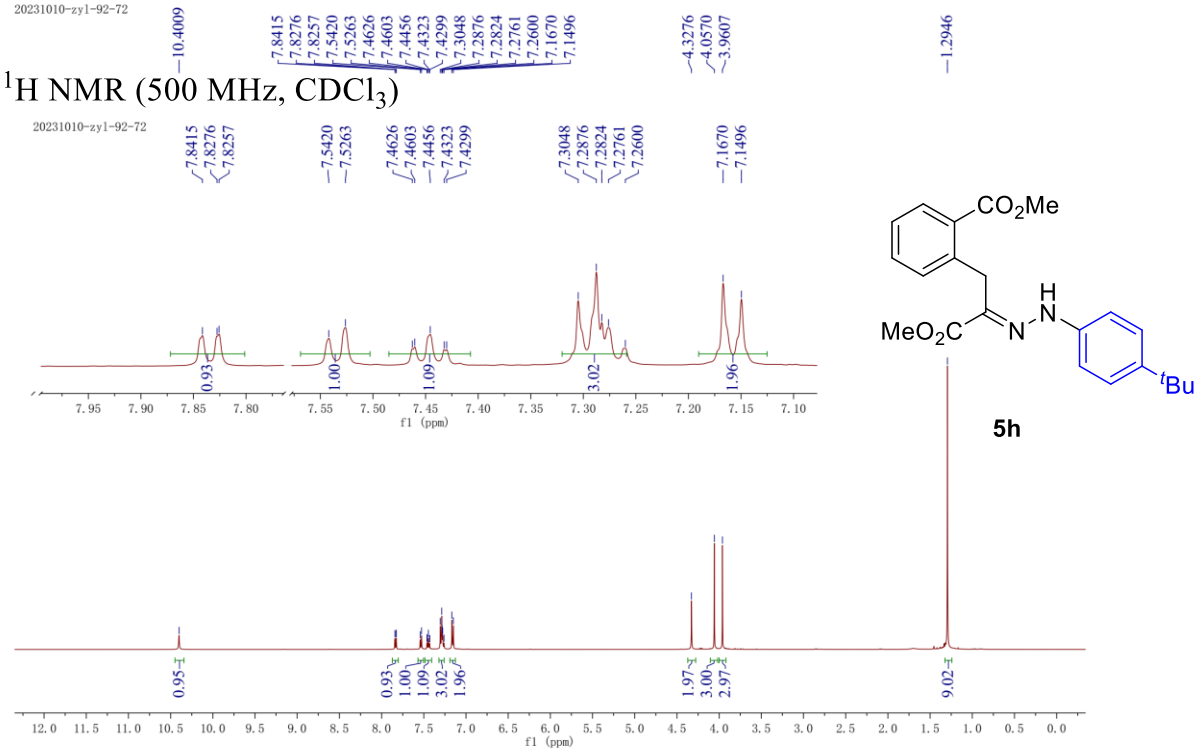




5g

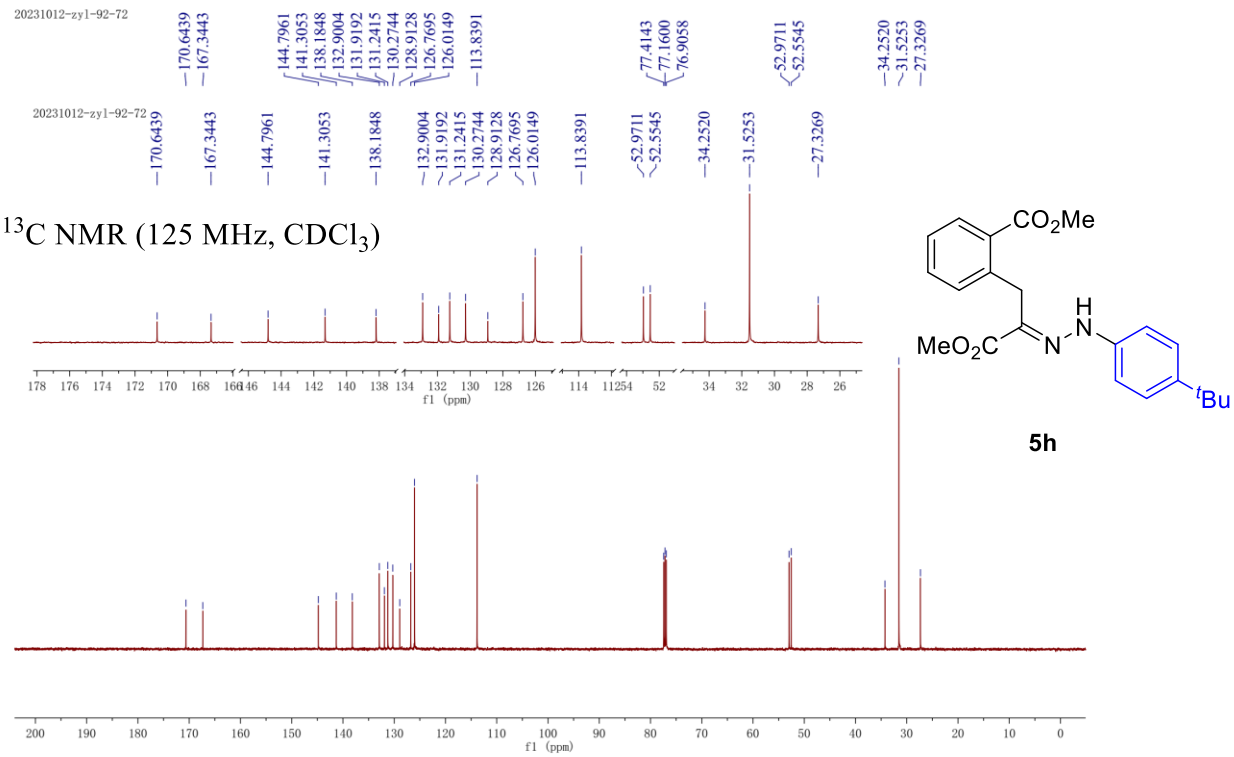


^{1}H NMR (500 MHz, $CDCl_3$)



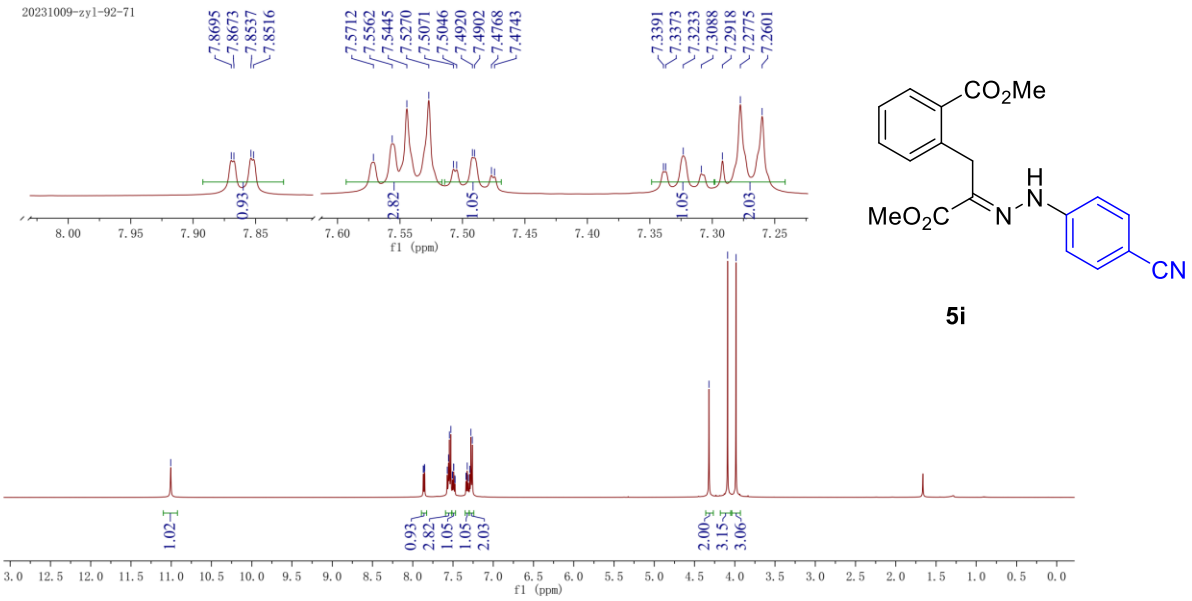
5h

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



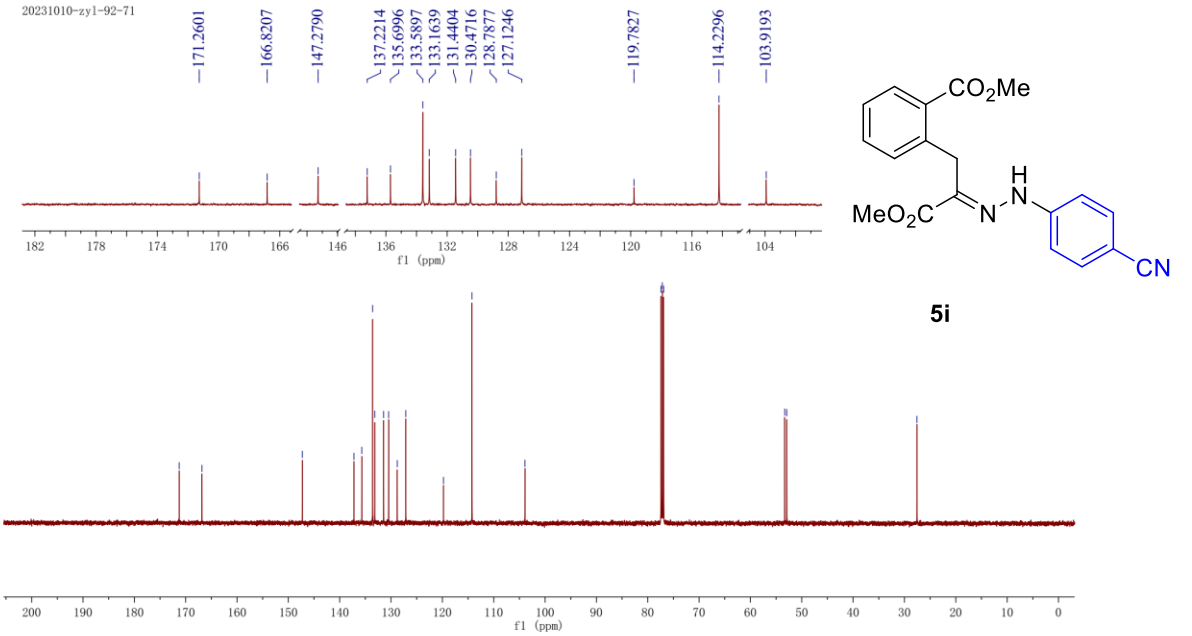
5h

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



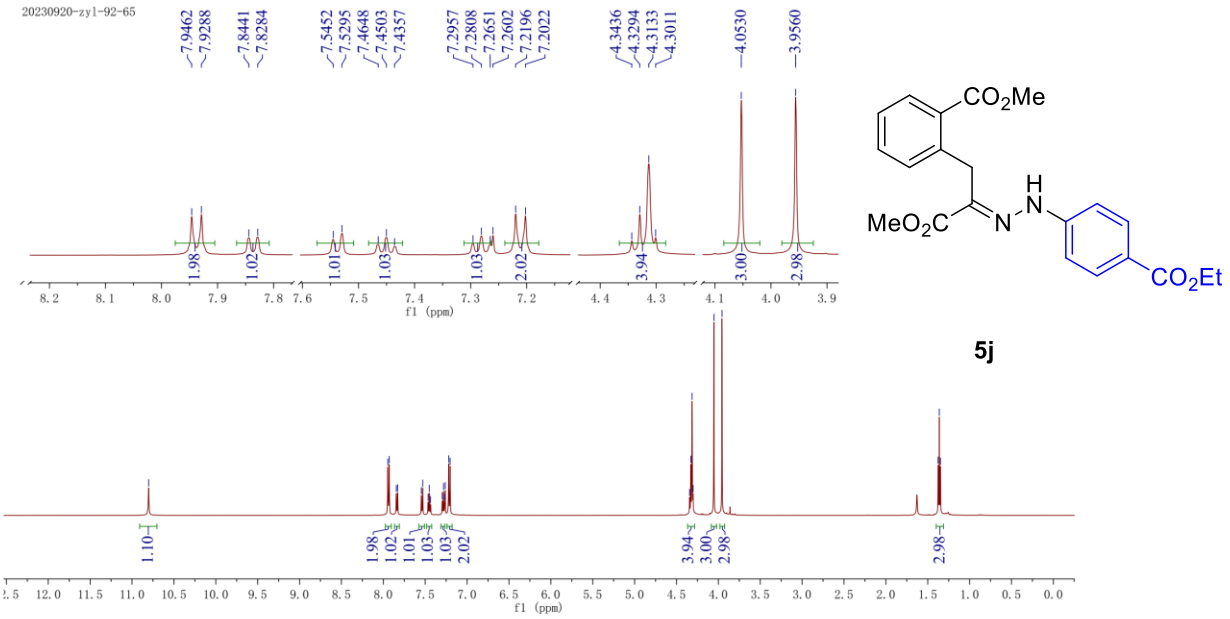
5i

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

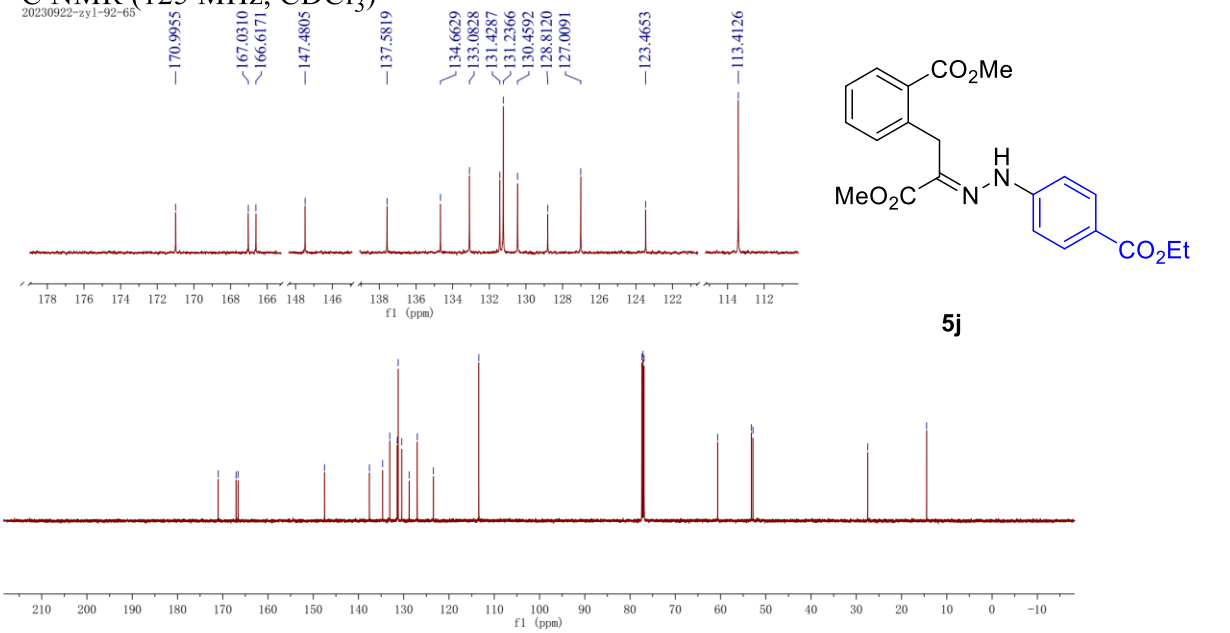


5i

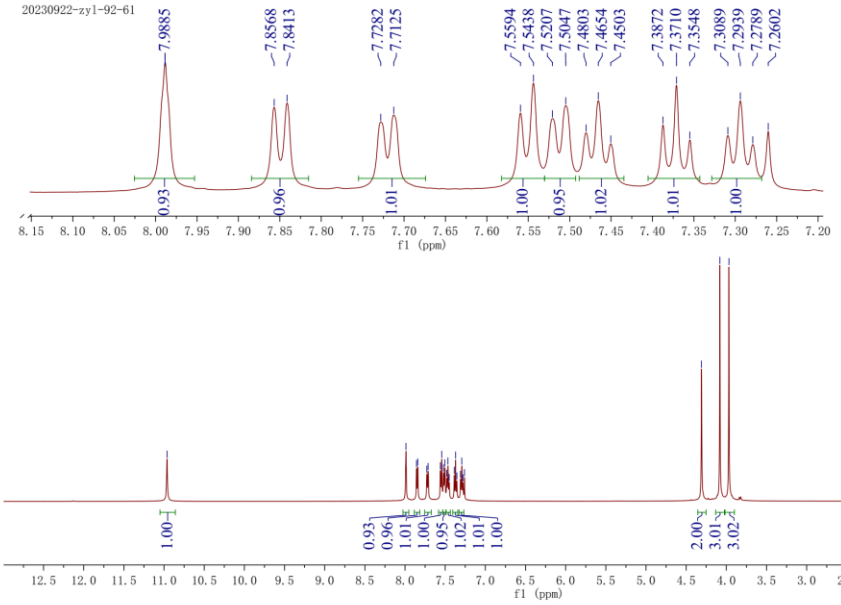
^{1}H NMR (500 MHz, $CDCl_3$)

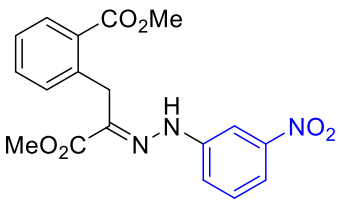


^{13}C NMR (125 MHz, $CDCl_3$)



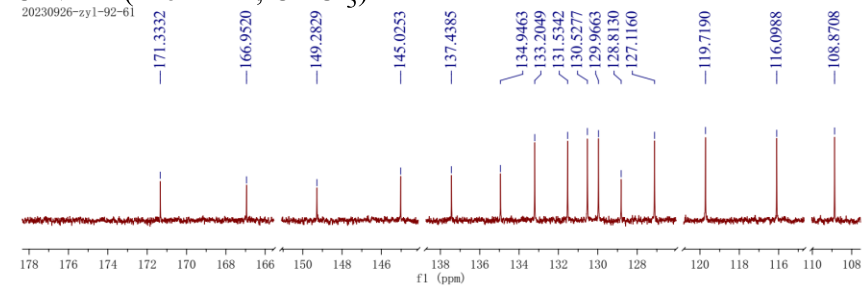
^{1}H NMR (500 MHz, $CDCl_3$)

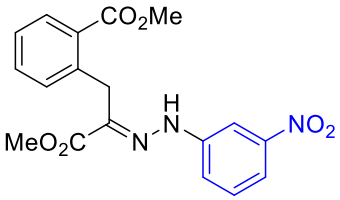




5k

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





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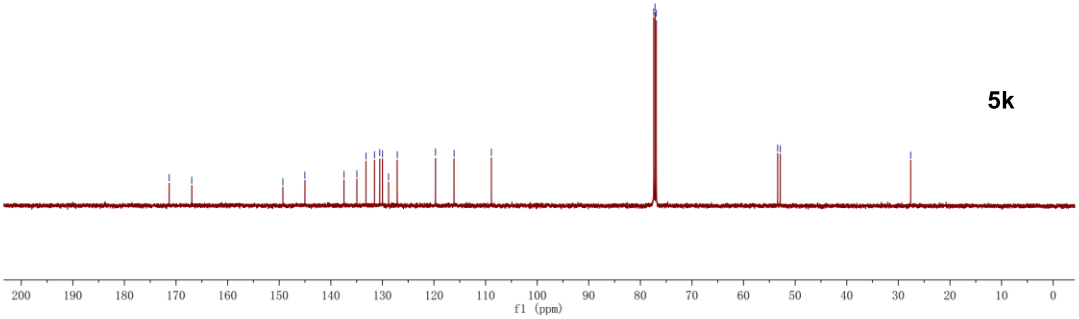
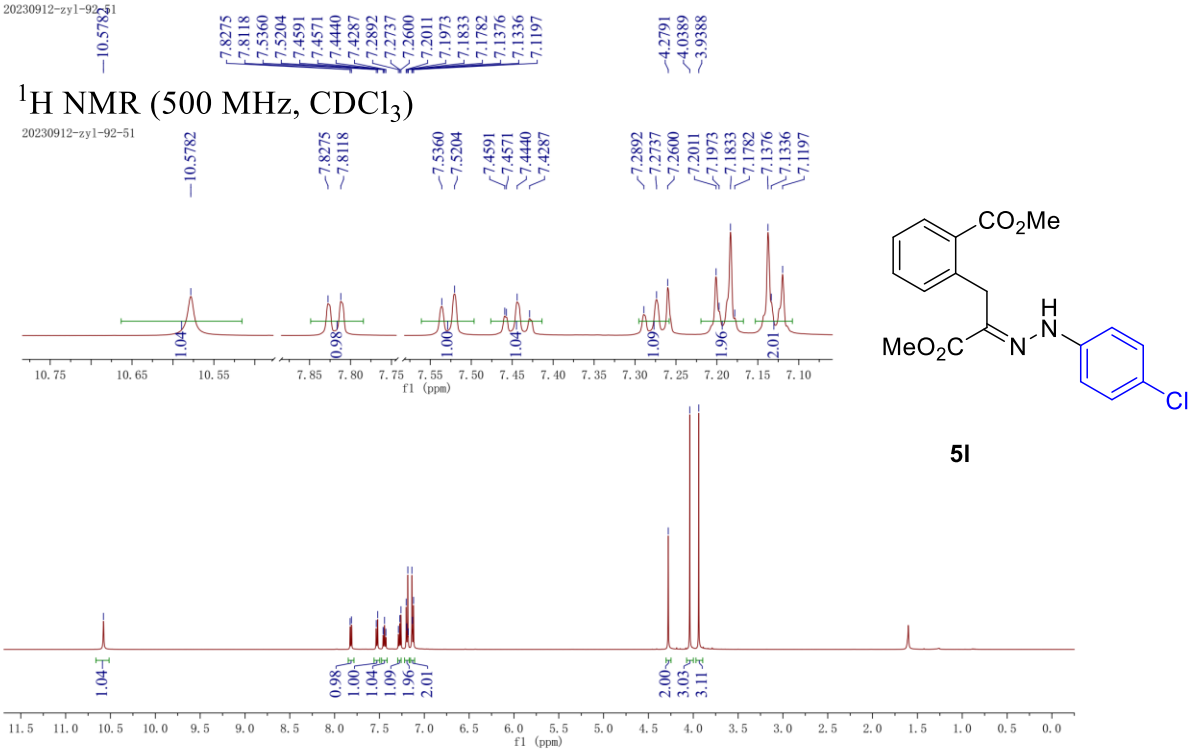
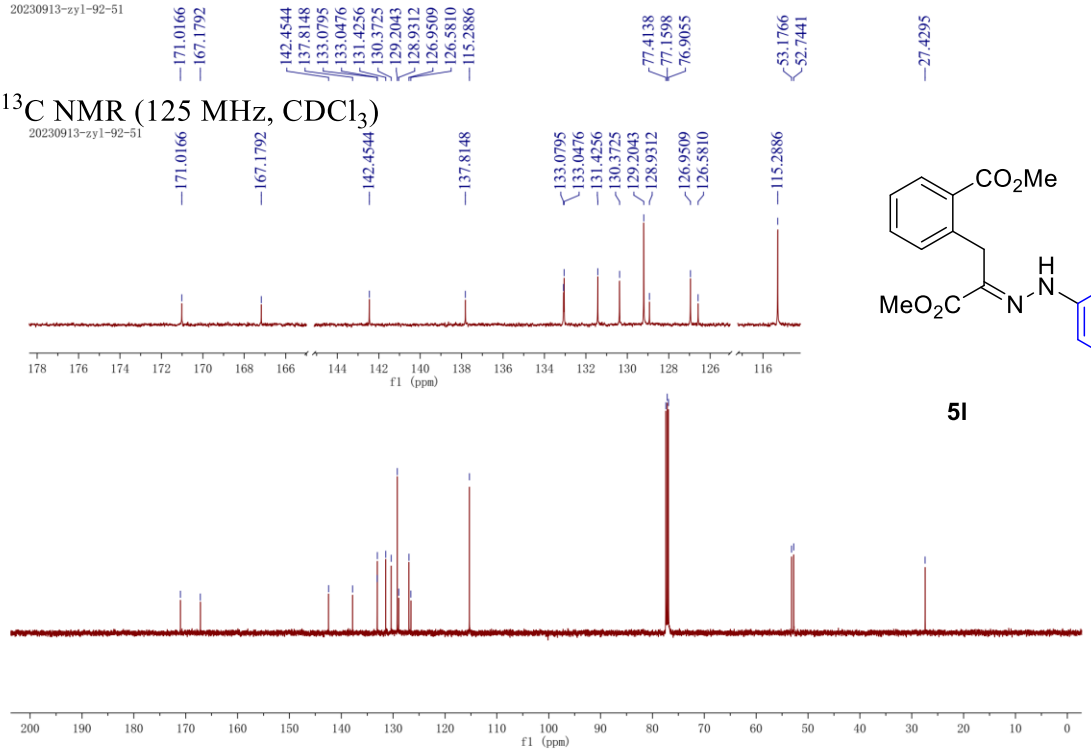


^{1}H NMR (500 MHz, $CDCl_3$)



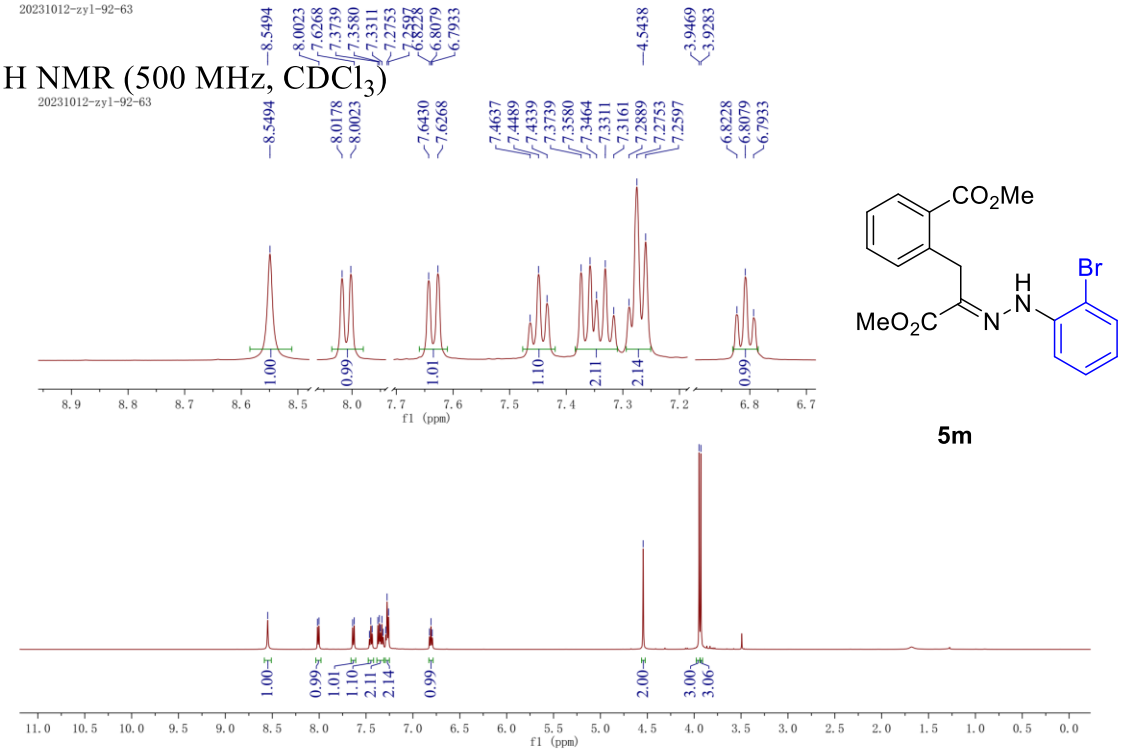
5l

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



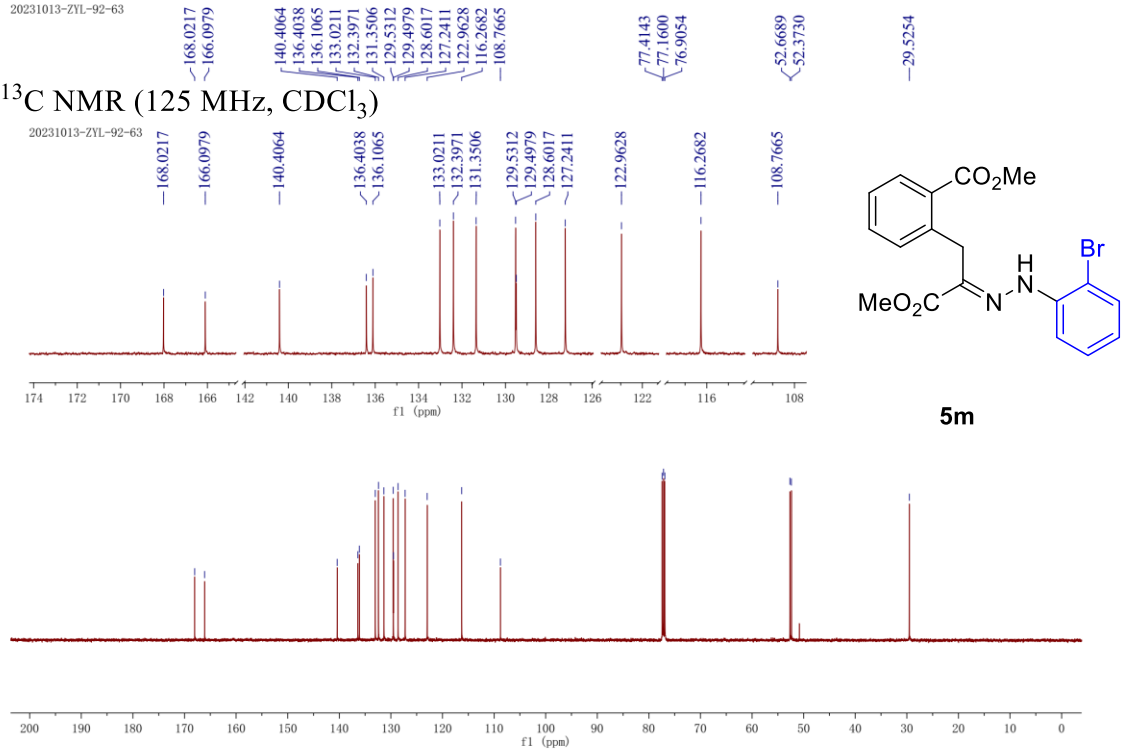
5l

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



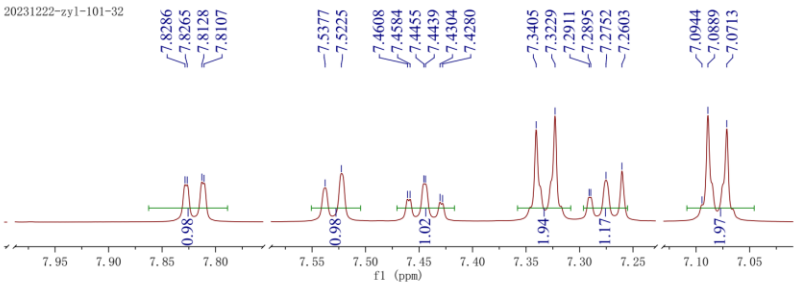
5m

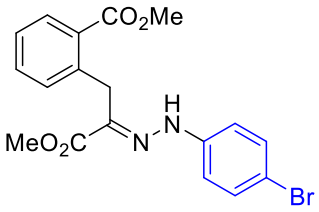
^{13}C NMR (125 MHz, $CDCl_3$)



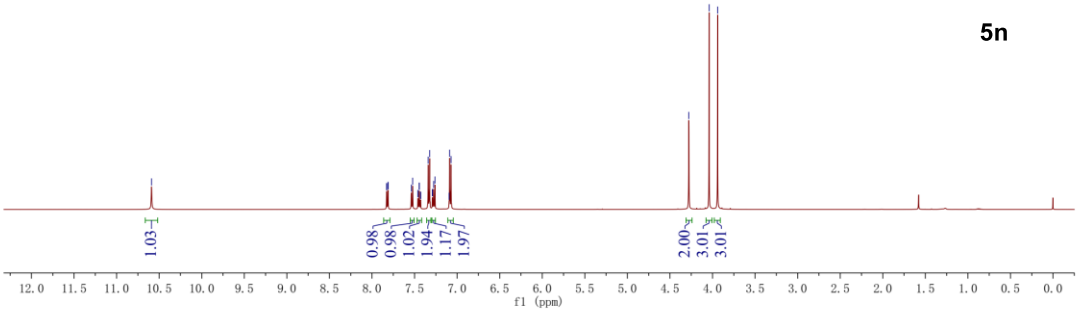
5m

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

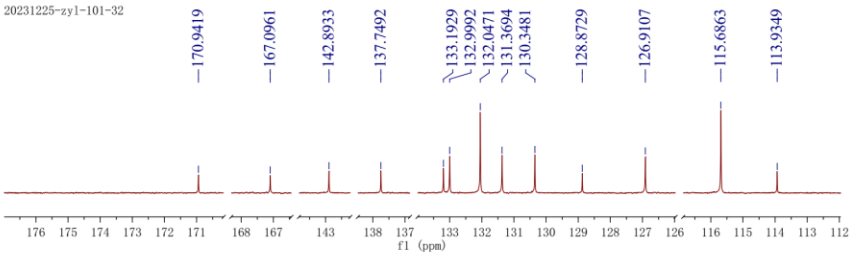


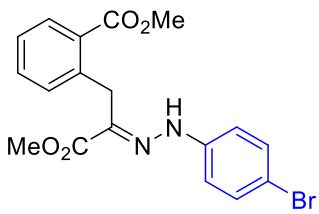


5n

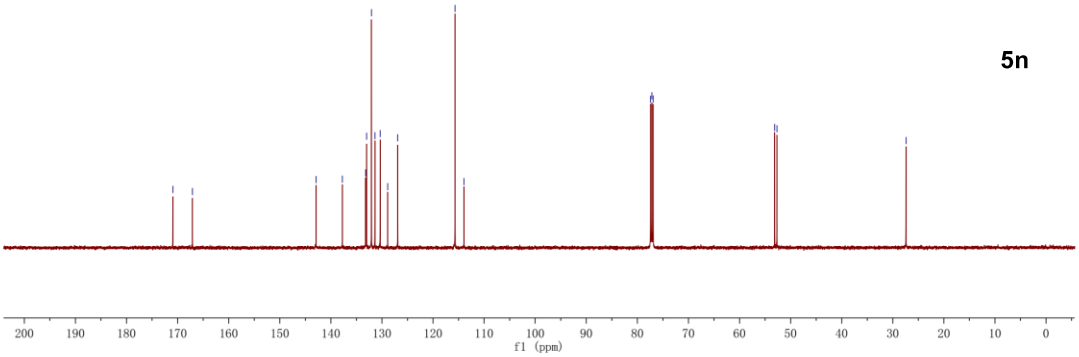


^{13}C NMR (125 MHz, $CDCl_3$)

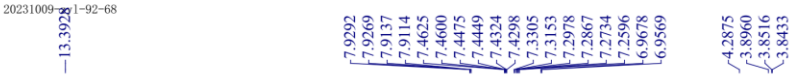




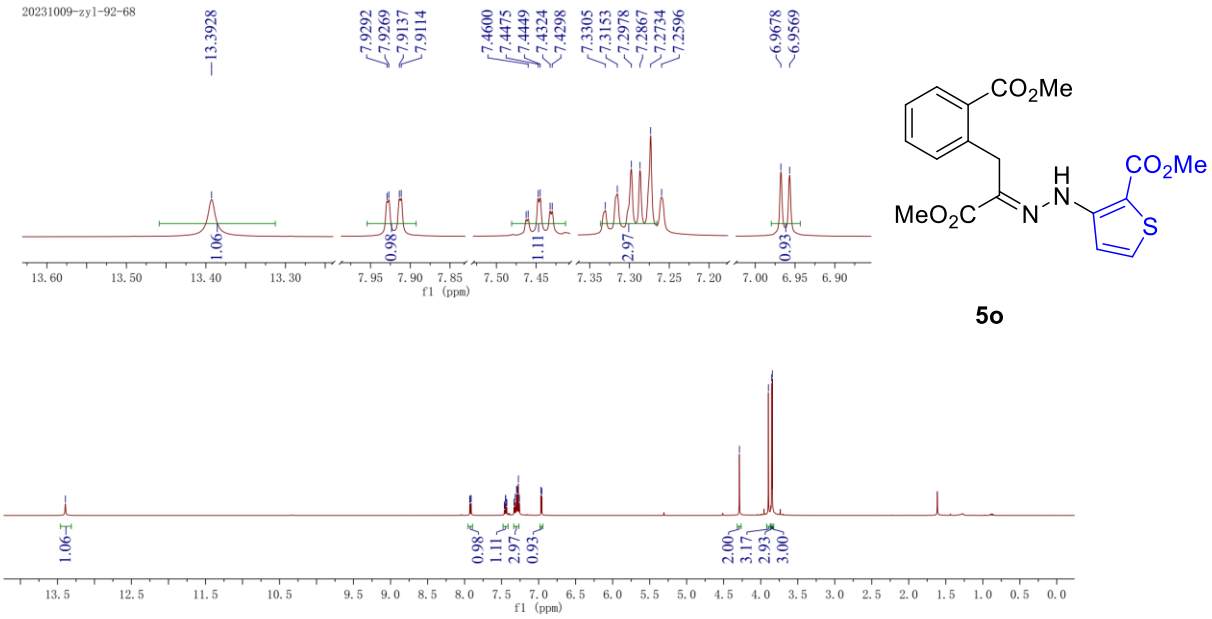
5n



20231009-zyl-92-68

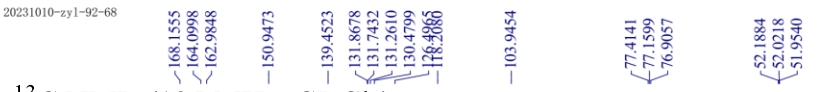


^{1}H NMR (500 MHz, $CDCl_3$)

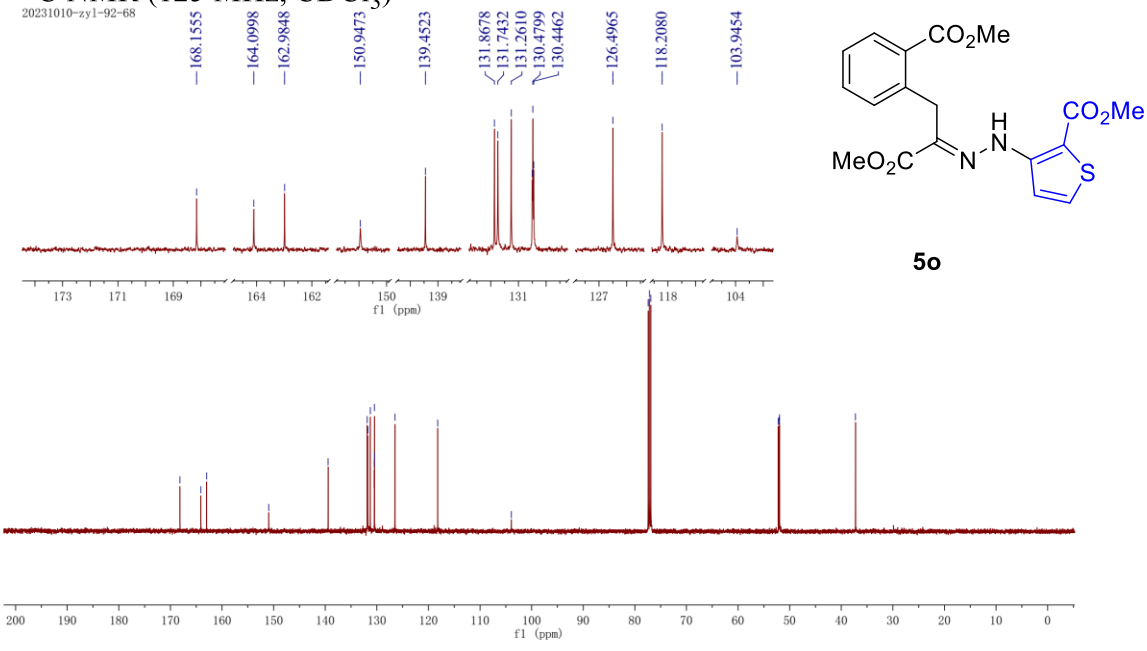


5o

20231010-zyl-92-68

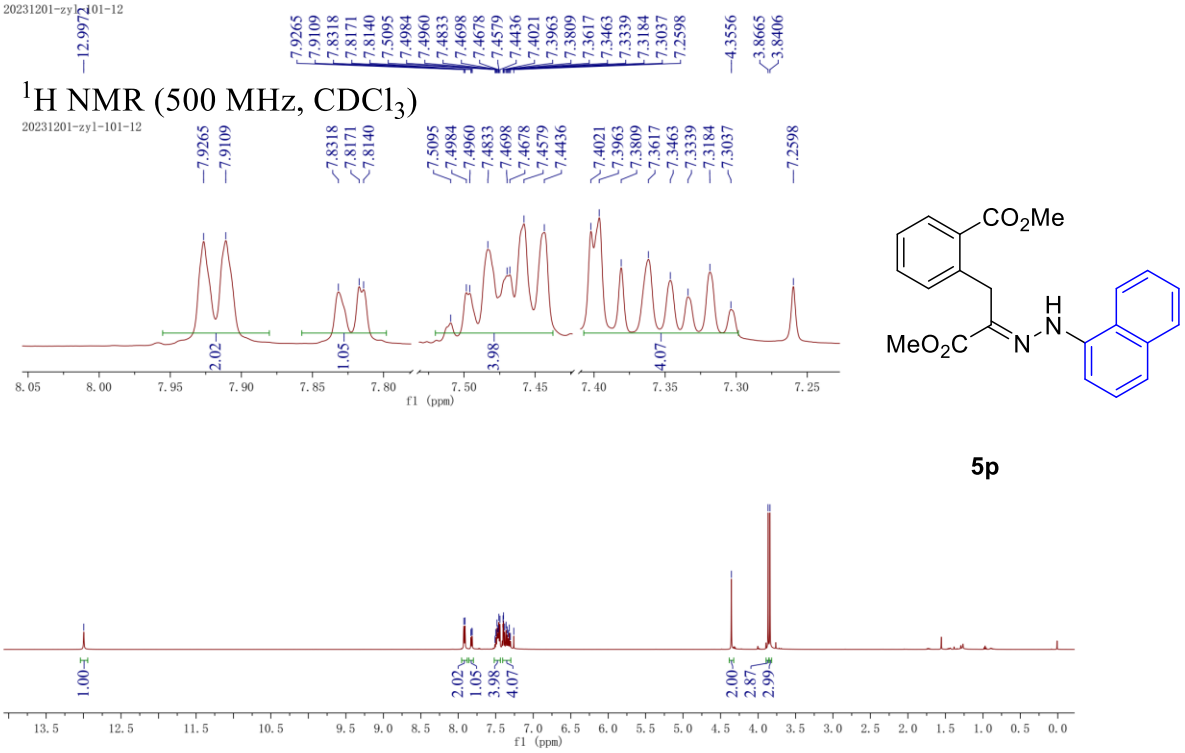


^{13}C NMR (125 MHz, $CDCl_3$)



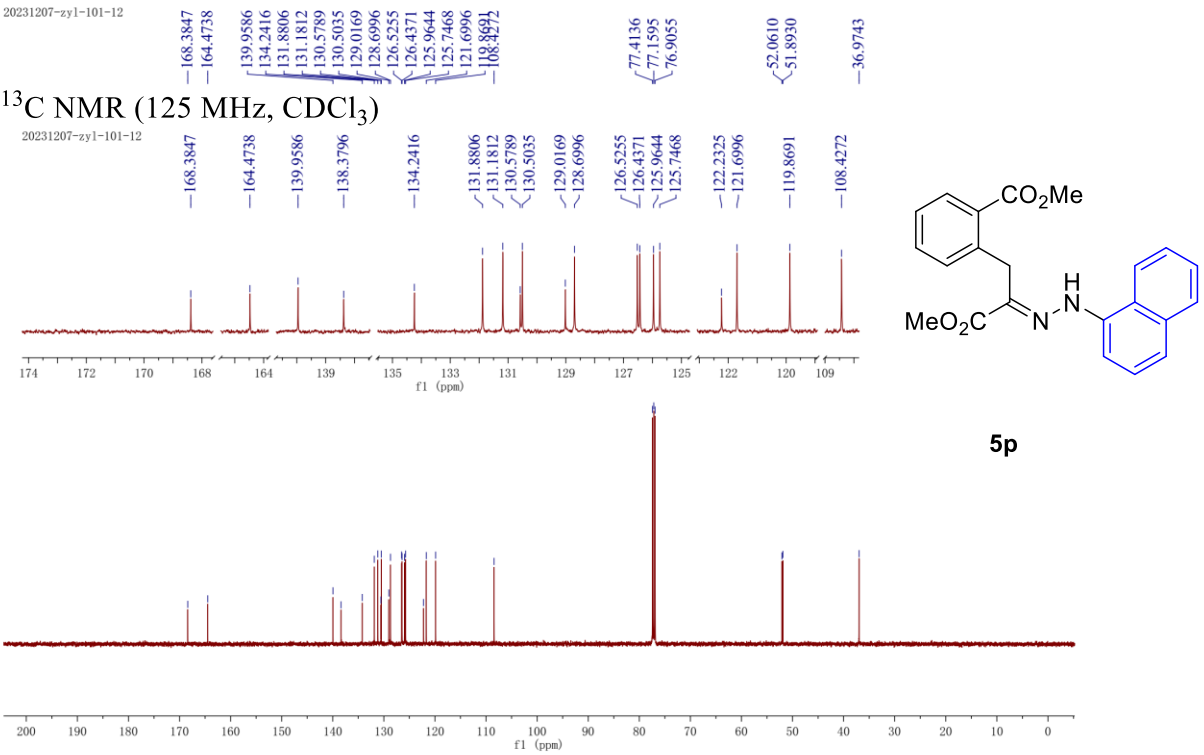
5o

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



5p

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



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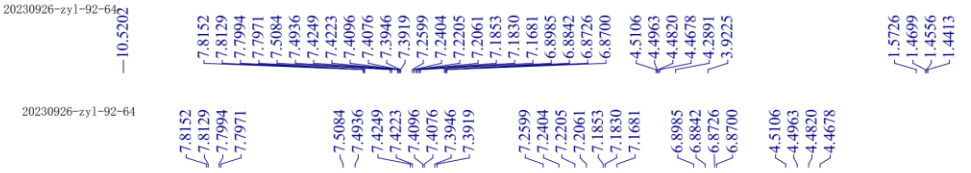
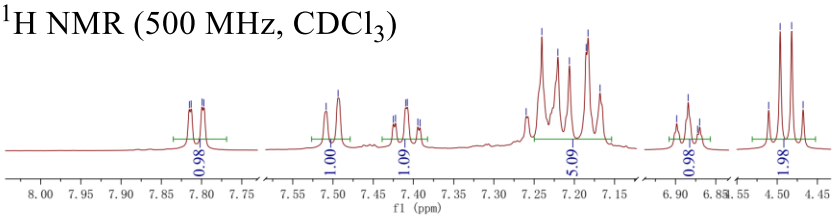
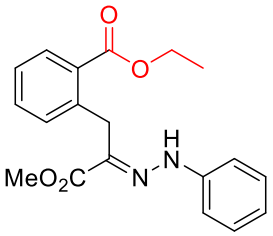
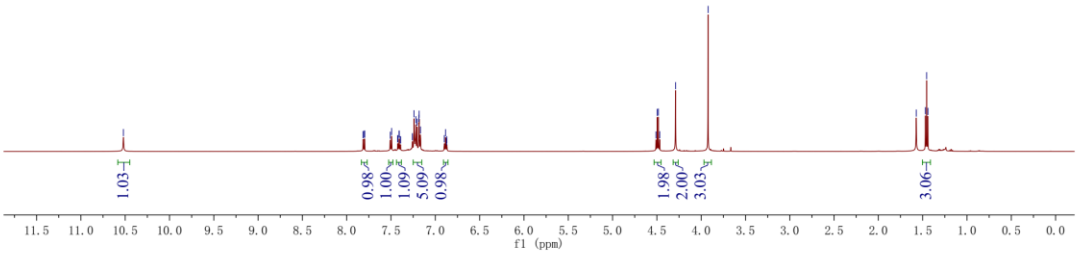


^{1}H NMR (500 MHz, $CDCl_3$)

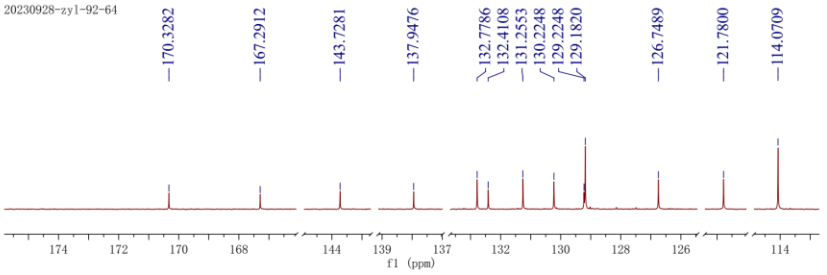


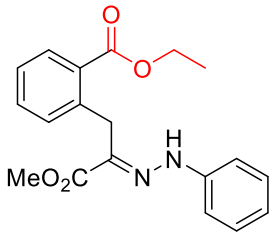


5q



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





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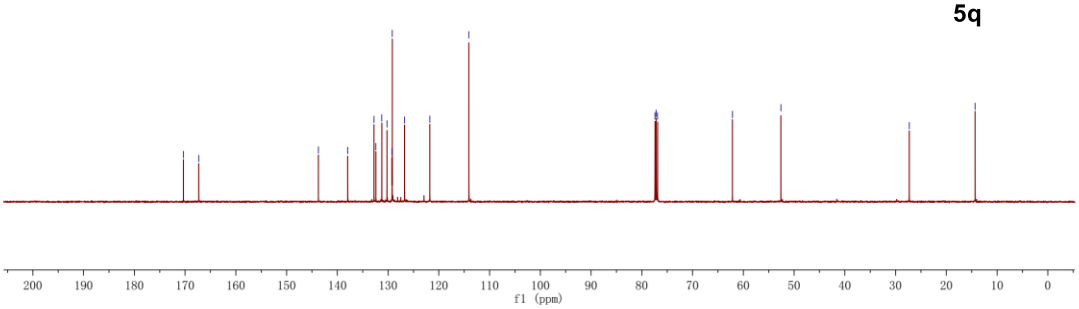
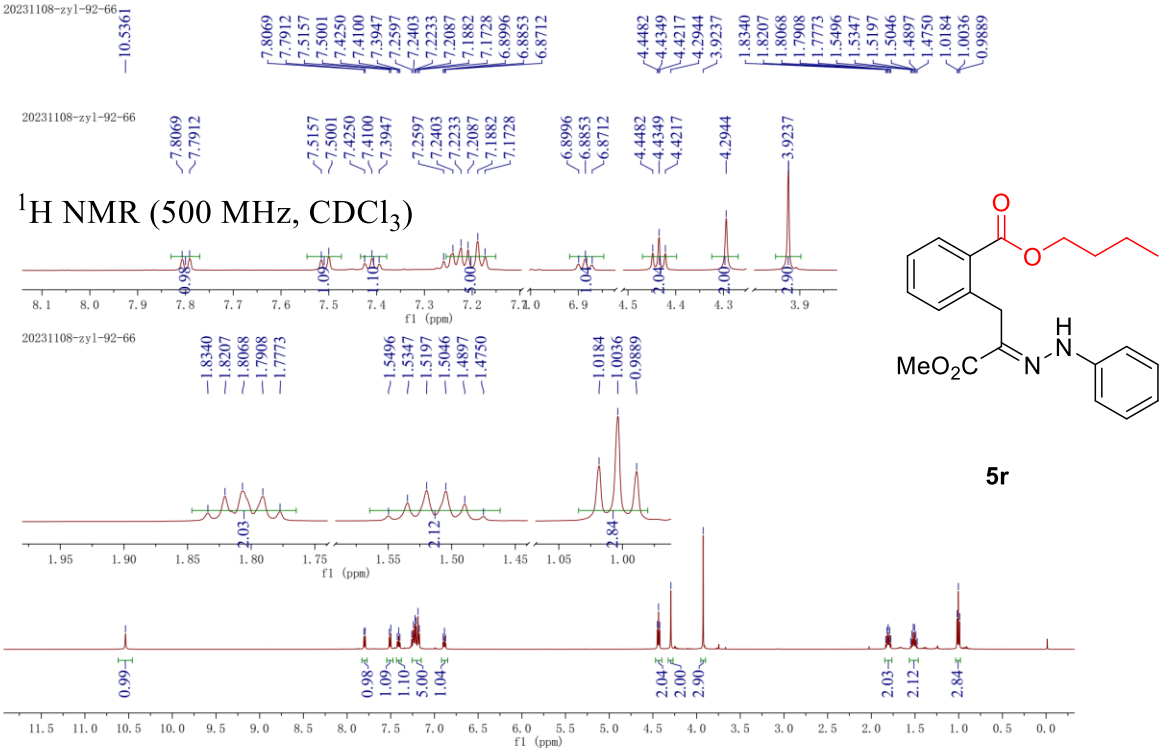
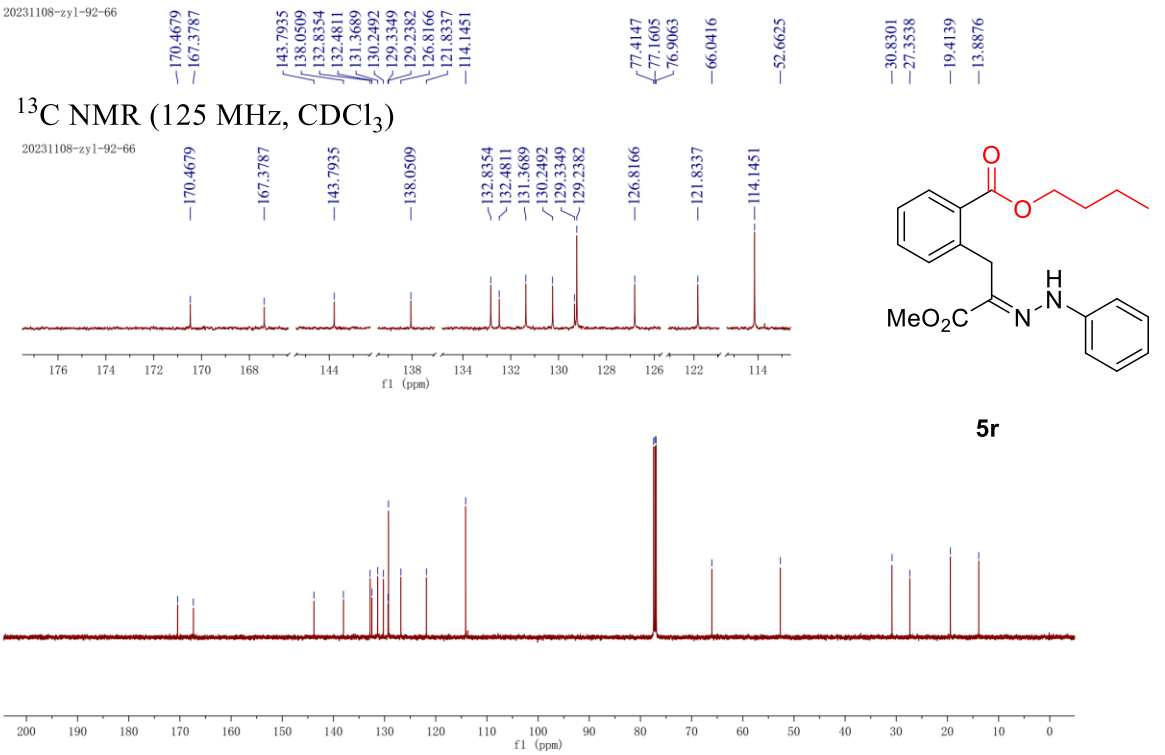
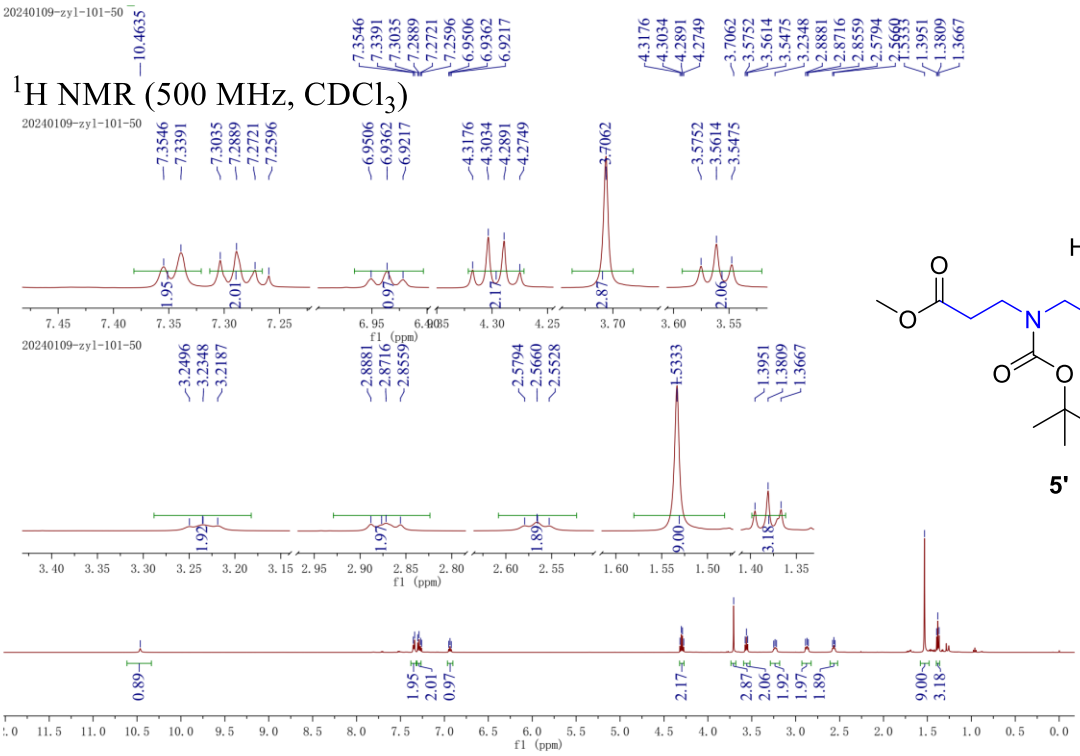



20231108-zyl-92-66
^{1}H NMR (500 MHz, $CDCl_3$)
5r

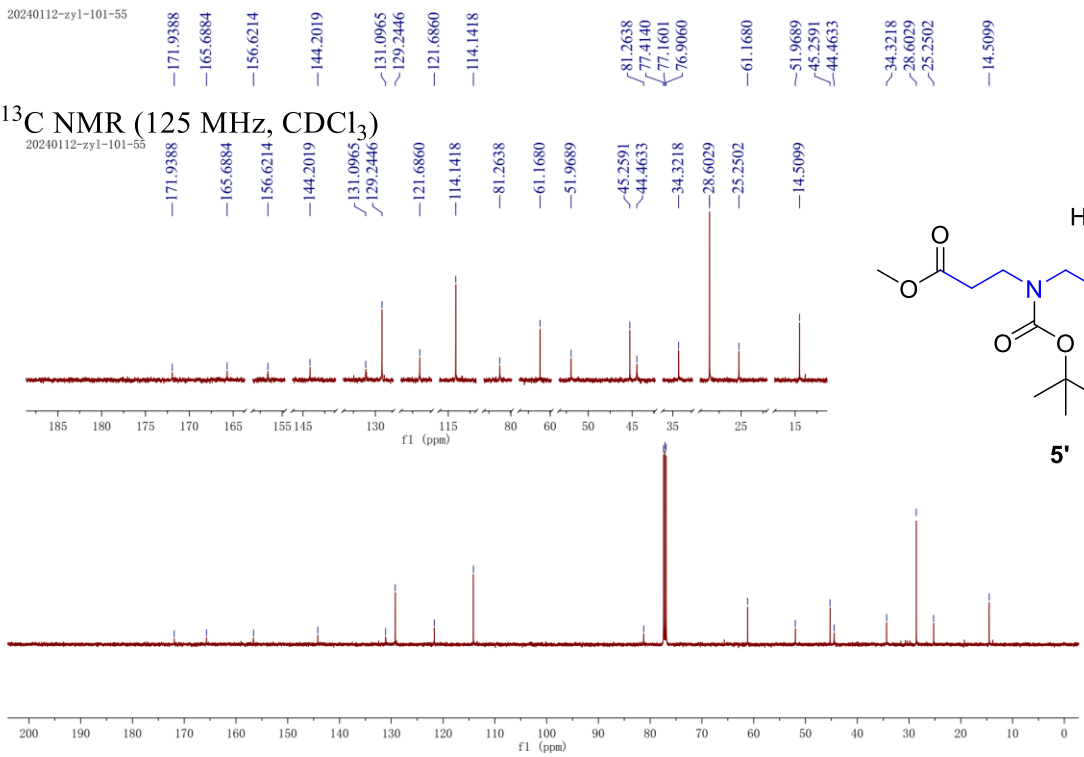

20231108-zyl-92-66
^{13}C NMR (125 MHz, $CDCl_3$)
5r

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



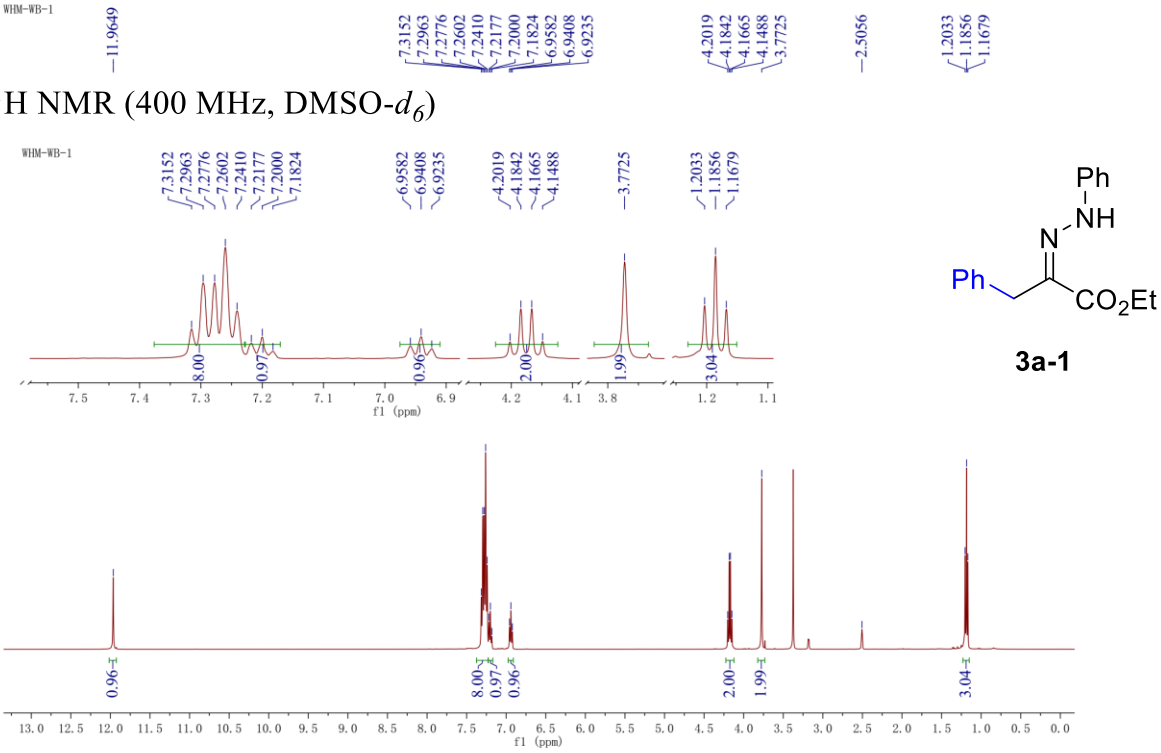
5'

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



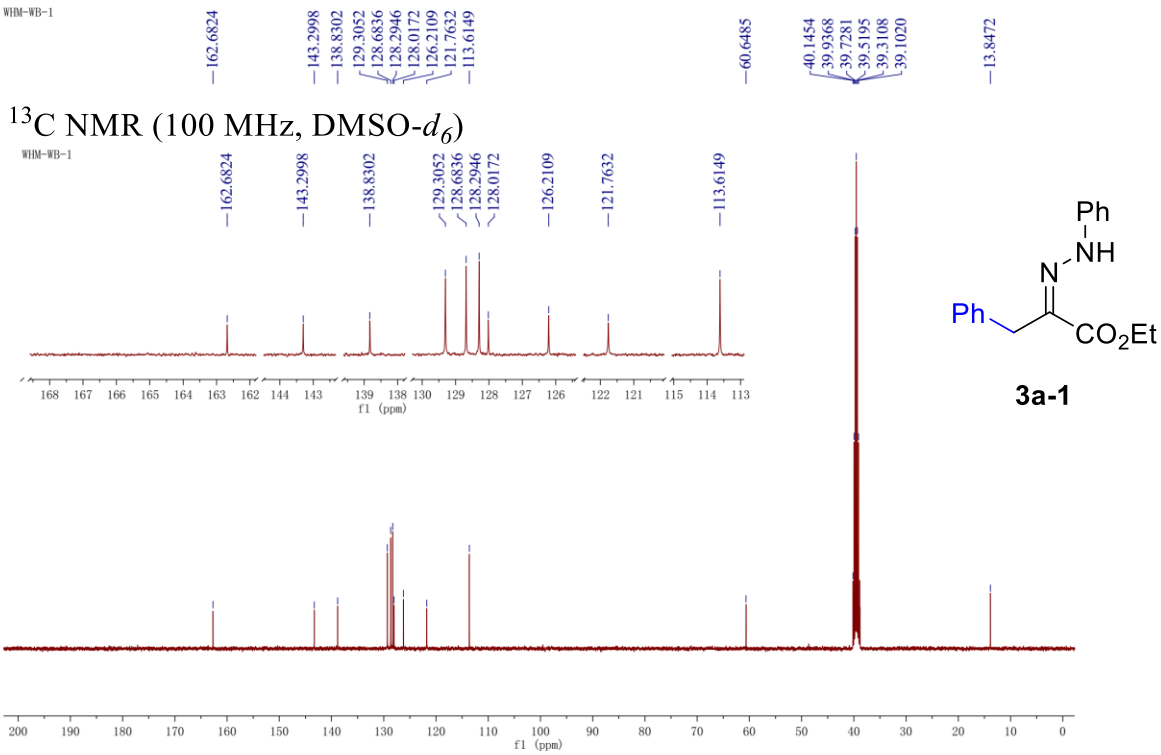
5'

^{1}H NMR (400 MHz, DMSO-d_6)



3a-1

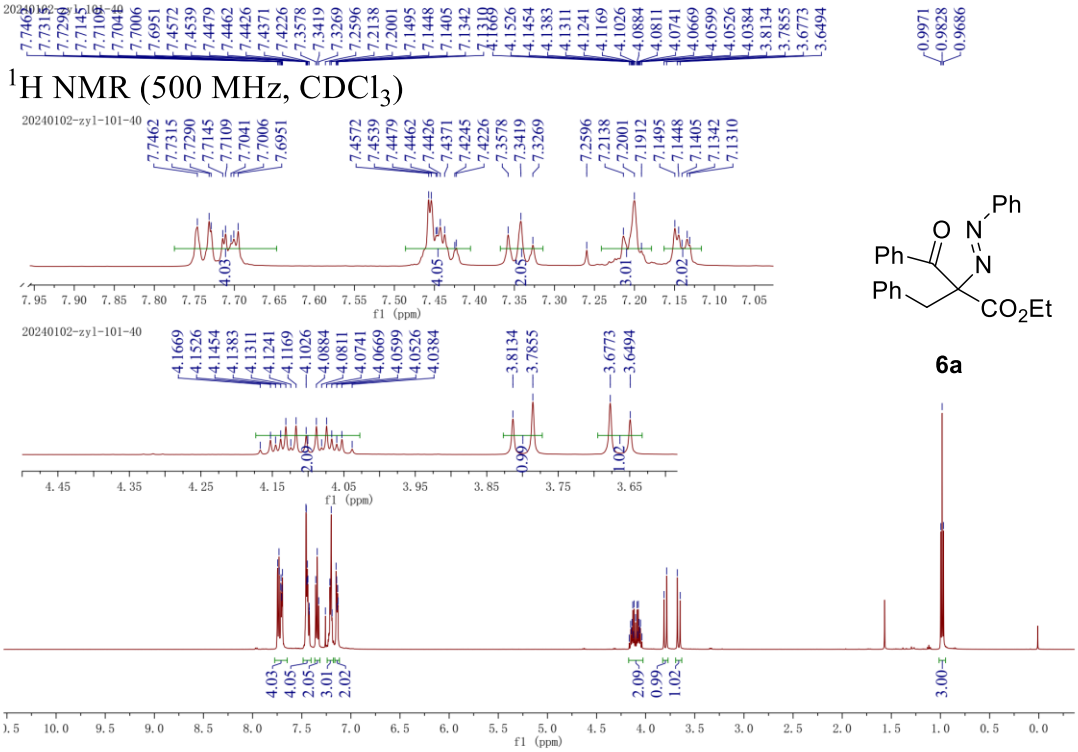
^{13}C NMR (100 MHz, DMSO-d_6)



3a-1

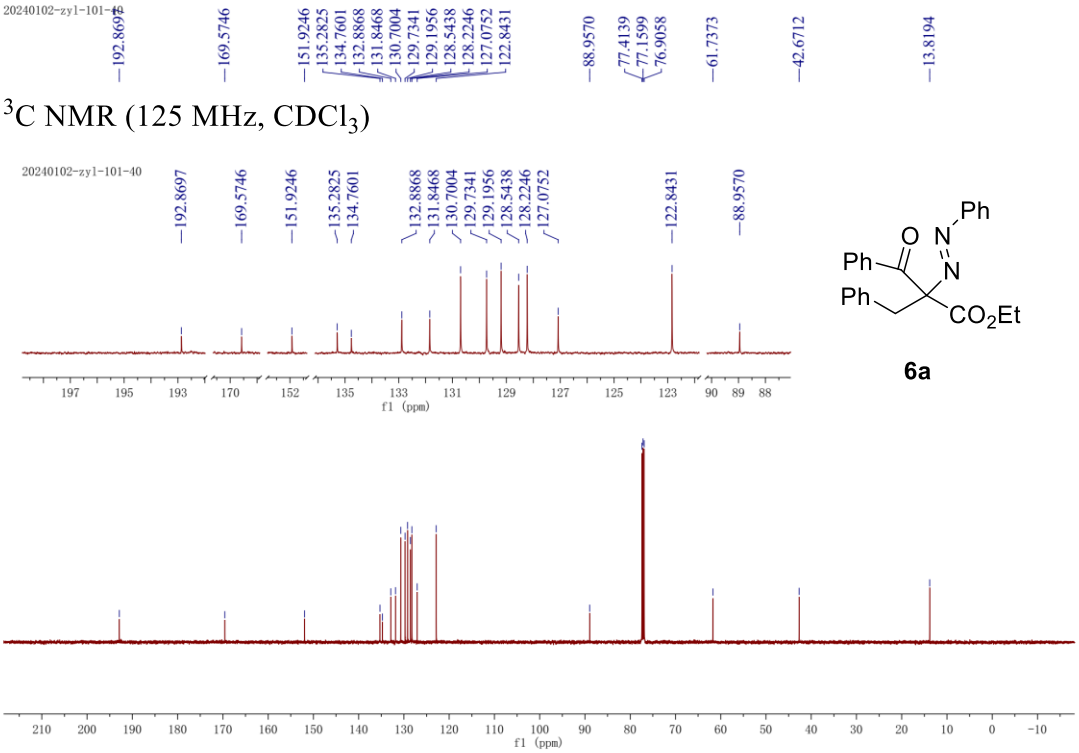
NMR spectra of compounds 6a

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



6a

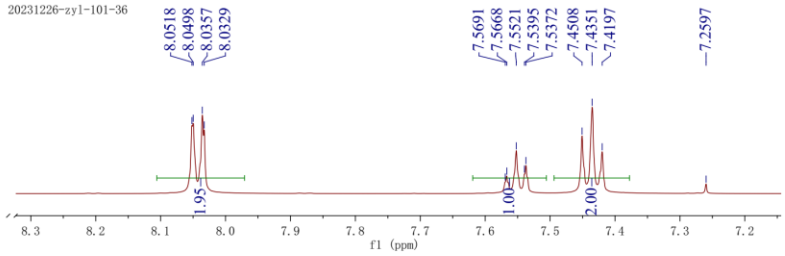
^{13}C NMR (125 MHz, $CDCl_3$)

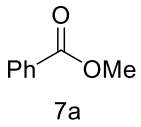


6a

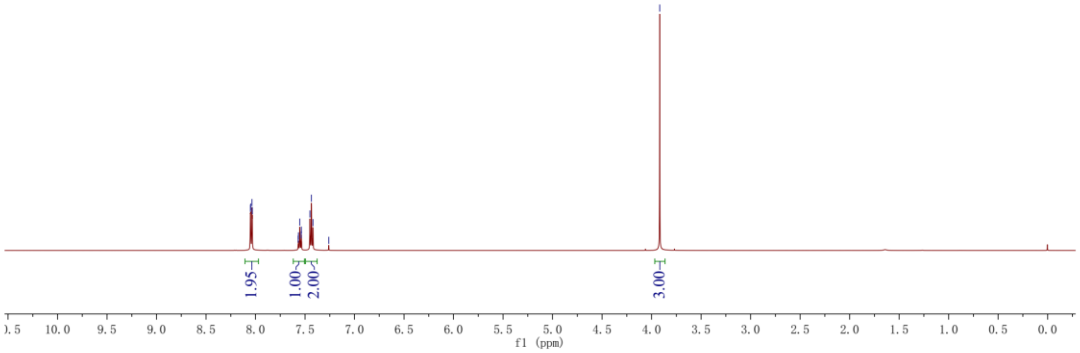
NMR spectra of compounds 7a

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

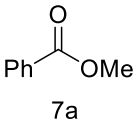




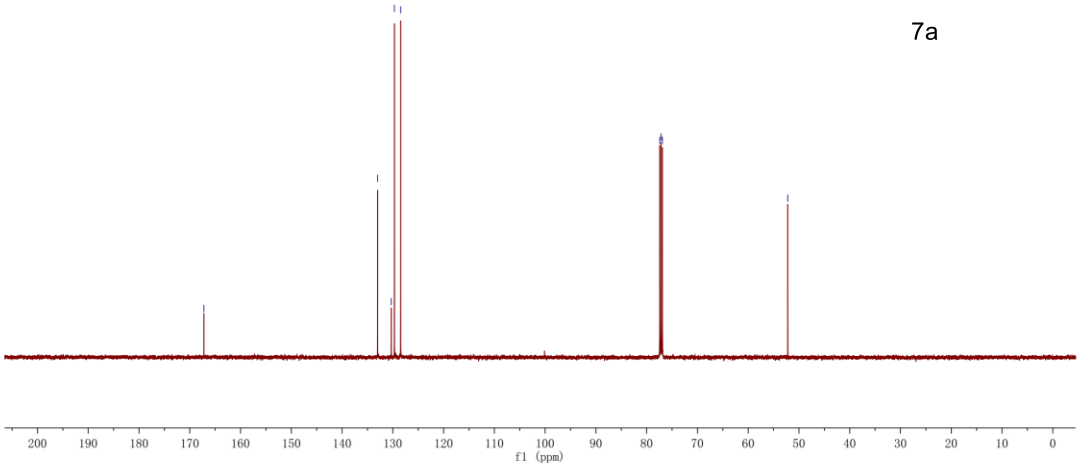
7a



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



7a



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