Supporting Information

Photocatalytic Phosphine-Mediated H_2O/D_2O as Only H/D Source for Radical Transfer Hydrogenation/Deuteration of α-Aryl Imino Esters

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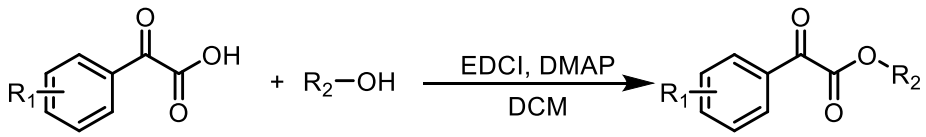
1. General information

Unless stated otherwise, all reactions were carried out under argon. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). All catalytic experiments were performed under an atmosphere of argon by using Glove Box. ^{1}H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. $^{13}C\{^{1}H\}$ NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were obtained at 376 MHz. ^{31}P NMR spectra are referenced according to the proton signal as the primary reference for the unified chemical shift scale. High resolution mass spectra (HRMS) were performed on an Agilent 6540 spectrometer with ESI ionization. Commercially available reagents were used without further purification unless indicated otherwise, all solvents were dried. The light source was 30 W blue LED (449 nm, 1 W*30, 30-50 cd/m^2, made in Everlight Electronics., Ltd.); borosilicate glass Schlenk tube was used as the irradiation vessel; the distance from the light source to the irradiation vessel; 2-3 cm and no filter was used.

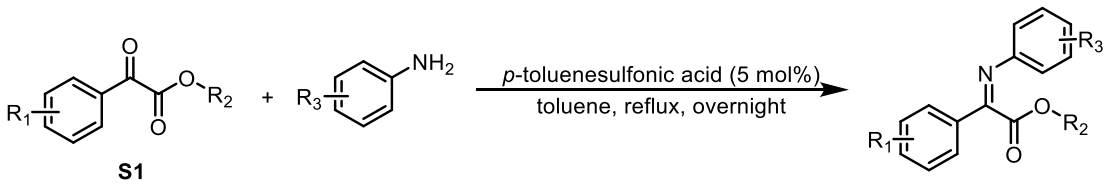
2. General procedure for the synthesis of α-aryl esters [1,2]



S1

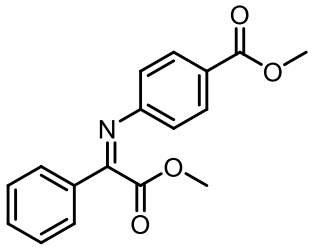
Step 1: Benzoylformic acid (1.50g, 10 mmol, 1.0 equiv.), alcohol (10 mmol, 1 equiv.), and EDCI (2.10 g, 11 mmol, 1.1 equiv.) were added to a dry flask and dissolved in DCM (30 mL). The mixture was then cooled to 0 °C, followed by the slow addition of DMAP (0.062g, 0.5 mmol, 0.05 equiv.) dissolved in DCM into the system. After stirring at 0 °C for 1 h, the reaction was allowed to proceed at room temperature overnight. When the reaction was completed as determined by TLC, the mixture was quenched with a saturated aqueous NH_4Cl solution (10 mL) and then extracted with DCM (3×30 mL). The organic phase was washed by brine, dried over Na_2SO_4, filtered and

concentrated under reduced pressure. The crude product was purified by flash column chromatography to give **S1**.



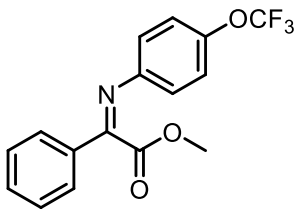
Step 2: The mixture of anisidine (1.05 equiv.), **S1** (1.0 equiv.) and *p*-toluenesulfonic acid (5 mol%) in toluene was refluxed overnight with azeotropic removal of water. The solvent was evaporated and the residue was purified by flash column chromatography to give the corresponding αaryl imino ester.

Methyl (Z)-4-((2-methoxy-2-oxo-1-phenylethylidene)amino)benzoate (9a)



Purified by silica gel chromatography (PE: EA/20:1), the desired product **9a** was obtained as a yellow solid, M.P. 100-102 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.01 (m, 2H), 7.89 – 7.85 (m, 2H), 7.54 – 7.44 (m, 3H), 6.99 – 6.96 (m, 2H), 3.90 (s, 3H), 3.62 (s, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 166.9, 164.9, 160.6, 154.4, 133.4, 132.4, 130.8, 129.0, 128.3, 126.7, 119.4, 52.2. HRMS (ESI) m/z calcd for $C_{17}H_{16}NO_4^+$ $(M+H)^+$ 298.1074, found 298.1071.

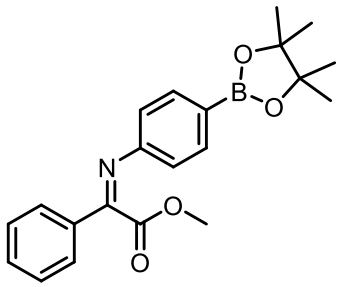
Methyl (Z)-2-phenyl-2-((4-(trifluoromethoxy)phenyl)imino)acetate (10a)



Purified by silica gel chromatography (PE: EA/50:1), the desired product **10a** was obtained as a yellow solid, M.P. 40-44 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.89 (m, 2H), 7.54 – 7.45 (m, 3H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.00 (dd, *J* = 8.8, 1.7 Hz, 2H), 3.65 (s, 3H), ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.11. ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.2, 161.0, 148.9 (d, $^{1}J_{C\text{-}F}$ = 3.1 Hz), 146.4 (d,

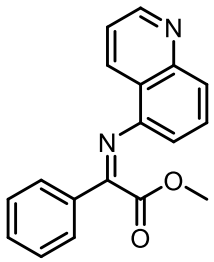
$^{2}J_{C\text{-}F}$ = 2.0 Hz), 133.6, 132.3, 128.9, 128.2, 124.6 – 116.7 (m), 121.7, 120.9, 52.0. HRMS (ESI) m/z calcd for $C_{16}H_{13}F_3NO_3^+$ $(M+H)^+$ 324.0842, found 324.0839.

Methyl (*Z*)-2-((4-(1,5-dimethyl-2,4-dioxa-3-borabicyclo[3.1.0]hexan-3-yl)phenyl)imino)-2-phenylacetate (14a)



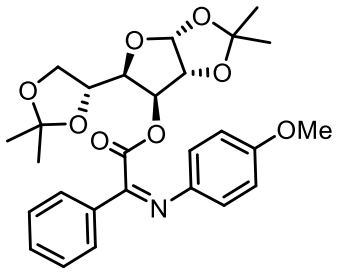
Purified by silica gel chromatography (PE: EA/2:1), the desired product **14a** was obtained as a yellow solid, M.P. 87-89 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.86 (m, 2H), 7.82 – 7.79 (m, 2H), 7.47 (dtd, *J* = 14.5, 7.0, 1.7 Hz, 3H), 6.98 – 6.95 (m, 2H), 3.63 (s, 3H), 1.35 (s, 12H), ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.3, 160.0, 152.8, 135.7, 133.8, 132.0, 128.9, 128.2, 118.9, 83.9, 52.1, 25.0. HRMS (ESI) m/z calcd for $C_{21}H_{25}BNO_4^+$ $(M+H)^+$ 366.1875, found 366.1872.

Methyl (Z)-2-phenyl-2-(quinolin-5-ylimino)acetate (29a)



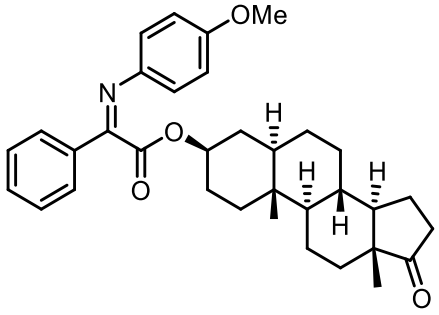
Purified by silica gel chromatography (PE: EA/10:1), the desired product **29a** was obtained as a yellow solid, M.P. 73-75 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 – 8.89 (m, 1H), 8.35 – 8.31 (m, 1H), 7.98 – 7.95 (m, 2H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.53 – 7.45 (m, 3H), 7.33 (dd, *J* = 8.5, 4.2 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 3.49 (s, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 161.1, 150.9, 148.5, 146.7, 133.5, 132.6, 132.4, 129.2, 129.0, 128.3, 126.5, 122.7, 120.8, 113.3, 52.1. HRMS (ESI) m/z calcd for $C_{18}H_{15}N_2O_2^+$ $(M+H)^+$ 291.1128, found 291.1117.

(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (Z)-2-((4-methoxyphenyl)imino)-2-phenylacetate (31a)



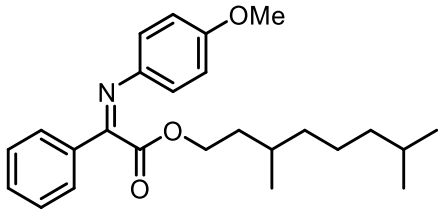
Purified by silica gel chromatography (PE: EA/10:1), the desired product **31a** was obtained as a yellow solid, M.P. 46-49 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.01 (m, 2H), 7.50 – 7.41 (m, 3H), 7.06 – 7.02 (m, 2H), 6.88 – 6.84 (m, 2H), 5.82 (d, *J* = 3.9 Hz, 1H), 4.85 (dd, *J* = 5.2, 3.8 Hz, 1H), 4.76 (ddd, *J* = 7.5, 5.2, 2.6 Hz, 1H), 4.12 – 4.08 (m, 2H), 3.89 – 3.84 (m, 1H), 3.79 (s, 3H), 3.54 – 3.49 (m, 1H), 1.44 (s, 3H), 1.35 – 1.31 (m, 9H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 164.8, 158.4, 157.7, 143.1, 134.2, 131.8, 128.6, 128.5, 121.7, 114.4, 113.4, 110.0, 104.5, 77.8, 77.7, 75.2, 74.0, 65.4, 55.4, 27.0, 26.8, 26.4, 25.3. HRMS (ESI) m/z calcd for $C_{27}H_{32}NO_8^+$ $(M+H)^+$ 498.2122, found 498.2100.

(3R,5R,8S,9R,10R,13R,14R)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl (Z)-2-((4-methoxyphenyl)imino)-2-phenylacetate (32a)



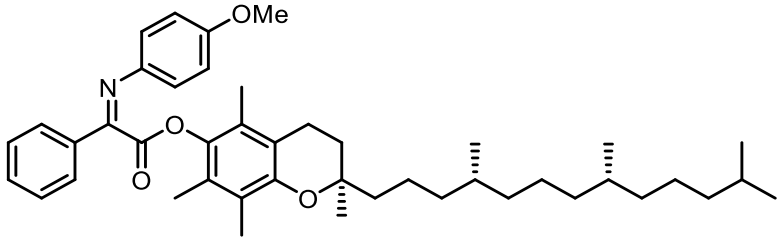
Purified by silica gel chromatography (PE: EA/15:1), the desired product **32a** was obtained as a yellow solid, M.P. 67-70 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.47 (tt, *J* = 9.0, 6.2 Hz, 3H), 6.96 – 6.92 (m, 2H), 6.88 – 6.83 (m, 2H), 4.79 (tt, *J* = 10.8, 4.9 Hz, 1H), 3.80 (s, 3H), 2.43 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.06 (dt, *J* = 18.9, 9.0 Hz, 1H), 1.92 (dt, *J* = 12.4, 4.3 Hz, 1H), 1.81 – 1.75 (m, 2H), 1.71 – 1.58 (m, 4H), 1.50 (qd, *J* = 9.2, 8.4, 5.1 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.29 – 1.22 (m, 4H), 1.17 – 1.09 (m, 2H), 1.02 – 0.92 (m, 2H), 0.84 (s, 3H), 0.76 (s, 3H), 0.67 (td, *J* = 11.1, 4.0 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.2, 160.2, 157.5, 143.7, 134.3, 131.7, 128.9, 128.0, 121.4, 114.2, 75.3, 55.7, 54.4, 51.5, 48.0, 44.8, 36.8, 36.0, 35.8, 35.2, 33.7, 31.7, 31.0, 28.4, 27.2, 22.0, 20.6, 14.0, 12.3. HRMS (ESI) m/z calcd for $C_{34}H_{42}NO_4^+$ $(M+H)^+$ 528.3108, found 528.3105.

3,7-dimethyloctyl (Z)-2-((4-methoxyphenyl)imino)-2-phenylacetate (34a)



Purified by silica gel chromatography (PE: EA/80:1), the desired product **34a** was obtained as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 2H), 7.50 – 7.42 (m, 3H), 7.02 – 6.97 (m, 2H), 6.90 – 6.85 (m, 2H), 4.17 (ddd, *J* = 7.2, 5.8, 3.3 Hz, 2H), 3.77 (q, *J* = 2.6, 1.9 Hz, 3H), 1.57 – 1.44 (m, 2H), 1.28 – 1.11 (m, 7H), 1.03 (td, *J* = 7.3, 6.5, 4.1 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 6H), 0.77 (d, *J* = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 165.7, 159.5, 157.4, 143.4, 134.2, 131.5, 128.7, 127.9, 121.3, 114.1, 63.9, 55.3, 39.2, 37.0, 35.2, 29.4, 28.0, 24.5, 22.8, 22.7, 19.2. HRMS (ESI) m/z calcd for $C_{25}H_{34}NO_3^+$ $(M+H)^+$ 396.2533, found 396.2518.

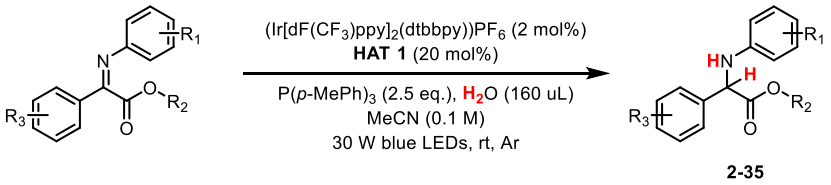
(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl (Z)-2-((4-methoxyphenyl)imino)-2-phenylacetate (35a)



Purified by silica gel chromatography (PE: EA/60:1), the desired product **35a** was obtained as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.08 (m, 2H), 7.59 – 7.50 (m, 3H), 7.12 – 7.07 (m, 2H), 6.97 – 6.92 (m, 2H), 3.84 (s, 3H), 2.54 (t, *J* = 6.8 Hz, 2H), 2.07 (s, 3H), 1.79 (dq, *J* = 13.7, 6.7 Hz, 2H), 1.66 (s, 3H), 1.61 – 1.54 (m, 6H), 1.42 (tt, *J* = 11.7, 6.0 Hz, 4H), 1.31 (dq, *J* = 13.3, 4.3, 3.8 Hz, 7H), 1.25 (s, 3H), 1.22 – 1.17 (m, 3H), 1.15 – 1.06 (m, 4H), 0.93 (s, 3H), 0.92 – 0.89 (m, 9H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 163.8, 159.7, 157.5, 149.9, 143.4, 139.8, 134.4, 131.8, 128.8, 128.2, 127.0, 125.4, 123.3, 121.6, 117.6, 114.6, 75.2, 55.7, 39.5, 37.6, 37.6, 37.4, 33.0, 32.8, 28.1, 25.0, 24.6, 22.9, 22.8, 21.2, 20.7, 19.9, 19.8, 13.0, 12.1, 12.0. HRMS (ESI) m/z calcd for $C_{44}H_{62}NO_4^+$ $(M+H)^+$ 668.4673, found 668.4678.

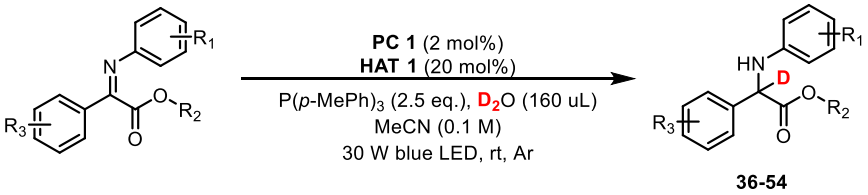
3. General Procedure for Photoredox Reactions

3.1 General procedure for the synthesis of α-aryl amino acid ester



To an oven dried 25 mL Schlenk-tube, αaryl imino esters (0.2 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (2 mol%), HAT (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), H_2O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature, the solution was concentrated in vacuum and the product was purified by flash column chromatography.

3.2 General procedure for the synthesis of deuterated α-aryl amino acid ester



To an oven dried 25 mL Schlenk-tube, αaryl imino ester (0.2 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (2 mol%), HAT (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), D_2O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography.

4. Emission Spectrum of blue LED Strip

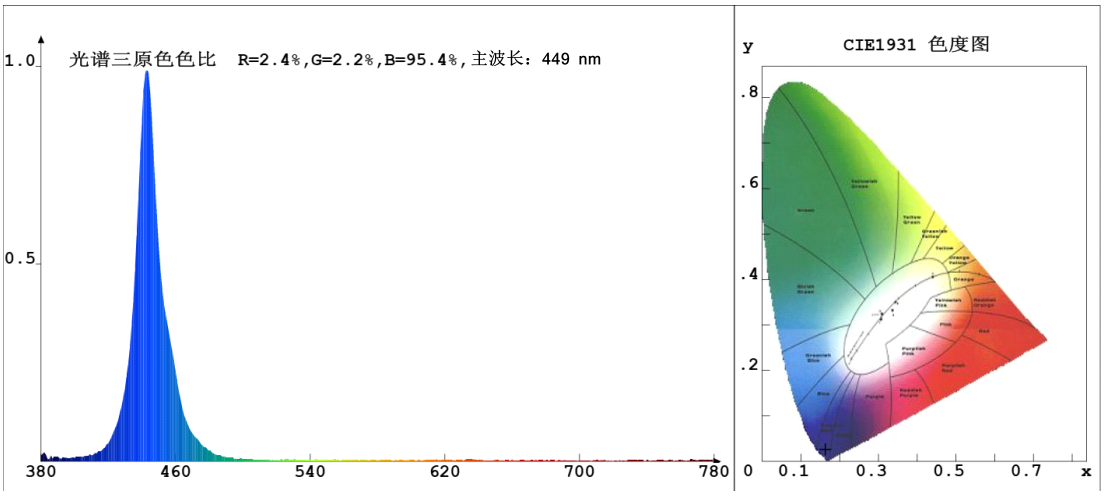
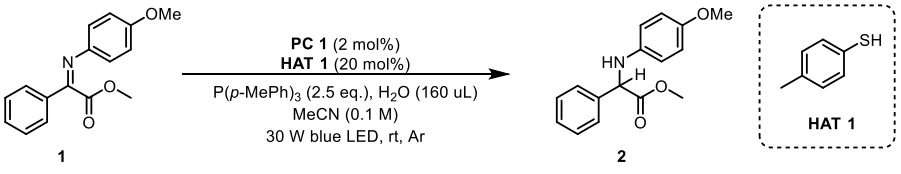
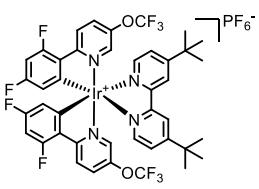


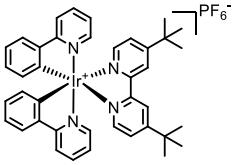
Figure S1 Emission spectrum of 30 W blue LED strip

5. Optimization of reaction condition

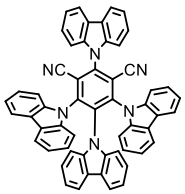




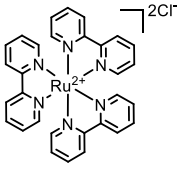
PC 1



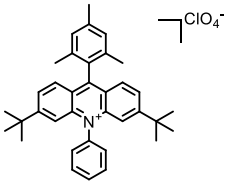
PC 2



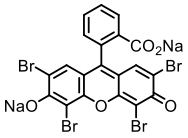
PC 3



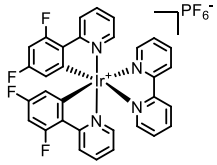
PC 4



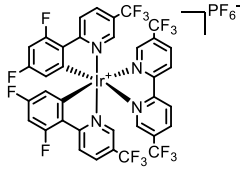
PC 5



PC 6



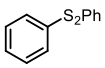
PC 7



PC 8

HAT 2

HAT 3



HAT 4

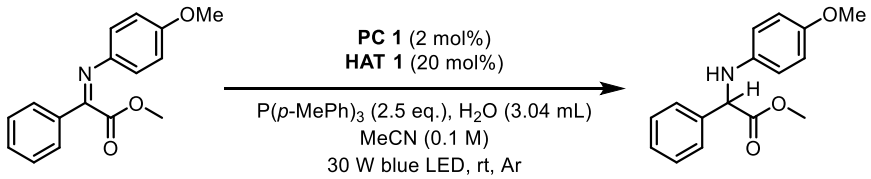
HAT 5

Entry	PC	HAT Reagent	Solvent	P Source	H_2O (uL)	Yield (%)[b]
1	**PC 1**	**HAT 1**	MeCN	Ph_3P	160	68
2	**PC 1**	**HAT 1**	MeCN	P(*p*-OMePh)$_3$	160	87

3	**PC 1**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	99
4	**PC 1**	**HAT 1**	MeCN	P(*p*-FPh)$_3$	160	23
5	**PC 1**	**HAT 1**	MeCN	P(*p*-CF_3Ph)$_3$	160	trace
6	**PC 1**	**HAT 2**	MeCN	P(*p*-MePh)$_3$	160	trace
7	**PC 1**	**HAT 3**	MeCN	P(*p*-MePh)$_3$	160	n.d.
8	**PC 1**	**HAT 4**	MeCN	P(*p*-MePh)$_3$	160	52
9	**PC 1**	**HAT 5**	MeCN	P(*p*-MePh)$_3$	160	trace
10	**PC 1**	**HAT 1**	THF	P(*p*-MePh)$_3$	160	93
11	**PC 1**	**HAT 1**	1,4-dioxane	P(*p*-MePh)$_3$	160	94
12	**PC 1**	**HAT 1**	DMF	P(*p*-MePh)$_3$	160	trace
13	**PC 1**	**HAT 1**	DCE	P(*p*-MePh)$_3$	160	72
14	**PC 1**	**HAT 1**	Toluene	P(*p*-MePh)$_3$	160	31
15	**PC 1**	**HAT 1**	EtOAc	P(*p*-MePh)$_3$	160	89
16	**PC 2**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	92
17	**PC 3**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	67
18	**PC 4**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	83
19	**PC 5**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	trace
20	**PC 6**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	87
21	**PC 7**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	88
22	**PC 8**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	160	95
23	**PC 1**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	36	n.d.
24	**PC 1**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	72	67
25	**PC 1**	**HAT 1**	MeCN	P(*p*-MePh)$_3$	200	87

[a]Reaction conditions of **2**: **1** (0.20 mmol), **PC 1** (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol, 2.5 eq.) and H_2O (160 uL) in MeCN (0.1 M), under 30 W blue LEDs irradiation at room temperature. [b]Isolated yield.

6. Gram-scale reaction



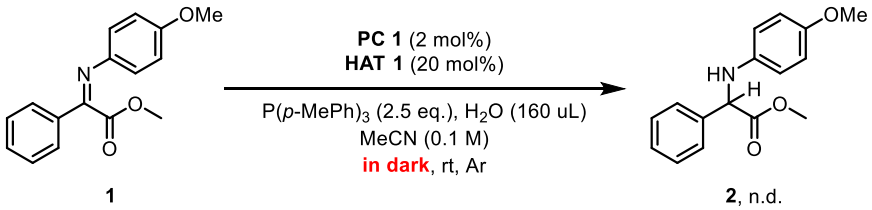
1
3.8 mmol (1.02 g)

2
0.94 g, 91%

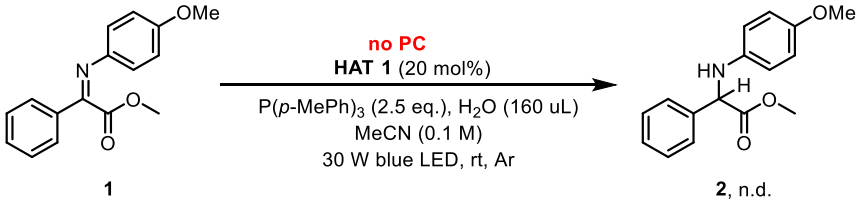
To an oven dried 100 mL Schlenk flask, *α*-aryl imino ester **1** (3.8 mmol, 1.02 g, 1 equiv), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (0.076 mmol, 83.6 mg), **HAT 1** (0.76 mmol, 95mg), P(*p*-MePh)$_3$ (9.50 mmol, 2.89g, 2.5 equiv), H_2O (3.04 mL) and MeCN (38 mL, 0.1M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature for 44 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography.

7. Mechanistic studies

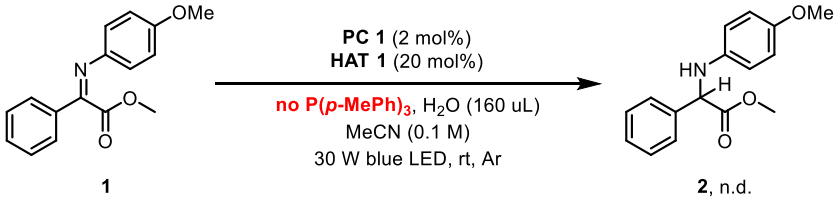
7.1 Control experiments



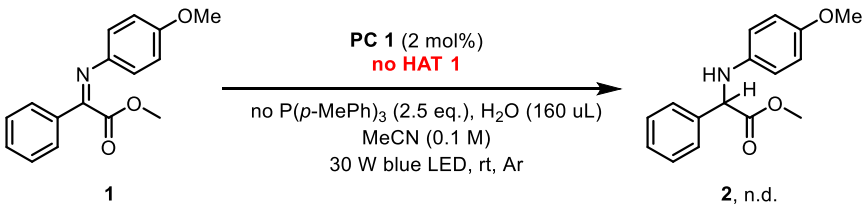
To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), H$_2$O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under dark at room temperature and the product **2** was not detected.



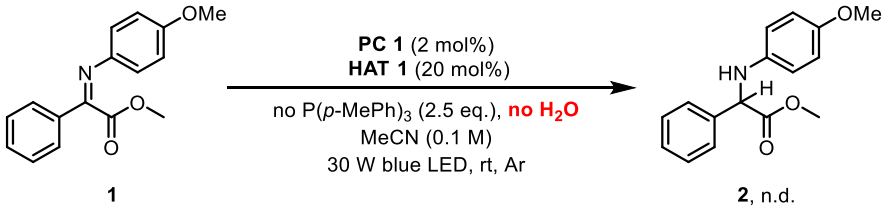
To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), H$_2$O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature and the product **2** was not detected.



To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), **HAT 1** (20 mol%), H$_2$O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature and the product **2** was not detected.



To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), P(*p*-MePh)$_3$ (0.5 mmol), H$_2$O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature and the product **2** was not detected.



To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), HAT (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature and the product **2** was not detected.

7.2 Radical trapping experiments

According to general procedure **2**, when DPE or TEMPO was added. After completion of the reaction, the crude residues were analyzed by GC-MS. Yield of **2** was reduced or no detected and the DPE-adduct and TEMPO-adduct products were detected by GC-MS.

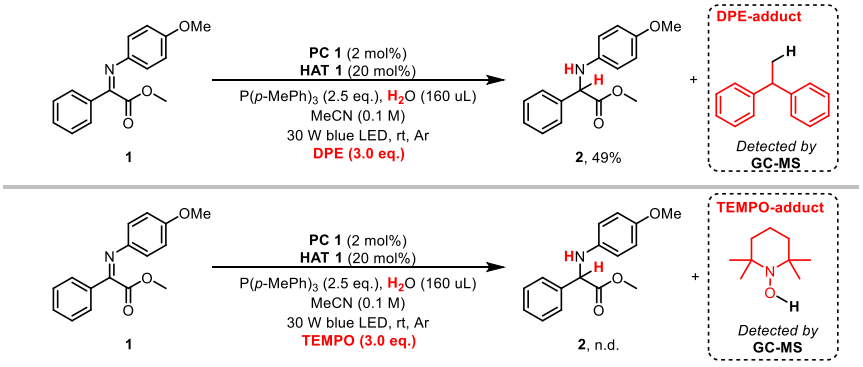


Figure S2 Radical trapping experiments

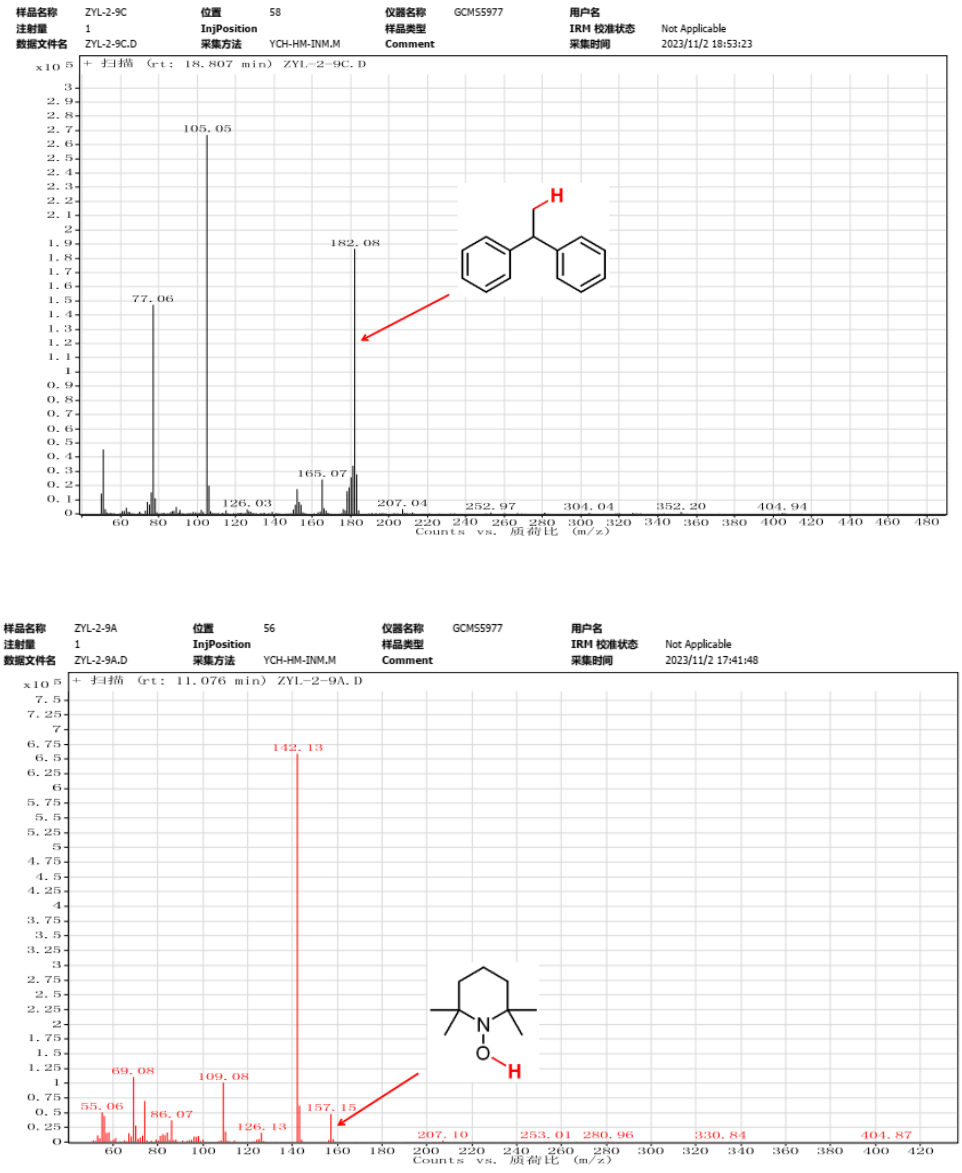
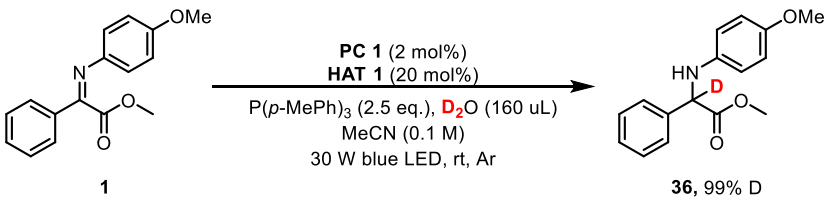


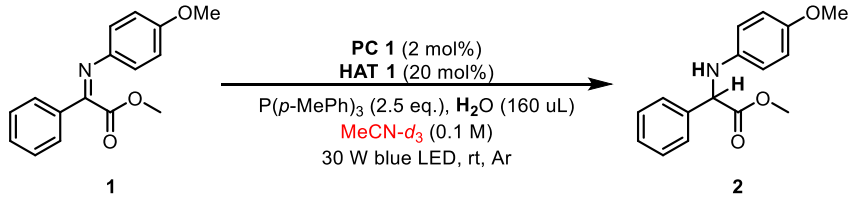
Figure S3 GC-MS analysis of radical trapping adducts

7.3 D-labeling experiment



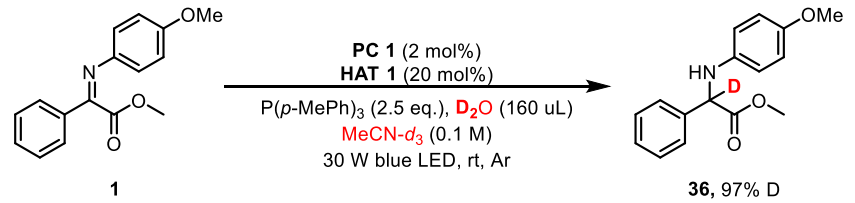
To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), D_2O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the

irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography, and the product detected by ^{1}H NMR (**Figure S4**).



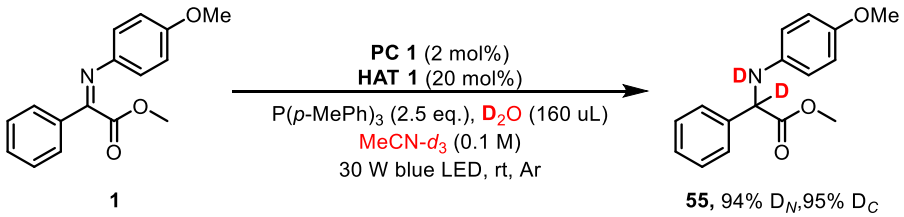
1 **2**

To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), H$_2$O (160 uL) and MeCN-d_3 (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography, and the product detected by ^{1}H NMR (**Figure S4**).



1 **36,** 97% D

To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), D$_2$O (160 uL) and MeCN-d_3 (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography, and the product detected by ^{1}H NMR (**Figure S4**).



1 **55,** 94% D_N,95% D_C

To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), D$_2$O (160 uL)

and MeCN-d_3 (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the reaction mixture was detected by ^{1}H NMR (**Figure S5**).

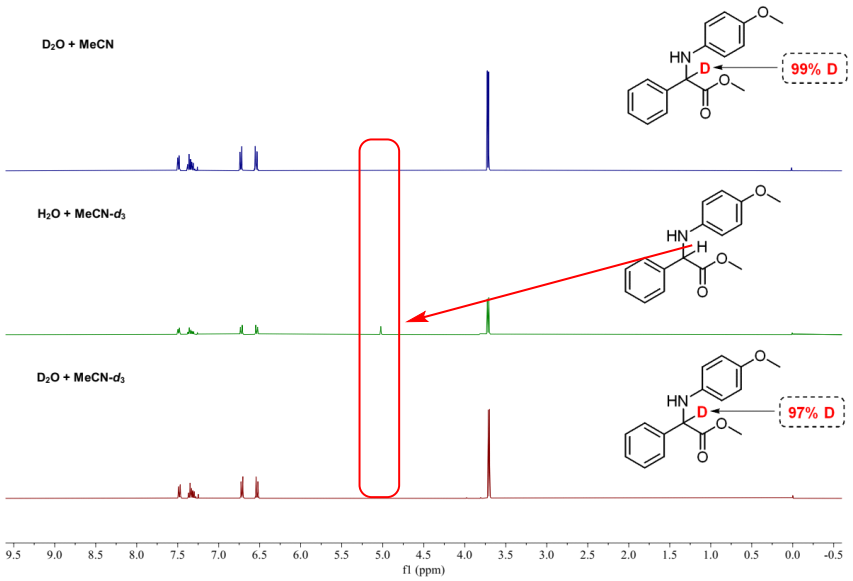


Figure S4 ^{1}H NMR of D-labeling product

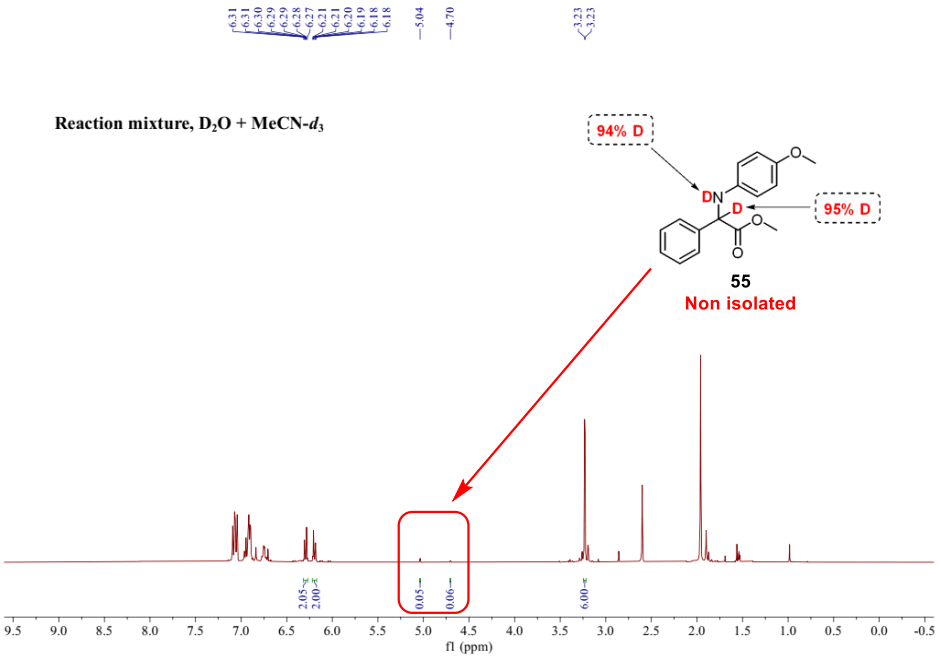
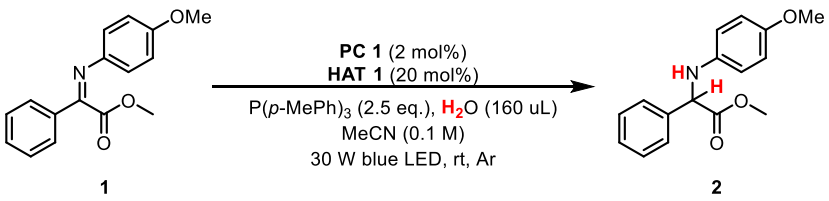


Figure S5 ^{1}H NMR of mixed reaction system.

7.4 ^{31}P NMR Tracer Experiments



To an oven dried 25 mL Schlenk-tube, α-aryl imino ester **1** (0.2 mmol), (Ir[dF(CF$_3$)ppy]$_2$(dtbbpy))PF$_6$ (2 mol%), **HAT 1** (20 mol%), P(*p*-MePh)$_3$ (0.5 mmol), H$_2$O (160 uL) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography, and the product detected by ^{31}P NMR (**Figure S6**).

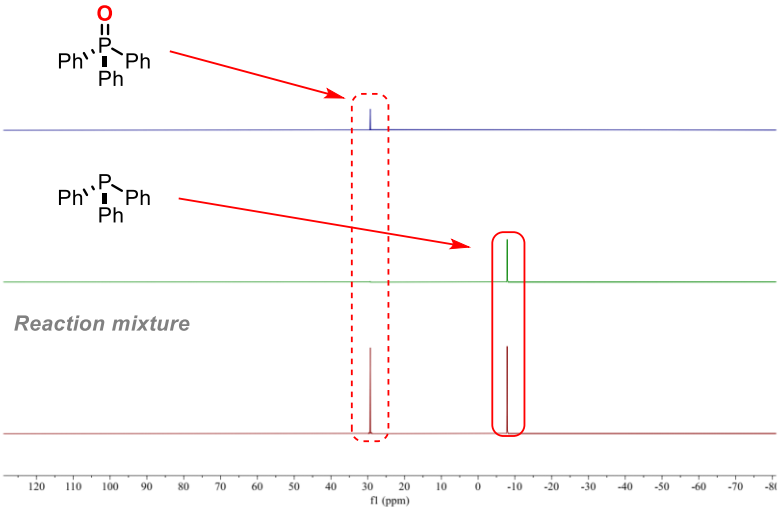


Figure S6 ^{31}P NMR of mixed reaction system.

7.5 Stern-Volmer Quenching Experiments

Formulation solution: *α*-aryl imino ester (**1**, 134.5 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.1 M. P(*p*-MePh)$_3$ (380.5 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.25 M. *p*-MePhSH (12.4 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.02 M. H$_2$O (400 uL) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 4.44 M.

Photocatalyst (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (1.1 mg) was dissolved in MeCN (5.0 mL) to set the concentration to be 0.2 mM.

Experimental procedure: The resulting 0.2 mM solution of (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 in MeCN (100 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding MeCN to prepare a 10 μM solution. The resulting mixture was sparged with argon for 3 minutes and then irradiated at 378 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 0.5 μL of a *α*-aryl imino ester (**1**) solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 3 minutes and irradiated at 378 nm. Fluorescence emission spectra of 0 μL, 0.5 μL, 1.0 μL, 1.5 μL, 2.0 μL, fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The results were shown in the following figures.

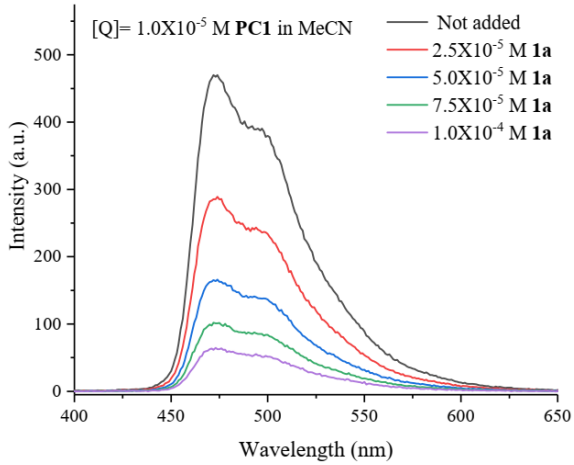


Figure S7 Emission quenching of **PC 1** with *α*-aryl imino ester (**1**) in MeCN

Experimental procedure: The resulting 0.2 mM solution of (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 in MeCN (100 μL) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding MeCN to prepare a 10 μM solution. The resulting mixture was sparged with argon for 3 minutes and then irradiated at 378 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0 μL of a P(*p*-MePh)$_3$ solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 3 minutes and irradiated at 378 nm. Fluorescence emission spectra of 0 uL, 20.0 μL, 40.0 μL, 60.0 μL, 80.0 μL, fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn. The results were shown in the following figures.

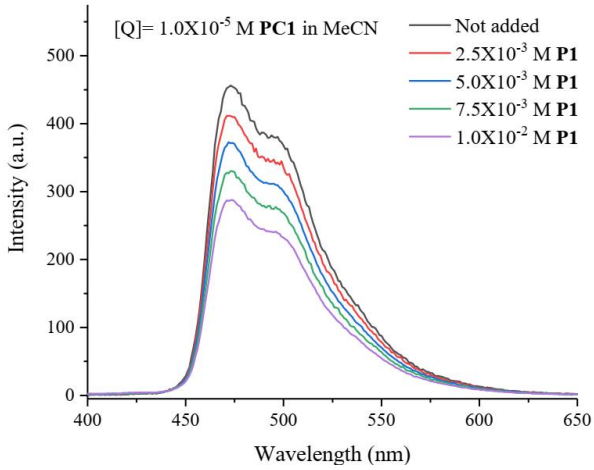


Figure S8 Emission quenching of **PC 1** with P(*p*-MePh)$_3$ in MeCN

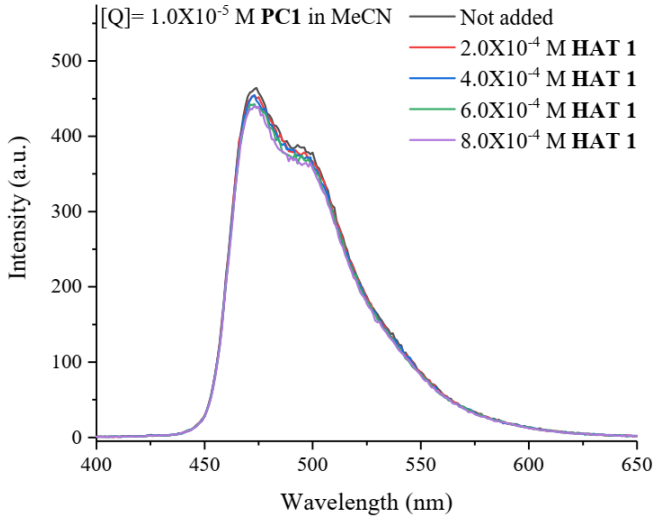


Figure S9 Emission quenching of **PC 1** with **HAT 1** in MeCN

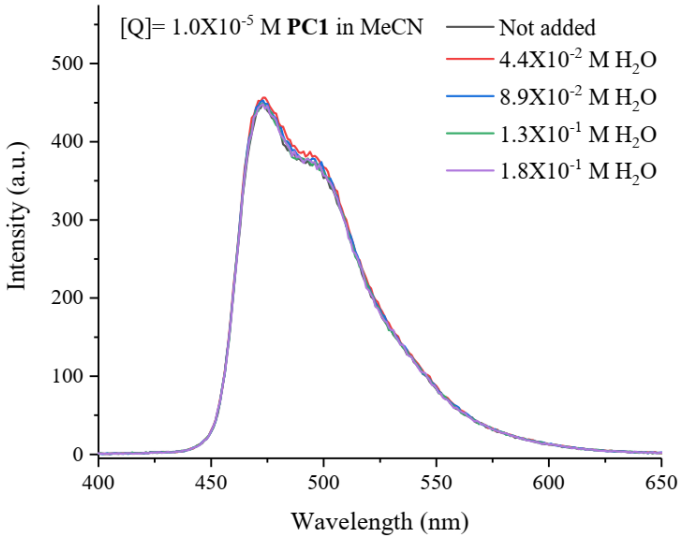


Figure S10 Emission quenching of **PC 1** with H_2O in MeCN

7.6 Cyclic voltammetry measurements

Cyclic voltammograms were taken on a CHI660E electrochemical analyzer/workstation (Shanghai Chen Hua Instrument Co., Ltd) in MeCN (Energy Chemical, 99.9%, with molecular sieves, water≤50 ppm (by K.F.)) at room temperature using a glass carbon working electrode, a S21 platinum auxiliary electrode and 0.1 M NBu_4PF_6 as supporting electrolyte. All potentials are referenced against the Ag/AgCl redox couple. 20 mM α-aryl imino ester **1** was dissolved in an anhydrous MeCN solution containing 0.1 M NBu_4PF_6. According to the above method, 20.0 mM **PC 1**, 20 mM and **P 1**, 20mM were prepared sequentially. The solution was degassed with nitrogen bubbling for 5 min prior to voltammetric studies. The scan rate was 100 mV/s.

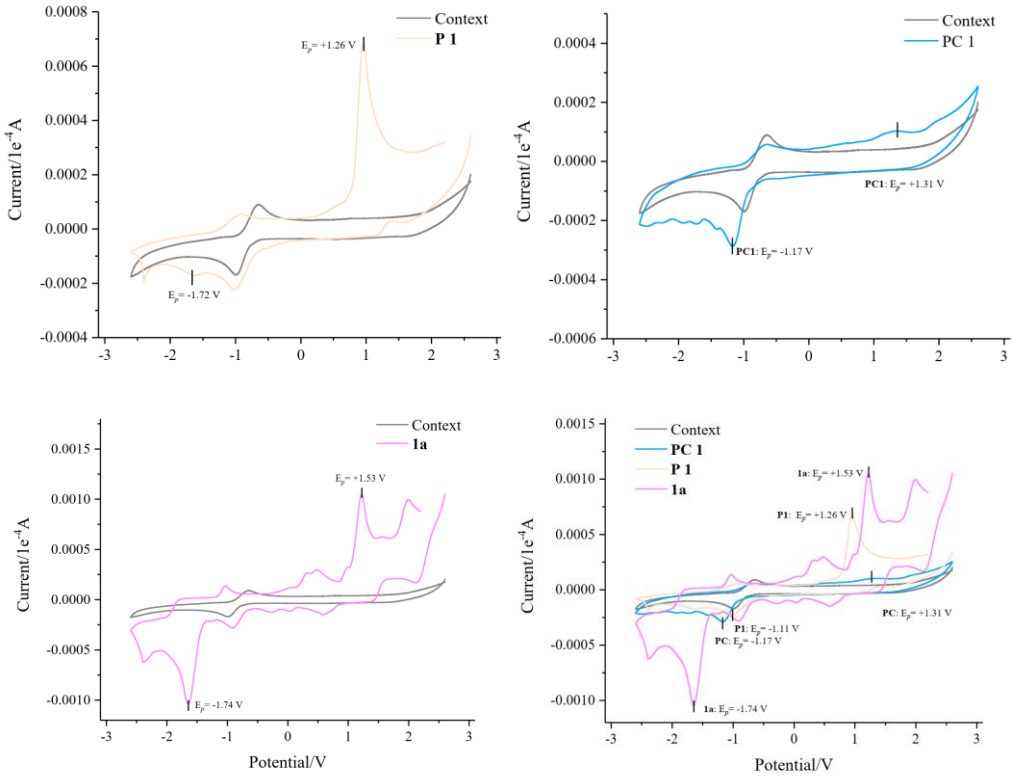
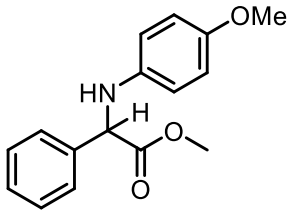


Figure S11 Cyclic Voltammetry of each reaction component

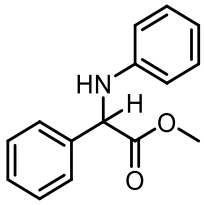
8. Characterization data of all products

Methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (2)[3]



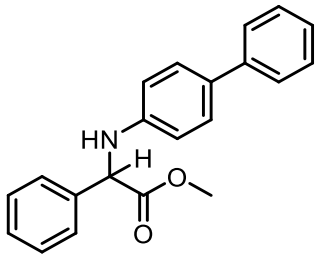
Purified by silica gel chromatography (PE: EA/30:1), the desired product **2** was obtained as a white solid, M.P. 105-107 °C, 53.7 mg, 99% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.47 (m, 2H), 7.42 – 7.28 (m, 3H), 6.79 – 6.70 (m, 2H), 6.60 – 6.51 (m, 2H), 5.05 (s, 1H), 4.71 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.7, 152.7, 140.3, 138.0, 129.0, 128.4, 127.4, 115.0 (d, *J* = 6.6 Hz), 61.8, 55.8, 52.8. (Known compounds, HRMS data detailed in Ref. 3.)

Methyl 2-phenyl-2-(phenylamino)acetate (3)[4]



Purified by silica gel chromatography (PE: EA/50:1), the desired product **3** was obtained as a white solid, M.P. 80-82 °C, 42.9 mg, 89% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.49 (m, 2H), 7.39 – 7.30 (m, 3H), 7.16 – 7.11 (m, 2H), 6.71 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.59 – 6.56 (m, 2H), 5.09 (s, 1H), 4.96 (s, 1H), 3.74 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.5, 146.1, 137.8, 129.4, 129.1, 128.5, 127.5, 118.3, 113.6, 61.0, 53.0. (Known compounds, HRMS data detailed in Ref. 4.)

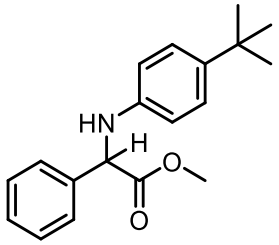
Methyl 2-([1,1'-biphenyl]-4-ylamino)-2-phenylacetate (4)[3]



Purified by silica gel chromatography (PE: EA/30:1), the desired product **4** was obtained as a white solid, M.P. 127-129 °C, 49.5 mg, 78% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (ddt, *J* = 10.8, 8.2, 1.4 Hz, 4H), 7.41 – 7.28 (m, 7H), 7.25 – 7.17 (m, 1H), 6.64 – 6.57 (m, 2H), 5.10 (s, 1H), 5.06 (s, 1H), 3.70 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.4, 145.5, 141.2, 137.7, 131.2, 129.1, 128.8,

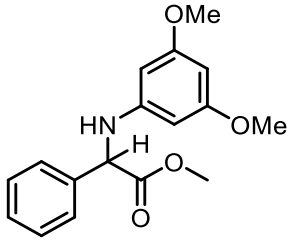
128.6, 128.1, 127.4, 126.5, 126.3, 113.9, 60.9, 53.0. (Known compounds, HRMS data detailed in Ref. 3.)

Methyl 2-((4-(tert-butyl)phenyl)amino)-2-phenylacetate (5)[5]



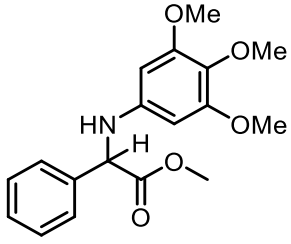
Purified by silica gel chromatography (PE: EA/30:1), the desired product **5** was obtained as a white solid, M.P. 115-117 °C, 44.6 mg, 75% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.37 – 7.29 (m, 3H), 7.17 – 7.12 (m, 2H), 6.53 – 6.49 (m, 2H), 5.04 (s, 1H), 4.85 (s, 1H), 3.70 (s, 3H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.7, 143.9, 141.0, 138.1, 129.0, 128.4, 127.5, 126.2, 113.3, 61.3, 52.9, 34.0, 31.7. (Known compounds, HRMS data detailed in Ref. 5.)

Methyl 2-((3,5-dimethoxyphenyl)amino)-2-phenylacetate (6)[6]



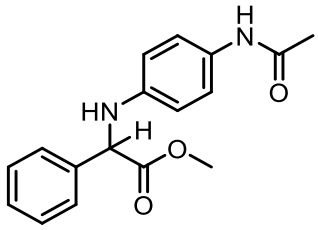
Purified by silica gel chromatography (PE: EA/4:1), the desired product **6** was obtained as a white solid, M.P. 98-101 °C, 53.6 mg, 89% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.37 – 7.28 (m, 3H), 5.86 (t, *J* = 2.2 Hz, 1H), 5.75 (d, *J* = 2.1 Hz, 2H), 5.05 (d, *J* = 4.5 Hz, 1H), 4.98 (d, *J* = 4.9 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.4, 161.8, 148.0, 137.8, 129.1, 128.5, 127.4, 92.5, 90.7, 60.9, 55.3, 53.0. (Known compounds, HRMS data detailed in Ref. 6.)

Methyl 2-phenyl-2-((3,4,5-trimethoxyphenyl)amino)acetate (7)[6]



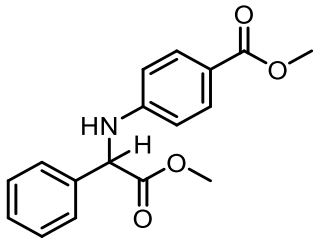
Purified by silica gel chromatography (PE: EA/2:1), the desired product **7** was obtained as a white solid, M.P. 105-107 ºC, 65.5 mg, 99% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.39 – 7.28 (m, 3H), 5.80 (s, 2H), 5.03 (s, 1H), 4.88 (s, 1H), 3.73 – 3.70 (m, 12H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.4, 154.0, 142.9, 137.9, 130.7, 129.1, 128.5, 127.3, 91.3, 61.4, 61.1, 55.9, 52.9. (Known compounds, HRMS data detailed in Ref. 6.)

Methyl 2-((4-acetamidophenyl)amino)-2-phenylacetate (8)[7]



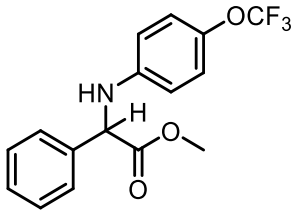
Purified by silica gel chromatography (PE: EA/2:1), the desired product **8** was obtained as a yellow oil, 59.0 mg, 99% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.46 (m, 2H), 7.36 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.03 – 6.99 (m, 2H), 6.69 – 6.65 (m, 1H), 6.27 (dd, *J* = 8.0, 2.3 Hz, 1H), 5.07 (d, *J* = 4.3 Hz, 1H), 5.00 (d, *J* = 5.8 Hz, 1H), 3.71 (s, 3H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.4, 168.6, 146.8, 139.2, 137.6, 129.8, 129.1, 128.5, 127.4, 109.6, 109.4, 105.1, 60.8, 53.0, 24.8. (Known compounds, HRMS data detailed in Ref. 7.)

Methyl 4-((2-methoxy-2-oxo-1-phenylethyl)amino)benzoate (9)



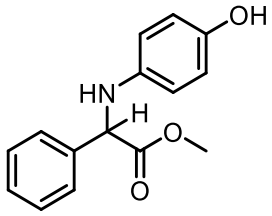
Purified by silica gel chromatography (PE: EA/10:1), the desired product **9** was obtained as a white solid, M.P. 100-102 ºC, 58.0 mg, 97% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 2H), 7.48 – 7.42 (m, 2H), 7.37 – 7.27 (m, 3H), 6.54 – 6.47 (m, 2H), 5.48 (s, 1H), 5.12 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.8, 167.3, 149.7, 136.9, 131.6, 129.2, 128.7, 127.3, 119.5, 112.5, 60.2, 53.1, 51.7. HRMS (ESI) m/z calcd for $C_{17}H_{18}NO_4^+$ $(M+H)^+$ 300.1230, found 300.1231.

Methyl 2-phenyl-2-((4-(trifluoromethoxy)phenyl)amino)acetate (10)



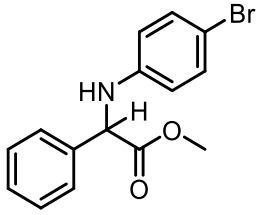
Purified by silica gel chromatography (PE: EA/30:1), the desired product **10** was obtained as a colorless oil, 62.4 mg, 96% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.45 (m, 2H), 7.38 – 7.28 (m, 3H), 7.00 – 6.93 (m, 2H), 6.52 – 6.46 (m, 2H), 5.07 (s, 1H), 5.02 (s, 1H), 3.72 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.44; ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.2, 144.9, 141.1 (d, $^{2}J_{C\text{-}F}$ = 2.2 Hz), 137.4, 129.2, 128.7, 127.4, 122.6, 120.9 (q, $^{1}J_{C\text{-}F}$ = 255.3 Hz), 113.9, 61.0, 53.1.HRMS (ESI) m/z calcd for $C_{16}H_{15}F_3NO_3^+$ $(M+H)^+$ 326.0999, found 326.0996.

Methyl 2-((4-hydroxyphenyl)amino)-2-phenylacetate (11)



Purified by silica gel chromatography (PE: EA/5:1), the desired product **11** was obtained as a white solid, M.P. 131-133 °C, 45.7 mg, 89% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 – 8.50 (m, 1H), 7.52 – 7.48 (m, 2H), 7.38 – 7.29 (m, 3H), 6.57 – 6.52 (m, 4H), 5.73 (dd, *J* = 8.7, 1.4 Hz, 1H), 5.13 (dd, *J* = 8.7, 2.2 Hz, 1H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 172.6, 149.1, 139.6, 138.1, 128.5, 127.9, 127.5, 115.6, 114.6, 60.7, 52.1. HRMS (ESI) m/z calcd for $C_{15}H_{16}NO_3^+$ $(M+H)^+$ 258.1125, found 258.1117.

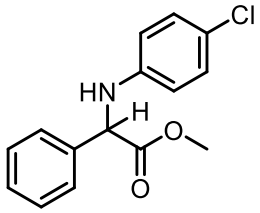
Nethyl 2-((4-bromophenyl)amino)-2-phenylacetate (12)[8]



Purified by silica gel chromatography (PE: EA/40:1), the desired product **12** was obtained as a white solid, M.P. 130-131 °C, 48.0 mg, 75% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 7.23 – 7.18 (m, 2H), 6.46 – 6.42 (m, 2H), 5.05 (s, 2H), 3.74 (s, 3H); ^{13}C{^{1}H} NMR

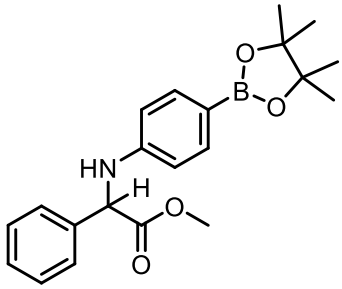
(101 MHz, Chloroform-*d*) δ 172.1, 145.0, 137.2, 132.1, 129.1, 128.6, 127.4, 115.2, 110.0, 60.7, 53.1. (Known compounds, HRMS data detailed in Ref. 8.)

Methyl 2-((4-chlorophenyl)amino)-2-phenylacetate (13)[8]



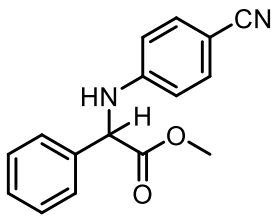
Purified by silica gel chromatography (PE: EA/40:1), the desired product **13** was obtained as a white solid, M.P. 90-93 °C, 39.6 mg, 72% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 2H), 7.38 – 7.28 (m, 3H), 7.07 – 7.02 (m, 2H), 6.51 – 6.41 (m, 2H), 5.02 (s, 2H), 3.72 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.2, 144.6, 137.3, 129.3, 129.2, 128.7, 127.4, 123.0, 114.7, 60.9, 53.1. (Known compounds, HRMS data detailed in Ref. 8.)

Methyl 2-phenyl-2-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)acetate (14)[9]



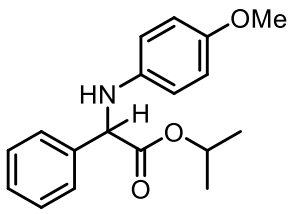
Purified by silica gel chromatography (PE: EA/30:1), the desired product **14** was obtained as a white solid, M.P. 114-117 °C, 52.8 mg, 72% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.57 (m, 2H), 7.49 – 7.46 (m, 2), 7.37 – 7.29 (m, 3H), 6.56 – 6.52 (m, 2H), 5.19 (s, 1H), 5.14 (s, 1H), 3.74 (s, 3H), 1.30 (d, *J* = 1.4 Hz, 12H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.3, 148.5, 137.4, 136.5, 129.1, 128.6, 127.4, 112.8, 83.4, 60.3, 53.0, 25.0, 25.0. (Known compounds, HRMS data detailed in Ref. 9.)

Methyl 2-((4-cyanophenyl)amino)-2-phenylacetate (15)[10]



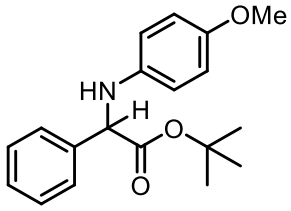
Purified by silica gel chromatography (PE: EA/10:1), the desired product **15** was obtained as a colorless oil, 36.2 mg, 68% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.43 (m, 2H), 7.39 – 7.36 (m, 2H), 7.36 – 7.30 (m, 3H), 6.54 – 6.49 (m, 2H), 5.58 (d, *J* = 5.6 Hz, 1H), 5.09 (d, *J* = 5.6 Hz, 1H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.6, 149.1, 136.4, 133.8, 129.3, 128.9, 127.3, 120.2, 113.3, 100.1, 60.0, 53.3. (Known compounds, HRMS data detailed in Ref. 10.)

Isopropyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (16)[11]



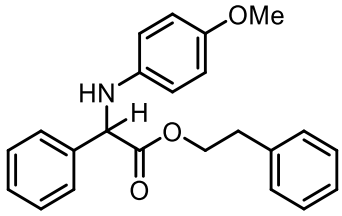
Purified by silica gel chromatography (PE: EA/40:1), the desired product **16** was obtained as a yellow oil, 57.4 mg, 96% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 2H), 7.39 – 7.30 (m, 3H), 6.76 – 6.72 (m, 2H), 6.59 – 6.54 (m, 2H), 5.09 – 5.02 (m, 1H), 5.01 (s, 1H), 4.70 (s, 1H), 3.71 (s, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.7, 152.6, 140.5, 138.1, 128.9, 128.2, 127.3, 115.0, 114.9, 69.5, 61.9, 55.8, 21.9, 21.5. (Known compounds, HRMS data detailed in Ref. 11.)

tert-butyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (17) [11]



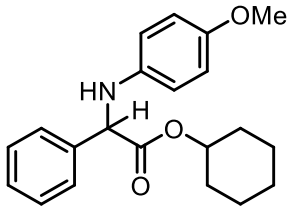
Purified by silica gel chromatography (PE: EA/30:1), the desired product **17** was obtained as a yellow solid, M.P. 86-87 ℃, 57.6 mg, 92% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 2H), 7.38 – 7.28 (m, 3H), 6.75 – 6.71 (m, 2H), 6.57 – 6.53 (m, 2H), 4.93 (s, 1H), 4.70 (s, 1H), 3.71 (s, 3H), 1.40 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.3, 152.5, 140.6, 138.6, 128.8, 128.1, 127.3, 115.0, 114.8, 82.3, 62.3, 55.9, 28.0. (Known compounds, HRMS data detailed in Ref. 11.)

Phenethyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (18)



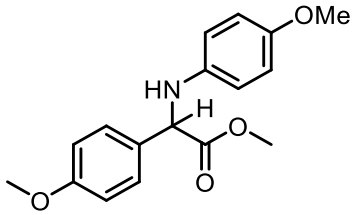
Purified by silica gel chromatography (PE: EA/25:1), the desired product **18** was obtained as a colorless oil, 68.6 mg, 95% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.30 (q, *J* = 6.6 Hz, 3H), 7.21 (td, *J* = 7.4, 5.4 Hz, 3H), 7.06 – 7.02 (m, 2H), 6.71 – 6.66 (m, 2H), 6.49 (d, *J* = 8.6 Hz, 2H), 4.97 (s, 1H), 4.64 (s, 1H), 4.31 (td, *J* = 6.8, 2.3 Hz, 2H), 3.67 (s, 3H), 2.84 (td, *J* = 6.9, 3.1 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.1, 152.7, 140.4, 137.9, 137.6, 129.0, 129.0, 128.6, 128.4, 127.5, 126.7, 115.0, 114.9, 66.2, 61.9, 55.8, 35.0. HRMS (ESI) m/z calcd for $C_{23}H_{24}NO_3^+$ $(M+H)^+$ 362.1751, found 362.1747.

Cyclohexyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (19)



Purified by silica gel chromatography (PE: EA/30:1), the desired product **19** was obtained as a yellow oil, 65.8 mg, 97% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.50 (m, 2H), 7.38 – 7.29 (m, 3H), 6.76 – 6.71 (m, 2H), 6.59 – 6.54 (m, 2H), 5.02 (s, 1H), 4.86 – 4.80 (m, 1H), 3.71 (s, 3H), 1.88 – 1.81 (m, 1H), 1.74 – 1.47 (m, 5H), 1.44 – 1.22 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.6, 152.6, 140.5, 138.3, 128.8, 128.2, 127.3, 115.0, 114.9, 74.0, 62.0, 55.8, 31.5, 31.1, 25.4, 23.5, 23.3. HRMS (ESI) m/z calcd for $C_{21}H_{26}NO_3^+$ $(M+H)^+$ 340.1907, found 340.1904.

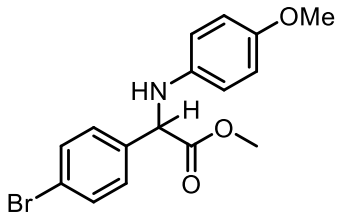
Methyl 2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)acetate (20)[12]



Purified by silica gel chromatography (PE: EA/20:1), the desired product **20** was obtained as a colorless oil, 57.8 mg, 96% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.39 (m, 2H), 6.90 – 6.87 (m, 2H),

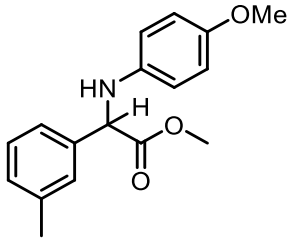
6.75 – 6.72 (m, 2H), 6.57 – 6.53 (m, 2H), 4.98 (s, 1H), 4.64 (s, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 173.0, 159.72, 152.7, 140.4, 129.9, 128.6, 115.0, 114.9, 114.4, 61.2, 55.8, 55.4, 52.8. (Known compounds, HRMS data detailed in Ref. 12.)

Methyl 2-(4-bromophenyl)-2-((4-methoxyphenyl)amino)acetate (21)[13]



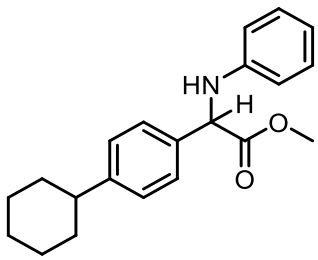
Purified by silica gel chromatography (PE: EA/30:1), the desired product **21** was obtained as a colorless oil, 47.6 mg, 68% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.46 (m, 2H), 7.39 – 7.36 (m, 2H), 6.74 – 6.70 (m, 2H), 6.51 – 6.48 (m, 2H), 4.98 (s, 1H), 4.71 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 172.1, 152.8, 140.0, 137.2, 132.2, 129.2, 122.4, 115.1, 115.0, 61.2, 55.9, 53.1. (Known compounds, HRMS data detailed in Ref. 13.)

Methyl 2-((4-methoxyphenyl)amino)-2-(m-tolyl)acetate (22)[9]



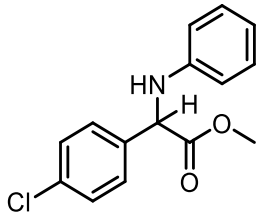
Purified by silica gel chromatography (PE: EA/30:1), the desired product **22** was obtained as a yellow oil, 48.5 mg, 85% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 3H), 7.13 – 7.09 (m, 1H), 6.74 – 6.69 (m, 2H), 6.57 – 6.50 (m, 2H), 4.97 (s, 1H), 4.63 (s, 1H), 3.69 (d, J = 4.3 Hz, 6H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 172.9, 152.7, 140.5, 138.8, 137.9, 129.3, 128.9, 128.0, 124.6, 115.0, 114.9, 61.9, 55.8, 52.8, 21.6. (Known compounds, HRMS data detailed in Ref. 9.)

Methyl 2-(4-cyclohexylphenyl)-2-(phenylamino)acetate (23)[6]



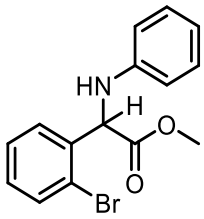
Purified by silica gel chromatography (PE: EA/50:1), the desired product **23** was obtained as a colorless oil, 34.2 mg, 53% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.40 (m, 2H), 7.23 – 7.20 (m, 2H), 7.17 – 7.13 (m, 2H), 6.72 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.61 – 6.58 (m, 2H), 5.08 (s, 1H), 4.90 (s, 1H), 3.74 (s, 3H), 2.51 (ddt, *J* = 11.5, 6.4, 3.7 Hz, 1H), 1.89 – 1.73 (m, 5H), 1.48 – 1.30 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.8, 148.4, 146.3, 135.0, 129.4, 127.5, 127.3, 118.2, 113.5, 60.7, 52.9, 44.4, 34.6, 34.5, 27.1, 26.3. (Known compounds, HRMS data detailed in Ref. 6.)

Methyl 2-(4-chlorophenyl)-2-(phenylamino)acetate (24)[6]



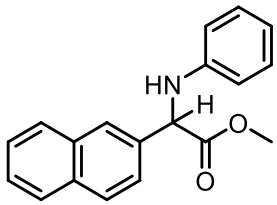
Purified by silica gel chromatography (PE: EA/40:1), the desired product **24** was obtained as a colorless oil, 34.1 mg, 62% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.44 (m, 2H), 7.35 – 7.32 (m, 2H), 7.16 – 7.11 (m, 2H), 6.75 – 6.71 (m, 1H), 6.56 – 6.53 (m, 2H), 5.07 (s, 1H), 5.01 (s, 1H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.0, 145.8, 136.4, 134.3, 129.5, 129.3, 128.8, 118.5, 113.6, 60.3, 53.1. (Known compounds, HRMS data detailed in Ref. 6.)

Methyl 2-(2-bromophenyl)-2-(phenylamino)acetate (25)[6]



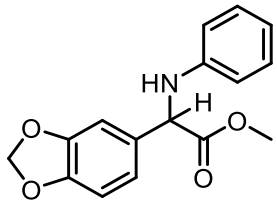
Purified by silica gel chromatography (PE: EA/40:1), the desired product **25** was obtained as a colorless oil, 49.9 mg, 78% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.25 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 – 7.08 (m, 3H), 6.69 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.56 (dt, *J* = 7.7, 1.1 Hz, 2H), 5.59 (s, 1H), 5.09 (s, 1H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.0, 145.8, 137.5, 133.5, 129.9, 129.5, 128.6, 128.3, 124.7, 118.5, 113.6, 59.7, 53.1. (Known compounds, HRMS data detailed in Ref. 6.)

Methyl 2-(naphthalen-2-yl)-2-(phenylamino)acetate (26)[6]



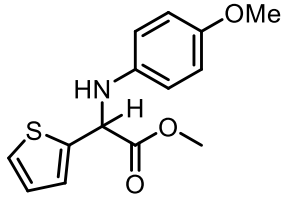
Purified by silica gel chromatography (PE: EA/40:1), the desired product **26** was obtained as a white solid, M.P. 101-105 ℃, 34.9 mg, 60% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 1.8 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.13 – 7.07 (m, 2H), 6.68 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.60 (dt, *J* = 7.7, 1.1 Hz, 2H), 5.23 (s, 1H), 5.08 (s, 1H), 3.72 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.5, 146.2, 135.3, 133.6, 133.5, 129.5, 129.0, 128.3, 127.9, 126.7, 126.5, 126.5, 125.1, 118.4, 113.7, 61.1, 53.1. (Known compounds, HRMS data detailed in Ref. 6.)

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(phenylamino)acetate (27)



Purified by silica gel chromatography (PE: EA/20:1), the desired product **27** was obtained as a colorless oil, 36.5 mg, 64% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.12 (m, 2H), 7.01 – 6.98 (m, 2H), 6.80 – 6.78 (m, 1H), 6.72 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.59 – 6.55 (m, 2H), 5.96 – 5.93 (m, 2H), 5.00 (s, 1H), 4.96 (s, 1H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.5, 148.3, 147.8, 146.0, 131.6, 129.4, 121.0, 118.31, 113.6, 108.7, 107.7, 101.4, 60.5, 53.0. HRMS (ESI) m/z calcd for $C_{16}H_{16}NO_4^+$ $(M+H)^+$ 286.1074, found 286.1068.

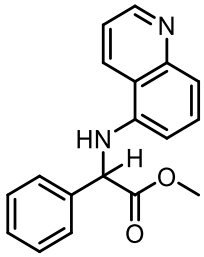
Methyl 2-((4-methoxyphenyl)amino)-2-(thiophen-2-yl)acetate (28) [9]



Purified by silica gel chromatography (PE: EA/20:1), the desired product **28** was obtained as a yellow oil, 44.9 mg, 81% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.12 (dt, *J* = 3.6, 1.1 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.63 – 6.58 (m, 2H), 5.28 (d, *J* = 0.9 Hz, 1H), 4.63 (s, 1H), 3.76 (s, 3H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.8,

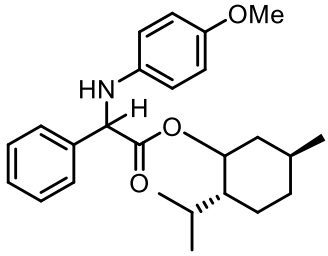
153.2, 141.6, 140.1, 127.2, 125.8, 125.7, 115.4, 115.0, 58.0, 55.8, 53.1. (Known compounds, HRMS data detailed in Ref. 9.)

Methyl 2-phenyl-2-(quinolin-5-ylamino)acetate (29)



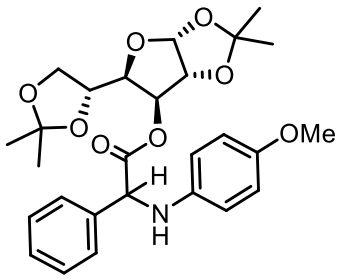
Purified by silica gel chromatography (PE: EA/6:1), the desired product **29** was obtained as a yellow solid, M.P. 190-191 °C, 36.2 mg, 62% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.37 (dt, *J* = 8.5, 1.3 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.48 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.38 – 7.33 (m, 3H), 6.37 (dd, *J* = 7.7, 1.0 Hz, 1H), 5.79 (d, *J* = 5.3 Hz, 1H), 5.22 (d, *J* = 5.2 Hz, 1H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.4, 150.3, 149.3, 141.3, 137.1, 130.3, 129.2, 129.0, 128.7, 127.4, 119.8, 119.5, 118.7, 106.2, 60.9, 53.2. HRMS (ESI) m/z calcd for $C_{18}H_{17}N_2O_2^+$ $(M+H)^+$ 293.1285, found 293.1280.

(2R,5S)-2-isopropyl-5-methylcyclohexyl2-((4-methoxyphenyl)amino)-2-phenylacetate (30)



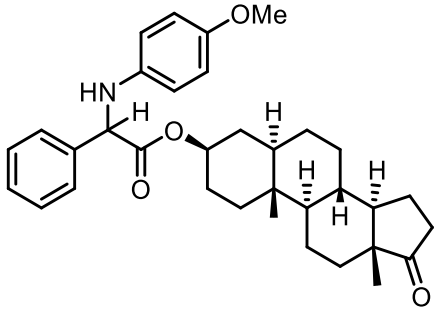
Purified by silica gel chromatography (PE: EA/60:1), the desired product **30** was obtained as a colorless oil, 62.4 mg, 79% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.46 (m, 2H), 7.36 – 7.29 (m, 3H), 6.73 – 6.70 (m, 2H), 6.57 – 6.53 (m, 2H), 4.99 (s, 1H), 4.73 – 4.59 (m, 2H), 3.70 (s, 3H), 1.84 (td, *J* = 7.0, 2.7 Hz, 1H), 1.70 – 1.63 (m, 3H), 1.38 (ddd, *J* = 14.6, 8.5, 3.1 Hz, 2H), 1.05 – 0.99 (m, 1H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 4H), 0.72 (d, *J* = 7.0 Hz, 4H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.9, 152.7, 140.6, 138.1, 128.9, 128.3, 127.4, 115.1, 115.1, 76.0, 62.1, 56.0, 47.1, 40.3, 34.3, 31.5, 26.5, 23.5, 22.1, 21.0, 16.4. HRMS (ESI) m/z calcd for $C_{25}H_{34}NO_3^+$ $(M+H)^+$ 396.2533, found 396.2530.

(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate (31)



Purified by silica gel chromatography (PE: EA/10:1), the desired product **31** was obtained as a colorless oil, 94.8 mg, 95% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (ddd, *J* = 7.9, 3.4, 1.5 Hz, 2H), 7.37 – 7.29 (m, 3H), 6.75 – 6.70 (m, 2H), 6.59 – 6.55 (m, 2H), 5.83 (d, *J* = 3.9 Hz, 0.5H), 5.78 (d, *J* = 3.7 Hz, 0.5H), 5.07 (d, *J* = 1.7 Hz, 1H), 4.88 (dd, *J* = 5.2, 3.9 Hz, 0.5H), 4.83 – 4.76 (m, 1.5H), 4.64 – 4.58 (m, 1H), 4.27 (dt, *J* = 6.8, 5.2 Hz, 0.5H), 4.16 – 4.06 (m, 2H), 3.90 (dd, *J* = 8.7, 5.5 Hz, 0.5H), 3.76 (dd, *J* = 8.7, 6.4 Hz, 0.5H), 3.70 (s, 3H), 3.25 (dd, *J* = 8.7, 6.7 Hz, 0.5H), 1.58 (s, 1.5H), 1.43 (s, 1.5H), 1.35 (d, *J* = 8.2 Hz, 3H), 1.24 (s, 1.5H), 1.18 (s, 1.5H), 1.11 (d, *J* = 10.8 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.3, 171.2, 152.8, 152.7, 140.4, 140.3, 137.4, 129.0, 128.7, 128.6, 128.3, 127.8, 127.6, 115.0, 114.9, 114.8, 113.2, 113.0, 110.1, 109.8, 104.5, 104.3, 78.0, 77.6, 77.5, 77.4, 77.2, 76.9, 75.3, 74.7, 74.0, 73.2, 66.0, 65.1, 61.9, 61.7, 55.8, 26.9, 26.8, 26.5, 26.2, 26.0, 25.4, 25.2. HRMS (ESI) m/z calcd for $C_{27}H_{34}NO_8^+$ $(M+H)^+$ 500.2279, found 500.2274.

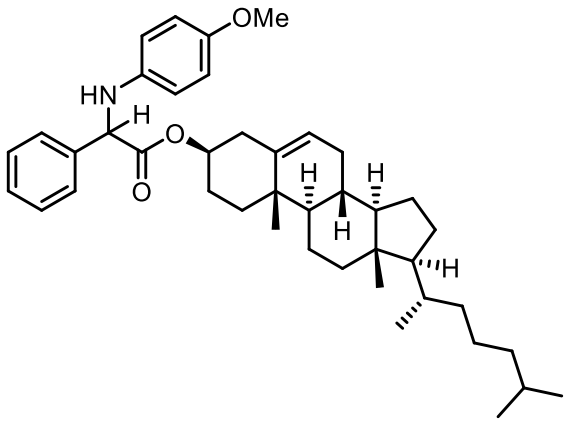
(3R,5R,8S,9R,10R,13R,14R)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate (32)



Purified by silica gel chromatography (PE: EA/15:1), the desired product **32** was obtained as a white solid, M.P. 88-90 ℃, 78.3 mg, 74% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.45 (m, 2H), 7.31 (dtd, *J* = 16.0, 6.9, 1.8 Hz, 2H), 6.73 – 6.68 (m, 3H), 6.55 – 6.50 (m, 2H), 4.97 (s, 2H), 4.71 (tt, *J* = 10.9, 4.9 Hz, 1H), 4.65 (s, 1H), 3.68 (s, 3H), 2.46 – 2.36 (m, 1H), 2.09 – 1.99 (m, 1H), 1.89 (ddd, *J* = 13.6, 8.5, 5.6 Hz, 1H), 1.77 (ddd, *J* = 12.2, 7.7, 3.6 Hz, 2H), 1.62 (tdd, *J* = 18.0, 8.6, 4.2 Hz, 3H), 1.55 –

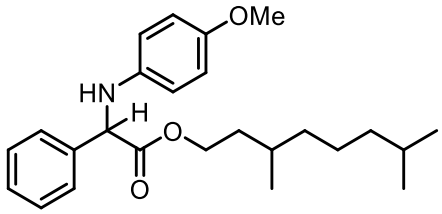
1.41 (m, 3H), 1.29 – 1.18 (m, 6H), 1.03 – 0.92 (m, 2H), 0.88 – 0.85 (m, 2H), 0.82 (d, *J* = 8.8 Hz, 6H), 0.67 (td, *J* = 11.4, 3.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 171.7, 152.6, 140.5, 138.1, 128.8, 128.2, 127.3, 114.9, 114.9, 75.1, 75.1, 61.9, 55.8, 54.4, 51.4, 47.9, 44.7, 44.7, 36.8, 36.6, 35.9, 35.7, 35.1, 35.1, 34.0, 33.5, 31.6, 30.9, 28.4, 28.3, 27.5, 27.1, 21.9, 20.6, 20.6, 13.9, 12.3. HRMS (ESI) m/z calcd for $C_{34}H_{44}NO_4^+$ $(M+H)^+$ 530.3265, found 530.3262.

(3R,8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate (33)[9]



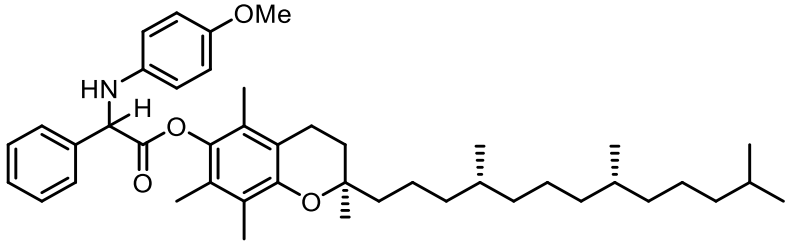
Purified by silica gel chromatography (PE: EA/80:1), the desired product **33** was obtained as a white solid, M.P. 114-116 ℃, 117.5 mg, 94% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.49 (m, 2H), 7.34 (ddd, *J* = 15.7, 7.7, 6.2 Hz, 3H), 6.76 – 6.71 (m, 2H), 6.58 – 6.53 (m, 2H), 5.41 – 5.28 (m, 1H), 5.01 (s, 1H), 4.66 (tt, *J* = 11.5, 4.7 Hz, 1H), 3.71 (s, 3H), 2.37 (d, *J* = 8.1 Hz, 1H), 2.20 – 2.08 (m, 1H), 2.06 – 1.96 (m, 2H), 1.92 – 1.78 (m, 3H), 1.65 – 1.41 (m, 7H), 1.39 – 1.26 (m, 4H), 1.21 – 1.06 (m, 8H), 1.01 (s, 4H), 0.93 (dd, *J* = 6.6, 1.5 Hz, 4H), 0.89 (dd, *J* = 6.6, 1.8 Hz, 7H), 0.69 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 171.6, 152.6, 140.5, 139.5, 139.4, 138.2, 128.9, 128.3, 127.4, 123.2, 123.1, 115.0, 114.9, 75.6, 62.0, 56.9, 56.3, 55.9, 50.2, 42.5, 39.9, 39.7, 38.2, 37.7, 37.1, 37.0, 36.7, 36.4, 36.0, 32.1, 32.0, 28.4, 28.2, 27.9, 27.5, 24.5, 24.0, 23.0, 22.8, 21.2, 19.5, 18.9, 12.0. (Known compounds, HRMS data detailed in Ref. 9.)

3,7-dimethyloctyl 2-((4-methoxyphenyl)amino)-2-phenylacetate (34)



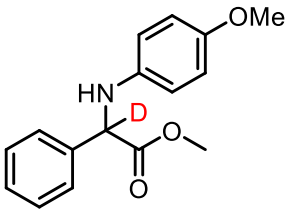
Purified by silica gel chromatography (PE: EA/60:1), the desired product **34** was obtained as a yellow oil, 67.5 mg, 85% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dt, *J* = 6.1, 1.5 Hz, 2H), 7.39 – 7.31 (m, 3H), 6.76 – 6.72 (m, 2H), 6.56 (dd, *J* = 9.0, 1.1 Hz, 2H), 5.03 (d, *J* = 1.4 Hz, 1H), 4.75 (s, 1H), 4.21 – 4.16 (m, 2H), 3.71 (s, 3H), 1.66 – 1.53 (m, 2H), 1.38 (dd, *J* = 7.8, 3.1 Hz, 1H), 1.27 – 1.06 (m, 7H), 0.90 (dt, *J* = 6.6, 1.9 Hz, 6H), 0.86 – 0.79 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.3, 152.6, 140.4, 138.2, 128.9, 128.3, 127.4, 115.0, 114.9, 64.3, 61.9, 55.8, 39.3, 37.2, 37.1, 35.6, 29.8, 28.1, 24.8, 22.9, 22.8, 19.5. HRMS (ESI) m/z calcd for $C_{25}H_{36}NO_3^+$ $(M+H)^+$ 398.2690, found 398.2682.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate (35)



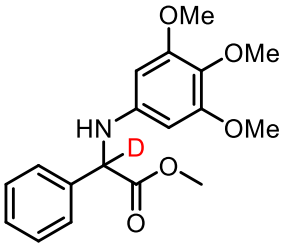
Purified by silica gel chromatography (PE: EA/40:1), the desired product **35** was obtained as a yellow oil, 95.0 mg, 71% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.63 (m, 2H), 7.43 – 7.34 (m, 3H), 6.79 – 6.74 (m, 2H), 6.66 – 6.62 (m, 2H), 5.34 (s, 1H), 4.88 (s, 1H), 3.73 (s, 3H), 2.52 (d, *J* = 34.1 Hz, 2H), 2.04 (d, *J* = 30.9 Hz, 6H), 1.75 (dd, *J* = 13.4, 6.9 Hz, 2H), 1.54 (q, *J* = 6.5 Hz, 3H), 1.43 – 1.33 (m, 7H), 1.31 – 1.26 (m, 5H), 1.22 (s, 5H), 1.19 – 1.04 (m, 7H), 0.90 (s, 3H), 0.87 (d, *J* = 3.7 Hz, 6H), 0.85 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 170.8, 152.8, 149.8, 140.4, 140.3, 138.1, 129.1, 128.7, 127.8, 126.9, 125.1, 123.3, 117.6, 115.1, 115.1, 75.3, 61.9, 55.9, 39.6, 37.7, 37.6, 37.5, 33.0, 32.9, 28.2, 25.0, 24.6, 22.9, 22.8, 21.2, 20.7, 20.0, 19.9. HRMS (ESI) m/z calcd for $C_{44}H_{64}NO_4^+$ $(M+H)^+$ 670.4830, found 670.4817.

Methyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (36)[14]



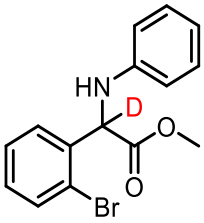
Purified by silica gel chromatography (PE: EA/30:1), the desired product **36** was obtained as a white solid, M.P. 107-109 ℃, 41.9 mg, 77% yield; 99% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.38 – 7.31 (m, 3H), 6.75 – 6.71 (m, 2H), 6.56 – 6.53 (m, 2H), 5.03 (s, 0.01H), 4.66 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.8, 152.8, 140.4, 137.9, 129.1, 128.5, 127.5, 115.1, 115.0, 61.7, 61.5, 61.3, 55.9, 52.9. (Known compounds, HRMS data detailed in Ref. 14.)

Methyl 2-phenyl-2-((3,4,5-trimethoxyphenyl)amino)acetate-*d* (37)[6]



Purified by silica gel chromatography (PE: EA/10:1), the desired product **37** was obtained as a white solid, M.P. 110-111 ℃, 55.8 mg, 84% yield; 97% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 2H), 7.38 – 7.30 (m, 3H), 5.80 (s, 2H), 5.03 (s, 0.03H), 4.86 (s, 1H), 3.72 (s, 3H), 3.71 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.4, 154.0, 142.9, 137.8, 130.6, 129.1, 128.5, 127.3, 91.2, 61.1, 61.0, 55.9, 52.9. (Known compounds, HRMS data detailed in Ref. 6.)

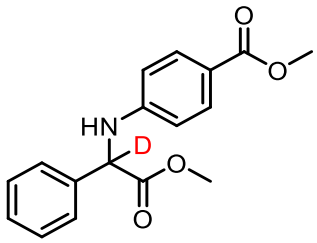
Methyl 2-(2-bromophenyl)-2-(phenylamino)acetate-*d* (38)



Purified by silica gel chromatography (PE: EA/40:1), the desired product **38** was obtained as a yellow oil, 48.2 mg, 75% yield; 96% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.25 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 (qd, *J* = 7.6, 7.2, 1.8 Hz, 3H), 6.69 (tt,

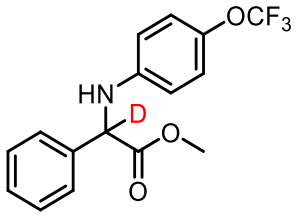
J = 7.3, 1.1 Hz, 1H), 6.58 – 6.52 (m, 2H), 5.59 (s, 0.04H), 5.08 (s, 1H), 3.72 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 172.0, 145.8, 137.4, 133.4, 129.9, 129.5, 128.5, 128.3, 124.7, 118.5, 113.6, 59.5, 59.3, 59.1, 53.1. HRMS (ESI) m/z calcd for $C_{15}H_{14}DBrNO_2^+$ $(M+H)^+$ 321.0343, found 321.0327.

Methyl 4-((2-methoxy-2-oxo-1-phenylethyl-1-*d*)amino)benzoate (39)



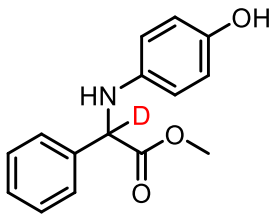
Purified by silica gel chromatography (PE: EA/10:1), the desired product **39** was obtained as a white solid, M.P. 146-149 ℃, 58.8 mg, 98% yield; 97% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 2H), 7.48 – 7.45 (m, 2H), 7.38 – 7.31 (m, 3H), 6.54 – 6.50 (m, 2H), 5.48 (s, 1H), 5.13 (s, 0.03H), 3.81 (s, 3H), 3.74 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 171.8, 167.3, 149.7, 136.8, 131.6, 129.2, 128.7, 127.3, 119.5, 112.5, 60.0, 59.8, 59.6, 53.2, 51.7. HRMS (ESI) m/z calcd for $C_{17}H_{17}DNO_4^+$ $(M+H)^+$ 301.1293, found 301.1283.

Methyl 2-phenyl-2-((4-(trifluoromethoxy)phenyl)amino)acetate-*d* (40)



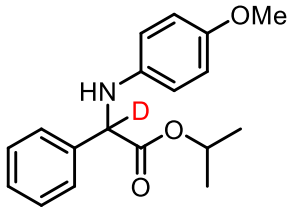
Purified by silica gel chromatography (PE: EA/40:1), the desired product **40** was obtained as a colorless oil, 57.4 mg, 88% yield; 90% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.40 – 7.33 (m, 3H), 7.01 – 6.97 (m, 2H), 6.54 – 6.49 (m, 2H), 5.08 (s, 1H), 5.05 (s, 0.10H), 3.74 (s, 3H); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -58.43; $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 172.2, 144.9, 141.1, 141.1, 137.3, 129.2, 128.7, 127.4, 122.6, 120.84 (d, $^{1}J_{C\text{-}F}$ = 255.3 Hz),113.9, 61.0, 60.6, 60.4, 53.1. HRMS (ESI) m/z calcd for $C_{16}H_{14}DF_3NO_3^+$ $(M+H)^+$ 327.1061, found 327.1056.

Methyl 2-((4-hydroxyphenyl)amino)-2-phenylacetate-*d* (41)



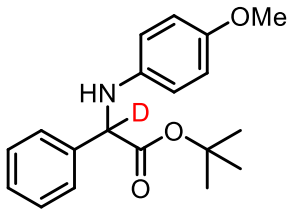
Purified by silica gel chromatography (PE: EA/10:1), the desired product **41** was obtained as a white solid, M.P. 130-132 ℃, 43.9 mg, 85% yield; 90% D, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 – 8.52 (m, 1H), 7.53 – 7.49 (m, 2H), 7.38 – 7.29 (m, 3H), 6.56 (dd, J = 6.3, 3.8 Hz, 4H), 5.75 (d, J = 2.1 Hz, 1H), 5.14 (d, J = 9.1 Hz, 0.10H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 172.7, 149.2, 139.7, 138.1, 128.6, 128.0, 127.6, 115.6, 114.7, 60.7, 60.4, 59.8, 52.1. HRMS (ESI) m/z calcd for $C_{15}H_{15}DNO_3^+$ $(M+H)^+$ 258.1115, found 258.1116.

Isopropyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (42)[14]



Purified by silica gel chromatography (PE: EA/40:1), the desired product **42** was obtained as a colorless oil, 40.2 mg, 67% yield; 93% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 2H), 7.37 – 7.26 (m, 3H), 6.75 – 6.70 (m, 2H), 6.57 – 6.51 (m, 2H), 5.03 (p, J = 6.3 Hz, 1H), 4.98 (s, 0.07H), 4.65 (s, 1H), 3.71 (s, 3H), 1.27 (d, J = 6.2 Hz, 3H), 1.08 (d, J = 6.3 Hz, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.8, 152.6, 140.5, 138.1, 128.9, 128.3, 127.3, 115.0, 114.9, 69.5, 55.9, 22.0, 21.6. (Known compounds, HRMS data detailed in Ref. 14.)

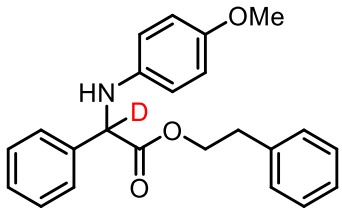
***Tert*-butyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (43)**



Purified by silica gel chromatography (PE: EA/40:1), the desired product **43** was obtained as a white solid, M.P. 83-84 ℃, 57.1 mg, 91% yield; 96% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.37 – 7.29 (m, 3H), 6.74 – 6.71 (m, 2H), 6.56 – 6.53 (m, 2H), 4.92 (s, 0.04H), 4.68 (s, 1H), 3.71

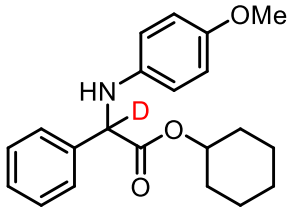
(s, 3H), 1.40 (s, 12H); $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 171.3, 152.5, 140.6, 138.5, 128.8, 128.1, 127.3, 115.0, 114.8, 82.3, 61.9, 55.9, 28.0. HRMS (ESI) m/z calcd for $C_{19}H_{23}DNO_3^+$ $(M+H)^+$ 315.1813, found 315.1809.

Phenethyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (44)



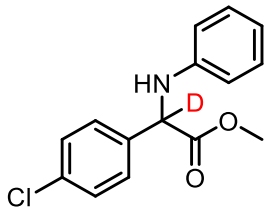
Purified by silica gel chromatography (PE: EA/30:1), the desired product **44** was obtained as a colorless oil, 50.7 mg, 70% yield; 95% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 2H), 7.36 – 7.30 (m, 3H), 7.23 (dt, *J* = 8.3, 2.3 Hz, 3H), 7.07 – 7.03 (m, 2H), 6.73 – 6.67 (m, 2H), 6.52 – 6.47 (m, 2H), 4.97 (s, 0.05H), 4.61 (d, *J* = 7.0 Hz, 1H), 4.33 (td, *J* = 6.8, 1.9 Hz, 2H), 3.69 (s, 3H), 2.86 (td, *J* = 6.8, 3.1 Hz, 2H), $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 172.2, 152.7, 140.4, 137.9, 137.6, 129.0, 128.7, 128.4, 127.5, 126.8, 115.0, 114.9, 66.2, 55.9, 35.1. HRMS (ESI) m/z calcd for $C_{23}H_{23}DNO_3^+$ $(M+H)^+$ 363.1813, found 363.1806.

Cyclohexyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (45)



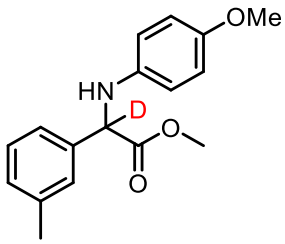
Purified by silica gel chromatography (PE: EA/40:1), the desired product **45** was obtained as a colorless oil, 55.1 mg, 81% yield; 93% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.49 (m, 2H), 7.37 – 7.28 (m, 3H), 6.75 – 6.71 (m, 2H), 6.57 – 6.53 (m, 2H), 5.01 (s, 0.07H), 4.82 (tt, *J* = 8.4, 3.8 Hz, 1H), 4.73 – 4.69 (m, 1H), 3.71 (s, 3H), 1.87 – 1.80 (m, 1H), 1.75 – 1.67 (m, 1H), 1.65 – 1.58 (m, 1H), 1.49 (ddt, *J* = 12.4, 8.4, 3.5 Hz, 3H), 1.42 – 1.35 (m, 1H), 1.28 (t, *J* = 9.7 Hz, 3H), $^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-*d*) δ 171.6, 152.5, 140.5, 138.2, 128.9, 128.2, 127.3, 115.0, 114.9, 74.1, 61.9, 61.8, 61.4, 55.9, 31.6, 31.1, 25.4, 23.6, 23.3. HRMS (ESI) m/z calcd for $C_{21}H_{25}DNO_3^+$ $(M+H)^+$ 341.1970, found 341.1967.

Methyl 2-(4-chlorophenyl)-2-(phenylamino)acetate-*d* (46)



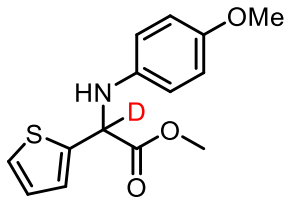
Purified by silica gel chromatography (PE: EA/40:1), the desired product **46** was obtained as a colorless oil, 27.6 mg, 50% yield; 93% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 2H), 5.06 (s, 0.07H), 4.97(s, 1H), 3.75 (s, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.0, 145.8, 136.3, 134.4, 129.5, 129.3, 128.8, 118.5, 113.6, 59.9, 59.7, 53.2. HRMS (ESI) m/z calcd for $C_{15}H_{14}DClNO_2^+$ $(M+H)^+$ 277.0849, found 277.0845.

Methyl 2-((4-methoxyphenyl)amino)-2-(m-tolyl)acetate-*d* (47)[14]



Purified by silica gel chromatography (PE: EA/30:1), the desired product **47** was obtained as a yellow oil, 36.0 mg, 63 % yield; 99% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 3H), 7.12 – 7.09 (m, 1H), 6.75 – 6.69 (m, 2H), 6.56 – 6.51 (m, 2H), 4.97 (s, 0.01H), 4.61 (s, 1H), 3.70 (d, *J* = 4.1 Hz, 6H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.9, 152.7, 140.5, 138.8, 137.8, 129.3, 128.9, 128.0, 124.6, 61.7, 61.5, 61.3, 55.8, 52.8, 21.6. (Known compounds, HRMS data detailed in Ref. 14.)

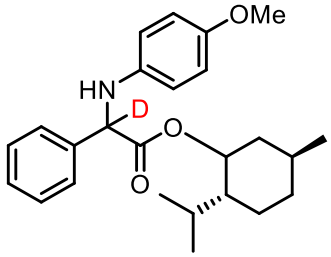
Methyl 2-((4-methoxyphenyl)amino)-2-(thiophen-2-yl)acetate-*d* (48)[6]



Purified by silica gel chromatography (PE: EA/30:1), the desired product **48** was obtained as a yellow oil, 41.1 mg, 74% yield; 99% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.12 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.77 – 6.72 (m, 2H), 6.63 – 6.59 (m, 2H), 5.28 (d, *J* = 1.0 Hz, 0.01H), 4.59 (s, 0.78H), 3.76 (s, 3H), 3.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz,

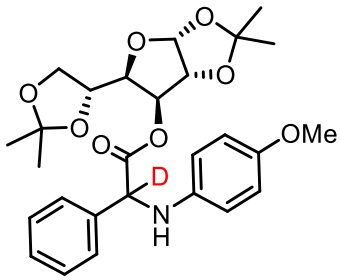
Chloroform-*d*) δ 171.8, 153.1, 141.5, 140.1, 127.3, 125.8, 125.7, 115.4, 115.0, 57.6, 57.4, 55.8, 53.1. (Known compounds, HRMS data detailed in Ref. 6.)

(2R,5S)-2-isopropyl-5-methylcyclohexyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-*d* (49)[14]



Purified by silica gel chromatography (PE: EA/80:1), the desired product **49** was obtained as a colorless oil, 68.9 mg, 87% yield; 97% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.45 (m, 2H), 7.31 (dt, *J* = 12.8, 6.9 Hz, 3H), 6.74 – 6.69 (m, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 4.96 (s, 0.03H), 4.73 (s, 1H), 4.62 (td, *J* = 10.9, 4.4 Hz, 1H), 3.70 (s, 3H), 2.03 – 1.97 (m, 1H), 1.67 – 1.46 (m, 3H), 1.24 (tt, *J* = 11.3, 3.2 Hz, 1H), 1.07 – 0.94 (m, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.81 (td, *J* = 12.5, 3.3 Hz, 1H), 0.58 (d, *J* = 7.0 Hz, 3H), 0.35 (d, *J* = 6.9 Hz, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.9, 152.5, 140.5, 138.4, 128.8, 128.3, 127.5, 115.0, 114.8, 76.0, 55.9, 47.3, 40.9, 34.3, 31.6, 25.4, 23.0, 22.2, 20.8, 15.7. (Known compounds, HRMS data detailed in Ref. 14.)

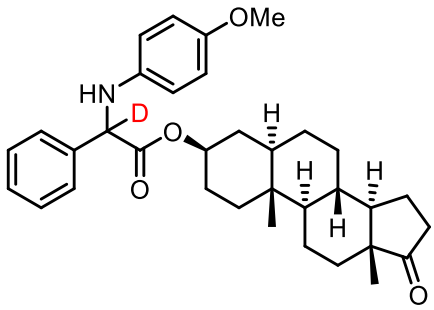
(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate-d (50)



Purified by silica gel chromatography (PE: EA/10:1), the desired product **50** was obtained as a yellow oil, 66.0 mg, 66% yield; 95%D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (dt, *J* = 7.9, 1.9 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.73 (dd, *J* = 9.0, 2.7 Hz, 2H), 6.59 – 6.54 (m, 2H), 5.83 (d, *J* = 3.9 Hz, 0.4H), 5.79 (d, *J* = 3.9 Hz, 0.6H), 5.06 (s, 0.05H), 4.89 (dd, *J* = 5.2, 3.9 Hz, 0.4H), 4.84 – 4.75 (m, 1.6H), 4.59 (s, 1H), 4.28 (dt, *J* = 6.7, 5.1 Hz, 0.6H), 4.18 – 4.05 (m, 2H), 3.91 (dd, *J* = 8.7, 5.6 Hz, 0.6H), 3.75 (dd, *J* = 8.7, 6.5 Hz, 0.4H), 3.71 (s, 3H), 3.21 (dd, *J* = 8.7, 6.9 Hz, 0.4H), 1.58 (s, 1H), 1.43 (s, 2H), 1.35 (d, *J* = 8.4 Hz, 3H), 1.24 (s, 1H), 1.17 (s, 2H), 1.09 (d, *J* = 11.0 Hz, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*)

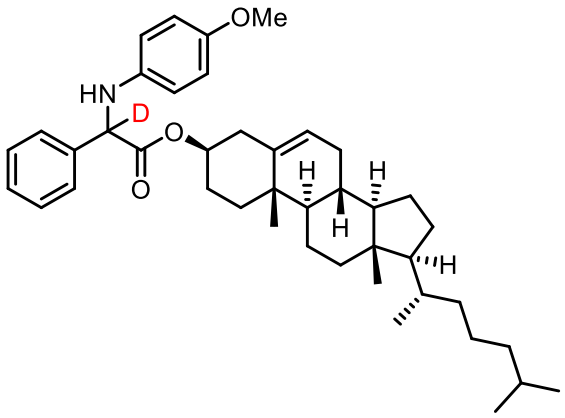
δ 171.4, 171.3, 152.8, 152.7, 140.4, 140.3, 137.3, 129.1, 128.8, 128.8, 128.5, 128.0, 127.7, 115.0, 115.0, 114.9, 113.3, 113.1, 110.2, 109.9, 104.6, 104.3, 78.0, 77.5, 77.4, 75.3, 74.7, 74.0, 73.2, 66.0, 65.1, 55.9, 27.0, 27.0, 26.6, 26.2, 26.0, 25.5, 25.2. HRMS (ESI) m/z calcd for $C_{27}H_{33}DNO_8^+$ $(M+H)^+$ 501.2342, found 501.2334.

(3R,5R,8S,9R,10R,13R,14R)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate-d (51)



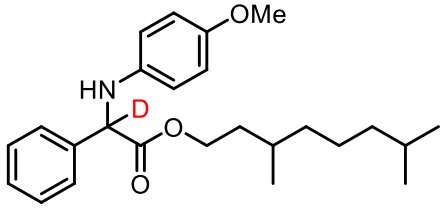
Purified by silica gel chromatography (PE: EA/20:1), the desired product **51** was obtained as a white solid, M.P. 63-65℃, 59.4 mg, 56% yield; 96%D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (dt, *J* = 8.0, 1.3 Hz, 2H), 7.32 (dtd, *J* = 15.3, 6.9, 1.8 Hz, 3H), 6.74 – 6.69 (m, 2H), 6.55 – 6.51 (m, 2H), 4.97 (s, 0.04H), 4.72 (dq, *J* = 11.4, 6.1, 5.5 Hz, 1H), 4.63 (s, 1H), 3.70 (s, 3H), 2.43 (dd, *J* = 19.2, 8.9 Hz, 1H), 2.10 – 2.02 (m, 1H), 1.90 (dd, *J* = 8.8, 5.5 Hz, 1H), 1.81 – 1.75 (m, 2H), 1.64 (ddd, *J* = 14.6, 8.9, 3.3 Hz, 3H), 1.55 – 1.45 (m, 3H), 1.30 – 1.22 (m, 6H), 1.18 – 1.08 (m, 2H), 1.02 – 0.94 (m, 2H), 0.86 – 0.81 (m, 6H), 0.68 (td, *J* = 11.5, 4.0 Hz, 1H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.8, 152.6, 140.5, 138.0, 128.9, 128.3, 127.3, 115.0, 114.9, 75.1, 55.9, 54.4, 51.5, 48.0, 44.8, 44.7, 36.8, 36.7, 36.0, 35.8, 35.1, 34.0, 33.5, 31.7, 30.9, 28.4, 28.3, 27.6, 27.1, 21.9, 20.6, 14.0, 12.4. HRMS (ESI) m/z calcd for $C_{34}H_{43}DNO_4^+$ $(M+H)^+$ 531.3328, found 531.3324.

(3R,8R,9R,10S,13S,14R,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate-d (52)



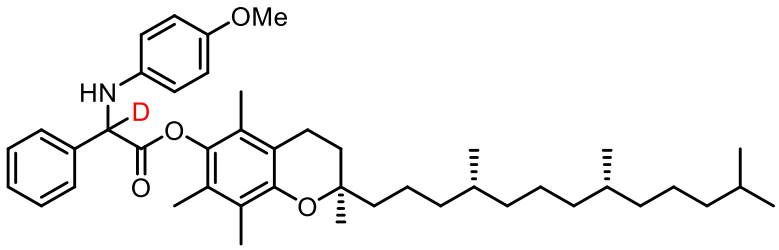
Purified by silica gel chromatography (PE: EA/80:1), the desired product **52** was obtained as a white solid, M.P. 97-100℃, 75.2 mg, 60% yield; 95%D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.29 (m, 3H), 6.75 – 6.70 (m, 2H), 6.56 – 6.52 (m, 2H), 5.33 (dd, *J* = 35.8, 5.1 Hz, 1H), 4.99 (s, 0.05H), 4.64 (ddt, *J* = 11.6, 6.9, 4.2 Hz, 1H), 3.71 (s, 3H), 2.35 (d, *J* = 8.1 Hz, 1H), 2.19 – 2.08 (m, 1H), 2.03 – 1.94 (m, 2H), 1.91 – 1.77 (m, 3H), 1.64 – 1.40 (m, 9H), 1.38 – 1.28 (m, 3H), 1.10 (ddd, *J* = 17.7, 13.8, 8.1 Hz, 7H), 0.99 (s, 4H), 0.91 (d, *J* = 6.3 Hz, 4H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 7H), 0.67 (s, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 171.7, 152.6, 140.5, 139.5, 139.4, 138.1, 128.9, 128.3, 127.4, 123.2, 123.1, 115.0, 114.9, 75.6, 56.8, 56.3, 55.9, 50.1, 42.5, 39.9, 39.7, 38.2, 37.7, 37.1, 37.0, 36.7, 36.4, 36.0, 32.1, 32.0, 28.4, 28.2, 27.9, 27.5, 24.5, 24.0, 23.0, 22.8, 21.2, 19.5, 18.9, 12.1. HRMS (ESI) m/z calcd for $C_{42}H_{59}DNO_3^+$ $(M+H)^+$ 627.4630, found 627.4626.

3,7-dimethyloctyl 2-((4-methoxyphenyl)amino)-2-phenylacetate-d (53)



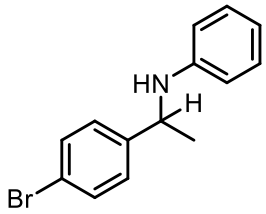
Purified by silica gel chromatography (PE: EA/60:1), the desired product **53** was obtained as a yellow oil, 49.4 mg, 62% yield; 98% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.47 (m, 2H), 7.37 – 7.29 (m, 3H), 6.74 – 6.70 (m, 2H), 6.55 – 6.52 (m, 2H), 5.00 (s, 0.02H), 4.70 (s, 1H), 4.19 – 4.11 (m, 2H), 3.71 (s, 3H), 1.61 – 1.48 (m, 2H), 1.35 (dt, *J* = 6.1, 3.5 Hz, 1H), 1.25 – 1.02 (m, 7H), 0.87 (dd, *J* = 6.6, 2.2 Hz, 6H), 0.80 (dd, *J* = 17.9, 6.1 Hz, 3H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 172.3, 152.6, 140.4, 138.0, 129.0, 128.4, 127.4, 115.0, 114.9, 64.4, 55.9, 39.3, 37.2, 37.1, 35.6, 35.6, 29.8, 28.2, 24.8, 24.8, 22.9, 22.8, 19.6, 19.4. HRMS (ESI) m/z calcd for $C_{25}H_{35}DNO_3^+$ $(M+H)^+$ 399.2752, found 399.2746.

(R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl 2-((4-methoxyphenyl)amino)-2-phenylacetate-d (54)



Purified by silica gel chromatography (PE: EA/60:1), the desired product **54** was obtained as a colorless oil, 85.9 mg, 64% yield; 99% D, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.65 (m, 2H), 7.44 – 7.34 (m, 3H), 6.80 – 6.75 (m, 2H), 6.68 – 6.64 (m, 2H), 5.36 (s, 0.01H), 4.91 (s, 1H), 3.74 (s, 3H), 2.54 (d, *J* = 42.5 Hz, 2H), 2.13 – 1.95 (m, 6H), 1.83 – 1.72 (m, 2H), 1.55 (h, *J* = 6.7 Hz, 3H), 1.39 (d, *J* = 16.6 Hz, 6H), 1.32 – 1.23 (m, 9H), 1.17 (td, *J* = 6.7, 6.1, 3.4 Hz, 3H), 1.13 – 1.06 (m, 4H), 0.89 (dd, *J* = 10.3, 6.4 Hz, 14H), ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 170.8, 152.7, 149.7, 140.3, 140.2, 137.9, 129.1, 128.7, 127.8, 125.1, 123.3, 117.6, 115.1, 115.0, 75.2, 55.8, 40.5, 39.6, 37.6, 37.6, 37.5, 33.0, 32.9, 31.1, 28.2, 25.0, 24.6, 22.9, 22.8, 21.2, 20.7, 20.0, 19.8. HRMS (ESI) m/z calcd for $C_{44}H_{63}DNO_4^+$ $(M+H)^+$ 671.4893, found 671.4888.

N-(1-(4-bromophenyl)ethyl)aniline (56)[15]



Purified by silica gel chromatography (PE: EA/60:1), the desired product **56** was obtained as a colorless oil, 18.2 mg, 66% yield; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 0H), 6.46 (d, *J* = 7.9 Hz, 1H), 4.42 (q, *J* = 6.8 Hz, 0H), 4.00 (s, 0H), 1.48 (d, *J* = 6.7 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 147.1, 144.6, 131.9, 129.3, 127.8, 120.7, 117.7, 113.5, 53.2, 25.3. (Known compounds, HRMS data detailed in Ref. 15.)

9. References

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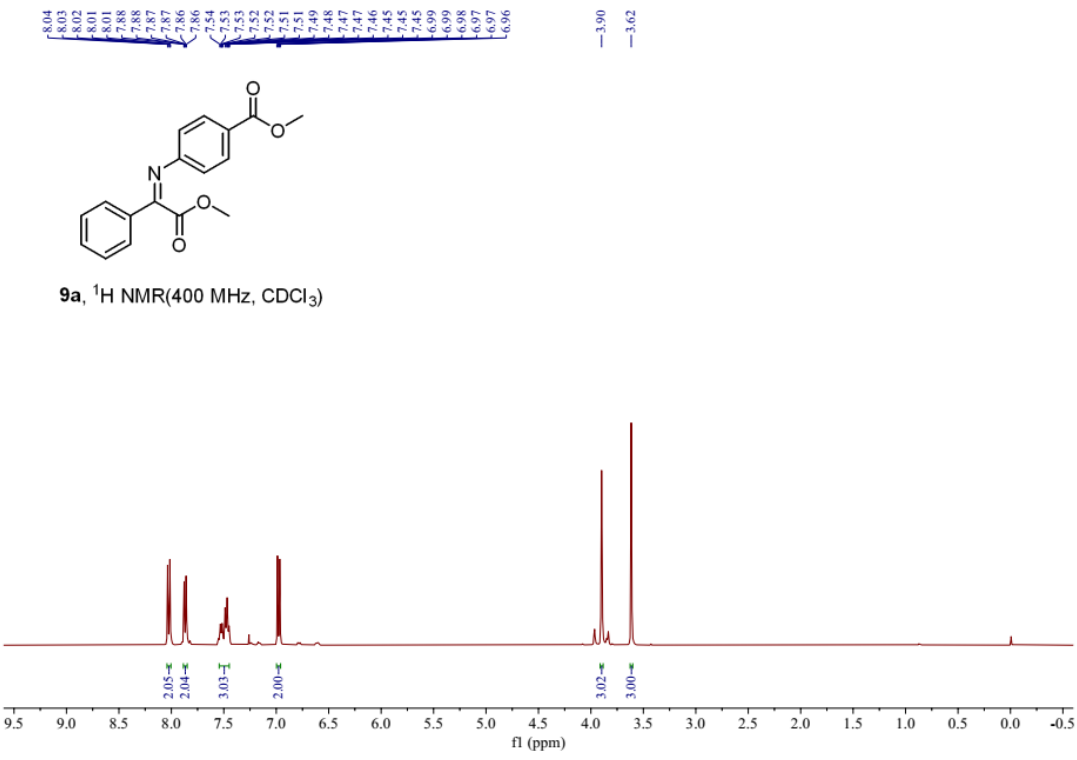
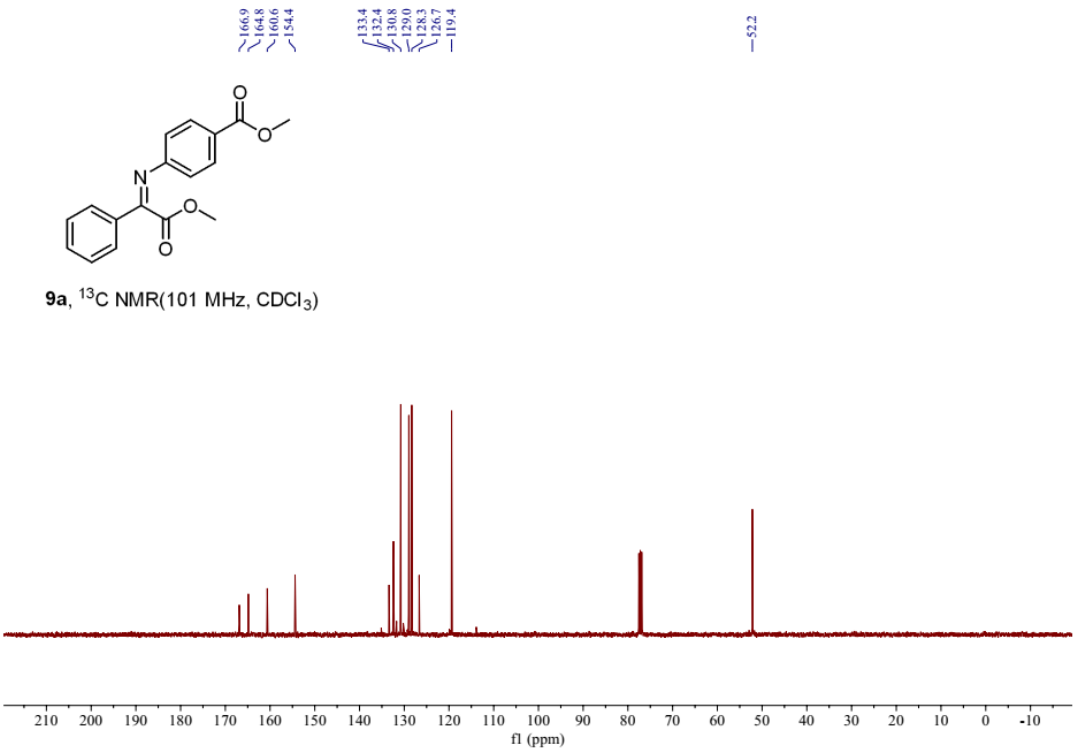
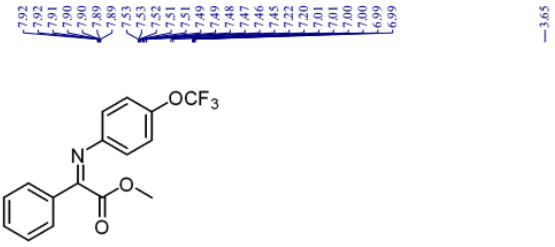
10. Copies of NMR spectra of all substrates



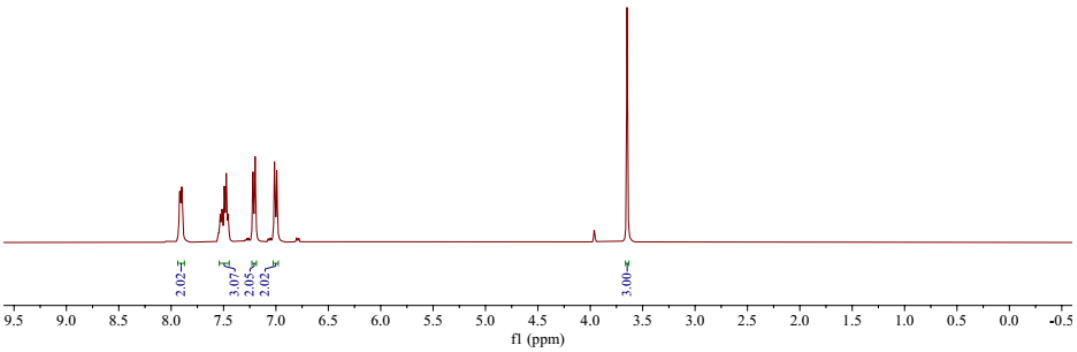
9a, ^{1}H NMR(400 MHz, $CDCl_3$)

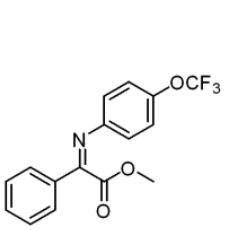


9a, ^{13}C NMR(101 MHz, $CDCl_3$)

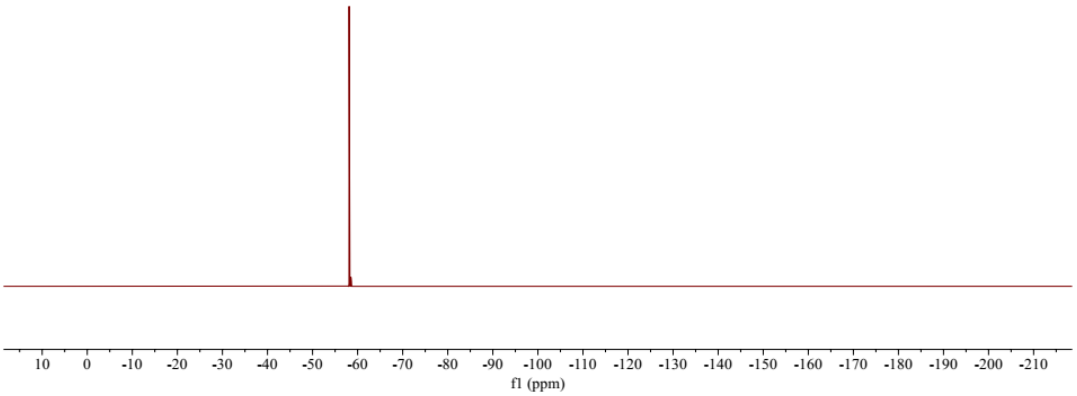


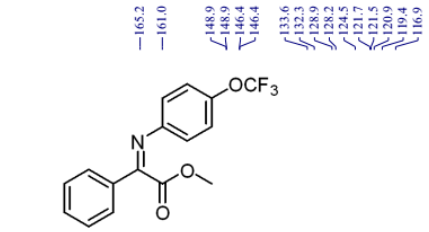
10a, ^{1}H NMR(400 MHz, $CDCl_3$)



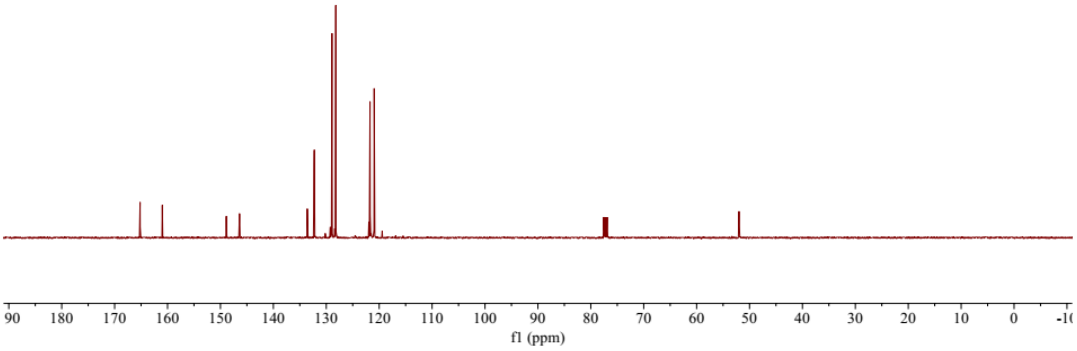


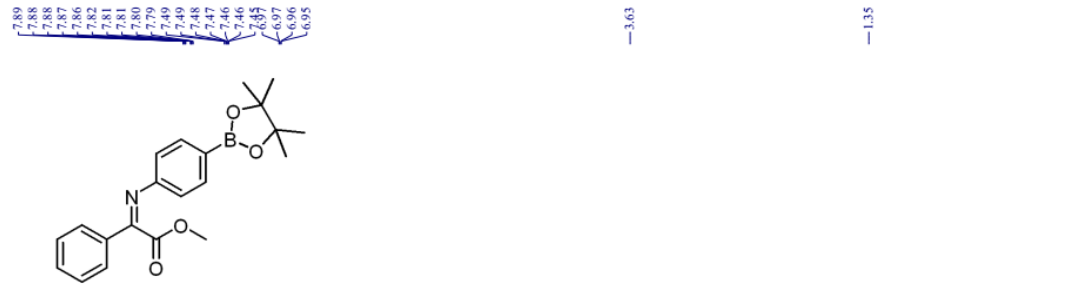
10a, ^{19}F NMR(376 MHz, $CDCl_3$)



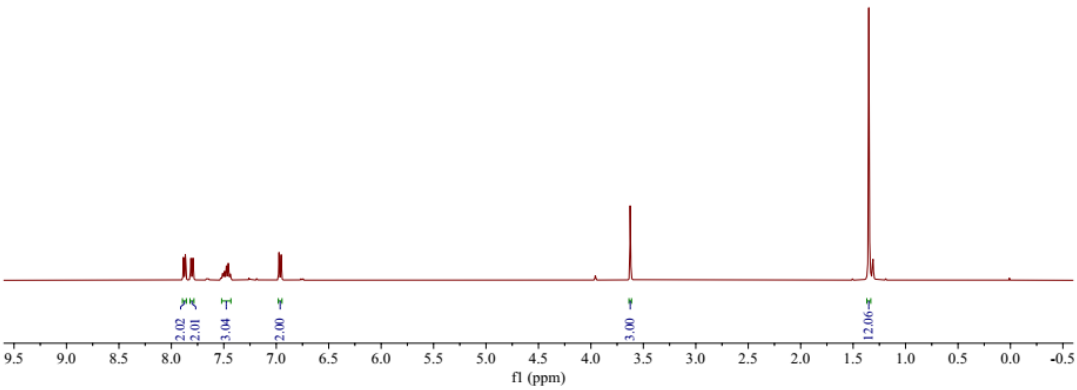


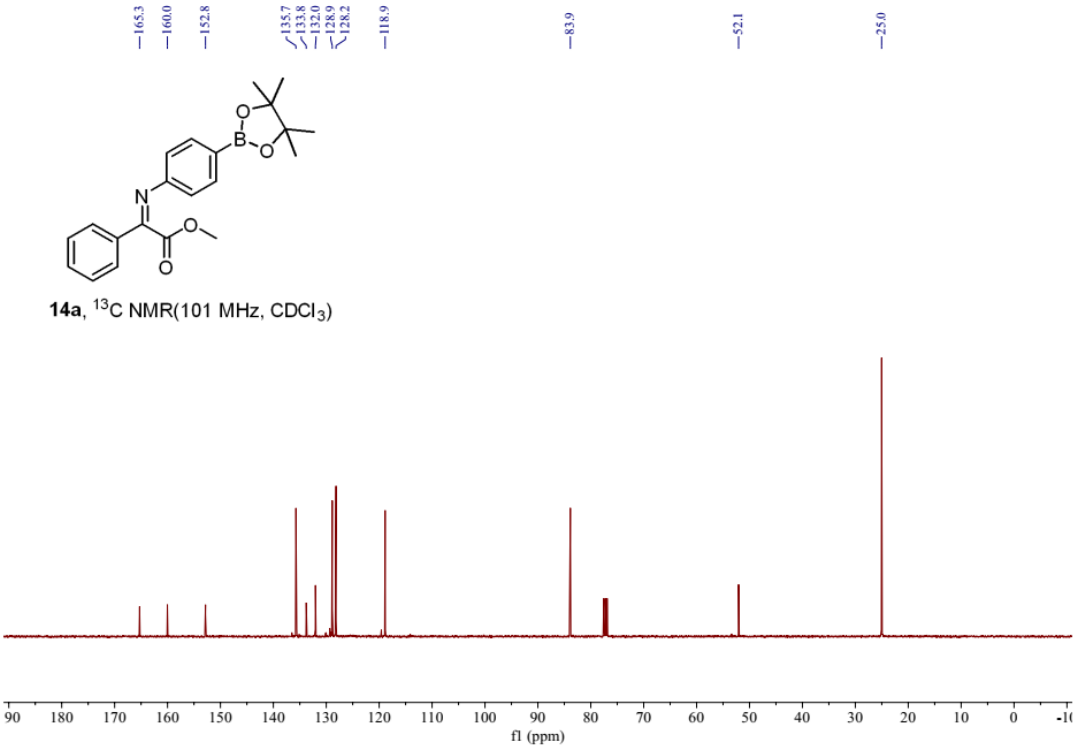
10a, ^{13}C NMR(101 MHz $CDCl_3$)



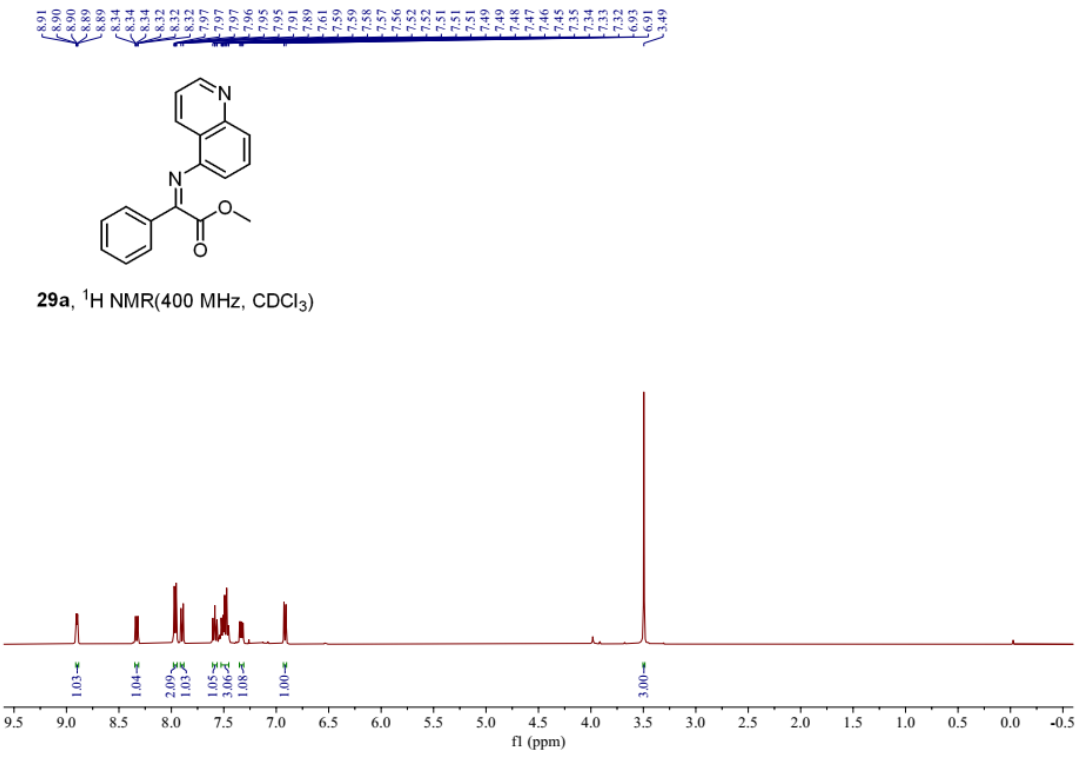


14a, ^{1}H NMR(400 MHz, $CDCl_3$)

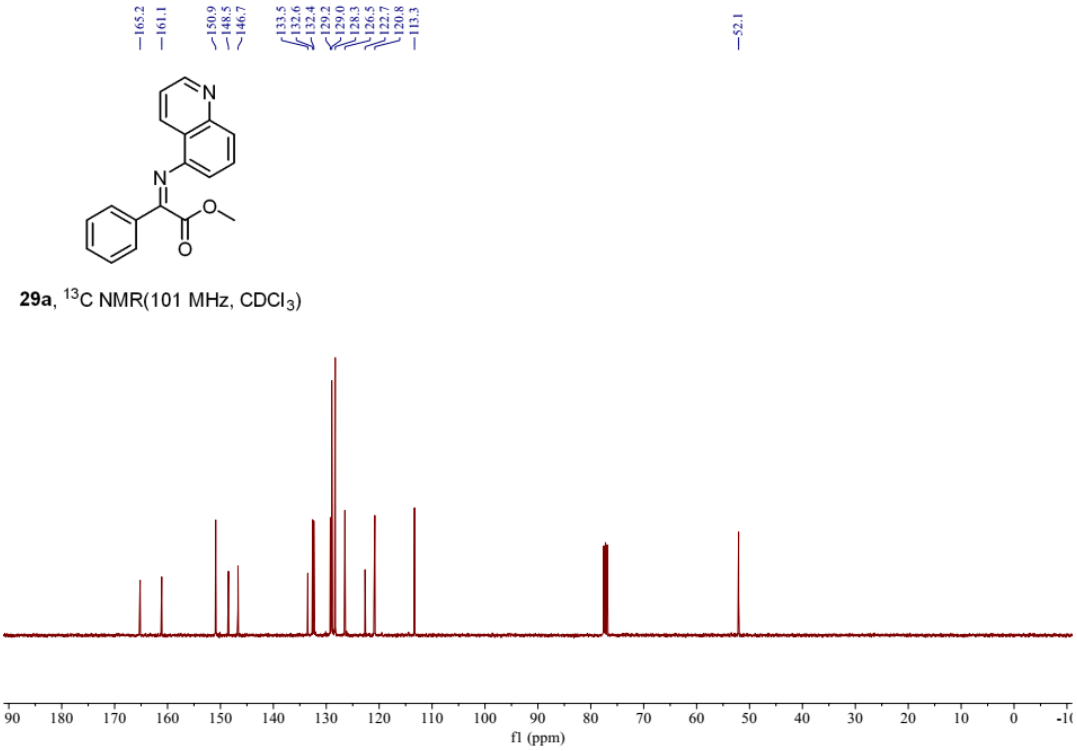




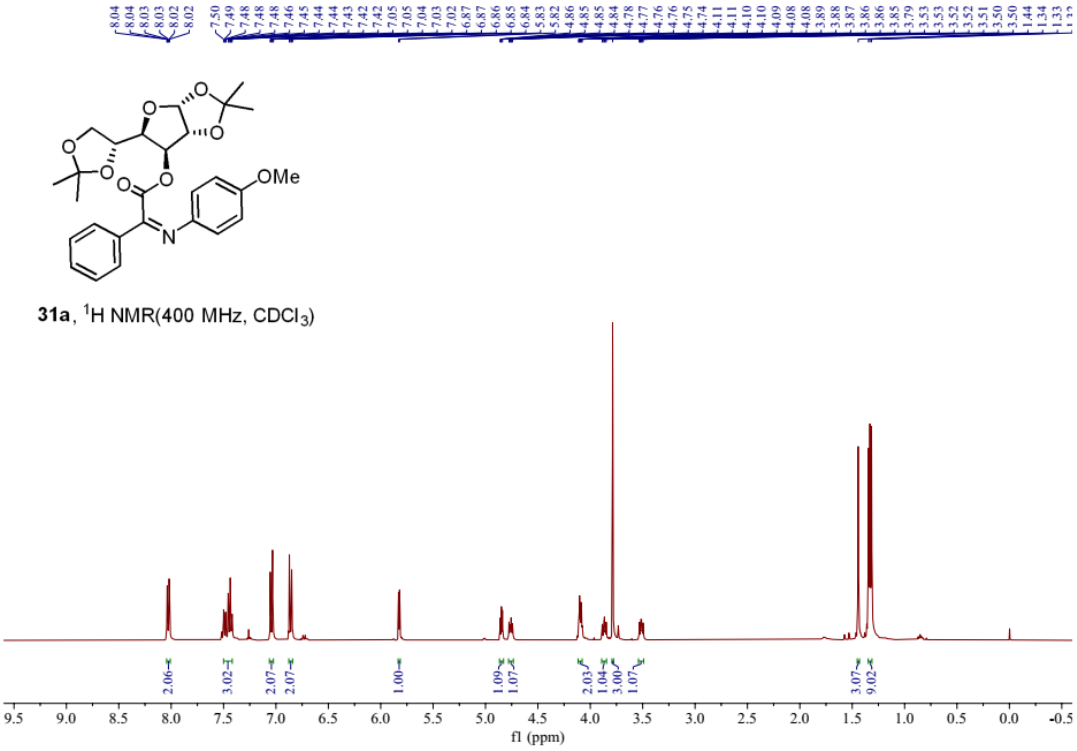
14a, ^{13}C NMR(101 MHz, $CDCl_3$)



29a, ^{1}H NMR(400 MHz, $CDCl_3$)



29a, ^{13}C NMR(101 MHz, $CDCl_3$)



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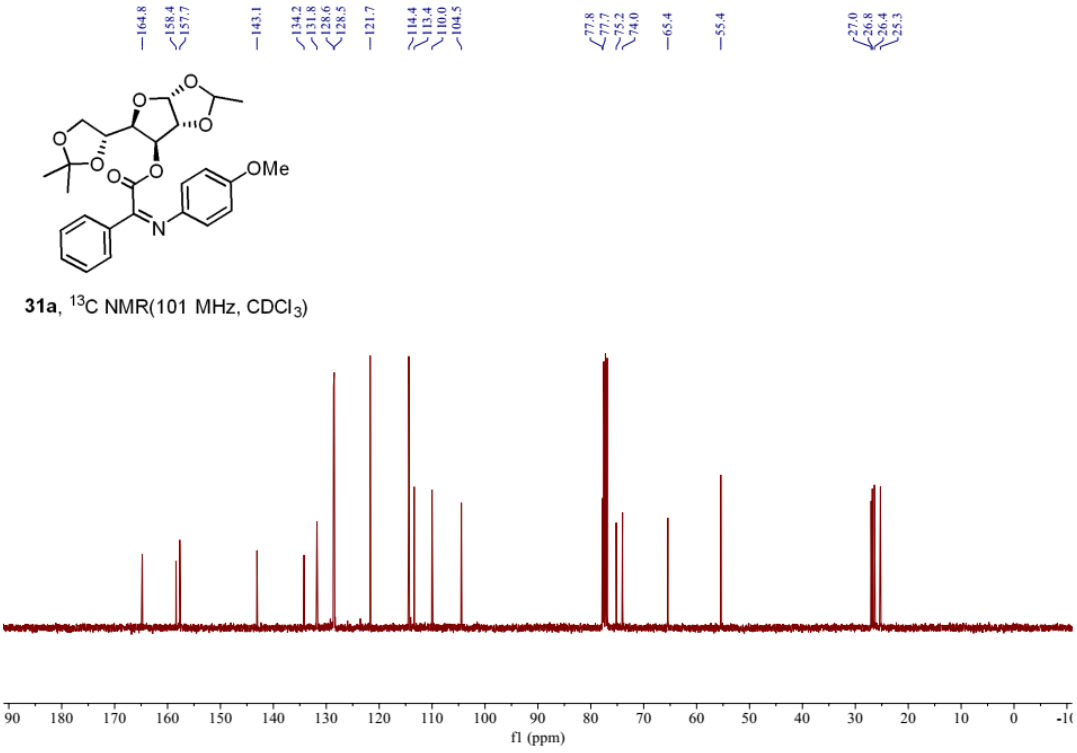
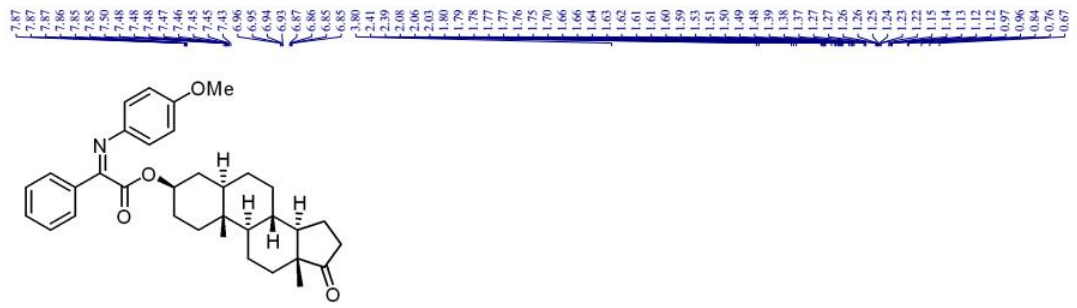


31a, ^{13}C NMR(101 MHz, $CDCl_3$)



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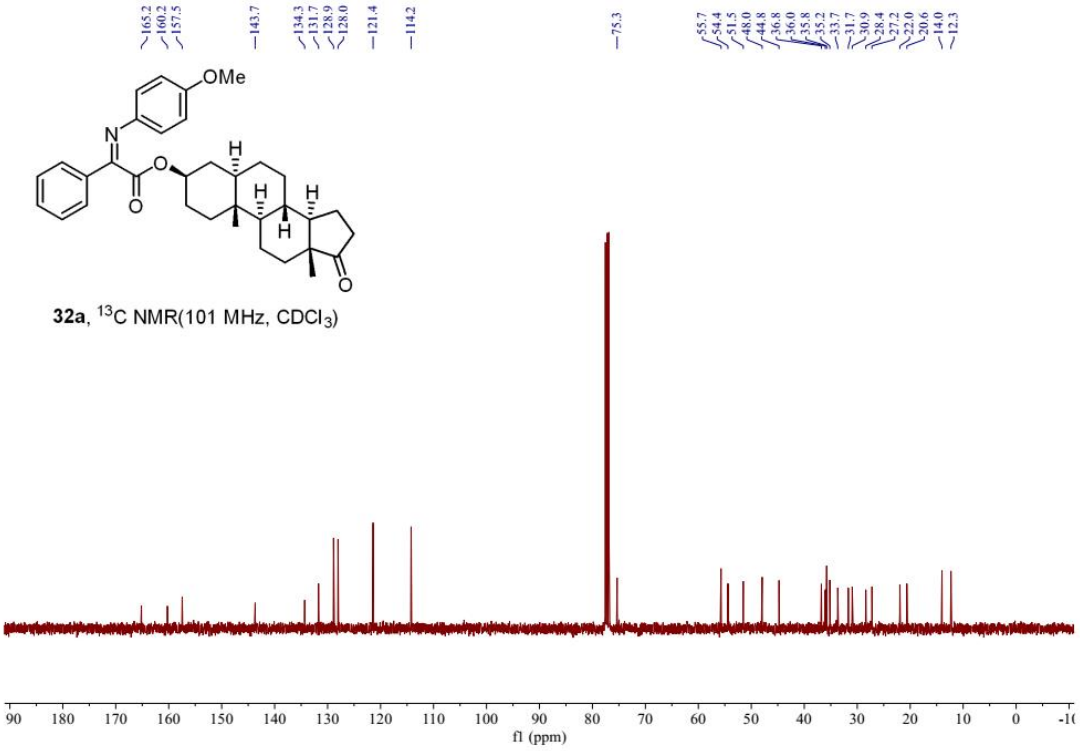

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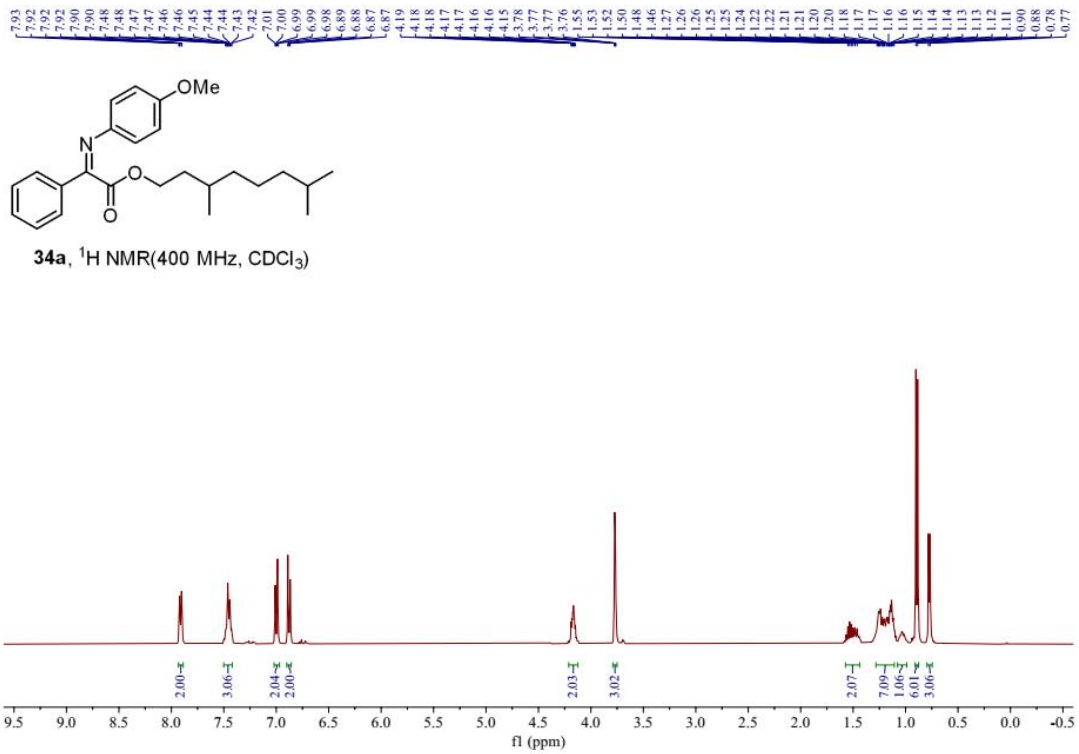
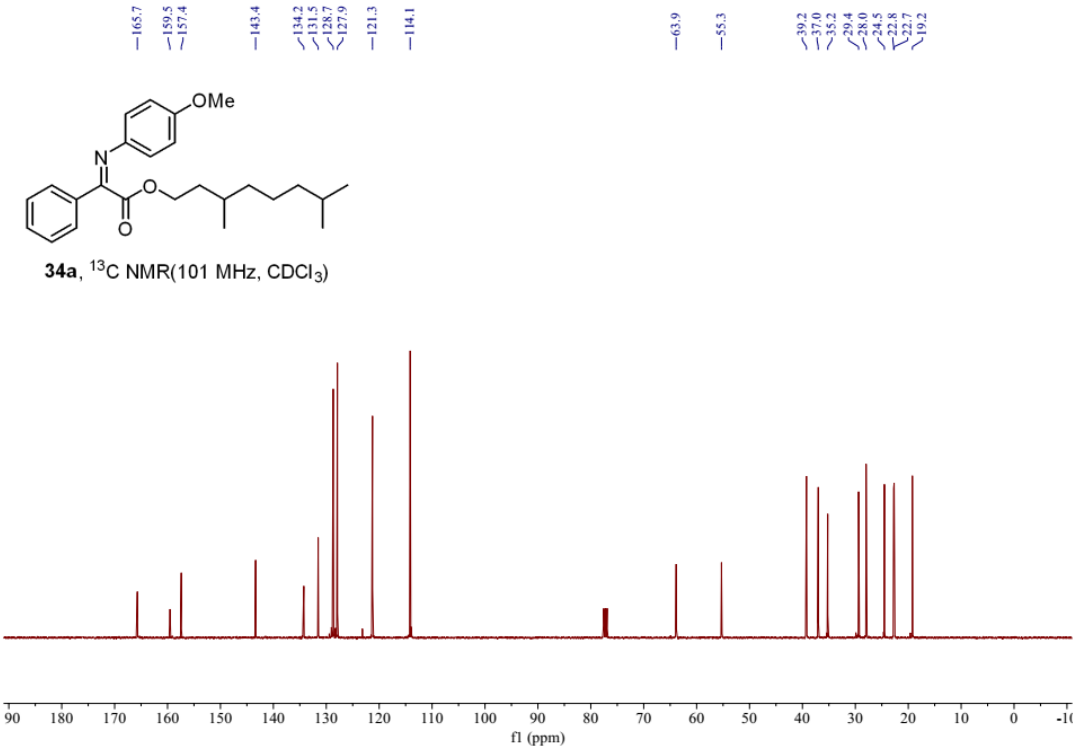
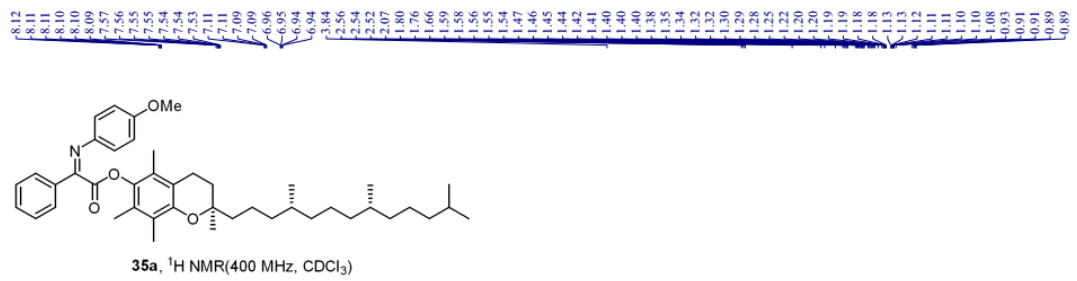


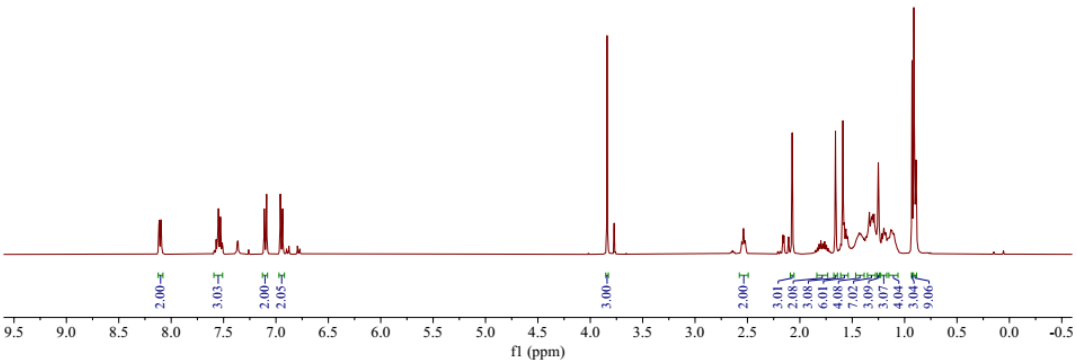
34a, ^{1}H NMR(400 MHz, $CDCl_3$)

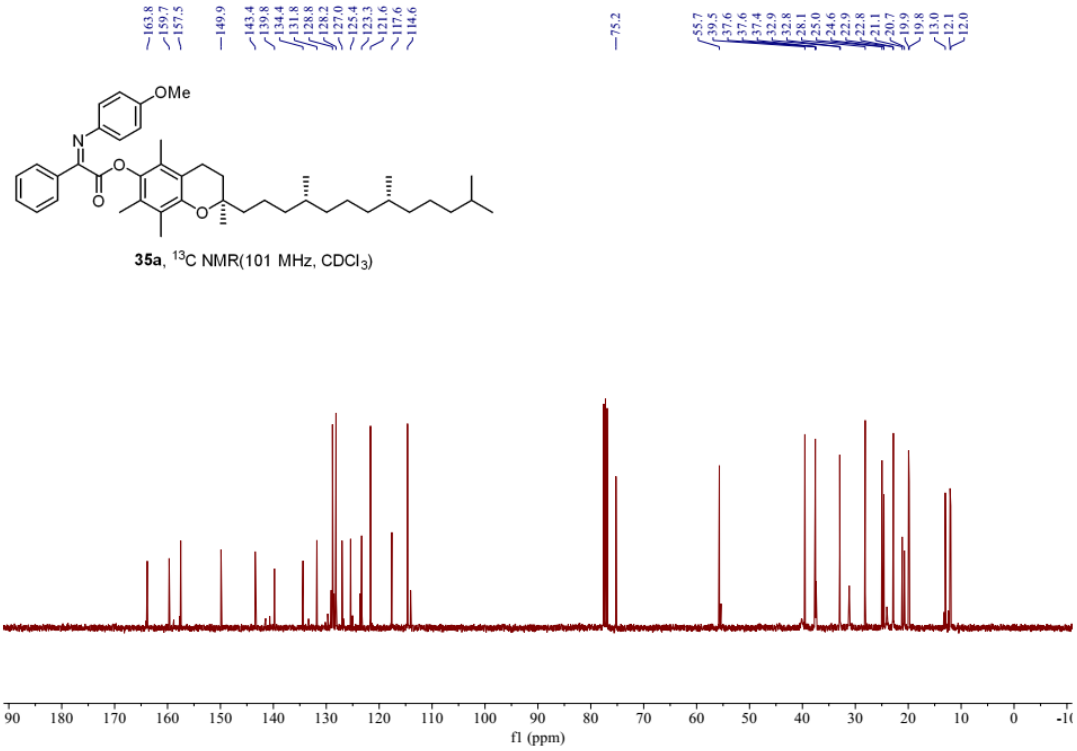


34a, ^{13}C NMR(101 MHz, $CDCl_3$)



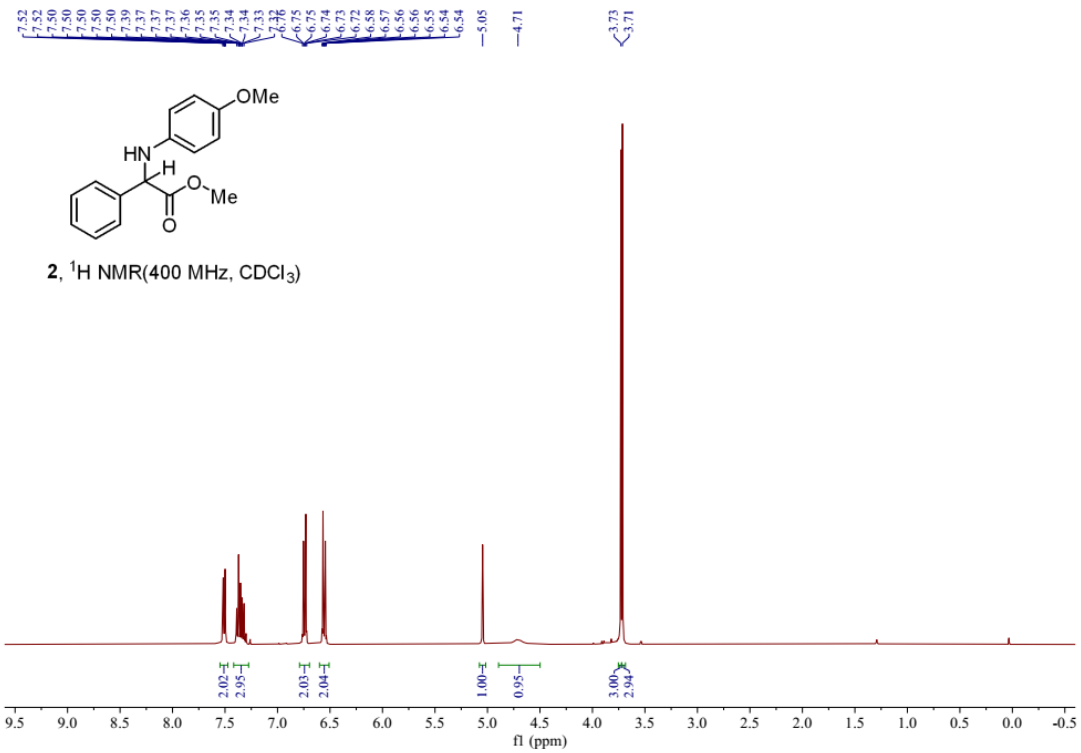
35a, ^{1}H NMR(400 MHz, $CDCl_3$)



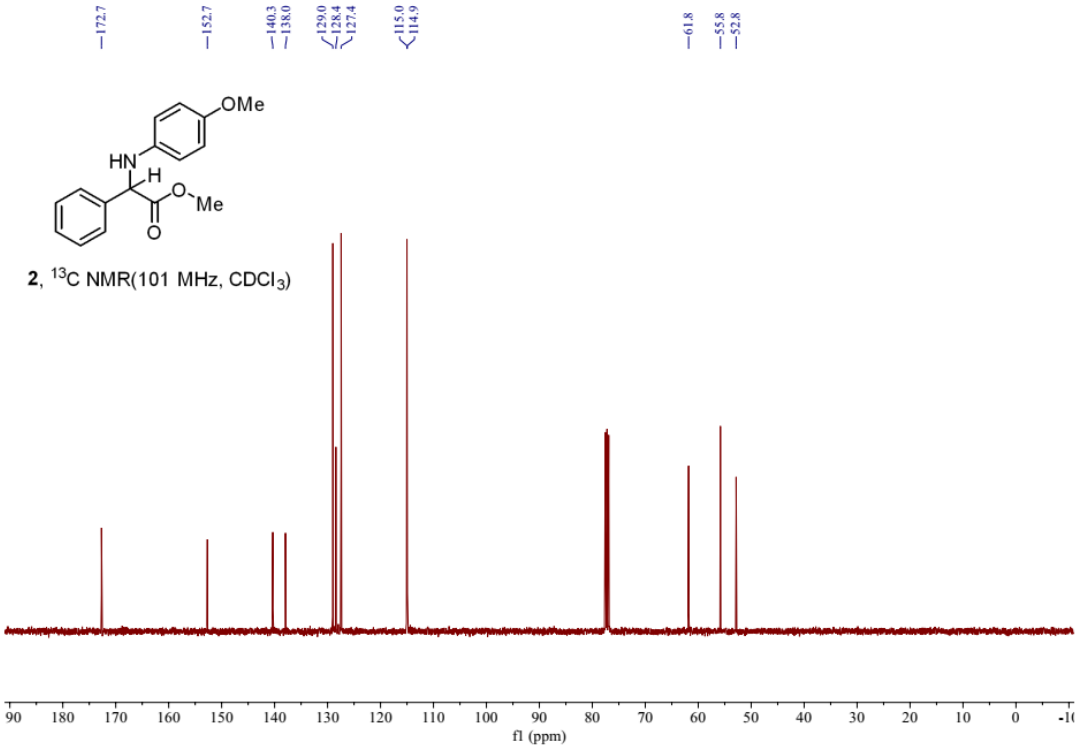


35a, ^{13}C NMR(101 MHz, $CDCl_3$)

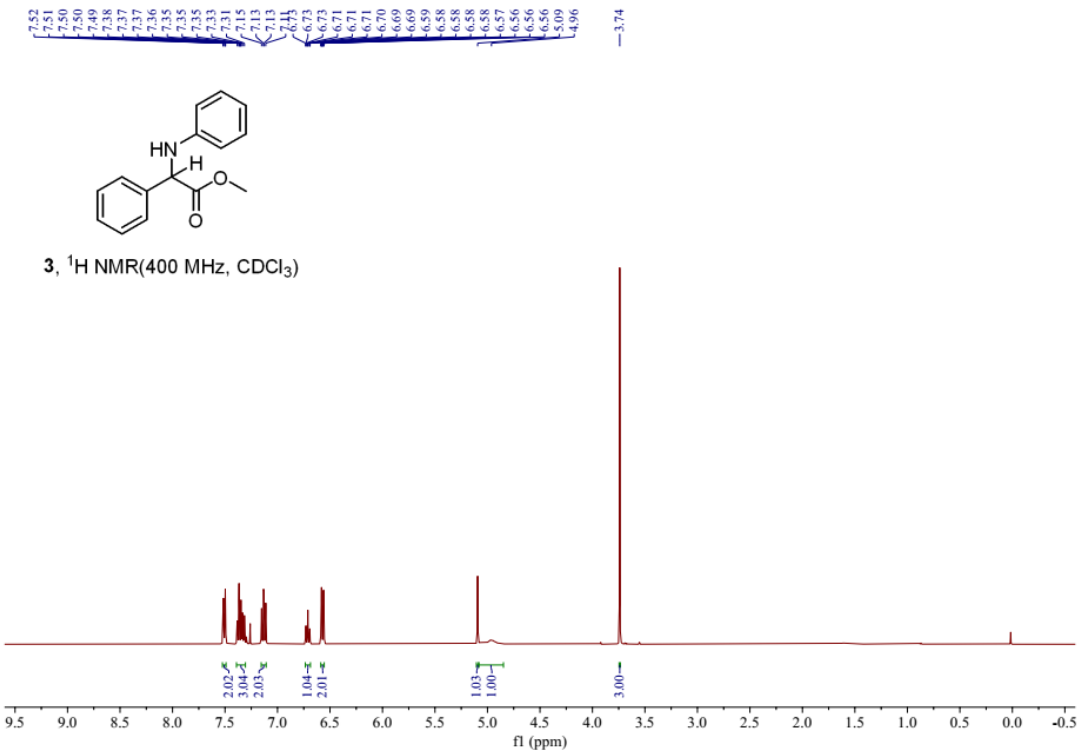
11. Copies of NMR spectra of all products



2, ^{1}H NMR(400 MHz, $CDCl_3$)



2, ^{13}C NMR(101 MHz, $CDCl_3$)



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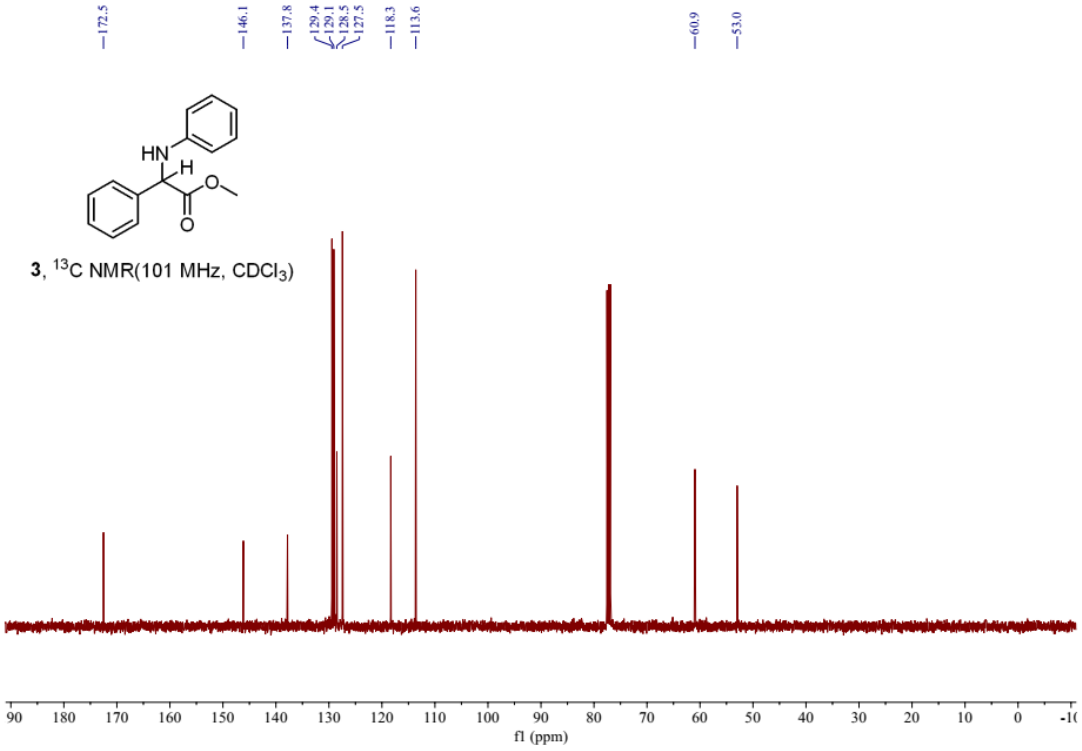
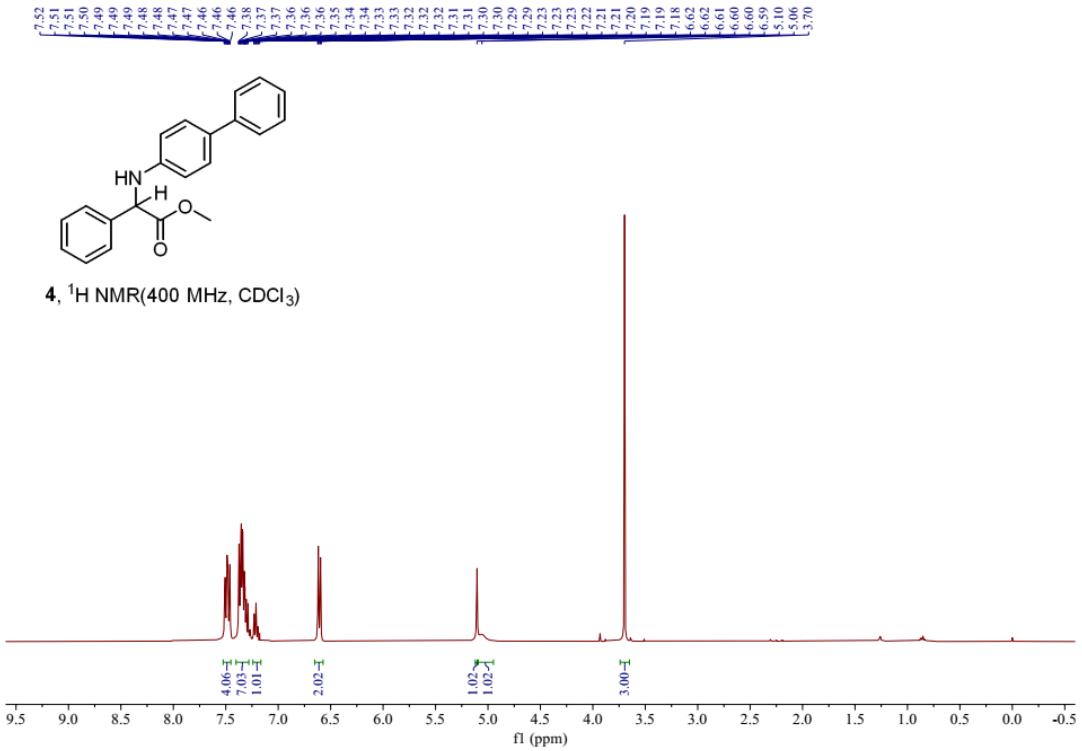
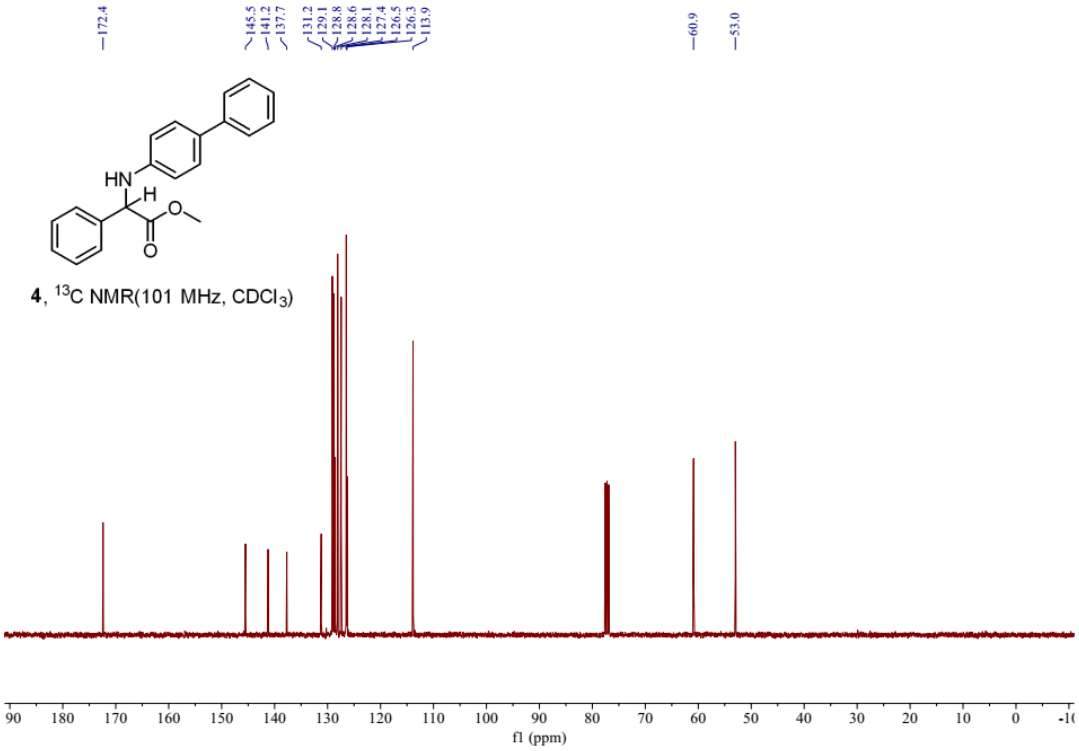
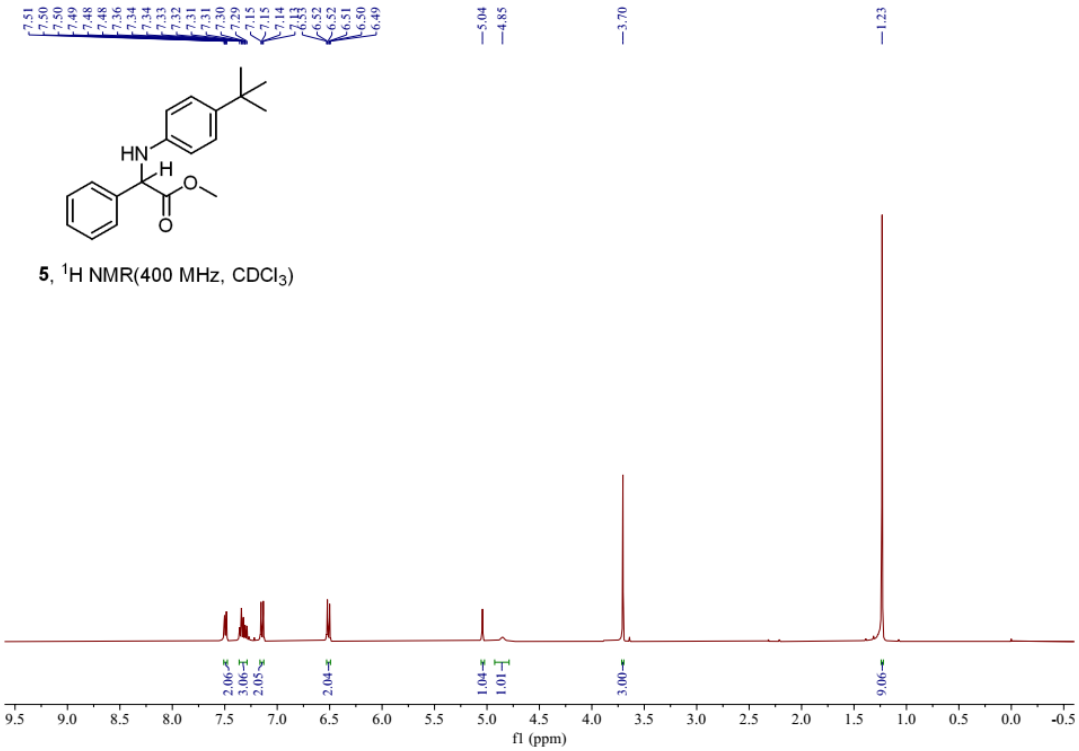

172.5
146.1
137.8
129.4
129.1
128.5
127.5
118.3
113.6
60.9
53.0
HN
H
O
O
3, 13C NMR(101 MHz, CDCl3)
f1 (ppm)

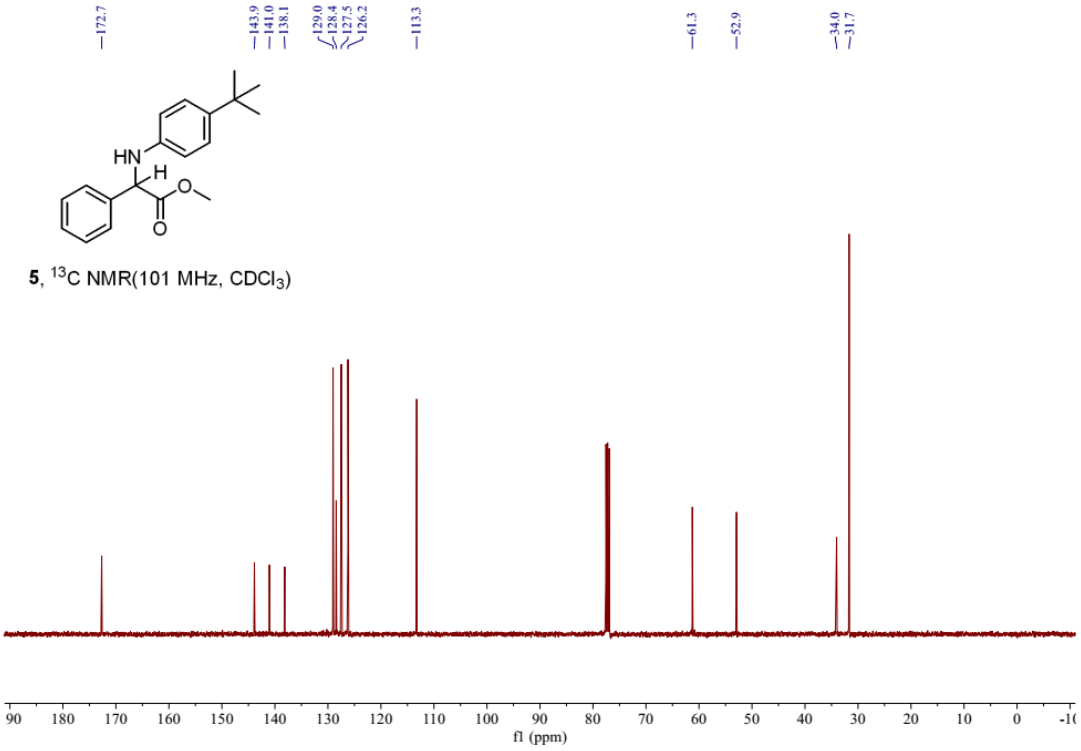

HN
H
O
O
4, 1H NMR(400 MHz, CDCl3)
4.06
7.03
1.01
2.02
1.02
1.02
3.00
f1 (ppm)



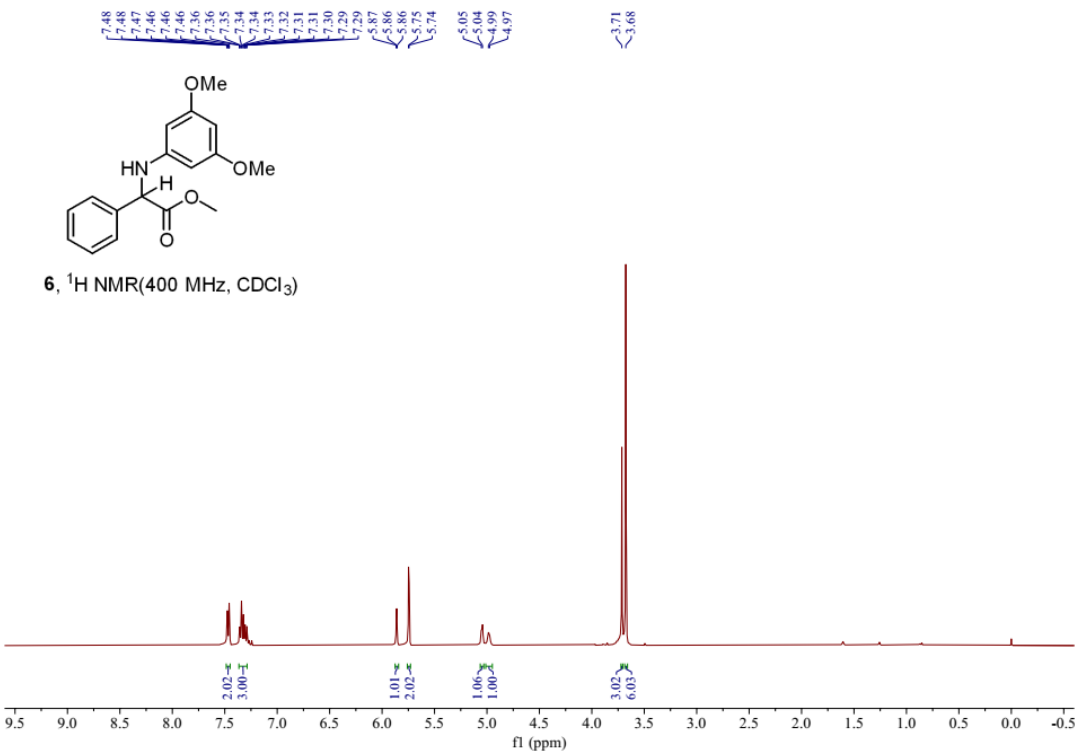
4, ^{13}C NMR(101 MHz, $CDCl_3$)



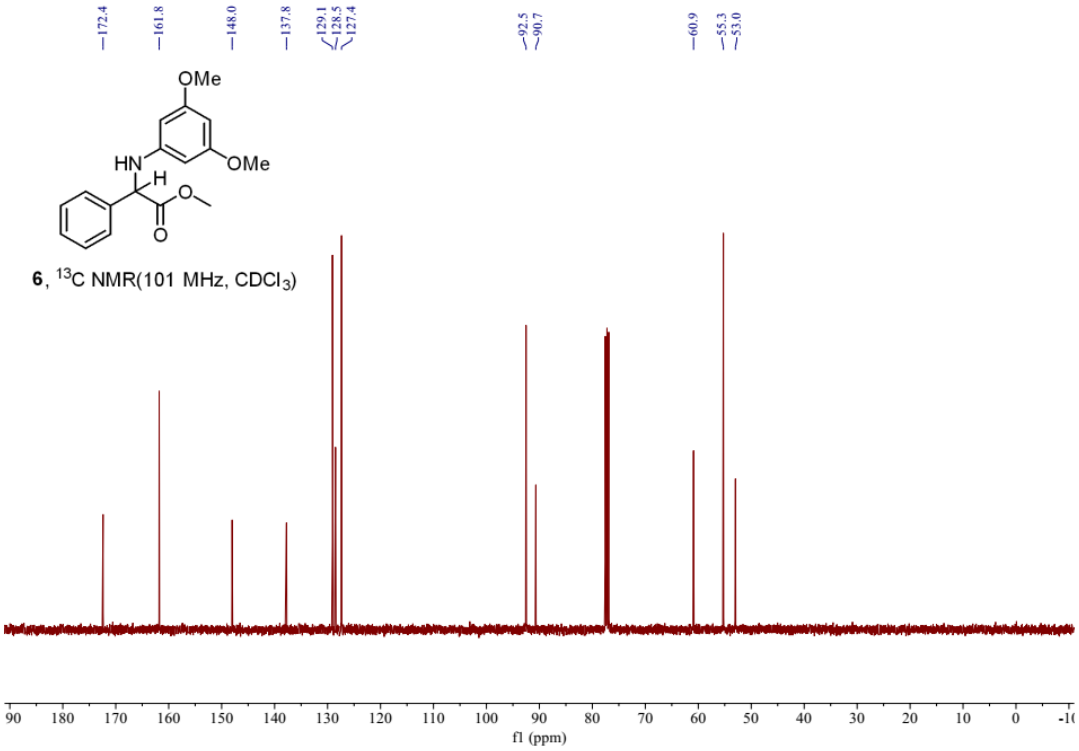
5, ^{1}H NMR(400 MHz, $CDCl_3$)



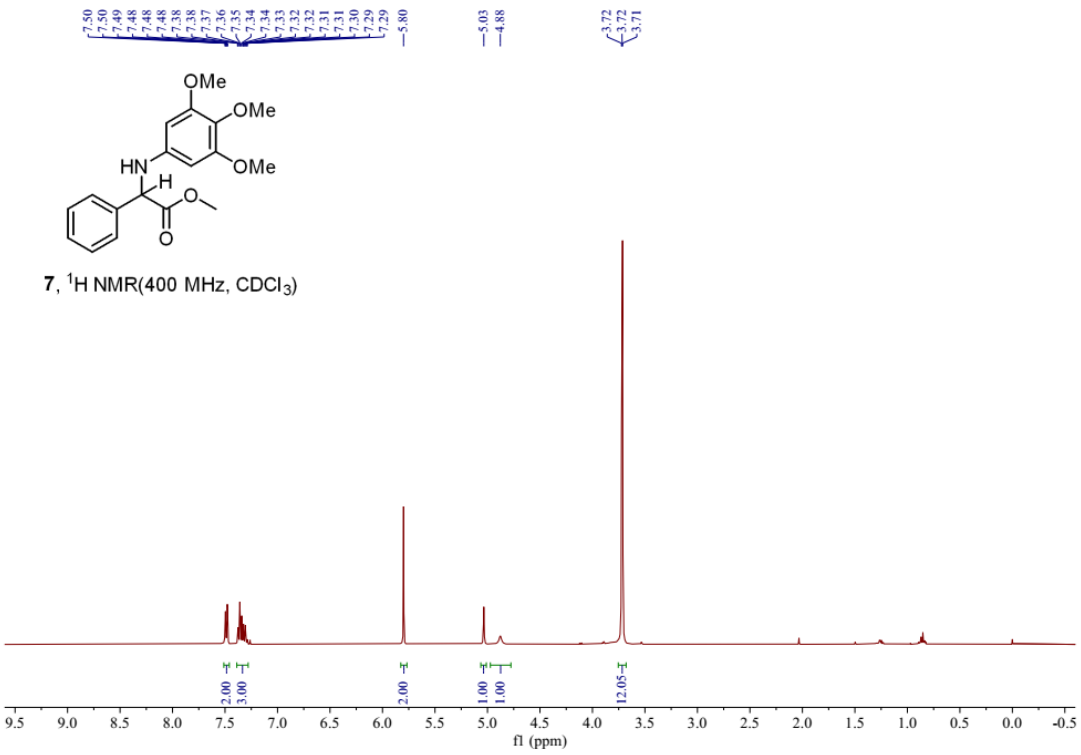
5, ^{13}C NMR(101 MHz, $CDCl_3$)



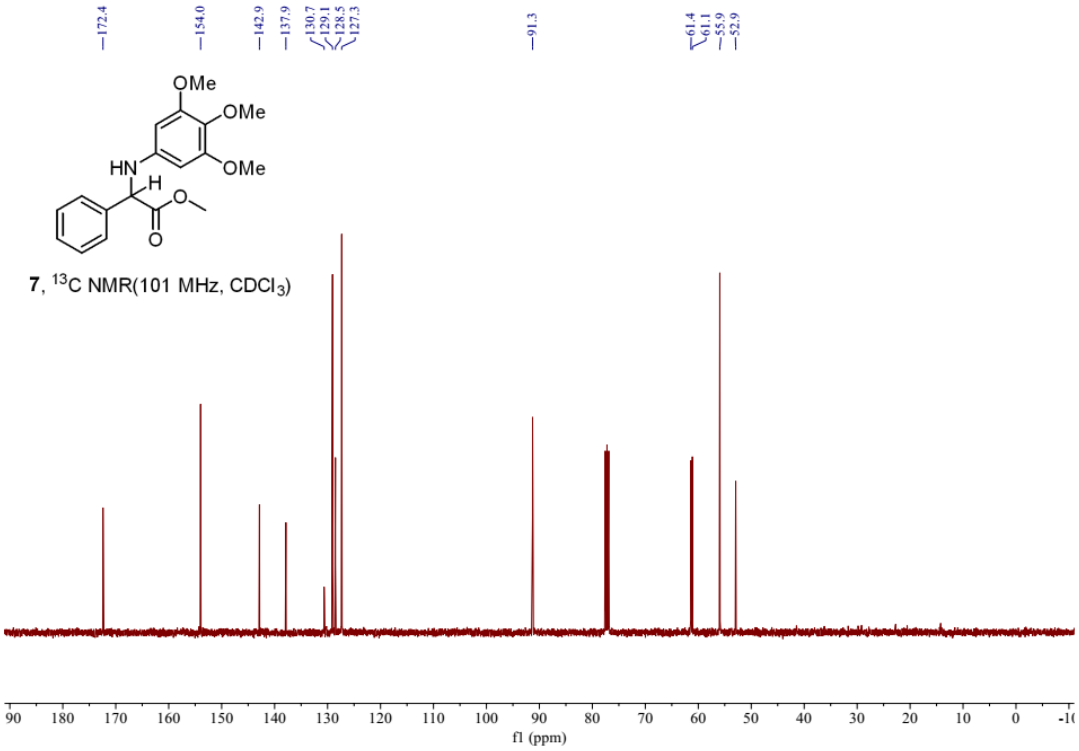
6, ^{1}H NMR(400 MHz, $CDCl_3$)



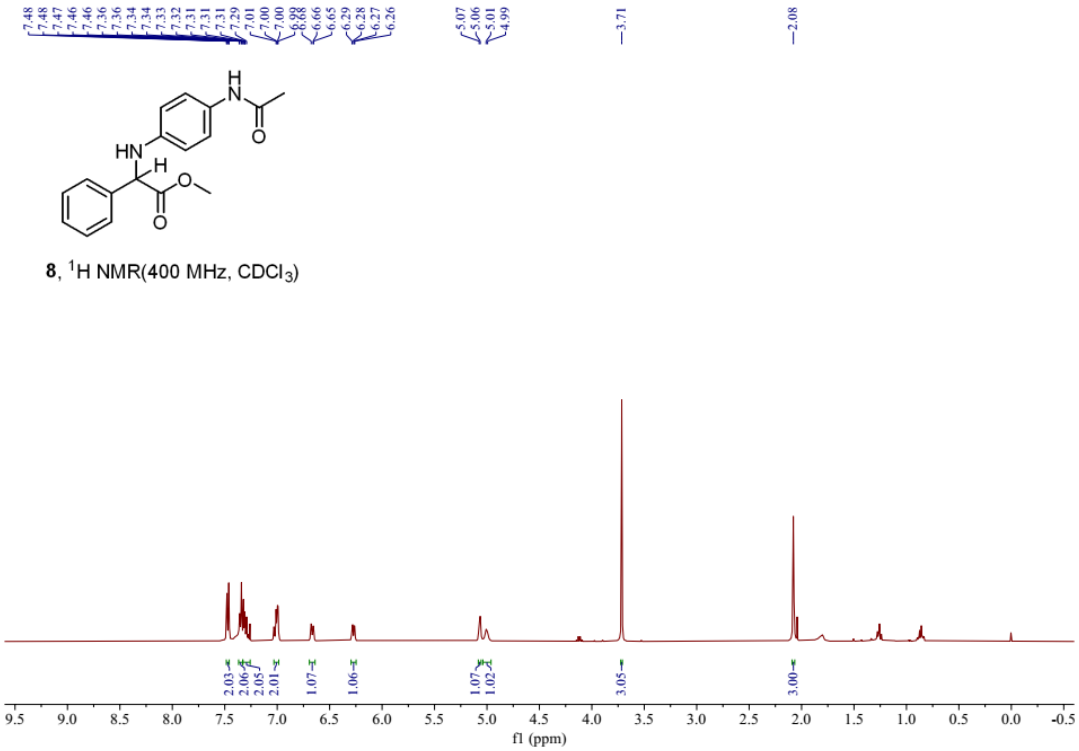
6, ^{13}C NMR(101 MHz, $CDCl_3$)



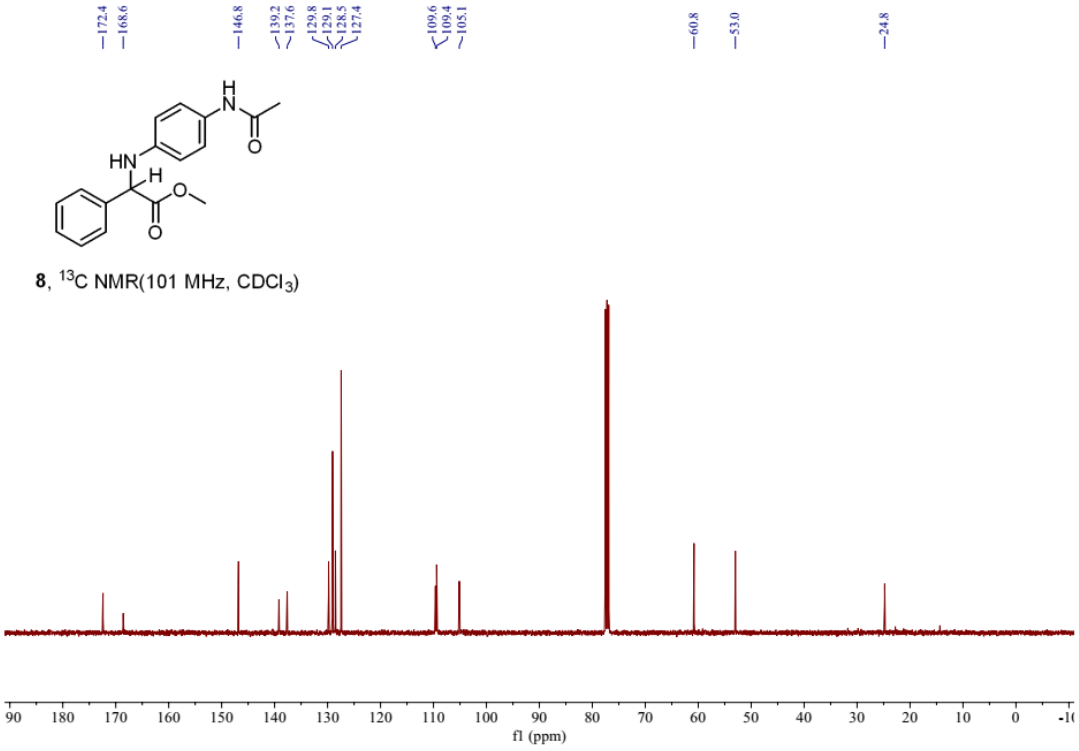
7, ^{1}H NMR(400 MHz, $CDCl_3$)



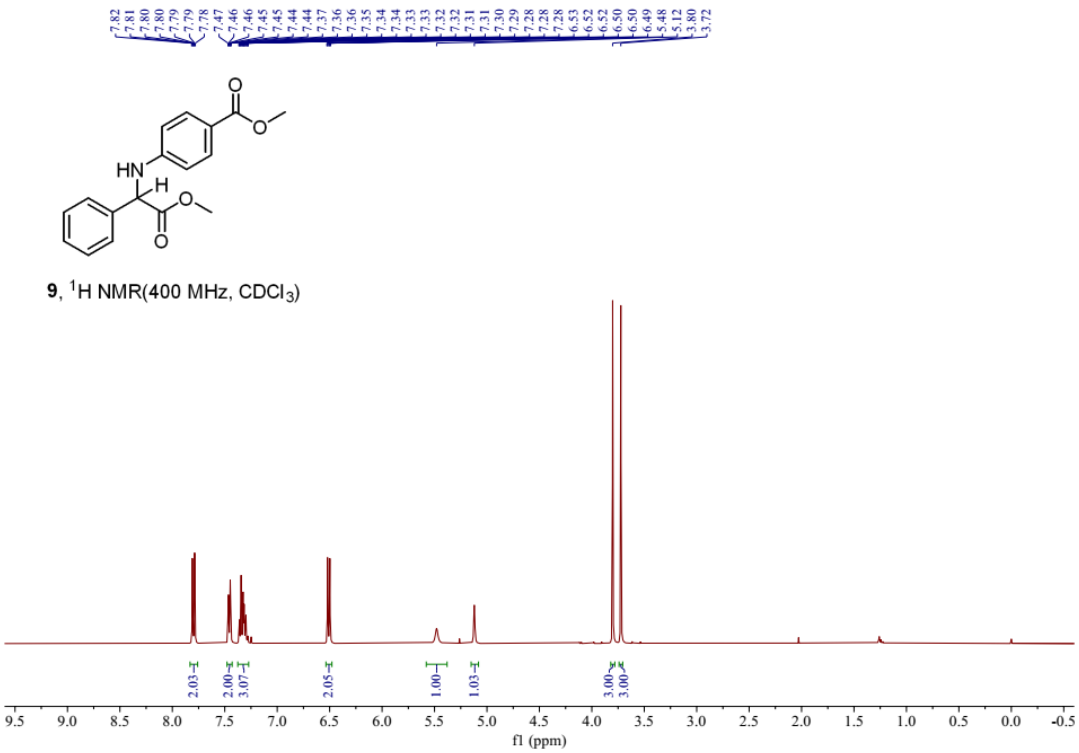
7, ^{13}C NMR(101 MHz, $CDCl_3$)



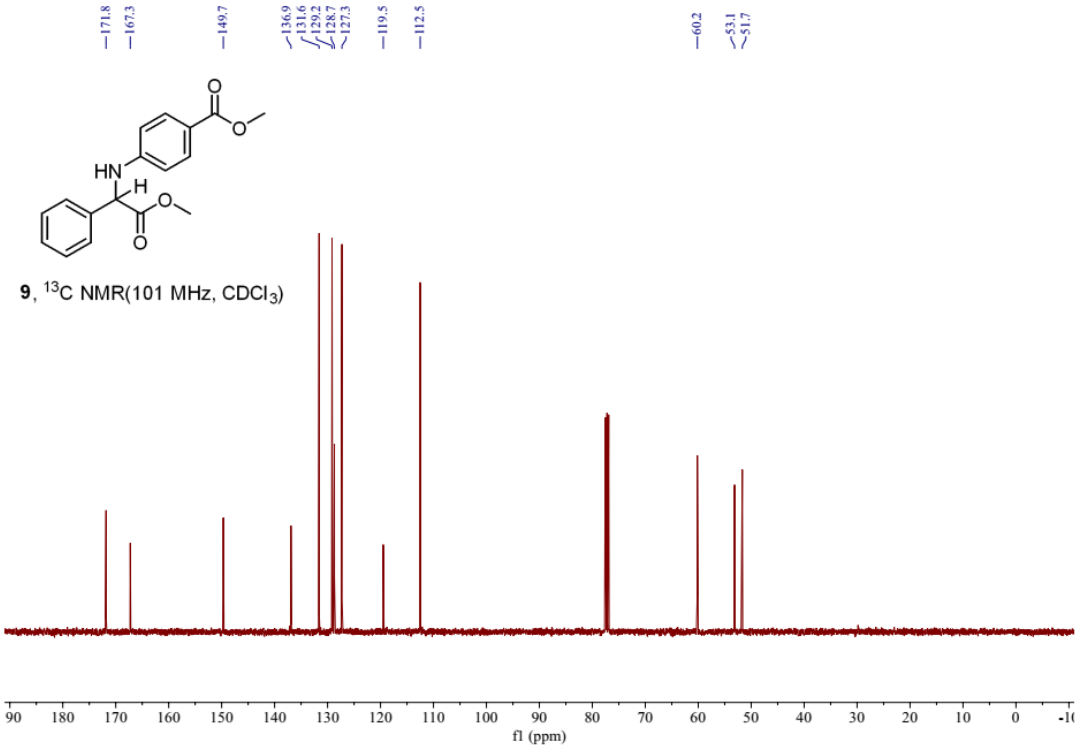
8, ^{1}H NMR(400 MHz, $CDCl_3$)



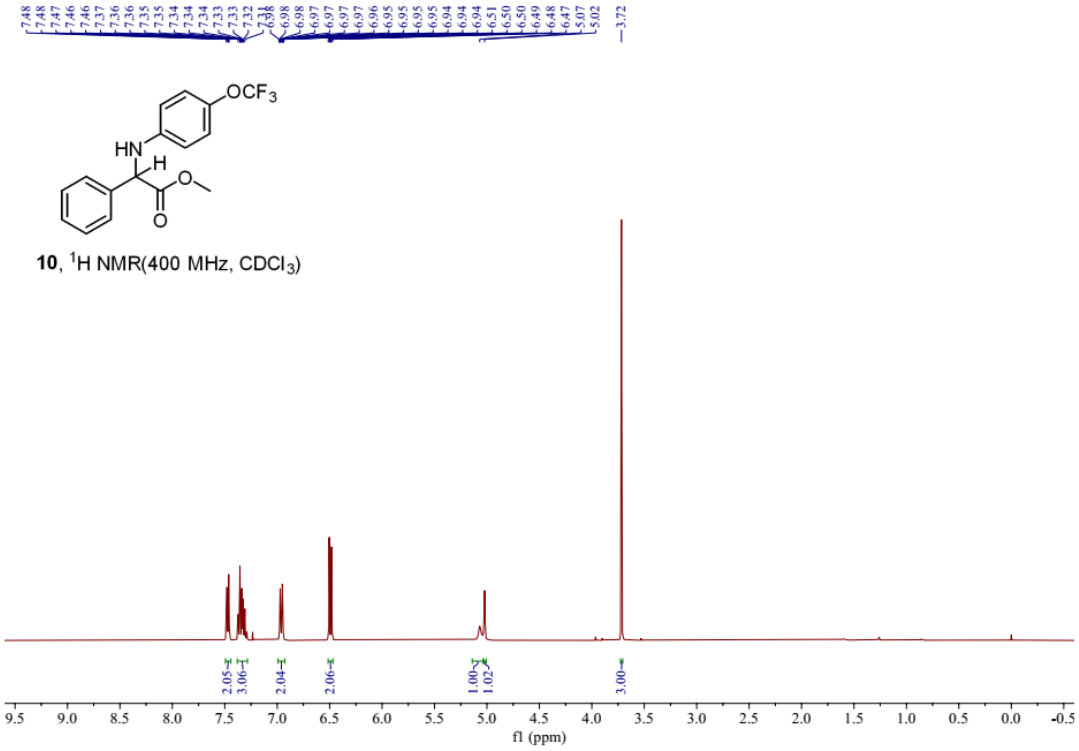
8, ^{13}C NMR(101 MHz, $CDCl_3$)



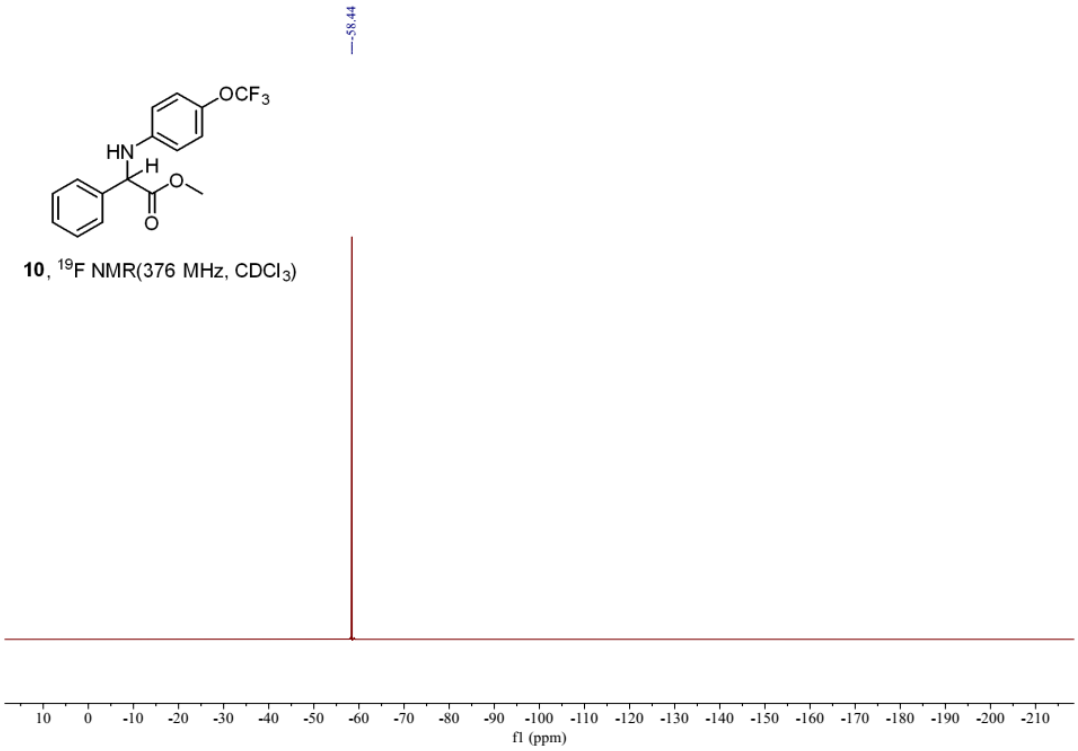
9, ^{1}H NMR(400 MHz, $CDCl_3$)



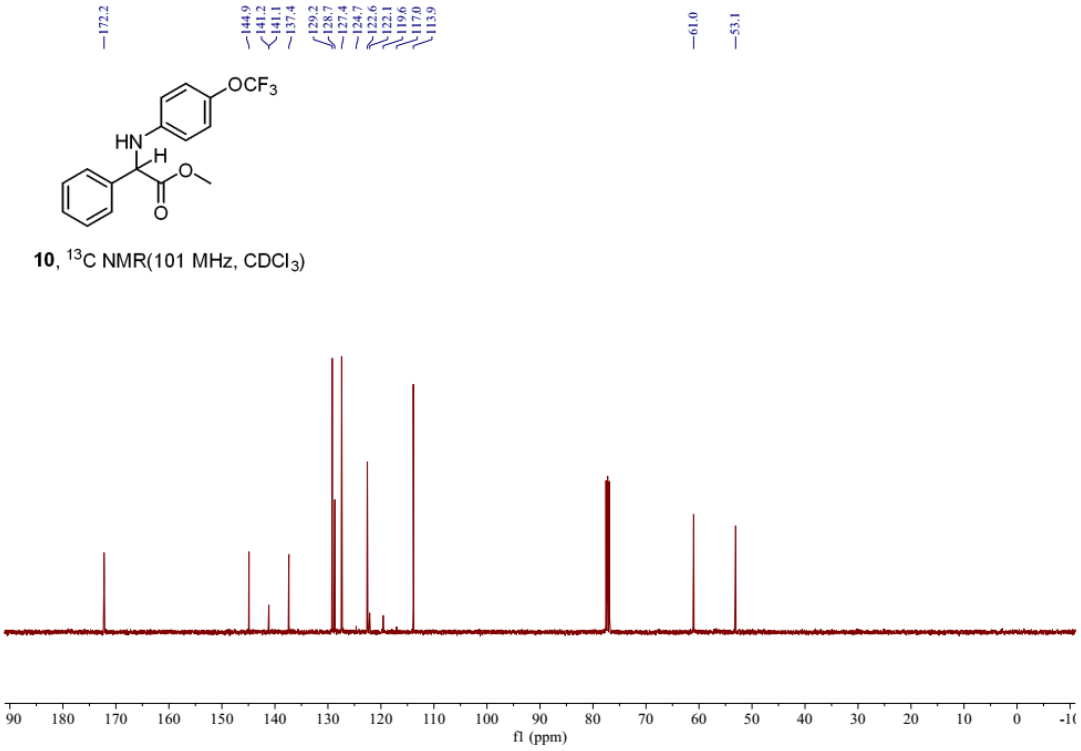
9, ^{13}C NMR(101 MHz, $CDCl_3$)



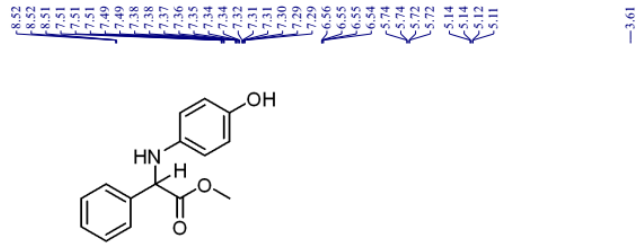
10, ^{1}H NMR(400 MHz, $CDCl_3$)



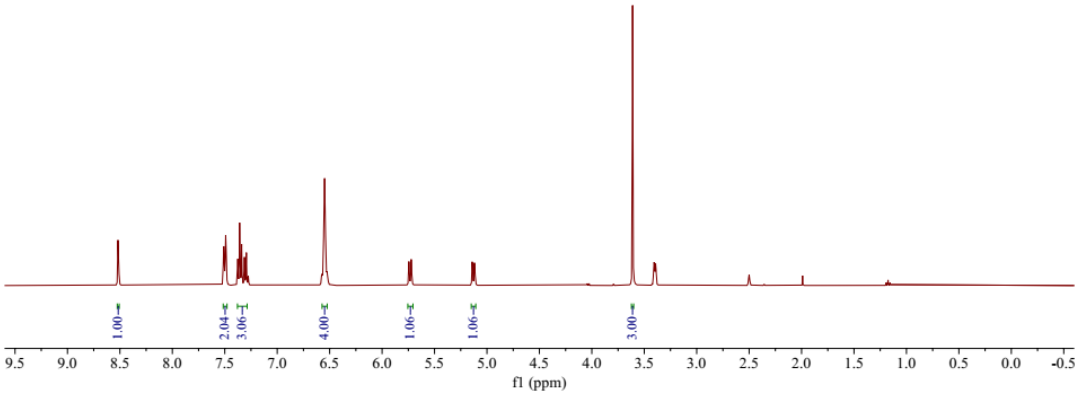
10, ^{19}F NMR(376 MHz, $CDCl_3$)

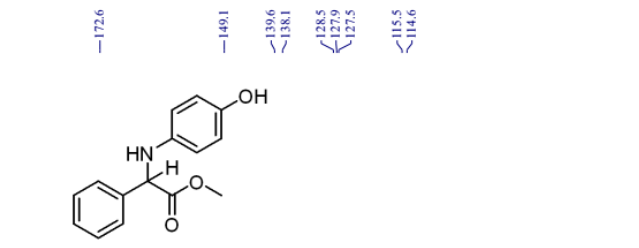


10, ^{13}C NMR(101 MHz, $CDCl_3$)

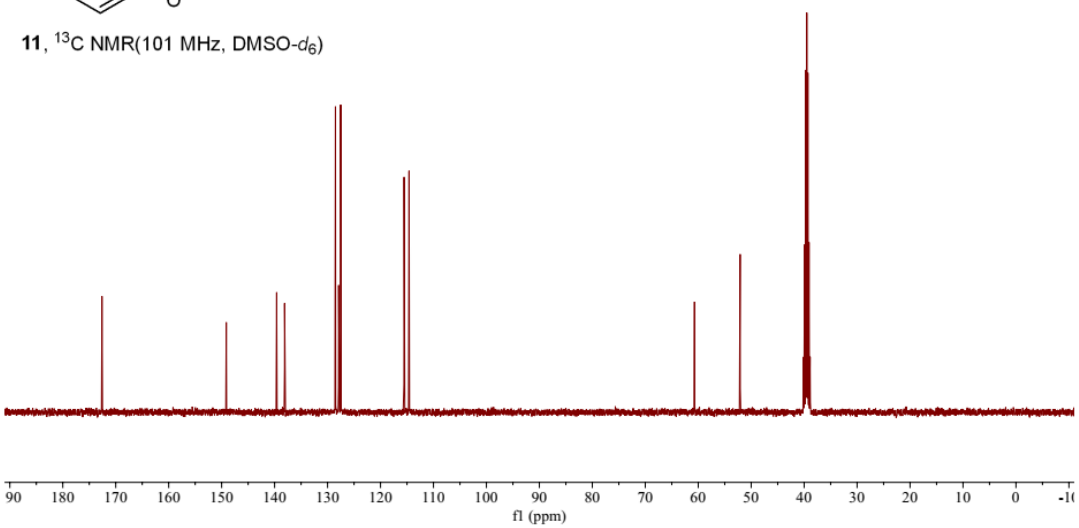


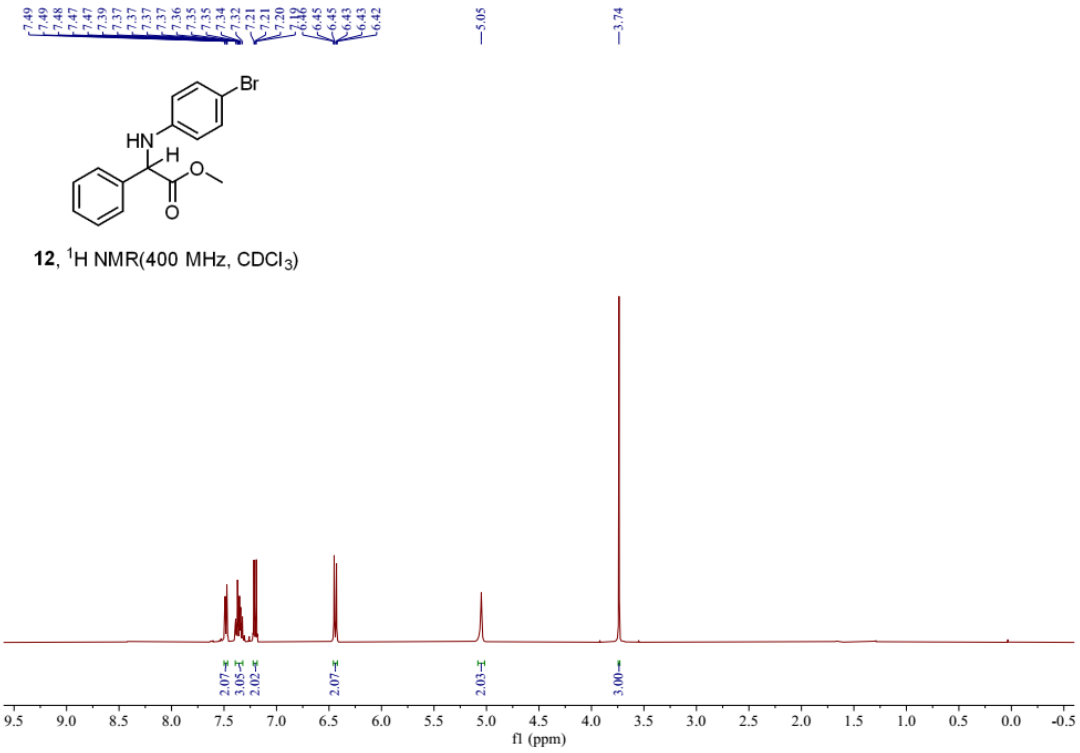
11, ^{1}H NMR(400 MHz, DMSO-d_6)



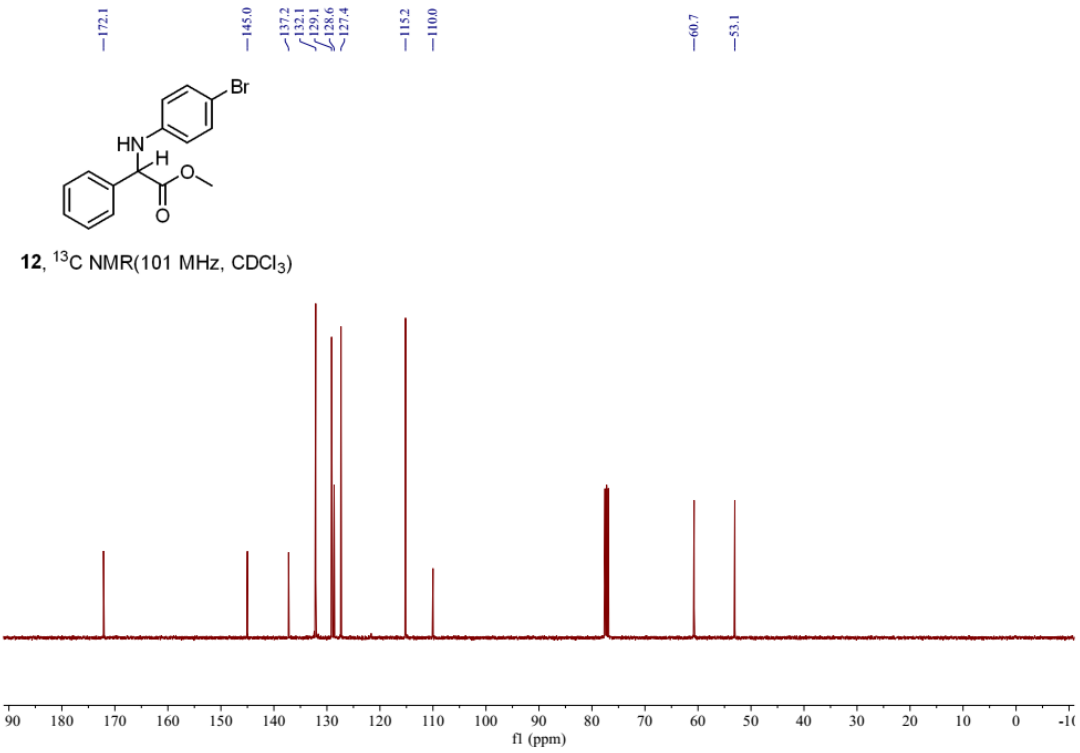


11, ^{13}C NMR(101 MHz, DMSO-d_6)

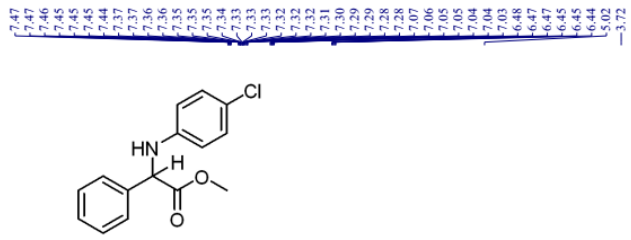




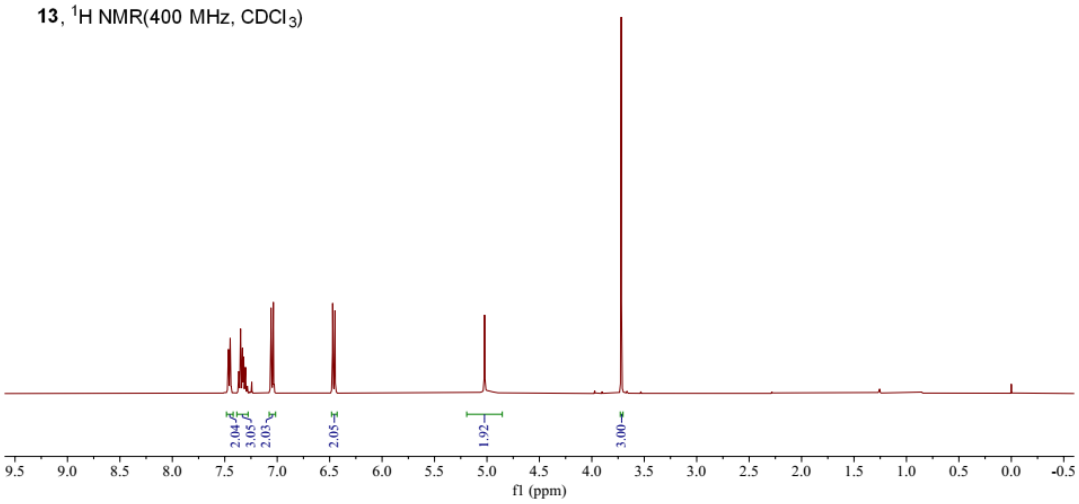
12, ^{1}H NMR(400 MHz, $CDCl_3$)

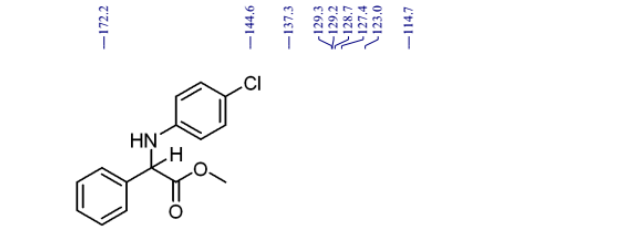


12, ^{13}C NMR(101 MHz, $CDCl_3$)

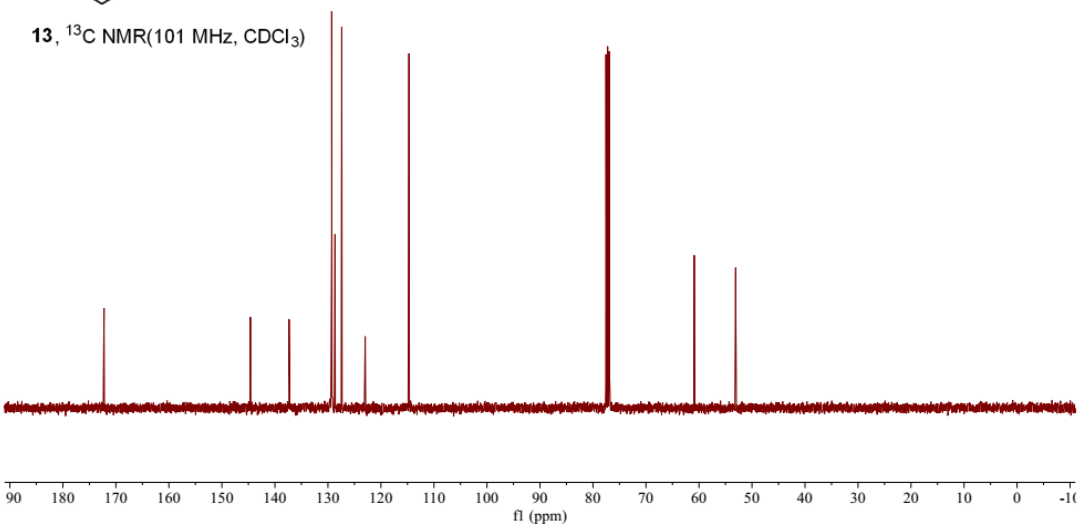


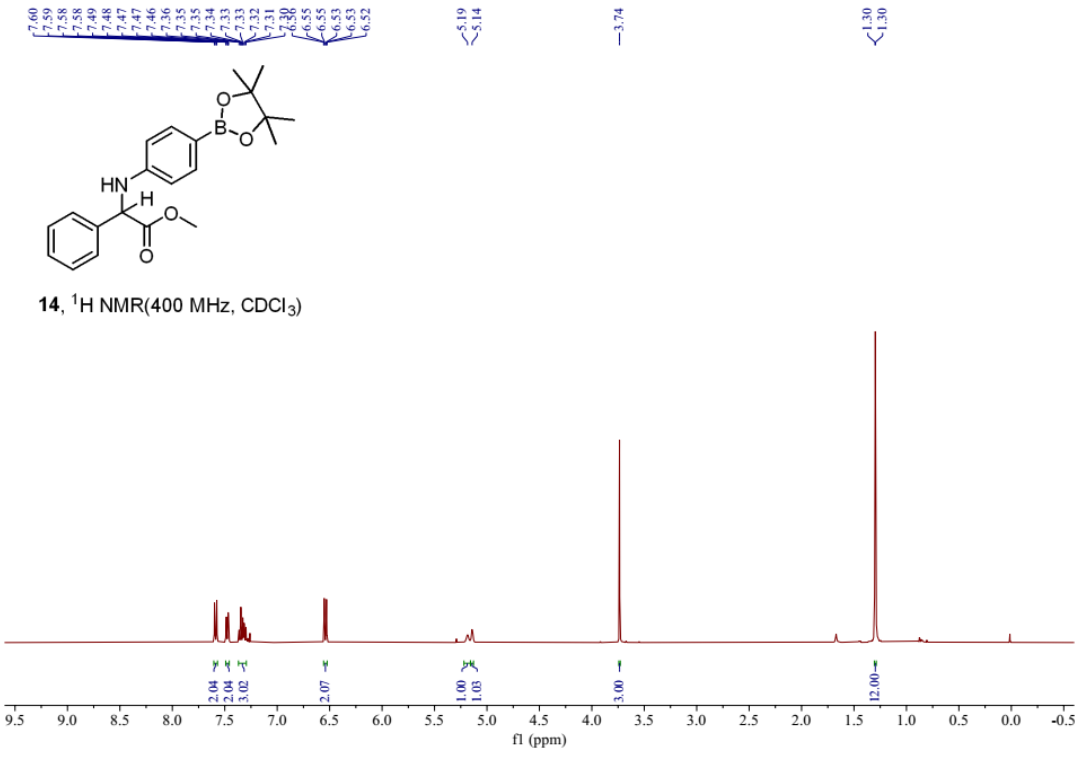
13, ^{1}H NMR(400 MHz, $CDCl_3$)



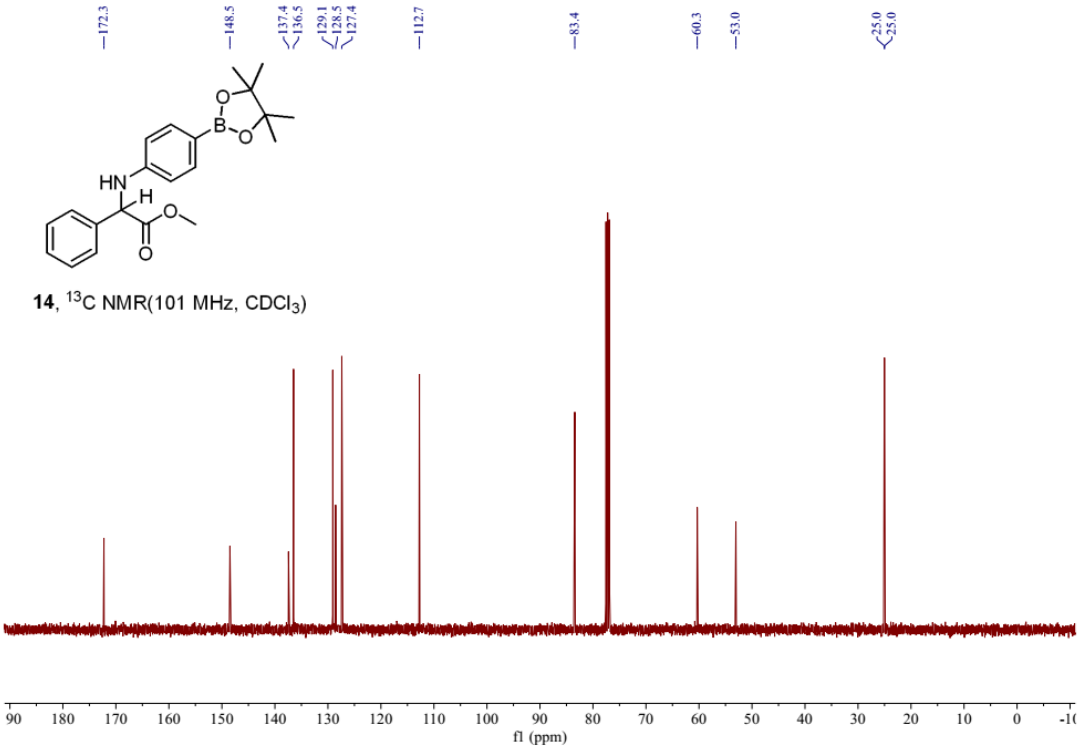


13, ^{13}C NMR(101 MHz, $CDCl_3$)

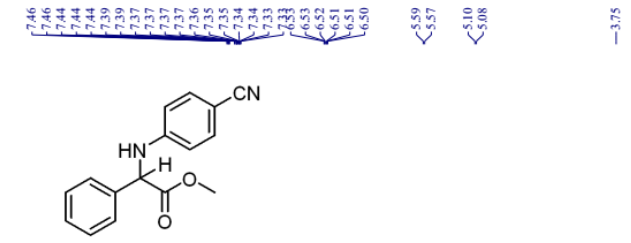




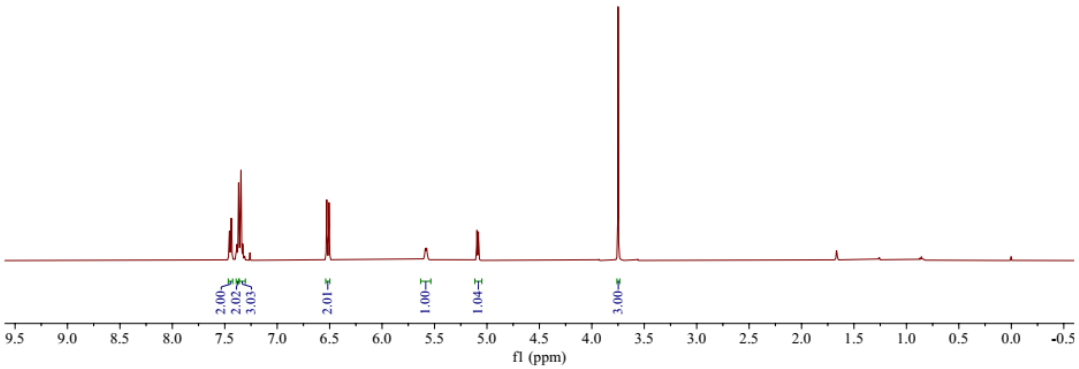
14, ^{1}H NMR(400 MHz, $CDCl_3$)

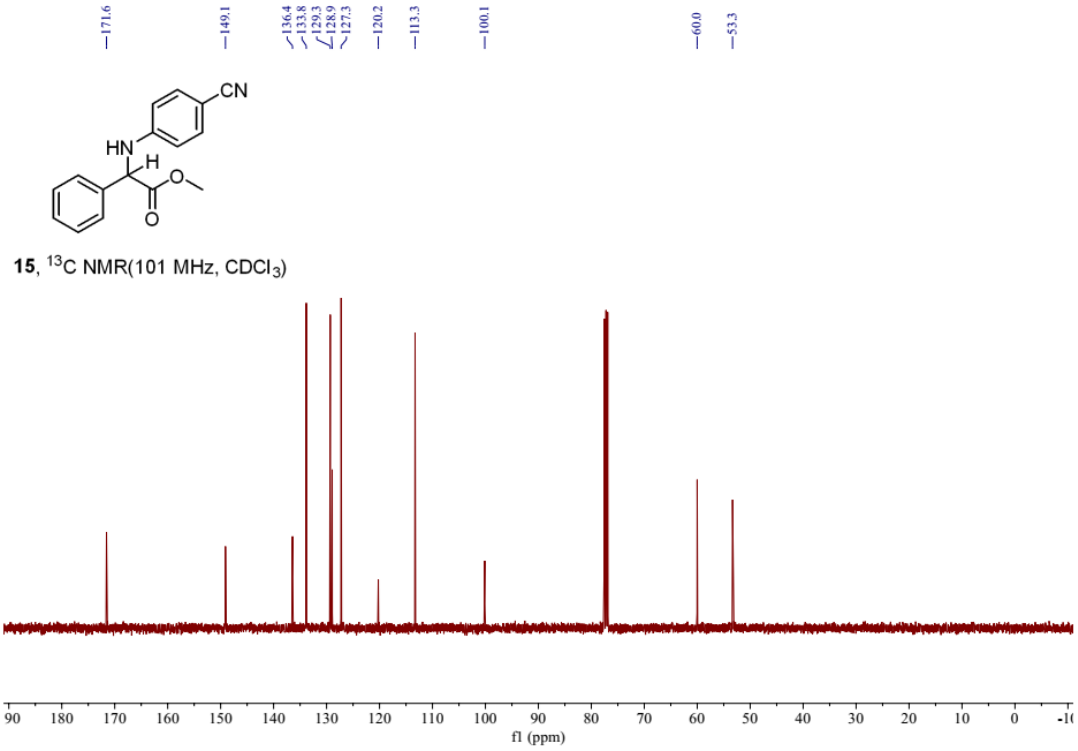


14, ^{13}C NMR(101 MHz, $CDCl_3$)

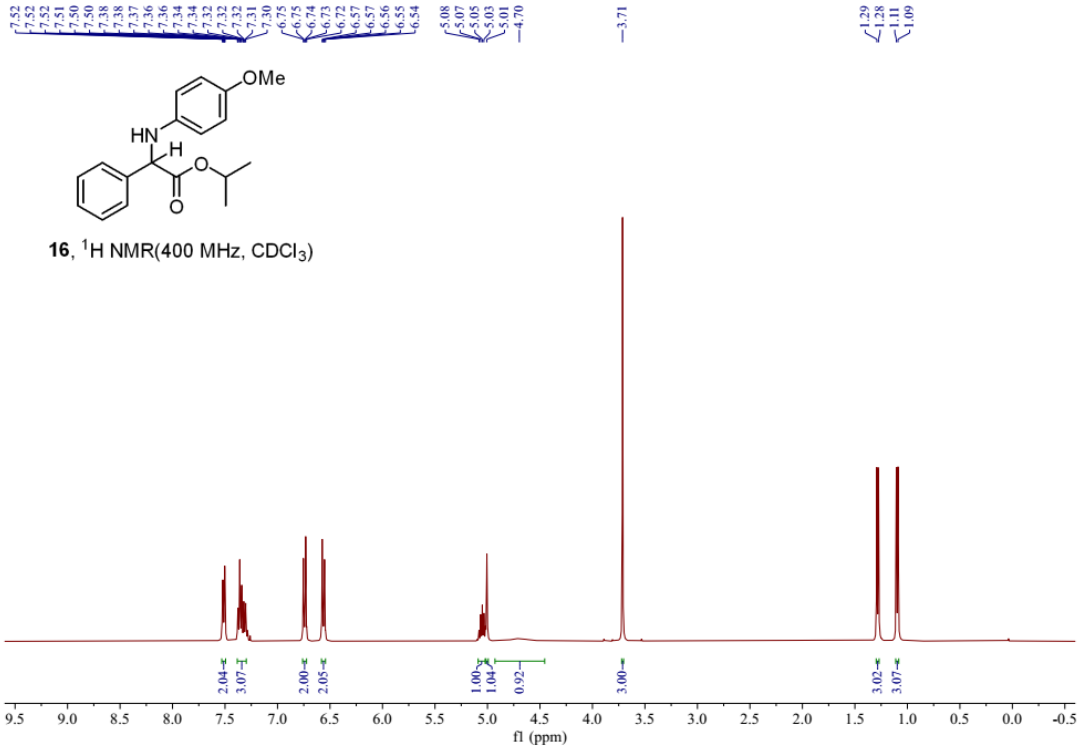


15, ^{1}H NMR(400 MHz, $CDCl_3$)

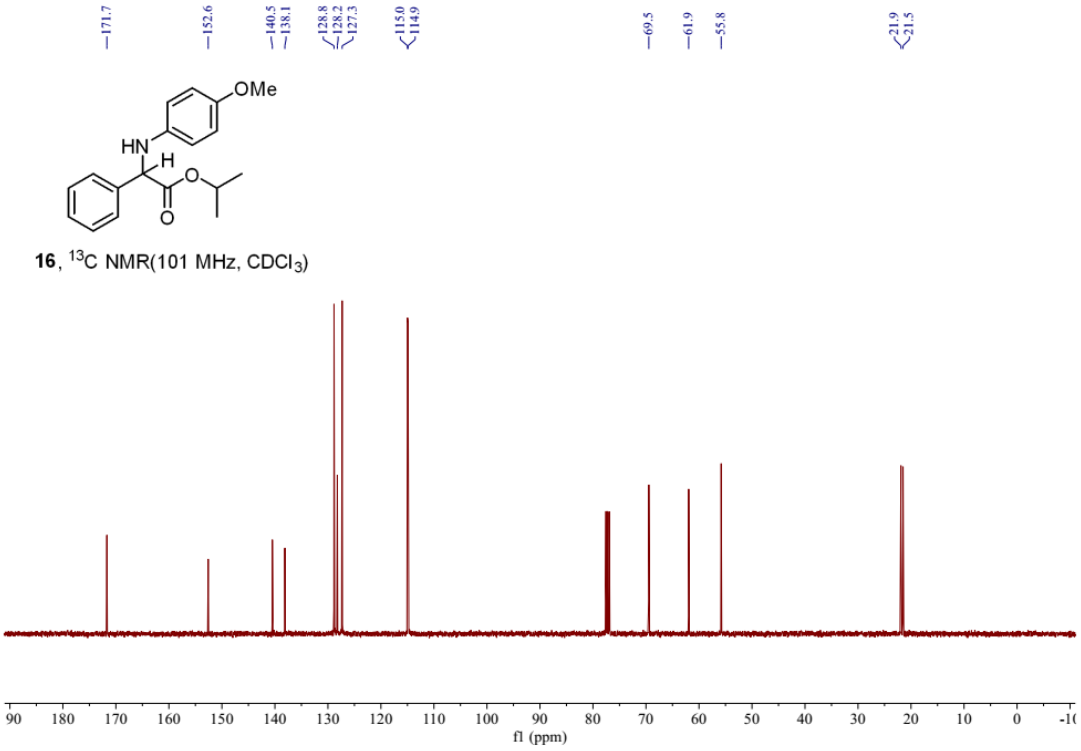




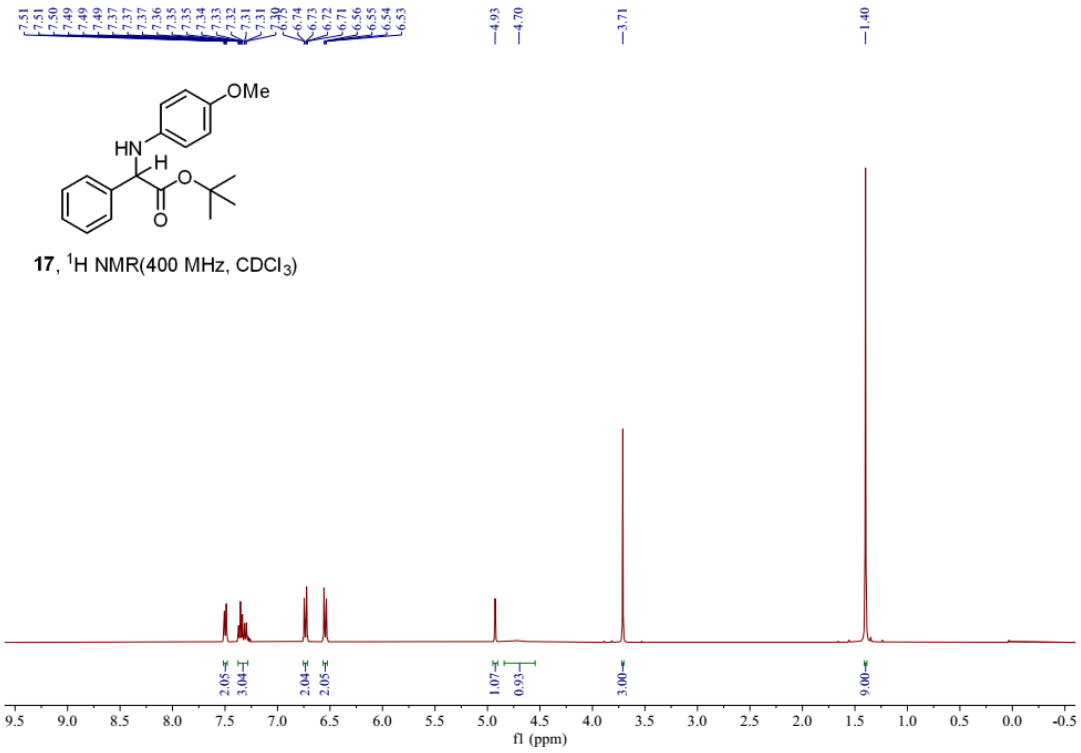
15, ^{13}C NMR(101 MHz, $CDCl_3$)



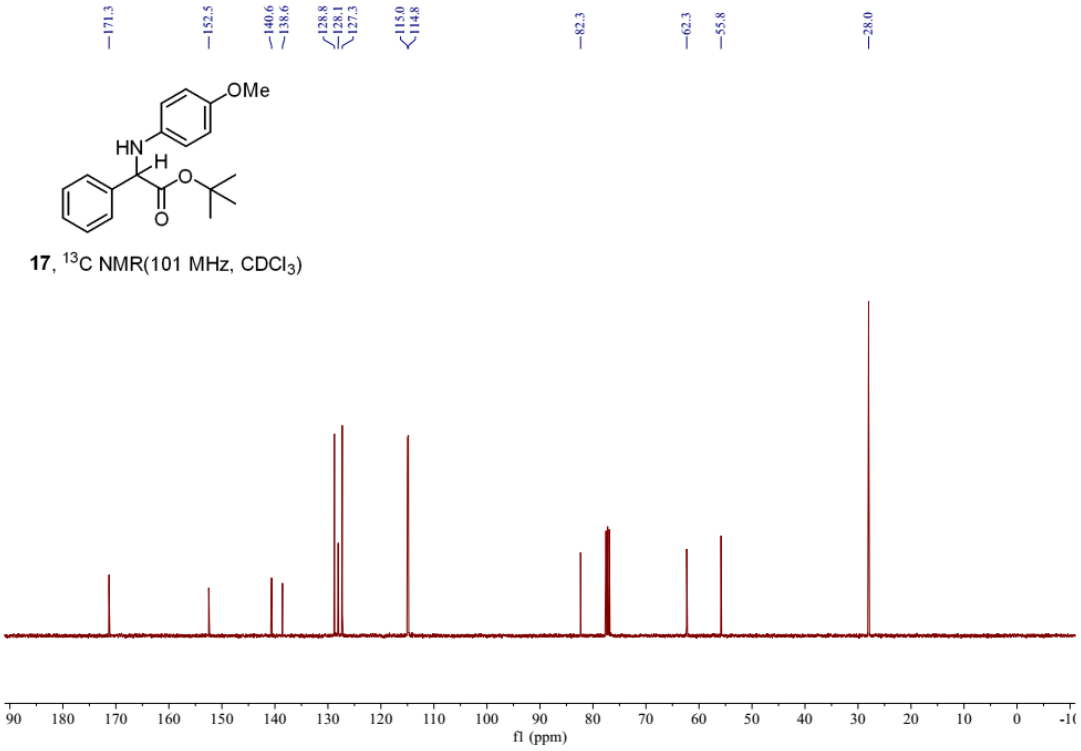
16, ^{1}H NMR(400 MHz, $CDCl_3$)



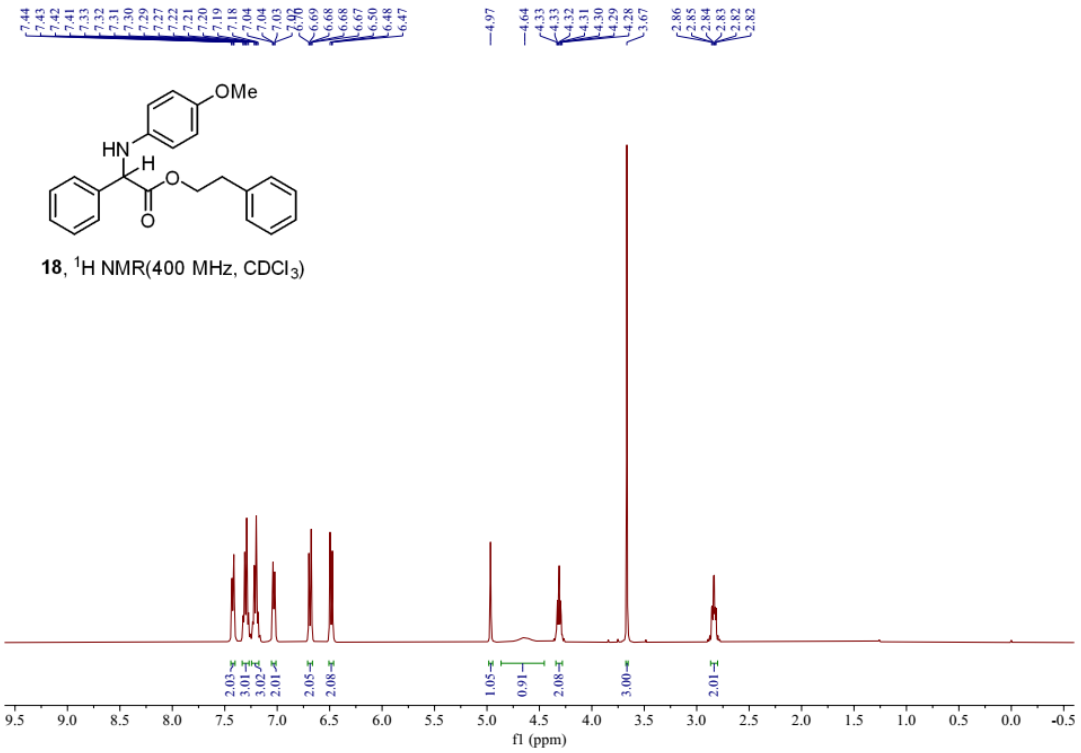
16, ^{13}C NMR(101 MHz, $CDCl_3$)



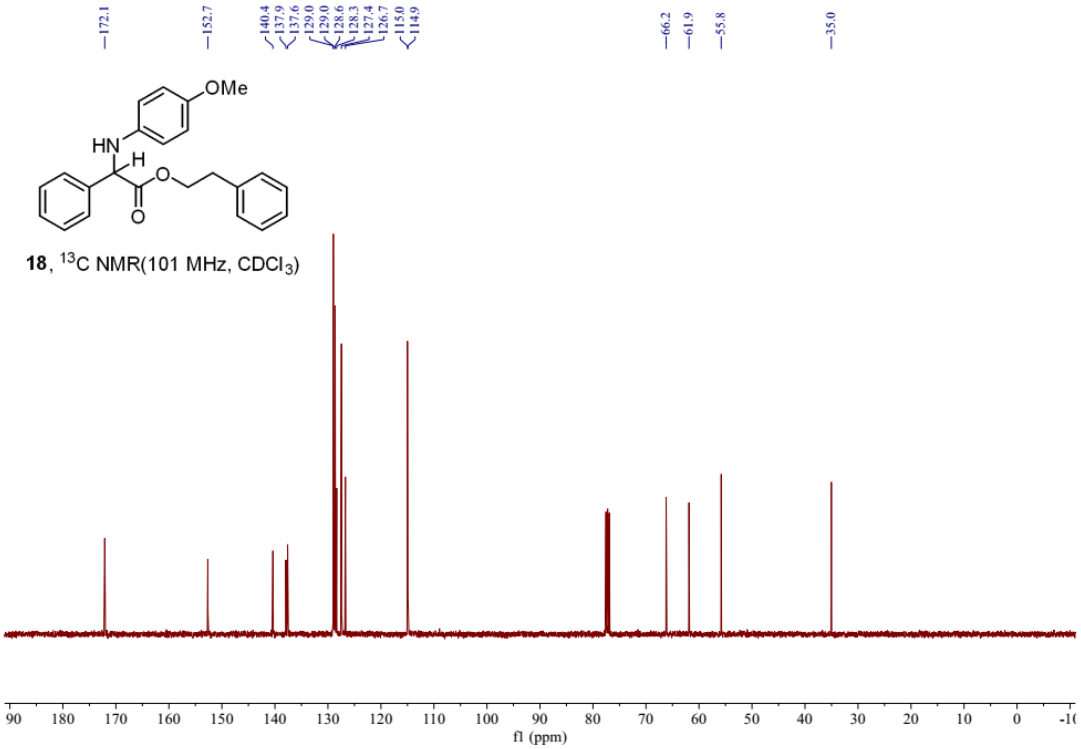
17, ^{1}H NMR(400 MHz, $CDCl_3$)



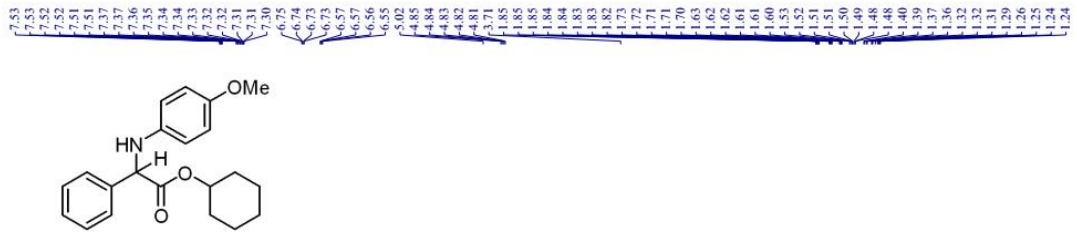
17, ^{13}C NMR(101 MHz, $CDCl_3$)



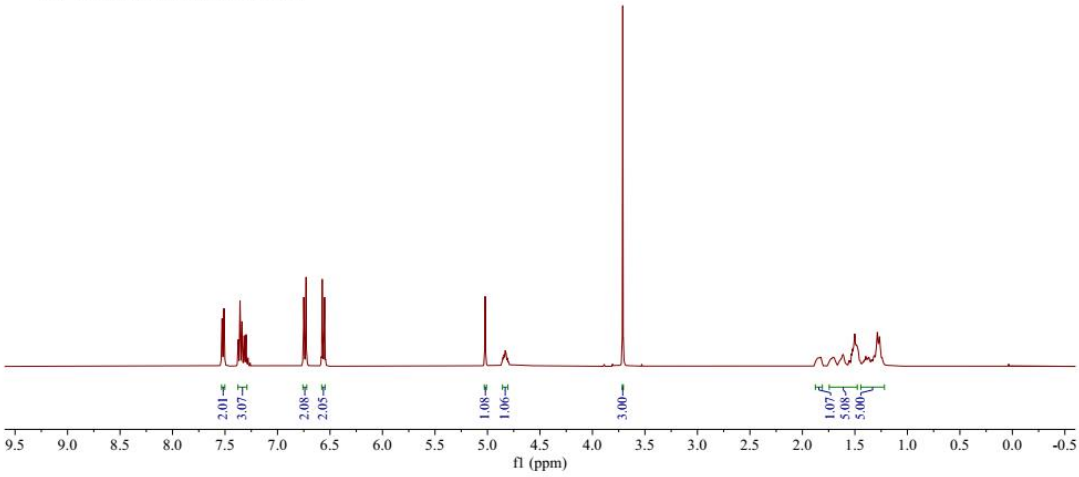
18, ^{1}H NMR(400 MHz, $CDCl_3$)



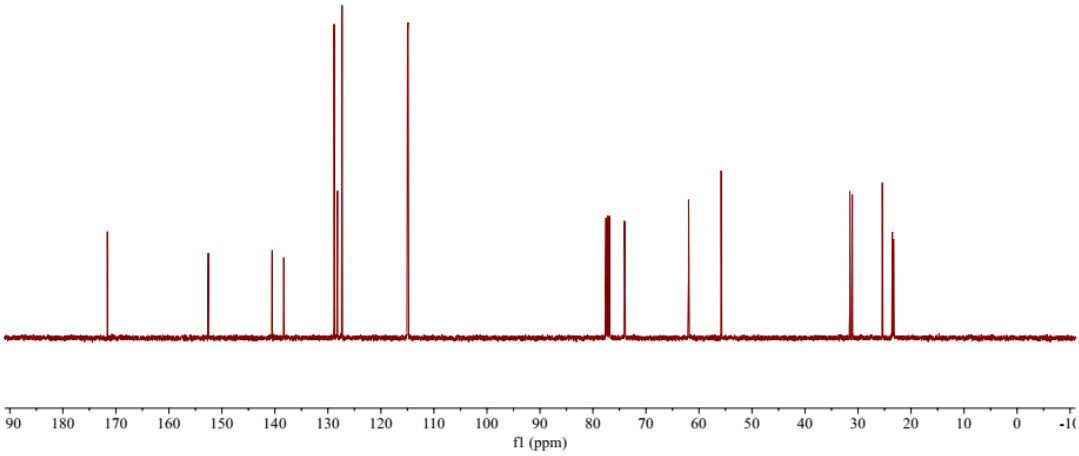
18, ^{13}C NMR(101 MHz, $CDCl_3$)

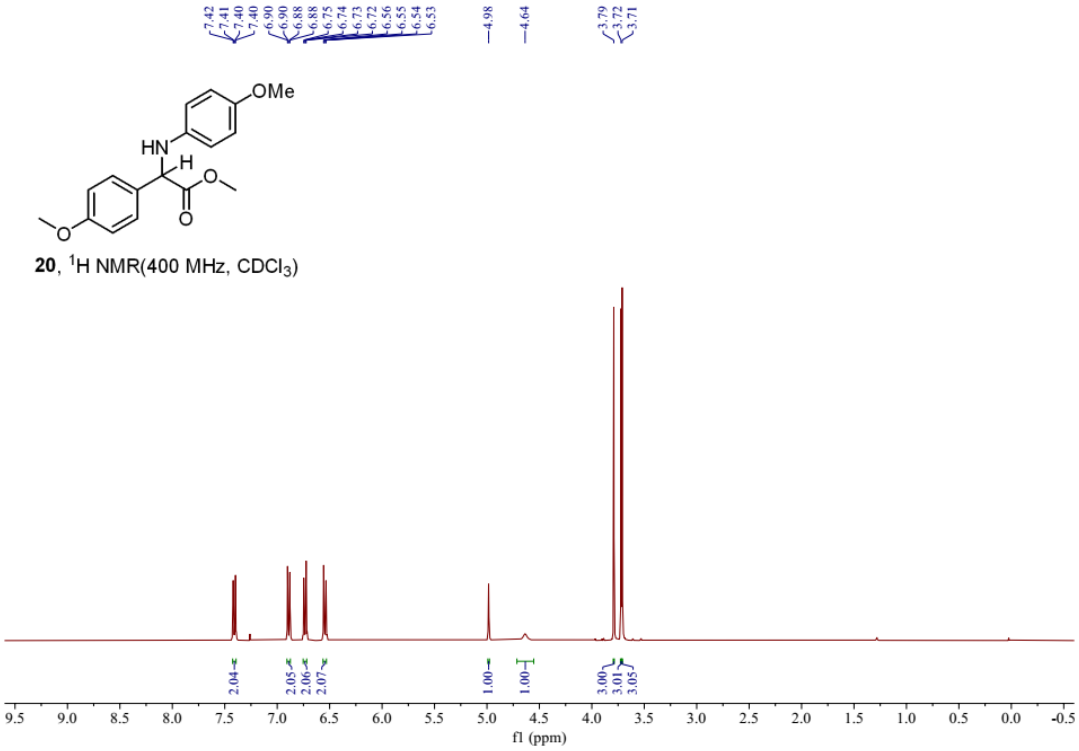


19, ^{1}H NMR(400 MHz, $CDCl_3$)

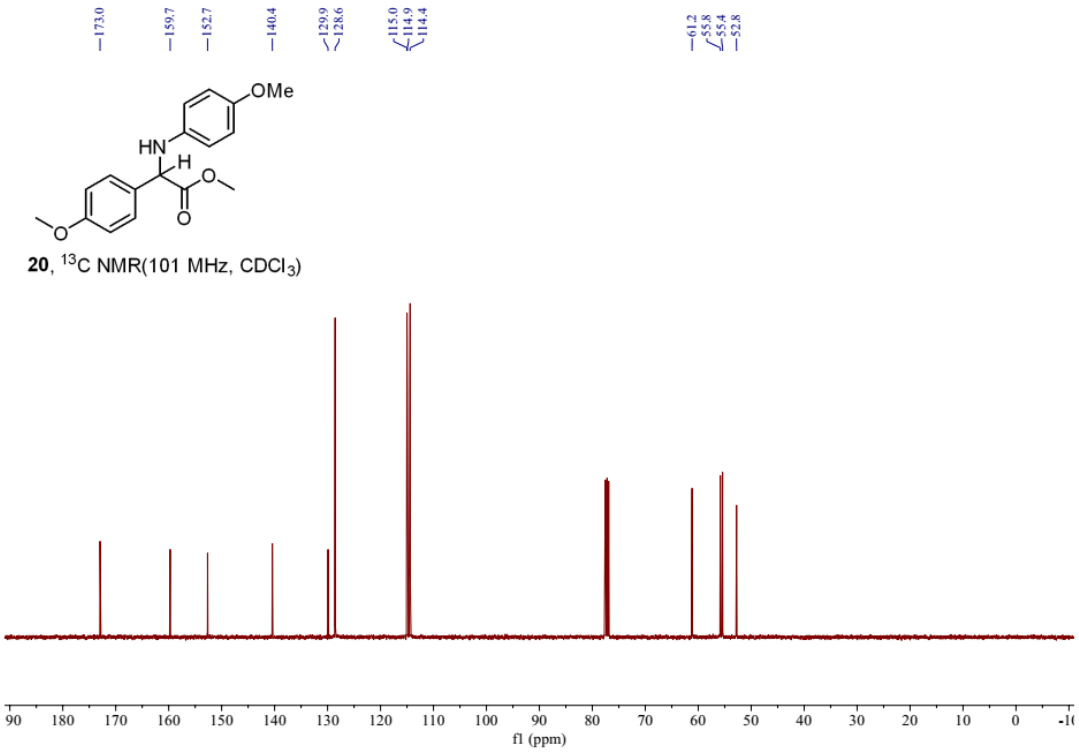


19, ^{13}C NMR(101 MHz, $CDCl_3$)

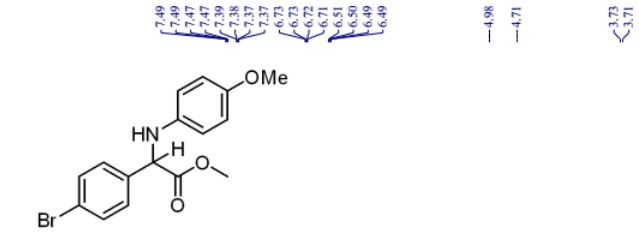




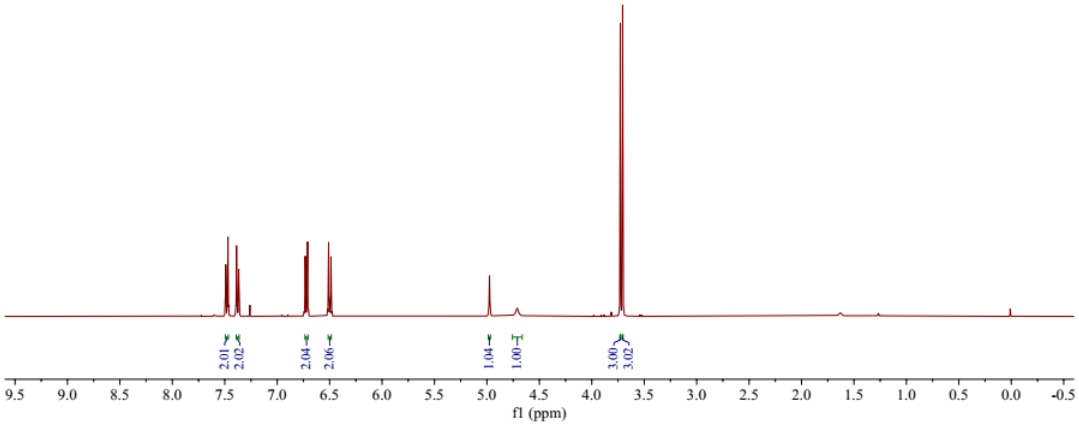
20, ^{1}H NMR(400 MHz, $CDCl_3$)

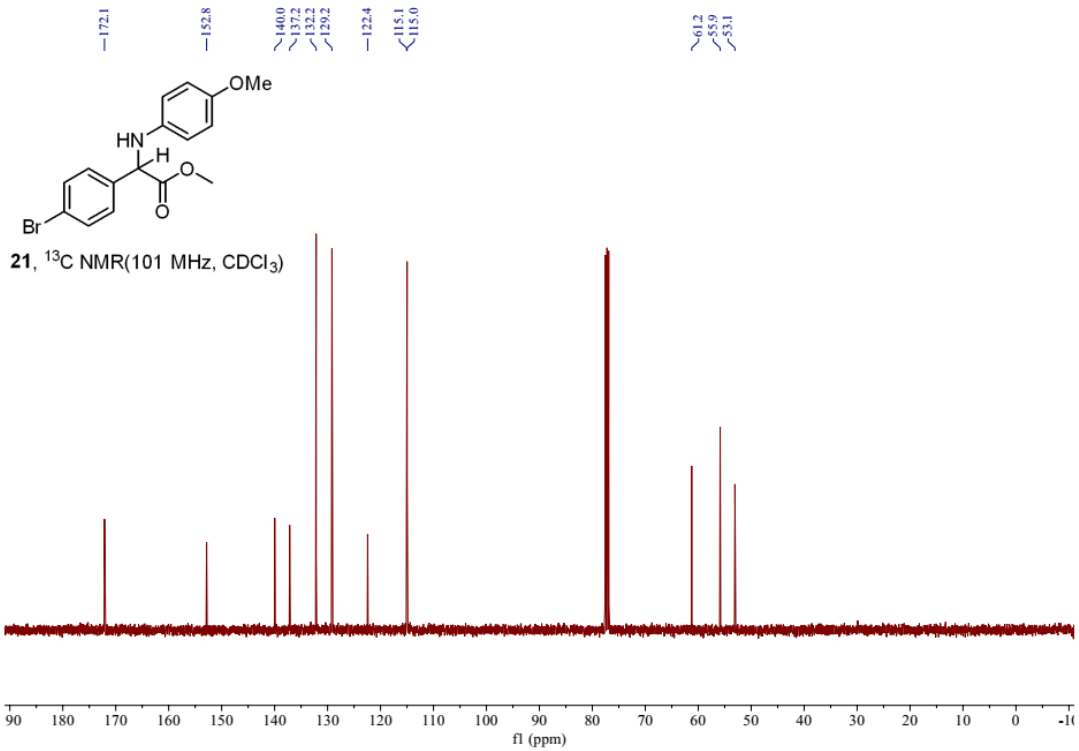


20, ^{13}C NMR(101 MHz, $CDCl_3$)

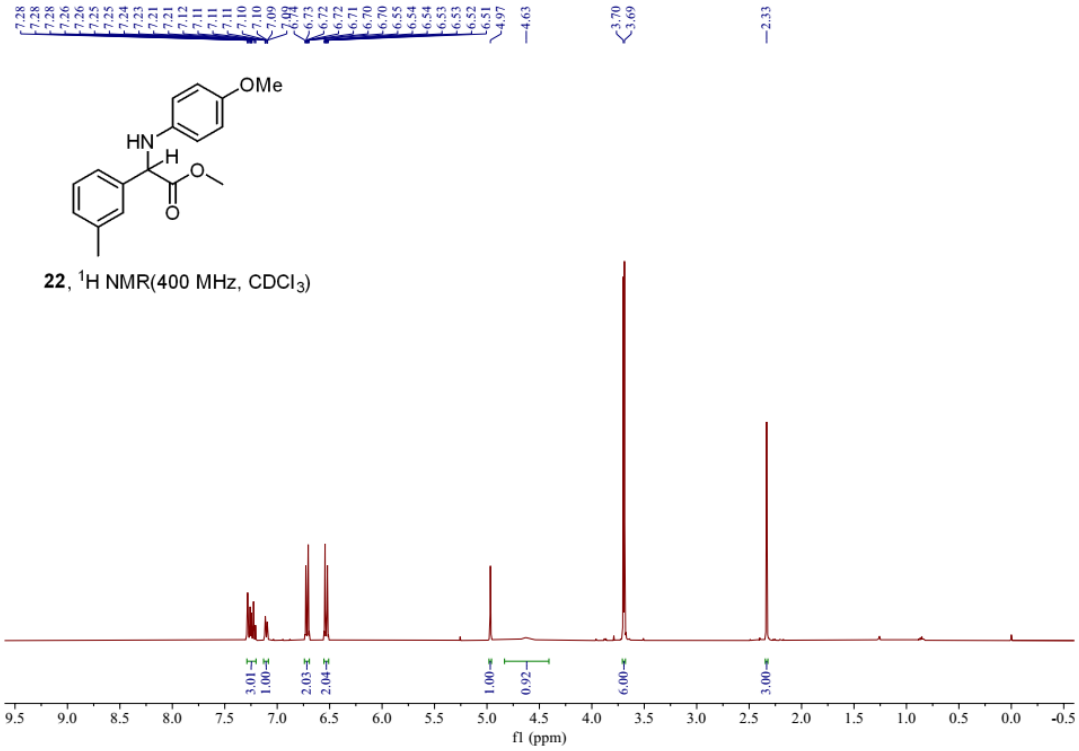


21, ^{1}H NMR(400 MHz, $CDCl_3$)

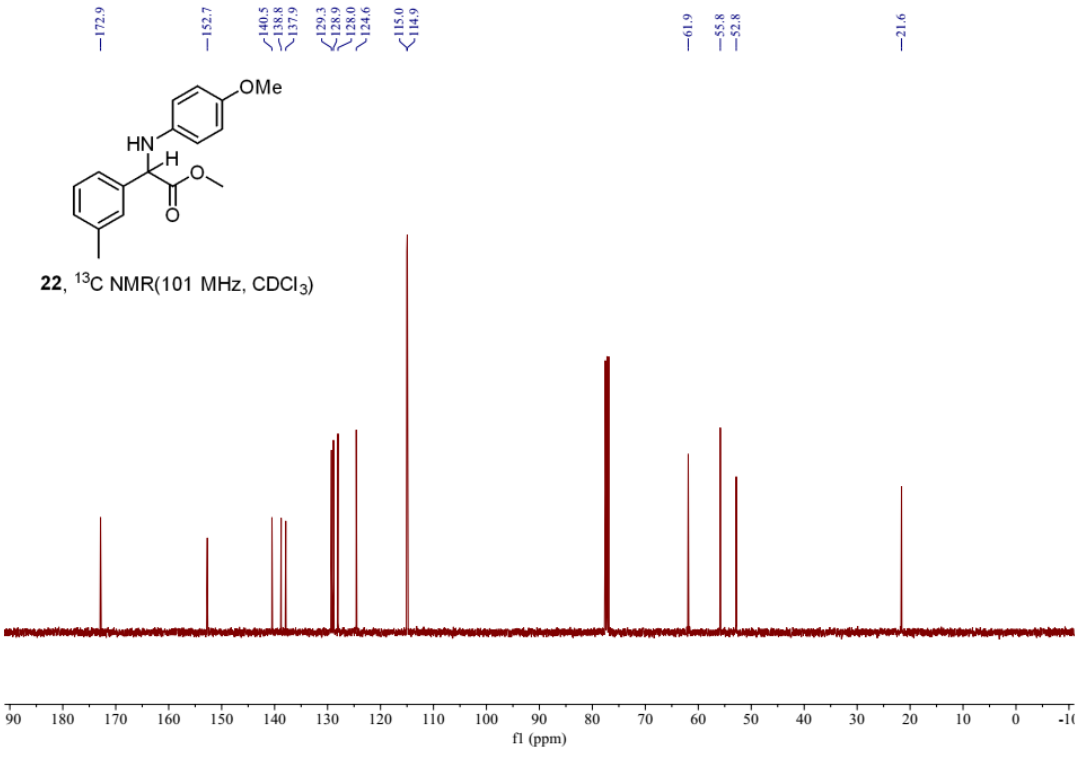




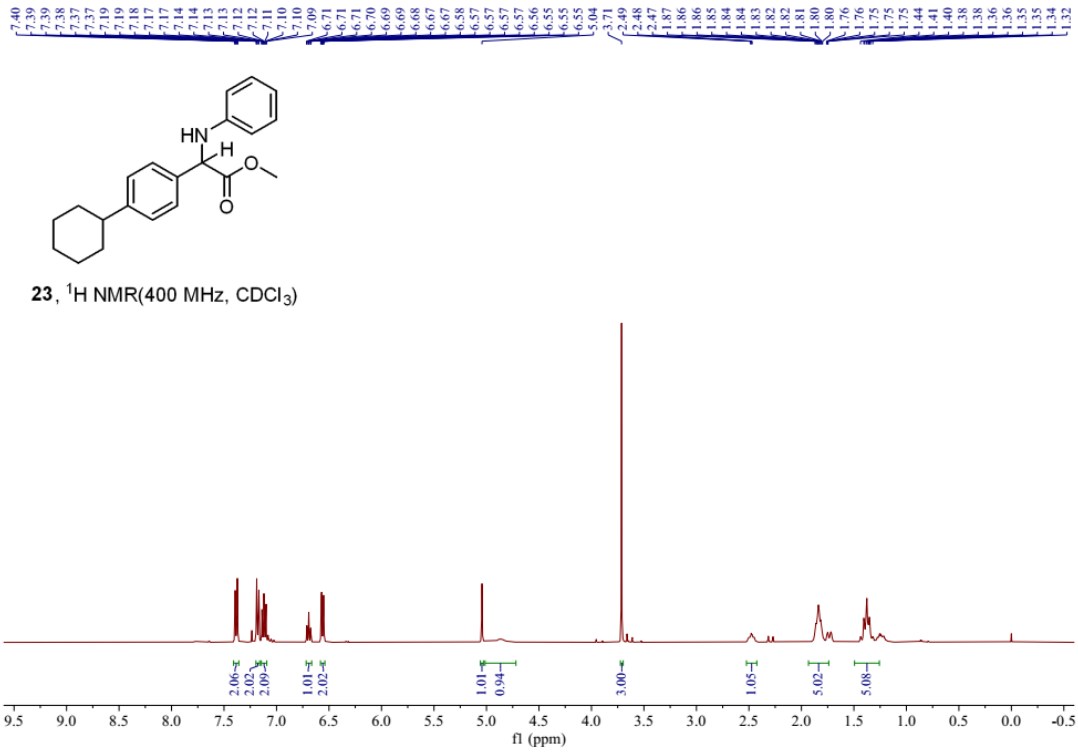
21, ^{13}C NMR(101 MHz, $CDCl_3$)



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

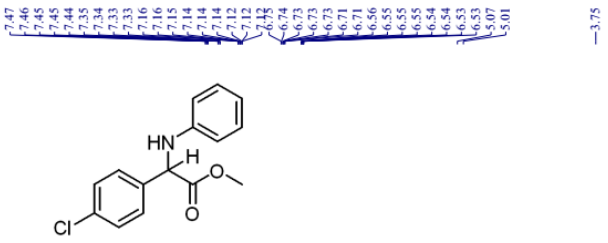


22, ^{13}C NMR(101 MHz, $CDCl_3$)

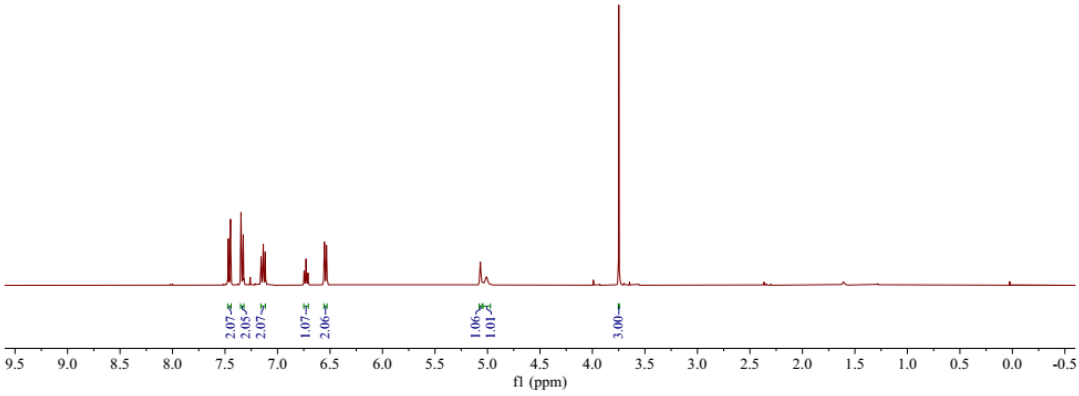


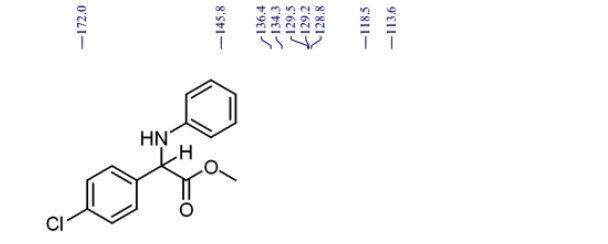
23, ^{1}H NMR(400 MHz, $CDCl_3$)

23, ^{13}C NMR(101 MHz, $CDCl_3$)

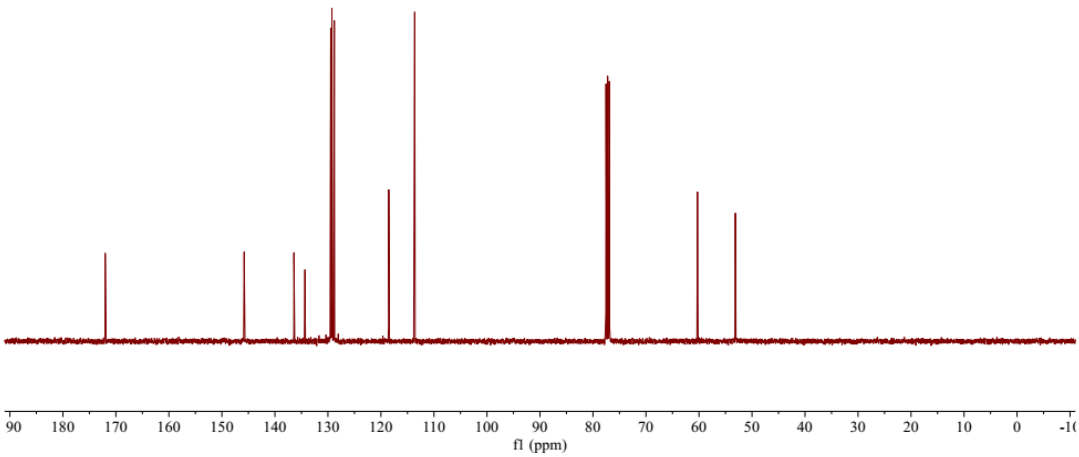


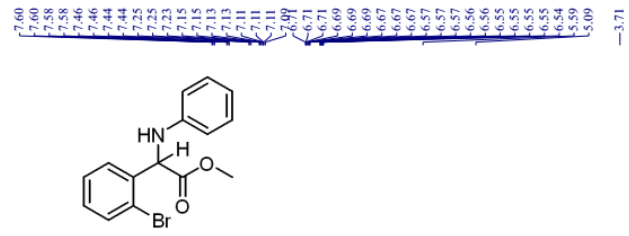
24, ^{1}H NMR(400 MHz, $CDCl_3$)



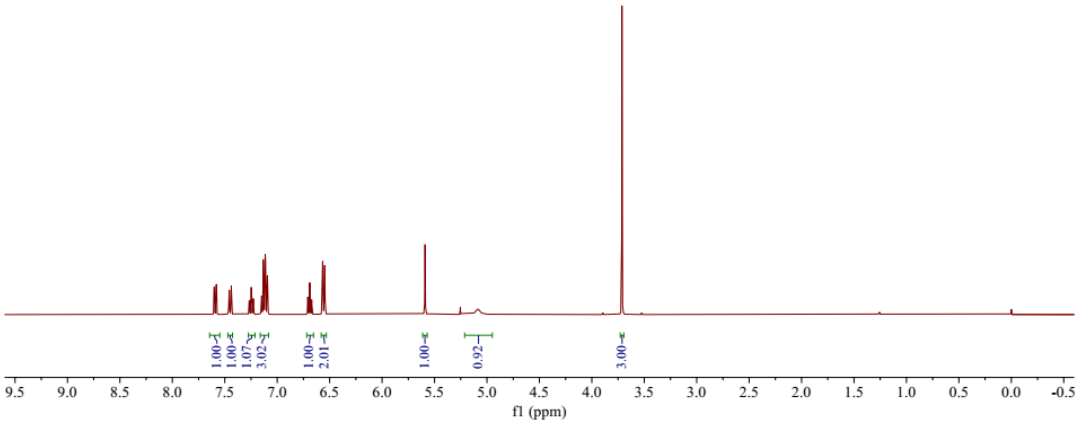


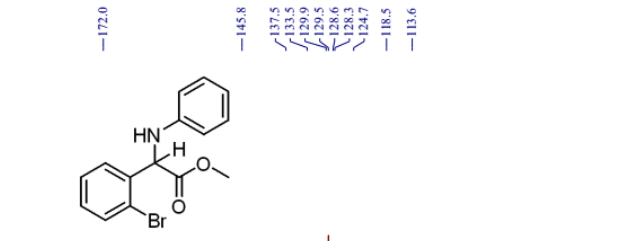
24, ^{13}C NMR(101 MHz, $CDCl_3$)



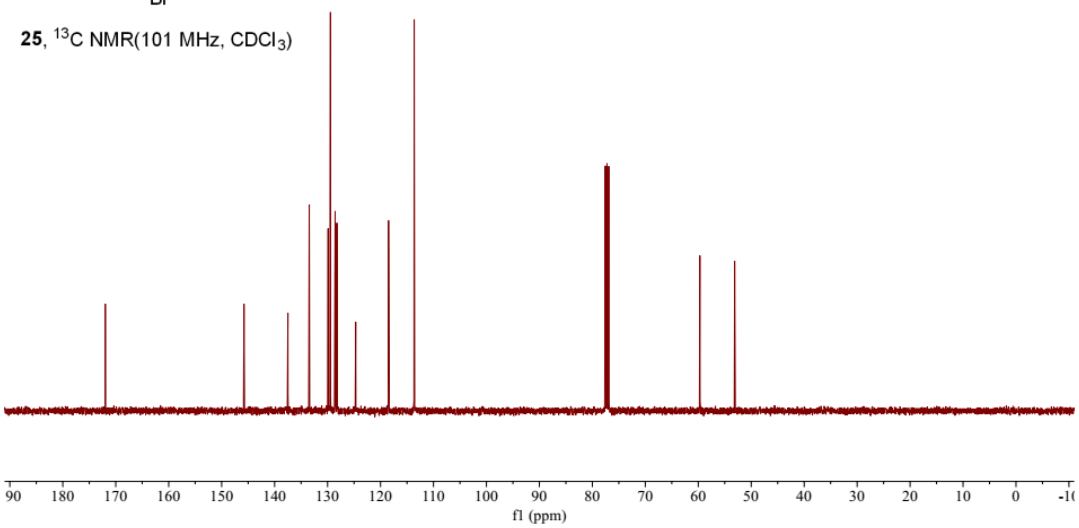


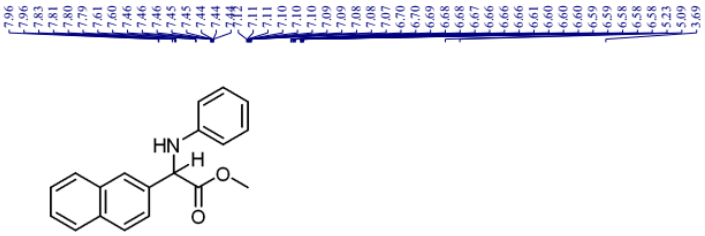
25, ^{1}H NMR(400 MHz, $CDCl_3$)



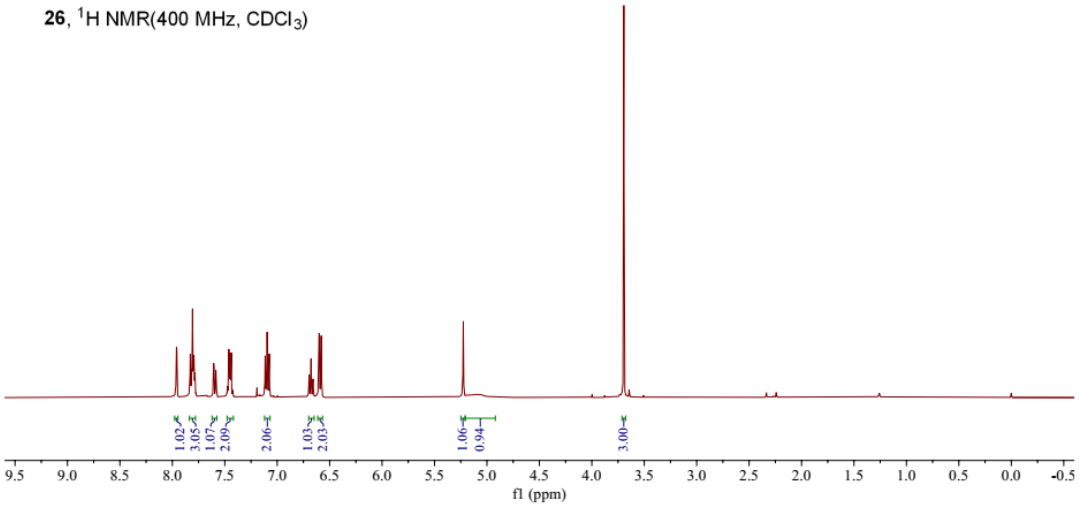


25, ^{13}C NMR(101 MHz, $CDCl_3$)

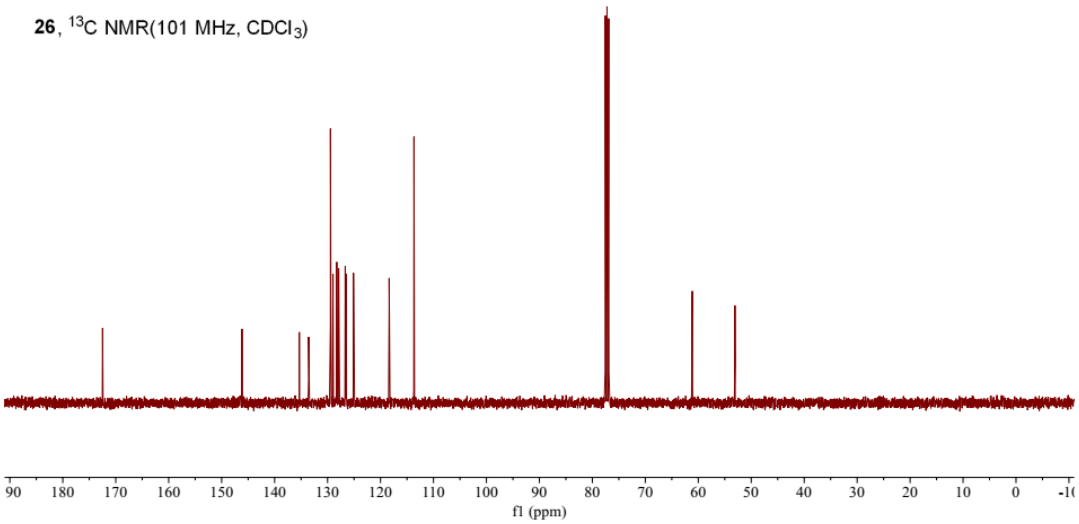


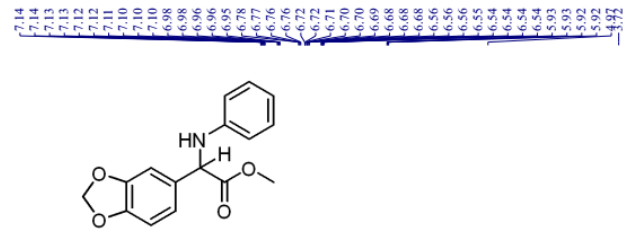


26, ^{1}H NMR(400 MHz, $CDCl_3$)

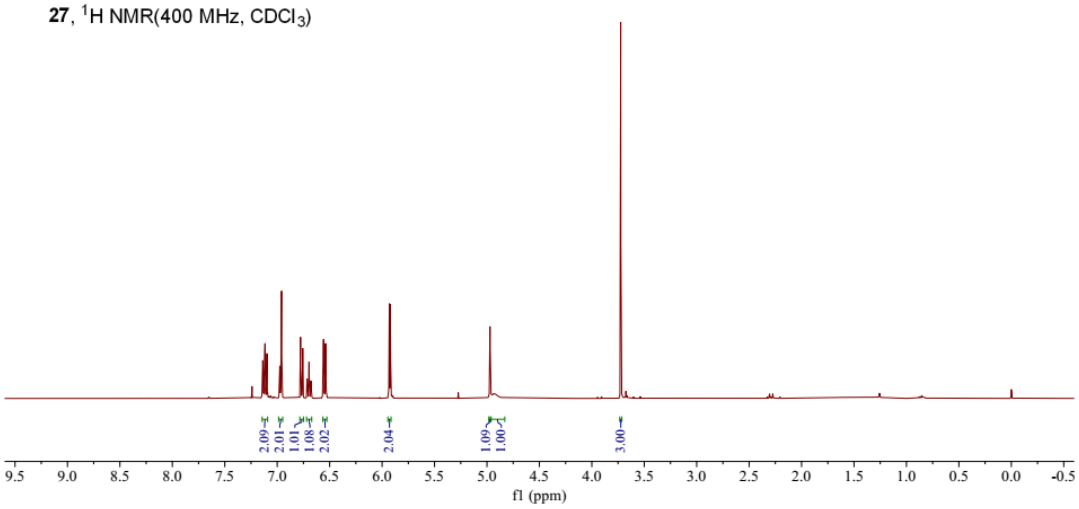


26, ^{13}C NMR(101 MHz, $CDCl_3$)

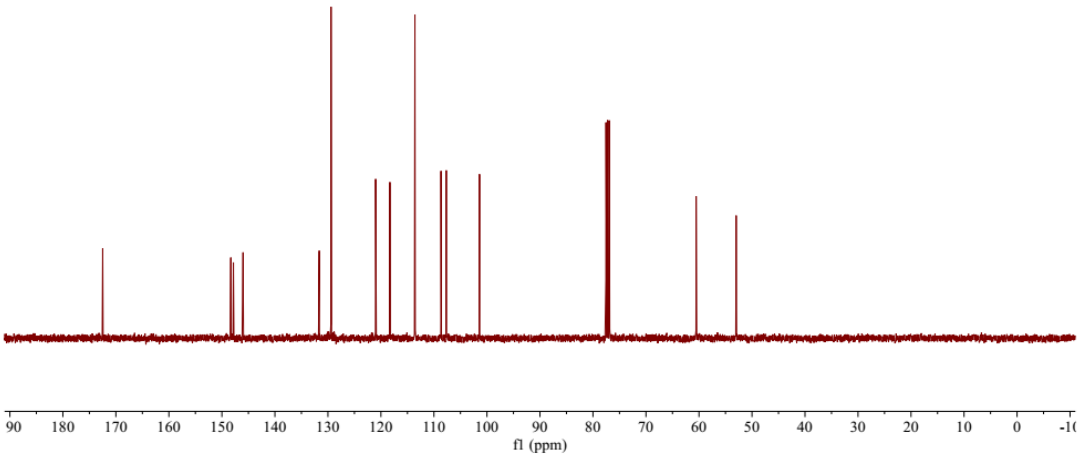


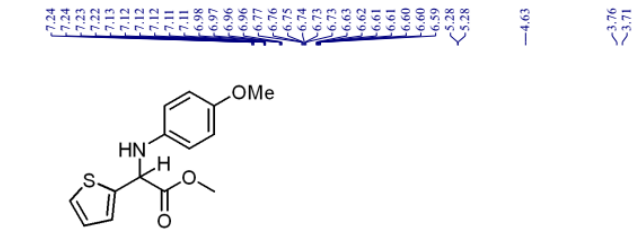


27, ^{1}H NMR(400 MHz, $CDCl_3$)

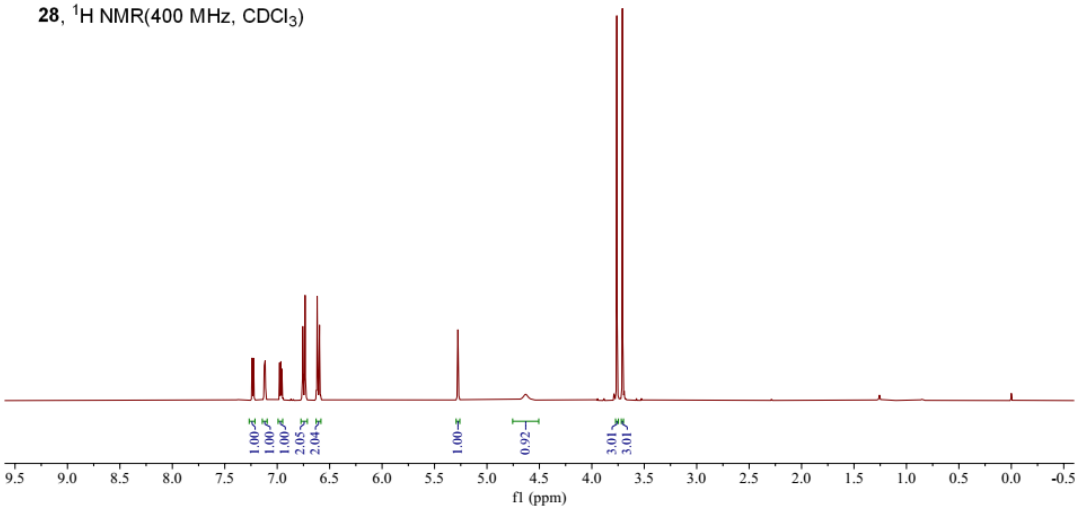


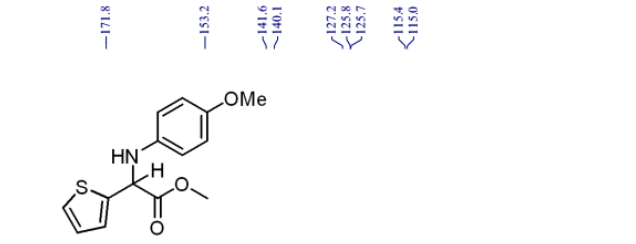
27, ^{13}C NMR(101 MHz, $CDCl_3$)



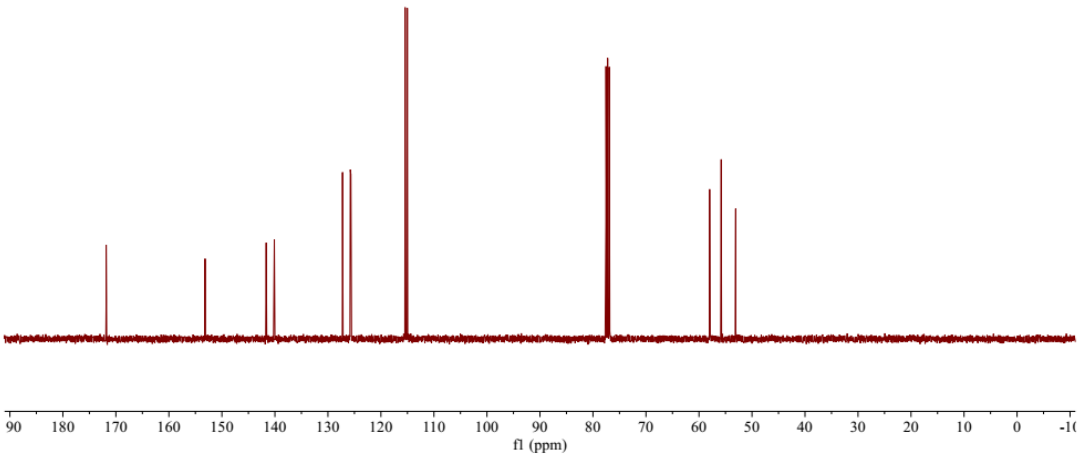


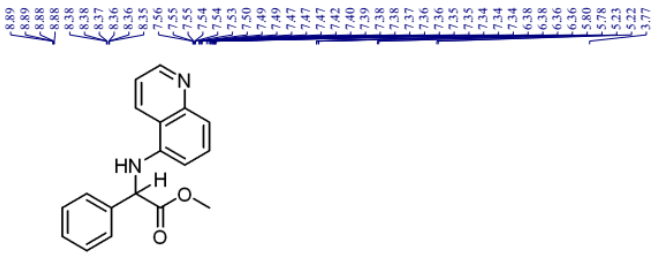
28, ^{1}H NMR(400 MHz, $CDCl_3$)



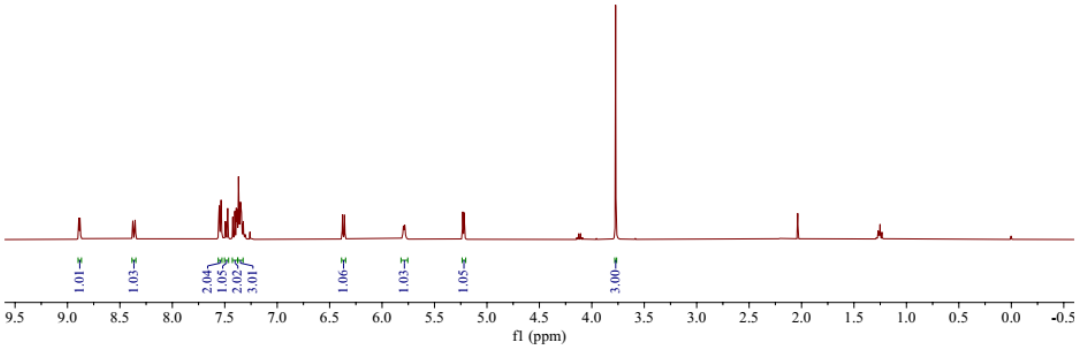


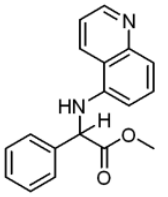
28, ^{13}C NMR(101 MHz, $CDCl_3$)



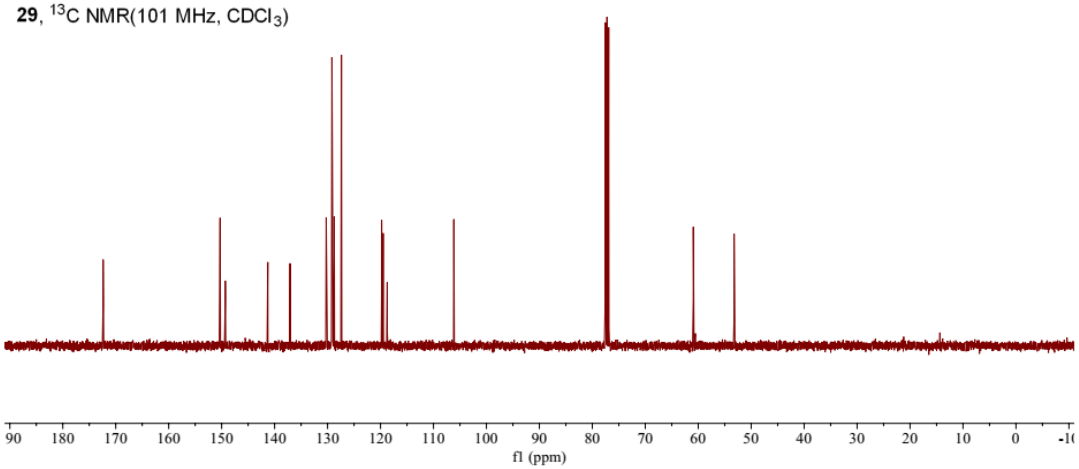


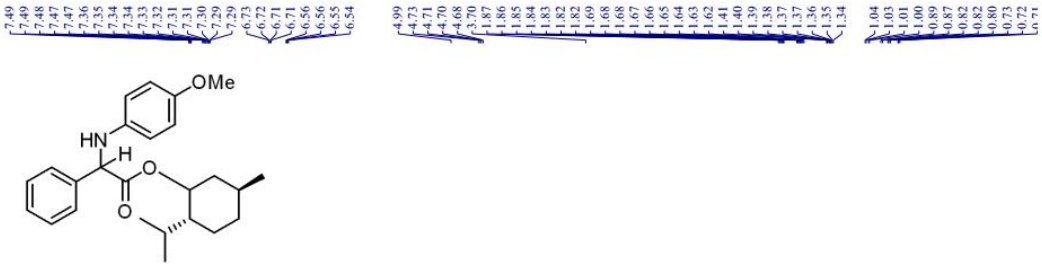
29, ^{1}H NMR(400 MHz, $CDCl_3$)



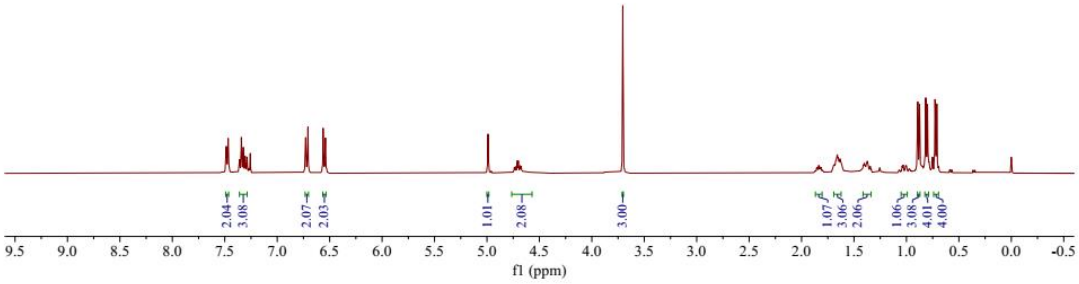


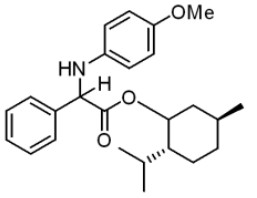
29, ^{13}C NMR(101 MHz, $CDCl_3$)



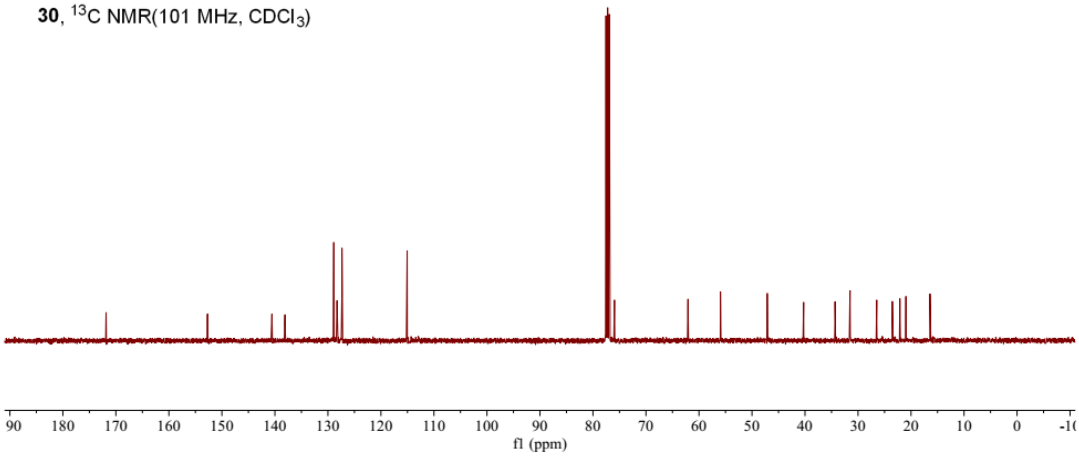


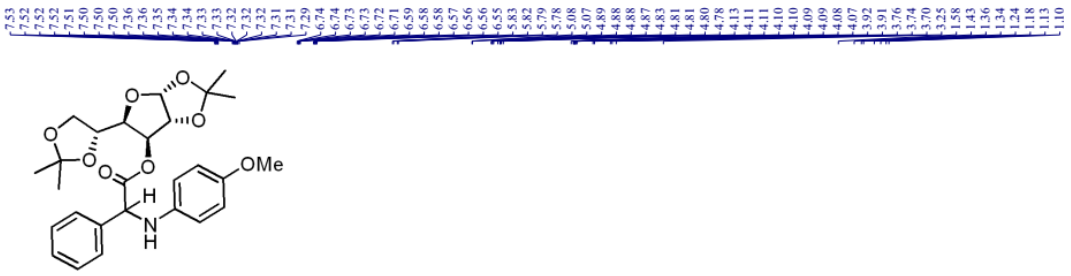
30, ^{1}H NMR(400 MHz, $CDCl_3$)



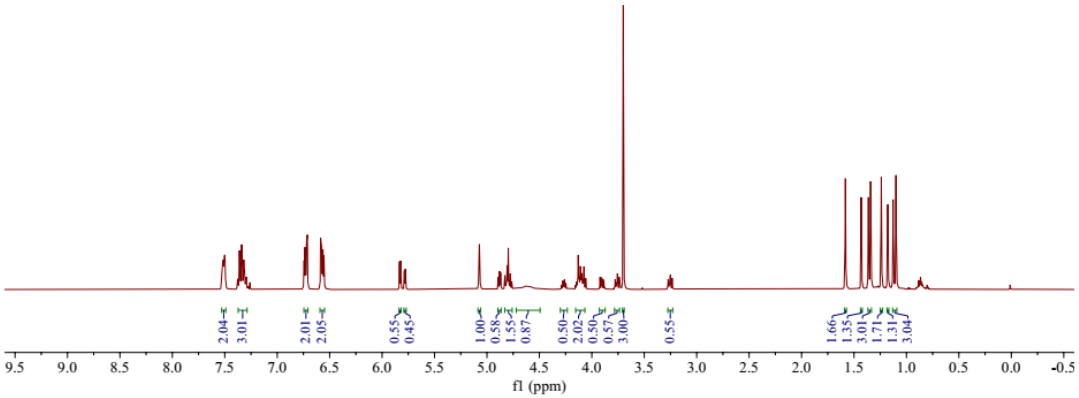


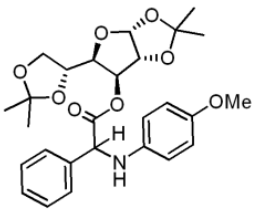
30, ^{13}C NMR(101 MHz, $CDCl_3$)



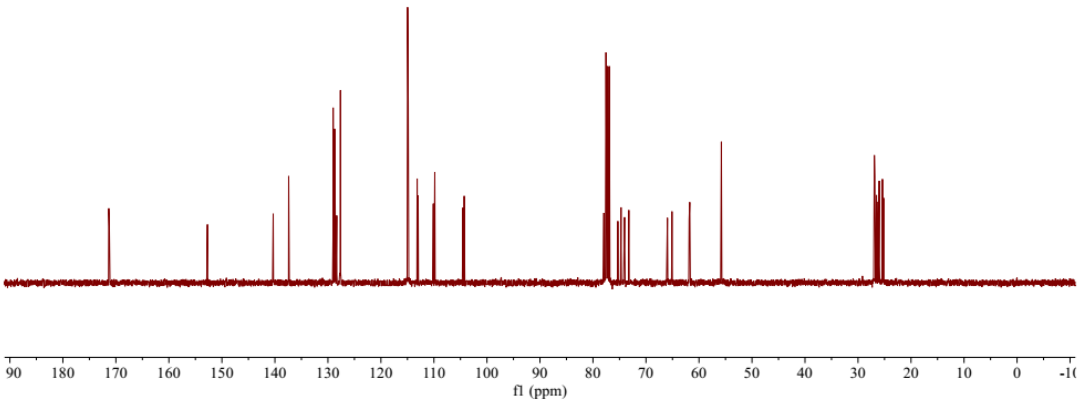


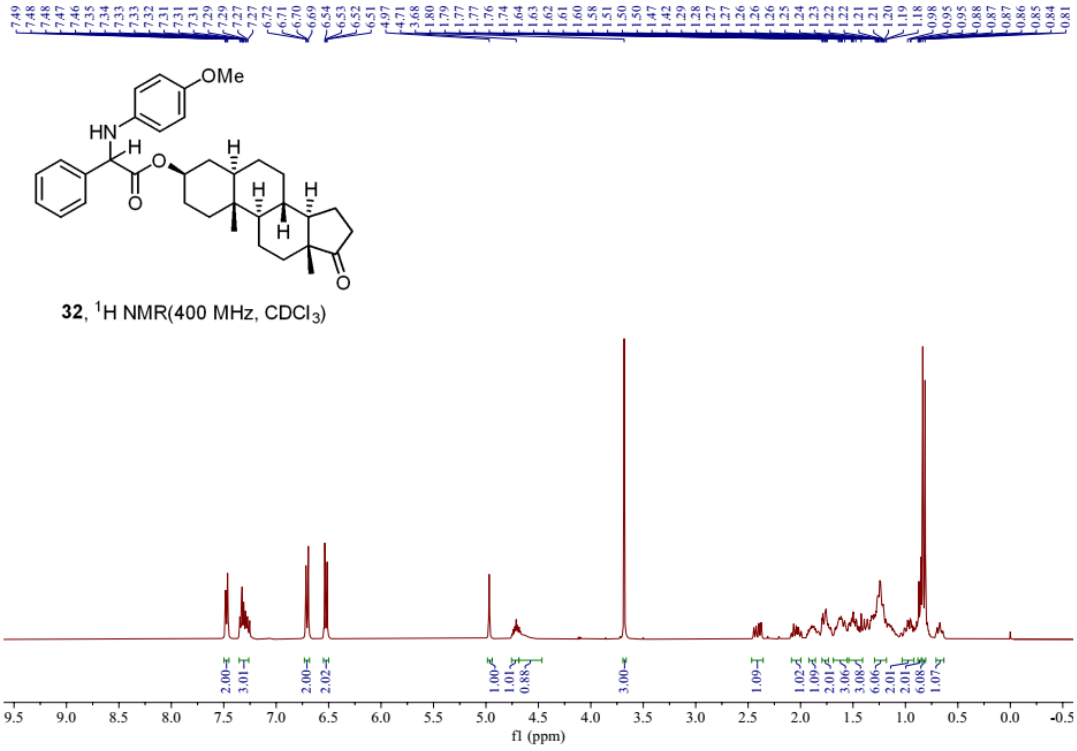
31, ^{1}H NMR(400 MHz, $CDCl_3$)



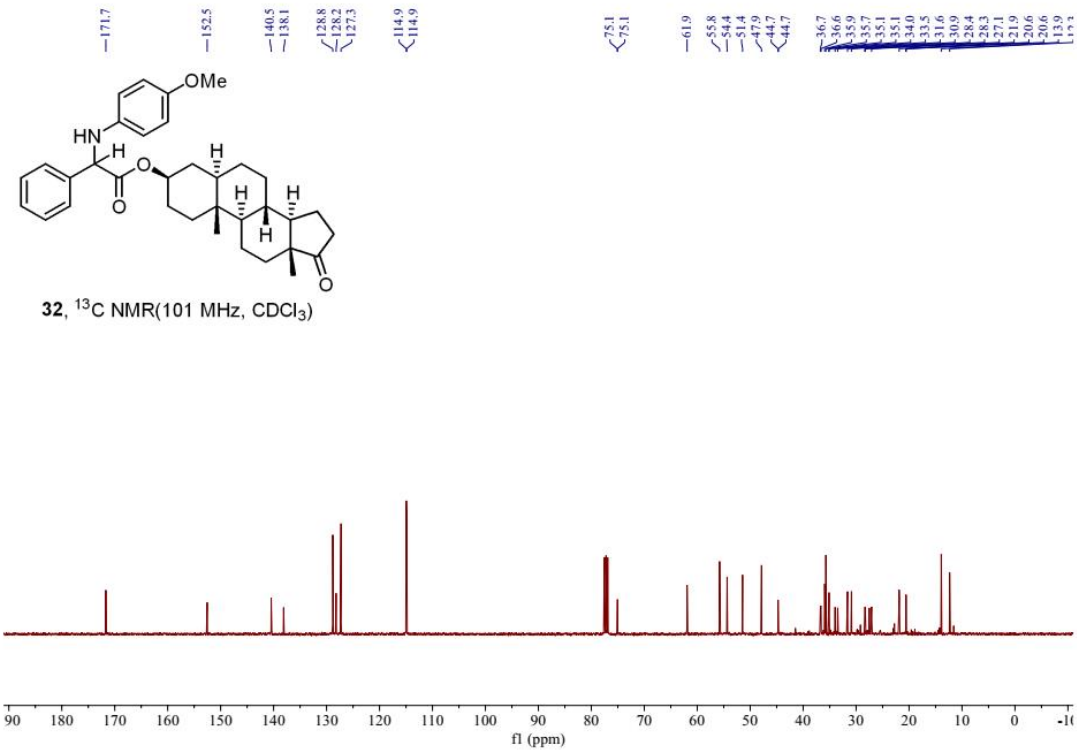


31, ^{13}C NMR(101 MHz, $CDCl_3$)



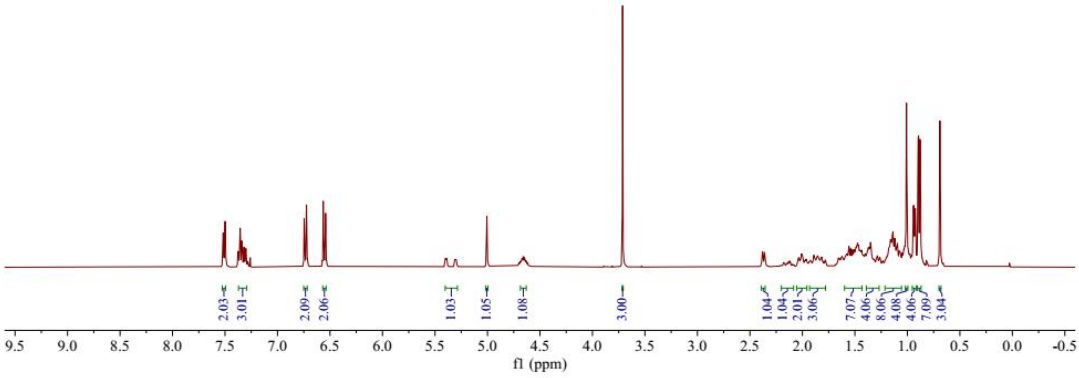


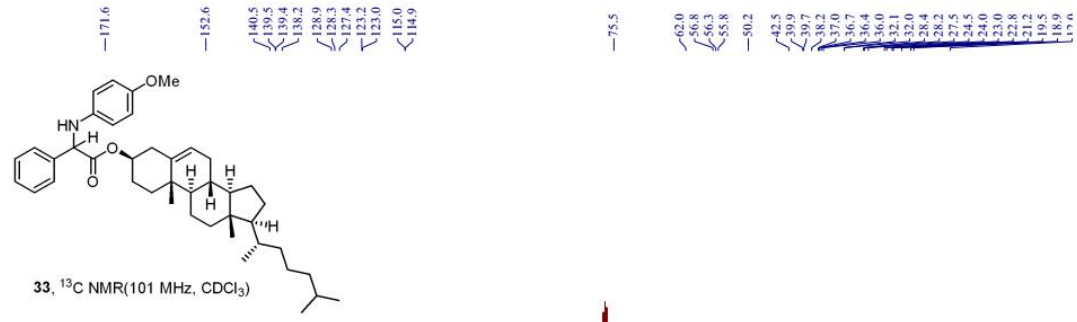
32, ^{1}H NMR(400 MHz, $CDCl_3$)



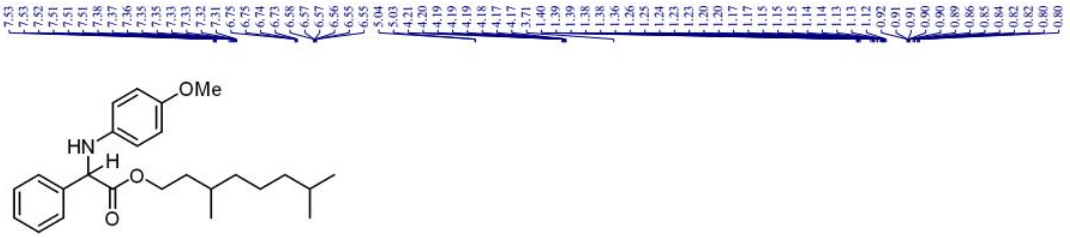
32, ^{13}C NMR(101 MHz, $CDCl_3$)

33, ^{1}H NMR(400 MHz, $CDCl_3$)

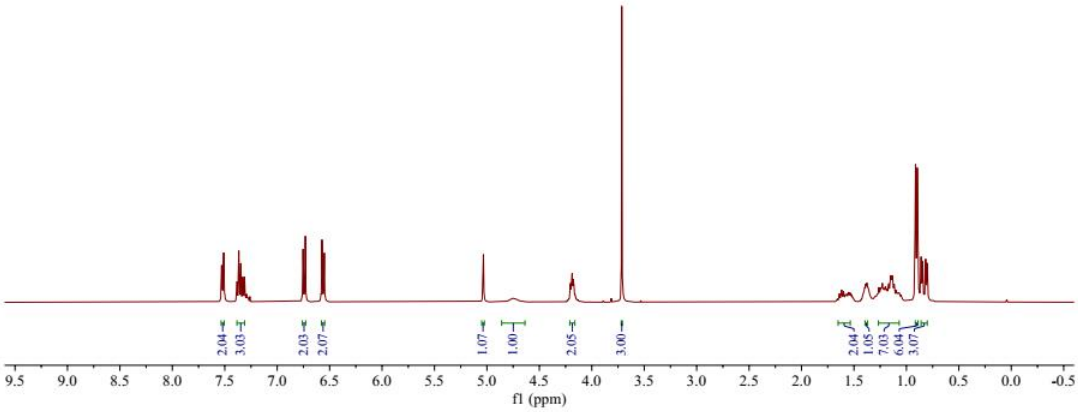




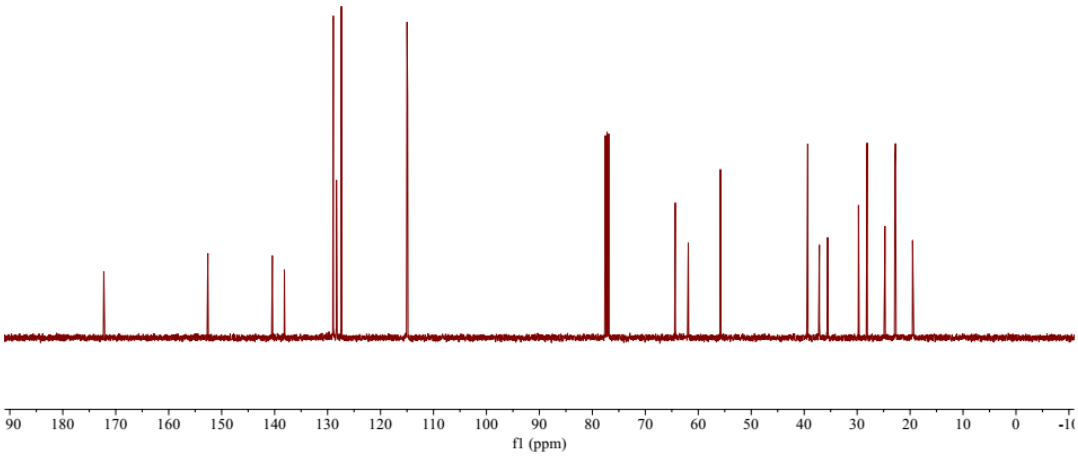
33, ^{13}C NMR(101 MHz, $CDCl_3$)

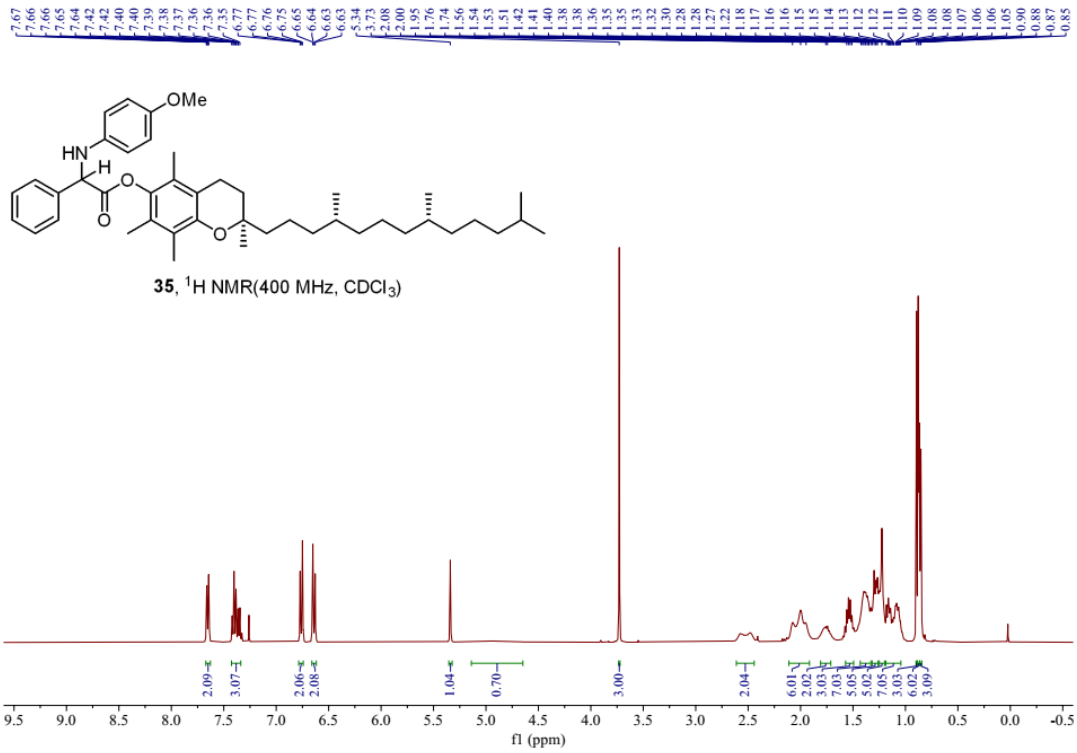


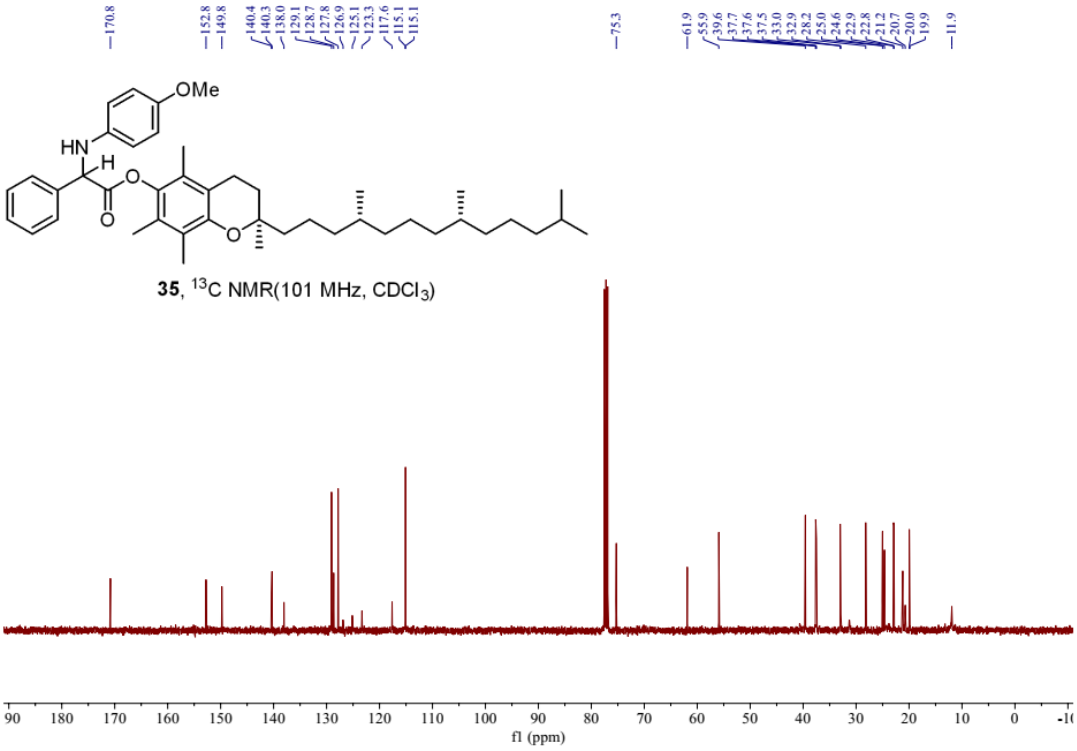
34, ^{1}H NMR(400 MHz, $CDCl_3$)

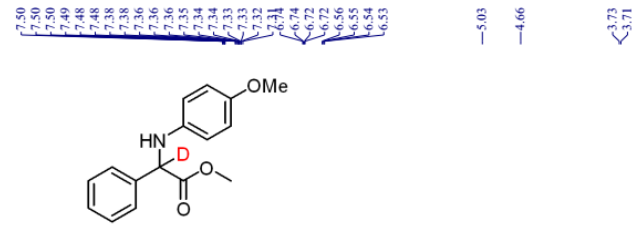


34, ^{13}C NMR(101 MHz, $CDCl_3$)

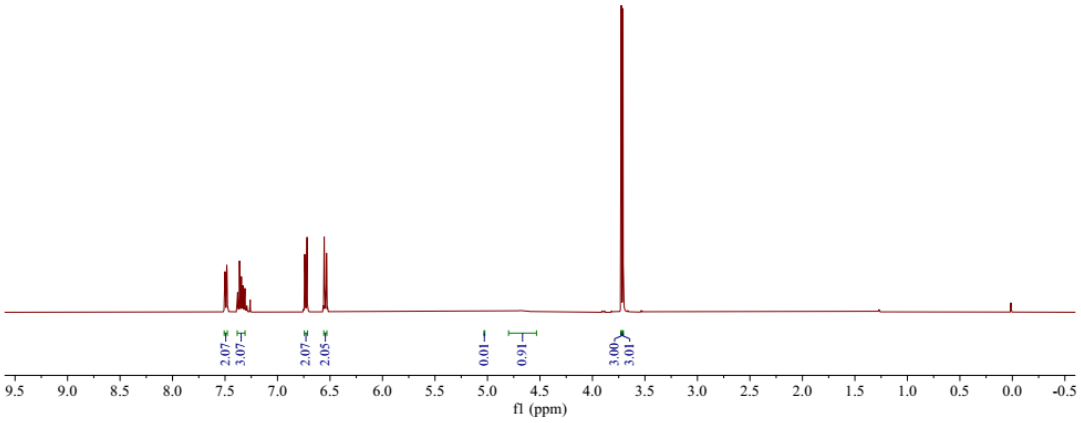


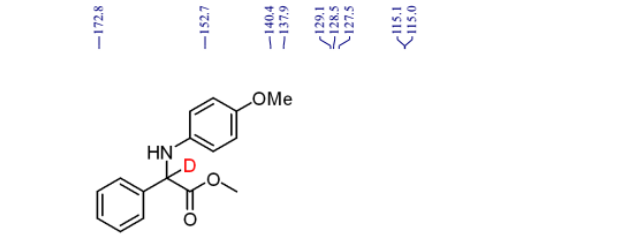

OMe
HN
H
O
O
O
35, 1H NMR(400 MHz, CDCl3)
fl (ppm)


OMe
HN
H
O
O
O
35, 13C NMR(101 MHz, CDCl3)
fl (ppm)

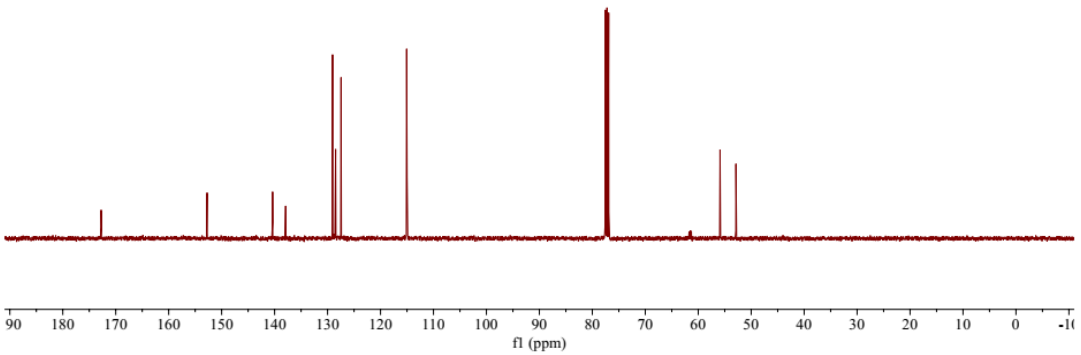


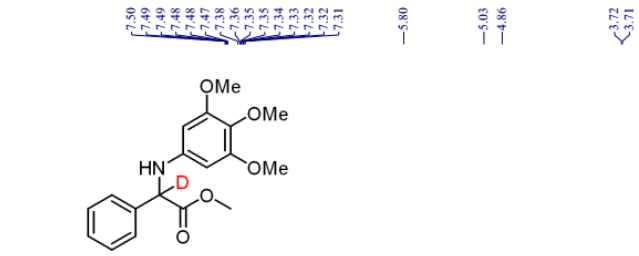
36, 99% D, ^{1}H NMR(400 MHz, $CDCl_3$)



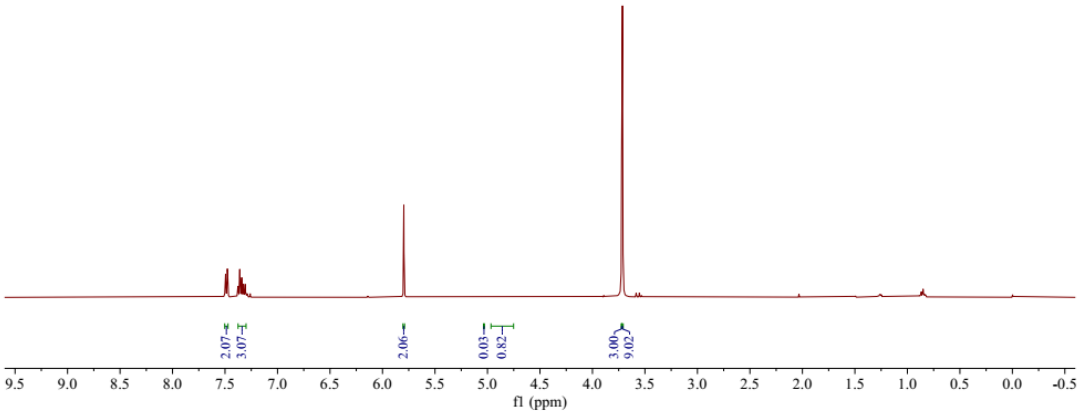


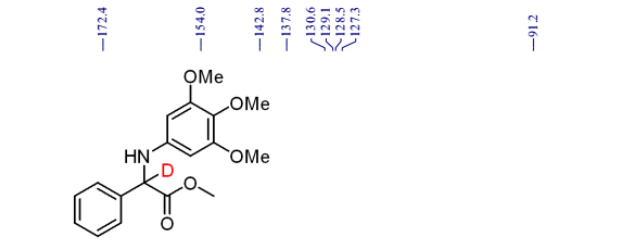
36, 99% D, ^{13}C NMR(101 MHz, $CDCl_3$)



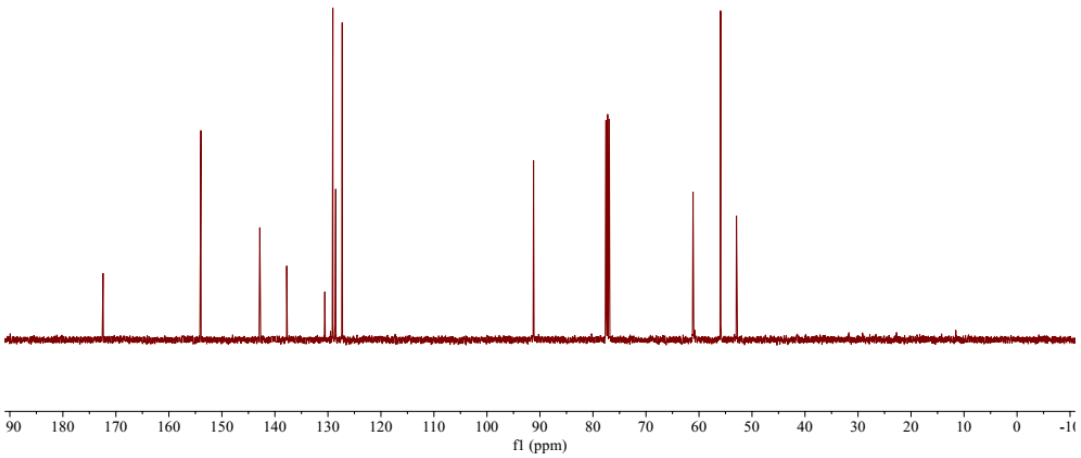


37, 97% D, ^{1}H NMR(400 MHz, $CDCl_3$)

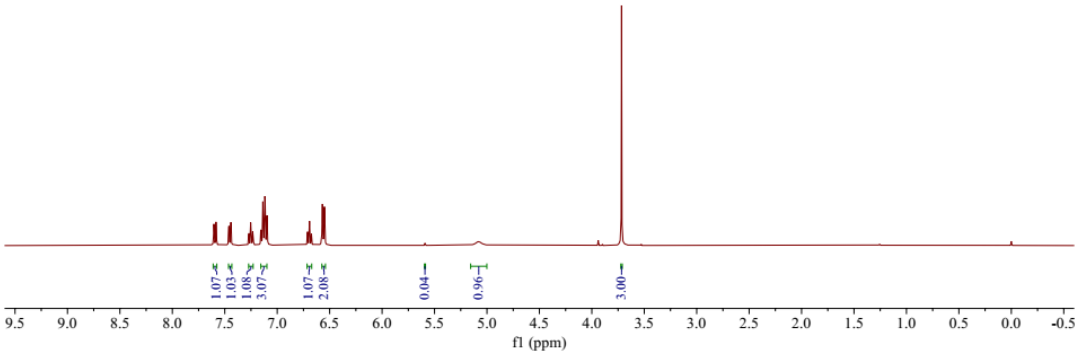




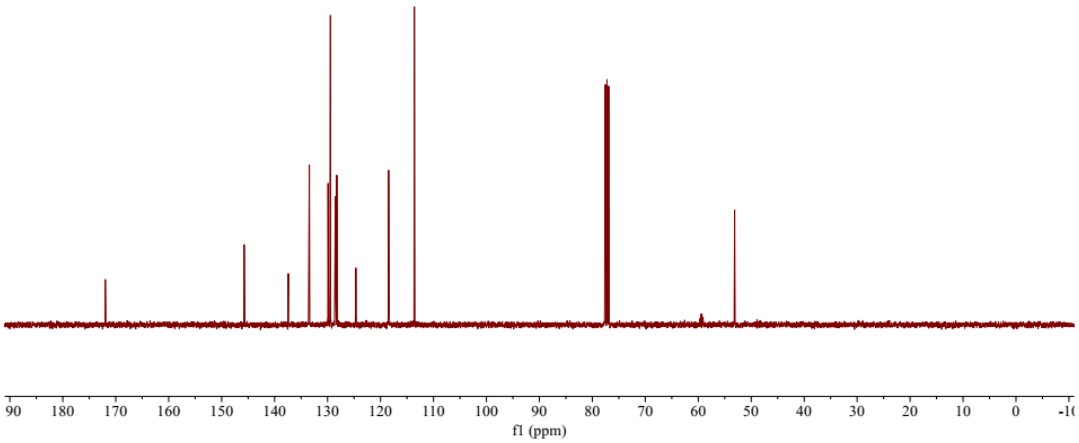
37, 97% D, ^{13}C NMR(101 MHz, $CDCl_3$)

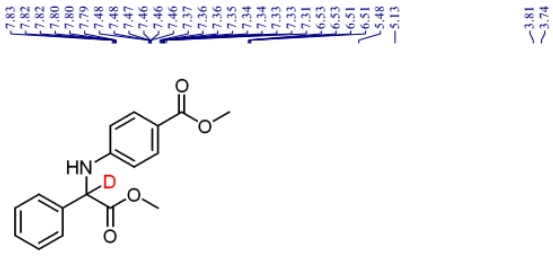


38, 96% D, ^{1}H NMR(400 MHz, $CDCl_3$)

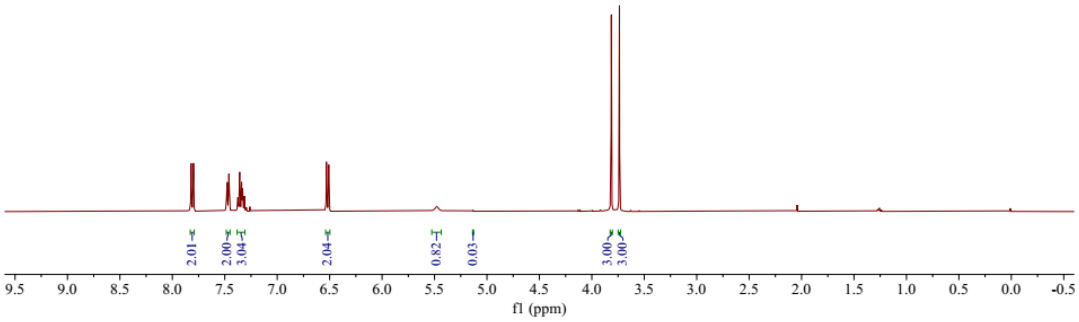


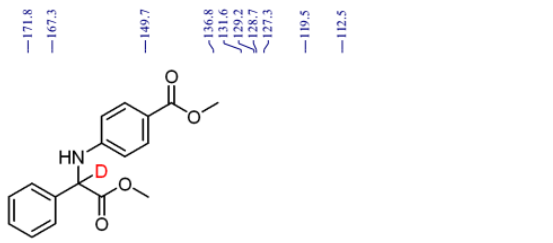
38, 96% D, ^{13}C NMR(101 MHz, $CDCl_3$)



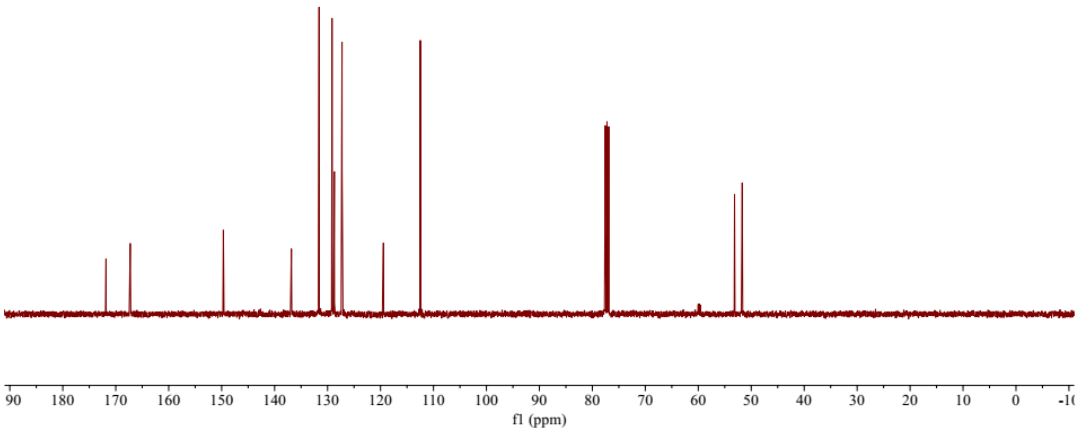


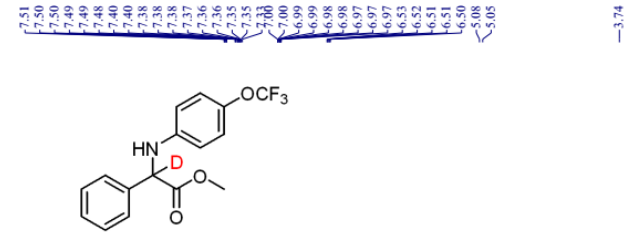
39, 97% D, ^{1}H NMR(400 MHz, $CDCl_3$)



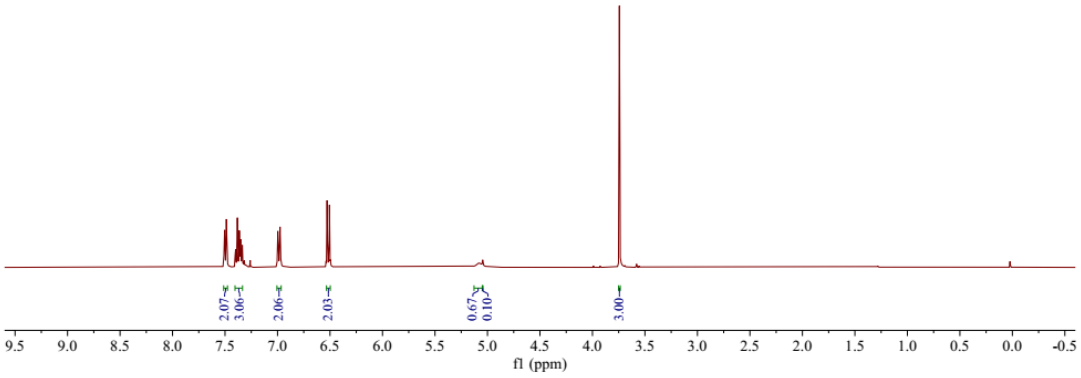


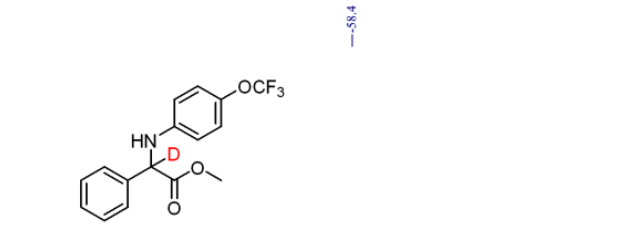
39, 97% D, ^{13}C NMR(101 MHz, $CDCl_3$)



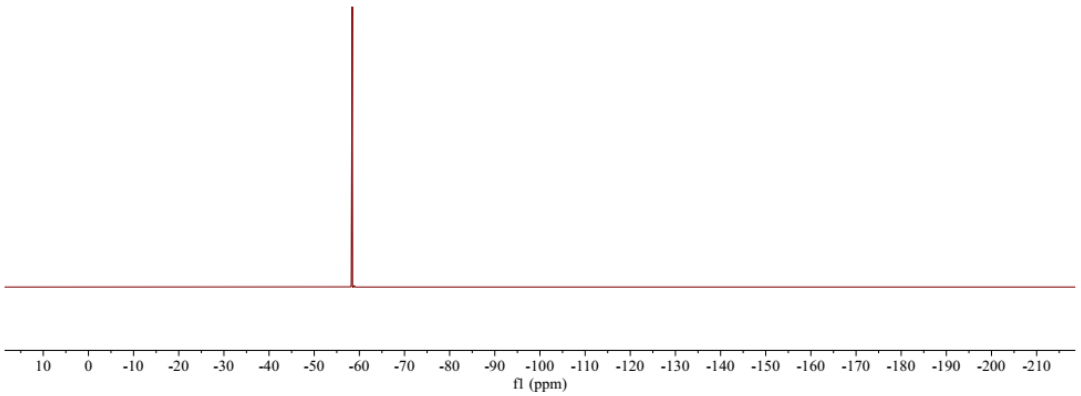


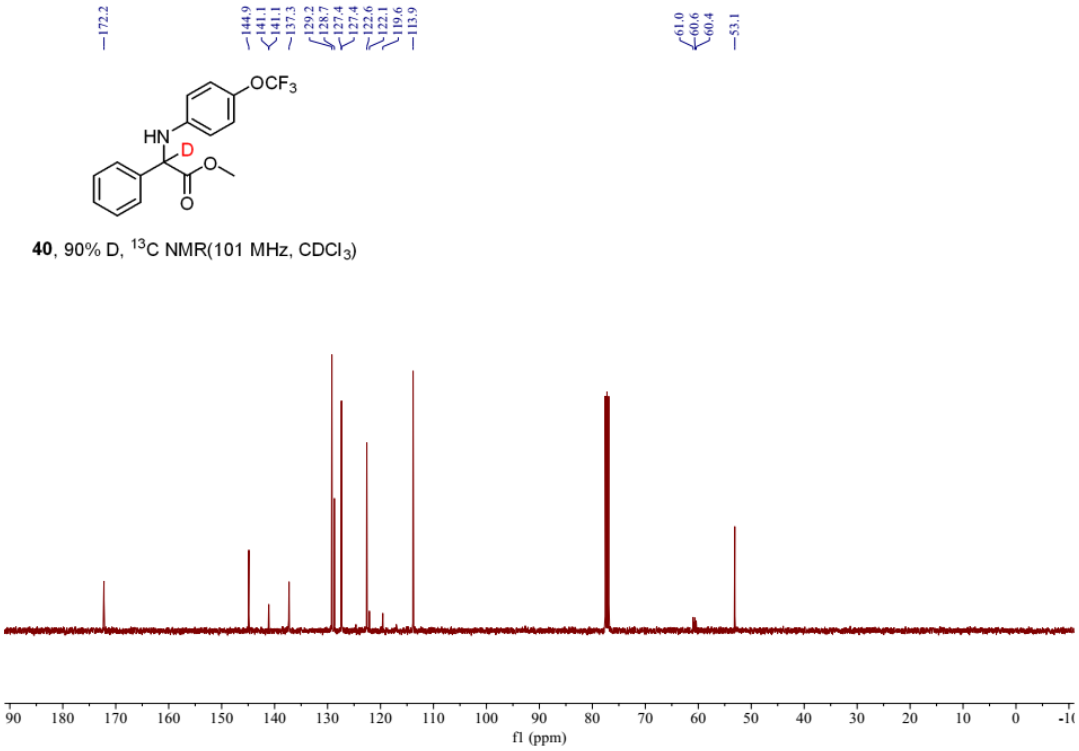
40, 90% D, ^{1}H NMR(400 MHz, $CDCl_3$)



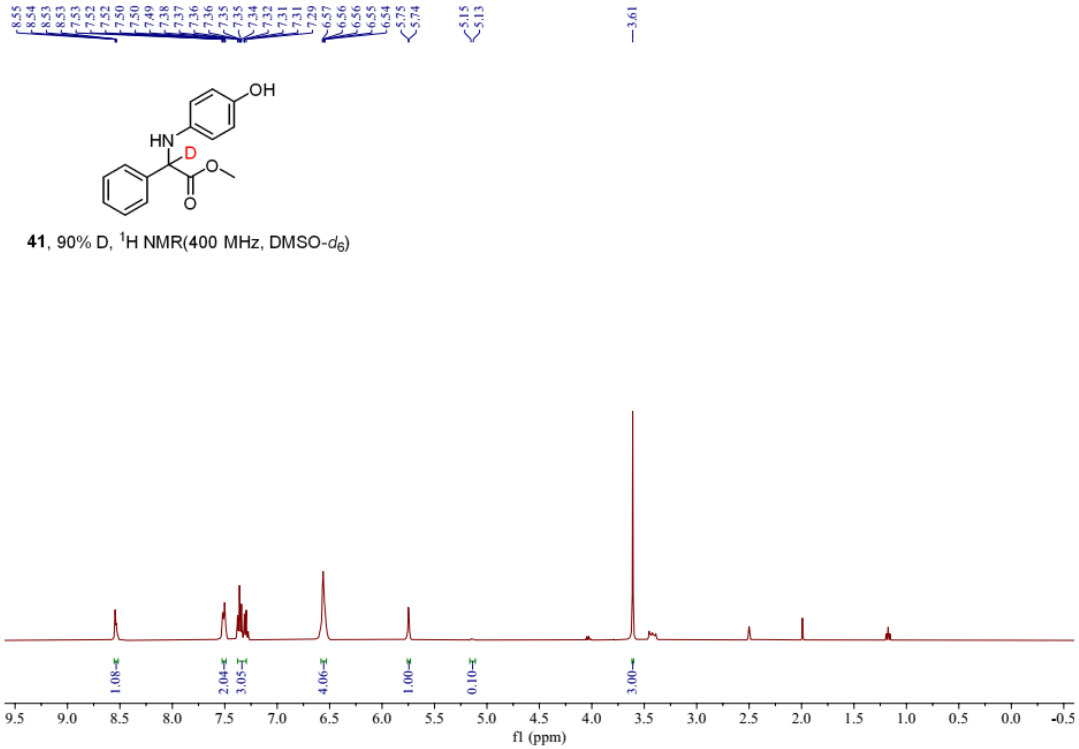


40, 90% D, ^{19}F NMR(376 MHz, $CDCl_3$)

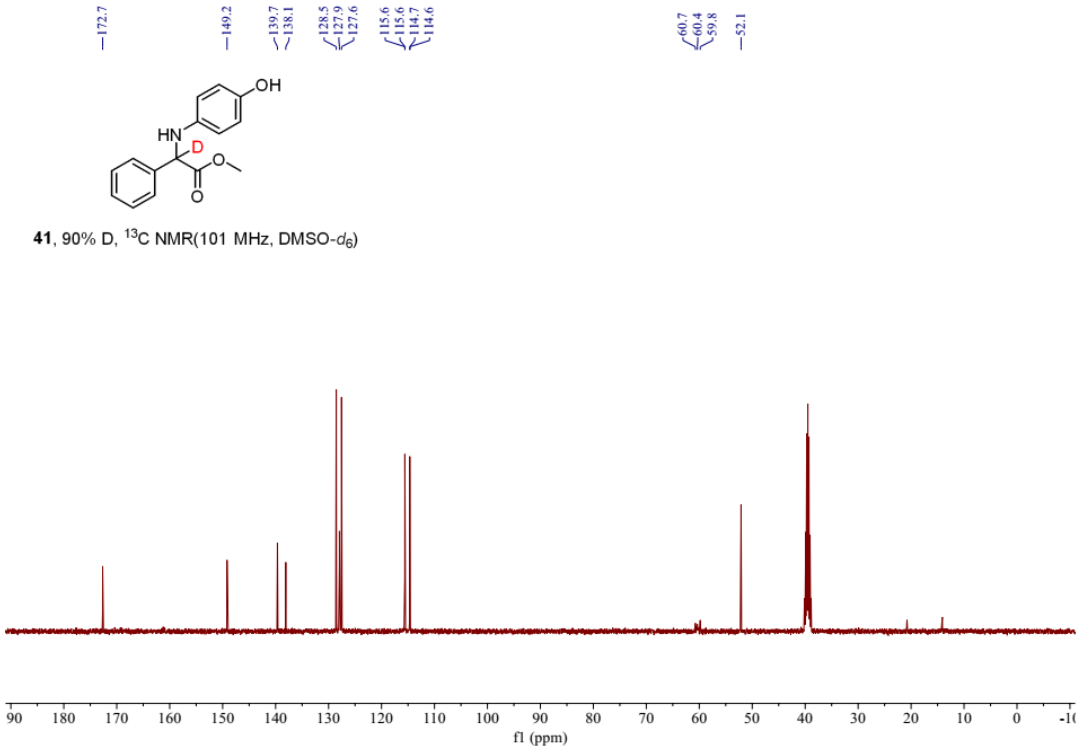




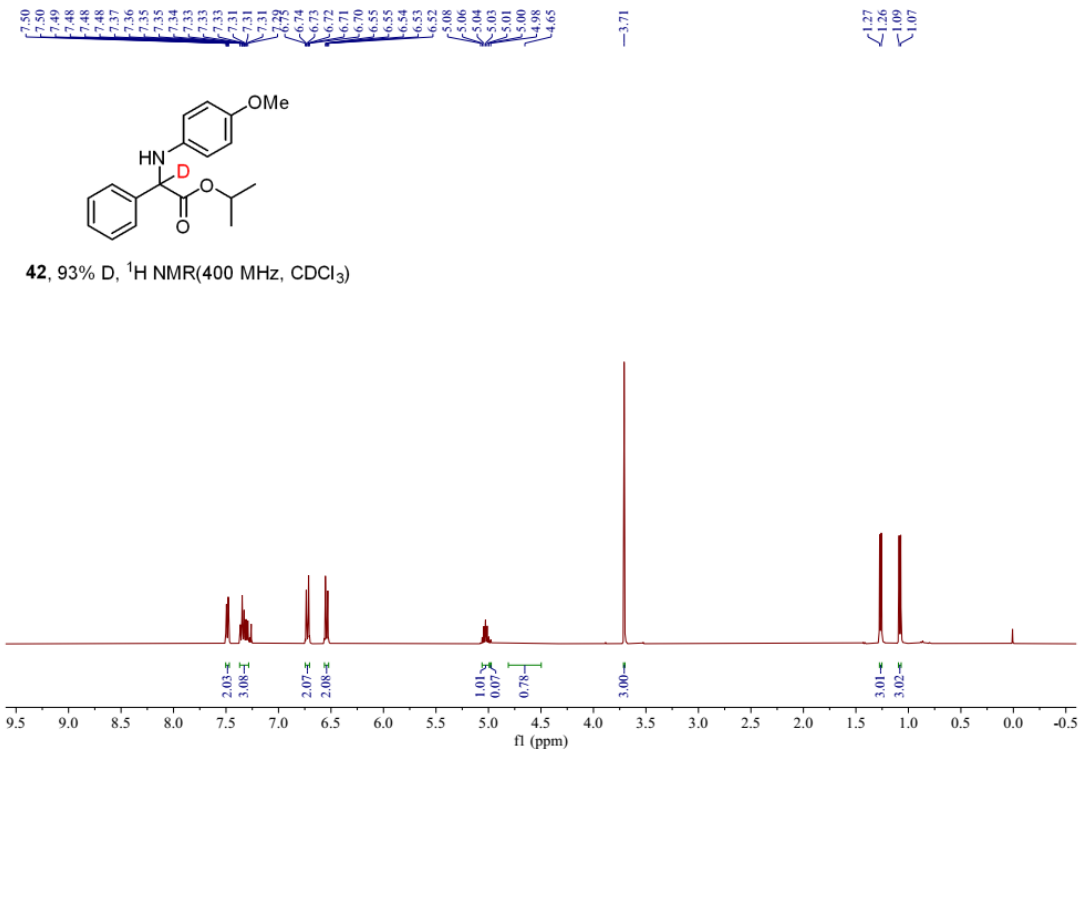
40, 90% D, ^{13}C NMR(101 MHz, $CDCl_3$)



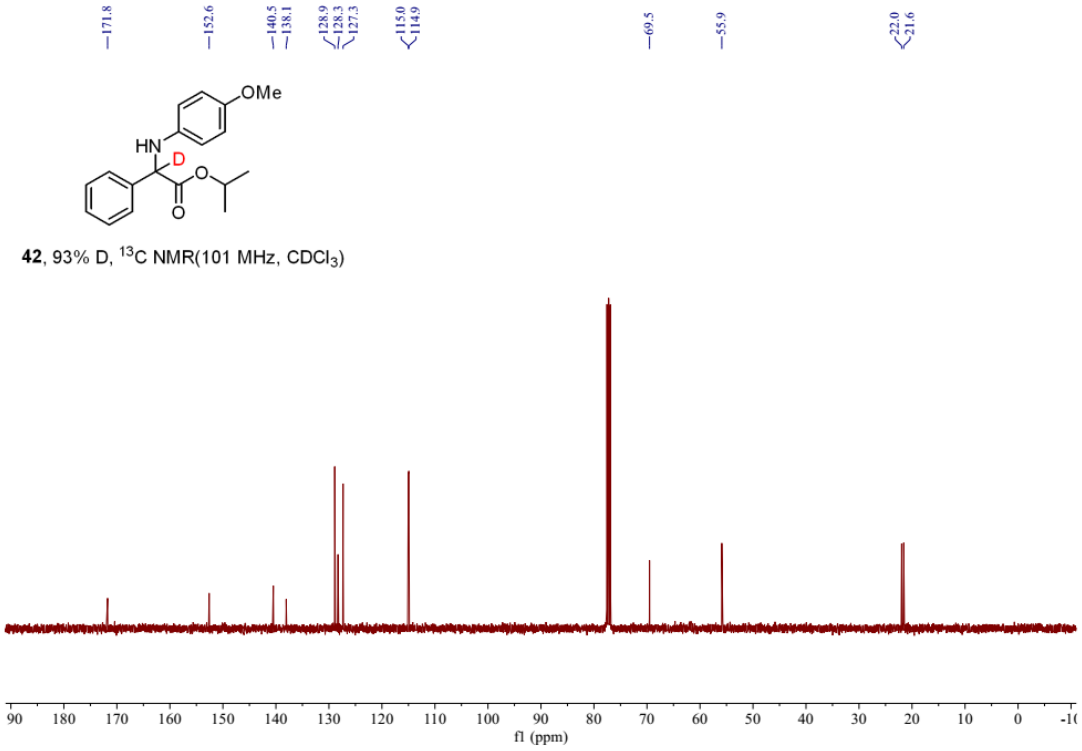
41, 90% D, ^{1}H NMR(400 MHz, DMSO-d_6)



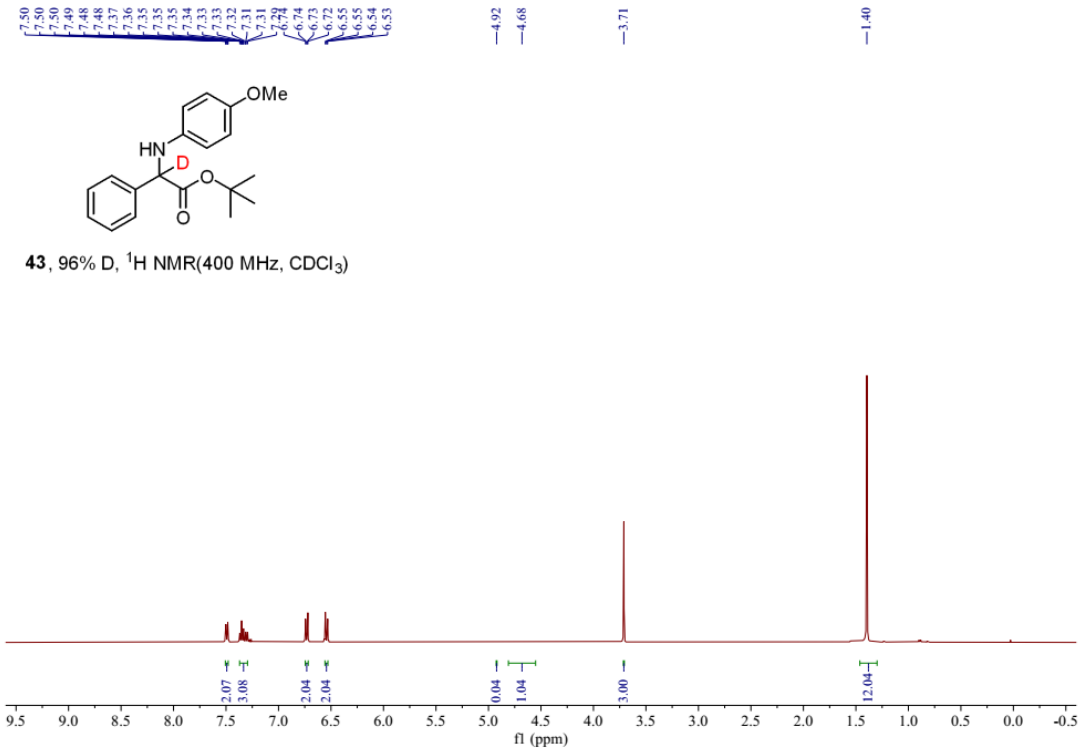
41, 90% D, ^{13}C NMR(101 MHz, DMSO-d_6)



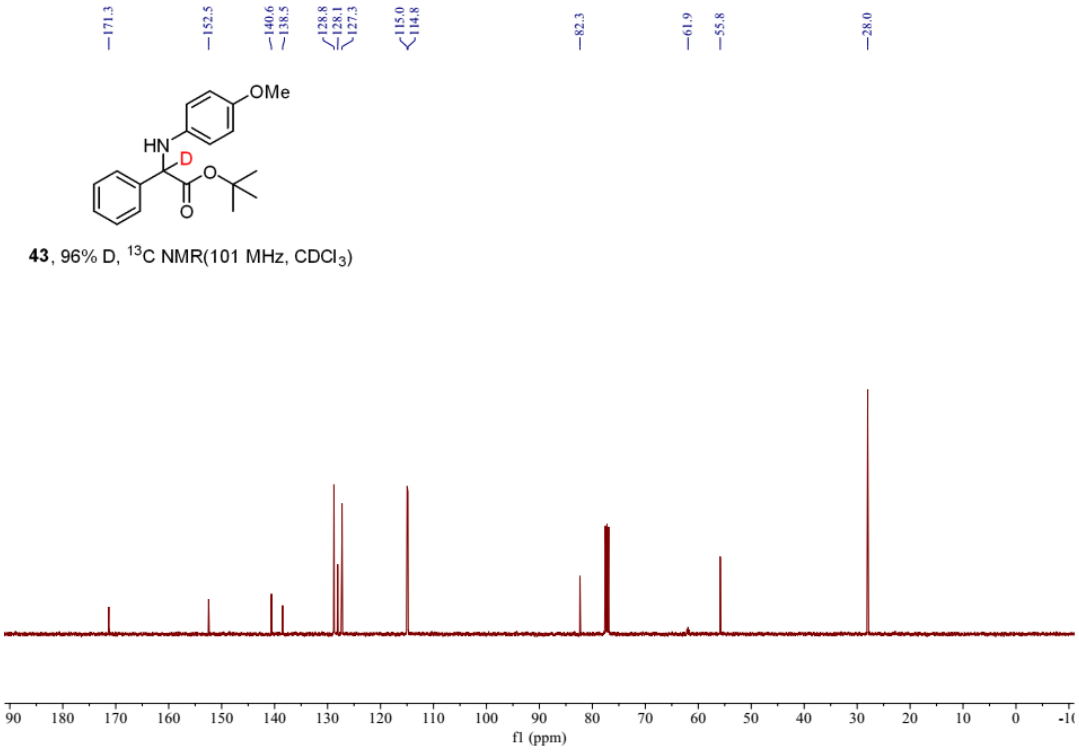
42, 93% D, ^{1}H NMR(400 MHz, $CDCl_3$)



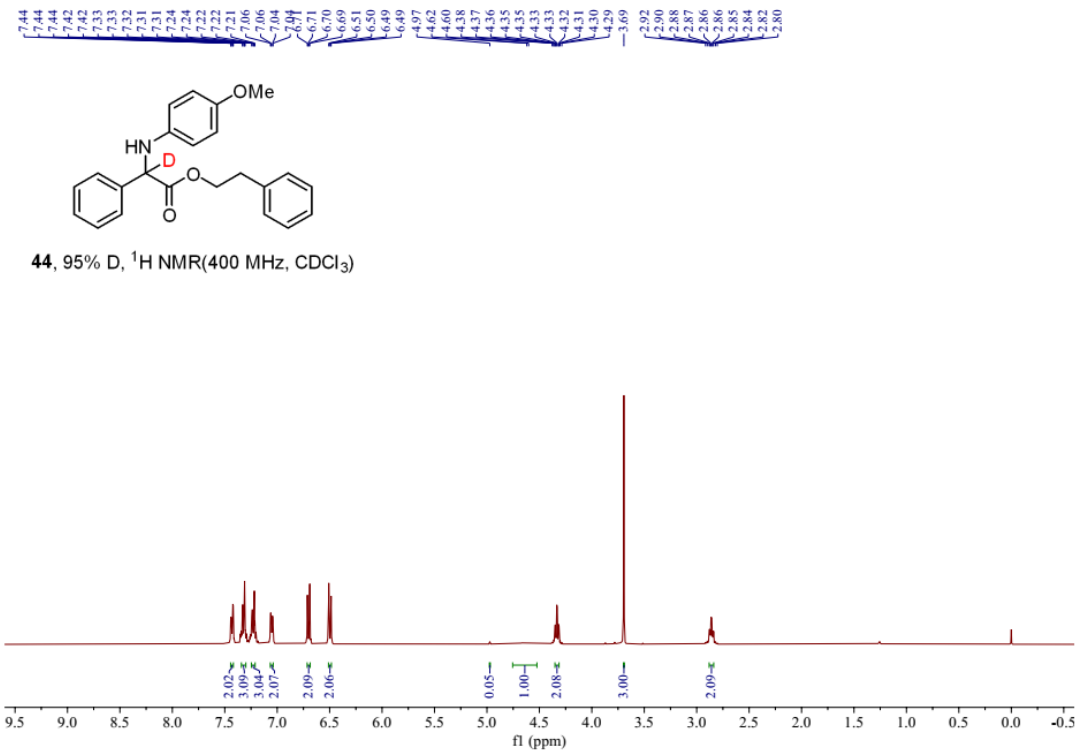
42, 93% D, ^{13}C NMR(101 MHz, $CDCl_3$)



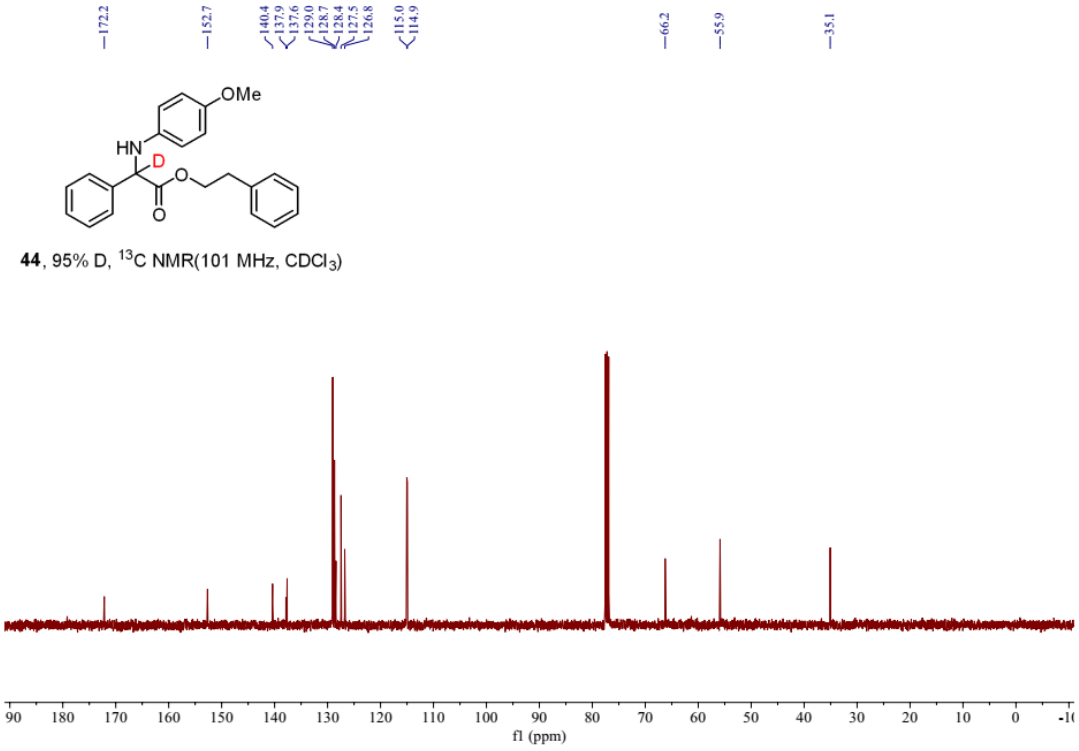
43, 96% D, ^{1}H NMR(400 MHz, $CDCl_3$)



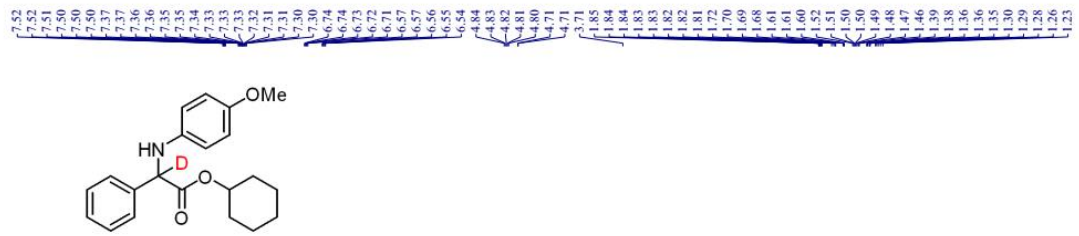
43, 96% D, ^{13}C NMR(101 MHz, $CDCl_3$)



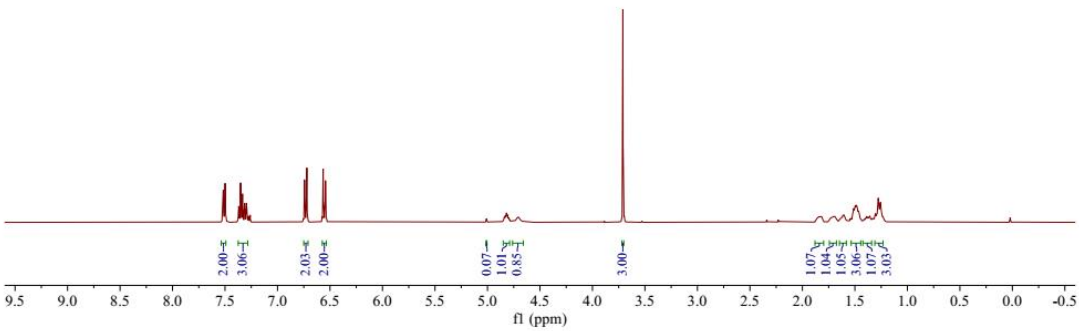
44, 95% D, ^{1}H NMR(400 MHz, $CDCl_3$)

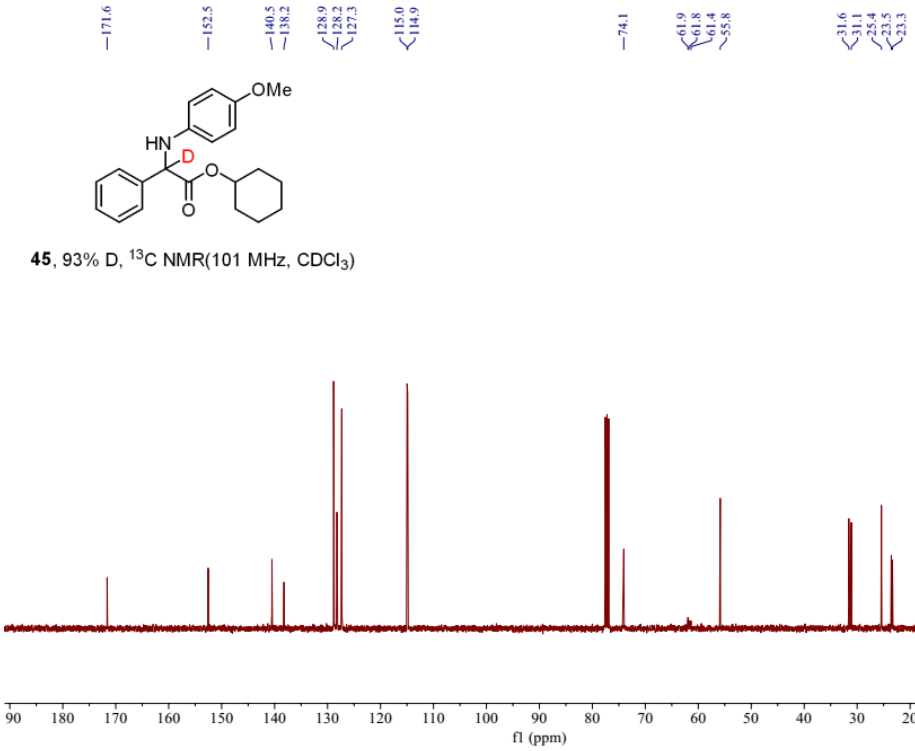


44, 95% D, ^{13}C NMR(101 MHz, $CDCl_3$)

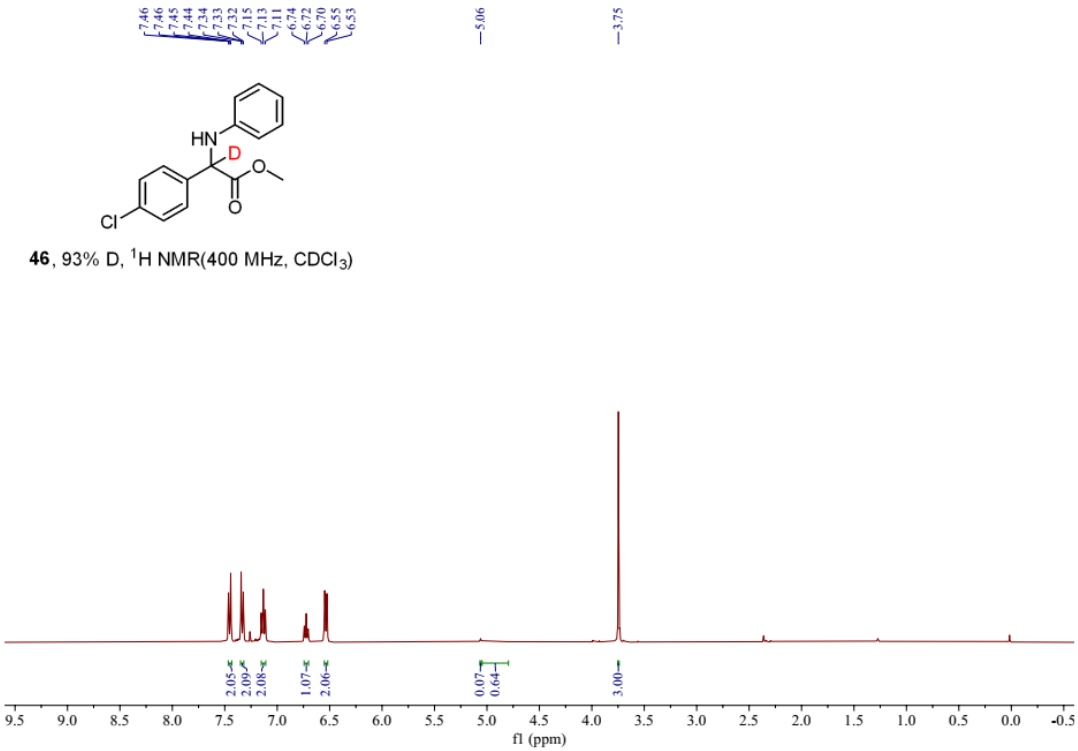


45, 93% D, ^{1}H NMR(400 MHz, $CDCl_3$)

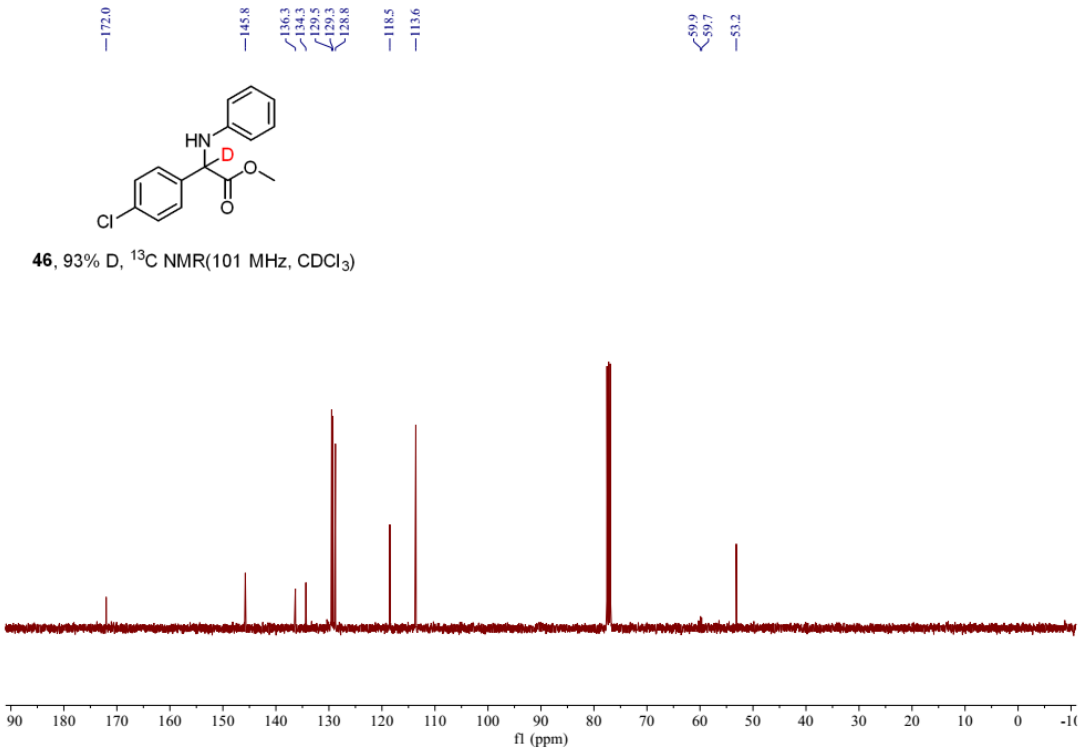




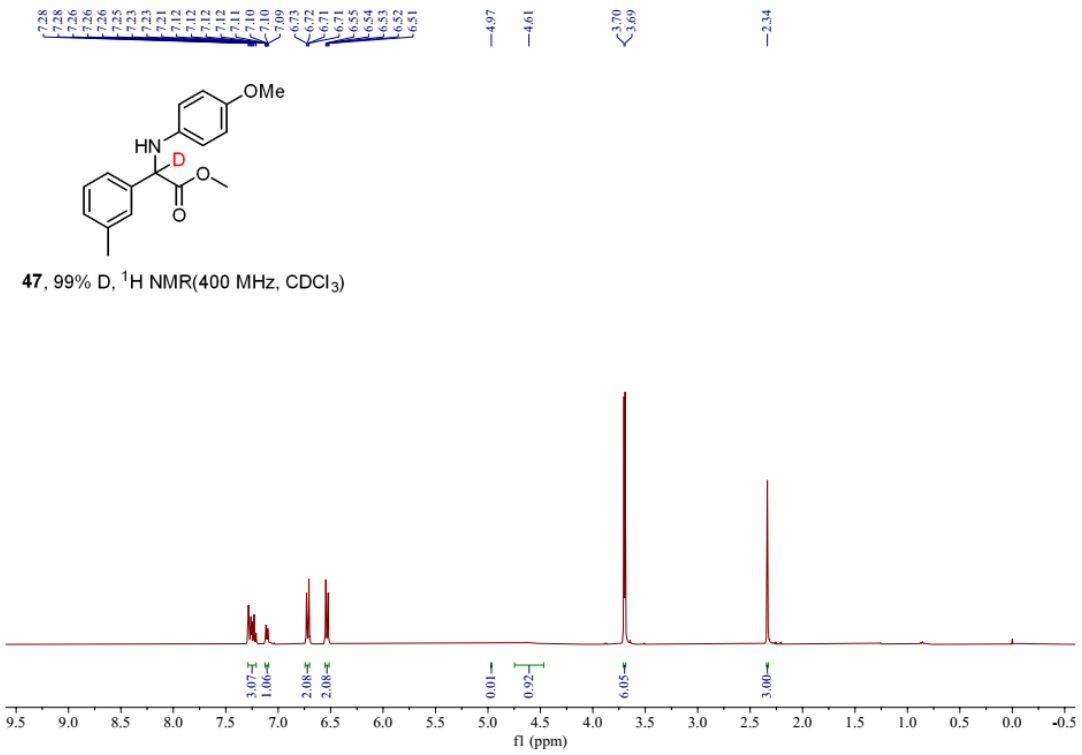
45, 93% D, ^{13}C NMR(101 MHz, $CDCl_3$)



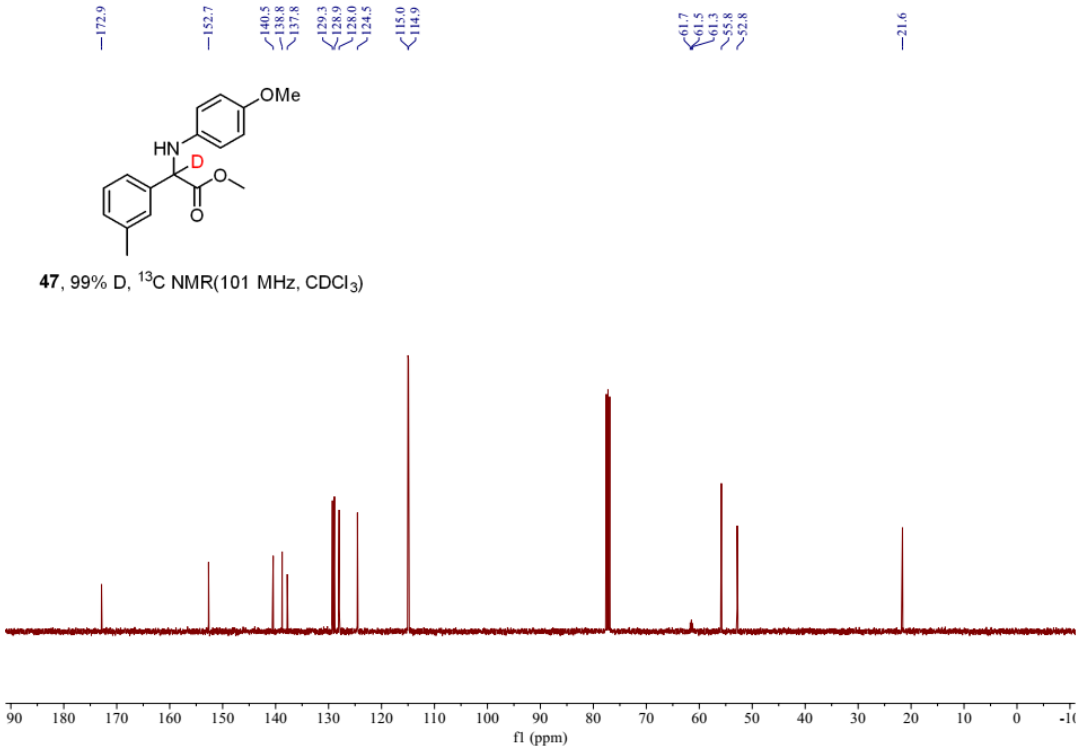
46, 93% D, ^{1}H NMR(400 MHz, $CDCl_3$)



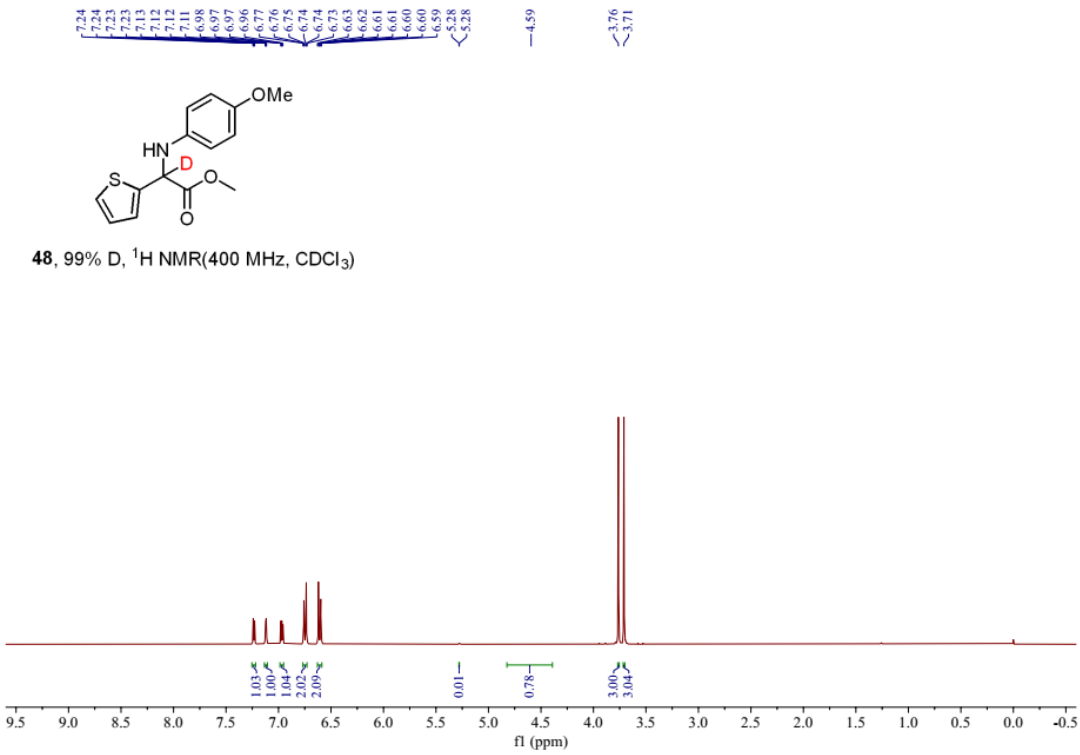
46, 93% D, ^{13}C NMR(101 MHz, $CDCl_3$)



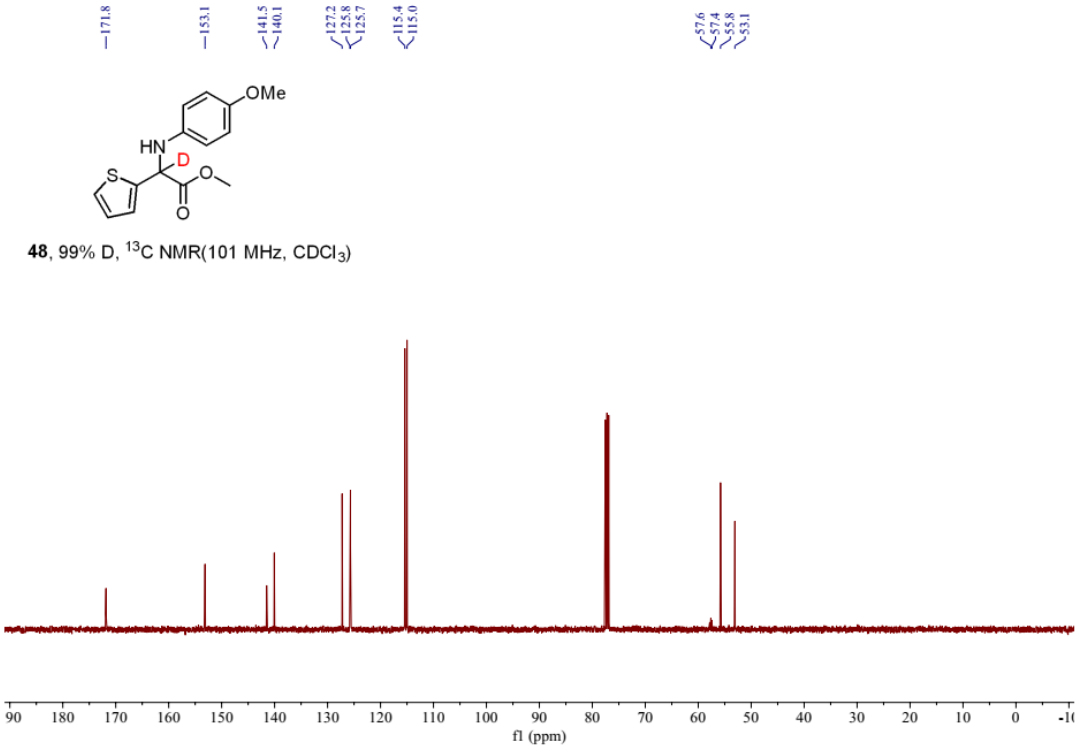
47, 99% D, ^{1}H NMR(400 MHz, $CDCl_3$)



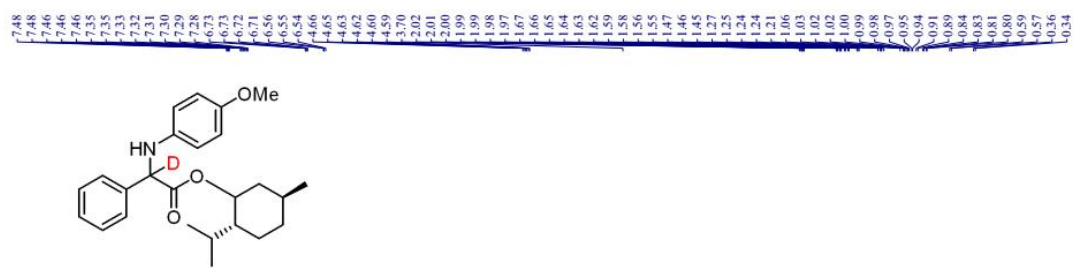
47, 99% D, ^{13}C NMR(101 MHz, $CDCl_3$)



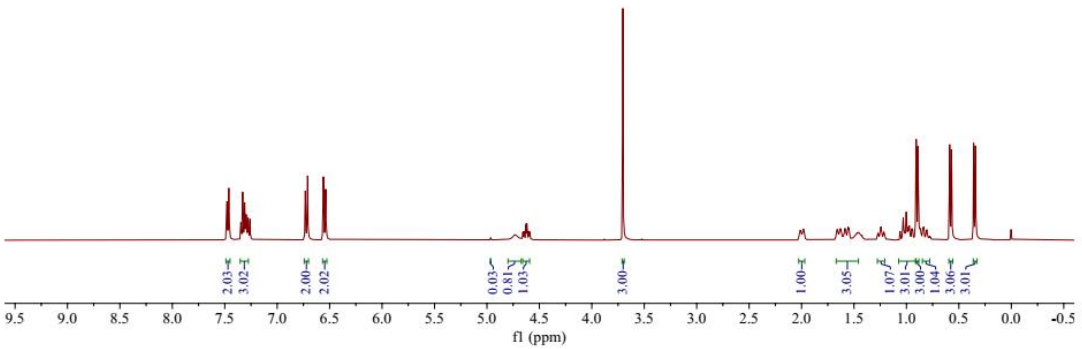
48, 99% D, ^{1}H NMR(400 MHz, $CDCl_3$)

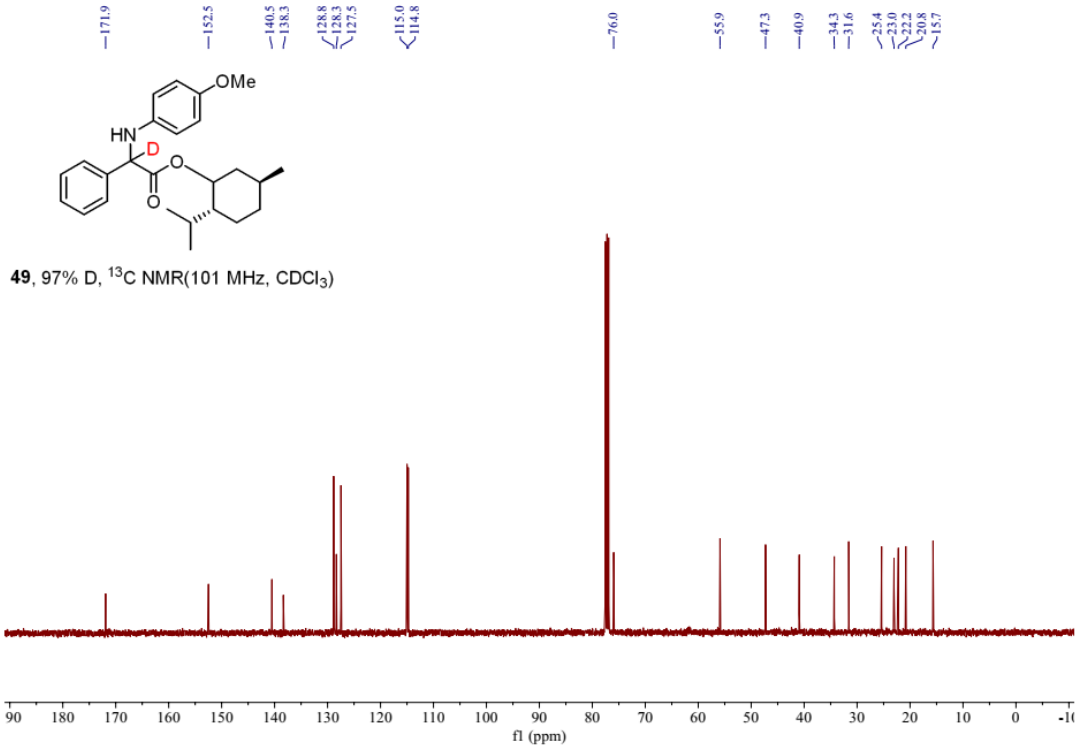


48, 99% D, ^{13}C NMR(101 MHz, $CDCl_3$)

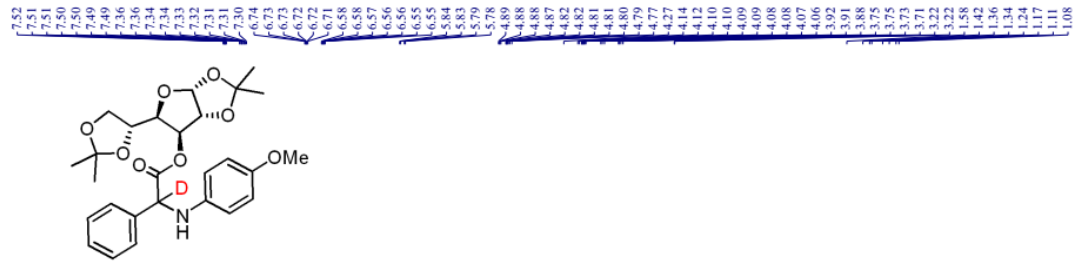


49, 97% D, ^{1}H NMR(400 MHz, $CDCl_3$)

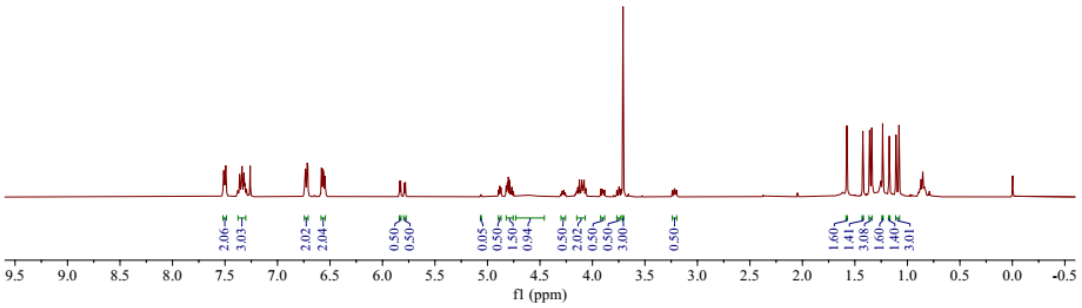


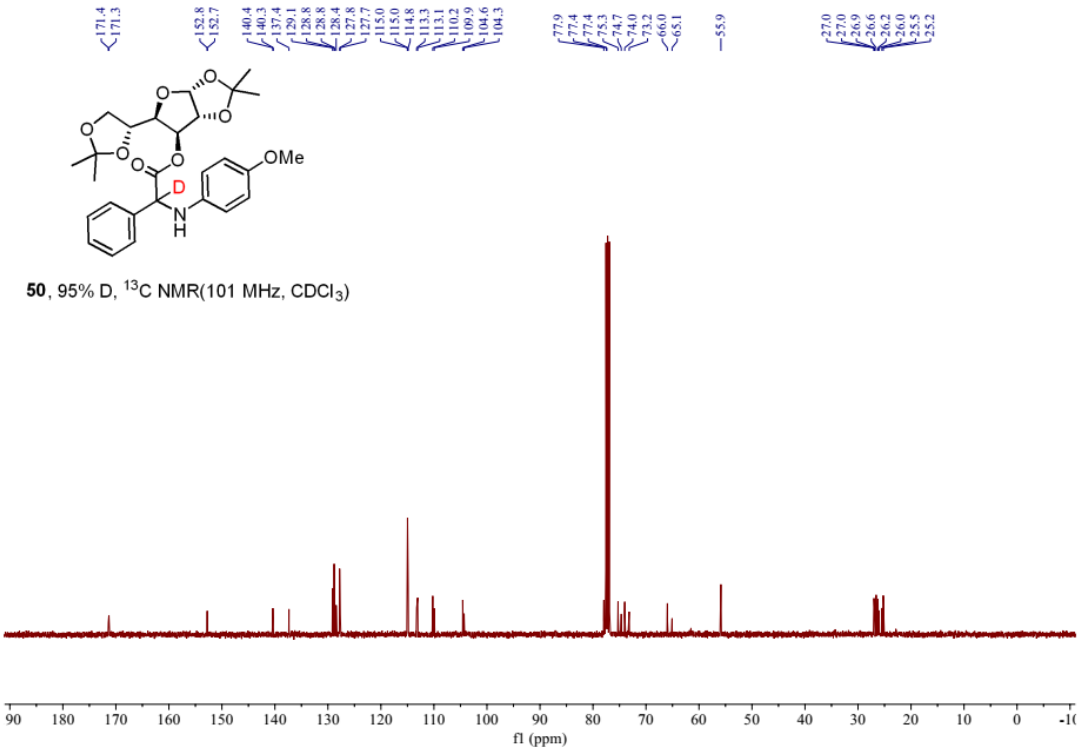


49, 97% D, ^{13}C NMR(101 MHz, $CDCl_3$)

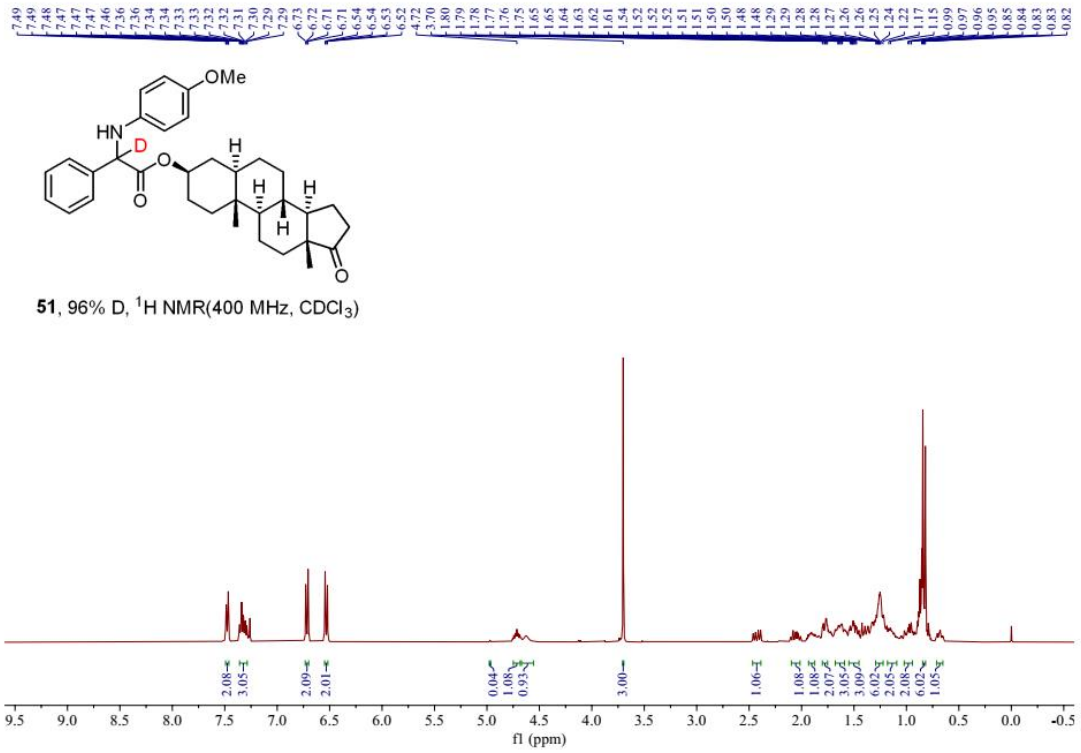


50, 95% D, ^{1}H NMR(400 MHz, $CDCl_3$)



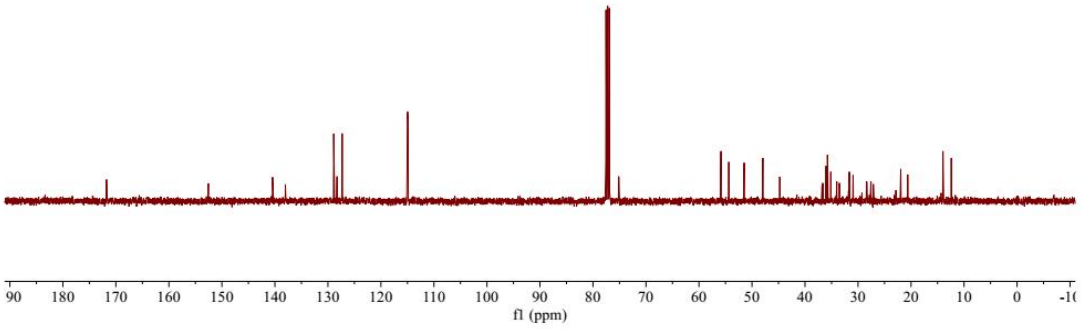


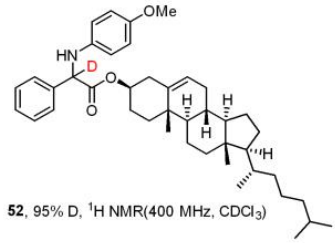
50, 95% D, ^{13}C NMR(101 MHz, $CDCl_3$)



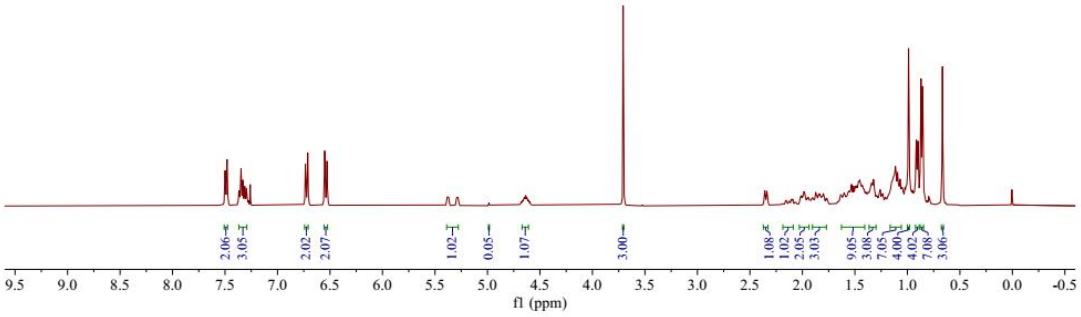
51, 96% D, ^{1}H NMR(400 MHz, $CDCl_3$)

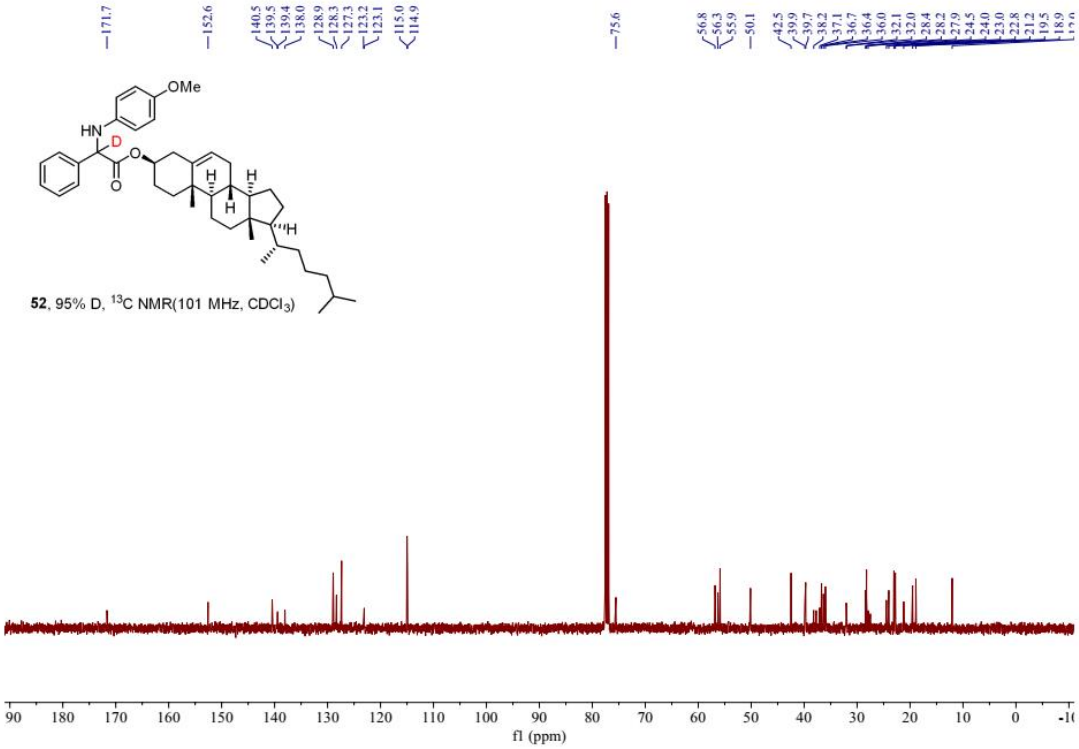
51, 96% D, ^{13}C NMR(101 MHz, $CDCl_3$)



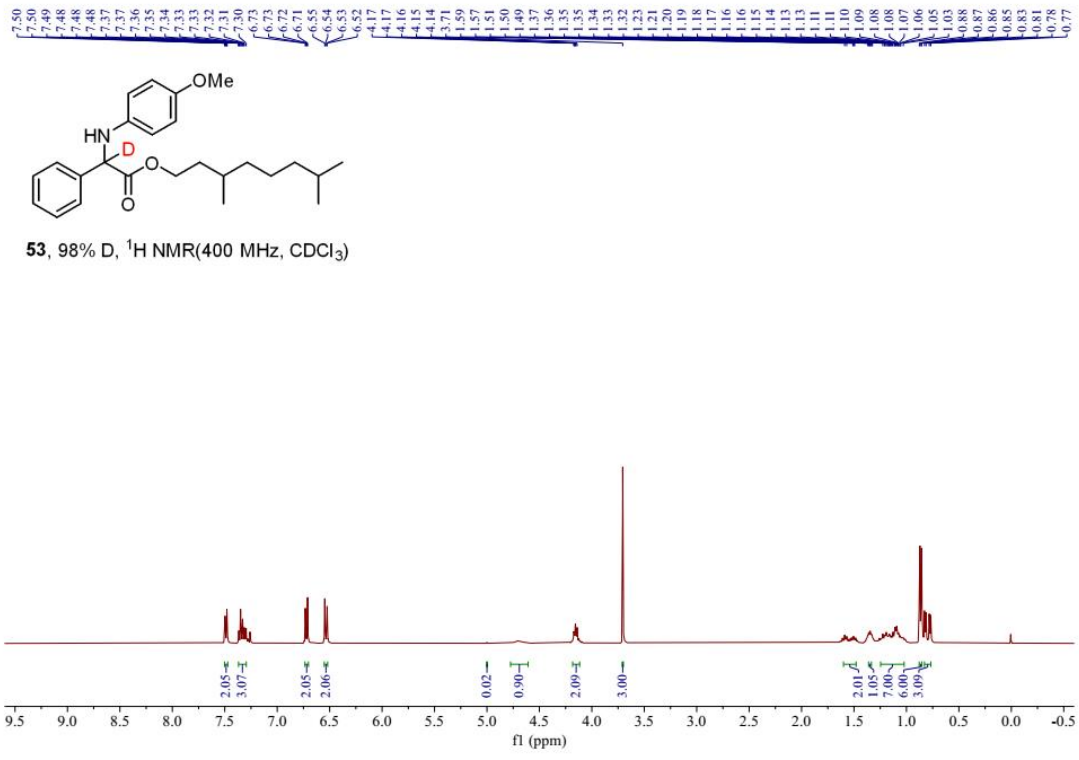


52, 95% D, ^{1}H NMR(400 MHz, $CDCl_3$)

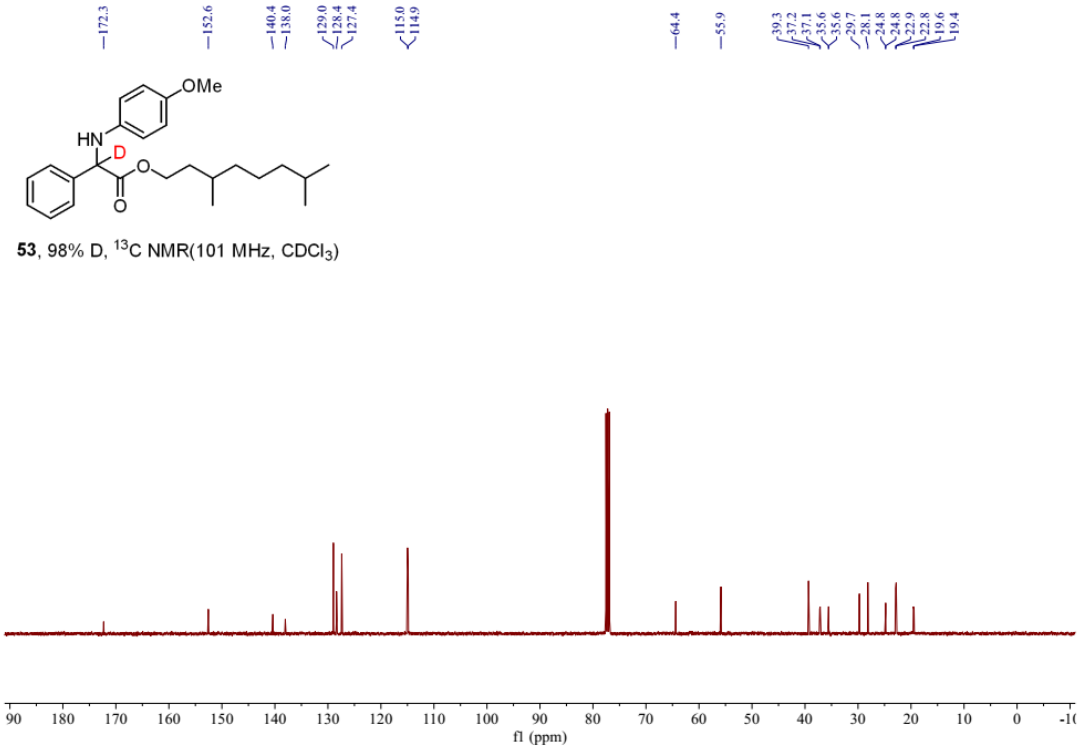




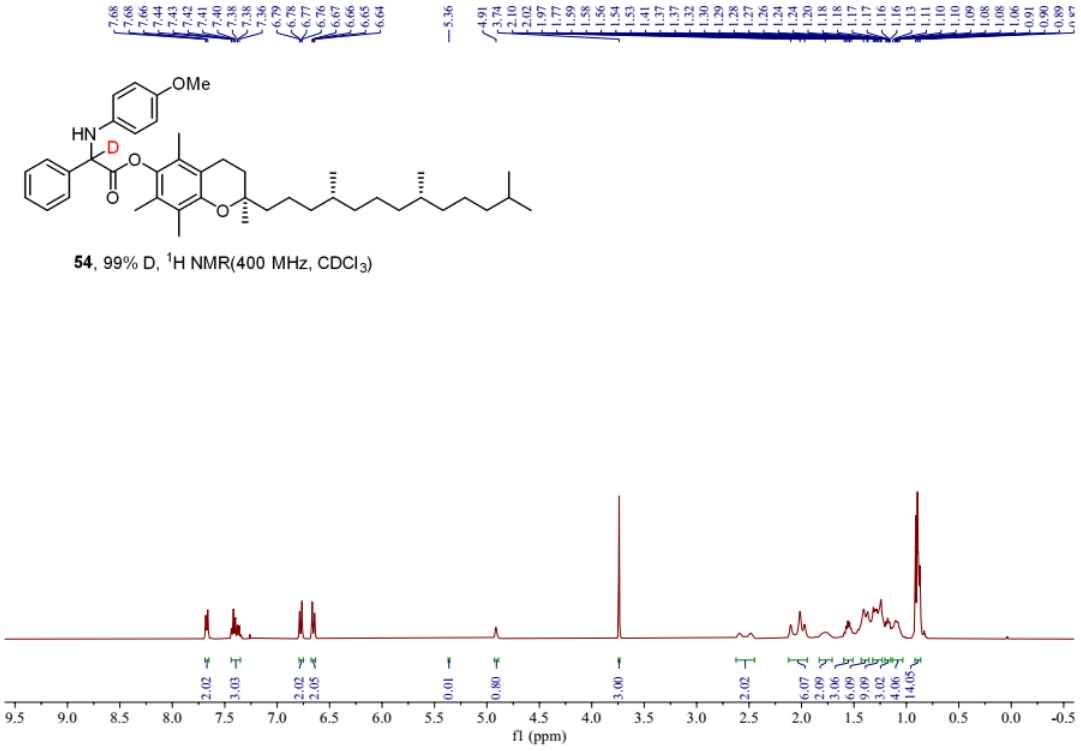
52, 95% D, ^{13}C NMR(101 MHz, $CDCl_3$)



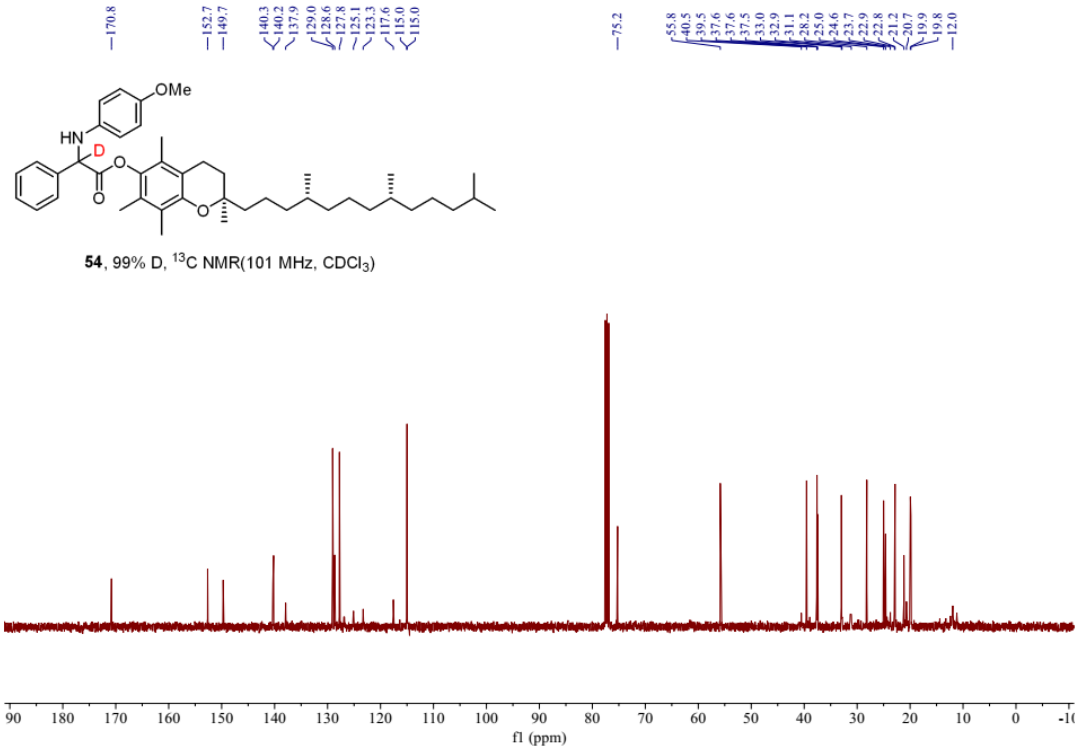
53, 98% D, ^{1}H NMR(400 MHz, $CDCl_3$)



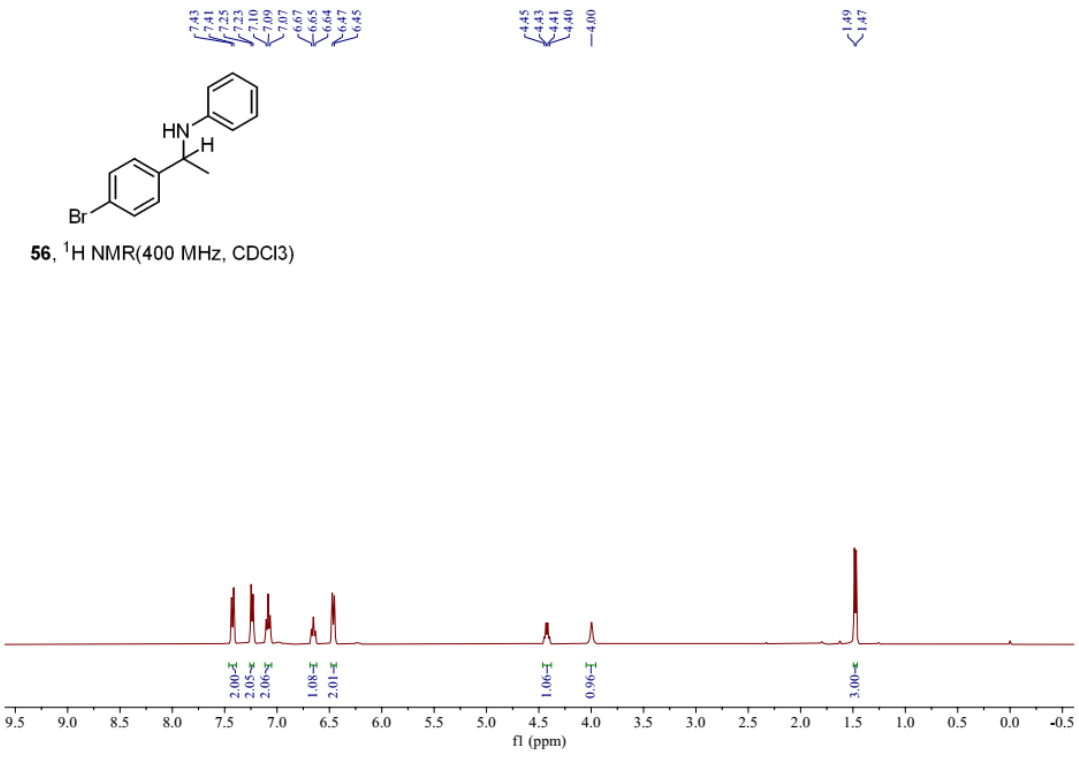
53, 98% D, ^{13}C NMR(101 MHz, $CDCl_3$)



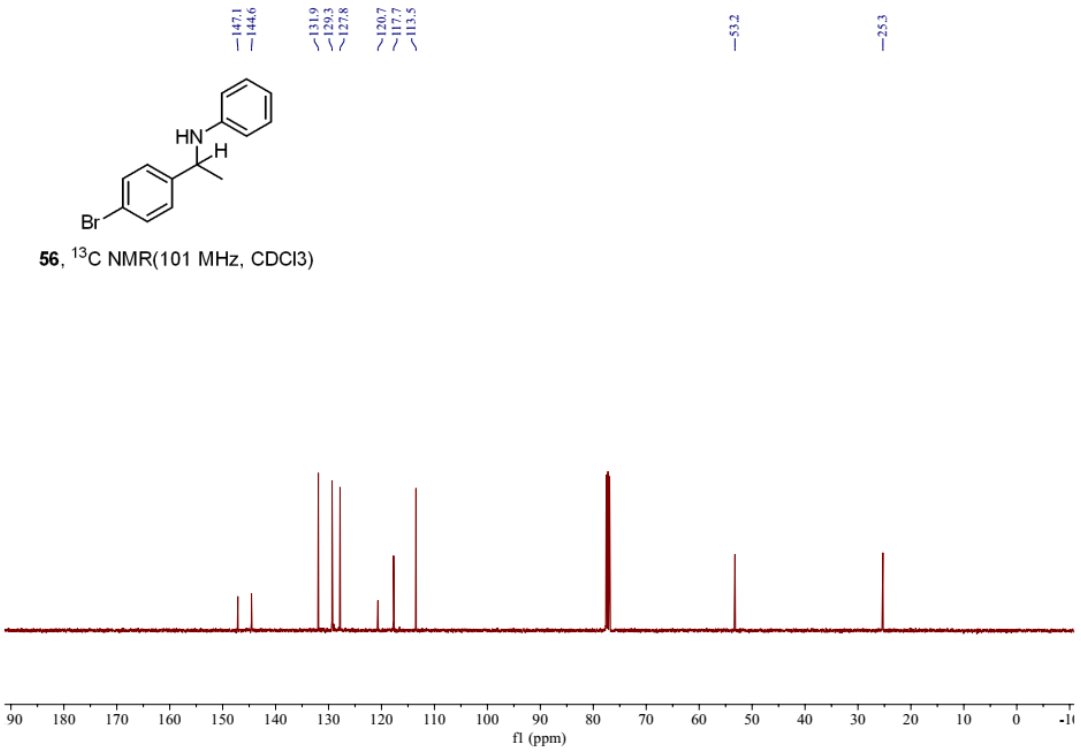
54, 99% D, ^{1}H NMR(400 MHz, $CDCl_3$)



54, 99% D, ^{13}C NMR(101 MHz, $CDCl_3$)



56, ^{1}H NMR(400 MHz, CDCl3)



56, ^{13}C NMR(101 MHz, CDCl3)