A Novel Approach for Synthesizing α-Amino Acids via Formate Mediated Hydrogen Transfer and Carbon Source

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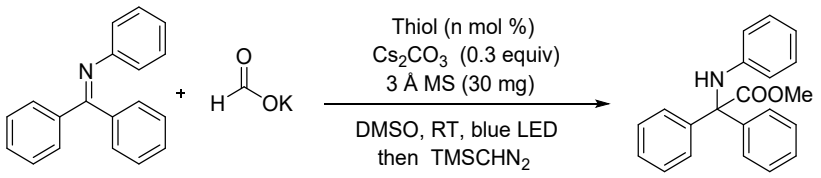
Contents

1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography was performed with 0.20 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (200-300 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker AM-40 spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from TMS scale. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants *J* are quoted in Hz. Data for ^{13}C NMR are reported as chemical shift. High resolution mass spectra (HRMS) were recorded on the Thermo Scientific Exactive Plus (orbitrap) equipped with ESI ionization source. Recycling preparative HPLC was provided by Shimadzu (Model LC20AR).

2. Optimization of reaction conditions.

Table S1 Screening of thiol catalyst.[a]

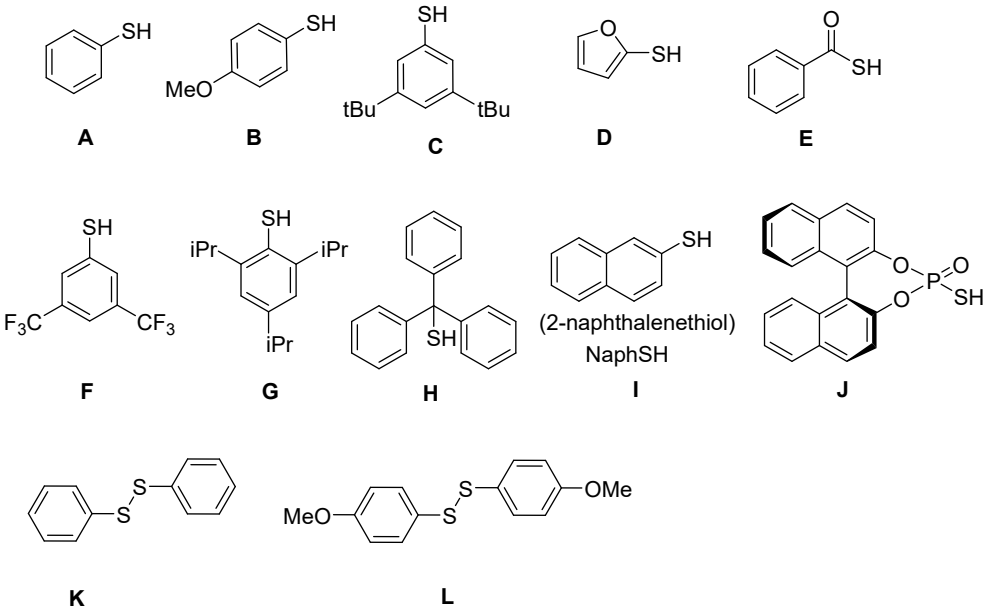


1 **2**

entry	thiol catalyst	n mol %	yield (%)[b]
1	**A**	30	34
2	**B**	30	17
3	**C**	30	10
4	**D**	30	0
5	**E**	30	0
6	**F**	30	6
7	**G**	30	12
8	**H**	30	0
9	**I**	30	68
10	**J**	30	0
11	**K**	30	57
12	**L**	30	45
13	**I** (NaphSH)	20	63
14	**I**	10	72

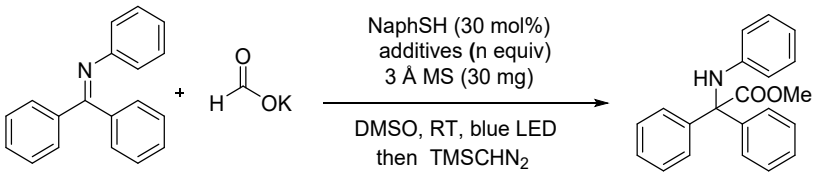
15	**I**	5	78

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), HCOOK (0.2 mmol, 2.0 equiv), thiol catalyst (n mol %), Cs_2CO_3 (0.03 mmol, 0.3 equiv), 3 Å MS (30 mg), DMSO (1.0 mL) at r.t. under the irradiation of blue LEDs (λ = 450-460 nm). [b]Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.



Scheme S1. The screen of thiol catalysts

Table S2 Effect of the additives utilized.[a]

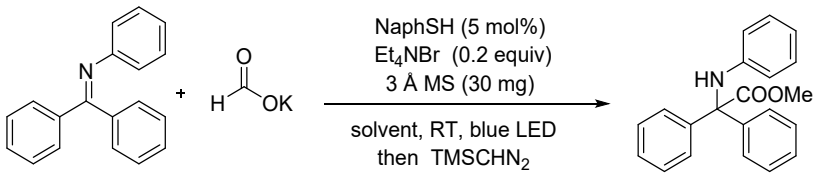


[a]Conditions: **1** (0.1

entry	additives	n equiv	yield (%)[b]
1	-	0.3	68
2	tBu$_4$NBF$_4$	0.3	77
3	tBu$_4$NI	0.3	52
4	Et$_4$NCl	0.3	63
5	tBu$_4$NF	0.3	58
6	tBu$_4$NBr	0.3	67
7	tBu$_4$PBr	0.3	80
8	Et$_4$NBr	0.3	88
9	Et$_4$NBr	0.2	91
10	Et$_4$NBr	1.0	77
11	Et$_4$NBr	2.0	68

mmol, 1.0 equiv.), HCOOK (0.2 mmol, 2.0 equiv), NaphSH (0.05 mmol, 5 mol%), additives (n equiv), 3 Å MS (30 mg), DMSO (1.0 mL) at r.t. under the irradiation of blue LEDs (λ = 450-460 nm). [b]Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

Table S3 Effect of the solvent utilized.[a]

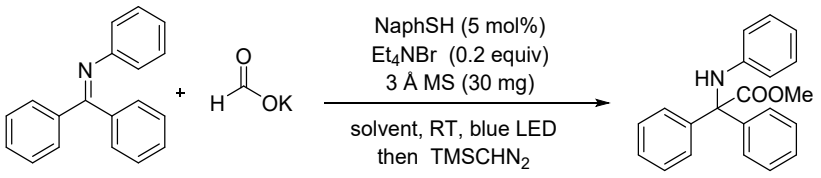


1 **2**

entry	solvent	volume (mL)	yield (%)[a,b]
1	MeCN	1.0	0
2	toluene	1.0	0
3	dixoane	1.0	0
4	THF	1.0	0
5	PhCl	1.0	0
6	DCE	1.0	0
7	DMSO	1.0	91
8	DMSO	0.5	78
9	DMSO	1.5	86
10	DMSO	2.0	74

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), HCOOK (0.2 mmol, 2.0 equiv), NaphSH (0.005 mmol, 5 mol%), Et_4NBr (0.02 mmol, 0.2 equiv), 3 Å MS (30 mg), solvent (n mL) at r.t. under the irradiation of blue LEDs (λ = 450-460 nm). [b]Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

Table S4 Screening of other reaction parameters.[a]



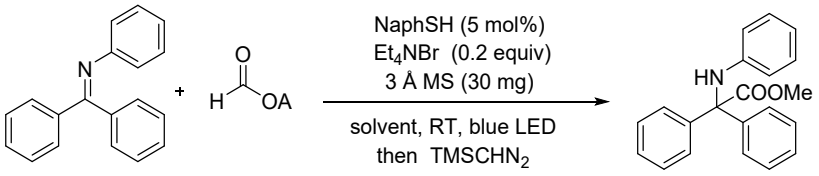
1 **2**

entry	conditionts	yield (%)[b]
1	40°C	77
2	3 Å MS (30 mg)	91
3	4Å MS (30 mg)	76
4	5Å MS (30 mg)	67
5	-	63

6	30 W blue LEDs	87
7	no light	0
8	no 2-naphthalenethiol	0

[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), HCOOK (0.2 mmol, 2.0 equiv), NaphSH (0.005 mmol, 5 mol%), Et_4NBr (0.02 mmol, 0.2 equiv), MS (n mg), DMSO (1.0 mL) at r.t. under the irradiation of blue LEDs (λ = 450-460 nm). [b]Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

Table S5 Screening of other formate.[a]

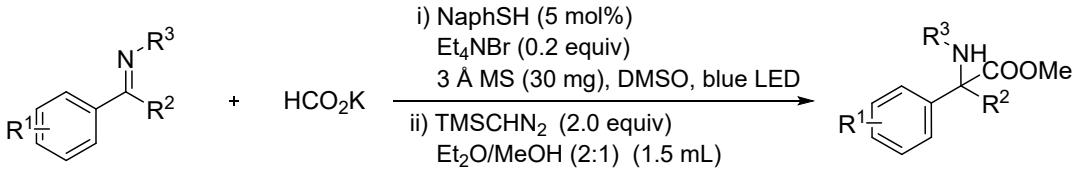


1 **2**

entry	HCOOA	yield (%)[b]
1	HCOOK	91
2	HCOONa	71
3	HCOOLi	26
4	HCOOCs	34
5	$HCOONH_4$	7

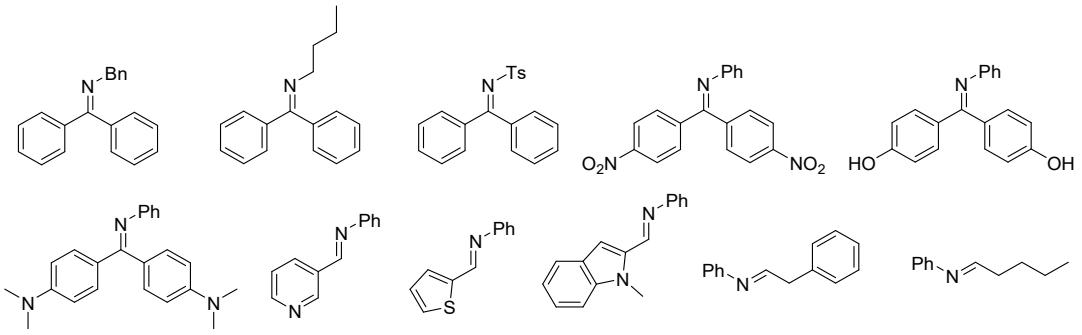
[a]Conditions: **1** (0.1 mmol, 1.0 equiv.), HCOOA (0.2 mmol, 2.0 equiv), NaphSH (0.005mol, 5 mol%), Et_4NBr (0.02 mmol, 0.2 equiv), 3 Å MS (30 mg), DMSO (1.0 mL) at r.t. under the irradiation of blue LEDs (λ = 450-460 nm). [b]Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

3. General procedure for the synthesis of α-amino acid derivatives.



A dried 10 mL reaction tube was charged with the imines (0.1 mmol, 1.0 equiv), formate (0.2 mmol, 2.0 equiv), activated 3 Å molecular sieves (30 mg), NaphSH (5 mol %, 0.8 mg), and Et_4NBr (0.02 mmol, 0.2 equiv). Then DMSO (1.0 mL) was added via a syringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was stirred at 1400 RPM for 24 h under irradiation by blue LEDs (λ = 450-460 nm). 2N HCl (2.0 mL) was added and then the reaction mixture was extracted with ethyl acetate (3 x 5 mL). The organic layer were removed using a rotary evaporator under reduced pressure. The crude residue was dissolved in 1.5 mL MeOH/Et_2O (1:2), $TMSCHN_2$ (0.15 mL, 0.3 mmol, 2 M in hexanes) was added dropwisely. The mixture was stirred

at ambient temperature until the completion of the methylation reaction. All the volatile materials were concentrated and the crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product.



Scheme S2. Unsuccessful examples.

3.1 DFT calculations for the tosylated ketimine and phenyl ketimine 1

The lowest reduction potential of the tosylated ketimine was -2.05v,[1] which indicated that NaphS- could reduce it. However, the tosylated ketimine didn't work in this reaction, , from which we performed DFT calculations. We calculated the charge density of C radical of 0.177e and 0.103e for the tosylated ketimine and phenyl ketimine **1**, respectively, from Gaussion 09w (b3lyp, 61-31d*). These results suggested that the C radical of the phenyl ketimine **1** was more stable than the C radical of the tosylated ketimine. Furthermore, the C radical of the phenyl ketimine **1** attached three conjugated groups in the optimization model, which makes the charge density of the C radical for the phenyl ketimine **1** be more delocalized[2] and improved the stability of the C radical. Therefore, we thought the stability of free radicals could play an important role in reactions involving free radicals.

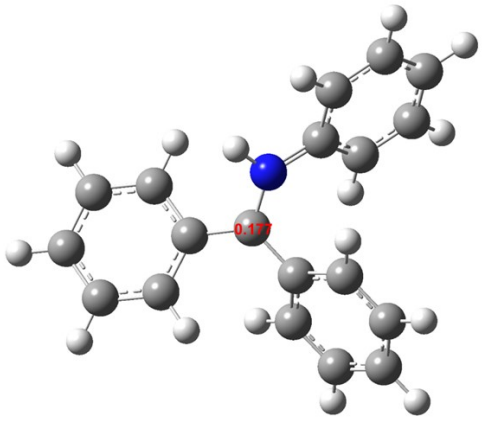


Figure S1. The optimization model of phenyl ketimine **1**.

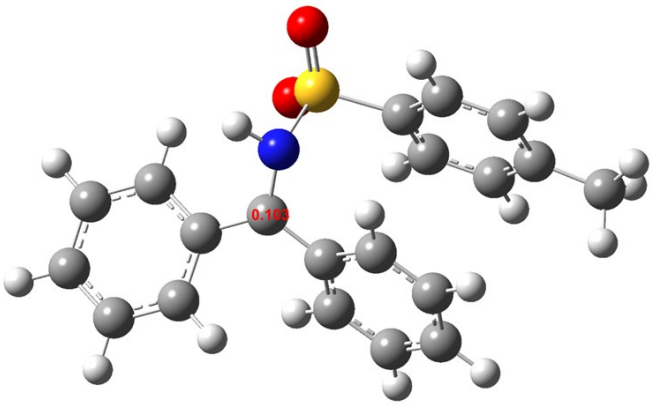
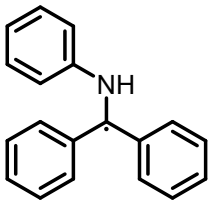


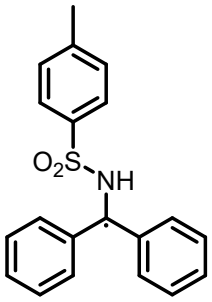
Figure S2. the optimization model of the tosylated ketimine.

Cartesian coordinates (Å) of all optimized structures.



C	-4.156729	-0.757825	0.732967
C	-4.156780	-2.152633	0.732941
C	-2.948779	-2.850046	0.733038
C	-1.740845	-2.152624	0.733038
C	-1.740784	-0.757840	0.732967
C	-2.948795	-0.060403	0.732967
C	-0.444329	-0.009365	0.732891
C	-0.365351	0.850296	-0.490120
C	-0.238223	2.233493	-0.363260
C	-0.164758	3.034481	-1.502853
C	-0.218302	2.452224	-2.769190
C	-0.345332	1.069043	-2.896059
C	-0.418896	0.268038	-1.756458
N	0.673449	-0.964075	0.732906
C	1.866841	-0.541499	0.732850
C	2.927422	-1.447401	0.732771
C	4.242276	-0.981773	0.732830
C	4.496453	0.389685	0.732847
C	3.435897	1.295579	0.732830
C	2.121018	0.829959	0.732866
H	-5.109350	-0.207813	0.732987
H	-5.109414	-2.702623	0.732845
H	-2.948762	-3.950046	0.733114
H	-0.788226	-2.702639	0.733094
H	-2.948805	1.039597	0.732967

H	-0.195902	2.692651	0.635431
H	-0.064595	4.125339	-1.402863
H	-0.160344	3.083915	-3.667860
H	-0.387500	0.609880	-3.894754
H	-0.519134	-0.822811	-1.856454
H	0.482082	-1.996489	0.732964
H	2.726944	-2.528978	0.732661
H	5.078728	-1.696159	0.732864
H	5.533367	0.756849	0.732874
H	3.636385	2.377154	0.732787
H	1.284570	1.544350	0.732909



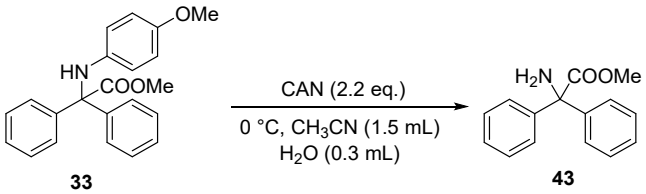
C	-4.426194	-1.341753	1.752564
C	-4.426246	-2.736561	1.752538
C	-3.218244	-3.433974	1.752635
C	-2.010310	-2.736552	1.752635
C	-2.010249	-1.341768	1.752564
C	-3.218260	-0.644331	1.752564
C	-0.713794	-0.593293	1.752487
C	-0.634816	0.266367	0.529477
C	-0.507688	1.649564	0.656337
C	-0.434223	2.450553	-0.483256
C	-0.487768	1.868295	-1.749594
C	-0.614797	0.485114	-1.876462
C	-0.688361	-0.315890	-0.736861
N	0.379651	-1.527221	1.752503
S	1.978382	-0.961115	1.752427
C	2.258850	0.033354	0.290760
C	2.920500	1.256721	0.396033
C	3.138931	2.031694	-0.742983
C	2.695817	1.583205	-1.987173
C	2.034263	0.359815	-2.092467
C	1.815737	-0.415136	-0.953430
C	2.930288	2.414943	-3.209566
O	2.890875	-2.087995	1.752458
O	2.205422	-0.156215	2.936948
H	-5.378815	-0.791742	1.752584

H	-5.378879	-3.286552	1.752442
H	-3.218228	-4.533974	1.752711
H	-1.057691	-3.286567	1.752691
H	-3.218271	0.455669	1.752564
H	-0.465367	2.108722	1.655028
H	-0.334060	3.541410	-0.383266
H	-0.429810	2.499987	-2.648263
H	-0.656966	0.025951	-2.875157
H	-0.788599	-1.406740	-0.836857
H	0.193752	-2.530137	1.752559
H	3.270030	1.610351	1.377243
H	3.660643	2.996541	-0.660004
H	1.684869	0.006123	-3.073704
H	1.293957	-1.379947	-1.036404
H	3.468207	3.347420	-2.926901
H	3.544625	1.838973	-3.937314
H	1.952840	2.676694	-3.673086

3.2 Gram-Scale Preparation of 2.

A dried 100 mL reaction tube was charged with N,1,1-triphenylmethanimine (4.0 mmol, 1.0 equiv, 1.028 g), potassium formate (8.0 mmol, 2.0 equiv, 0.672 g), activated 3 Å molecular sieves (1.2 g), NaphSH (5 mol %, 32 mg), and Et_4NBr (0.8 mmol, 0.2 equiv, 0.168 g). Then DMSO (40 mL) was added via a syringe. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was stirred at 1400 RPM for 48 h under irradiation by blue LEDs (λ = 450-460 nm). 2N HCl (60 mL) was added and then the reaction mixture was extracted with ethyl acetate (3 x 60 mL). The organic layer were removed using a rotary evaporator under reduced pressure. The crude residue was dissolved in 60 mL MeOH/Et_2O (1:2), $TMSCHN_2$ (6 mL, 0.3 mmol, 2 M in hexanes) was added dropwise. The mixture was stirred at ambient temperature until the completion of the methylation reaction. All the volatile materials were concentrated and the crude mixture was purified by flash chromatography (silica gel, mixtures of petroleum/ethyl acetate) to afford the pure product **2** (1.052 g, 83% yield).

4. Experimental procedure for CAN mediated deprotection of 33.



33 **43**

To a CH_3CN (1.5 mL) solution of **33** (150 mg, 0.2 mmol, 1 eq) at 0 °C was added a H_2O (0.4 mL) solution

of cerium ammonium nitrate (CAN, 667 mg, 0.44 mmol, 2.2 eq). The resulting dark solution was stirred at 0 °C for 30 min before treated with 2N HCl to pH = 1. The aqueous phase was washed with EtOAc (5 mL × 3) and brought to basic by saturated $NaHCO_3$. The resulting suspension was then extracted with CH_2Cl_2 (5 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4. Methyl 2-amino-2,2-diphenylacetate **43** (78.0 mg, 86% yield) was obtained by removal of the solvent under vacuum.[3]

5. Mechanism studies

5.1 NaphSK solubility test.

We prepared MeCN-d_3, DMSO-d_6 and $CDCl_3$ solutions of NaphSH and HCOOK, and DMSO solution of NaphSH, respectively, and performed NMR hydrogen spectroscopy. By ^{1}H NMR spectrum control, the characteristic hydrogen chemical shift of NaphSH shifted to the lower field with increasing solvent polarity, and the characteristic hydrogen of NaphSH disappeared in the DMSO basic solution. This indicates that in the polar solvent DMSO base solution, NaphSH mostly exists in the form of thiol negative ions.

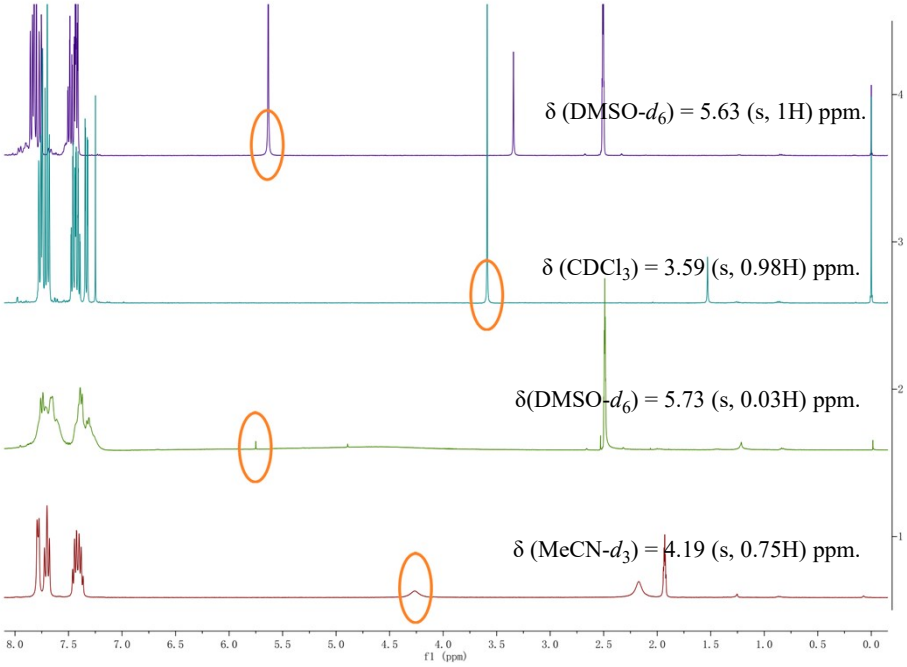


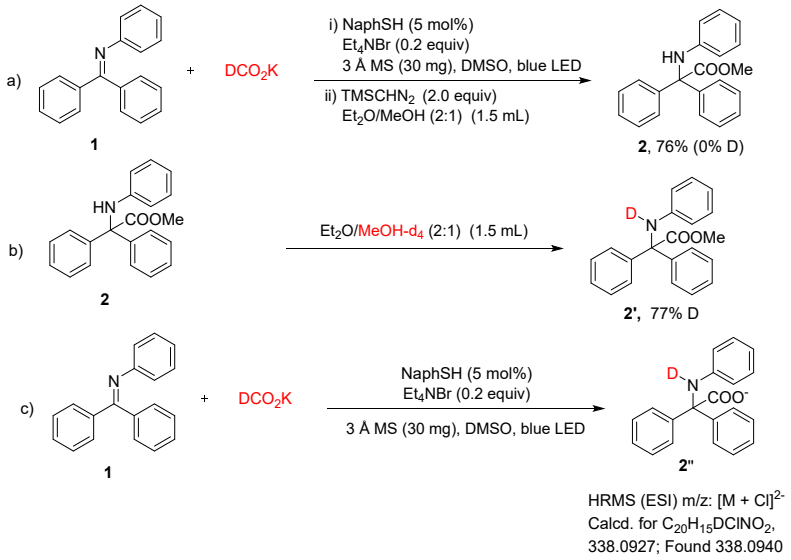
Figure S3. NMR hydrogen spectra of NaphSH in MeCN-d_3, DMSO-d_6, $CDCl_3$ basic solution and DMSO-d_6 solution.

5.2 Specific isotope labeling of α-amino acid derivative.

DCO_2K.[4] To DCO_2D (Formic-*d* 99$^+$ atom % D, acid-*d* 90$^+$ atom % D) (250 mg, 5.2 mmol) was added K_2CO_3 (552 mg, 4.0 mmol), and the mixture was stirred 5 h at 100 °C in an argon atmosphere. The mixture was concentrated in vacuo to yield 333 mg (98%) of the corresponding DCO_2K as a

colorless solid.

Under standard conditions, DCO_2K was added to the reaction system instead of HCO_2K. When the reaction was finished, the reaction system was acidified and esterified, however, the isolated product was not deuterated (Scheme S3a). Subsequently, product **2** (0.1 mmol) and 1.5 mL Et_2O/MeOH-d_4 (2:1) were added to a 1 dram vial at room temperature.[5] After 5 h, 77%-D of the product were observed by ^{1}H NMR (Scheme S3b and Figure S4). Finally, the deuterated product **2″** was detected in the photocatalytic reaction system of DCO_2K (Scheme S3c and Figure S5). These results suggested the hydrogen on the amine might come from the formate.



Scheme S3. Deuterium labeling experiments.

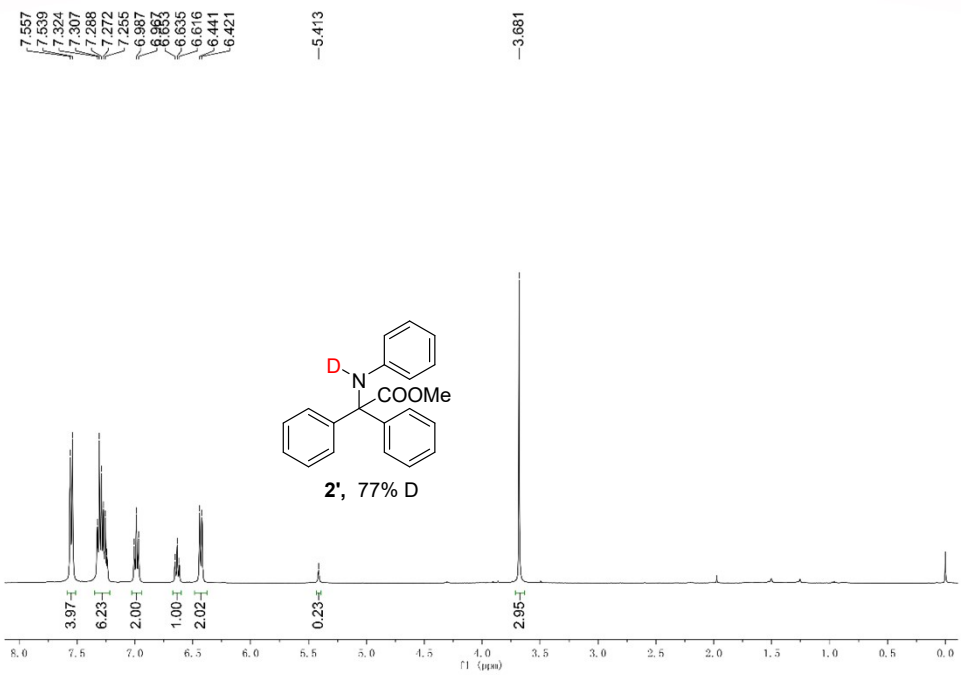


Figure S4. ^{1}H-NMR measurements of α-amino acid derivative **2'**.

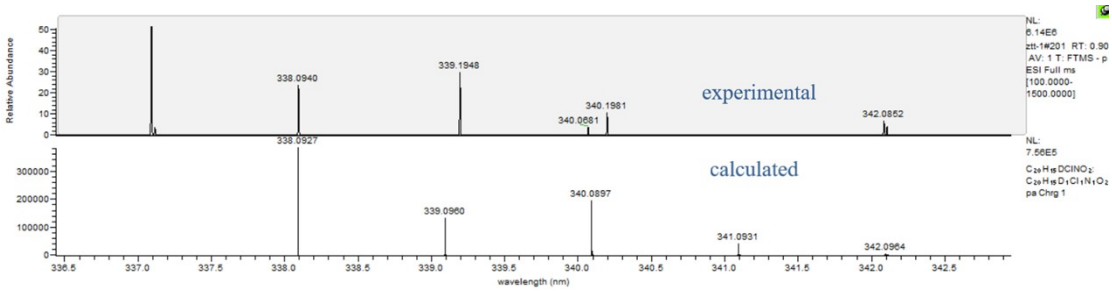
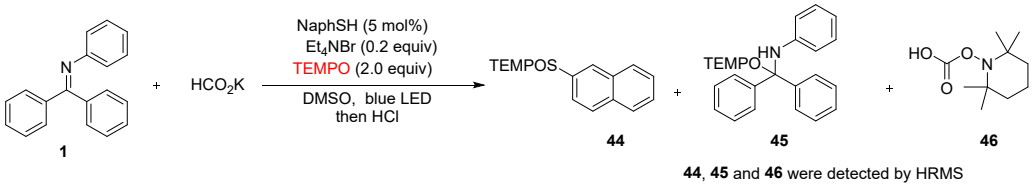


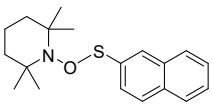
Figure S5. HRMS detection **2″** compound.

5.3 Radical trapping experiment.

When 2.0 equiv. of the radical scavenger TEMPO were added to the system under standard conditions, the reaction mixture was irradiated under a blue LEDs. After 24 hours, the reaction was quenched with a 2N solution of hydrochloric acid. The target product **2** was not produced and the TEMPO-trapped product **44**, **45** and **46** was detected by HRMS, which implied that a radical process was involved in the reaction system.



Scheme S4. Radical trapping experiment



44

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{25}NNaOS$, 338.1549; Found 338.1551.

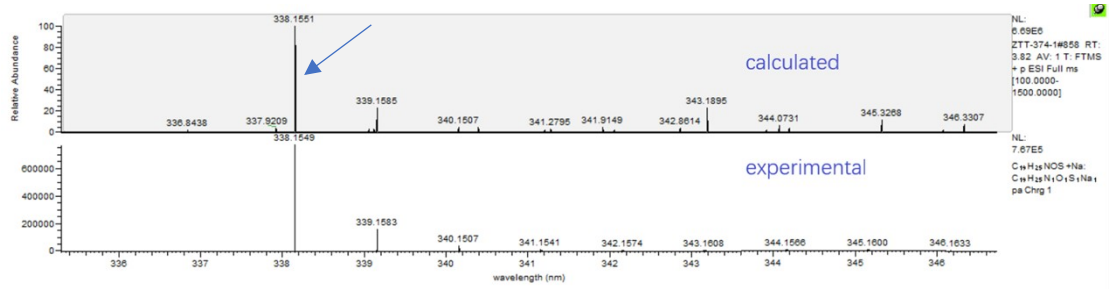
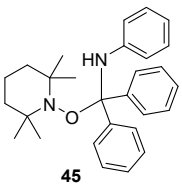


Figure S6. HRMS of the mixture **44**.



45

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{28}H_{34}N_2NaO$, 437.2563; Found 437.2559.

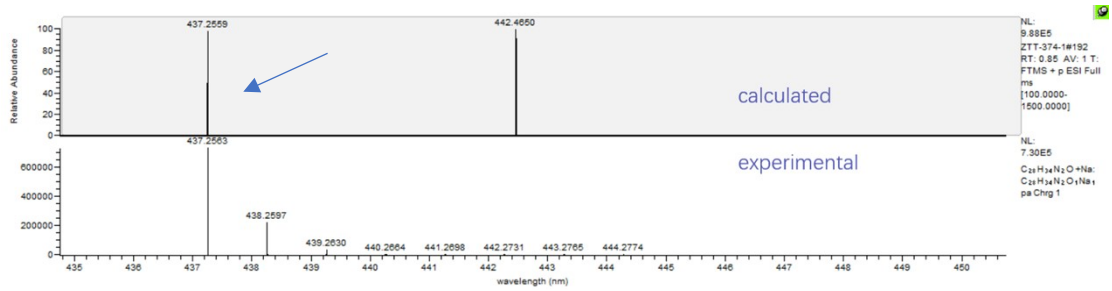
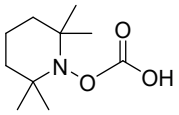


Figure S7. HRMS of the mixture **45**.



46

HRMS (ESI) m/z: $[M + Na]^+$ Calcd. for $C_{10}H_{19}NNaO_3$, 224.1257; Found 224.1264.

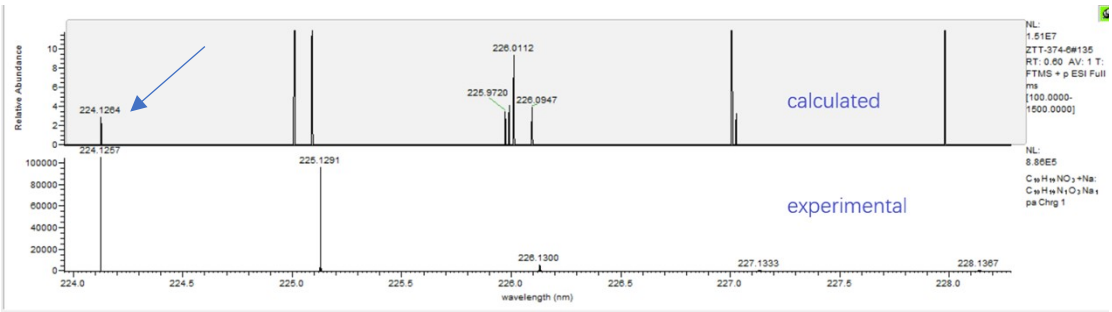
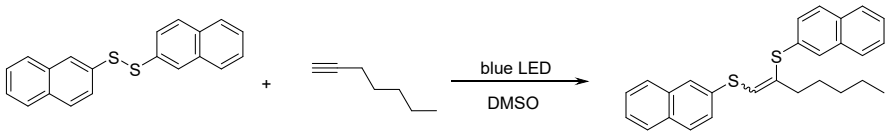


Figure S8. HRMS of the mixture **46**.

5.4 Procedure for the addition reaction of 2-naphthalenyl disulfide and 1-heptyne.

In a clear glass vial, 2-naphthalenyl disulfide (31.8 mg, 0.10 mmol) and 1-heptyne (9.6 mg, 0.10 mmol) were dissolved in DMSO (1.0 mL). Under LED irradiation, the mixture was stirred at 25 °C for 8 hours.[6] Analysis by HRMS showed formation of the addition product (Figure S9), indicating that the S-S bond of 2-naphthalenyl disulfide could be cleaved to give thiyl radicals with light from an blue LED lamp.



HRMS (ESI) m/z: $[M + Na]^+$
Calcd. for $C_{27}H_{26}NaS_2$,
437.1368; Found 437.1368.

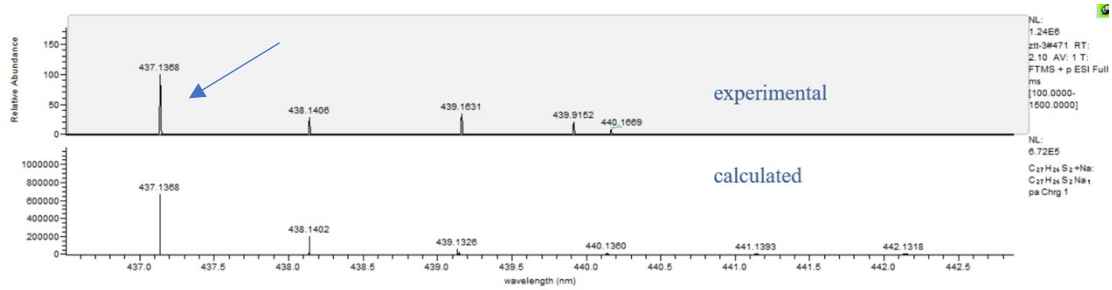


Figure S9. HRMS detection additive product.

5.5 UV-vis absorption spectra.

UV-visible spectroscopy was performed for each reaction component and combination of reaction components using a U-3900H spectrophotometer (Japan Hitachi). The solution was made up and their UV/vis absorption spectra immediately taken.

Stock solutions of NaphSK, NaphSH, ketimine **1**, aldimine **47** and $(NaphS)_2$ dimer were prepared with the same concentration used in the reaction. HCOOK was used in 40 mol % to ensure generation of NaphSH anion under measurement condition. The solutions were prepared in the presence of air using DMSO as solvent.

A new peak (λ_{max} = 403 nm) in NaphSH absorption upon HCOOK addition was observed (Figure S10). This peak was attributed to the thiolate anion's absorption (deprotonated NaphSH) and is supported by the upfield peak of the NMR signal when NaphSH and HCOOK were mixed. Furthermore, we observed no significant absorption peak changes when imines and $NaphS^-$ were combined (Figure S11). Thus, we speculate that no major electron donor-acceptor (EDA) complex was formed by the association of the thiolate anion and imines, but rather a single electron transfer (SET) from $NaphS^-$ to the substrate.

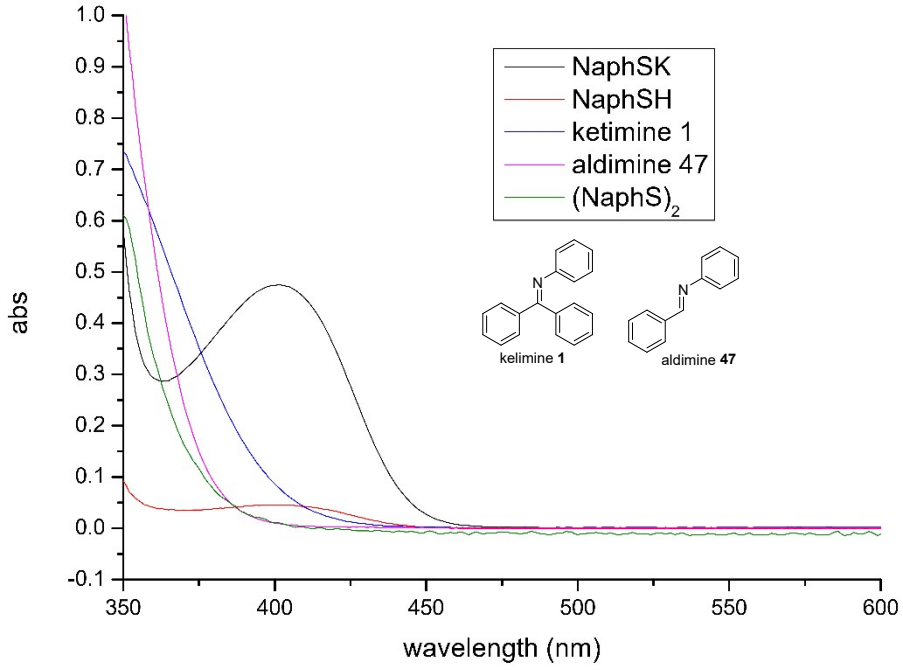


Figure S10. UV/vis absorption spectra of catalyst, substrate.

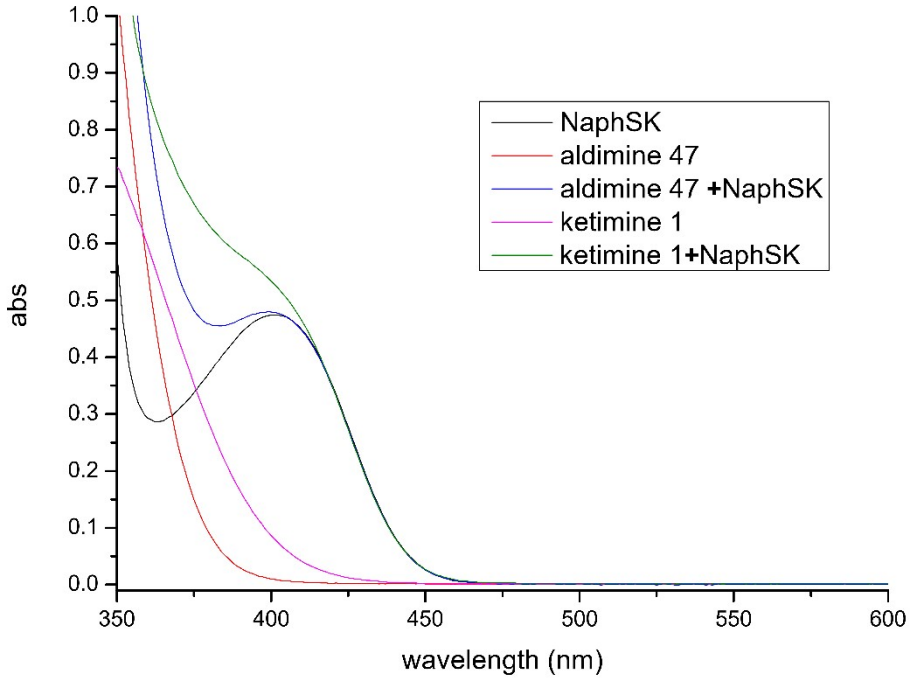


Figure S11. UV/vis absorption spectra of catalyst, substrate, and the mixture.

5.6 Stern-volmer fluorescence quenching experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously purged (with nitrogen) solutions of each component were prepared prior to each set of experiments. Luminescence quenching experiments were run with DMSO as the solvent. The solutions were irradiated at 403 nm and the luminescence was measured from 400 nm to 650 nm (emission maximum is at 485 nm). The concentration of $NaphS^-$ and $(NaphS)_2$ stock solution was 0.3 mM in DMSO. After being stirred with a thin glass rod, the emission spectrum was collected. Linear regression of I_0/I against concentration is done in Origin.

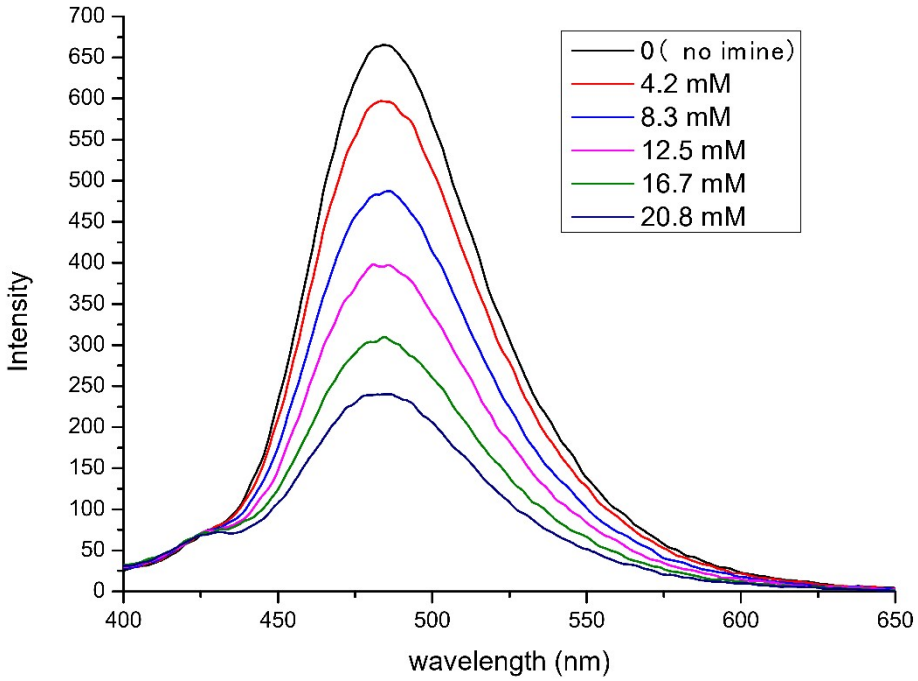


Figure S12. Fluorescence quenching data with $NaphS^-$ and variable aldimine **47**.

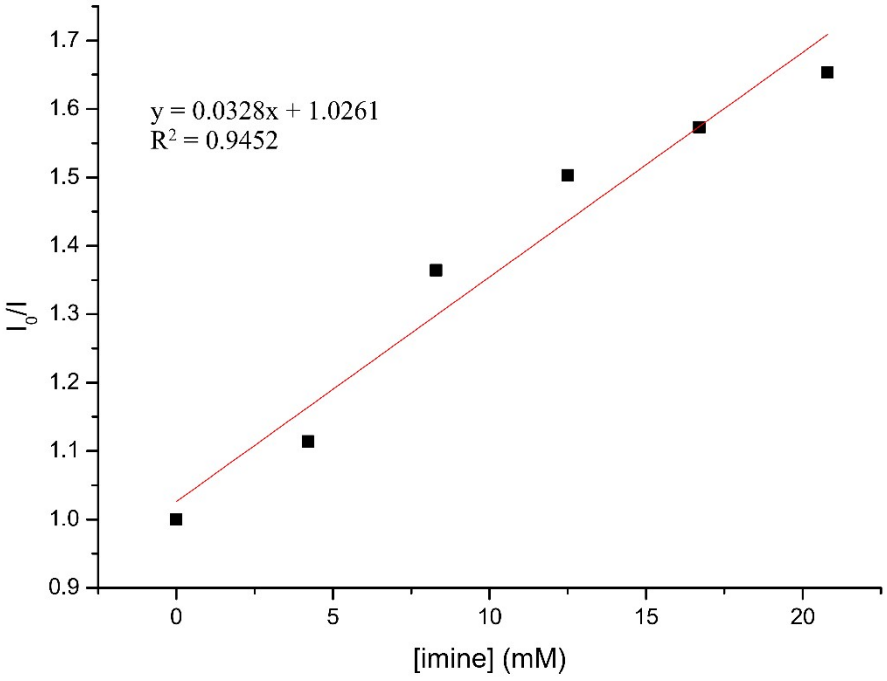


Figure S13. Stern-Volmer quenching plot of aldimine **47**.

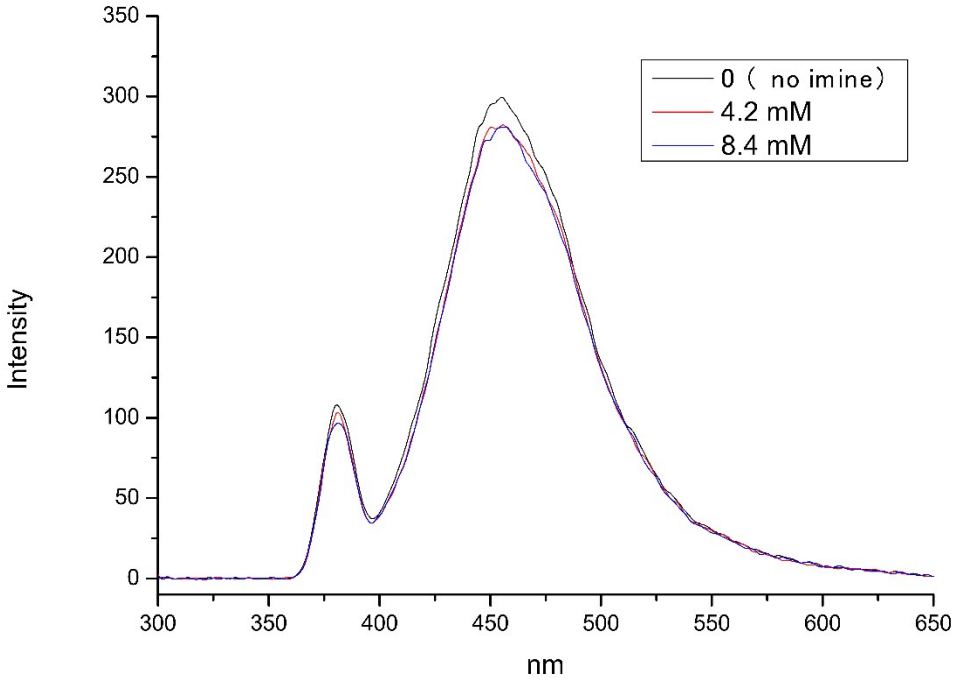


Figure S14. Fluorescence quenching data with $(NaphS)_2$ and variable aldimine **47**.

5.7 Cyclic voltammetry experiments

Determination of the potential of $NaphS^-$ and imines were performed by cyclic voltammetry using a CHI660D potentiostation. The electrochemical measurements were made using a polished glassy carbon electrode (Ø = 2 mm) as the working electrode, platinum mesh as counter electrode and a double junction $Ag/AgNO_3$ as reference electrode. Measurements of $NaphS^-$ and imines (0.01M) were performed in 0.1 M of Bu_4NBF_4/DMSO with a sweep rate of 100 mV/s under anhydrous and anaerobic conditions. Half-wave potentials ($E_{p/2}$) were displayed in Table S6.

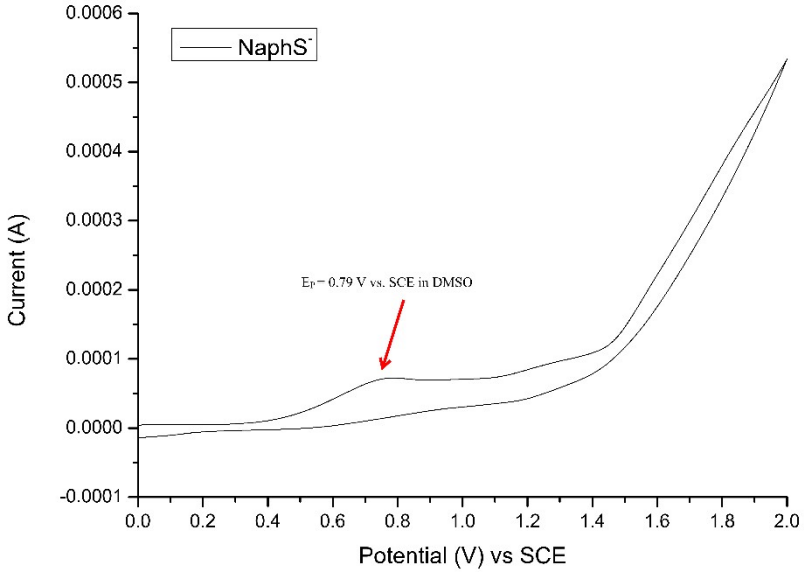


Figure S15. CV of $NaphS^-$

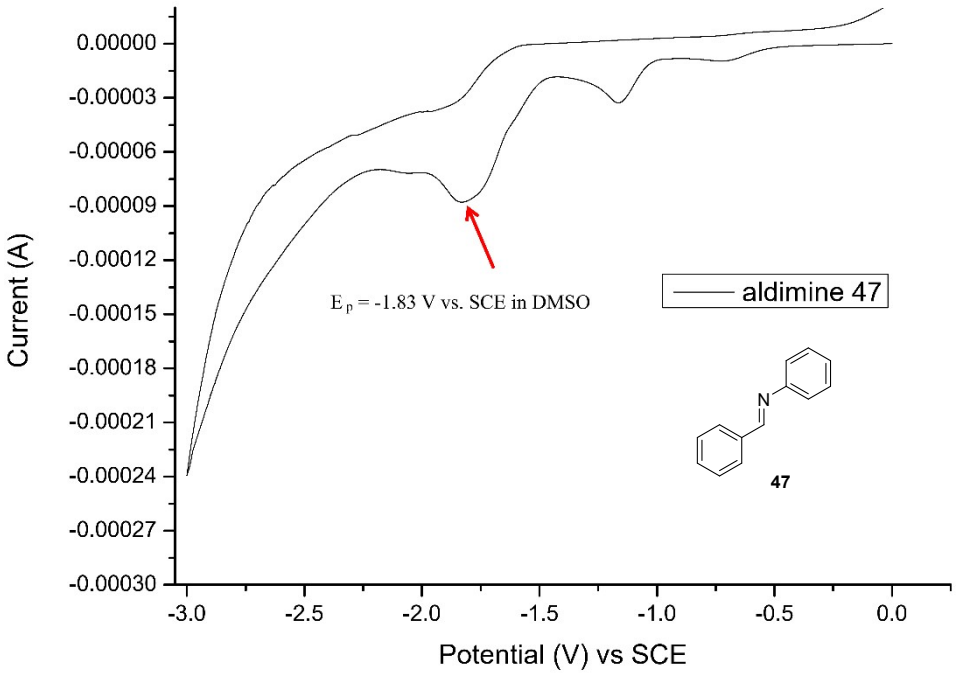


Figure S16. CV of aldimine **47**.

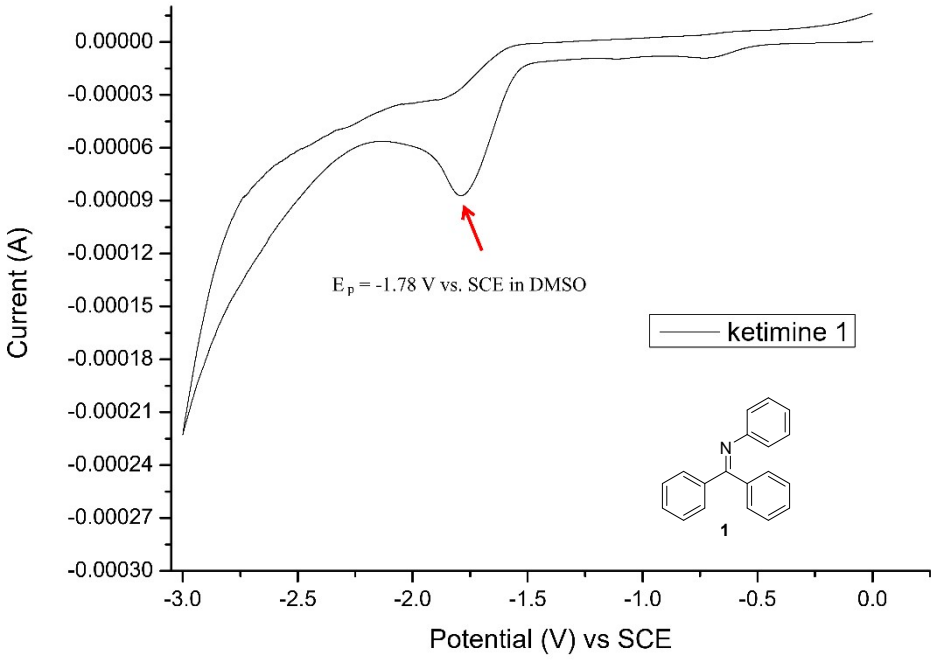


Figure S17. CV of ketimine **1**.

The excited-state potentials were calculated with the equation $E_{1/2}^* = E^{ox}_{1/2} - E_{0,0}$ (the energy of the excited state), which was important for designing organic reactions. With this data in hand, we calculated the redox potential of the excited S1 anion employing the following equation:[7,8]

$$^*E_{p/2} = E_{p/2} - E_0$$

$E_{p/2}$ = 0.58 V vs. SCE, In the absence of vibrational structures, E_0 can be roughly estimated from the absorption spectrum.[9] This corresponds to 403 nm, which translates into an E_0 of 3.08 eV for the $NaphS^-$.

$^*E_{p/2} = E_{p/2} - E_0 = 0.58 - 3.08 = -2.5$ V vs. SCE

Table S6. Half-wave potentials of substrate

Substrate	E_p/V (vs SCE)	$E_{p/2}$/V (vs SCE)	$^*E_{p/2}$/V (vs SCE)
$NaphS^-$	0.79	0.58	-2.5
aldimine **47**	-1.83	-1.61	-
ketimine **1**	-1.78	-1.50	-

5.8 On/off lamp experiment

On/off lamp experiment was performed following *General procedure 3* with ketimine **1**, formate, activated 3 Å molecular sieves, NaphSH, Et_4NBr, and DMSO (12 mL) in 1.2 mmol scale. The reaction was placed in light and dark in every alternative 2 hour. After every time interval of 2 hour the reaction aliquot (1.0 mL) from the reaction mixture was extracted for acidification, extraction, concentration, esterification, and separation. The yield of the product hardly changed significantly after the lights were turned off (Figure S18), from which we deduced that the reaction was not a chain reaction mechanism.

Time (h)	yield (%)
0	0
2	0
4	30.0
6	29.0
8	33.8
10	34.0
12	39.4
14	40.0
16	46.4
18	45.7
20	51.8
22	52.1

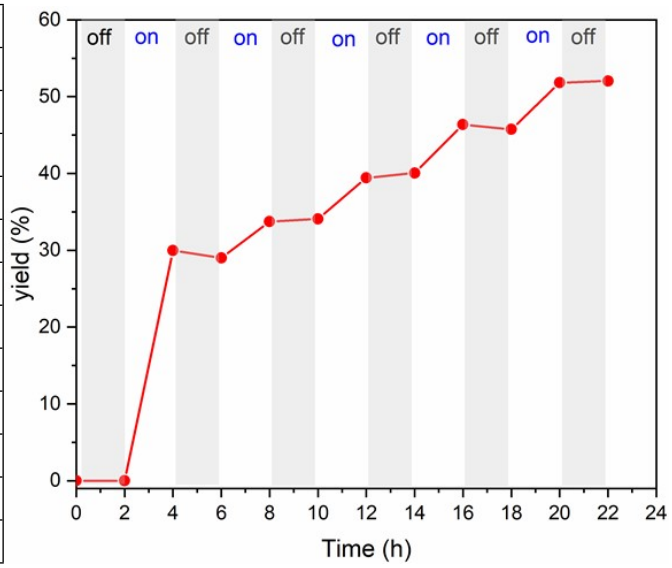
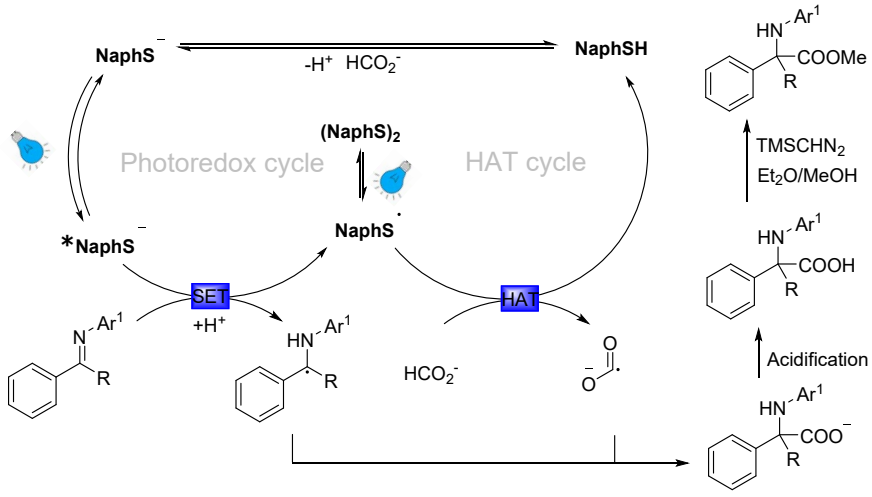


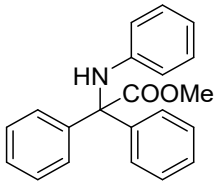
Figure S18. On/off light experiments of the template reaction.

5.9 Propossed mechanism.



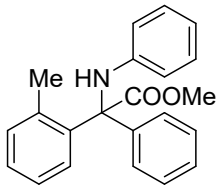
6. Characterization of products.

Methyl 2,2-diphenyl-2-(phenylamino)acetate (**2**)



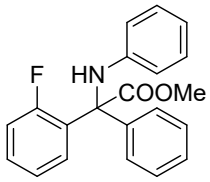
Yield: 87%; 27.6 mg; white solid; m.p. 104-106 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 4H), 7.25 (dt, *J* = 21.7, 7.1 Hz, 6H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 7.8 Hz, 2H), 5.41 (s, 1H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 145.3, 140.2, 128.7, 128.5, 128.3, 127.8, 118.2, 115.6, 71.7, 53.2. HRMS (ESI, m/z): Calcd. for $C_{21}H_{19}NNaO_2$ $[M+Na]^+$: 340.1308, found: 340.1318.

Methyl 2-phenyl-2-(phenylamino)-2-(*o*-tolyl)acetate (**3**)



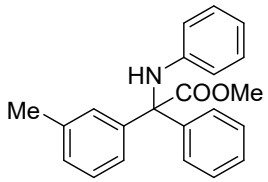
Yield: 76%; 25.2 mg; white solid; m.p. 116-118 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.41 – 7.32 (m, 4H), 7.19 – 7.02 (m, 3H), 6.98 – 6.87 (m, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.38 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.62 (s, 1H), 3.75 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 144.6, 138.3, 137.7, 137.7, 132.3, 130.6, 129.3, 128.5, 128.2, 128.1, 124.9, 117.4, 115.2, 71.6, 53.5, 20.6. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_2$ $[M+Na]^+$: 354.1465, found: 354.1473.

Methyl 2-(2-fluorophenyl)-2-phenyl-2-(phenylamino)acetate (**4**)



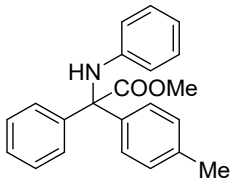
Yield: 81%; 27.1 mg; white solid; m.p.126-128 ºC, PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.45 (td, *J* = 7.9, 1.5 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.23 – 7.13 (m, 1H), 7.02 (td, *J* = 7.7, 1.1 Hz, 1H), 6.98 – 6.86 (m, 3H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.9 Hz, 2H), 5.57 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 162.1, 159.6, 144.5, 136.8, 131.0 (d, *J* = 2.9 Hz), 129.8 (d, *J* = 8.9 Hz), 129.2, 128.4, 128.3, 128.1 (d, *J* = 11.1 Hz), 122.8 (d, *J* = 3.7 Hz), 118.1, 116.0 (d, *J* = 22.1 Hz), 115.9, 68.8, 53.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9. HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}FNNaO_2$ $[M+Na]^+$: 358.1214; found358.1223.

Methyl 2-phenyl-2-(phenylamino)-2-(m-tolyl)acetate (**5**)



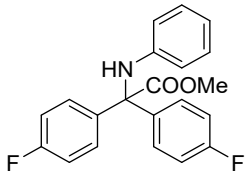
Yield: 68%; 22.5 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.35 – 7.24 (m, 5H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.64 (dd, *J* = 10.5, 4.1 Hz, 1H), 6.47 – 6.39 (m, 2H), 5.37 (s, 1H), 3.68 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 145.4, 140.4, 140.0, 137.9, 128.8, 128.6, 128.5, 128.5, 128.1, 128.1, 127.6, 125.3, 118.0, 115.6, 71.6, 53.1, 21.7. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_2$ $[M+Na]^+$: 354.1465; found 354.1472.

Methyl 2-phenyl-2-(phenylamino)-2-(p-tolyl)acetate (**6**)



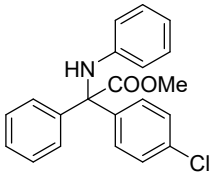
Yield: 77%; 25.5 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.27 (ddd, *J* = 14.7, 5.1, 3.6 Hz, 3H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.97 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 2H), 5.41 (s, 1H), 3.65 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 145.3, 140.2, 137.5, 137.2, 129.0, 128.6, 128.5, 128.4, 128.2, 127.7, 118.0, 115.6, 71.4, 53.2, 21.1. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_2$ $[M+Na]^+$: 354.1465, found: 354.1470.

Methyl 2,2-bis(4-fluorophenyl)-2-(phenylamino)acetate (**7**)



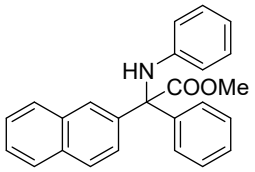
Yield: 85%; 30.0 mg; white solid; m.p. 136-138 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.6, 5.3 Hz, 4H), 7.04 – 6.93 (m, 6H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 8.5 Hz, 2H), 5.42 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 162.2 (d, *J* = 246.1 Hz), 144.8, 135.6 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 8.1 Hz), 128.8, 118.5, 115.3 (t, *J* = 28.9 Hz), 70.6, 53.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3. HRMS (ESI, m/z): Calcd. for $C_{21}H_{17}F_2NNaO_2$ $[M+Na]^+$: 376.1120, found: 376.1128.

Methyl 2-(4-chlorophenyl)-2-phenyl-2-(phenylamino)acetate (**8**)



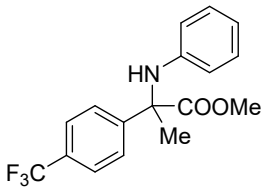
Yield: 67%; 23.5 mg; colourless oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.50 – 7.45 (m, 2H), 7.33 – 7.26 (m, 5H), 7.02 – 6.95 (m, 2H), 6.69 – 6.63 (m, 1H), 6.45 – 6.37 (m, 2H), 5.39 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 144.9, 140.2, 138.2, 133.6, 130.2, 128.7, 128.5, 128.3, 128.2, 128.0, 118.4, 115.6, 71.2, 53.3. HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}ClNNaO_2$ $[M+Na]^+$: 374.0918, found: 374.0921.

Methyl 2-(naphthalen-2-yl)-2-phenyl-2-(phenylamino)acetate (**9**)



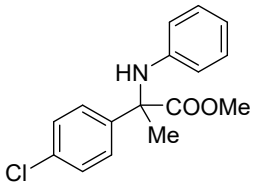
Yield: 52%; 19.1 mg; yellow oil; PE/EA = 30/1;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.7 Hz, 1H), 7.83 – 7.74 (m, 3H), 7.66 – 7.57 (m, 3H), 7.50 – 7.40 (m, 2H), 7.36 – 7.25 (m, 3H), 6.97 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.54 – 6.46 (m, 2H), 5.52 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 145.2, 139.9, 137.4, 132.9, 132.7, 128.7, 128.57, 128.5, 128.3, 127.9, 127.8, 127.5, 126.5, 126.4, 126.2, 118.2, 115.7, 71.8, 53.3. HRMS (ESI, m/z): Calcd. for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465; found 390.1475.

Methyl 2-(phenylamino)-2-(4-(trifluoromethyl)phenyl)propanoate (**10**)



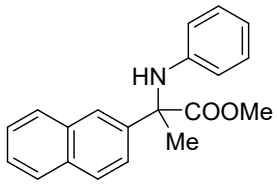
Yield: 67%; 21.6 mg; colourless oil; PE/EA = 30/1;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.11 – 6.96 (m, 2H), 6.76 – 6.58 (m, 1H), 6.42 – 6.25 (m, 2H), 5.23 (s, 1H), 3.69 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 145.1, 144.1, 129.6, 129.0, 127.5, 125.6 (dd, *J* = 3.7 Hz, 3.8 Hz), 122.8, 118.1, 115.3, 63.0, 53.4, 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. HRMS (ESI, m/z): Calcd. for $C_{17}H_{16}F_3NNaO_2$ $[M+Na]^+$: 369.0923; found 369.0930.

Methyl 2-(4-chlorophenyl)-2-(phenylamino)propanoate (**11**)



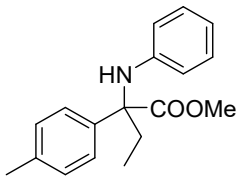
Yield:53%; 15.3 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.38 – 7.25 (m, 2H), 7.07 – 6.98 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.39 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.23 (s, 1H), 3.67 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 144.6, 141.2, 128.9, 128.7, 128.5, 127.6, 126.9, 117.7, 115.4, 63.0, 53.2, 23.0. HRMS (ESI, m/z): Calcd. for $C_{16}H_{16}ClNNaO_2$ $[M+Na]^+$: 312.0762; found 312.0769.

Methyl 2-(naphthalen-2-yl)-2-(phenylamino)propanoate (**12**)



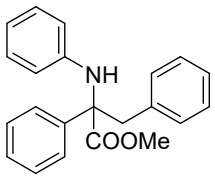
Yield: 62%; 18.9 mg; yellow solid; m.p. 78-80 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.5 Hz, 1H), 7.91 – 7.78 (m, 3H), 7.68 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.08 – 6.94 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.43 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.35 (s, 1H), 3.66 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 144.6, 138.9, 133.4, 132.8, 128.9, 128.5, 128.4, 127.6, 126.3, 126.2, 126.0, 124.9, 117.8, 115.4, 63.2, 53.2, 22.9. HRMS (ESI, m/z): Calcd. for $C_{20}H_{19}NNaO_2$ $[M+Na]^+$: 328.1308; found 328.1318.

Methyl 2-(phenylamino)-2-(p-tolyl)butanoate (**13**)



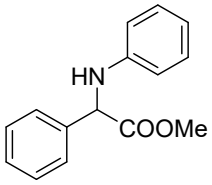
Yield: 68%; 19.2 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.00 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.42 – 6.33 (m, 2H), 5.35 (s, 1H), 3.66 (s, 3H), 2.53 (ddt, *J* = 21.1, 13.8, 7.0 Hz, 2H), 2.33 (s, 3H), 0.80 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 144.4, 137.8, 137.2, 129.4, 128.8, 126.9, 117.2, 115.0, 66.6, 53.1, 25.6, 21.1, 8.5. HRMS (ESI, m/z): Calcd. for $C_{18}H_{21}NNaO_2$ $[M+Na]^+$: 306.1465; found 306.1470.

Methyl 2,3-diphenyl-2-(phenylamino)propanoate (**14**)



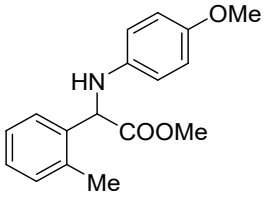
Yield: 62%; 20.5 mg; yellow solid; m.p. 116-118 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.34 – 7.30 (m, 1H), 7.23 – 7.16 (m, 3H), 7.09 – 7.00 (m, 2H), 6.91 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.35 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.21 (s, 1H), 3.90 – 3.78 (m, 2H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 144.3, 140.2, 136.0, 130.2, 129.0, 128.9, 128.1, 127.8, 127.1, 127.0, 117.2, 114.9, 67.2, 52.9, 37.8. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_2$ $[M+Na]^+$: 354.1465; found 354.1471.

Methyl 2-phenyl-2-(phenylamino)acetate (**15**)



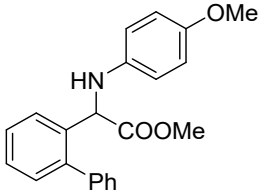
Yield: 63%; 15.2 mg; yellow solid; m.p. 70-72 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.26 (m, 3H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 2H), 5.07 (d, *J* = 5.9 Hz, 1H), 4.96 (d, *J* = 5.7 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 146.0, 137.7, 129.3, 129.0, 128.4, 127.3, 118.2, 113.5, 60.8, 52.9. HRMS (ESI, m/z): Calcd. for $C_{15}H_{15}NNaO_2$ $[M+Na]^+$: 264.0995, found: 264.1002.

Methyl 2-((4-methoxyphenyl)amino)-2-(o-tolyl)acetate (**16**)



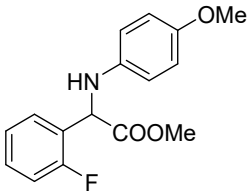
Yield: 43%; 12.3 mg; yellow solid; m.p. 98-100 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.8 Hz, 1H), 7.23 – 7.14 (m, 3H), 6.77 – 6.68 (m, 2H), 6.56 – 6.45 (m, 2H), 5.22 (s, 1H), 4.52 (s, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 152.6, 140.5, 136.6, 136.1, 130.9, 128.2, 126.6, 126.5, 114.9, 114.6, 58.3, 55.7, 52.6, 19.5. HRMS (ESI, m/z): Calcd. for $C_{17}H_{19}NNaO_3$ $[M+Na]^+$: 308.1263, found: 308.1264.

Methyl 2-([1,1'-biphenyl]-2-yl)-2-((4-methoxyphenyl)amino)acetate (**17**)



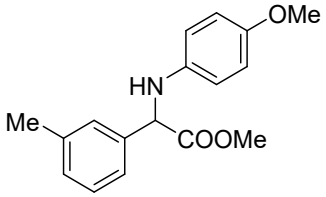
Yield: 52%; 18.0 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.42 (ddd, *J* = 8.6, 7.6, 3.6 Hz, 3H), 7.38 – 7.29 (m, 3H), 6.63 (d, *J* = 8.9 Hz, 2H), 6.34 (d, *J* = 8.9 Hz, 2H), 5.19 (s, 1H), 4.41 (s, 1H), 3.69 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 152.7, 142.4, 140.5, 140.2, 135.6, 130.7, 129.7, 128.3, 128.2, 127.5, 126.6, 115.1, 114.7, 57.9, 55.7, 52.6. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_3$ $[M+Na]^+$: 370.1419, found: 370.1423.

Methyl 2-(2-fluorophenyl)-2-(phenylamino)acetate (**18**)



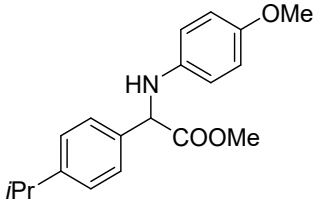
Yield: 53%; 13.7 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 (ddd, *J* = 7.3, 4.8, 1.9 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 5.31 (s, 1H), 4.62 (s, 1H), 3.66 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 162.0, 159.6, 152.7, 139.8, 129.9 (d, *J* = 8.2 Hz), 128.3 (d, *J* = 3.4 Hz), 125.3 (d, *J* = 13.8 Hz), 124.7 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 21.7 Hz), 114.9, 55.7, 54.7, 52.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.5. HRMS (ESI, m/z): Calcd. for $C_{16}H_{16}FNNaO_3$[M+Na]$^+$: 282.0901, found: 282.0909.

Methyl 2-(phenylamino)-2-(m-tolyl)acetate (**19**)



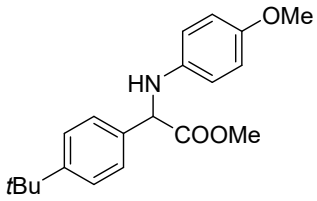
Yield: 45%; 11.5 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 9.6 Hz, 3H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 1H), 4.62 (s, 1H), 3.71 (d, *J* = 4.4 Hz, 6H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 152.5, 140.3, 138.6, 137.7, 129.1, 128.7, 127.9, 124.4, 114.9, 114.8, 61.7, 55.7, 52.7, 21.5. HRMS (ESI, m/z): Calcd. for $C_{17}H_{19}NNaO_3$ [M+Na]$^+$: 308.1257, found: 308.1266.

Methyl 2-(4-isopropylphenyl)-2-(phenylamino)acetate (**20**)



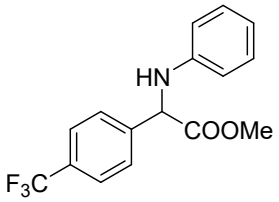
Yield: 36%; 10.2 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.97 (d, *J* = 5.0 Hz, 1H), 4.57 (s, 1H), 3.70 (d, *J* = 4.2 Hz, 6H), 2.94 – 2.82 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 152.5, 149.0, 140.4, 135.0, 127.2, 127.0, 114.9, 114.7, 61.5, 55.7, 52.6, 33.8, 23.9. HRMS (ESI, m/z): Calcd. for $C_{19}H_{23}NNaO_3$[M+Na]$^+$: 336.1576; found 336.1570.

Methyl 2-(4-(tert-butyl)phenyl)-2-((4-methoxyphenyl)amino)acetate (**21**)



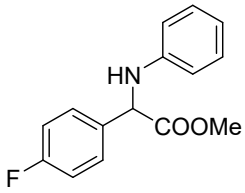
Yield: 42%; 13.7 mg; pink solid; m.p. 62-64 ºC; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 6.77 – 6.69 (m, 2H), 6.58 – 6.51 (m, 2H), 4.99 (s, 1H), 4.59 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 152.5, 151.2, 140.4, 134.6, 126. 9, 125.8, 114.9, 114.7, 61.4, 55.7, 52.7, 34.6, 31.3. HRMS (ESI, m/z): Calcd. for $C_{20}H_{25}NNaO_3$ $[M+Na]^+$: 350.1727, found: 350.1735.

Methyl 2-(phenylamino)-2-(4-(trifluoromethyl)phenyl)acetate (**22**)



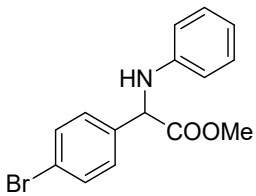
Yield: 64%; 19.8 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (q, J = 8.6 Hz, 4H), 7.27 – 7.22 (m, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.65 – 6.62 (m, 2H), 5.25 (d, J = 5.3 Hz, 1H), 5.18 (d, J = 5.1 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 145.5, 141.8, 130.5 (d, J = 32.3 Hz), 129.4, 127.7, 125.9 (dd, J = 3.8 Hz, 3.7 Hz), 118.5, 113.8, 113.4, 60.4, 53.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. HRMS (ESI, m/z): Calcd. for $C_{16}H_{14}F_3NNaO_2$ $[M+Na]^+$: 332.0869, found: 332.0876.

Methyl 2-(4-fluorophenyl)-2-(phenylamino)acetate (**23**)



Yield: 58%; 15.0 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.14 – 7.07 (m, 2H), 7.05 – 6.98 (m, 2H), 6.69 (t, J = 7.3 Hz, 1H), 6.52 (dd, J = 8.6, 0.9 Hz, 2H), 5.04 (d, J = 5.4 Hz, 1H), 4.94 (d, J = 4.8 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 145.7, 133.4 (d, J = 3.3 Hz), 129.3, 128.9 (d, J = 8.2 Hz), 118.3, 115.9 (d, J = 21.5 Hz), 113.4, 60.0, 52.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9. HRMS (ESI, m/z): Calcd. for $C_{15}H_{14}FNNaO_2$ $[M+Na]^+$: 282.0901, found: 282.0906.

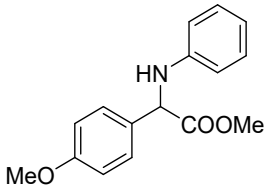
Methyl 2-(4-bromophenyl)-2-(phenylamino)acetate (**24**)



Yield: 22%; 7.0 mg; yellow solid; m.p. 72-74ºC; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.35 – 7.29 (m, 2H), 7.15 – 7.06 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.58 – 6.51 (m, 2H),

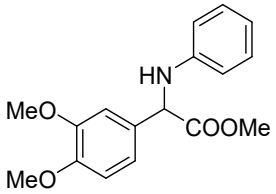
5.06 (d, *J* = 5.8 Hz, 1H), 4.93 (d, *J* = 5.4 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 145.9, 137.6, 129.3, 128.9, 128.3, 127.3, 118.1, 113.4, 60.7, 52.8. HRMS (ESI, m/z): Calcd. for $C_{15}H_{14}BrNNaO_2$ $[M+Na]^+$: 342.0100, found: 342.0109.

Methyl 2-(4-methoxyphenyl)-2-(phenylamino)acetate (**25**)



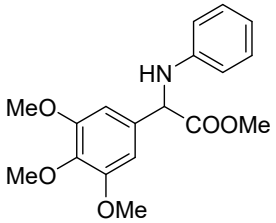
Yield: 32%; 8.7 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.16 – 7.08 (m, 2H), 6.91 – 6.84 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.55 (dd, *J* = 8.5, 0.9 Hz, 2H), 5.02 (d, *J* = 5.4 Hz, 1H), 4.89 (d, *J* = 5.1 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.6, 146.0, 129.6, 129.2, 128.4, 118.1, 114.3, 113.4, 60.1, 55.3, 52.8. HRMS (ESI, m/z): Calcd. for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$: 294.1101, found: 294.1108.

Methyl 2-(3,4-dimethoxyphenyl)-2-(phenylamino)acetate (**26**)



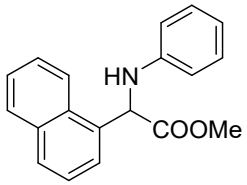
Yield: 38%; 11.4 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 2H), 7.04 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.57 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.00 (s, 1H), 4.89 (s, 1H), 3.86 (d, *J* = 3.2 Hz, 6H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 149.3, 149.1, 146.1, 130.0, 129.3, 119.7, 118.2, 113. 5, 111.3, 110.0, 60.6, 55.9, 55.9, 52.8. HRMS (ESI, m/z): Calcd. for $C_{17}H_{19}NNaO_4$ $[M+Na]^+$: 324.1214, found: 324.1206.

Methyl 2-(phenylamino)-2-(3,4,5-trimethoxyphenyl)acetate (**27**)



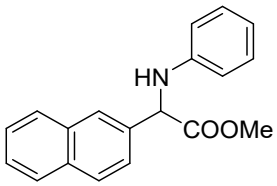
Yield: 42%; 13.9 mg; white solid; m.p. 112-114 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.5, 7.4 Hz, 2H), 6.75 – 6.70 (m, 3H), 6.58 (dd, *J* = 8.6, 0.9 Hz, 2H), 4.97 (d, *J* = 5.0 Hz, 1H), 4.91 (d, *J* = 4.9 Hz, 1H), 3.85 (s, 6H), 3.83 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 153.6, 146.0, 137.8, 133.2, 129.3, 118.3, 113.5, 104.1, 61.1, 60.8, 56.2, 52.9. HRMS (ESI, m/z): Calcd. for $C_{18}H_{21}NNaO_5$ $[M+Na]^+$: 354.1312, found: 354.1317.

Methyl 2-(naphthalen-1-yl)-2-(phenylamino)acetate (**28**)



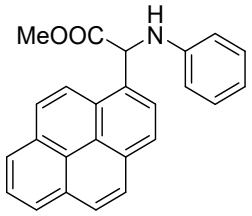
Yield: 58%; 16.9 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 4.98 (s, 1H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 146.2, 134.2, 133.4, 131.3, 129.3, 129.2, 129.1, 126.7, 126.0, 125.6, 125.1, 123.4, 118.3, 113.3, 57.4, 52.8. HRMS (ESI, m/z): Calcd. for $C_{19}H_{17}NNaO_2$ $[M+Na]^+$: 314.1152, found: 314.1157.

Methyl 2-(naphthalen-2-yl)-2-(phenylamino)acetate (**29**)



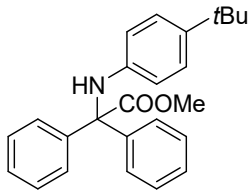
Yield: 52%; 15.1 mg; yellow oil; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.61 – 7.49 (m, 2H), 7.46 – 7.39 (m, 1H), 7.10 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.7 Hz, 2H), 5.83 (d, *J* = 2.8 Hz, 1H), 4.99 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 146.2, 134.2, 133.4, 131.3, 129.4, 129.2, 129.1, 126.8, 126.0, 125.6, 125.1, 123.4, 118.3, 113.3, 57.4, 52.9. HRMS (ESI, m/z): Calcd. for $C_{19}H_{17}NNaO_2$ $[M+Na]^+$: 314.1152, found: 314.1155.

Methyl 2-(phenylamino)-2-(pyren-1-yl)acetate (**30**)



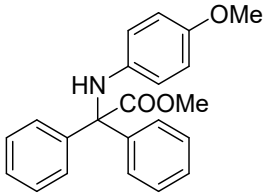
Yield: 51%; 18.6 mg; yellow solid; m.p. 118-120 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 9.4 Hz, 1H), 8.26 – 8.12 (m, 5H), 8.09 – 7.99 (m, 3H), 7.06 (t, *J* = 7.9 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 6.14 (s, 1H), 5.26 (d, *J* = 7.2 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 146.1, 131.4, 131.3, 131.2, 130.7, 129.3, 129.1, 128.4, 127.8, 127.4, 126.2, 125.6, 125.4, 125.4, 125.3, 124.8, 124.6, 122.6, 118.2, 113.4, 57.5, 53.0. HRMS (ESI, m/z): Calcd. for $C_{25}H_{19}NNaO_2$ $[M+Na]^+$: 388.1308, found: 388.1320.

Methyl 2-((4-(tert-butyl)phenyl)amino)-2,2-diphenylacetate (**32**)



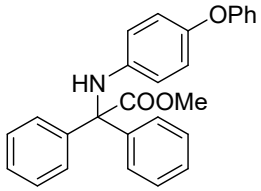
Yield: 80%; 29.8 mg; white solid; m.p. 114-116 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.6, 3.7 Hz, 4H), 7.39 – 7.12 (m, 6H), 7.06 – 6.91 (m, 2H), 6.43 – 6.27 (m, 2H), 5.25 (d, *J* = 4.3 Hz, 1H), 3.63 (d, *J* = 6.5 Hz, 3H), 1.18 (d, *J* = 5.7 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 142.8, 140.7, 140.6, 128.4, 128.2, 127.6, 125.5, 115.2, 71.7, 53.1, 33.9, 31.6. HRMS (ESI, m/z): Calcd. for $C_{25}H_{27}NNaO_2$[M+Na]$^+$: 396.1934; found 396.1944.

Methyl 2-((4-methoxyphenyl)amino)-2,2-diphenylacetate (**33**)



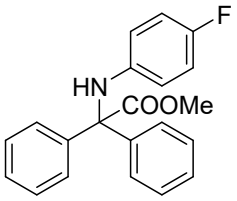
Yield: 75%; 26.0 mg; white solid; m.p. 108-110 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.33 – 7.23 (m, 6H), 6.60 – 6.54 (m, 2H), 6.42 – 6.35 (m, 2H), 5.09 (s, 1H), 3.67 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 152.5, 140.7, 139.2, 128.3, 128.1, 127.6, 117.2, 114.1, 72.1, 55.5, 53.0. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_3$[M+Na]$^+$: 370.1419; found 370.1414.

Methyl 2-((4-phenoxyphenyl)amino)-2,2-diphenylacetate (**34**)



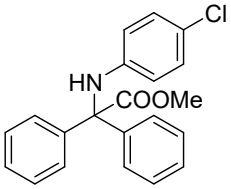
Yield: 83%; 33.9 mg; white solid; m.p. 112-114 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 4H), 7.35 – 7.18 (m, 8H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 2H), 6.72 – 6.65 (m, 2H), 6.46 – 6.36 (m, 2H), 5.33 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.76, 158.6, 148.5, 141.7, 140.2, 129.5, 128.5, 128.3, 127.8, 122.2, 120.2, 117.5, 117.0, 72.0, 53.2. HRMS (ESI, m/z): Calcd. for $C_{27}H_{23}NNaO_3$[M+Na]$^+$: 432.1570; found 432.1580.

Methyl 2-((4-fluorophenyl)amino)-2,2-diphenylacetate (**35**)



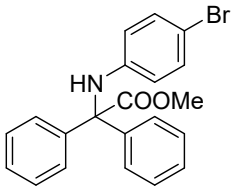
Yield: 84%; 28.1 mg; white solid; m.p. 114-116 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 4H), 7.36 – 7.21 (m, 6H), 6.68 (dd, *J* = 12.0, 5.5 Hz, 2H), 6.39 – 6.31 (m, 2H), 5.33 (s, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 156.2 (d, *J* = 234.8 Hz), 141.4, 139.9, 128.3 (d, *J* = 16.8 Hz), 127.8, 116.7 (d, *J* = 7.4 Hz), 115.1 (d, *J* = 22.2 Hz), 71.9, 53.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -126.9. HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}FNNaO_2$[M+Na]$^+$: 358.1214; found 358.1222.

Methyl 2-((4-chlorophenyl)amino)-2,2-diphenylacetate (**36**)



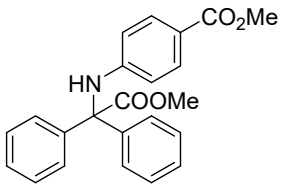
Yield: 78%; 27.4 mg; white solid; m.p. 140-142 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 4H), 7.36 – 7.24 (m, 6H), 6.97 – 6.85 (m, 2H), 6.37 – 6.28 (m, 2H), 5.52 (s, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 143.7, 139.4, 128.5, 128.5, 128.3, 127.9, 122.8, 116.7, 71.5, 53.7. HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}ClNNaO_2$[M+Na]$^+$: 374.0918; found 374.0927.

Methyl 2-((4-bromophenyl)amino)-2,2-diphenylacetate (**37**)



Yield: 54%; 21.4 mg; yellow solid; m.p. 126-128 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 4H), 7.38 – 7.27 (m, 6H), 7.09 – 7.02 (m, 2H), 6.33 – 6.24 (m, 2H), 5.55 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 144.1, 139.2, 131.3, 128.5, 128.3, 127.9, 117.1, 109.9, 71.4, 53.4. HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}BrNNaO_2$ [M+Na]$^+$: 418.0413; found 418.0421.

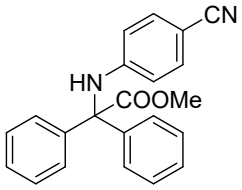
Methyl 4-((2-methoxy-2-oxo-1,1-diphenylethyl)amino)benzoate (**38**)



Yield: 84%; 31.5 mg; white solid; m.p. 124-126 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.52 (dd, *J* = 8.1, 1.4 Hz, 4H), 7.37 – 7.27 (m, 6H), 6.40 (d, *J* = 8.8 Hz, 2H), 6.05 (s,

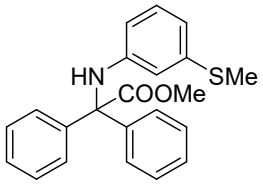
1H), 3.78 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 167.2, 149.0, 138.6, 130.8, 128.6, 128.4, 128.1, 119.1, 114.4, 71.2, 53.6, 51.6. HRMS (ESI, m/z): Calcd. for $C_{23}H_{21}NNaO_4$ $[M+Na]^+$: 398.1363; found 398.1368.

Methyl 2-((4-cyanophenyl)amino)-2,2-diphenylacetate (**39**)



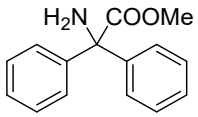
Yield: 63%; 21.5 mg; white solid; m.p. 154-156 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.39 – 7.29 (m, 6H), 7.29 – 7.19 (m, 2H), 6.40 (d, *J* = 8.8 Hz, 2H), 6.17 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 148.4, 137.9, 133.0, 128.5, 128.5, 128.3, 120.1, 115.1, 99.9, 71.1, 53.7. HRMS (ESI, m/z): Calcd. for $C_{22}H_{18}N_2NaO_2$ $[M+Na]^+$: 365.1260; found 365.1257.

Methyl 2-((3-(methylthio)phenyl)amino)-2,2-diphenylacetate (**40**)



Yield: 71%; 25.7 mg; white solid; m.p. 102-104 °C; PE/EA = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 4H), 7.29 – 7.18 (m, 6H), 6.80 (t, *J* = 7.9 Hz, 1H), 6.45 (d, *J* = 7.7 Hz, 1H), 6.23 (s, 1H), 6.12 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.46 (s, 1H), 3.62 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 145.6, 139.6, 138.5, 128.9, 128.5, 128.3, 127.8, 116.3, 113.2, 112.5, 71.4, 53.3, 15.5. HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NNaO_2S$ $[M+Na]^+$: 363.1288; found 363.1284.

Methyl 2-amino-2,2-diphenylacetate (**43**)



Yield: 84%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 10H), 3.79 (s, 3H), 2.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 143.8, 128.2, 127.6, 127.6, 68.5, 52.9. HRMS (ESI, m/z): Calcd. for $C_{15}H_{15}NNaO_2$ $[M+Na]^+$: 264.100; found 264.1004.

7. Crystallographic data

X-ray data for 27 (CCDC 2244895)

Single crystal of product **27** was obtained through slow evaporation of a solution in dichloromethane-diethyl ether at room temperature.

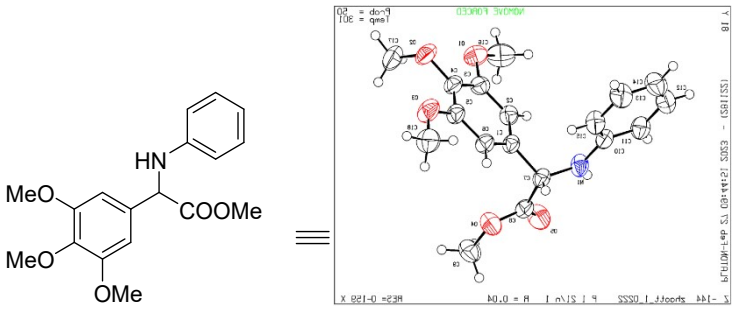


Table S7. Crystal data and structure refinement for **27.**

Empirical formula	$C_{18}H_{21}NO_5$
Formula weight	331.36
Temperature/K	300.88(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.78002(17)
b/Å	18.6163(6)
c/Å	15.8540(5)
α/°	90
β/°	95.564(3)
γ/°	90
Volume/Å^3	1697.89(9)
Z	4
ρ_{calc}g/cm^3	1.296
μ/mm^{-1}	0.783
F(000)	704.0
Crystal size/mm^3	0.17 × 0.02 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.344 to 152.828
Index ranges	-3 ≤ h ≤ 7, -22 ≤ k ≤ 22, -19 ≤ l ≤ 19
Reflections collected	10981
Independent reflections	3377 [R_{int} = 0.0502, R_{sigma} = 0.0520]
Data/restraints/parameters	3377/0/222
Goodness-of-fit on F^2	1.082

Final R indexes [I>=2σ (I)]	$R_1 = 0.0440$, $wR_2 = 0.1198$
Final R indexes [all data]	$R_1 = 0.0544$, $wR_2 = 0.1268$
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15

X-ray data for 36 (CCDC 2244897)

Single crystal of product **36** was obtained through slow evaporation of a solution in dichloromethane-diethyl ether at room temperature.

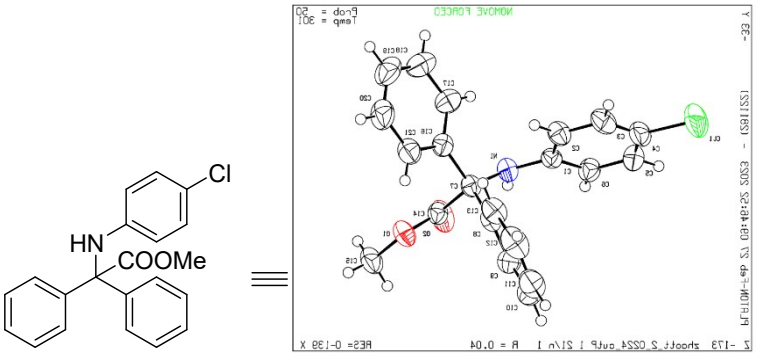


Table S8. Crystal data and structure refinement for **36**

Empirical formula	$C_{21}H_{18}ClNO_2$
Formula weight	351.81
Temperature/K	300.88(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.4508(2)
b/Å	12.4654(2)
c/Å	14.1577(3)
α/°	90
β/°	99.135(2)
γ/°	90
Volume/Å^3	1820.98(6)
Z	4
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	1.960
F(000)	736.0
Crystal size/mm^3	0.14 × 0.11 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.506 to 153.056
Index ranges	$-12 \le h \le 13$, $-11 \le k \le 15$, $-17 \le l \le 17$
Reflections collected	12011
Independent reflections	3599 [$R_{int} = 0.0187$, $R_{sigma} = 0.0169$]
Data/restraints/parameters	3599/0/232

Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0414, wR_2 = 0.1009
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.35

8. Reference

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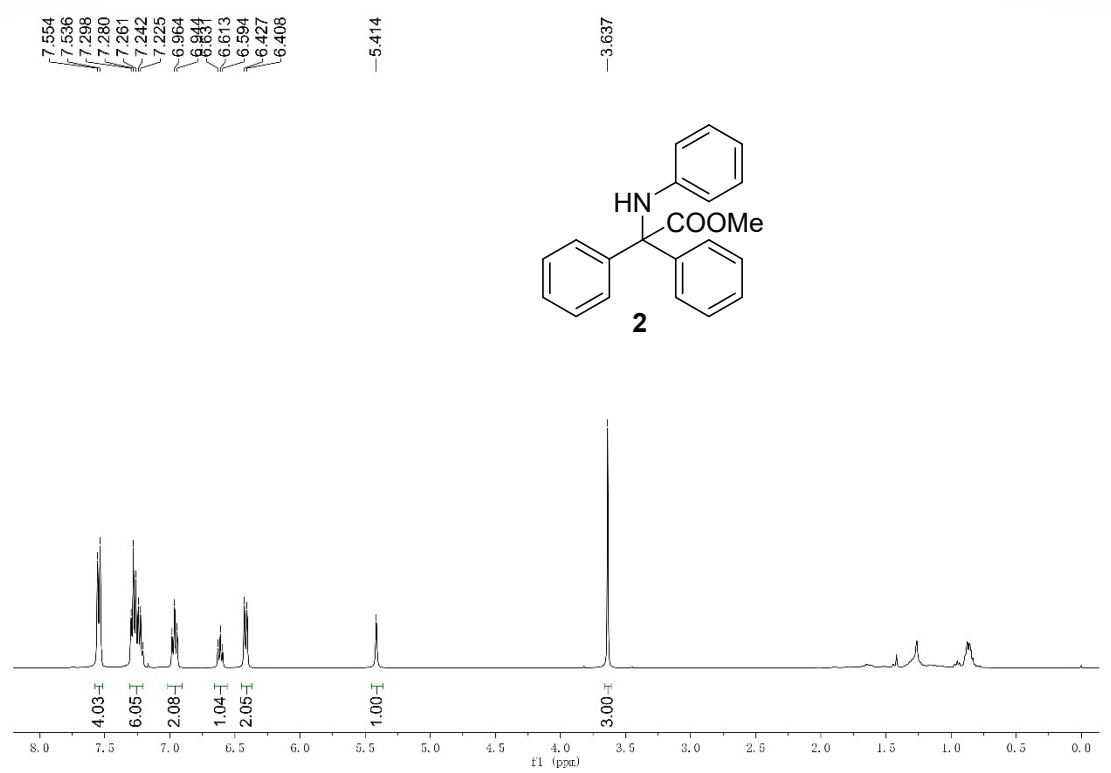
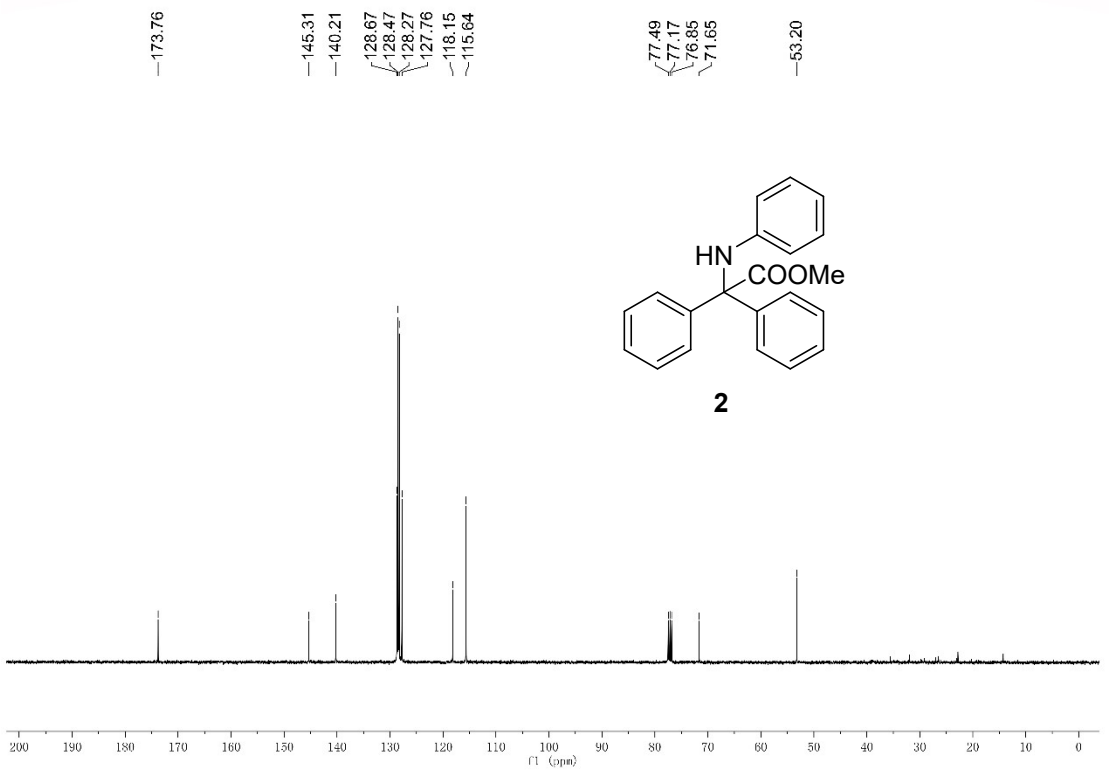
9. NMR Spectra of Coupounds.

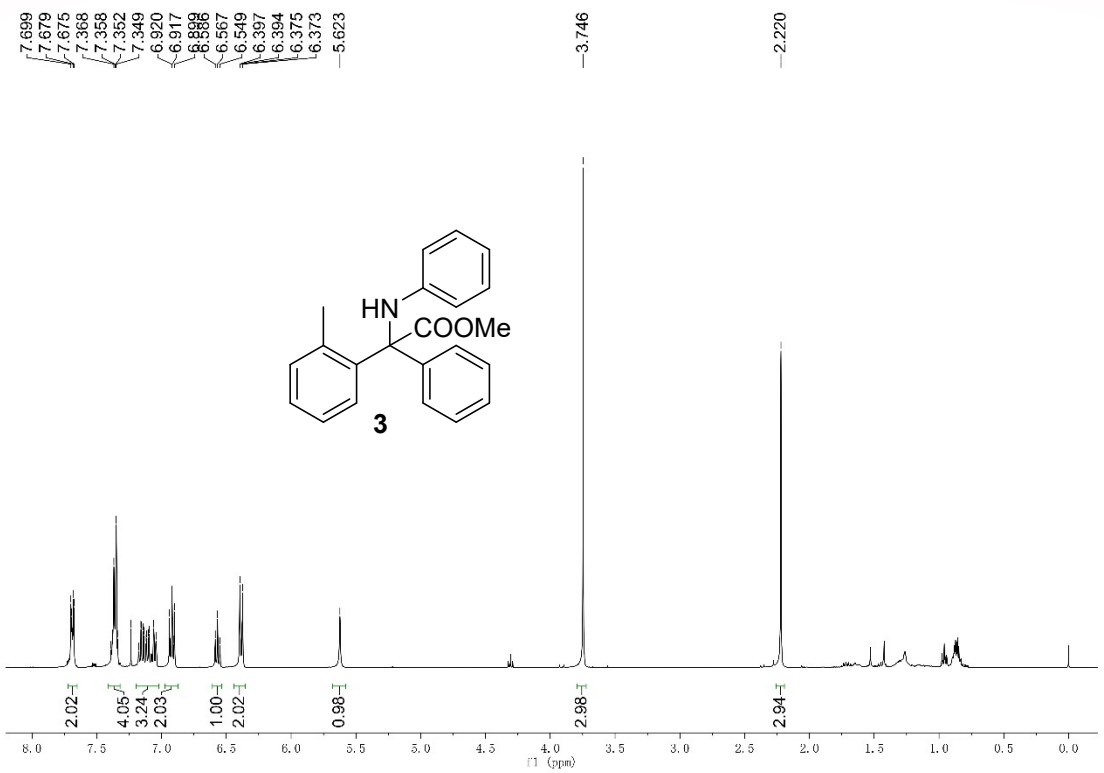
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.



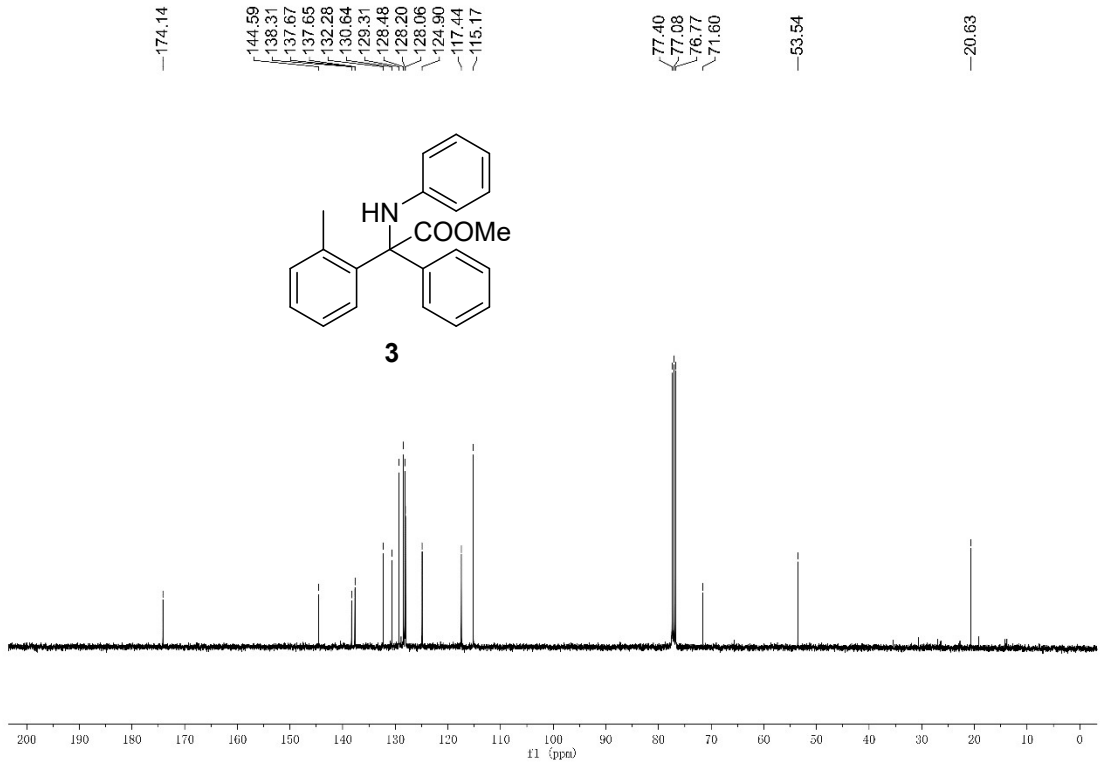
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2.**



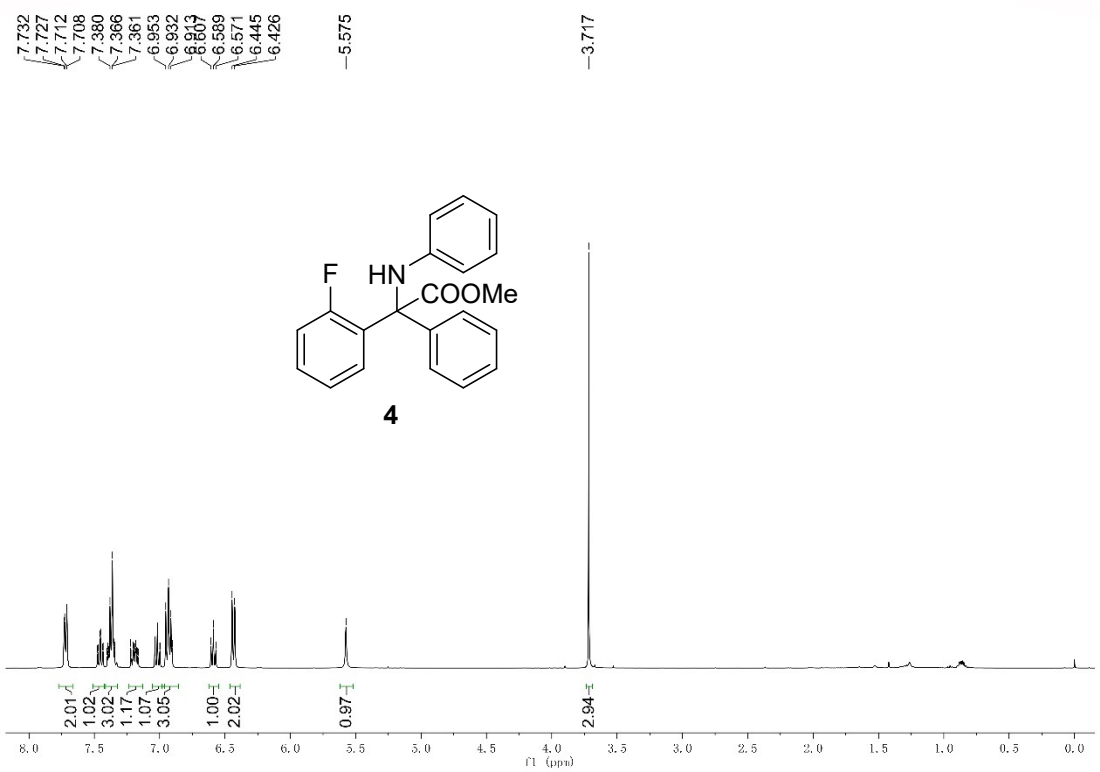
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.



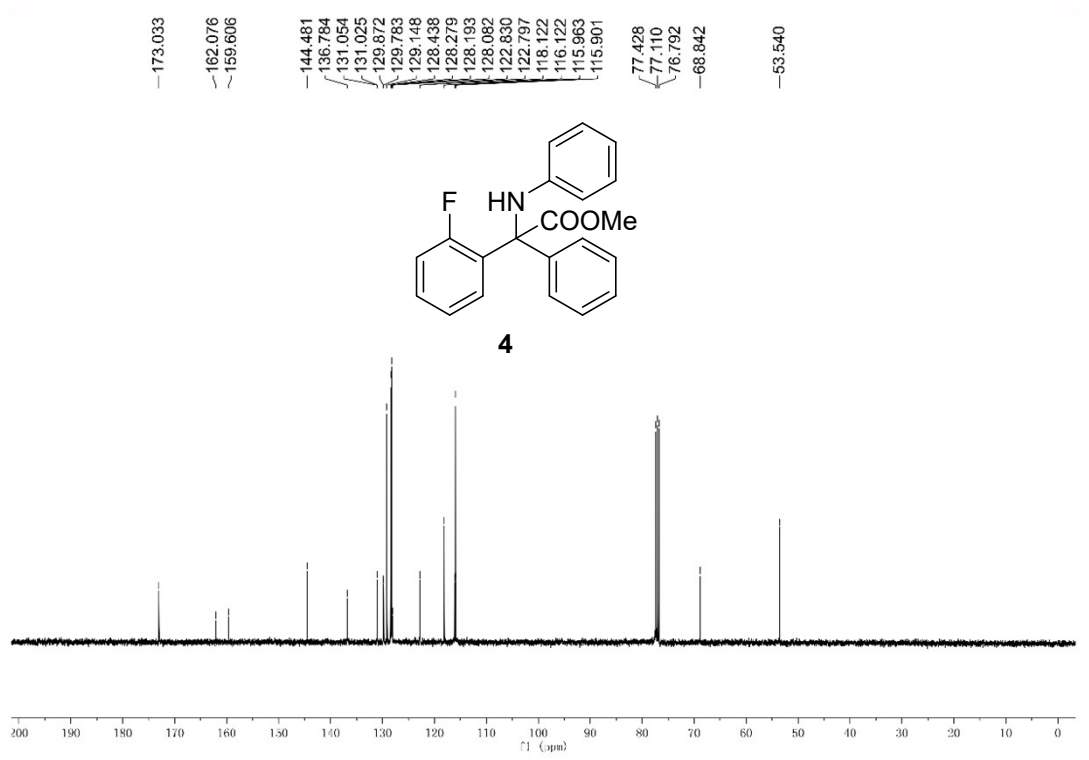
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**



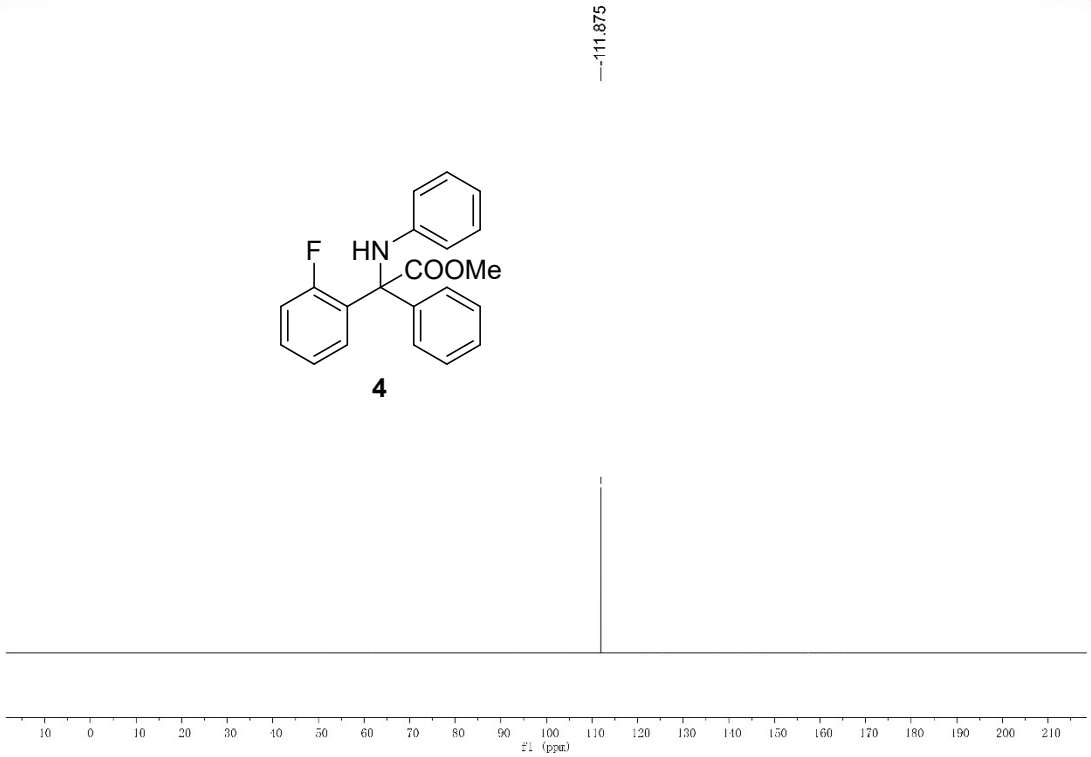
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**.



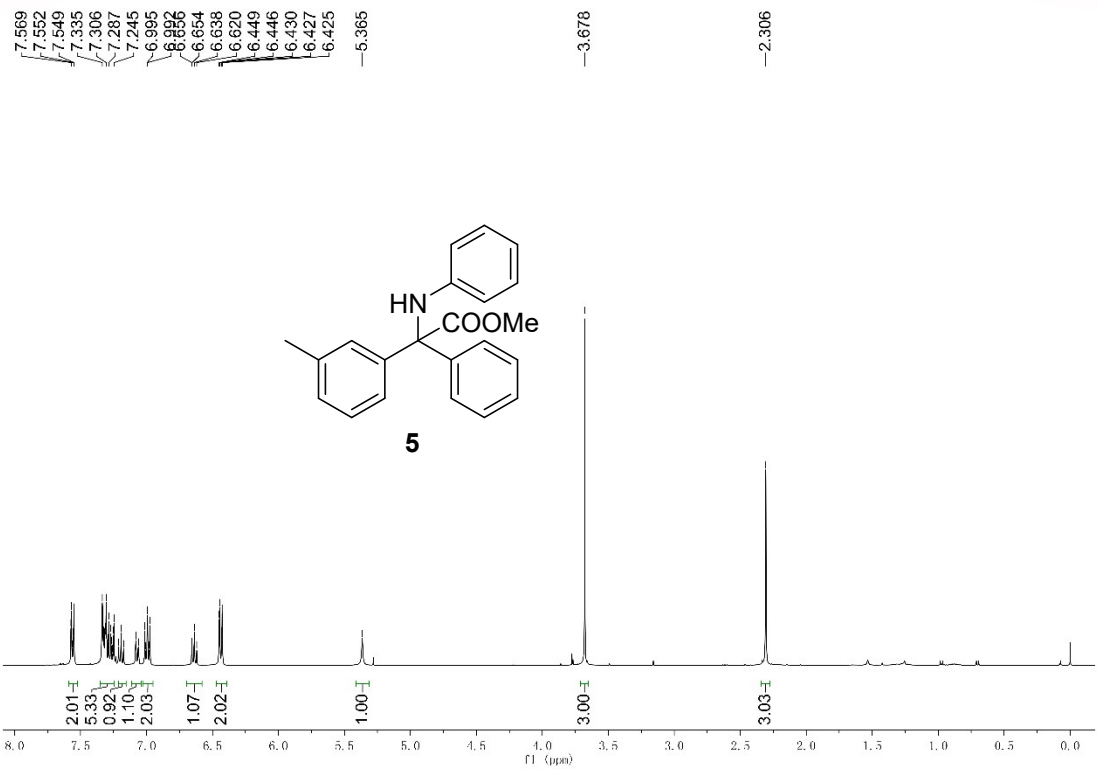
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**



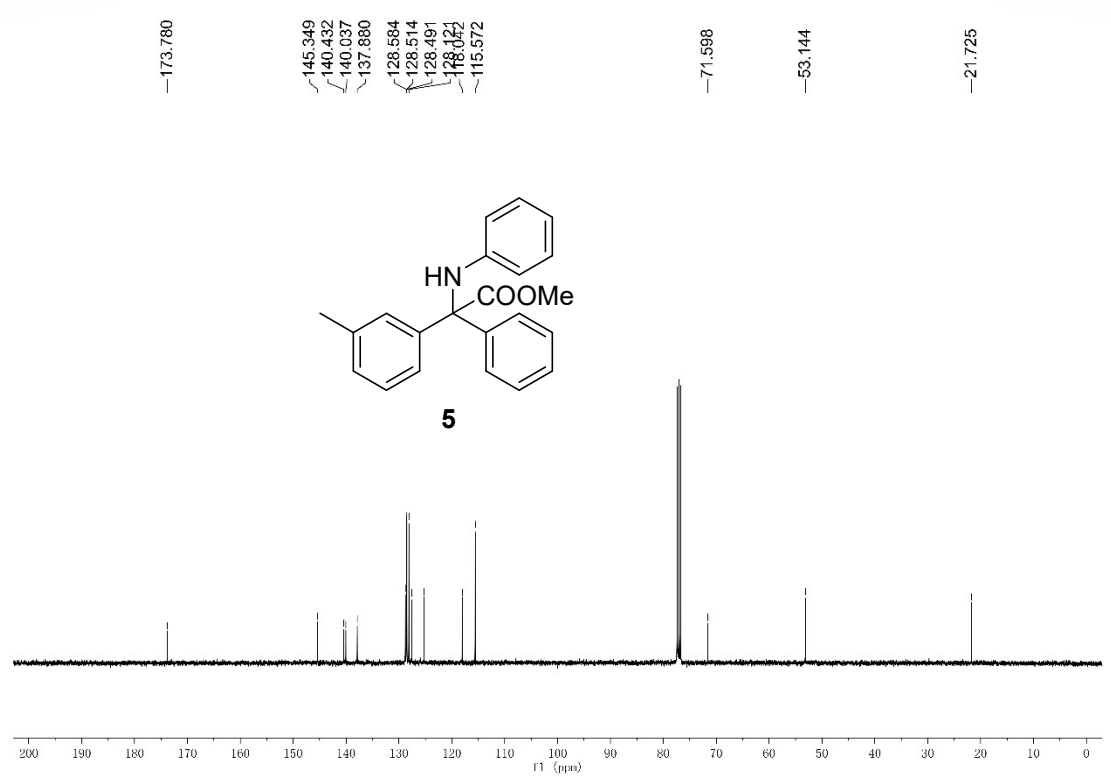
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **4.**



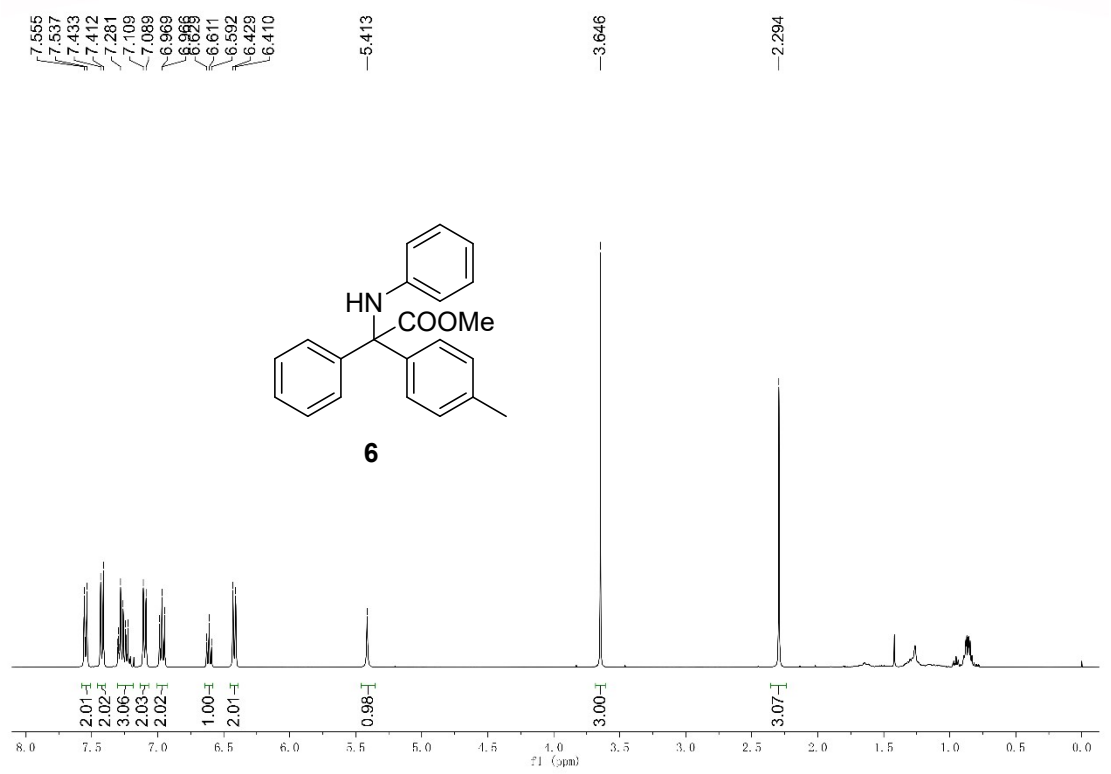
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**.



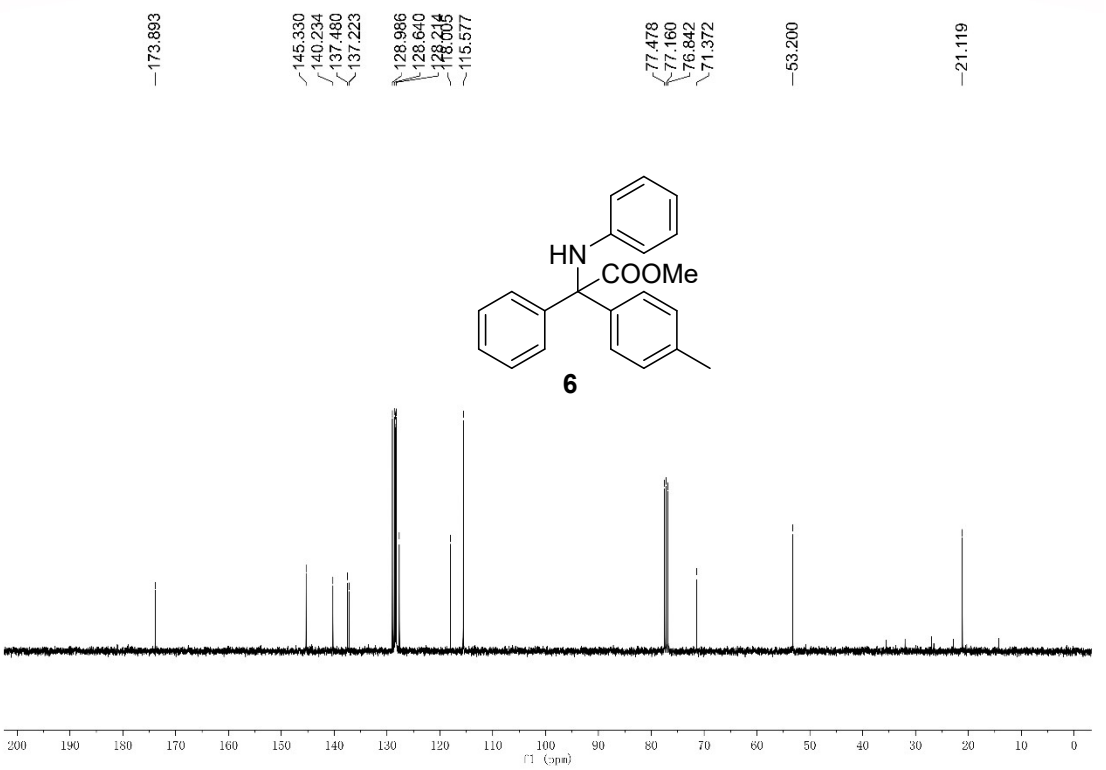
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**



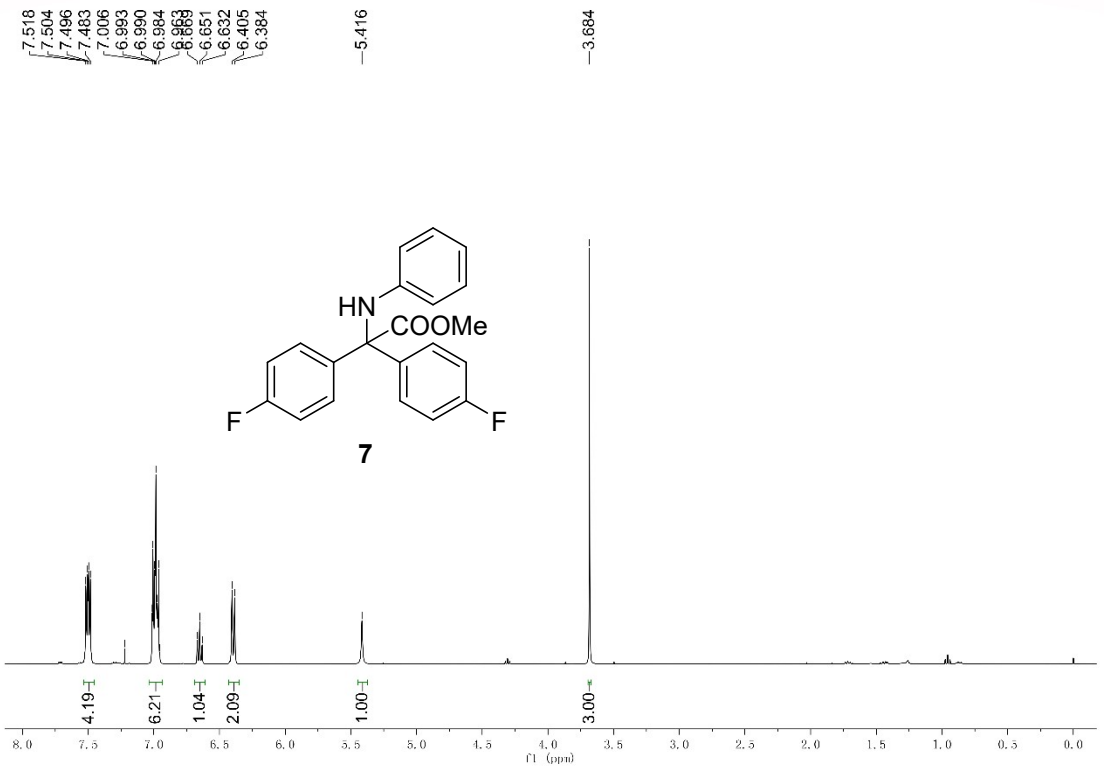
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**.



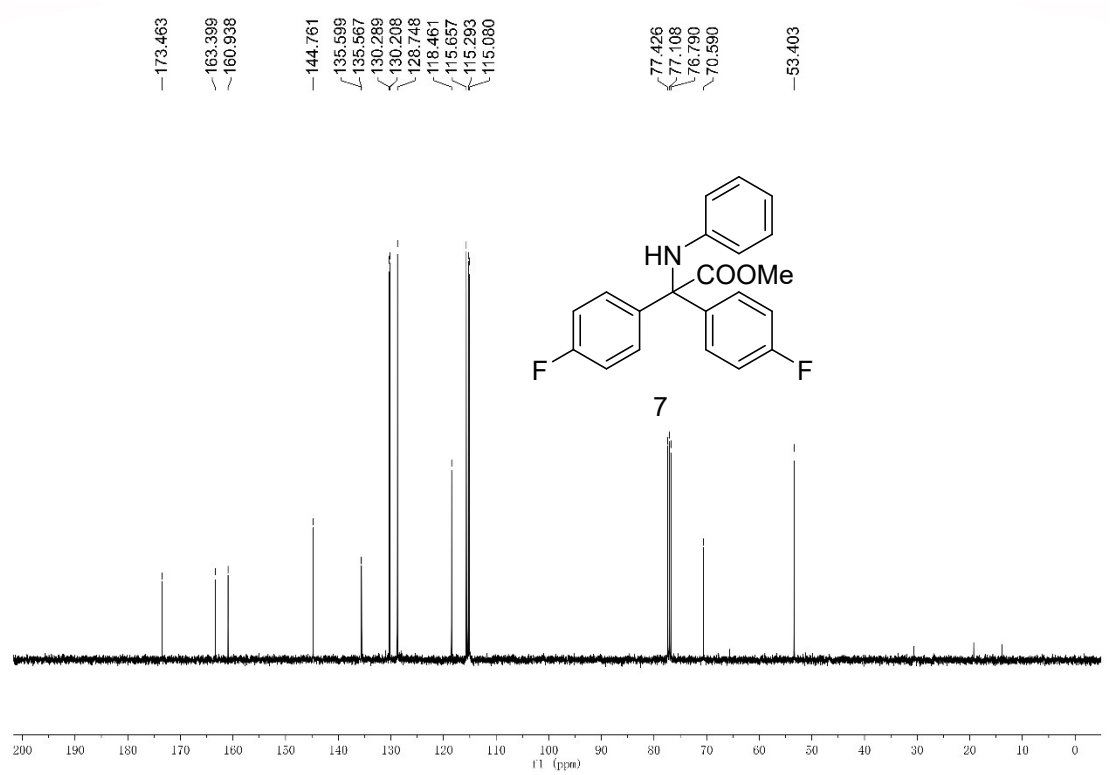
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**



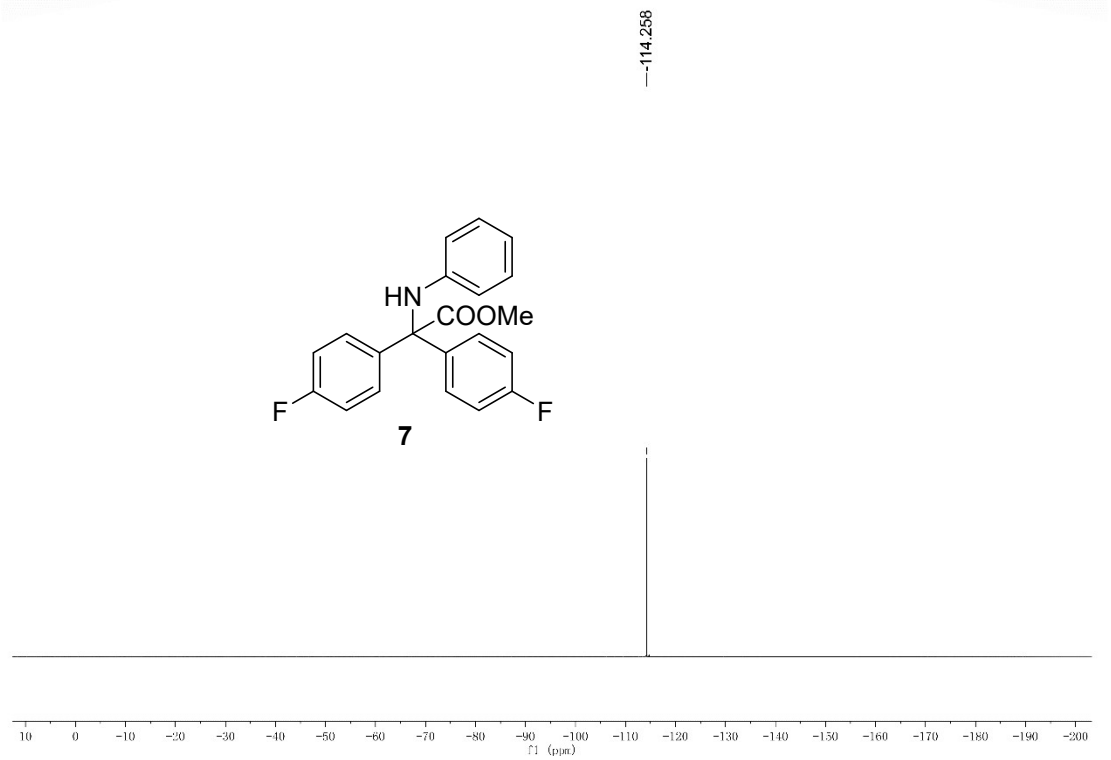
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**.



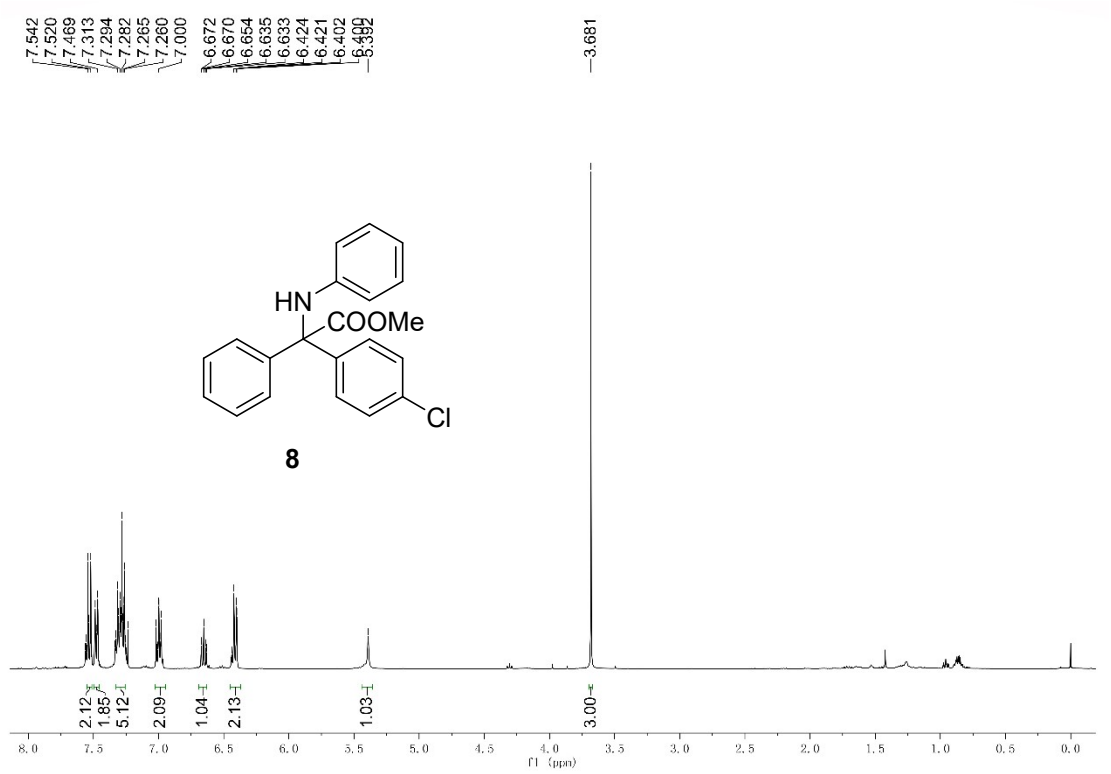
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7**



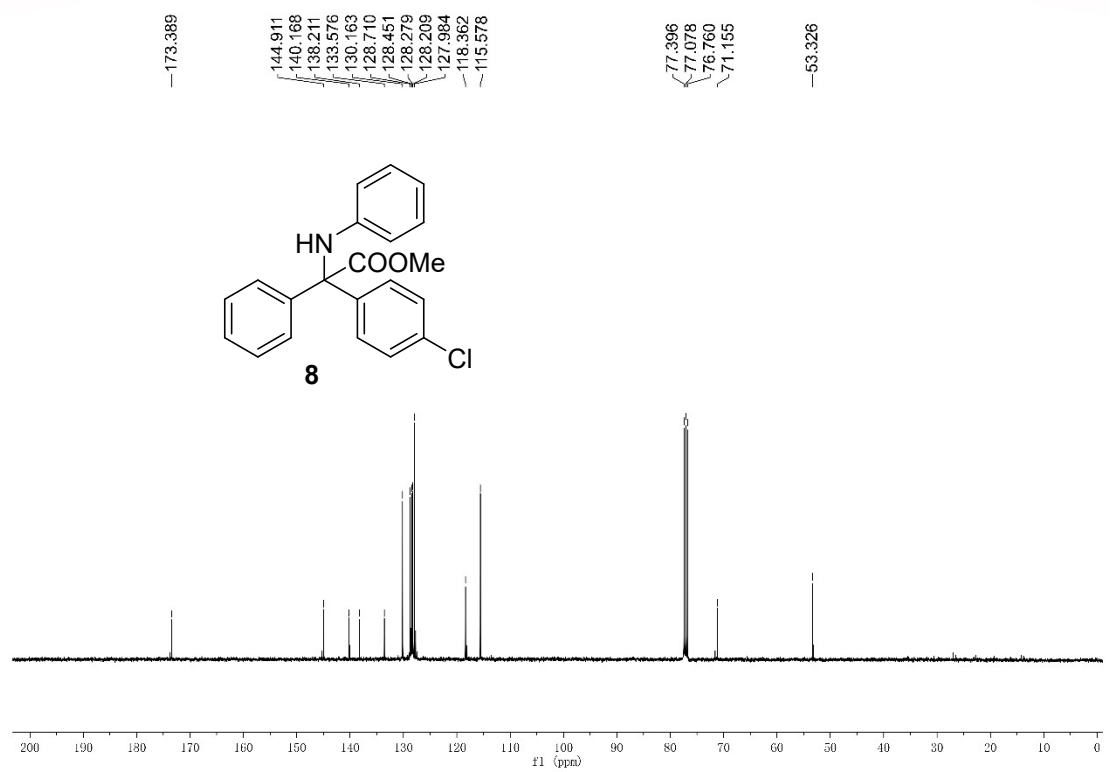
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **7.**



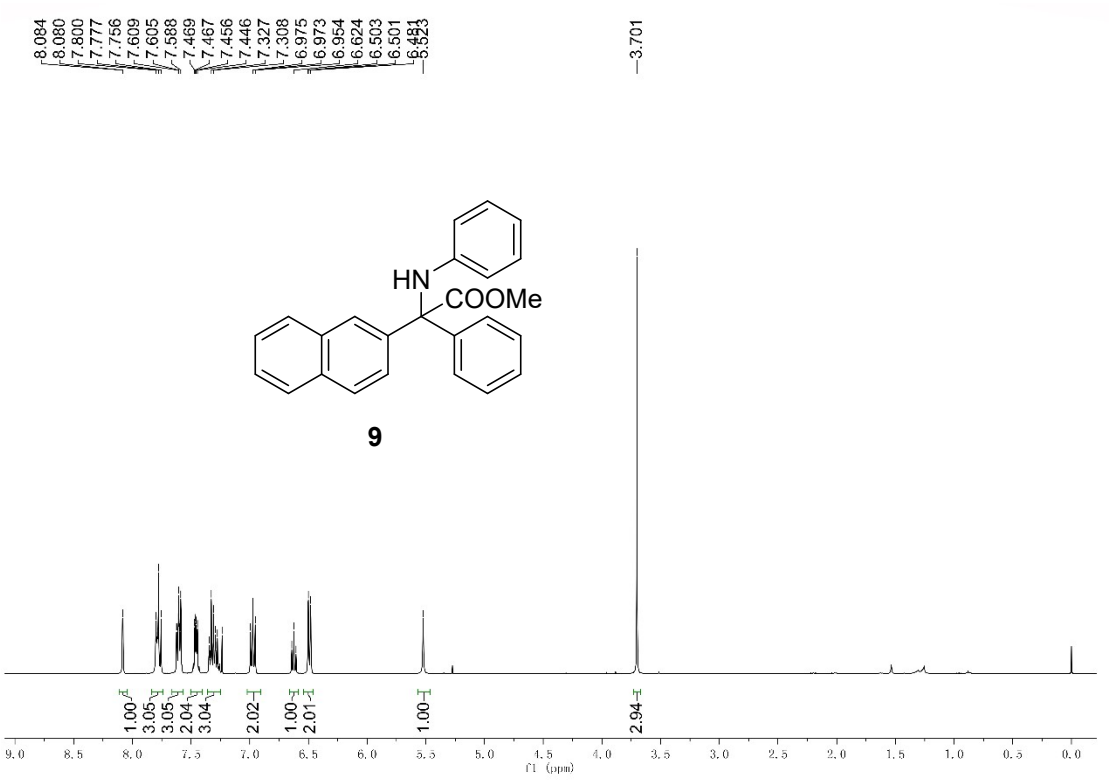
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**.



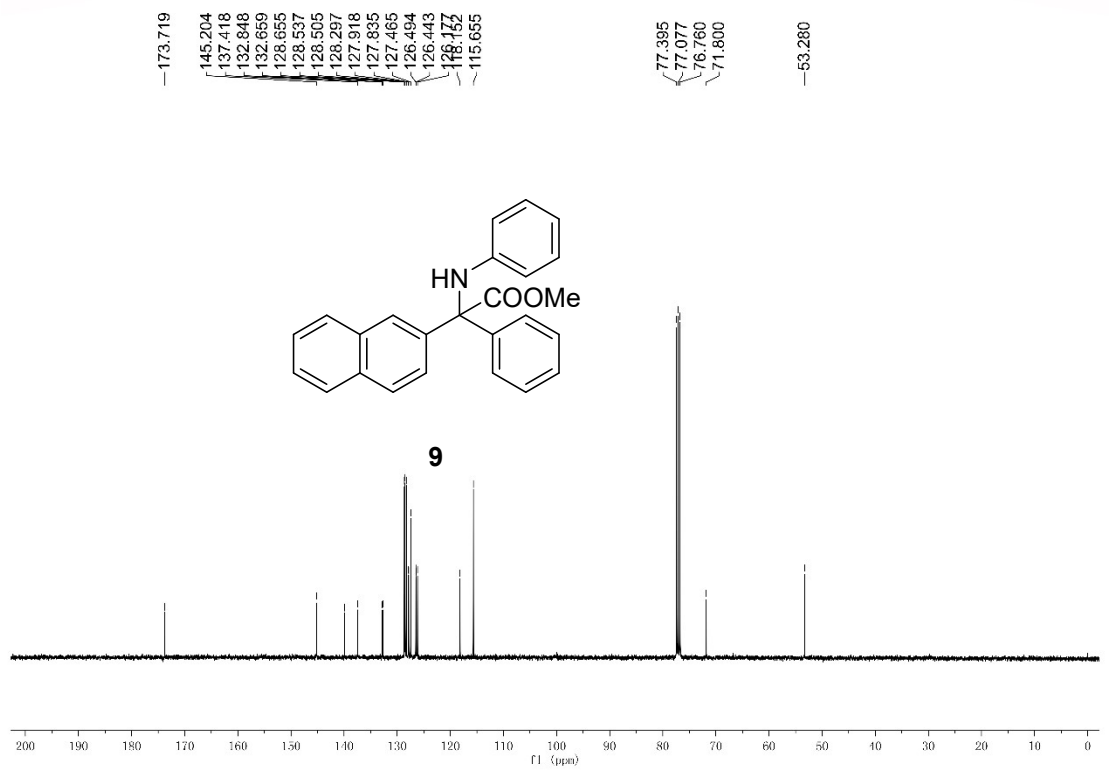
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8**



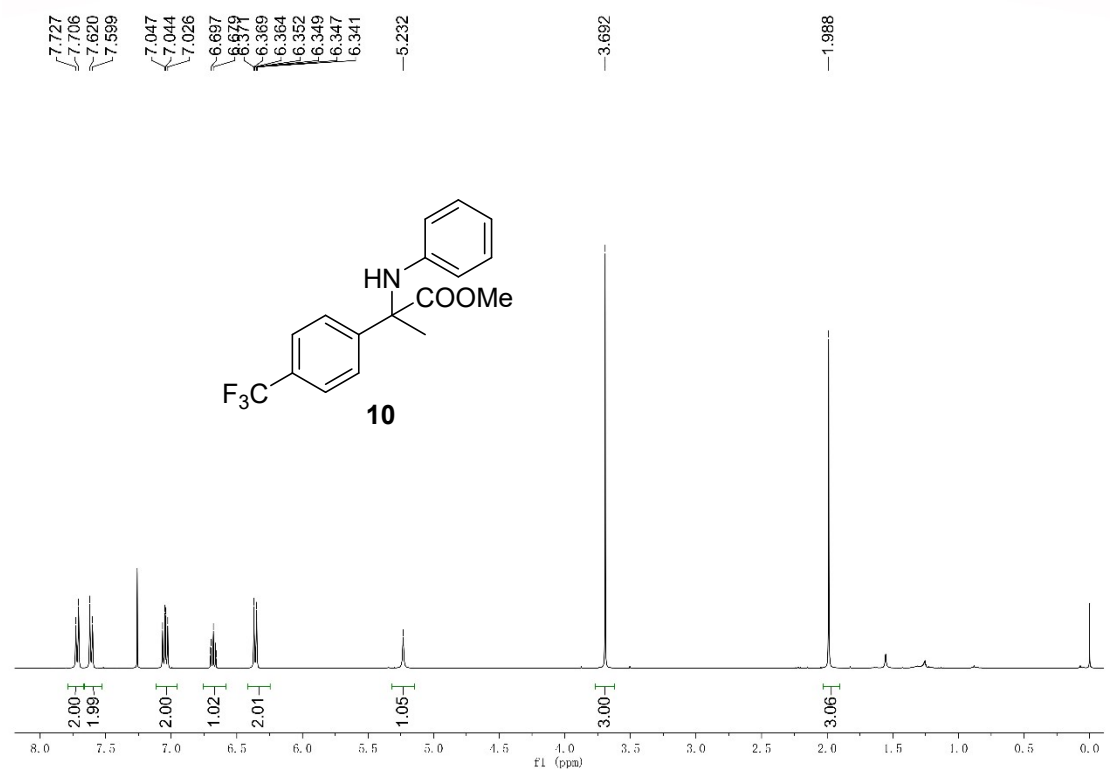
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9**.



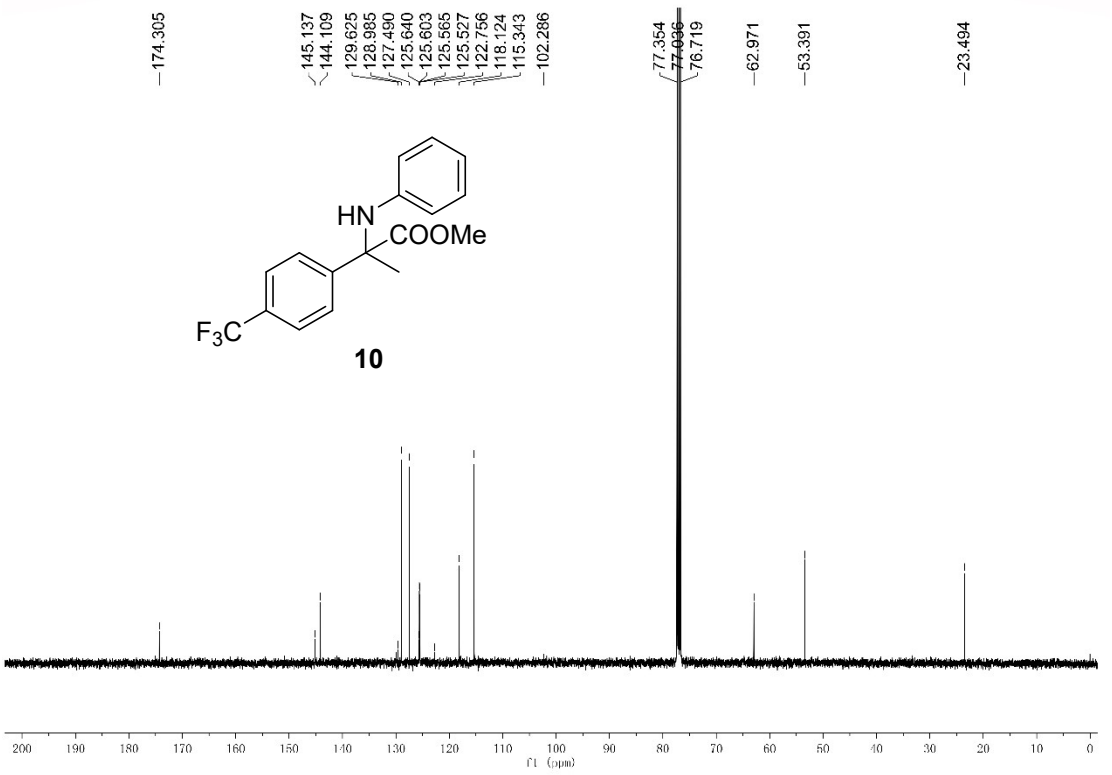
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9**



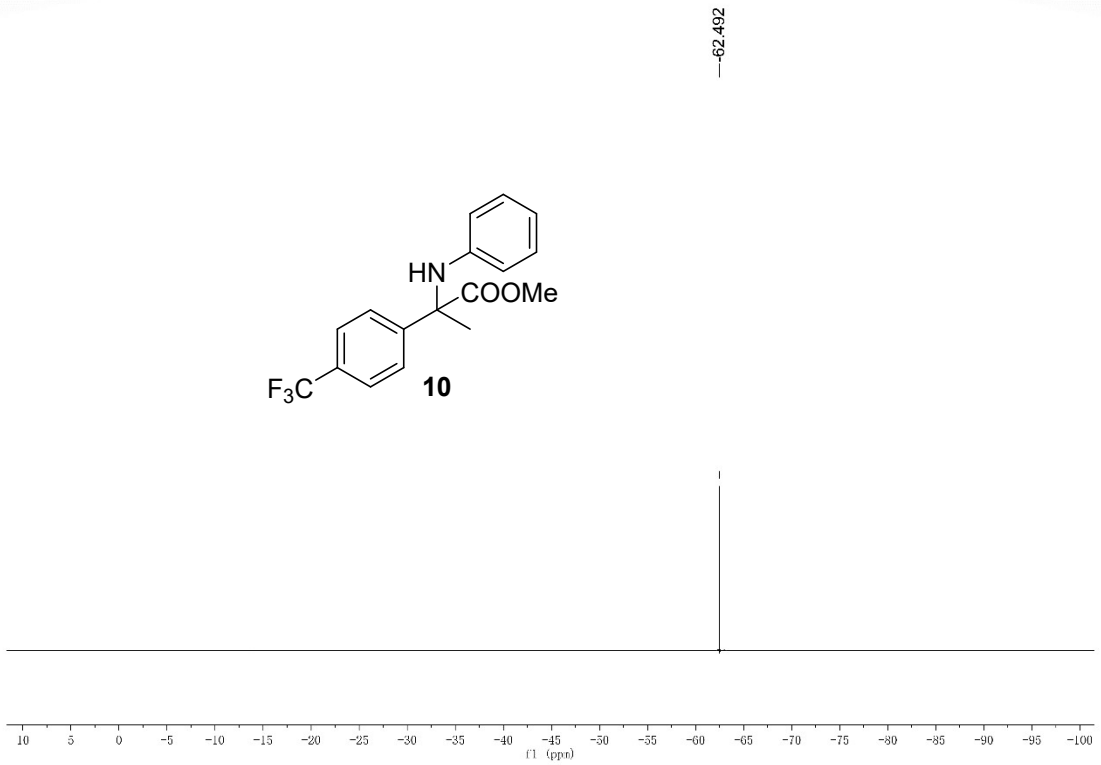
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**.



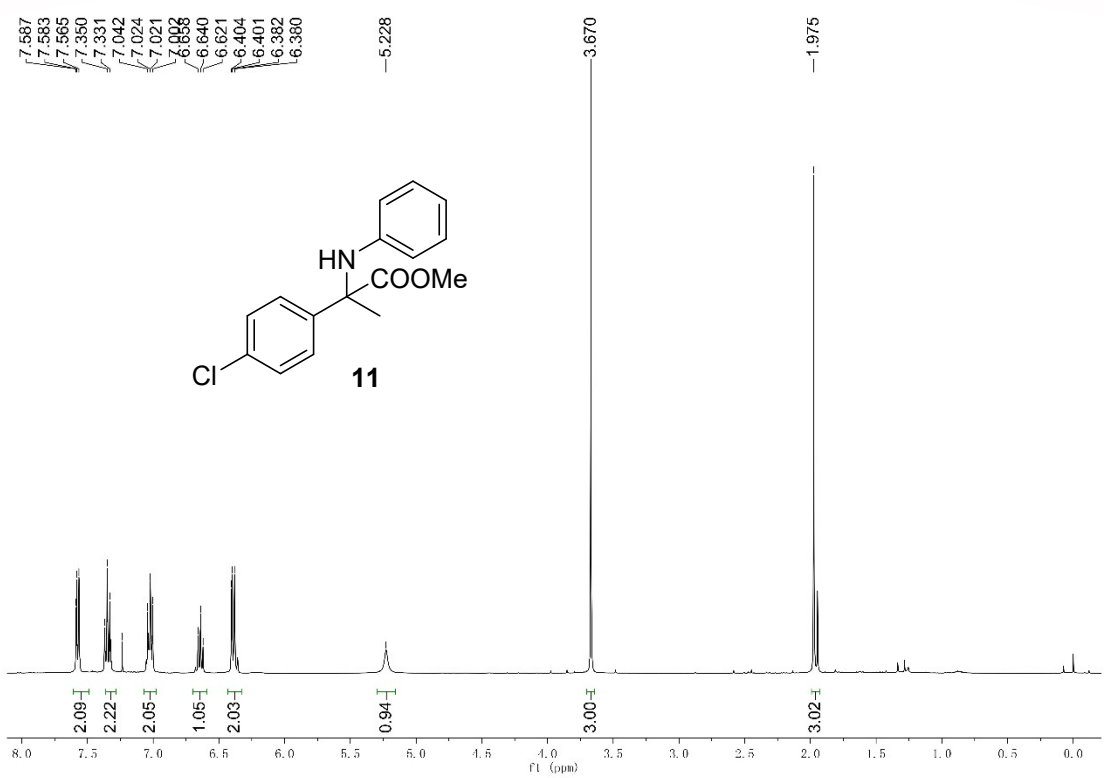
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**



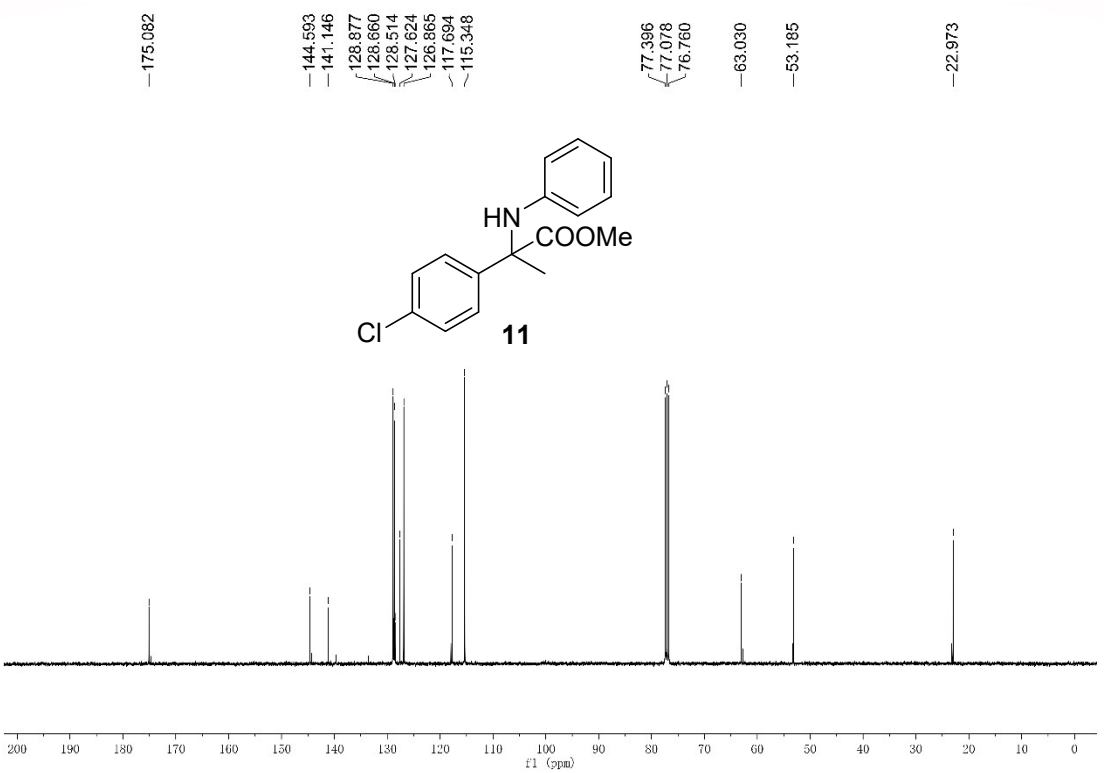
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **10.**



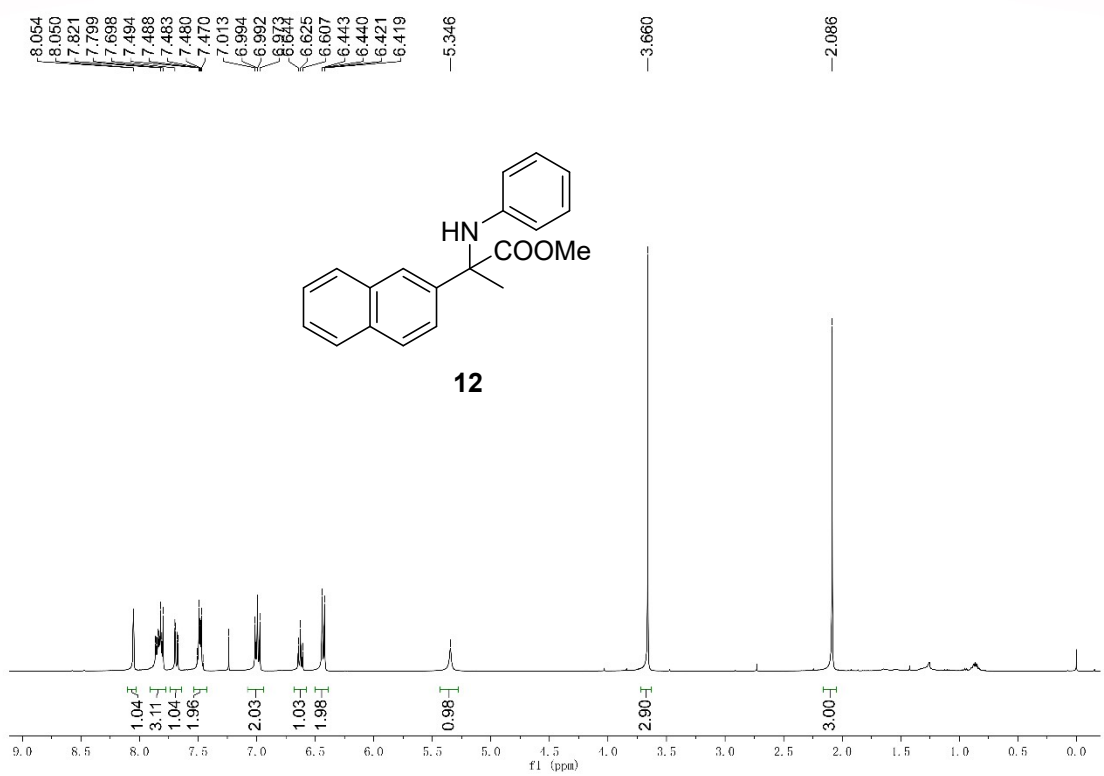
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**.



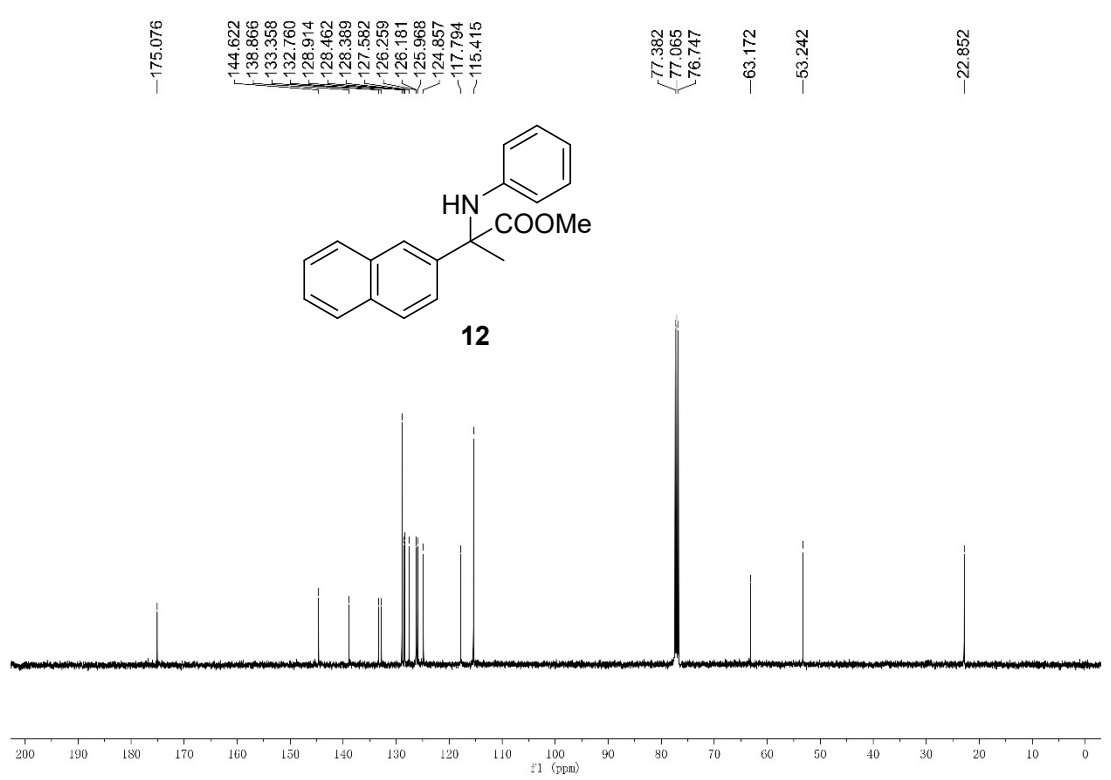
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11**



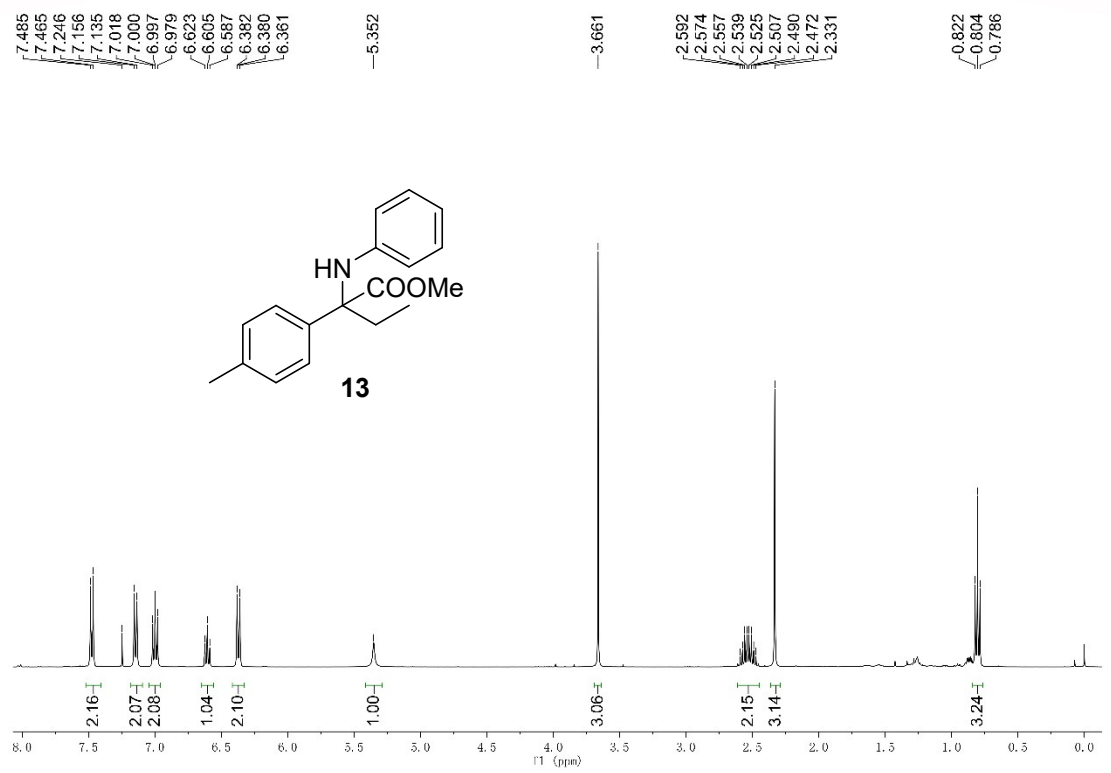
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**.



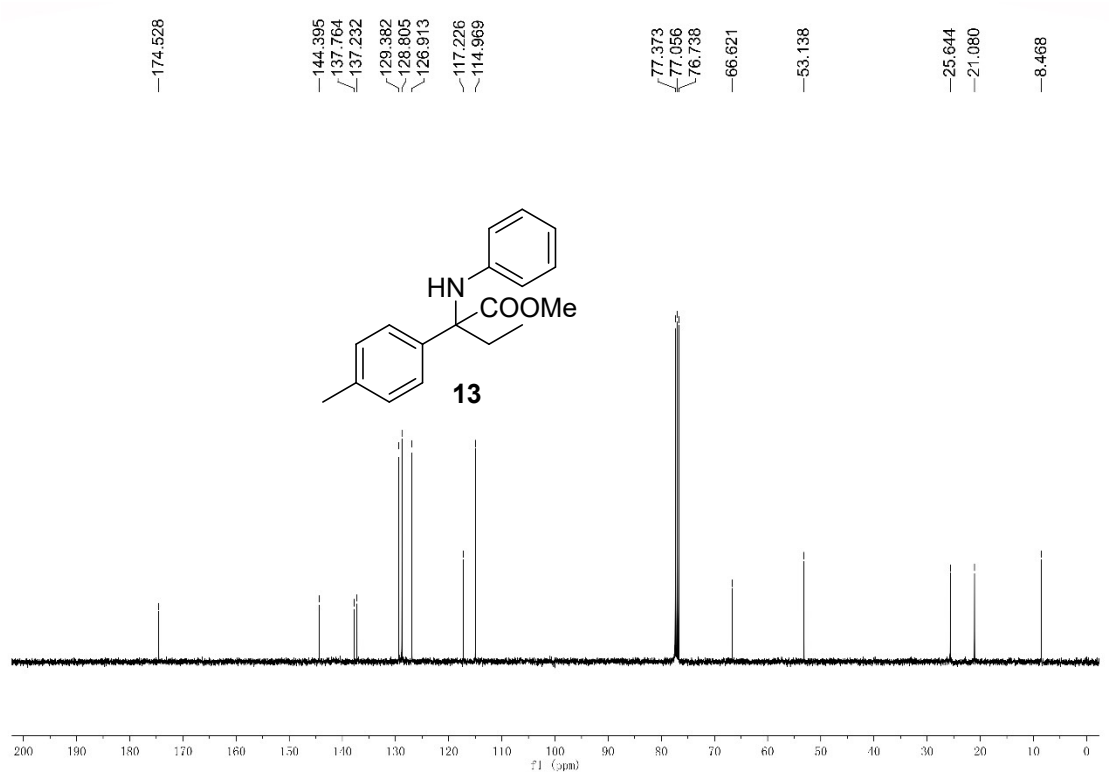
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12**



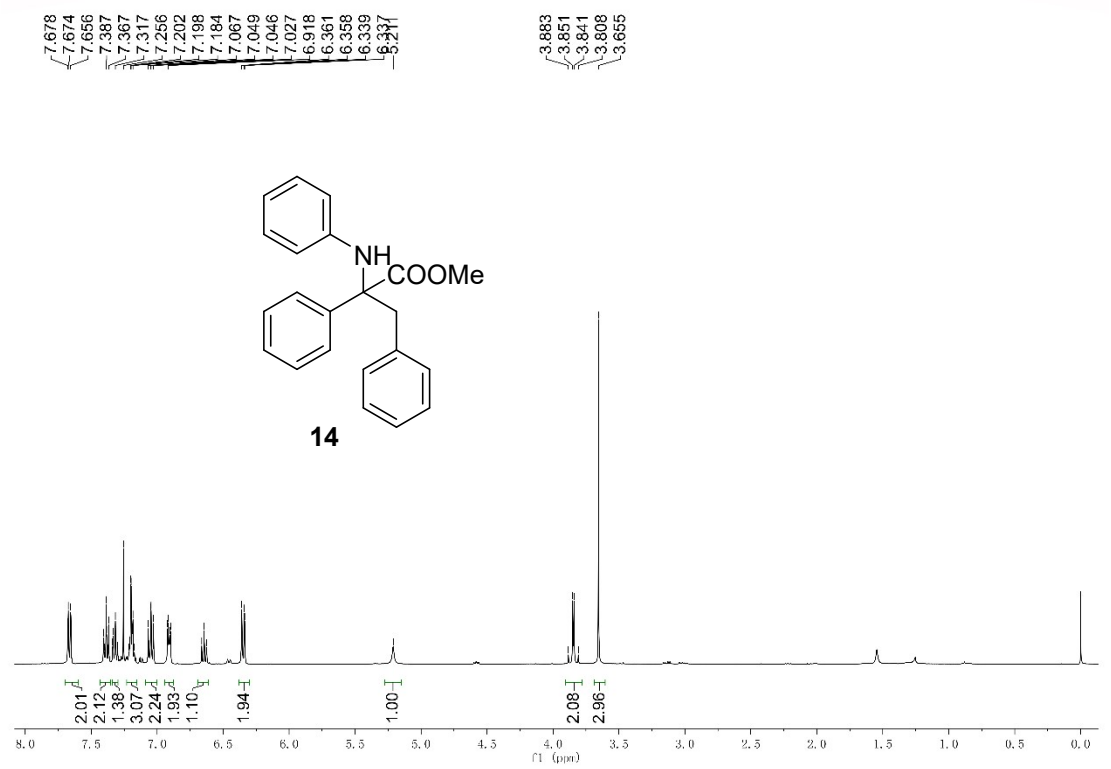
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**.



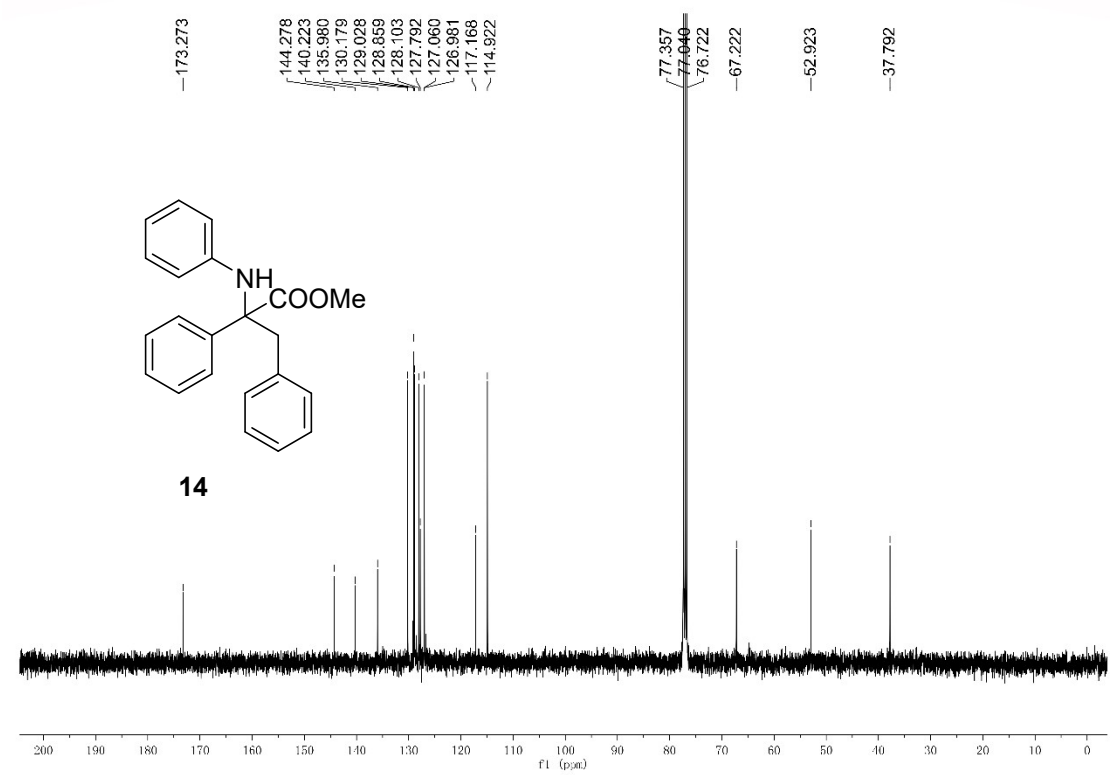
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13**



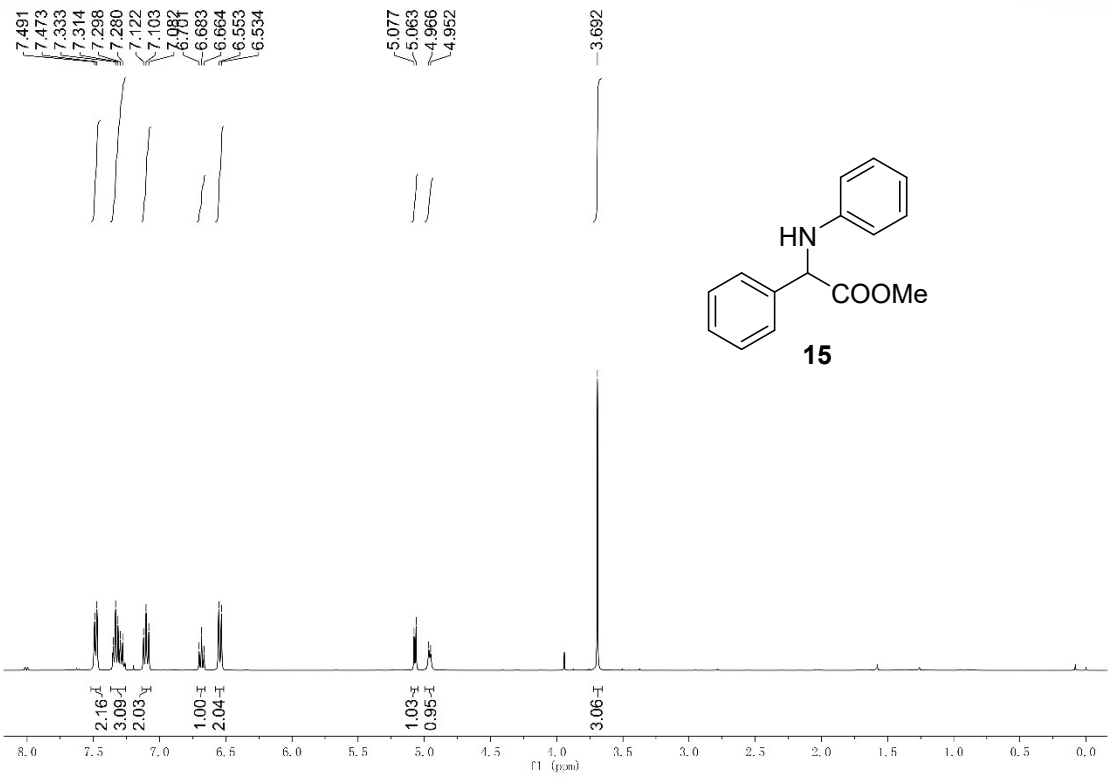
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14**.



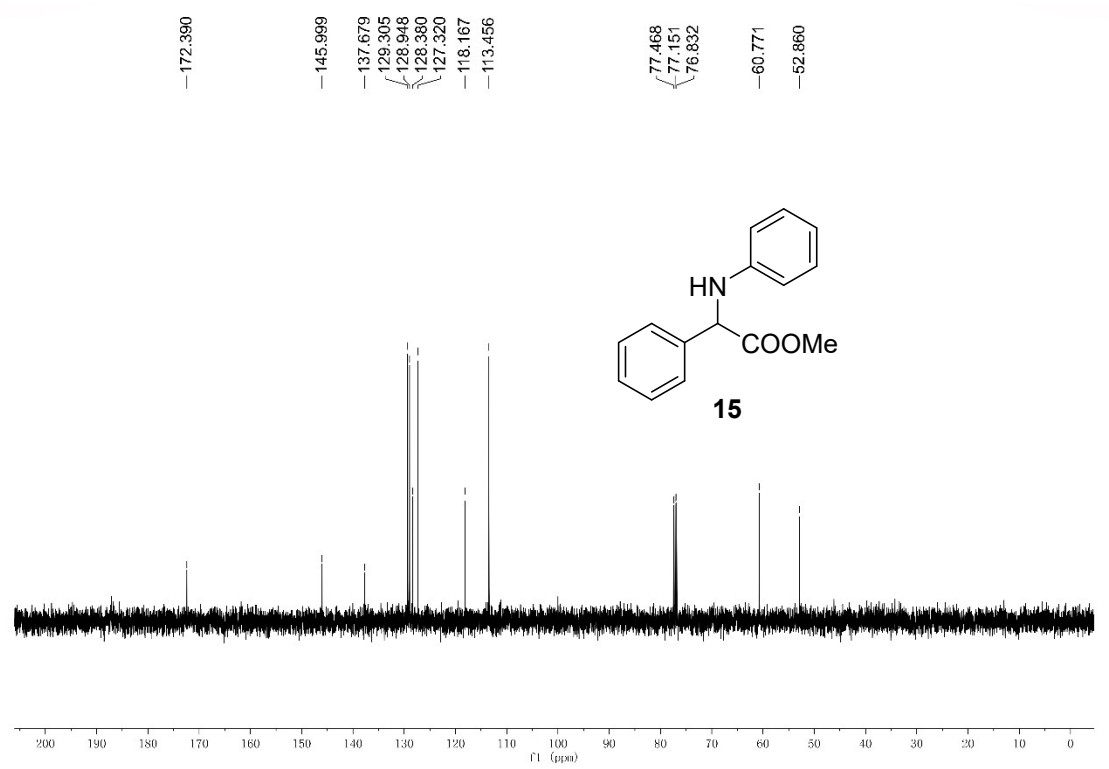
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **14**



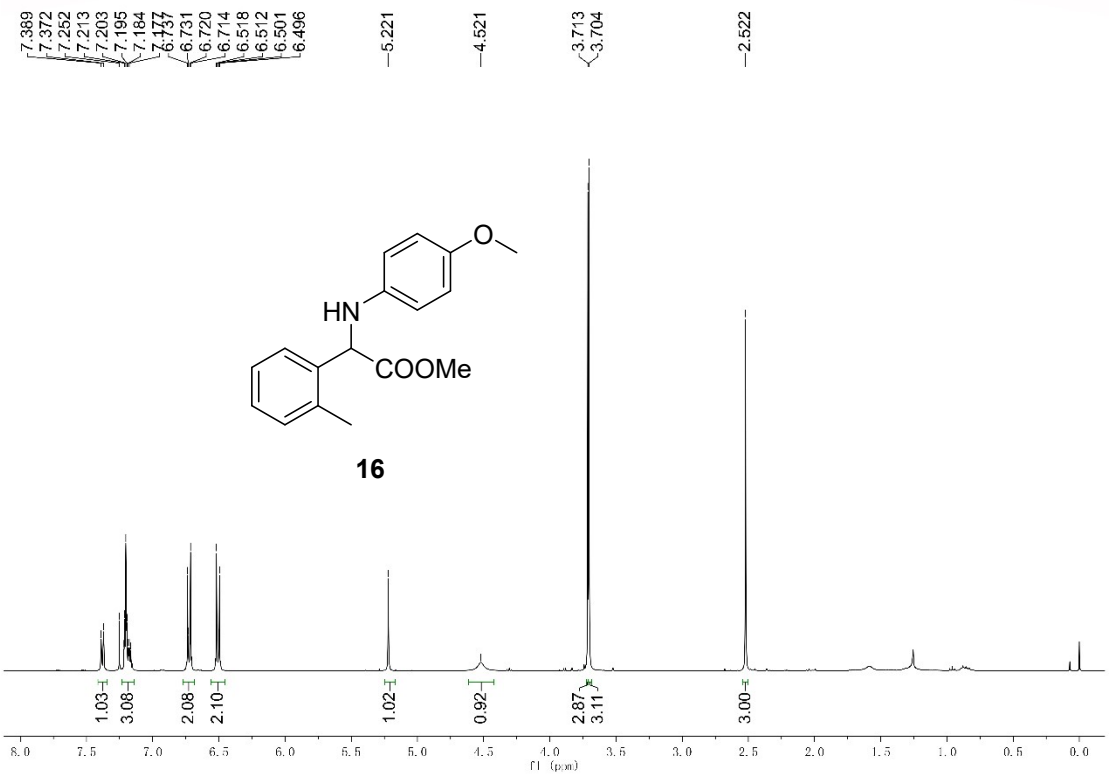
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15**.



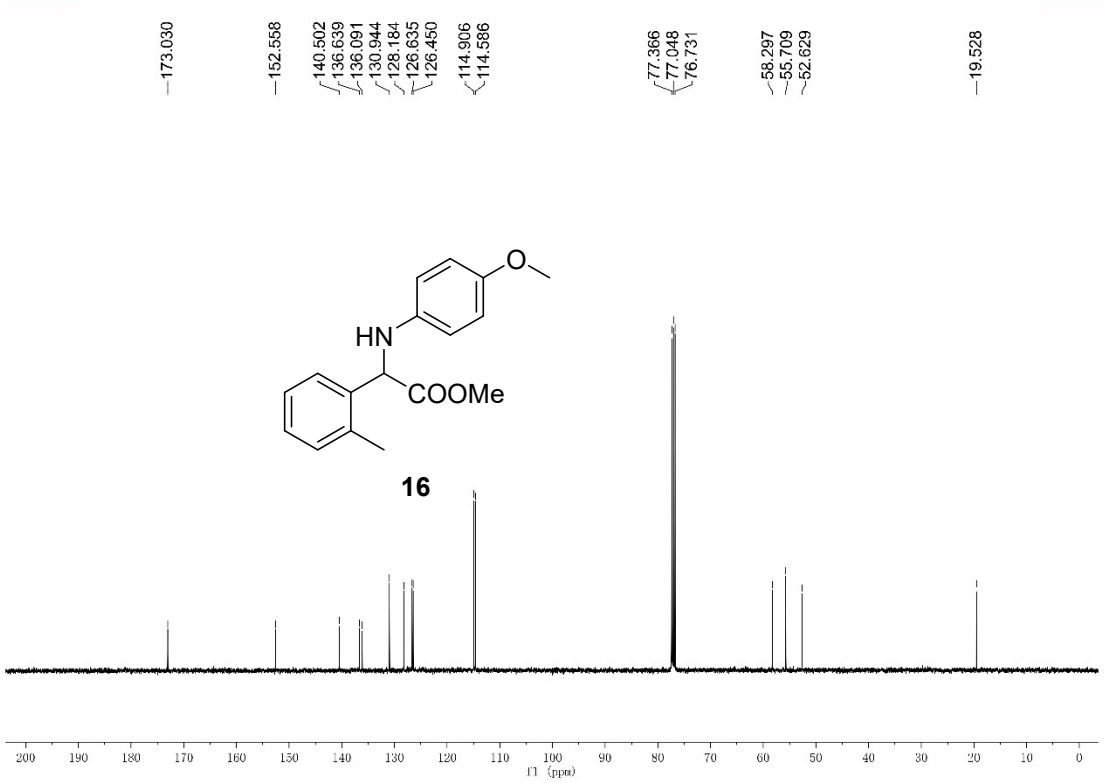
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **15**



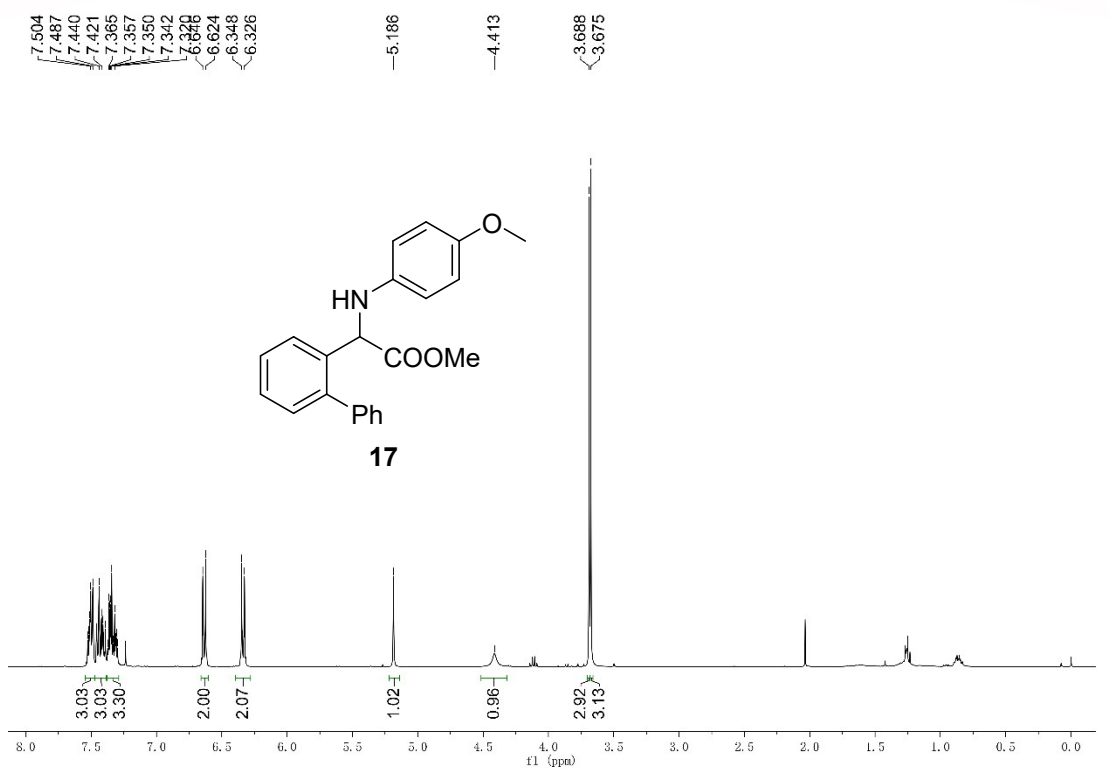
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16**.



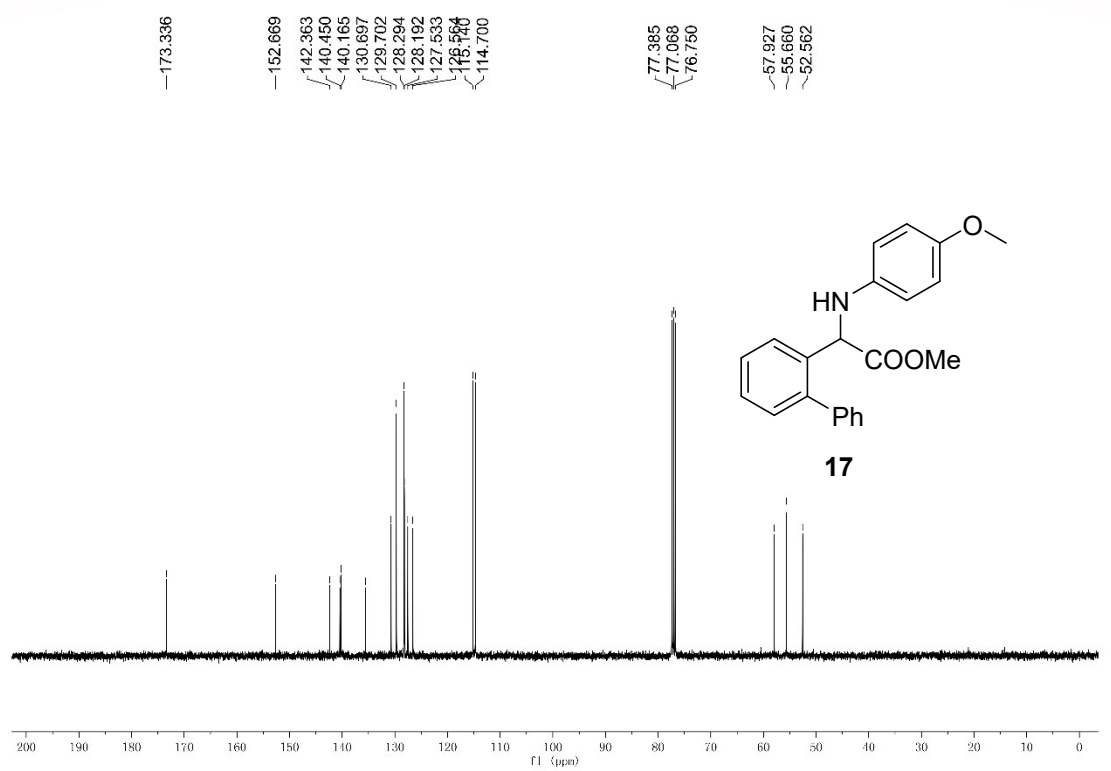
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16**



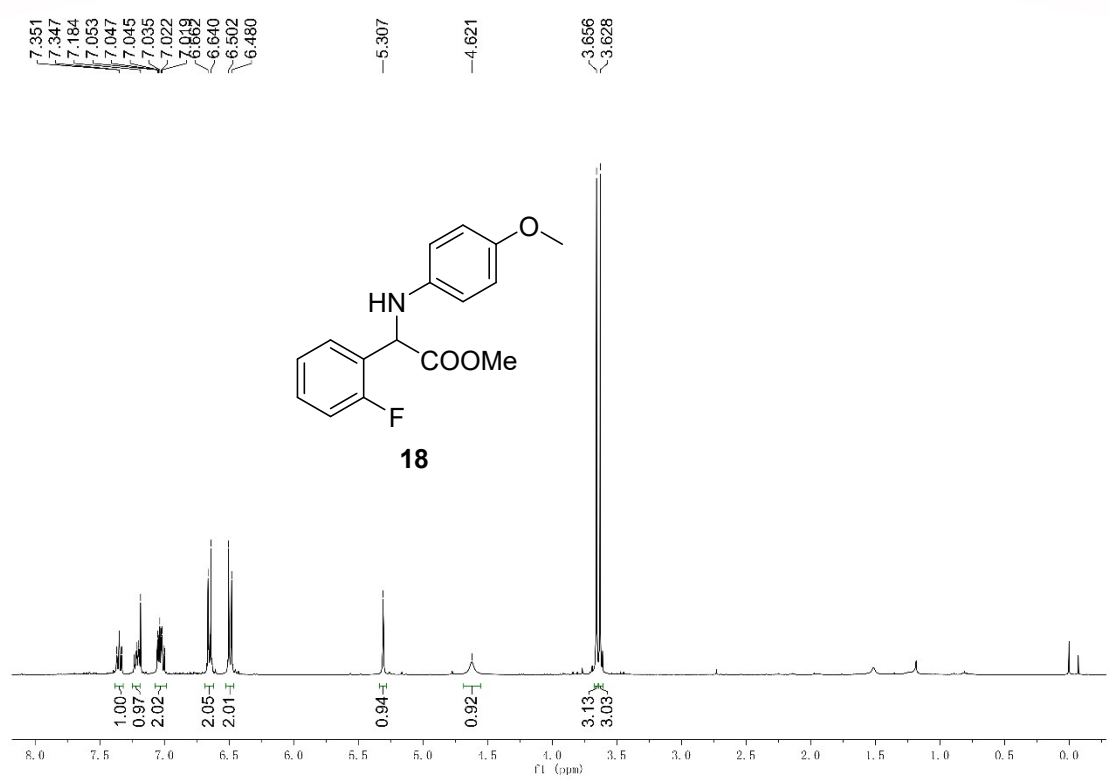
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **17**.



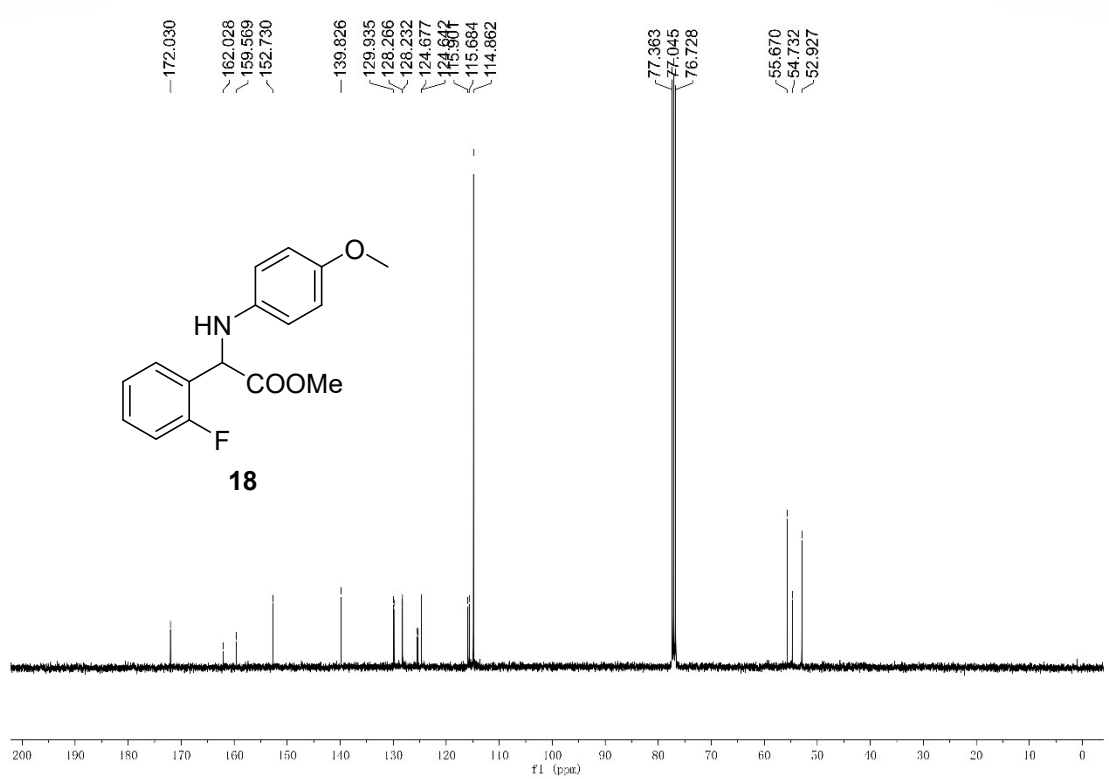
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **17**



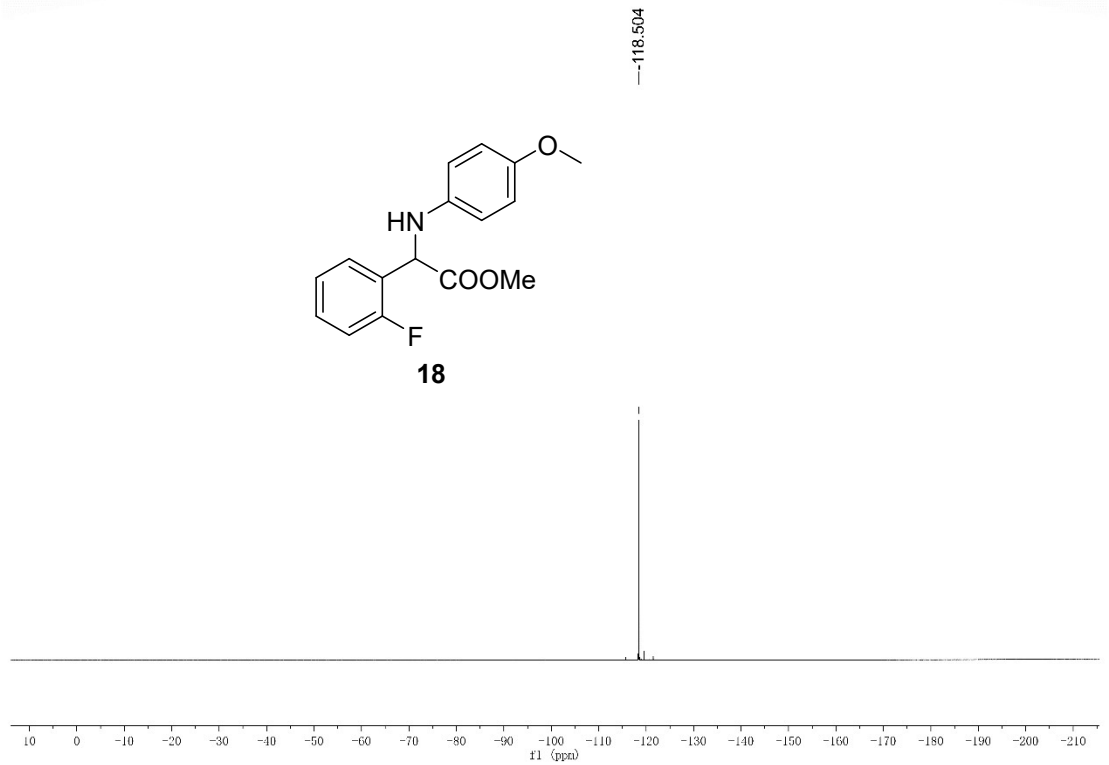
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18**.



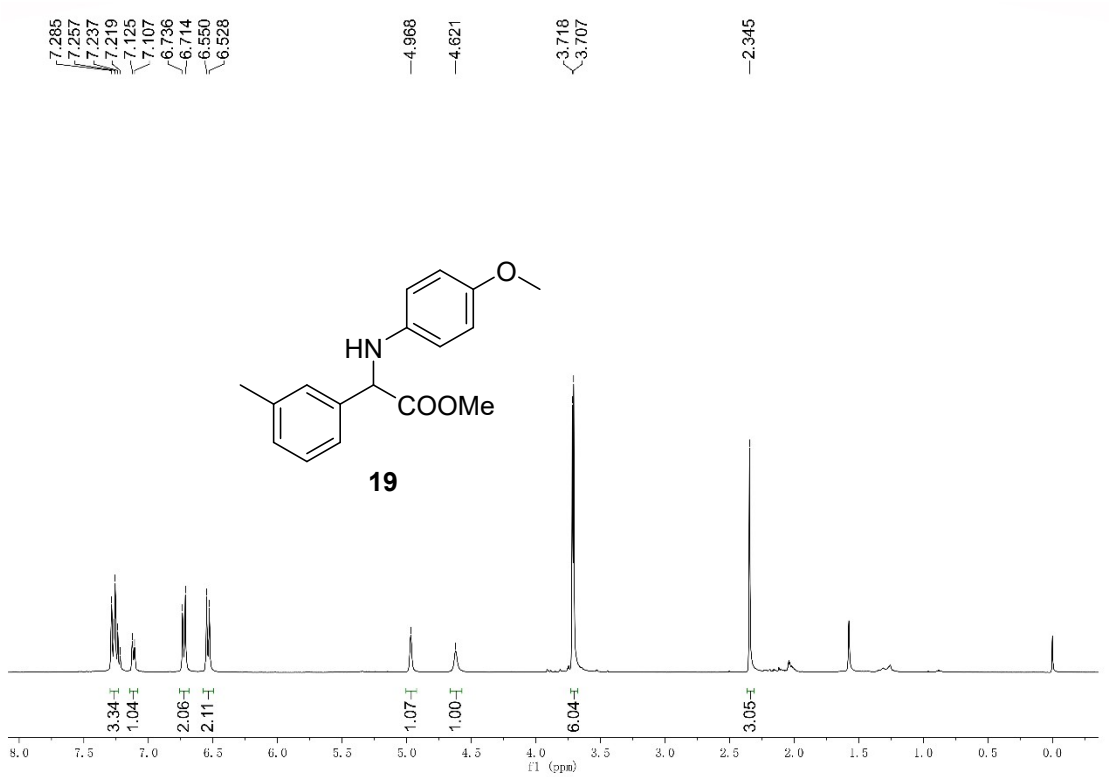
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **18**



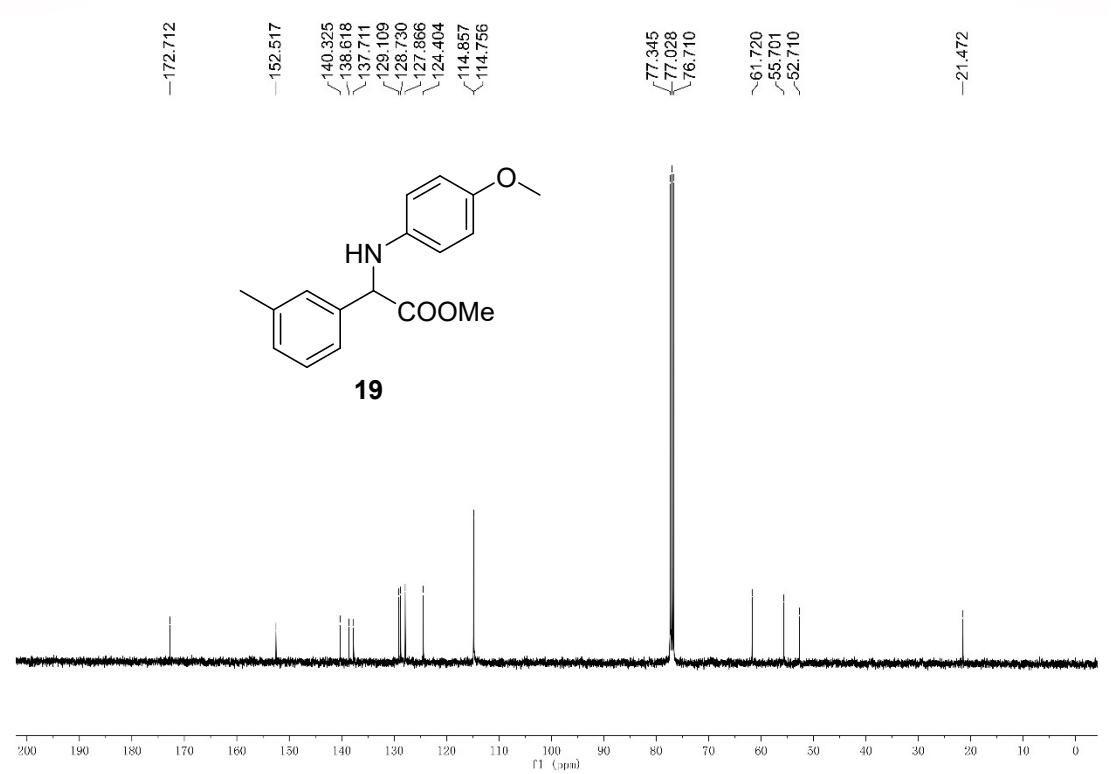
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **18**



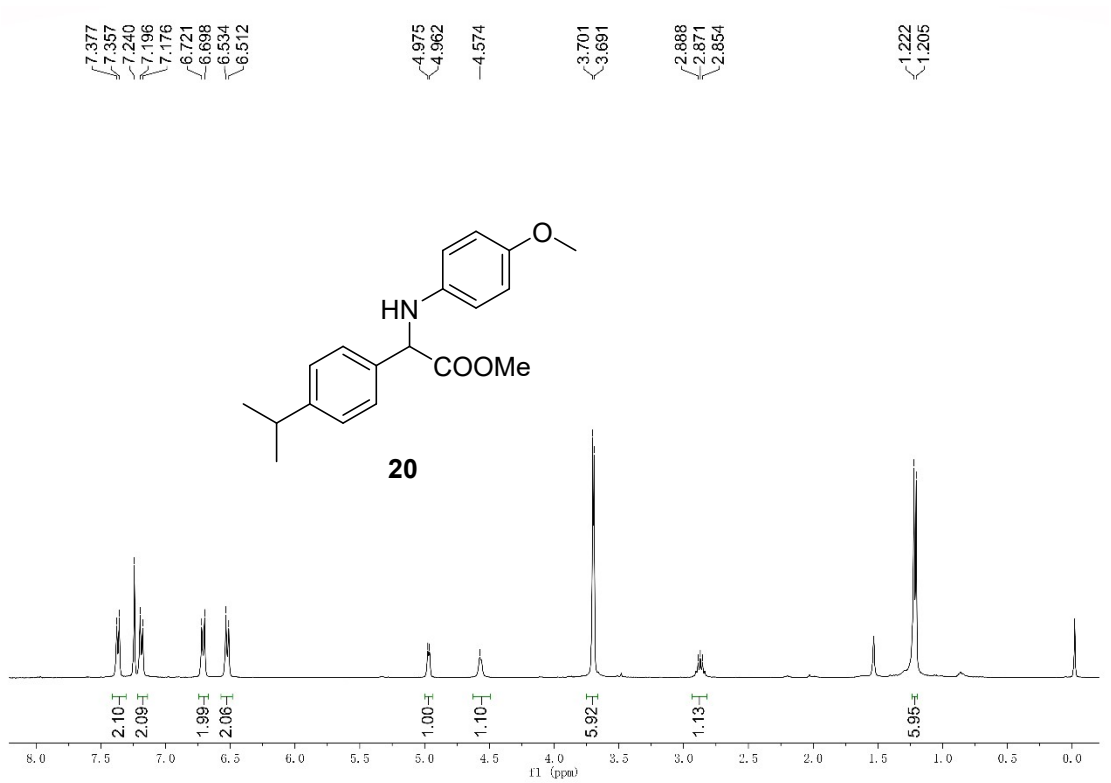
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**.



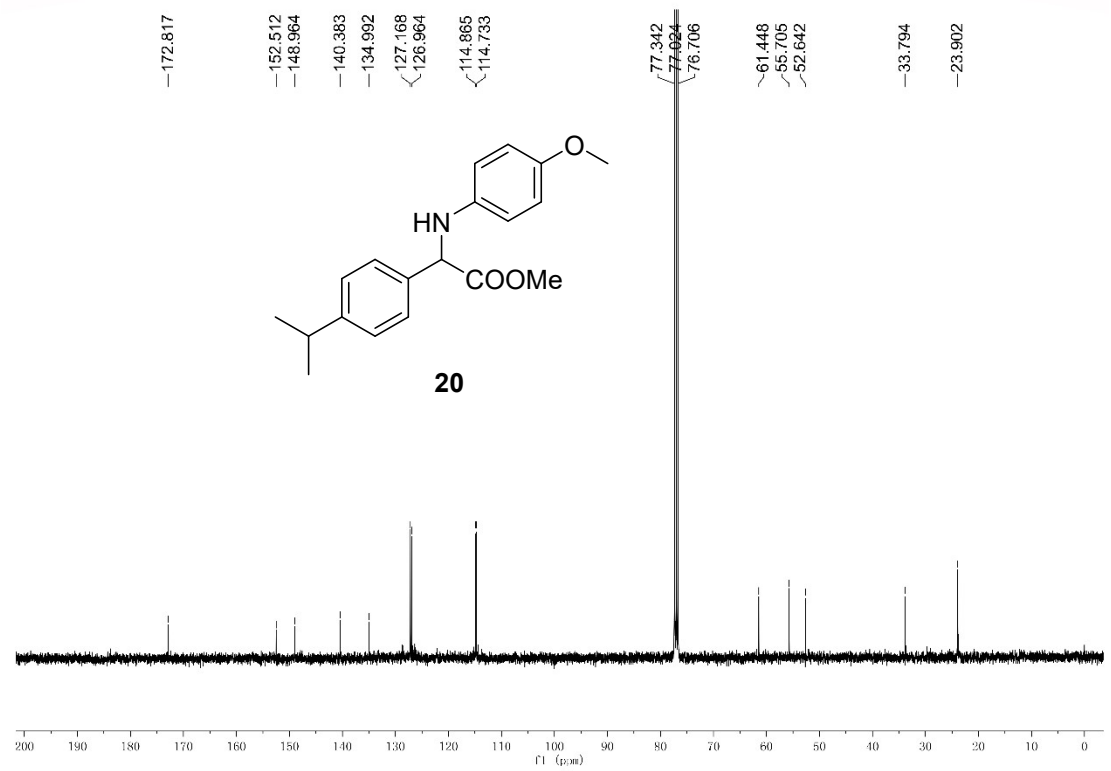
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **19**



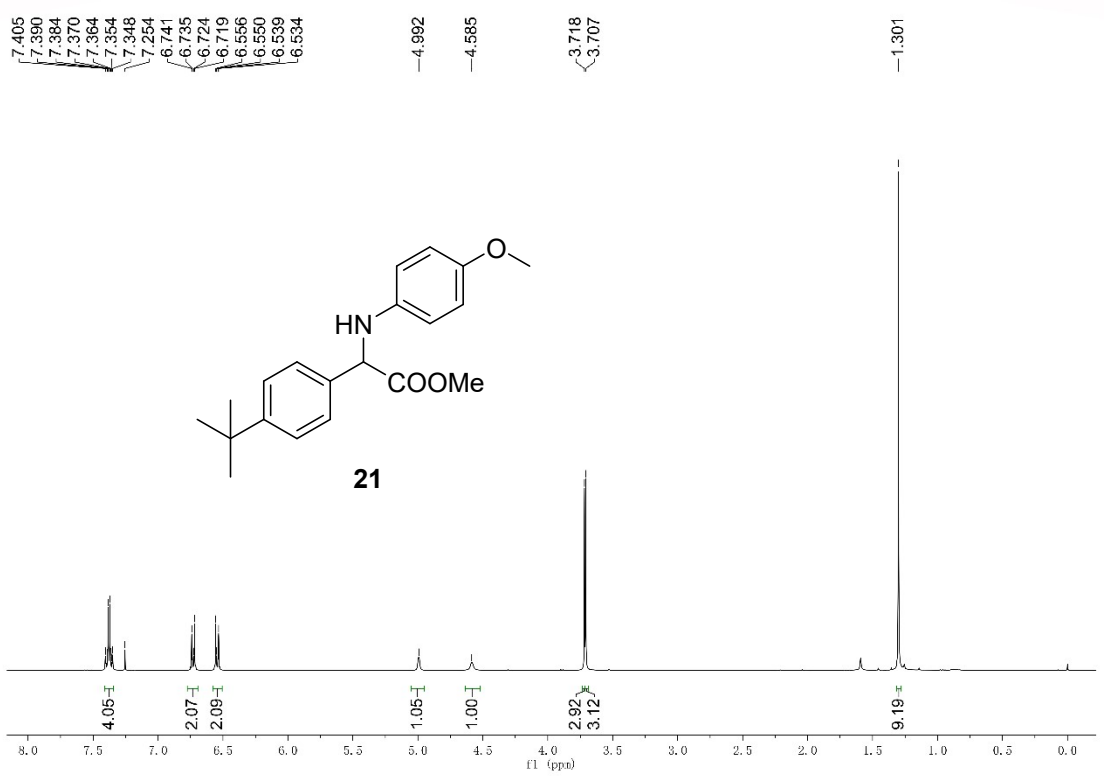
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **20**.



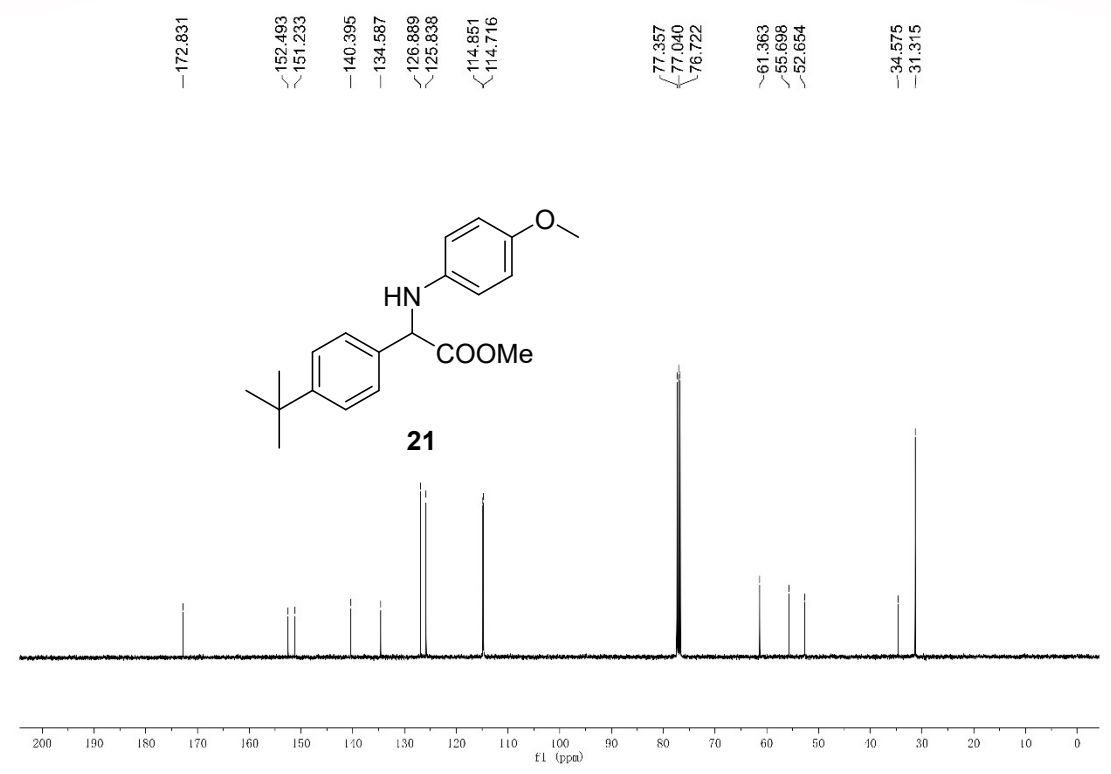
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **20**



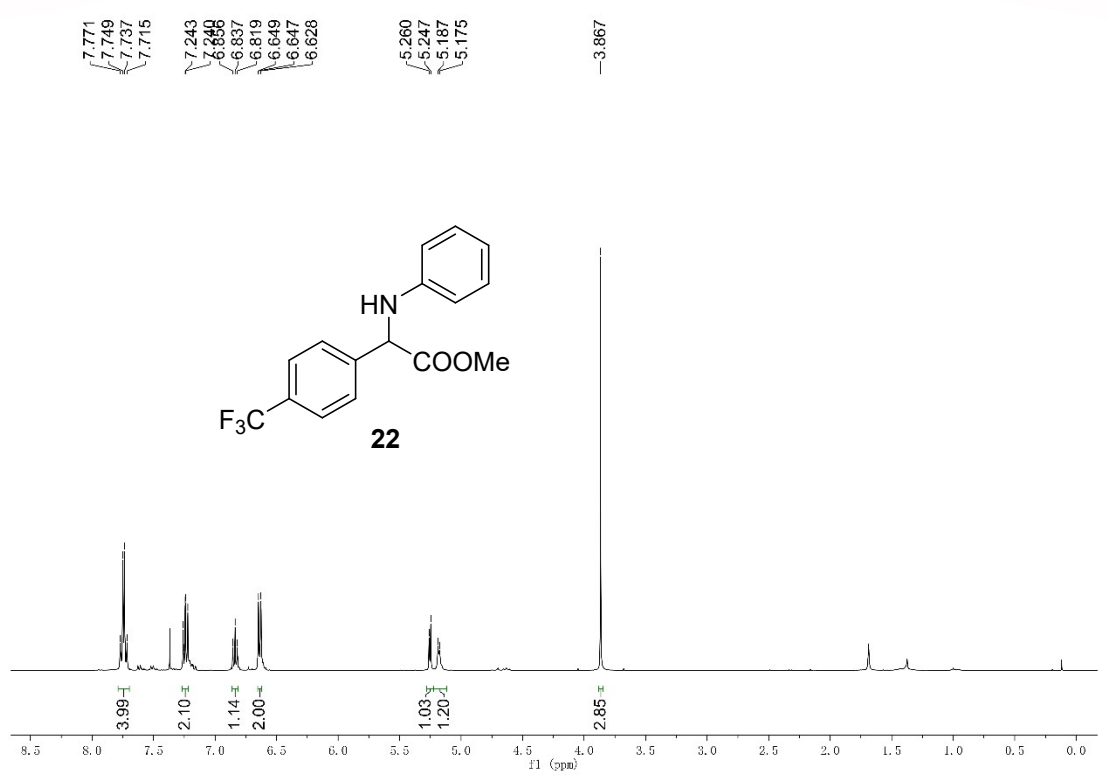
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **21**.



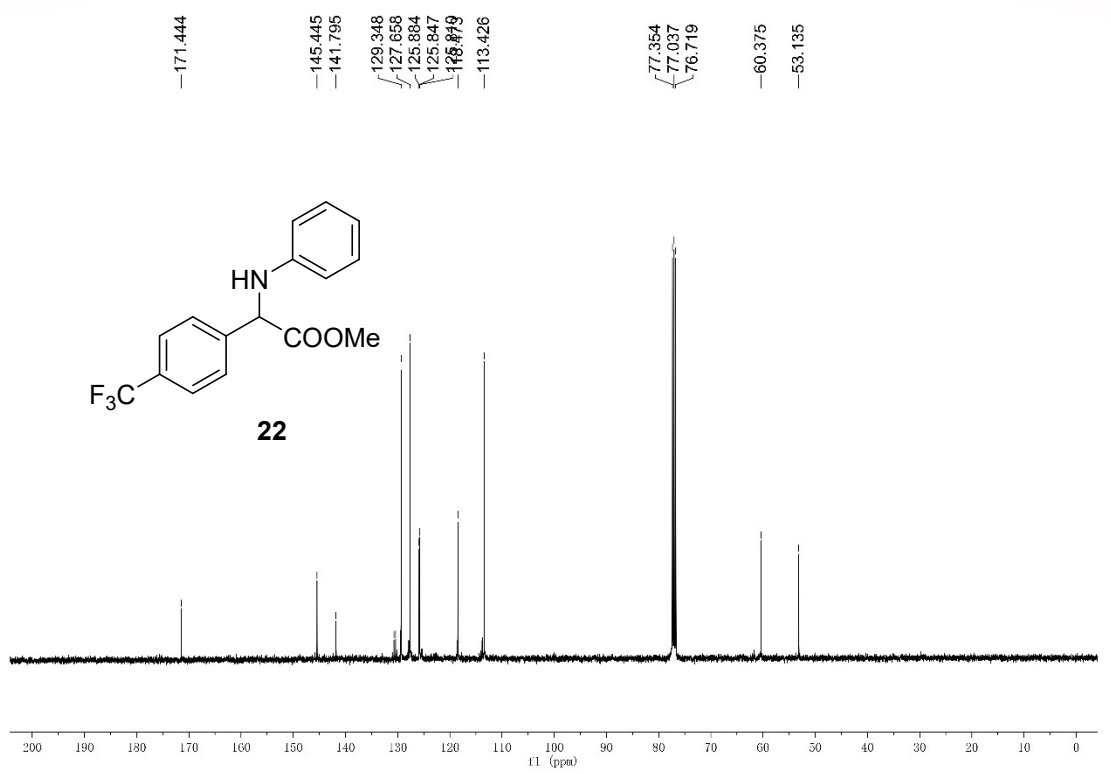
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **21**



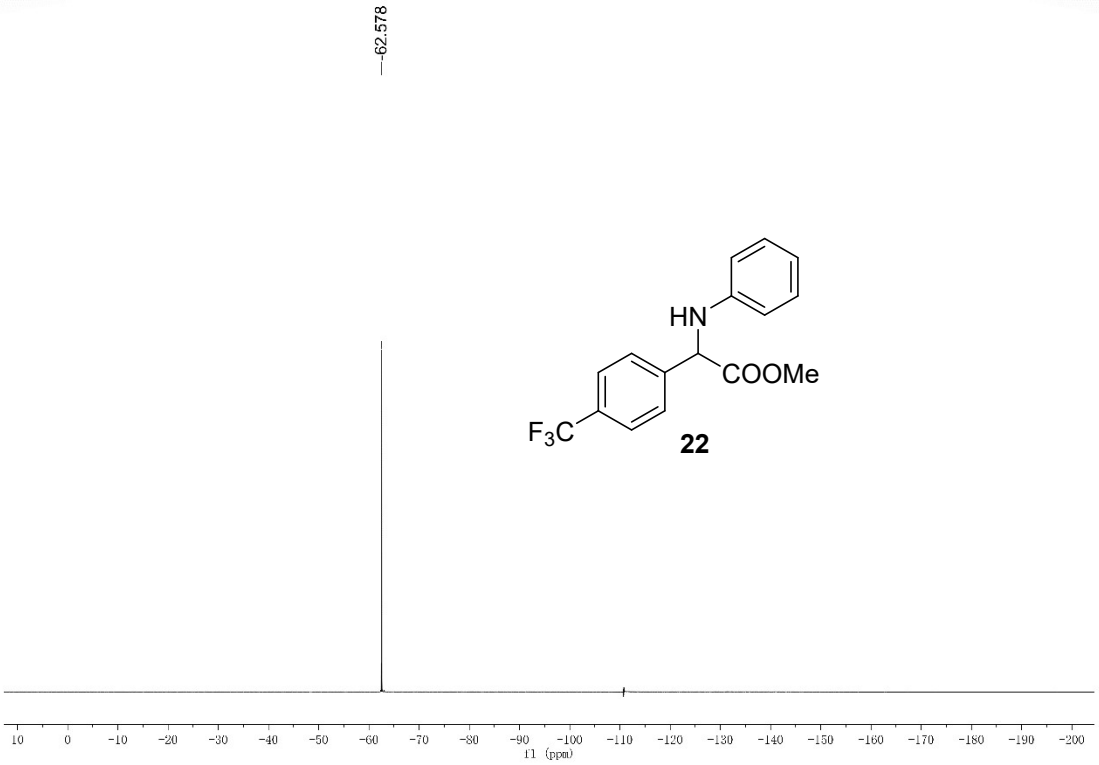
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **22**.



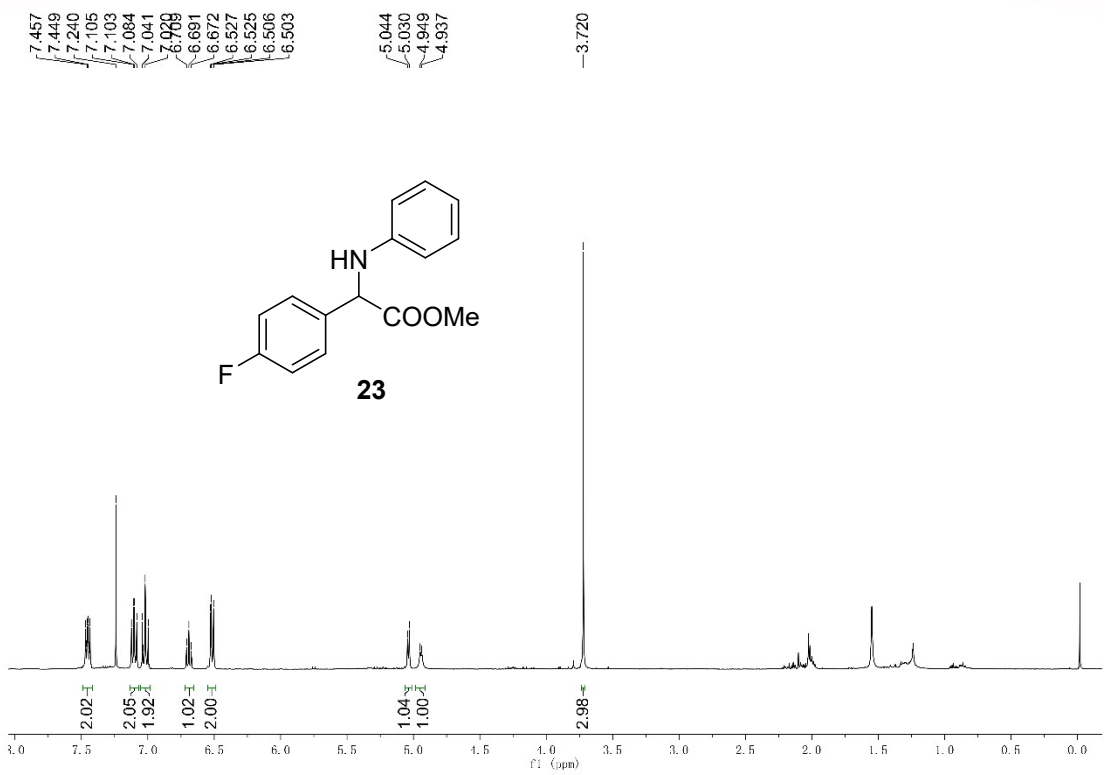
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **22**



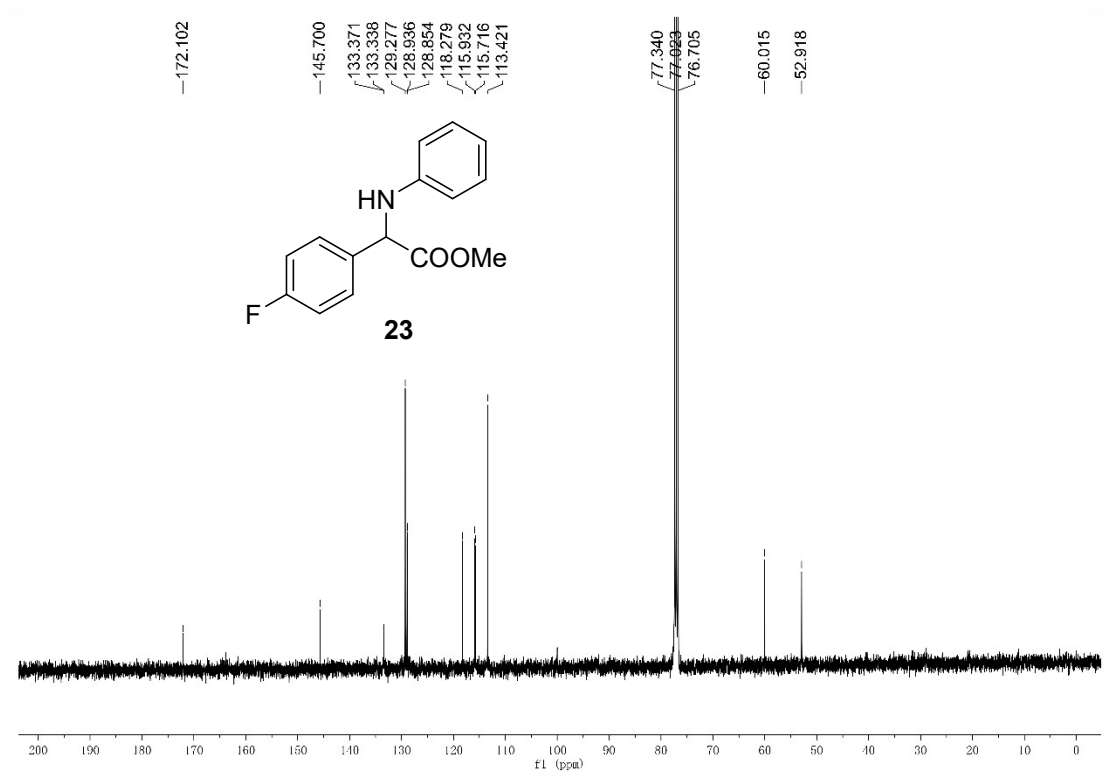
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **22**.



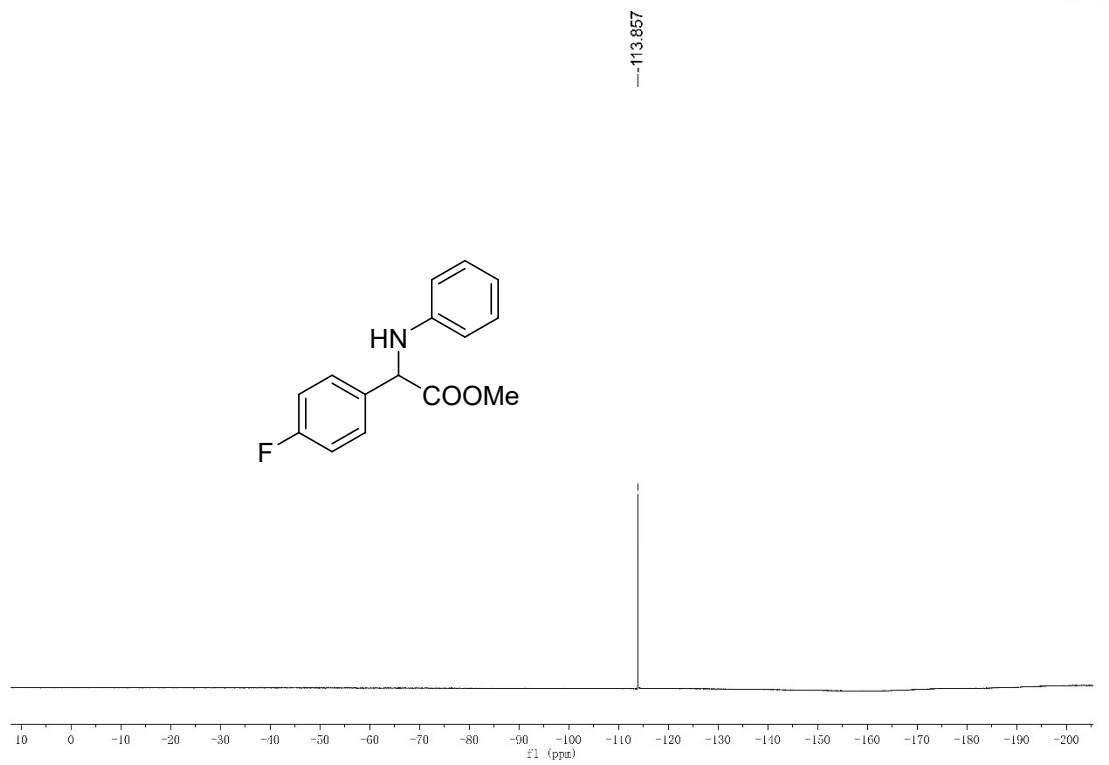
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **23**.



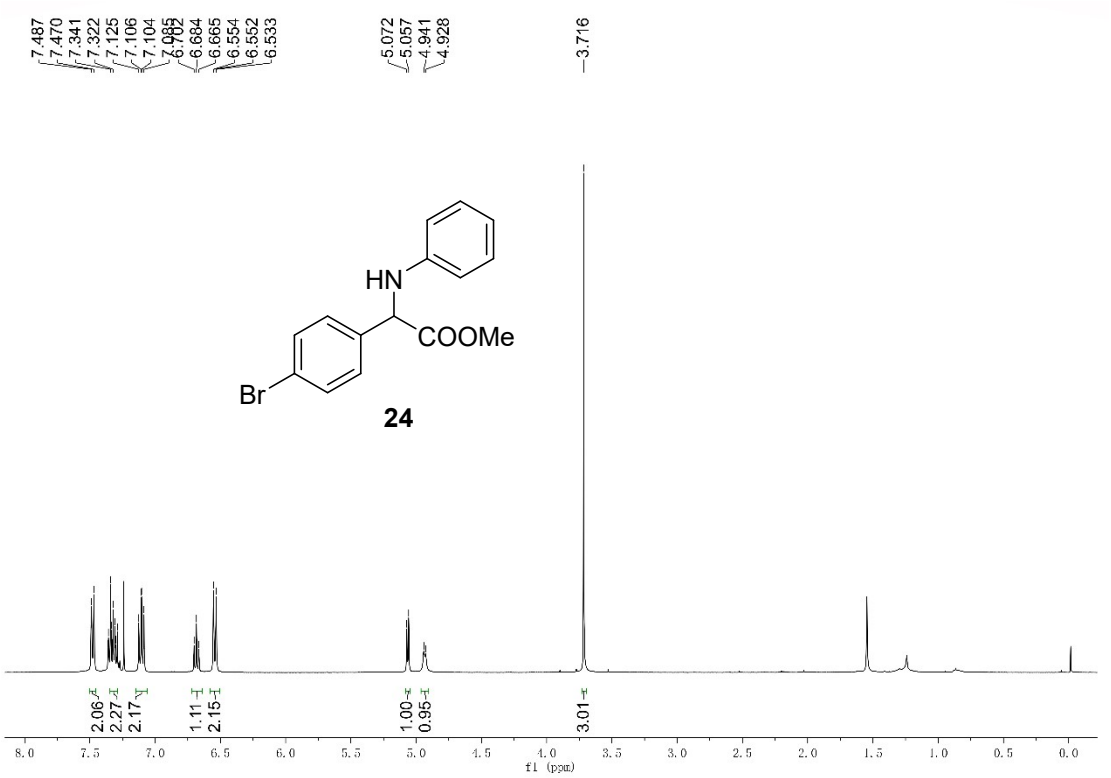
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **23**



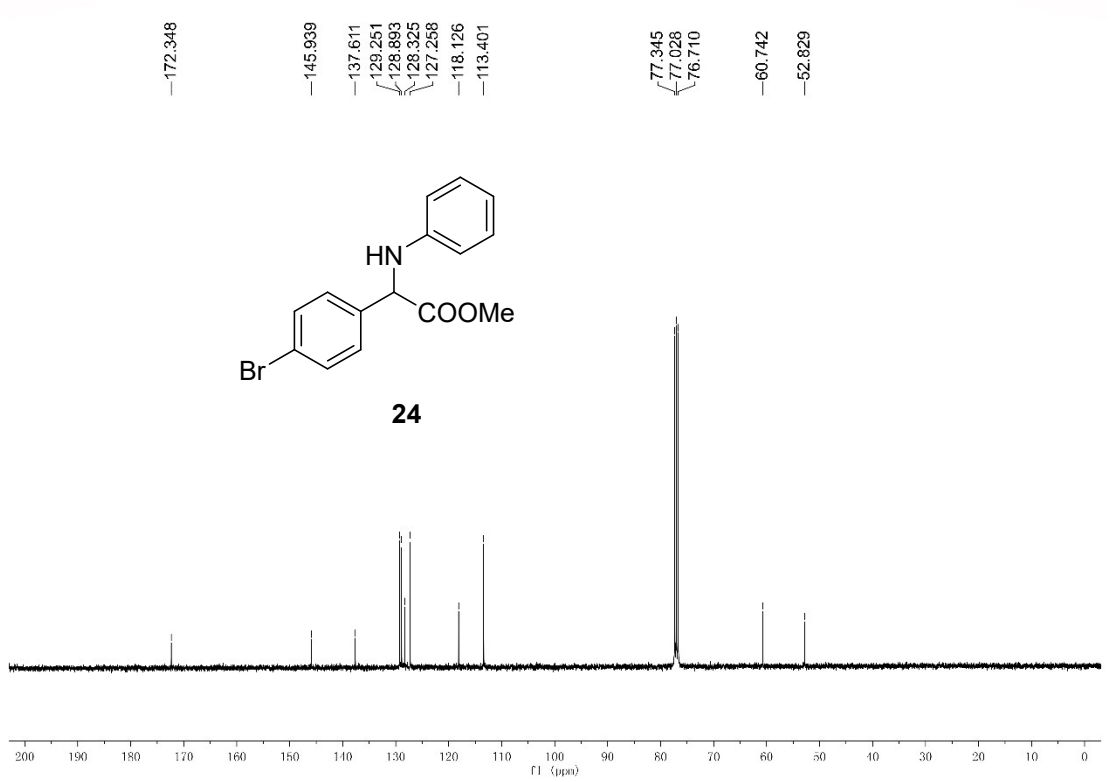
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **23**



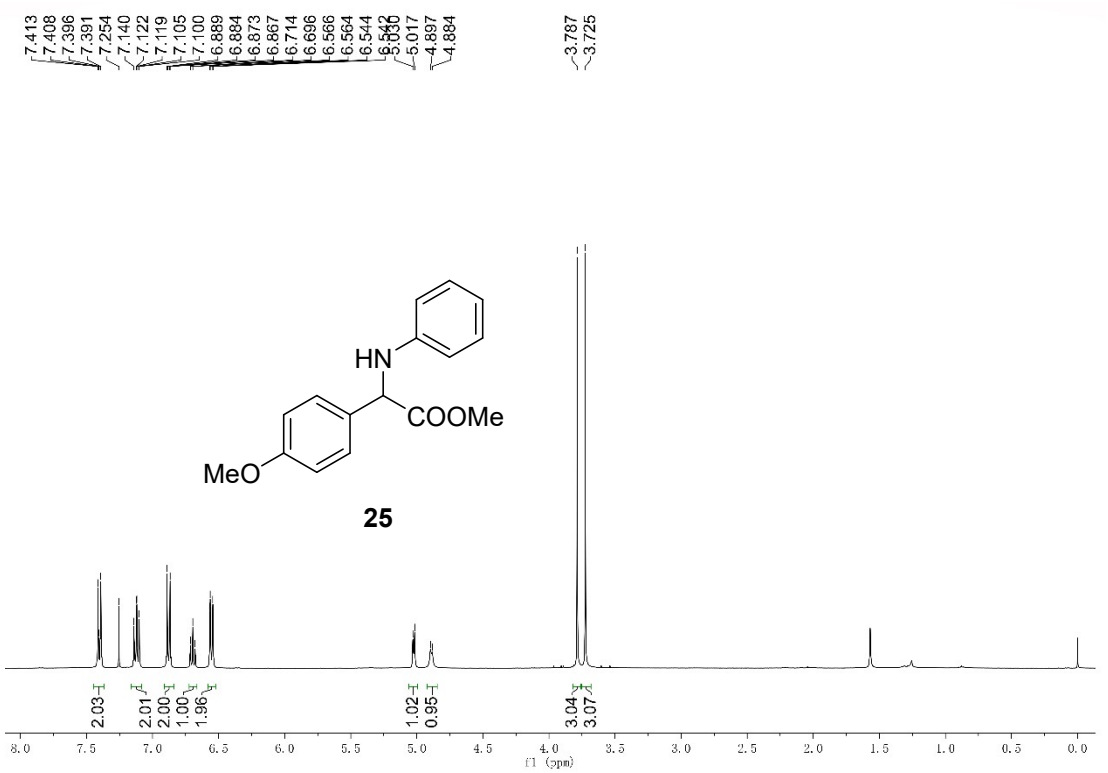
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **24**.



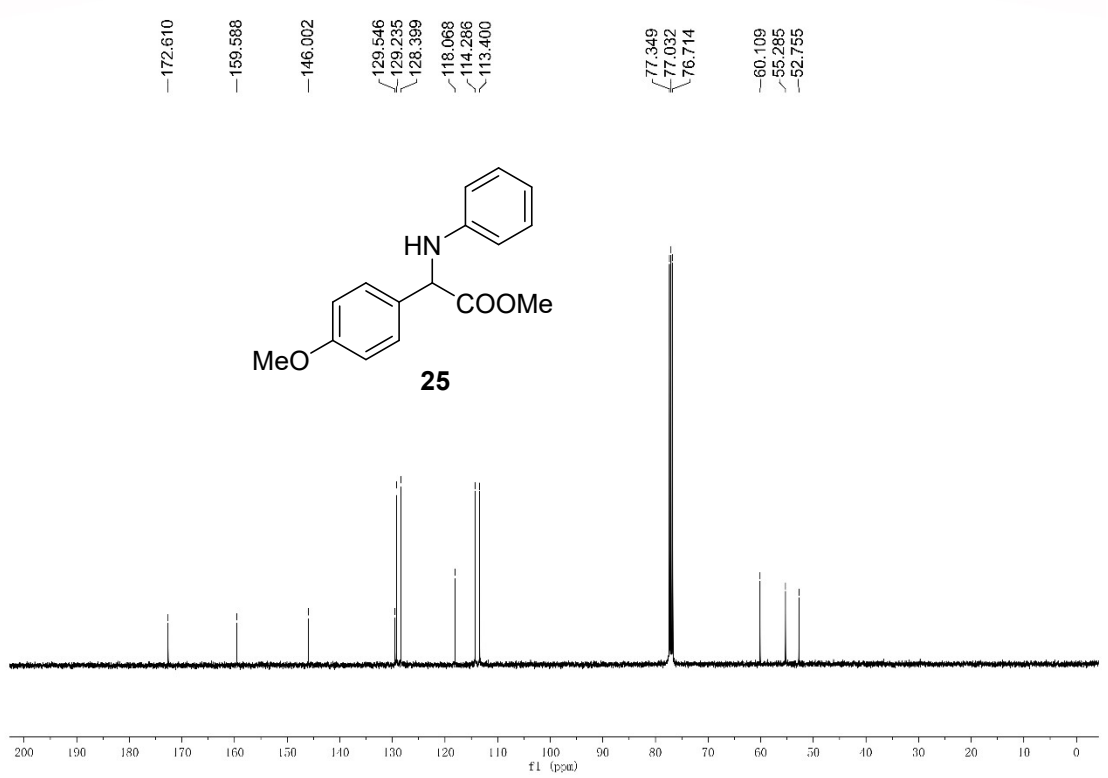
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **24**



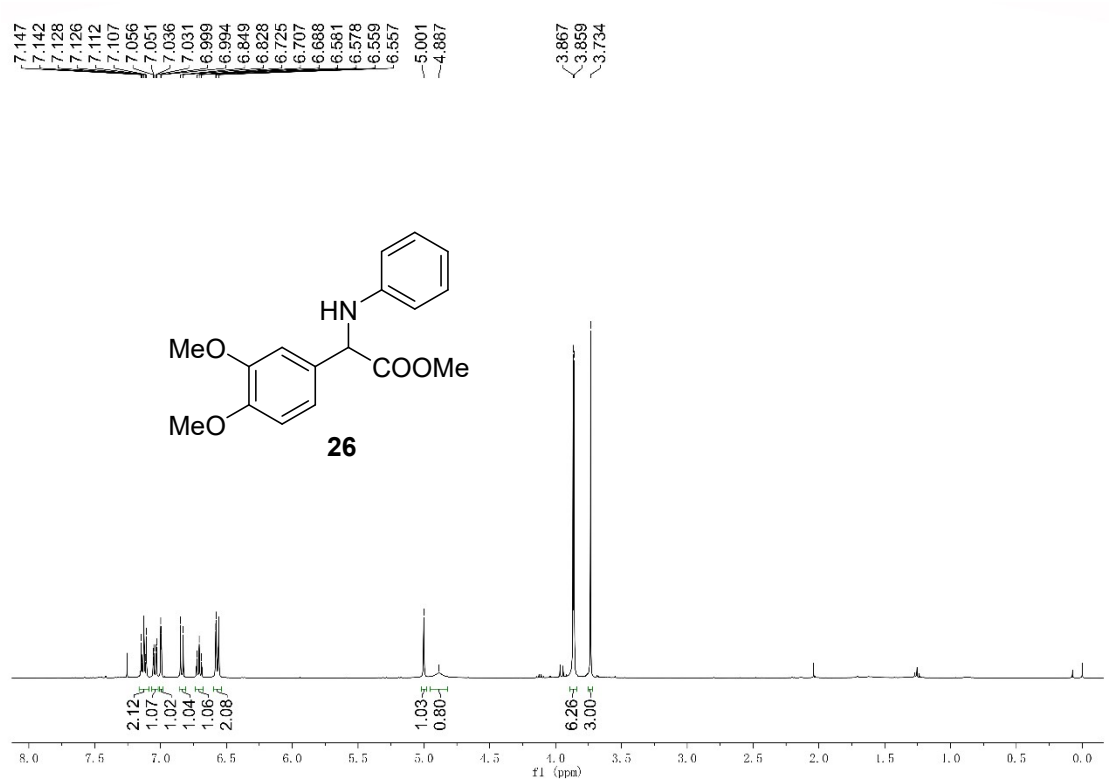
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **25**.



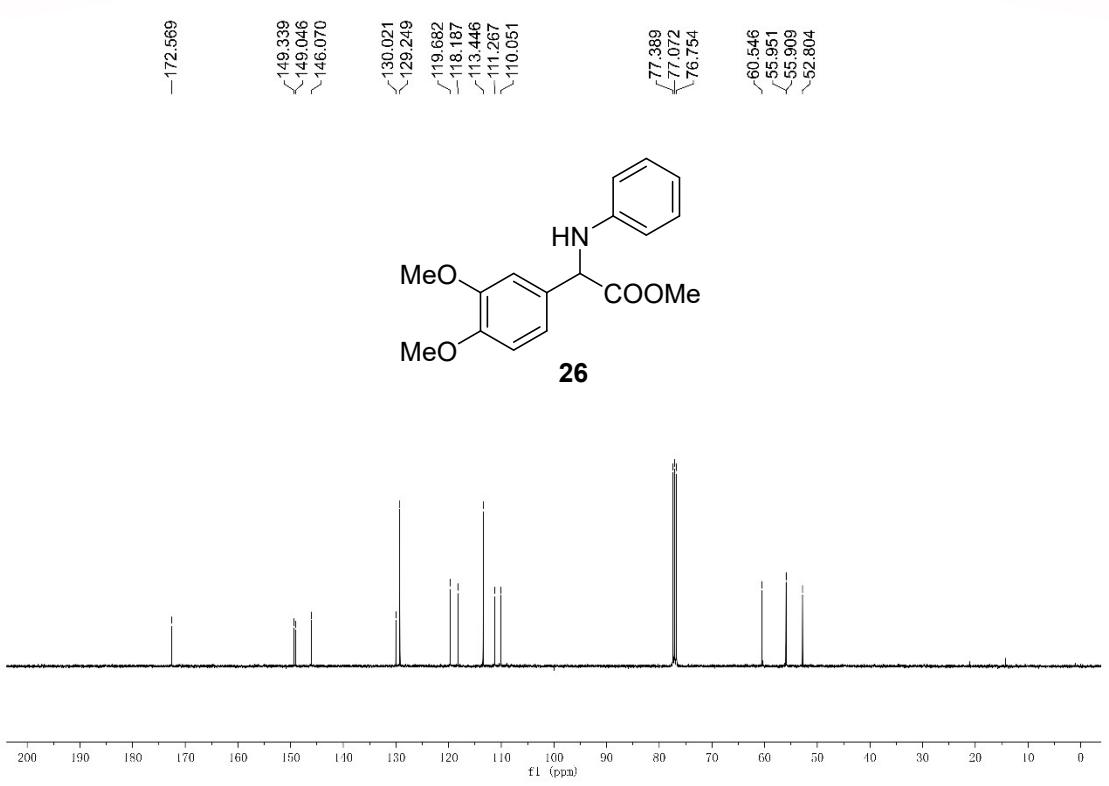
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **25**



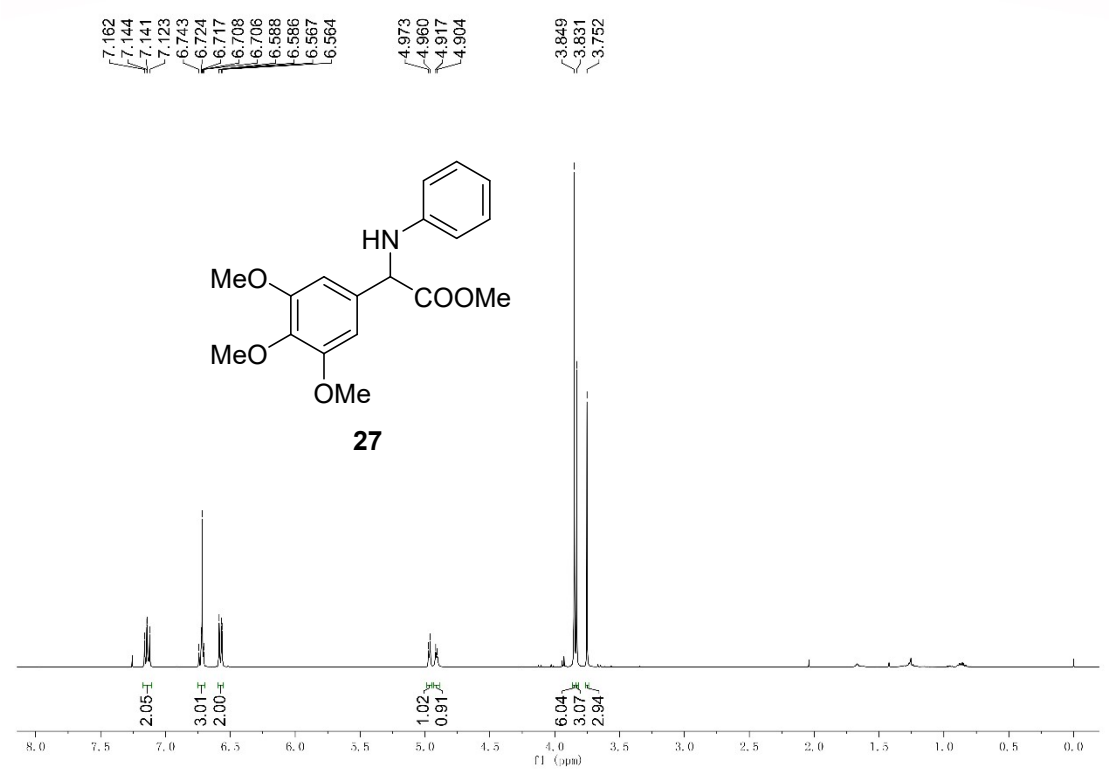
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **26**.



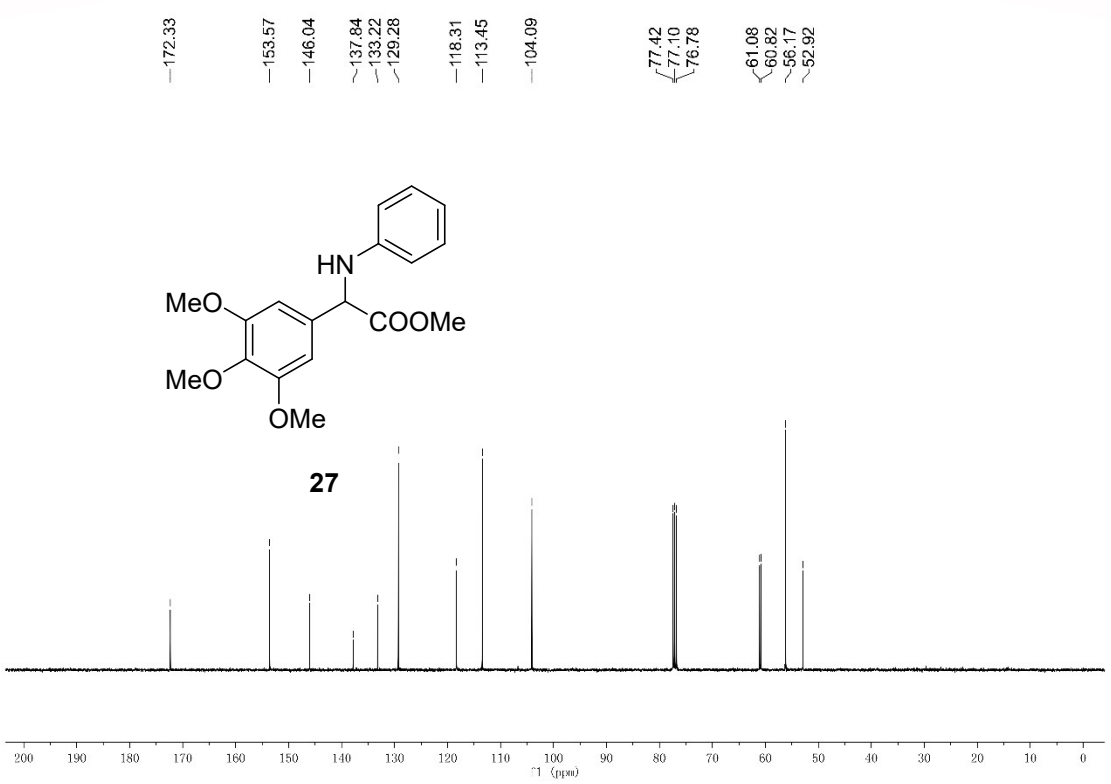
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **26.**



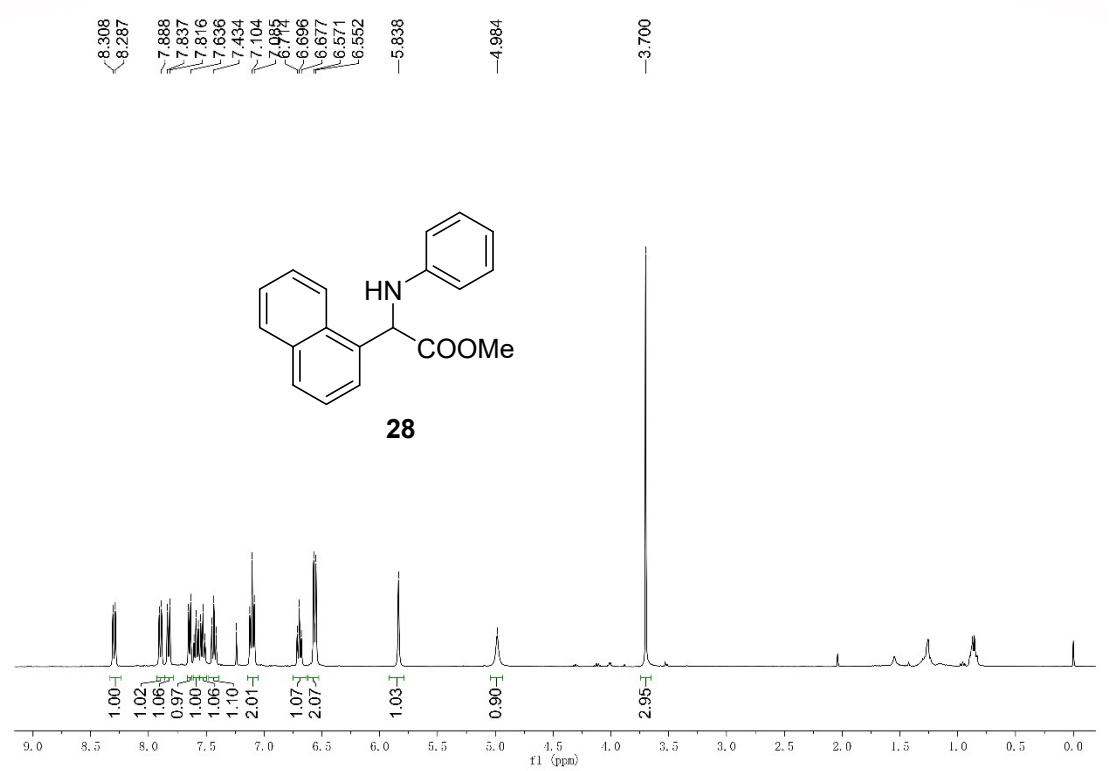
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **27**.



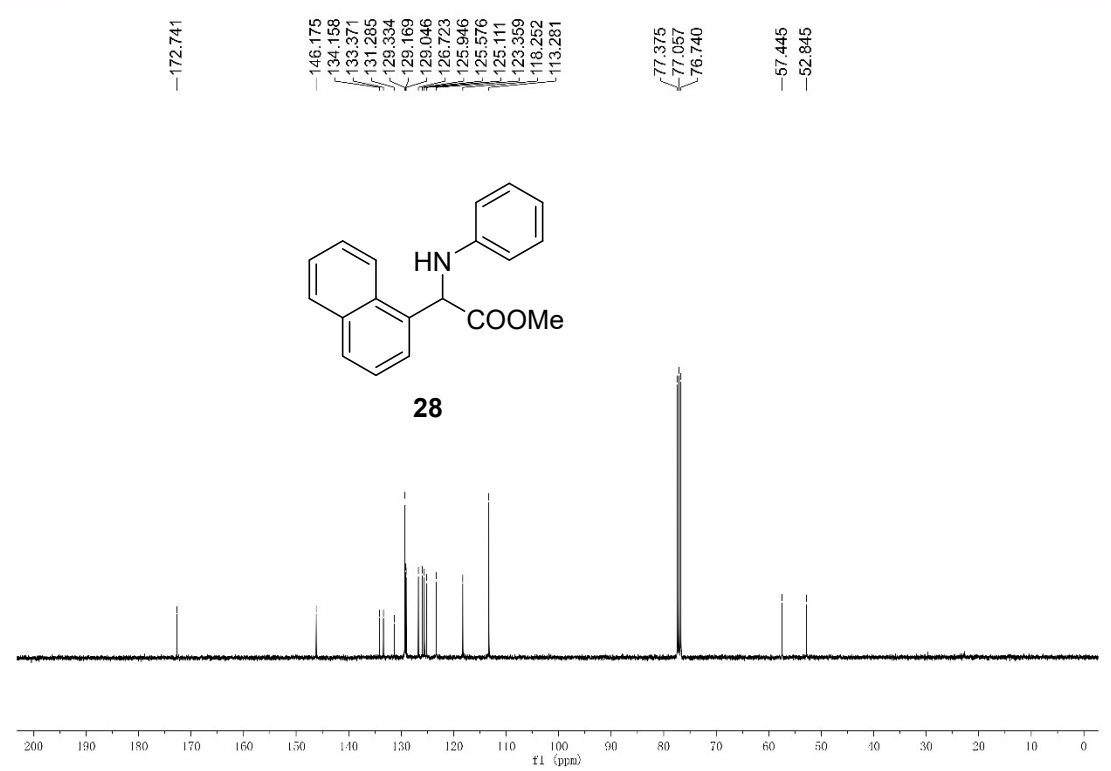
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **27**.



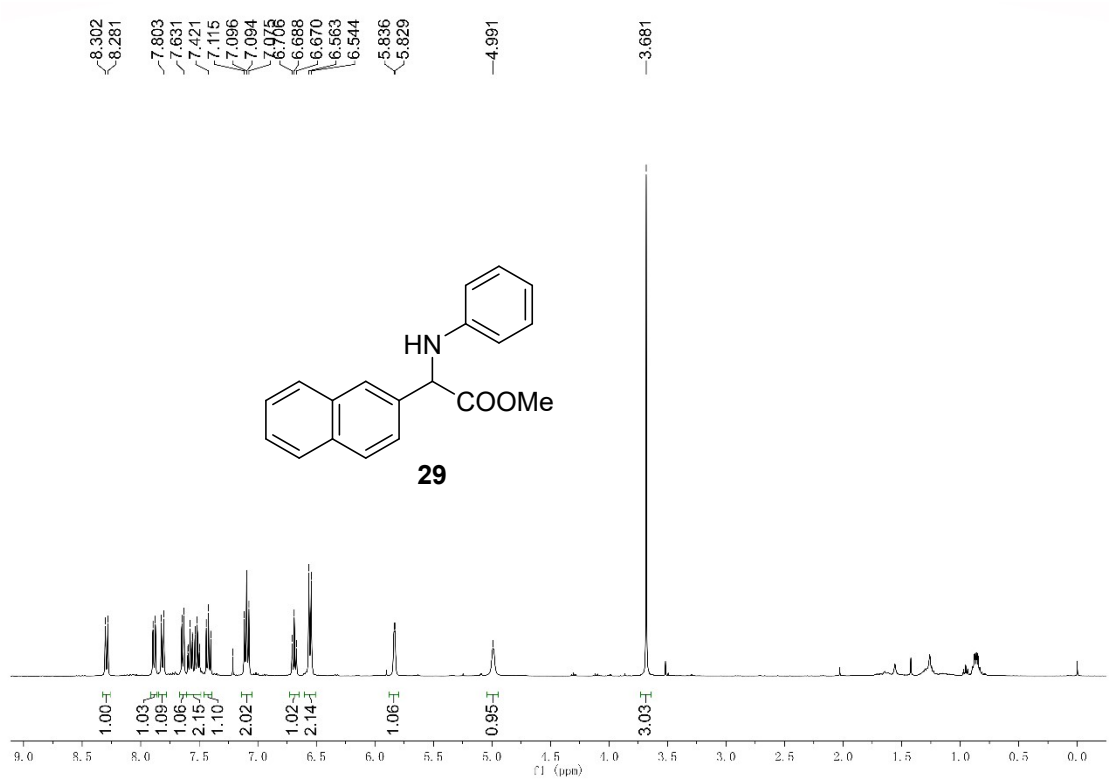
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **28**.



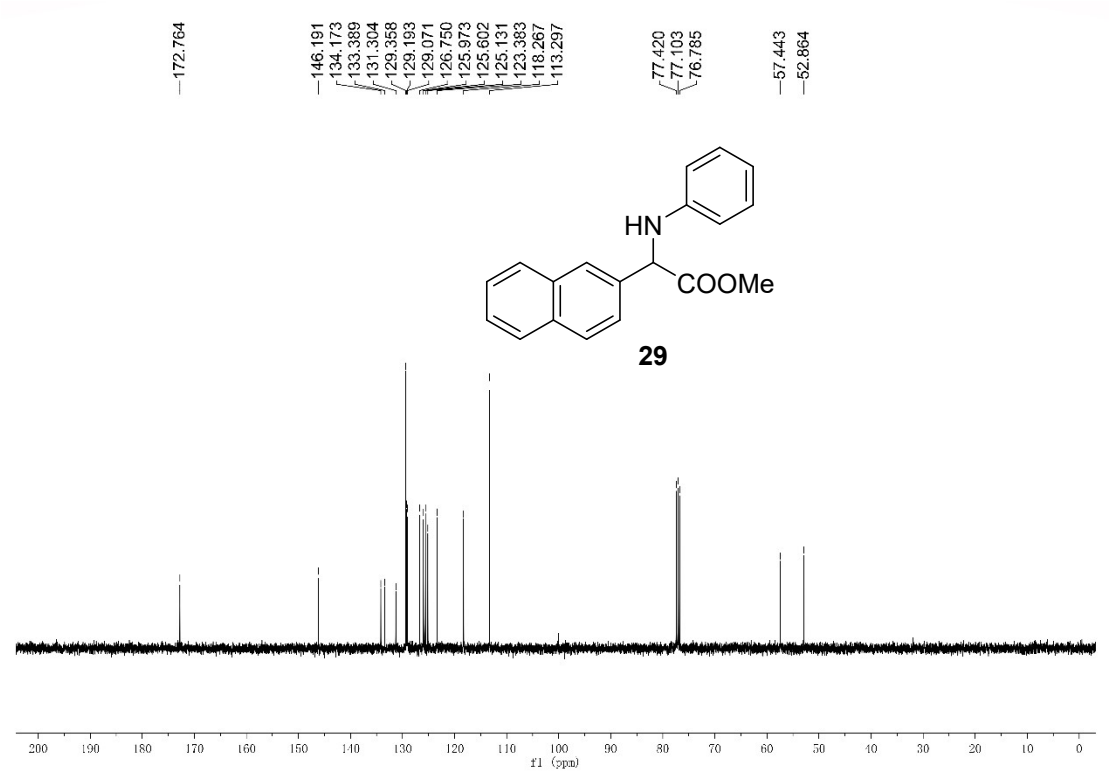
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **28**.



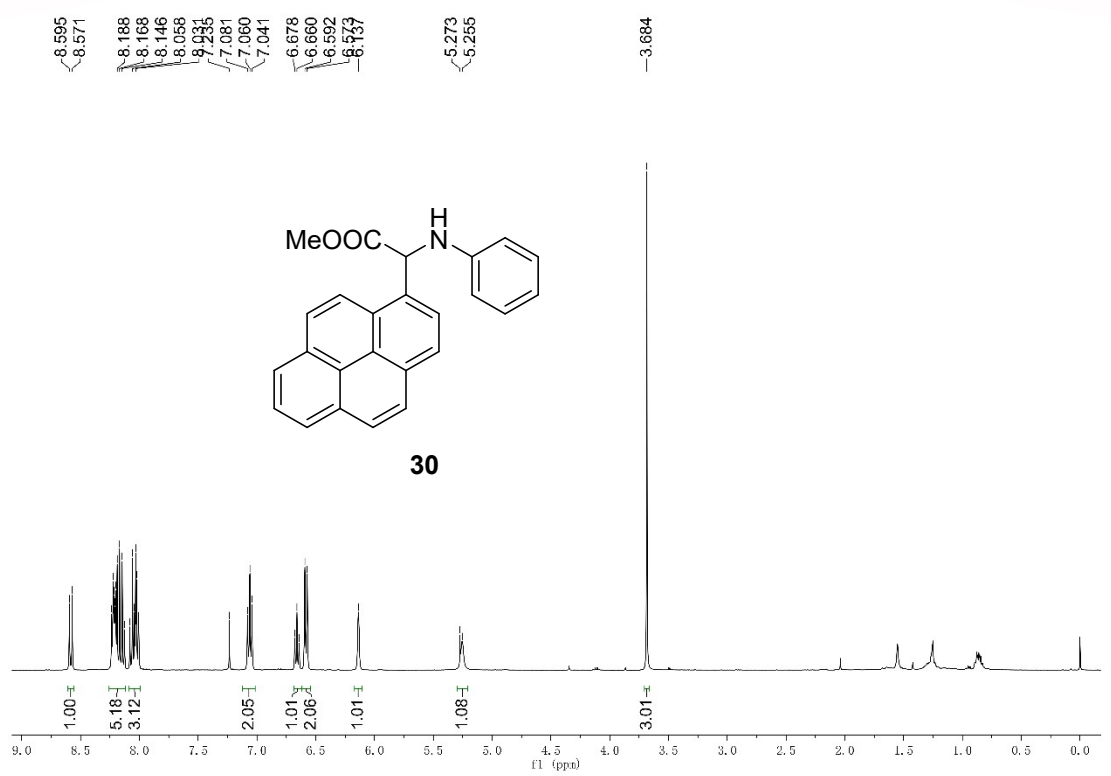
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **29**.



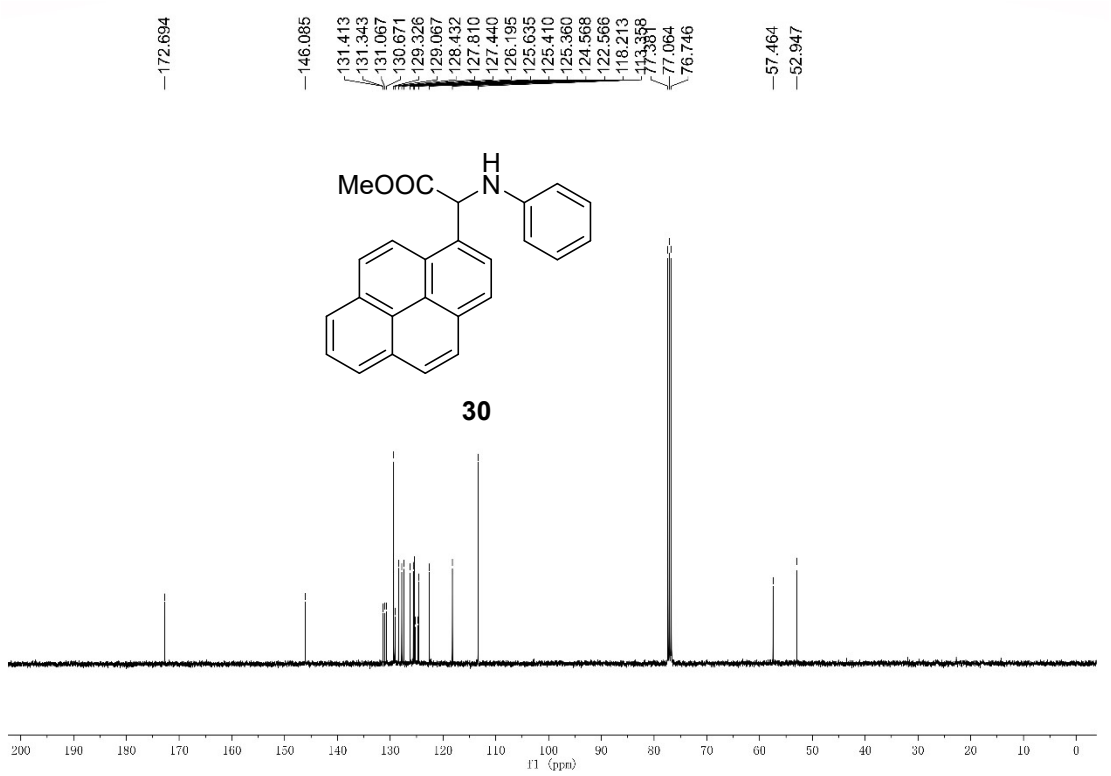
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **29**.



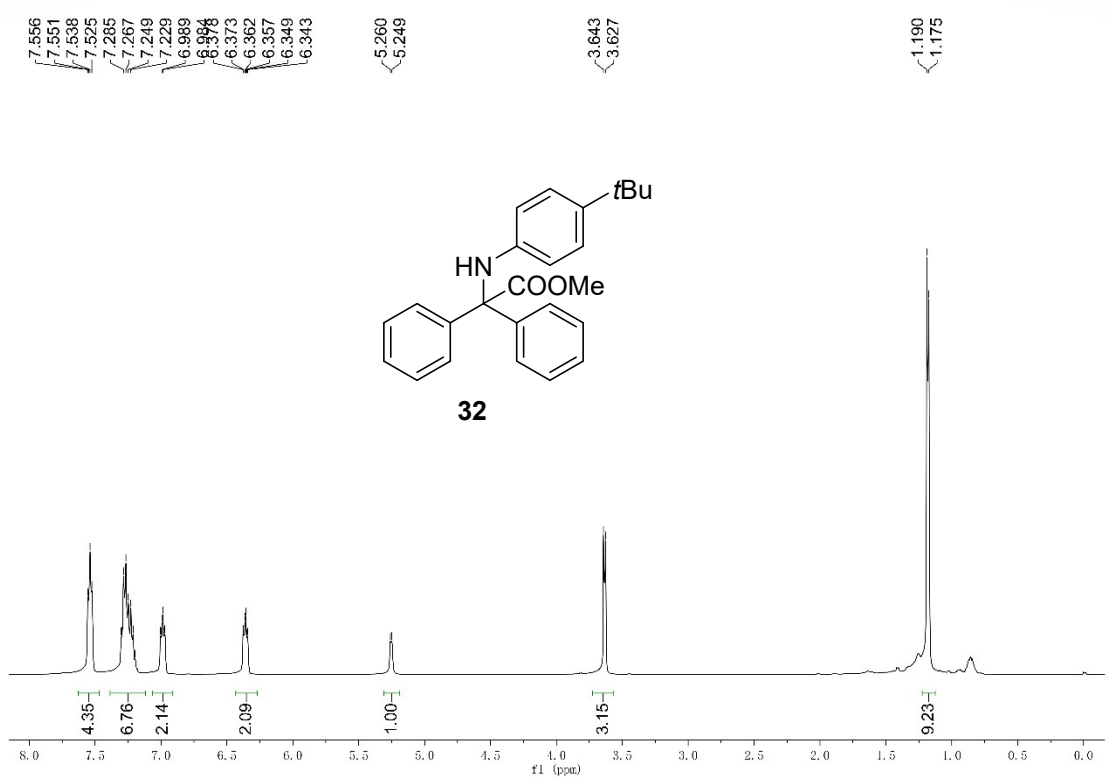
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **30**.



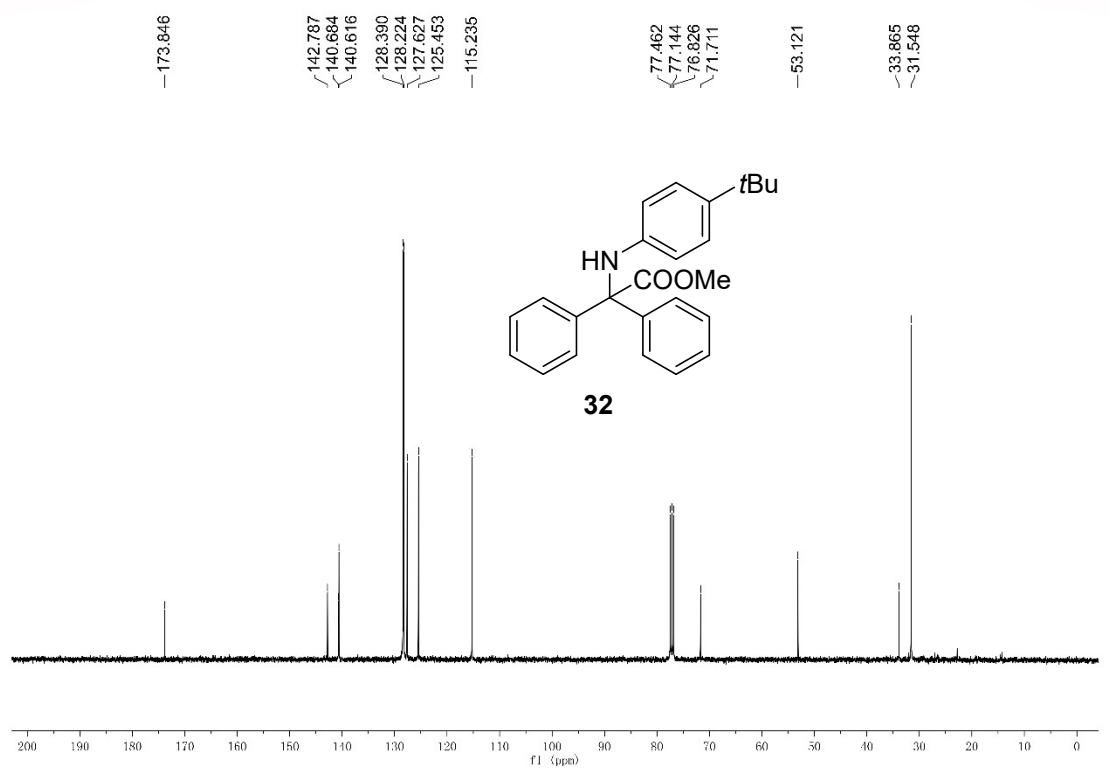
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **30**.



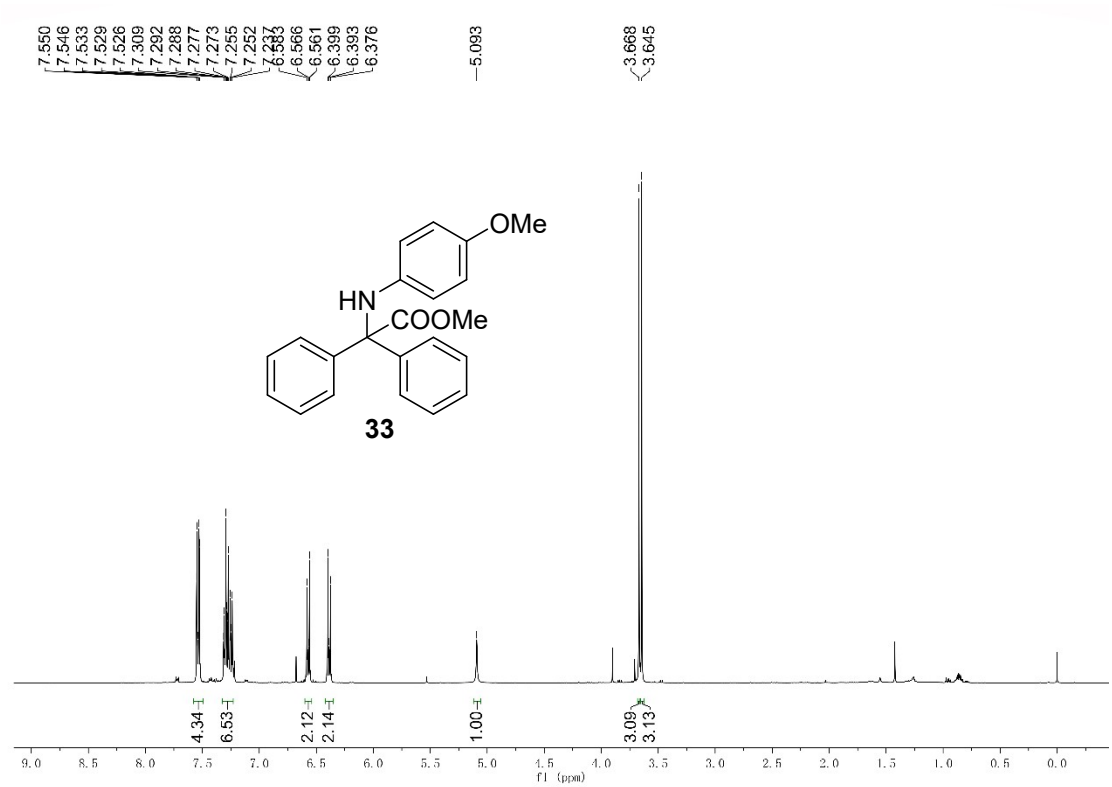
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **32**.



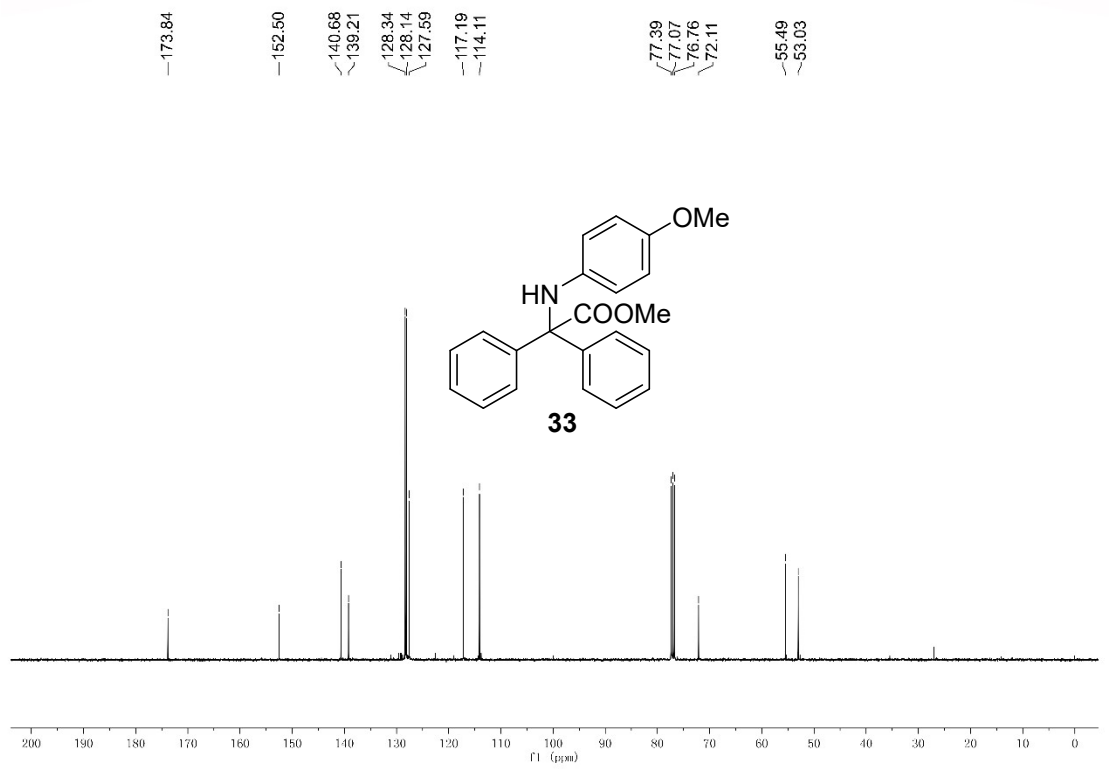
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **32**.



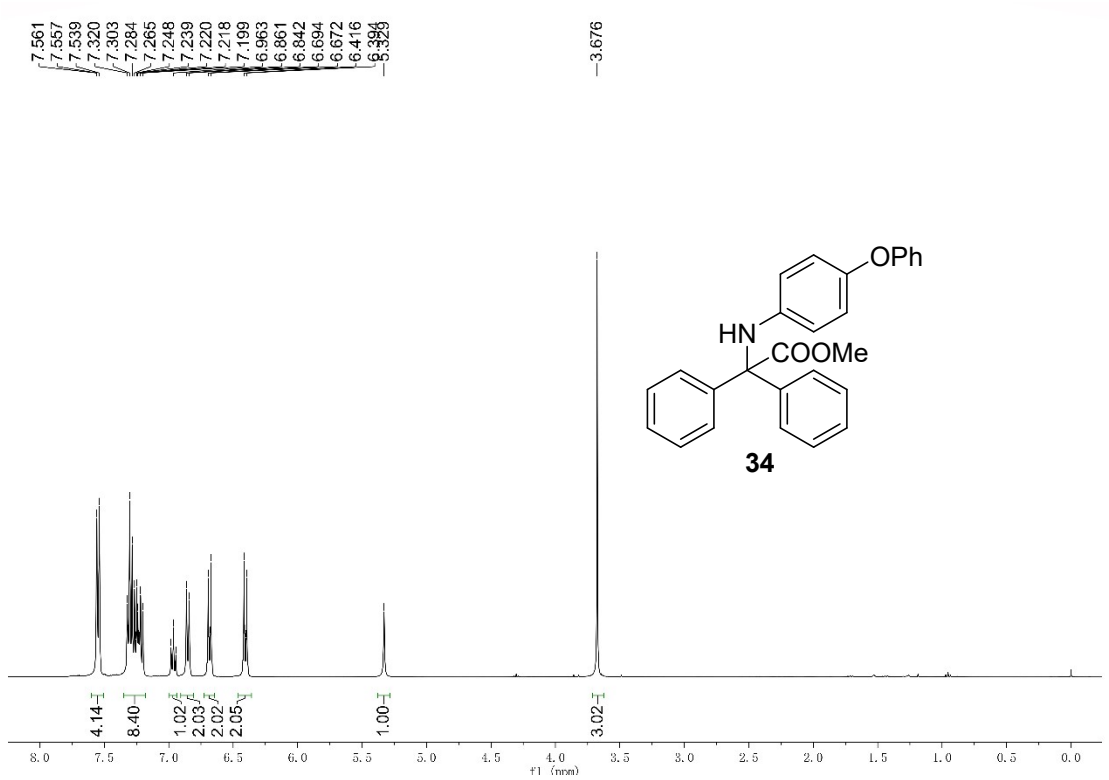
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **33**.



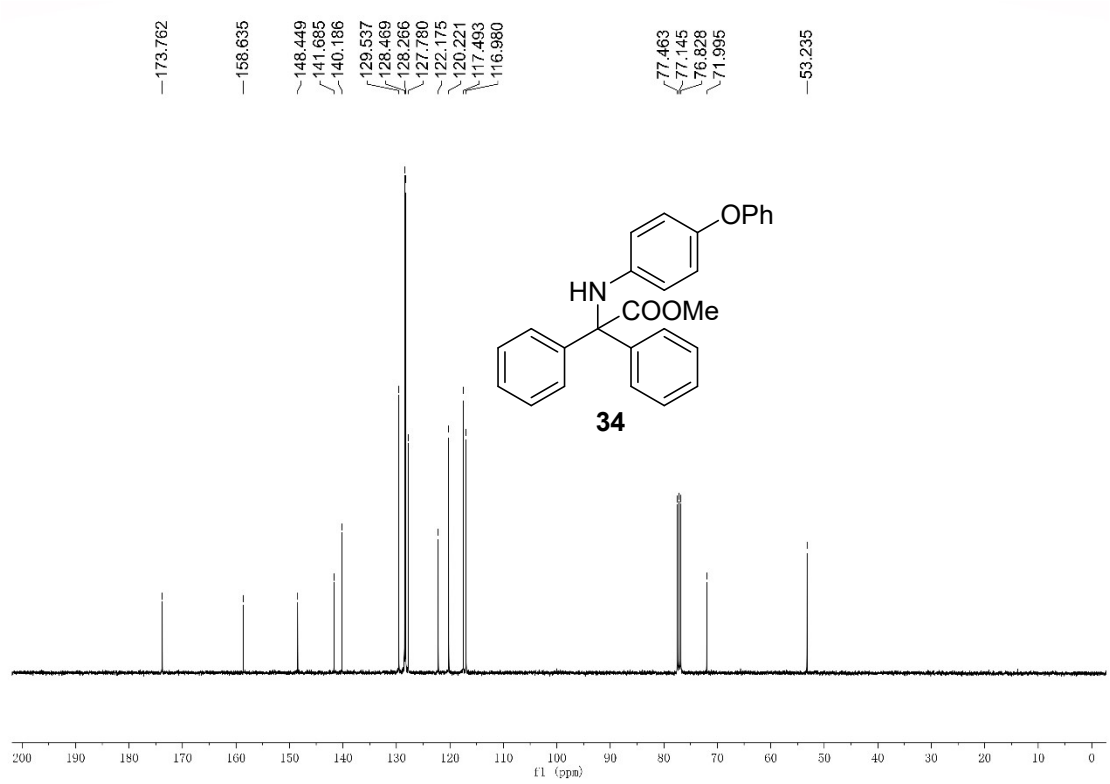
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **33**.



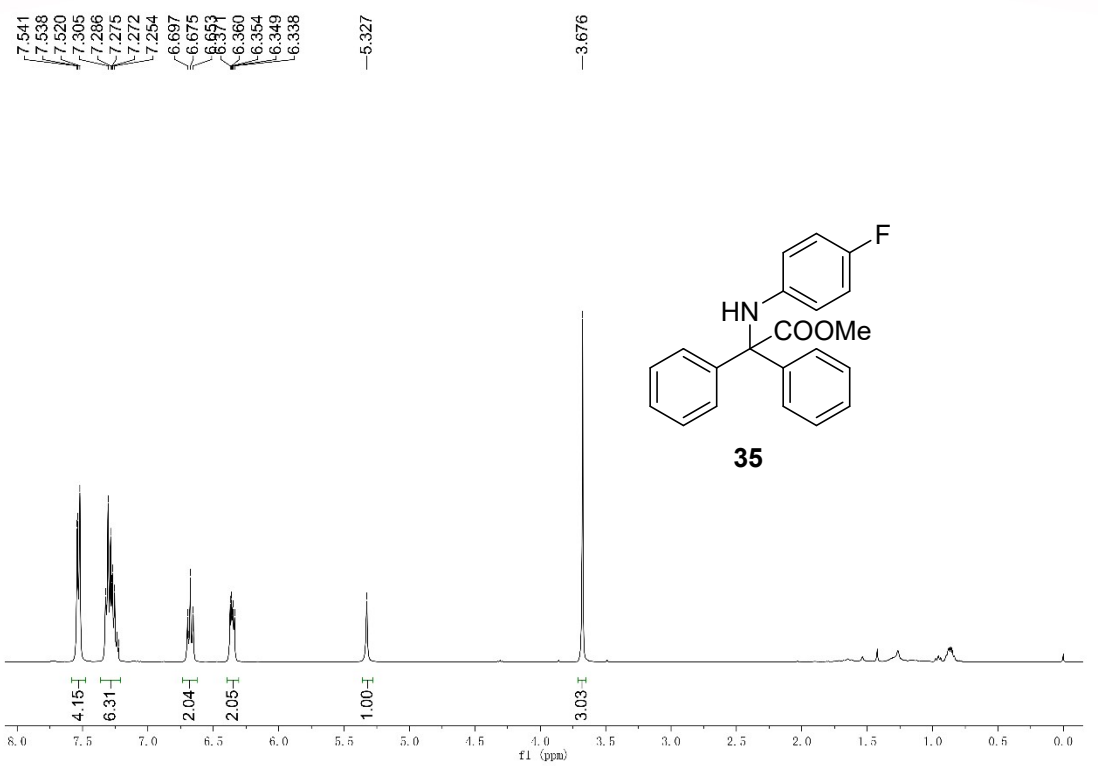
^{1}H NMR (100 MHz, $CDCl_3$) spectrum of **34**.



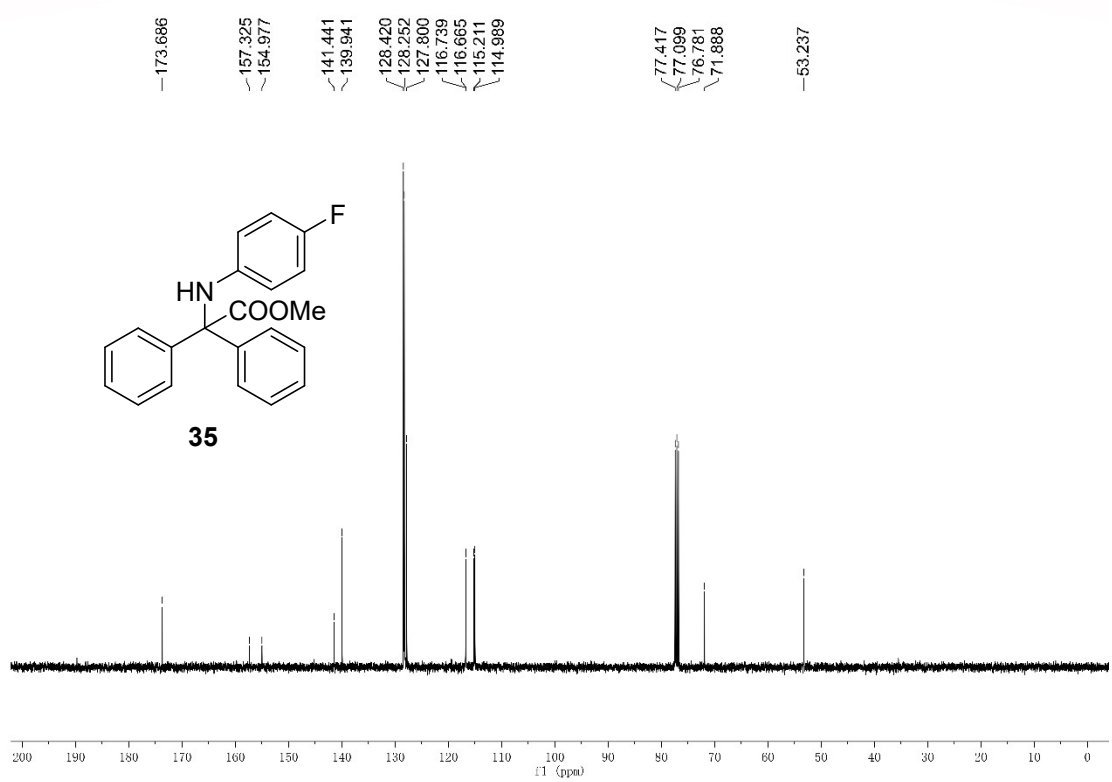
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **34**.



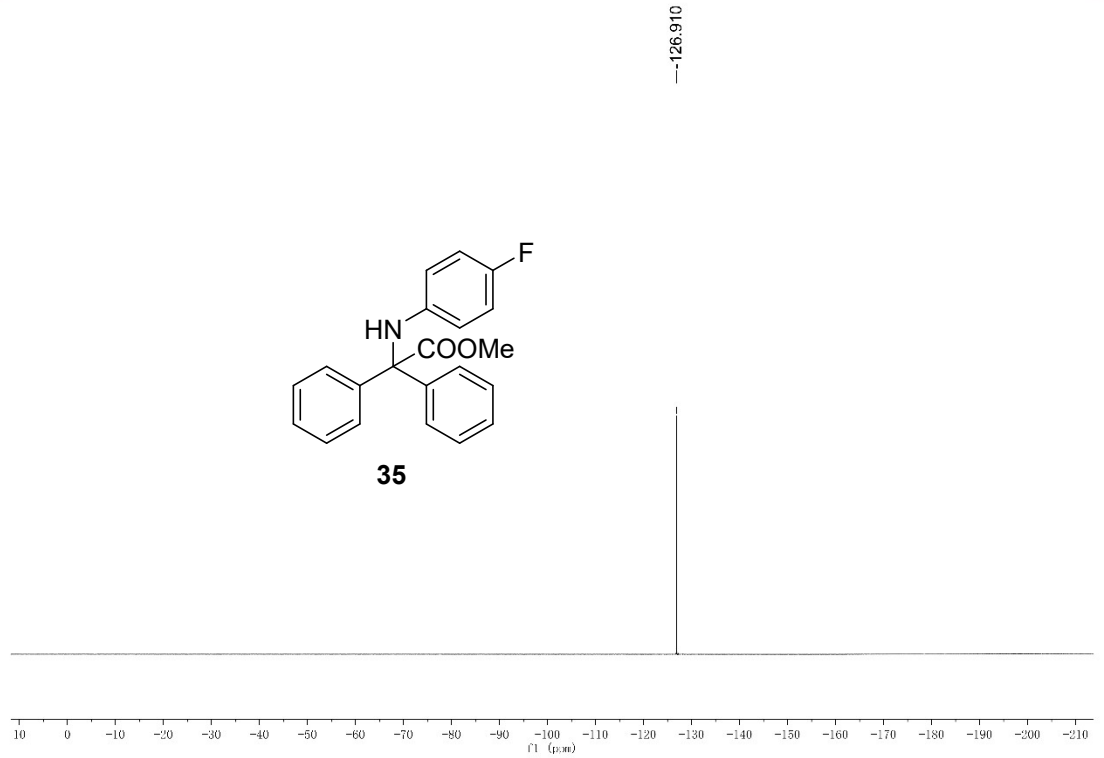
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **35**.



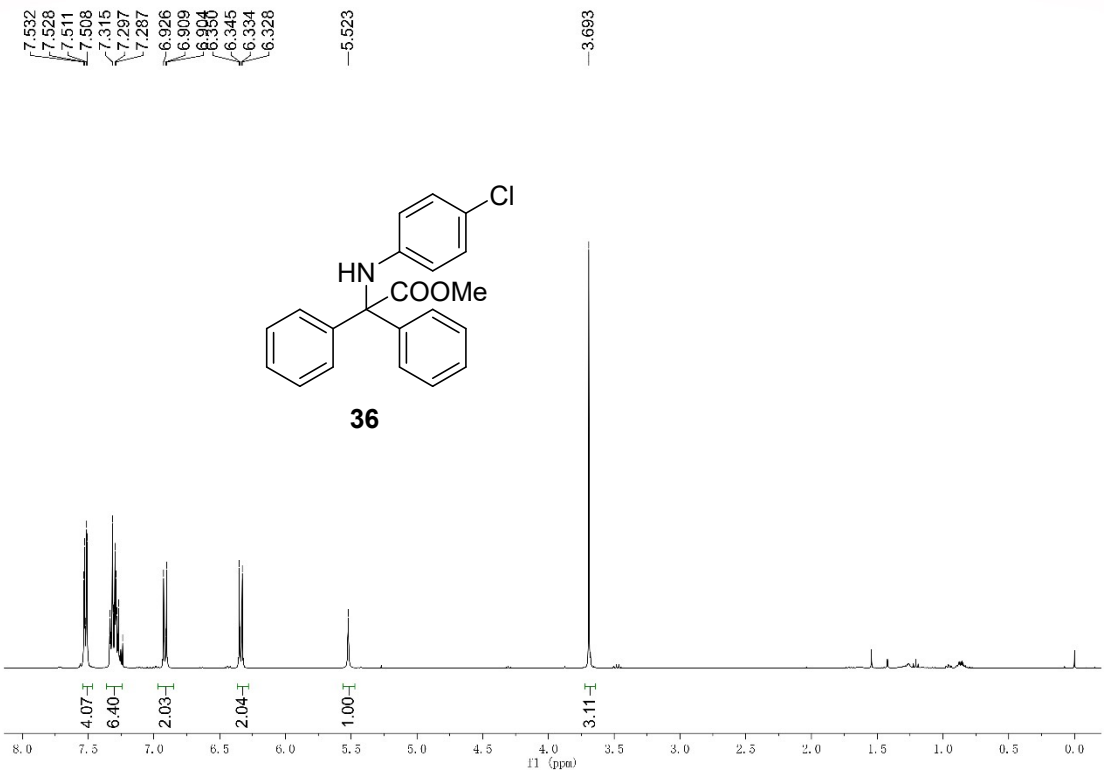
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **35**.



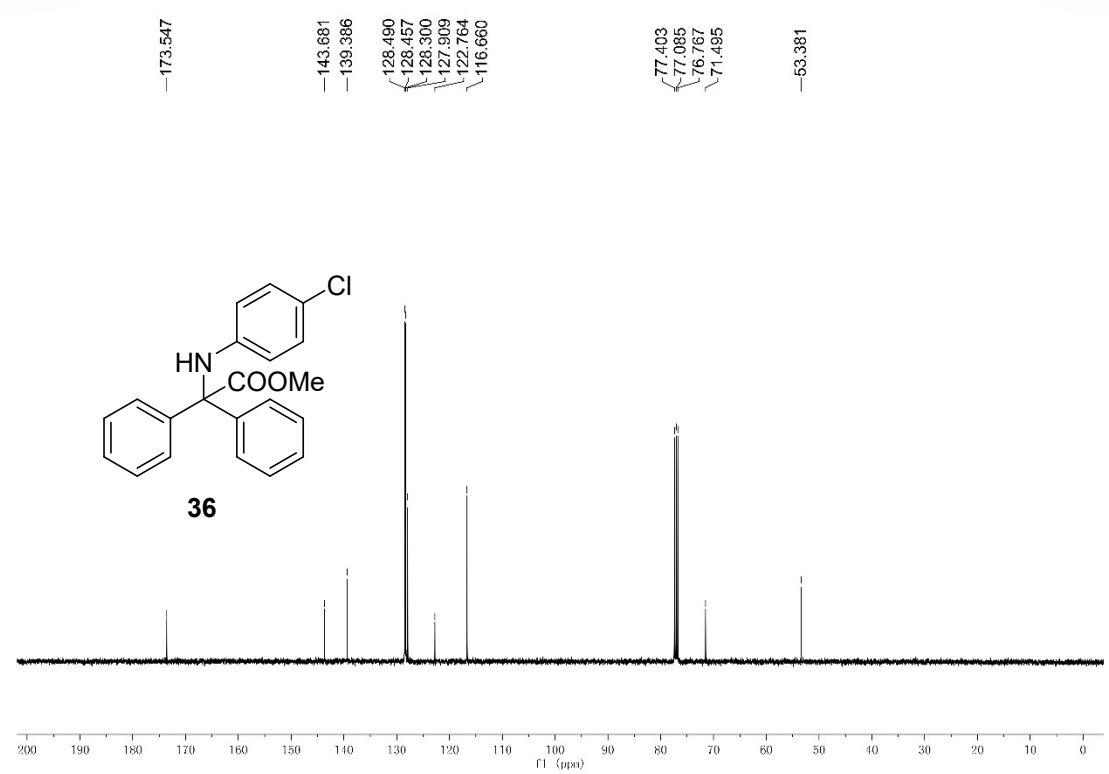
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **35**.



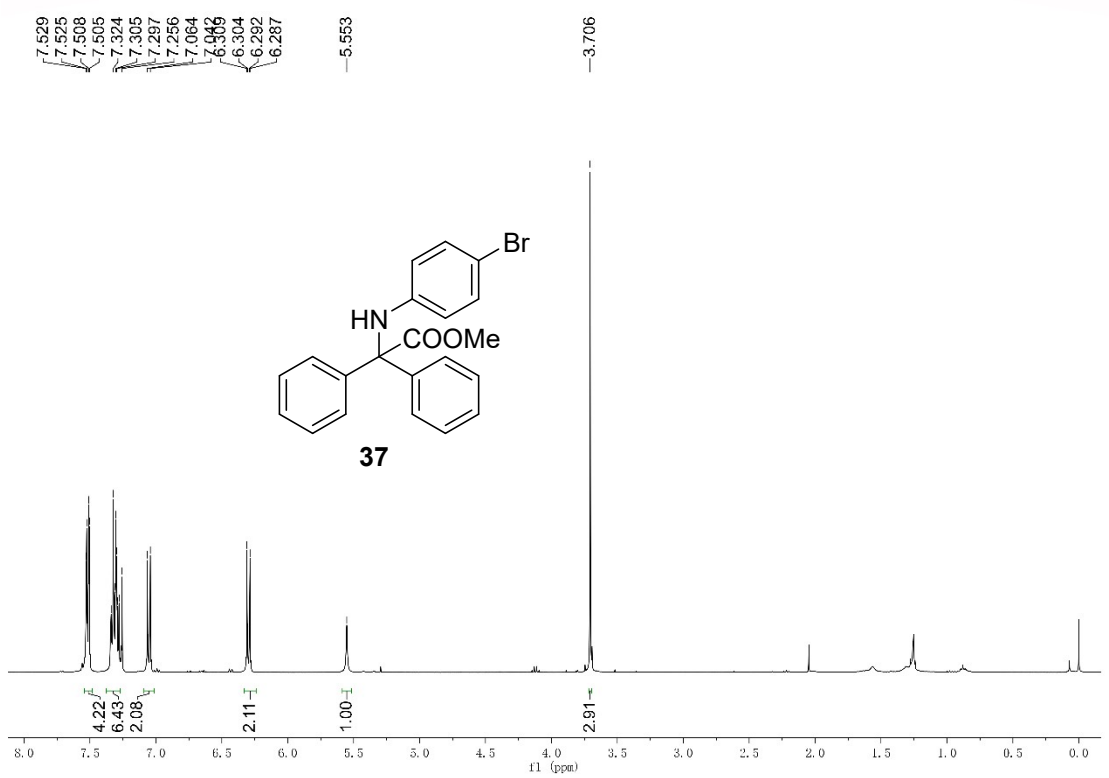
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **36**.



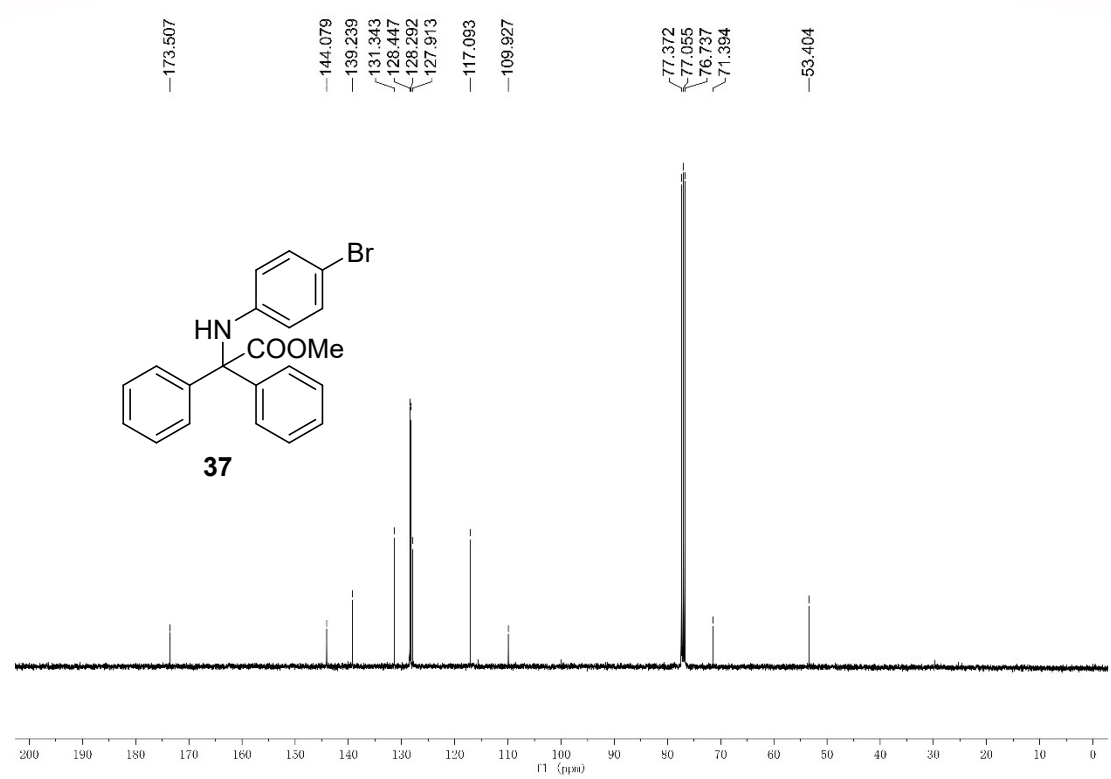
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **36**.



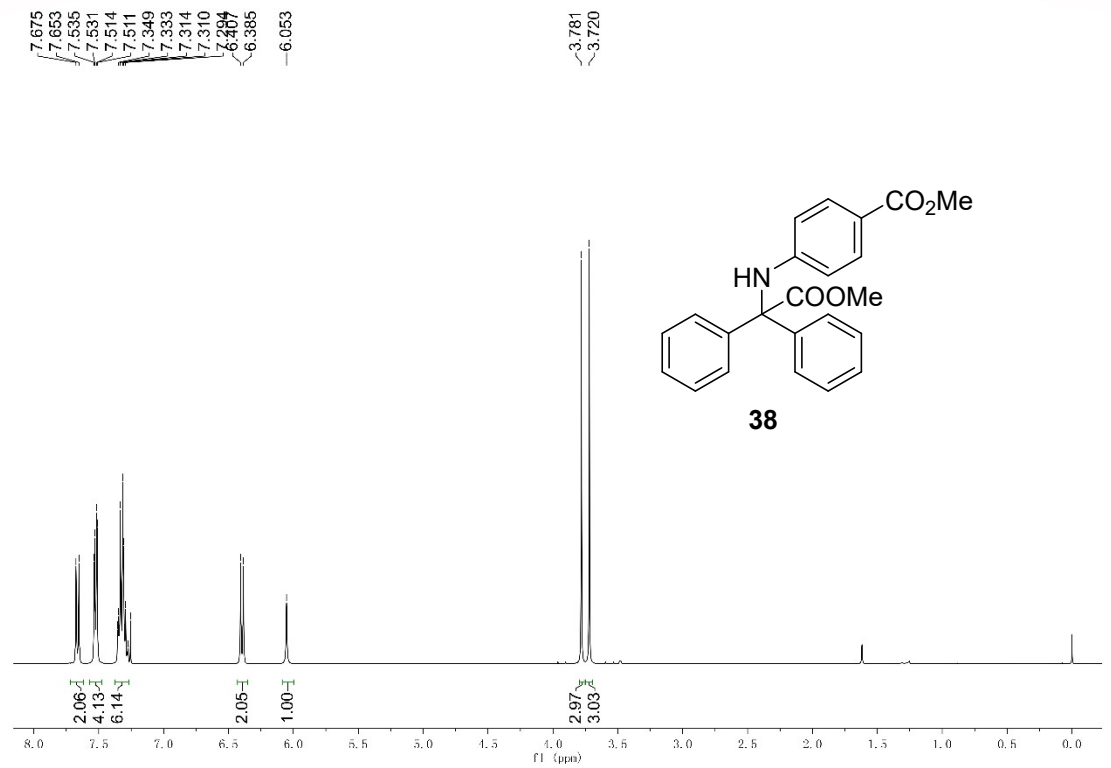
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **37**.



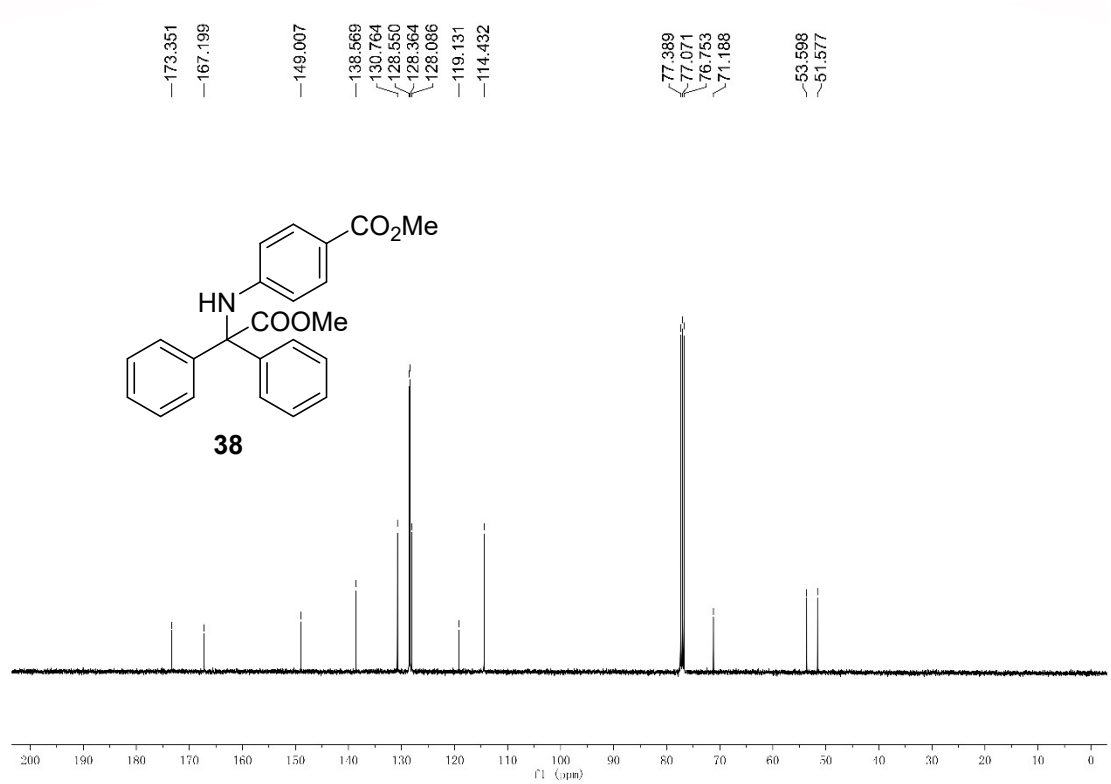
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **37**.



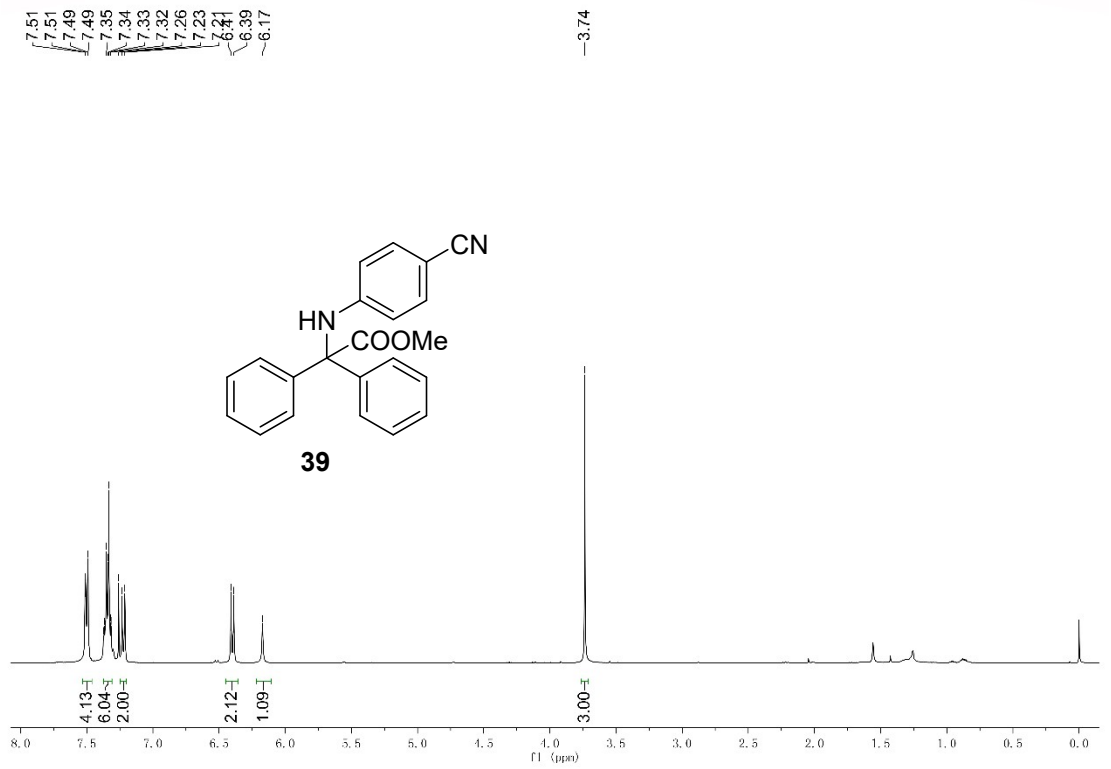
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **38**.



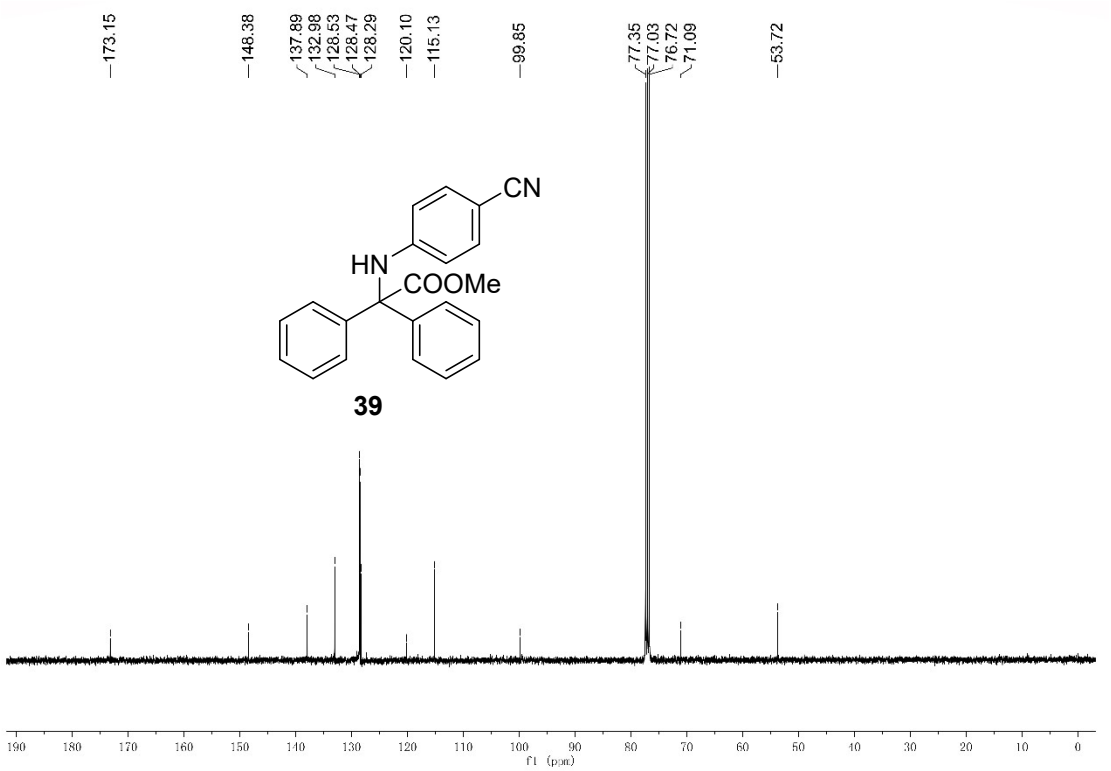
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **37**.



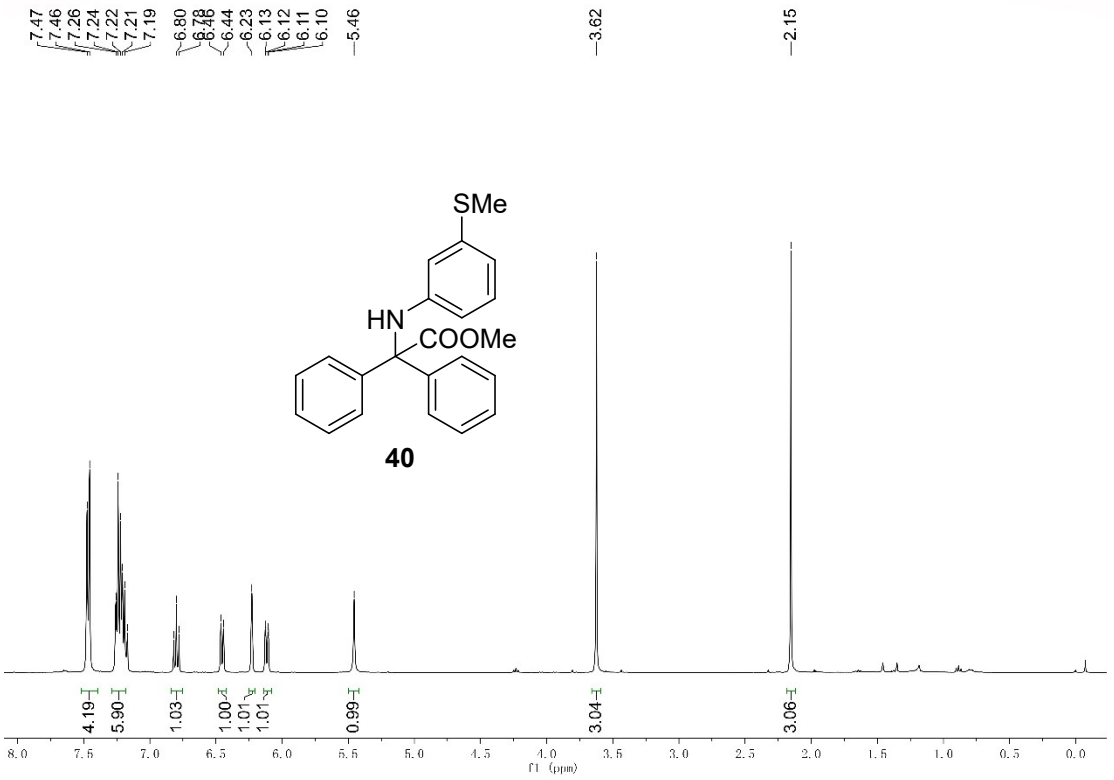
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **39**.



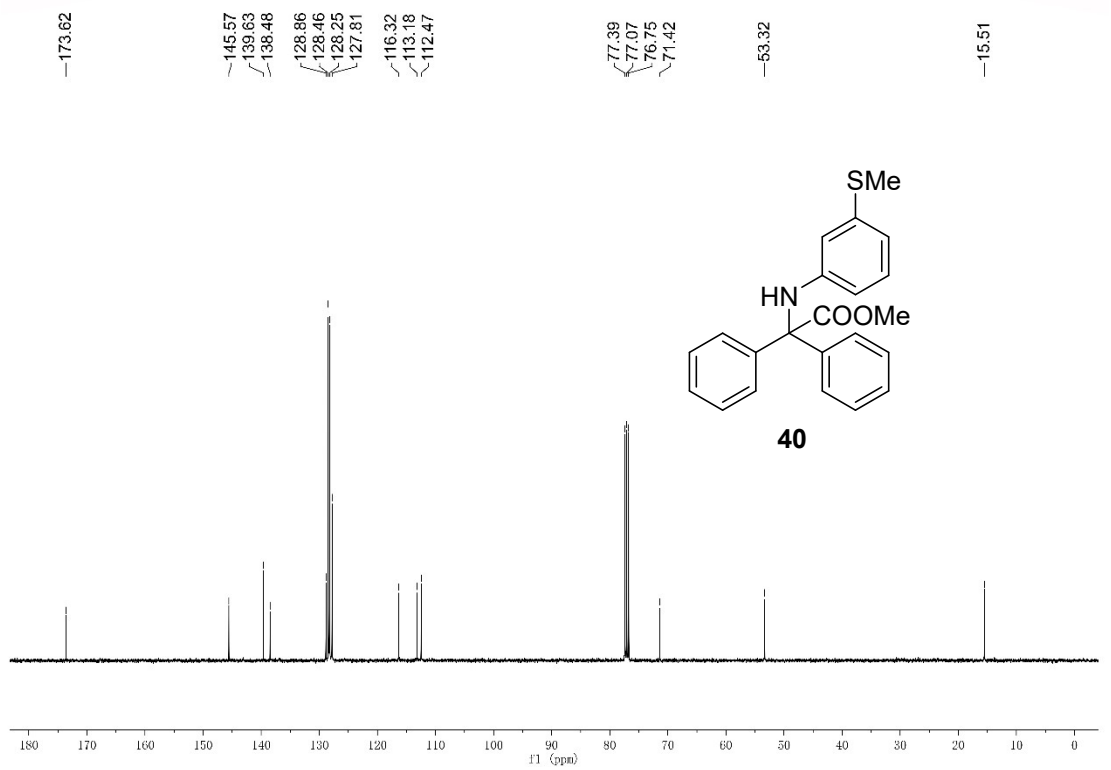
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **39**.



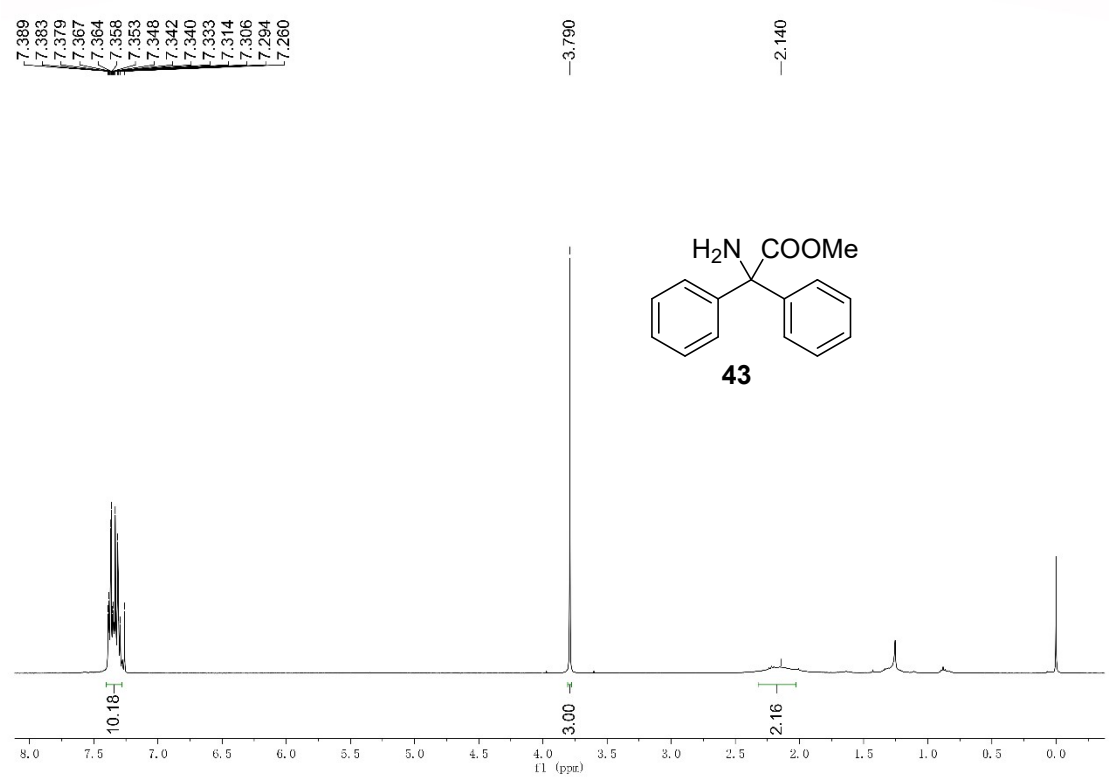
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **40**.



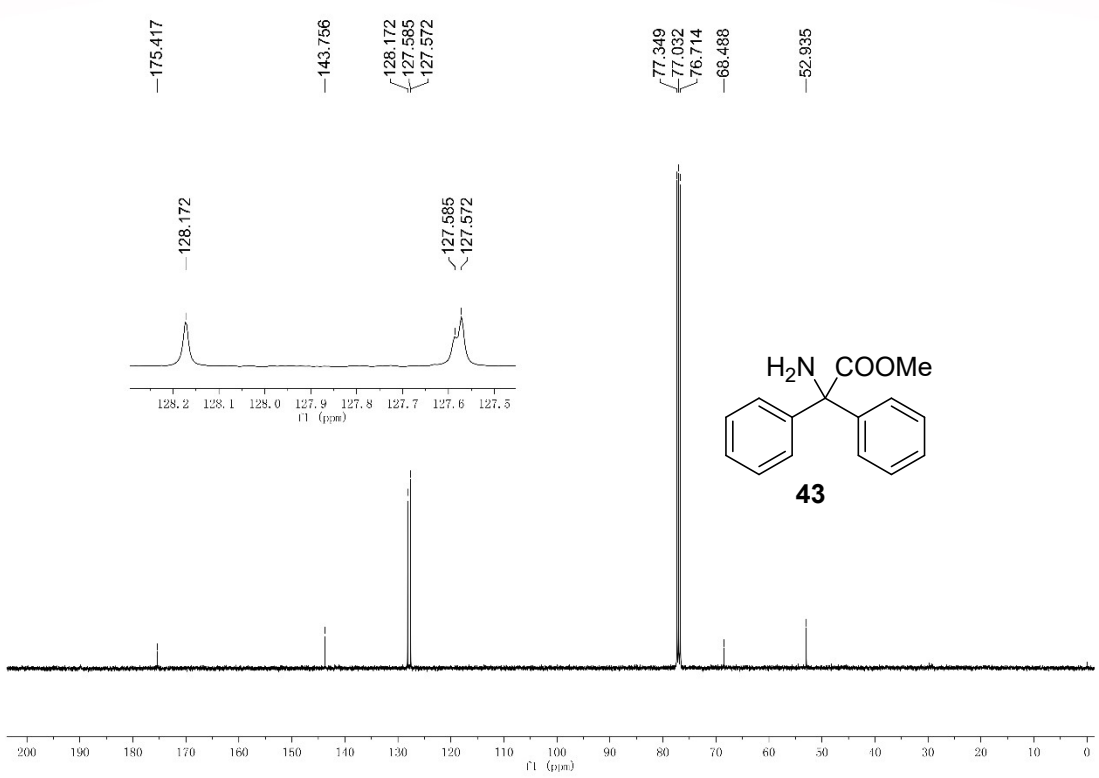
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **40**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **43**.



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **43**.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128.172
127.585
127.572
77.349
77.032
76.714
68.488
52.935
128.172
127.585
127.572
128.2 128.1 128.0 127.9 127.8 127.7 127.6 127.5
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
H2N COOMe
43