Supporting Information

Deoxygenative *ortho*-Benzylation of Aryl Iodides with Benzyl Alcohol via Palladium/Norbornene Cooperative Catalysis

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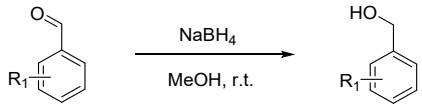
General Information

DMF, DMA, DMSO, toluene and CH_3CN solvents were dried from CaH and purified by distillation before being used. Purifications of reactions products were carried out by column chromatography on silica gel (200-300 mesh) using a mixture of petroleum ether (60-90°C), dichloromethane and ethyl acetate as eluent. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (377 MHz) were measured on a Brucker Avance 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal ($CDCl_3$ δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets) or m (multiplet). Electrospray mass spectra were obtained using Bruker micrOTOF-Q II 10410 Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

Preparation of substrates

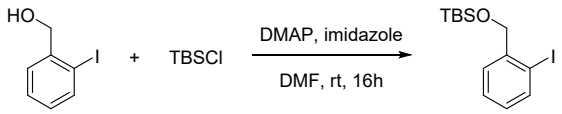
General Procedure 1 (2r-2t, 2w-2z, 2A-2C)



Benzaldehyde derivatives (1.00 mmol) in methanol (15 mL), sodium borohydride (2.00 mmol) and stirred at room temperature for 1 h. Usual work-up, quantitative yield.[2]

These substrates were prepared according to the **general procedure 1**. Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature reports.[1-5]

General Procedure 2

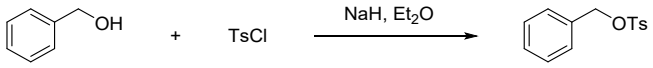


To a solution of 2-iodobenzyl alcohol (4.27 mmol, 1.0 equiv) in dry DMF (7 mL) were successively added imidazole (6.42 mmol, 1.5 equiv), DMAP (0.43 mmol, 10.0

mol%) and TBSCl (6.42 mmol, 1.5 equiv). The reaction mixture was stirred overnight at room temperature before quenching with H_2O and extracting with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. Purification by flash column chromatography on silica afforded iodide as a colourless oil.

Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature reports.[6]

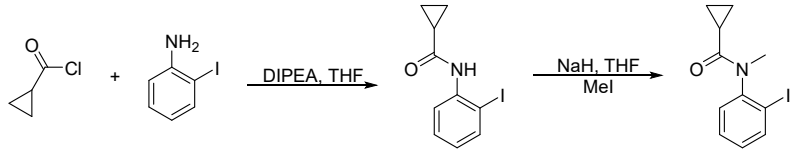
General Procedure 3



Sodium hydride (60% dispersion in oil, 420 mg, 10.50 mmol) was added to a solution of benzyl alcohol (1.08 g, 10.00 mmol) in diethyl ether (10 mL) and the mixture was stirred at reflux for 16 h. The mixture was cooled to -20 °C and a solution of p-toluenesulfonyl chloride (1.91 g, 10.00 mmol) in diethyl ether (10 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature over 3 h and was stirred at room temperature for a further hour. The mixture was filtered to give a clear solution, which was then cooled to -78 °C. The resultant white precipitate was collected and dried to give the product as a white solid (1.04 g, 3.96 mmol, 40%).

Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature reports.[7]

General Procedure 4

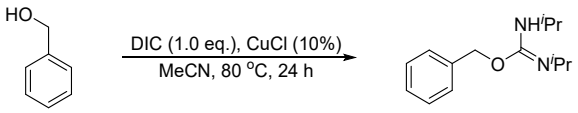


Cyclopropane carbonyl chloride (1.04 g, 10.40 mmol) was added dropwise to a solution of 2-iodoaniline (2.00 g, 9.13 mmol) and *N*, *N*-diisopropylethylamine (1.53 g, 11.90 mmol) in THF (20 mL) at 0 °C under nitrogen. The solution was then allowed to warm to room temperature and stirring was continued for a further four hours. The reaction mixture was then diluted with diethyl ether (50 mL) and washed with brine (2 × 30 mL) and then water (30 mL). The ether layer was then dried with Na_2SO_4 and filtered, and the solvent was removed at reduced pressure. The product was purified by

recrystallization from the mixed solvents of dichloromethane and hexane, yielding cyclopropane carboxylic acid (2-iodo-phenyl)-amide as a white solid.

Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature reports.[8]

Synthesis of isourea

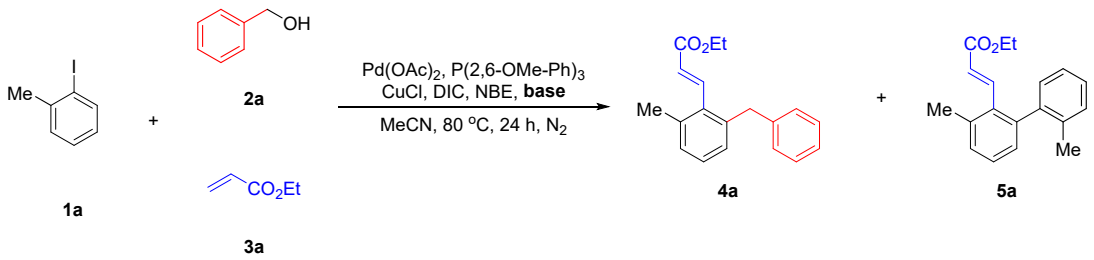


DIC (10.00 mmol, 1.0 eq.) was added to a mixture of phenylmethanol (10.00 mmol, 1.0 eq.) and anhydrous CuCl (1.00 mmol, 10 mol%) in MeCN (10 mL). The reaction mixture was stirred at room temperature for 24 h. Thereafter, pentane (80 mL) was added and the suspension filtered over alumina (neutral, activity grade I) and the filter plug was flushed with DCM. Thereafter, the filtrate was washed twice with aq. ammonia (2 M) The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Drying under high vaccum afforded the compound as a liquid.

Analytical data (^{1}H NMR, ^{13}C NMR) matches with the literature reports.[9]

Optimization of Reaction Conditions

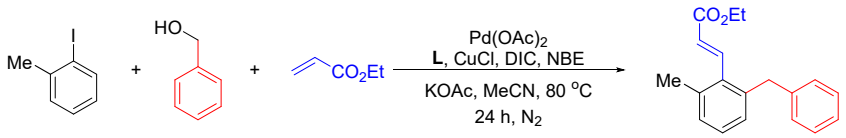
Table 1. Screening of Base[a]



entry	base	yield (%)
1	K_2CO_3	14
2	Na_2CO_3	N.R.
3	Cs_2CO_3	5
4	CsOAc	10
5	**KOAc**	**22**

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **3a** (0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), P(2,6-OMe-Ph)$_3$ (0.05 mmol, 25 mol%), NBE (0.6 mmol, 3.0 equiv), DIC (0.6 mmol, 3.0 equiv), base (0.4 mmol, 2.0 equiv), CuCl (0.02 mmol, 10 mol%), MeCN (2.0 mL), 80 °C, 24 h, N_2. Isolated yields.

Table 2. Screening of Ligand[a]

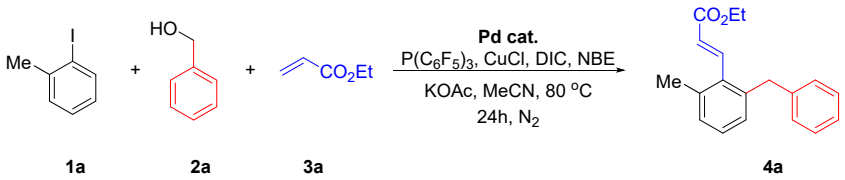


1a **2a** **3a** **4a**

entry	ligand	yield (%)
1	P(2,6-OMe-Ph)$_3$	22
2	$AsPh_3$	20
3	TFP	30
4	PPh_3	24
5[b]	**$P(C_6F_5)_3$**	**48**
6	Xantphos	30
7	DPEphos	trace

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **3a** (0.24 mmol, 1.2 equiv), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), L (0.05 mmol, 25 mol%), NBE (0.6 mmol, 3.0 equiv), DIC (0.6 mmol, 3.0 equiv), KOAc (0.4 mmol, 2.0 equiv), CuCl (0.02 mmol, 10 mol%), MeCN (2.0 mL), 80 °C, 24 h, N_2. Isolated yields.

Table 3. Screening of [Pd][a]

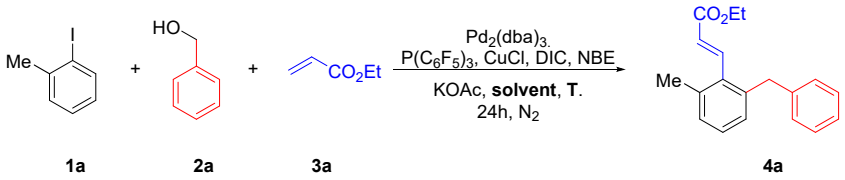


1a **2a** **3a** **4a**

entry	[Pd]	yield (%)
1	$Pd(OAc)_2$	48
2	$Pd(PPh_3)_4$	8
3	$Pd(dba)_2$	47
4	$PdCl_2$	40
5	$PdCl_2(dppf)$	7
6	$Pd(TFA)_2$	39
7	$[Pd(allyl)Cl]_2$	45
8	$Pd(PPh_3)_2Cl_2$	35
9	$Pd_2(dba)_3$	50
10[b]	$Pd_2(dba)_3$	78
11[c]	**$Pd_2(dba)_3$**	**88**

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **3a** (0.24 mmol, 1.2 equiv), [Pd] (0.02 mmol, 10 mol%), $P(C_6F_5)_3$ (0.05 mmol, 25 mol%), NBE (0.6 mmol, 3.0 equiv), DIC (0.6 mmol, 3.0 equiv), KOAc (0.4 mmol, 2.0 equiv), CuCl (0.02 mmol, 10 mol%), MeCN (2.0 mL), 80 °C, 24 h, N_2. Isolated yields. [b] **2a** (0.5 mmol, 2.5 equiv). [c] **2a** (0.6 mmol, 3.0 equiv).

Table 4. Screening of Temperature and Solvent[a]

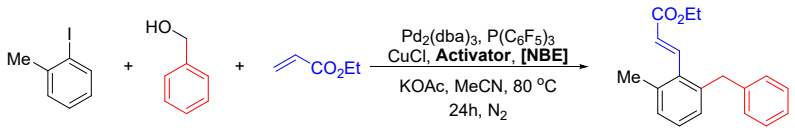


1a **2a** **3a** **4a**

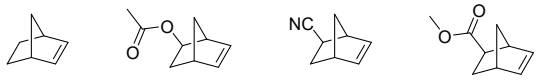
entry	solvent	T (°C)	yield (%)
1	**MeCN**	**80**	**88**
2	MeCN	90	64
3	MeCN	100	55
4	MeCN	110	43
5	MeCN	120	20
6	toluene	80	trace
7	dioxane	80	trace
8	DCE	80	trace

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3a** (0.24 mmol, 1.2 equiv), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), $P(C_6F_5)_3$ (0.05 mmol, 25 mol%), NBE (0.6 mmol, 3.0 equiv), DIC (0.6 mmol, 3.0 equiv), KOAc (0.4 mmol, 2.0 equiv), CuCl (0.02 mmol, 10 mol%), solvent (2.0 mL), T, 24 h, N_2. Isolated yields.

Table 5. Screening of [NBE] and Activator [a]



1a **2a** **3a** **4a**



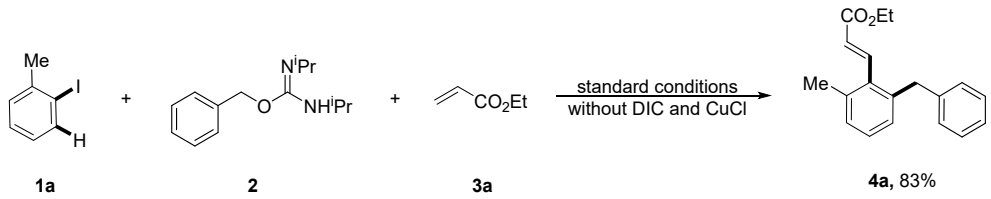
N1 N2 N3 N4

entry	[NBE]	Activator	yield (%)
1	**N1**	DIC	**88**
2	N2	DIC	18
3	N3	DIC	23
4	N4	DIC	15
5	N1	DMO	0
6	N1	DCC	65

[a] Reaction conditions: substrate **1a** (0.2 mmol, 1.0 equiv), **2a** (0.6 mmol, 3.0 equiv), **3a** (0.24 mmol, 1.2 equiv), $Pd_2(dba)_3$ (0.01 mmol, 5 mol%), $P(C_6F_5)_3$ (0.05 mmol, 25 mol%), [NBE] (0.6 mmol, 3.0 equiv), Activator (0.6 mmol, 3.0 equiv), KOAc (0.4 mmol, 2.0 equiv), CuCl (0.02 mmol, 10 mol%), MeCN (2.0 mL), 80 °C, 24 h, N_2. Isolated yields.

Mechanistic Experiments

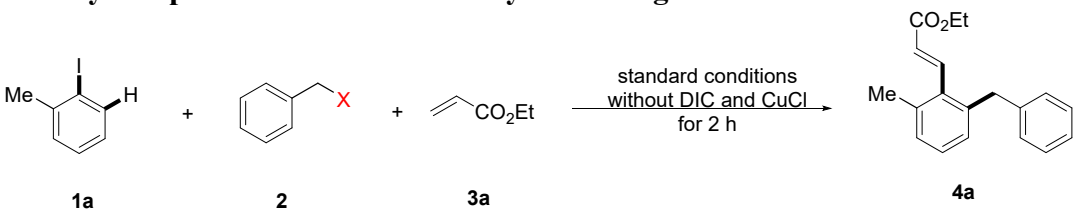
Reaction with preformed isourea



1a **2** **3a** **4a**, 83%

A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.01 mmol), $P(C_6F_5)_3$ (25 mol%, 0.05 mmol), KOAc (2.0 equiv, 0.4 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, 1-iodo-2-methylbenzene **1a** (1.0 equiv, 0.2 mmol), norbornene (3.0 equiv, 0.6 mmol), isourea **2** (3.0 equiv, 0.6 mmol), ethyl acrylate **3a** (1.2 equiv, 0.24 mmol), MeCN (2 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 80 °C in the oil bath for 24 h. Upon the completion of the reaction, removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **4a**.

Reactivity comparison of different benzylation reagents

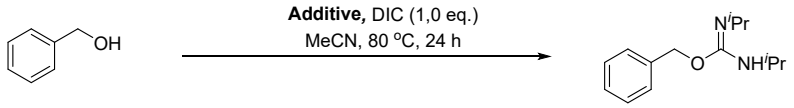


1a **2** **3a** **4a**

X	Yield / %
OTs	20
Br	15
Cl	12
methyl oxalate	< 5
OCN^{i}PrNH^{i}Pr	32

A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.01 mmol), $P(C_6F_5)_3$ (25 mol%, 0.05 mmol), KOAc (2.0 equiv, 0.4 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, 1-iodo-2-methylbenzene **1a** (1.0 equiv, 0.2 mmol), norbornene (3.0 equiv, 0.6 mmol), benzylation reagents **2** (3.0 equiv, 0.6 mmol), ethyl acrylate **3a** (1.2 equiv, 0.24 mmol), MeCN (2 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 80 °C in the oil bath for 2 h. Upon the completion of the reaction, removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **4a**.

Investigation of the Isourea Formation

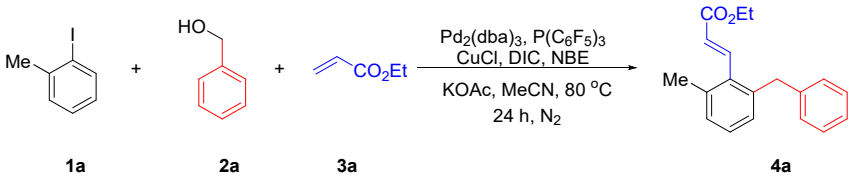


Entry	Additive	Yield/%[a]
1	$Pd_2(dba)_3$ (10 mol %)	< 10
2	$P(C_6F_5)_3$ (25 mol %)	N.D.
3	CuCl (10 mol %)	93
4	$Pd_2(dba)_3$ (10 mol %), $P(C_6F_5)_3$ (25 mol %)	< 10

[a] Reaction was analyzed via GC-MS.

A Schlenk-tube equipped with a magnetic stir bar was evacuated and backfilled with N_2 for 3 times. Afterwards, phenylmethanol **2a** (0.6 mmol), DIC (1.0 eq.), MeCN (2 mL) and addictive were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 80 °C in the oil bath for 24 h. An aliquot was taken, filtered over a short plug of silica and analyzed via GC-MS.

Scale-up of the model reaction

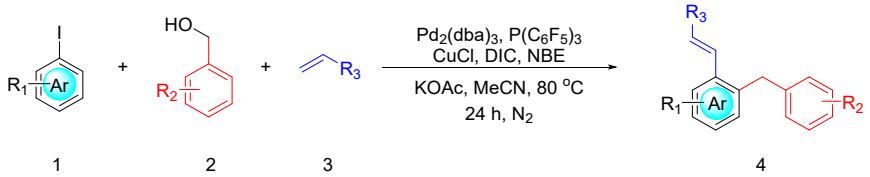


1a **2a** **3a** **4a**

A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.25 mmol), $P(C_6F_5)_3$ (25 mol%, 1.25 mmol), KOAc (2.0 equiv, 10.0 mmol), CuCl (10 mol%, 0.5 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, 1-iodo-2-methylbenzene **1a** (1.0 equiv, 5.0 mmol), norbornene (3.0 equiv, 15.0 mmol), benzyl alcohol **2a** (3.0 equiv, 15.0 mmol), ethyl acrylate **3a** (1.2 equiv, 6.0 mmol), DIC (3.0 equiv, 15.0 mmol), MeCN (50 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 80 °C in the oil bath for 24 h. Upon the completion of the reaction, removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **4a** (937.6 mg, 67%).

Synthesis and Characterization of Compound 4

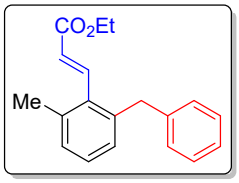
General Procedure 6



1 2 3 4

A Schlenk-tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (5 mol%, 0.01 mmol), $P(C_6F_5)_3$ (25 mol%, 0.05 mmol), KOAc (2.0 equiv, 0.4 mmol), CuCl (10 mol%, 0.02 mmol) and then evacuated and backfilled with N_2 for 3 times. Afterwards, 1-iodo-2-methylbenzene **1** (1.0 equiv, 0.2 mmol), norbornene (3.0 equiv, 0.6 mmol), benzyl alcohol **2** (3.0 equiv, 0.6 mmol), alkene **3** (1.2 equiv, 0.24 mmol), DIC (3.0 equiv, 0.6 mmol), MeCN (2 mL) were added consecutively under N_2 atmosphere. The tight tube was stirred and heated at 80 °C in the oil bath for 24 h. Upon the completion of the reaction, removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel to give the product **4**.

ethyl (*E*)-3-(2-benzyl-6-methylphenyl)acrylate (4a)[10]



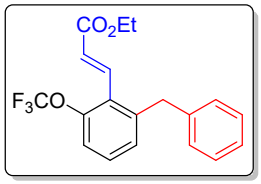
Compound **4a** was prepared from 1-iodo-2-methylbenzene **1a**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4a** as a white solid. 88% yield (49.4 mg). m.p. 65-66 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 16.0 Hz, 1H), 7.27-7.21 (m, 2H), 7.18-7.13 (m, 2H), 7.10-7.07 (m, 3H), 7.01 (d, *J* = 7.0 Hz, 1H), 5.94 (d, *J* = 16.0 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 4.00 (s, 2H), 2.32 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.48, 143.31, 140.43, 139.17, 136.50, 134.38, 128.84, 128.69, 128.38, 128.22, 128.08, 126.02, 124.39, 60.50, 39.73, 21.13, 14.26;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O_2$ 281.1536; Found 281.1541.

ethyl (*E*)-3-(2-benzyl-6-(trifluoromethoxy)phenyl)acrylate (4b)



Compound **4b** was prepared from 1-iodo-2-(trifluoromethyl) benzene **1b**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4b** as colorless oil 68% yield (47.3 mg).

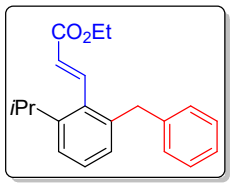
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.33-7.27 (m, 3H), 7.22 (t, *J* = 7.0 Hz, 2H), 7.15-7.12 (m, 3H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 4.11 (s, 2H), 1.34 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.38, 147.40, 142.23, 139.30, 136.99, 129.56, 128.89, 128.75, 128.60, 127.65, 126.42, 125.58, 120.36(q, *J* = 256 Hz), 119.06, 60.61, 39.45, 14.18;

^{19}F NMR (377 MHz, $CDCl_3$): δ -56.93;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}F_3O_3$ 351.1203; Found 351.1206.

ethyl (*E*)-3-(2-benzyl-6-isopropylphenyl)acrylate (4c)[10]



Compound **4c** was prepared from 1-iodo-2-isopropylbenzene **1c**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4c** as a white solid. 80% yield (49.3 mg). m.p. 64-65 °C.

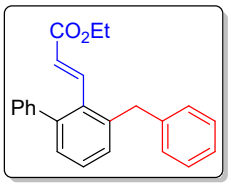
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 16.0 Hz, 1H), 7.26-7.20 (m, 4H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.0 Hz, 2H), 6.99 (dd, *J* = 6.0, 2.0 Hz, 1H), 5.88 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 2H), 3.12 (hept, *J* = 7.0 Hz, 1H), 1.32 (t, *J* = 7.0 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.19, 146.93, 143.82, 140.49, 138.43, 133.79, 128.91,

128.33, 128.29, 127.62, 125.95, 124.84, 123.43, 60.49, 39.93, 29.94, 23.85, 14.25;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_2$ 309.1849; Found 309.1850.

ethyl (*E*)-3-(3-benzyl-[1,1'-biphenyl]-2-yl)acrylate (4d)[10]



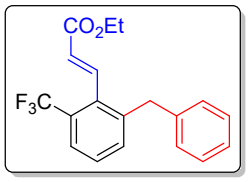
Compound **4d** was prepared from 2-iodo-1,1'-biphenyl **1d**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4d** as a white solid. 75% yield (51.3 mg). m.p. 77-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.37-7.26 (m, 8H), 7.23-7.14 (m, 5H), 5.63 (d, *J* = 16.0 Hz, 1H), 4.14-4.09 (m, 4H), 1.21 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.25, 143.08, 142.30, 141.11, 140.32, 139.59, 133.15, 129.71, 128.88, 128.78, 128.47, 128.36, 128.07, 127.08, 126.12, 124.82, 60.22, 39.84, 14.15;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{23}O_2$ 343.1693; Found 343.1687.

ethyl (*E*)-3-ethyl-2-(*p*-tolylthio)benzoate (4e)[10]



Compound **4e** was prepared from 1-iodo-2-(trifluoromethyl)benzene **1e**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 70:1) afforded **4e** as a white solid. 65% yield (43.4 mg). m.p. 75-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 16.0 Hz, 1H), 7.61-7.55 (m, 1H), 7.35 (d, *J* = 4.0 Hz, 2H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 2H), 5.96 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 4.02 (s, 2H), 1.32 (t, *J* = 7.0 Hz, 3H);

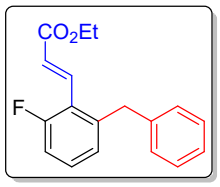
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.63, 140.58, 140.37, 139.45, 134.24, 133.67, 128.88,

128.78(q, J = 29 Hz), 128.60, 128.02, 126.49, 126.41, 124.18(q, J = 6 Hz), 123.90(q, J = 273 Hz), 60.72, 39.32, 14.20;

^{19}F NMR (377 MHz, $CDCl_3$): δ -58.14;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}F_3O_2$ 335.1253; Found 335.1261.

ethyl (*E*)-3-(2-benzyl-6-fluorophenyl)acrylate (4f)[10]



Compound **4f** was prepared from 1-fluoro-2-iodobenzene **1f**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4f** as a white solid. 80% yield (45.5 mg). m.p. 67-68 °C.

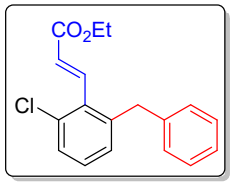
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 16.0 Hz, 1H), 7.31-7.25 (m, 3H), 7.23-7.19 (m, 1H), 7.14 (d, J = 7.0 Hz, 2H), 7.03-6.99 (m, 2H), 6.53 (dd, J = 16.0, 1.0 Hz, 1H), 4.24 (q, J = 7.0 Hz, 2H), 4.13 (s, 2H), 1.32 (t, J = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.03, 161.94 (d, J = 252.0 Hz), 142.63 (d, J = 2.0 Hz), 139.49, 135.80, 130.36 (d, J = 10.0 Hz), 128.68, 128.62, 126.41, 126.38, 124.25(d, J = 13.0 Hz), 121.66(d, J = 11.0 Hz), 114.42(d, J = 24.0 Hz), 60.52, 39.31(d, J = 3.0 Hz) , 14.25;

^{19}F NMR (377 MHz, $CDCl_3$): -110.68;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}FO_2$ 285.1285; Found 285.1282.

ethyl (*E*)-3-(2-benzyl-6-chlorophenyl)acrylate (4g) [10]



Compound **4g** was prepared from 1-chloro-2-iodobenzene **1g**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4g** as a white solid. 75% yield

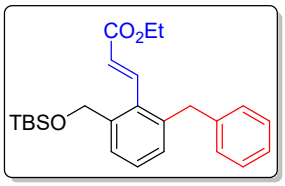
(44.8 mg). m.p. 75-76 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 16.0 Hz, 1H), 7.33-7.25 (m, 3H), 7.22-7.16 (m, 2H), 7.08 (d, *J* = 7.0 Hz, 3H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 4.05 (s, 2H), 1.32 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.17, 141.25, 140.39, 139.69, 133.74, 133.38, 129.21, 129.03, 128.79, 128.55, 128.06, 126.34, 125.81, 60.65, 39.79, 14.24;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}ClO_2$ 301.0990; Found 301.0988.

ethyl (*E*)-3-(2-benzyl-6-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)acrylate (4h)



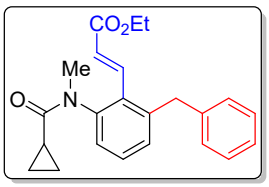
Compound **4h** was prepared from *tert*-butyl((2-iodobenzyl)oxy) dimethylsilane **1h**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4h** as colorless oil. 73% yield (59.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.31-7.25 (m, 3H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.12-7.10 (m, 3H), 6.06 (d, *J* = 16.0 Hz, 1H), 4.67 (s, 2H), 4.26 (q, *J* = 7.0 Hz, 2H), 4.04 (s, 2H), 1.33 (t, *J* = 7.0 Hz, 3H), 0.94 (s, 9H), 0.11 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.32, 142.09, 140.28, 139.35, 138.99, 133.47, 129.30, 128.86, 128.39, 126.11, 126.06, 124.83, 63.40, 60.48, 39.53, 25.90, 18.32, 14.24, -5.32;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{35}O_3Si$ 411.2350; Found 411.2353.

ethyl (*E*)-3-(2-benzyl-6-(*N*-methylcyclopropanecarboxamido)phenyl)acrylate (4i)



Compound **4i** was prepared from *N*-(2-iodophenyl)-*N*-methylcyclopropanecarboxamide **1i**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by

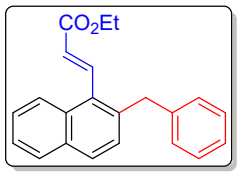
flash column chromatography on silica gel (PE/EA = 10:1) afforded **4i** as colorless oil. 30% yield (21.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.36-7.26 (m, 3H), 7.23-7.17 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 6.05 (d, *J* = 16.0 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.09 (s, 2H), 3.15 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.26-1.21 (m, 1H), 1.01-0.95 (m, 2H), 0.62-0.57 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.47, 166.06, 142.61, 141.51, 139.57, 139.33, 133.18, 130.17, 129.71, 128.78, 128.58, 127.16, 126.38, 124.76, 60.68, 39.61, 36.82, 14.18, 12.47, 8.58, 8.14;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}NO_3$ 364.1907; Found 364.1900.

ethyl (*E*)-3-(2-benzylnaphthalen-1-yl)acrylate (4j)[10]



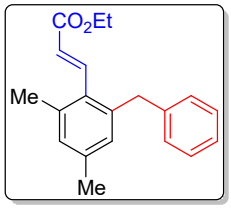
Compound **4j** was prepared from 1-iodonaphthalene **1j**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4j** as a white solid. 90% yield (56.9 mg). m.p. 73-75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 16.0 Hz, 1H), 8.06-8.04 (m, 1H), 7.84-7.81 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.49 (td, *J* = 7.0 Hz, *J* = 2.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28-7.24 (m, 2H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.0 Hz, 2H), 4.21 (s, 2H), 1.36 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.34, 142.51, 140.51, 136.39, 132.28, 131.52, 131.42, 128.83, 128.76, 128.48, 128.40, 128.27, 126.59, 126.14, 126.08, 125.61, 125.09, 60.67, 39.61, 14.31;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}O_2$ 317.1536; Found 317.1542.

ethyl (*E*)-3-(2-benzyl-4,6-dimethylphenyl)acrylate (4k)[10]



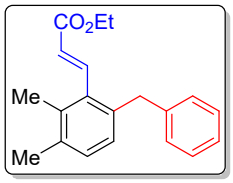
Compound **4k** was prepared from 1-iodo-2,4-dimethylbenzene **1k**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4k** as a white solid. 91% yield (53.5 mg). m.p. 77-78 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.16-7.12 (m, 2H), 7.06 (t, *J* = 7.0 Hz, 1H), 6.99 (d, *J* = 7.0 Hz, 2H), 6.82 (s, 1H), 6.74 (s, 1H), 5.83 (d, *J* = 16.0 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.88 (s, 2H), 2.20 (s, 3H), 2.16 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.64, 143.26, 140.54, 139.26, 138.16, 136.59, 131.35, 129.67, 128.96, 128.77, 128.35, 125.96, 123.73, 60.39, 39.70, 21.15, 21.09;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H23O_2$ 295.1693; Found 295.1696.

ethyl (*E*)-3-(6-benzyl-2,3-dimethylphenyl)acrylate (4l)[10]



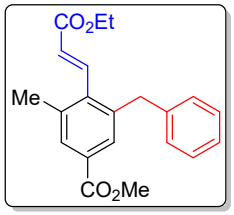
Compound **4l** was prepared from 1-iodo-2,3-dimethylbenzene **1l**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4l** as a white solid. 72% yield (52.3 mg). m.p. 64-65 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 16.0 Hz, 1H), 7.24 (t, *J* = 7.0 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.10-7.06 (m, 3H),, 6.92 (d, *J* = 8.0 Hz, 1H), 5.87 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.40, 144.42, 140.67, 136.44, 135.17, 134.84, 134.64, 129.69, 128.84, 128.34, 127.48, 125.93, 124.72, 60.46, 39.70, 20.41, 17.13, 14.28;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_2$ 295.1693; Found 295.1688.

methyl (*E*)-3-benzyl-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-5-methylbenzoate (4m)



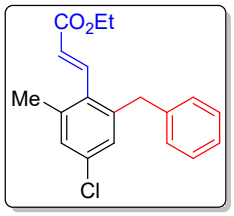
Compound **4m** was prepared from methyl 4-iodo-3-methylbenzoate **1m**, phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 20:1) afforded **4m** as colorless oil. 70% yield (47.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.72 (m, 3H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 2H), 5.95 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 7.0 Hz, 2H), 4.03 (s, 2H), 3.88 (s, 3H), 2.35 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.76, 165.96, 142.36, 139.76, 139.36, 139.20, 136.77, 129.59, 129.47, 129.03, 128.67, 128.43, 126.18, 125.34, 60.61, 52.07, 39.68, 20.99, 14.19.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_4$ 339.1591; Found 339.1596.

ethyl (*E*)-3-(2-benzyl-4-chloro-6-methylphenyl)acrylate (4n)



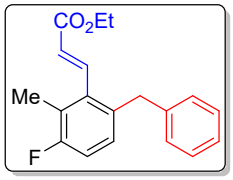
Compound **4n** was prepared from 4-chloro-1-iodo-2-methylbenzene **1n,** phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4n** as colorless oil. 90% yield (56.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.11-7.08 (m, 3H), 7.01 (d, *J* = 2.0 Hz, 1H), 5.95 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 2H), 2.31 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.19, 142.11, 141.07, 139.51, 138.37, 133.78, 132.85, 128.81, 128.56, 128.52, 127.87, 126.32, 124.92, 60.58, 39.56, 20.99, 14.24;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}ClO_2$ 315.1146; Found 315.1147.

ethyl (*E*)-3-(6-benzyl-3-fluoro-2-methylphenyl)acrylate (4o)



Compound **4o** was prepared from 1-fluoro-3-iodo-2-methylbenzene **1o,** phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4o** as colorless oil. 87% yield (51.8 mg).

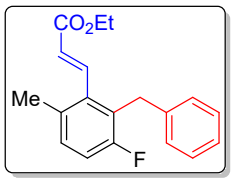
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.89-6.84 (m, 2H), 5.84 (d, *J* = 16.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.86 (s, 2H), 2.14 (d, *J* = 2.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.21, 160.05 (d, *J* = 243.0 Hz), 142.33 (d, *J* = 2.8 Hz), 140.27, 136.44 (d, *J* = 4.4 Hz), 134.71 (d, *J* = 3.5 Hz), 128.83, 128.76, 128.52, 126.23, 125.46, 123.41 (d, *J* = 16.8 Hz), 114.82 (d, *J* = 23.1 Hz), 60.70, 39.36, 12.46, 12.40;

^{19}F NMR (377 MHz, $CDCl_3$): δ -117.81;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}FO_2$ 299.1442; Found 299.1450.

ethyl (*E*)-3-(2-benzyl-3-fluoro-6-methylphenyl)acrylate (4p)



Compound **4p** was prepared from 4-fluoro-2-iodo-1-methylbenzene **1p,** phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4p** as colorless oil. 90% yield (53.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.15 (t, *J* = 7.0 Hz, 2H), 7.08-6.97 (m, 4H), 6.88 (t, *J* = 9.0 Hz, 1H), 5.82 (d, *J* = 16.0 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.95 (s, 2H), 2.18 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 3H);

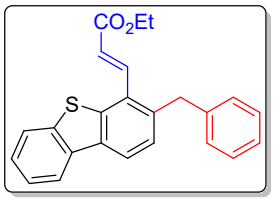
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.27, 159.67 (d, *J* = 242.0 Hz), 142.35 (d, *J* = 3.0 Hz), 139.66, 136.35 (d, *J* = 4.0 Hz), 132.08 (d, *J* = 4.0 Hz), 129.80 (d, *J* = 9.0 Hz), 128.50,

128.31, 126.16, 126.01 (d, J = 16.0 Hz), 125.21, 115.07 (d, J = 23.0 Hz), 60.69, 32.00, 20.65, 14.32;

^{19}F NMR (377 MHz, $CDCl_3$): δ -119.23;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}FO_2$ 299.1442; Found 299.1439.

ethyl *(E)*-3-(3-benzyldibenzo[*b*,*d*]thiophen-4-yl)acrylate (4q) (8:2 *E/Z* ratio)



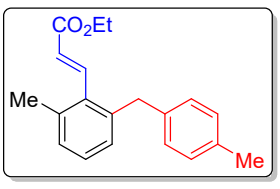
Compound **4q** was prepared from 4-iododibenzo[*b*,*d*]thiophene **1q,** phenylmethanol **2a** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 10:1) afforded **4q** as a white solid with a 8:2 *E/Z* ratio. 40% yield (29.8 mg). m.p. 102-103 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 16.0 Hz, 0.8H), 8.14-8.08 (m, 2H), 8.02 (d, J = 8.0 Hz, 1H), 7.87-7.85 (m, 0.8H), 7.81-7.79 (m, 0.2H), 7.48-7.46 (m, 1.6H), 7.44-7.41 (m, 1.6H), 7.35 (d, J = 8.0 Hz, 0.8H), 7.31-7.27 (m, 2H), 7.22-7.15 (m, 3.2H), 6.73 (d, J = 16.0 Hz, 0.8H), 6.26 (d, J = 12.0 Hz, 0.2H), 4.33-4.27 (m, 3.2H), 4.11 (s, 0.4H), 3.92 (q, J = 7.0 Hz, 0.4H), 1.37 (t, J = 7.0 Hz, 2.4H), 0.90 (t, J = 7.0 Hz, 0.6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.79, 164.96, 141.41, 141.12, 140.17, 140.05, 139.49, 139.18, 139.11, 135.10, 128.92, 128.73, 128.57, 128.53, 128.36, 127.64, 126.83, 126.58, 126.36, 126.28, 126.07, 125.02, 124.63, 124.28, 123.16, 122.68, 122.53, 122.34, 121.42, 121.37, 120.69, 60.71, 60.24, 39.57, 39.44, 14.31, 13.67;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{21}O_2S$ 373.1257; Found 373.1257.

ethyl (*E*)-3-(2-methyl-6-(4-methylbenzyl)phenyl)acrylate (4r)



Compound **4r** was prepared from 1-iodo-2-methylbenzene **1a,** p-tolylmethanol **2r** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4r** as colorless oil. 76%

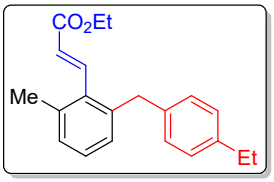
yield (44.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 16.0 Hz, 1H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.14-7.09 (m, 3H), 7.06-7.02 (m, 3H), 6.01 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 2H), 4.01 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.50, 146.51, 143.40, 139.46, 137.71, 136.41, 134.36, 128.71, 128.61, 128.19, 128.05, 126.41, 124.35, 60.46, 39.30, 33.63, 24.00, 21.14, 14.26;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_2$ 295.1442; Found 295.1444.

ethyl (*E*)-3-(2-(4-ethylbenzyl)-6-methylphenyl)acrylate (4s)



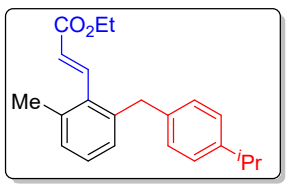
Compound **4s** was prepared from 1-iodo-2-methylbenzene **1a,** (4-ethylphenyl)methanol **2s** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4s** as colorless oil. 78% yield (48.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 16.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 3H), 7.04 (d, *J* = 8.0 Hz, 3H), 6.00 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 4.00 (s, 2H), 2.63 (q, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 8.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.49, 143.37, 141.88, 139.48, 137.57, 134.32, 128.75, 128.60, 128.19, 128.01, 127.86, 124.33, 60.45, 39.31, 28.37, 21.13, 15.58, 14.26;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_2$ 309.1849; Found 309.1843.

ethyl (*E*)-3-(2-(4-isopropylbenzyl)-6-methylphenyl)acrylate (4t)



Compound **4t** was prepared from 1-iodo-2-methylbenzene **1a,** (4-isopropylphenyl)methanol **2t** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column

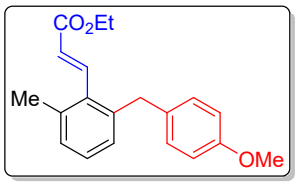
chromatography on silica gel (PE/EA = 50:1) afforded **4t** as colorless oil. 80% yield (51.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 16.0 Hz, 1H), 7.20-7.11 (m, 4H), 7.06-7.04 (m, 3H), 5.99 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 4.00 (s, 2H), 2.88 (hept, *J* = 7.0 Hz, 1H), 2.35 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.24 (d, *J* = 7.0 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.50, 146.51, 143.40, 139.46, 137.71, 136.41, 134.36, 128.71, 128.61, 128.19, 128.05, 126.41, 124.35, 60.46, 39.30, 33.63, 24.00, 21.14, 14.26;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}O_2$ 323.2006; Found 323.2010.

ethyl (*E*)-3-(2-(4-methoxybenzyl)-6-methylphenyl)acrylate (4u)



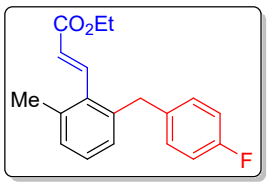
Compound **4u** was prepared from 1-iodo-2-methylbenzene **1a,** (4-methoxyphenyl)methanol **2u** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 20:1) afforded **4u** as colorless oil. 67% yield (41.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 16.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.04-7.02 (m, 3H), 6.83-6.81 (m, 2H), 5.98 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.50, 157.84, 143.33, 139.65, 136.47, 134.26, 132.47, 129.76, 128.61, 128.20, 127.91, 124.29, 113.77, 60.47, 55.17, 38.86, 21.13, 14.27;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_3$ 311.1642; Found 311.1643.

ethyl (*E*)-3-(2-(4-fluorobenzyl)-6-methylphenyl)acrylate (4v)



Compound **4v** was prepared from 1-iodo-2-methylbenzene **1a,** (4-fluorophenyl)methanol **2v** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column

chromatography on silica gel (PE/EA = 50:1) afforded **4v** as colorless oil. 67% yield (39.9 mg).

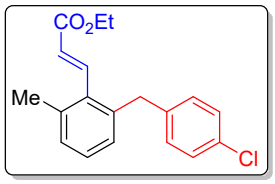
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 7.08-6.99 (m, 3H), 6.95 (t, *J* = 9.0 Hz, 2H), 5.95 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.99 (s, 2H), 2.34 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.49, 161.36 (d, *J* = 244.1 Hz), 143.22, 139.05, 136.70, 136.15 (d, *J* = 3.2 Hz), 134.41, 130.23 (d, *J* = 7.8 Hz), 128.92, 128.36, 128.02, 124.51, 115.22 (d, *J* = 21.2 Hz), 60.60, 39.04, 21.17, 14.33;

^{19}F NMR (377 MHz, $CDCl_3$): δ -117.27;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}FO_2$ 299.1442; Found 299.1437.

ethyl (*E*)-3-(2-(4-chlorobenzyl)-6-methylphenyl)acrylate (4w)



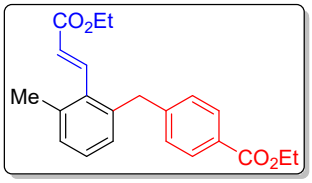
Compound **4w** was prepared from 1-iodo-2-methylbenzene **1a,** (4-chlorophenyl)methanol **2w** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4w** as colorless oil. 48% yield (30.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.24-7.21 (m, 2H), 7.19-7.13 (m, 2H), 7.04-7.01 (m, 3H), 5.95 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.99 (s, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.35, 143.05, 138.92, 138.57, 136.64, 134.36, 131.80, 130.11, 128.92, 128.47, 128.30, 127.98, 124.50, 60.52, 39.11, 21.07, 14.25;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}ClO_2$ 315.1146; Found 315.1143.

ethyl (*E*)-4-(2-(3-ethoxy-3-oxoprop-1-en-1-yl)-3-methylbenzyl)benzoate (4x)



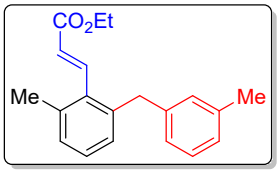
Compound **4x** was prepared from 1-iodo-2-methylbenzene **1a,** ethyl 4-(hydroxymethyl)benzoate **2x** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 30:1) afforded **4x** as colorless oil. 53% yield (37.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.20-7.12 (m, 4H), 7.01 (d, *J* = 7.0 Hz, 1H), 5.93 (d, *J* = 16.0 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 4.07 (s, 2H), 2.34 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.52, 166.33, 145.81, 143.03, 138.21, 136.69, 134.44, 129.68, 128.98, 128.78, 128.34, 128.33, 128.09, 124.57, 60.78, 60.54, 39.80, 21.08, 14.29, 14.24;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}O_4$ 353.1747; Found 353.1749.

ethyl (*E*)-3-(2-methyl-6-(3-methylbenzyl)phenyl)acrylate (4y)



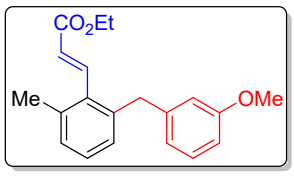
Compound **4y** was prepared from 1-iodo-2-methylbenzene **1a,** m-tolylmethanol **2y** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4y** as colorless oil. 82% yield (48.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.22-7.13 (m, 3H), 7.07-7.02 (m, 2H), 6.97-6.93 (m, 2H), 6.01 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.0 Hz, 2H), 4.02 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.37 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.42, 143.31, 140.30, 139.28, 137.87, 136.40, 134.34, 129.61, 128.59, 128.22, 128.16, 128.03, 126.74, 125.88, 124.35, 60.42, 39.64, 21.33, 21.08, 14.24;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_2$ 295.1693; Found 295.1686.

ethyl (*E*)-3-(2-(3-methoxybenzyl)-6-methylphenyl)acrylate (4z)



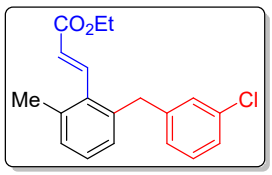
Compound **4z** was prepared from 1-iodo-2-methylbenzene **1a,** (3-methoxyphenyl)methanol **2z** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4z** as colorless oil. 80% yield (49.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 16.0 Hz, 1H), 7.21-7.16 (m, 2H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.75-6.66 (m, 3H), 5.98 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 4.00 (s, 2H), 3.76 (s, 3H), 2.34 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.48, 159.61, 143.28, 142.07, 138.96, 136.50, 134.37, 129.33, 128.71, 128.24, 128.06, 124.39, 121.29, 114.63, 111.30, 60.49, 55.05, 39.75, 21.12, 14.25;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_3$ 311.1642; Found 311.1644.

ethyl (*E*)-3-(2-(3-chlorobenzyl)-6-methylphenyl)acrylate (4A)



Compound **4A** was prepared from 1-iodo-2-methylbenzene **1a,** (3-chlorophenyl)methanol **2A** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4A** as colorless oil. 87% yield (54.6 mg).

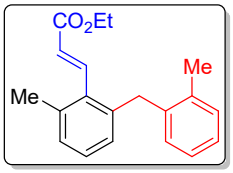
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.21-7.13 (m, 4H), 7.08 (s, 1H), 7.04-6.98 (m, 2H), 5.94 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.99 (s, 2H), 2.34 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.34, 143.02, 142.53, 138.17, 136.68, 134.43, 134.18, 129.59, 129.00, 128.88, 128.34, 128.08, 127.02, 126.28, 124.61, 60.57, 39.43, 21.08,

14.26;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}ClO_2$ 315.1146; Found 315.1147.

ethyl (*E*)-3-(2-methyl-6-(2-methylbenzyl)phenyl)acrylate (4B)



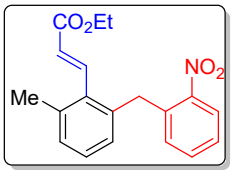
Compound **4B** was prepared from 1-iodo-2-methylbenzene **1a,** *o*-tolylmethanol **2B** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4B** as colorless oil. 73% yield (42.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 16.0 Hz, 1H), 7.19-7.12 (m, 5H), 6.93 (d, *J* = 7.0 Hz, 1H), 6.83 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.01 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.98 (s, 2H), 2.38 (s, 3H), 2.22 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.46, 143.07, 138.67, 138.47, 136.38, 136.37, 134.27, 130.10, 129.49, 128.47, 128.21, 127.31, 126.32, 125.96, 124.32, 60.47, 37.20, 21.08, 19.57, 14.22;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O_2$ 295.1693; Found 295.1688.

ethyl (*E*)-3-(2-methyl-6-(2-nitrobenzyl)phenyl)acrylate (4C)



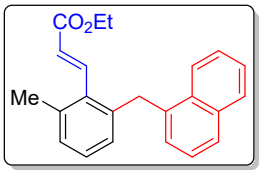
Compound **4C** was prepared from 1-iodo-2-methylbenzene **1a,** (2-nitrophenyl)methanol **2C** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 10:1) afforded **4C** as colorless oil. 60% yield (39.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.73 (d, *J* = 16.0 Hz, 1H), 7.49 (td, *J* = 7.0, 1.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.15-7.08 (m, 3H), 6.84-6.82 (m, 1H), 5.93 (d, *J* = 16.0 Hz, 1H), 4.34 (s, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.17, 149.12, 142.73, 136.80, 136.69, 135.49, 134.65, 133.00, 132.08, 129.06, 128.33, 127.44, 127.37, 124.83, 124.78, 60.59, 36.53, 20.99, 14.19;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}NO_4$ 326.1387; Found 326.1392.

ethyl (*E*)-3-(2-methyl-6-(naphthalen-1-ylmethyl)phenyl)acrylate (4D)



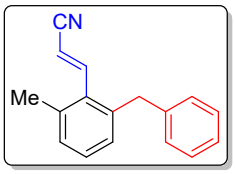
Compound **4D** was prepared from 1-iodo-2-methylbenzene **1a,** naphthalen-1-ylmethanol **2D** and ethyl acrylate **3a** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4D** as colorless oil. 83% yield (54.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.89-7.85 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.50-7.44 (m, 2H), 7.42-7.38 (m, 1H), 7.14-7.06 (m, 3H), 6.81 (d, *J* = 7.0 Hz, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 4.46 (s, 2H), 4.21 (q, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.46, 143.02, 138.73, 136.48, 136.26, 134.25, 133.79, 131.99, 128.65, 128.57, 128.30, 127.60, 127.18, 127.10, 126.00, 125.57, 125.52, 124.55, 123.97, 60.52, 36.84, 21.15, 14.19;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}O_2$ 331.1693; Found 331.1698.

(*E*)-3-(2-benzyl-6-methylphenyl)acrylonitrile (4E)



Compound **4E** was prepared from 1-iodo-2-methylbenzene **1a,** phenylmethanol **2a** and acrylonitrile **3E** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 20:1) afforded **4E** as colorless oil. 72% yield (33.5 mg).

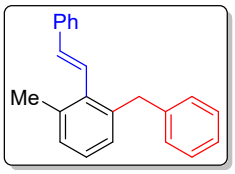
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 17 Hz, 1H), 7.31-7.28 (m, 2H), 7.25-7.20 (m,

2H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.11-7.06 (m, 3H), 5.40 (d, *J* = 17.0 Hz, 1H), 4.01 (s, 2H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.73, 140.01, 138.59, 136.48, 133.48, 129.15, 129.04, 128.73, 128.62, 128.47, 126.30, 117.52, 102.88, 39.73, 20.93;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}N$ 234.1277; Found 234.1285.

(*E*)-1-benzyl-3-methyl-2-styrylbenzene (4F)



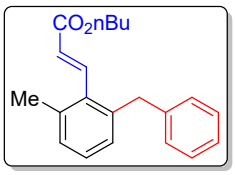
Compound **4F** was prepared from 1-iodo-2-methylbenzene **1a,** phenylmethanol **2a** and styrene **3F** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4F** as colorless oil. 58% yield (32.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 17.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.25-7.20 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 7.11-7.06 (m, 3H), 5.40 (d, *J* = 17.0 Hz, 1H), 4.01 (s, 2H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.73, 140.01, 138.59, 136.48, 133.48, 129.15, 129.04, 128.73, 128.62, 128.47, 126.30, 117.52, 102.88, 39.73, 20.93;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}$ 285.1638; Found 285.1645.

(*E*)-1-benzyl-3-methyl-2-styrylbenzene (4G)



Compound **4G** was prepared from 1-iodo-2-methylbenzene **1a,** phenylmethanol **2a** and butyl acrylate **3G** according to **general procedure 6**, and purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded **4G** as colorless oil. 80% yield (49.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 16.0 Hz, 1H), 7.27 (t, *J* = 7.0 Hz, 2H), 7.21-7.17 (m, 2H), 7.13-7.10 (m, 3H), 7.04 (d, *J* = 7.0 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 4.20

(t, *J* = 7.0 Hz, 2H), 4.03 (s, 2H), 2.35 (s, 3H), 1.72-1.65 (m, 2H), 1.47-1.38 (m, 2H), 0.97 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.55, 143.23, 140.43, 139.13, 136.51, 134.41, 128.81, 128.71, 128.38, 128.21, 128.11, 126.02, 124.43, 64.41, 39.77, 30.68, 21.12, 19.16, 13.74;

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_2$ 309.1849; Found 309.1855.

References

[1] S. Parihar, A. Kumar, A. K. Chaturvedi, N. K. Sachan, S. Luqman, B. Changkija, M. Manohar, O. Prakash, D. Chanda, F. Khan, C. S. Chanotiya, K. Shanker, A. Dwivedi, R. Konwar, A. S. Negi, Synthesis of combretastatin A4 analogues on steroidal framework and their anti-breast cancer activity, *J. Steroid Biochem. Mol. Biol.*, **2013**, *137*, 332-344.

[2] Q. Yu, D. Zhou, Y. Liu, X. Huang, C. Song, J. Ma, J. Li, Iron-Catalyzed, Directed Benzylic Borylation, *Org. Lett.*, **2023**, *25*, 47-52.

[3] S. S. Kotha, N. Sharma, G. Sekar, An Efficient, Stable and Reusable Palladium Nanocatalyst: Chemoselective Reduction of Aldehydes with Molecular Hydrogen in Water, *Adv. Synth. Catal.*, **2016**, *358*, 1694-1698.

[4] S. Okumura, S. Hattori, L. Fang, Y. Uozumi, Multielectron Reduction of Esters by a Diazabenzacenaphthenium Photoredox Catalyst, *J. Am. Chem. Soc.*, **2024**, *146*, 16990-16995.

[5] F. J. Ruiz-Mendoza, E. Campos-Dominguez, A. Álvarez-Hernández, D. Mendoza-Espinosa, Synthesis and catalytic applications of NHC–metal complexes supported on *p-tert*-butylcalix[4]arene frameworks, *New J. Chem.*, **2024**, *48*, 14021-14028.

[6] S. Zhao, S. Yang, G. Du, D. Zhang, H. Liu, F. G. Sun, *ortho*-Acylation of Aryl Iodides Enabled with Imides via Palladium/Norbornene/CuI Catalysis, *Adv. Synth. Catal.*, **2022**, *364*, 3506-3511.

[7] E. C. Frye, C. J. O'Connor, D. G. Twigg, B. Elbert, L. Laraia, D. G. Hulcoop, A. R. Venkitaraman, D. R. Spring, Palladium-Catalysed Cross-Coupling of Vinyldisiloxanes with Benzylic and Allylic Halides and Sulfonates, *Chem. Eur. J.*, **2012**, *18*, 8774-8779.

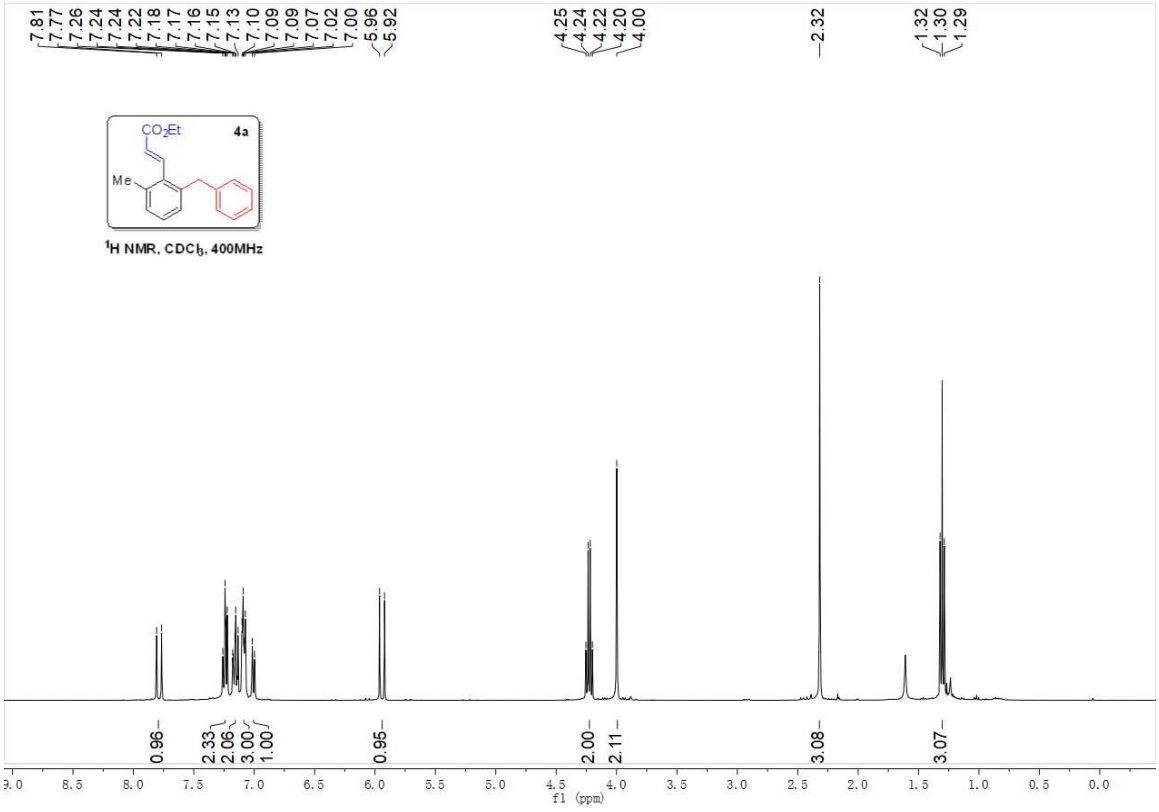
[8] A. Ishaq, J. M. Storey, W. T. Harrison, Short I···O Interactions in the Crystal

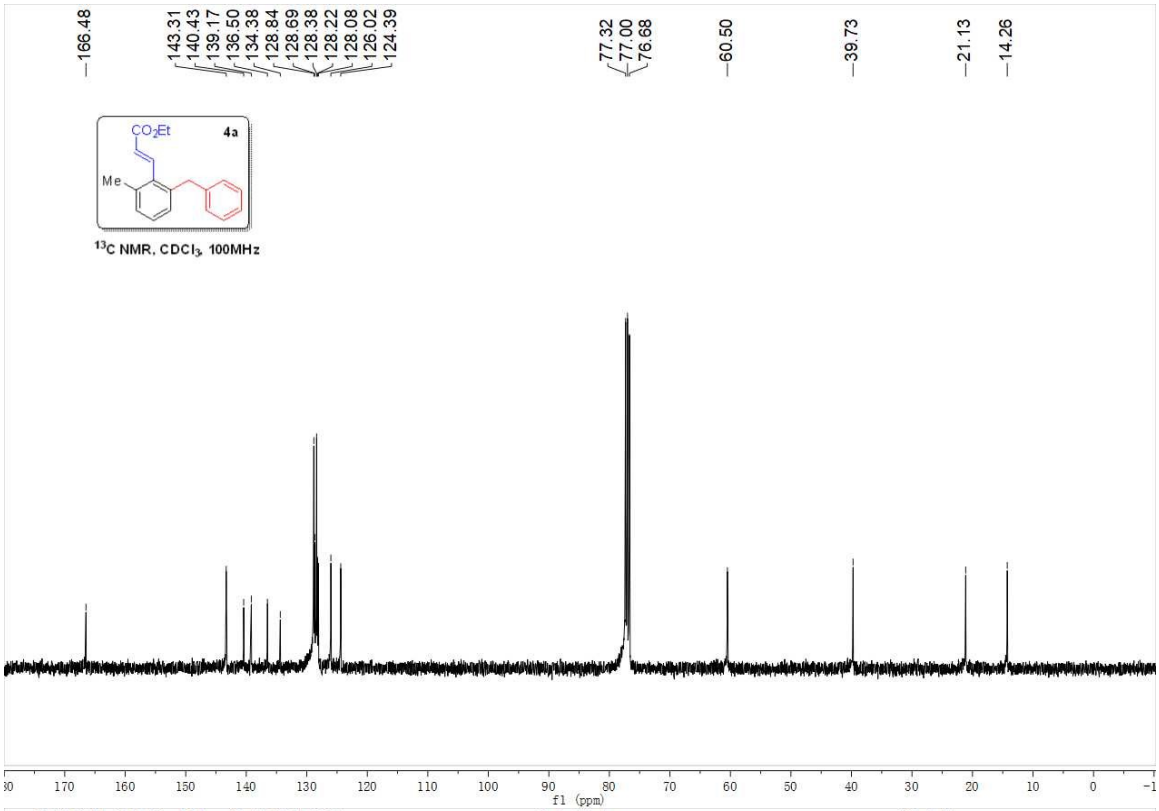
Structures of Two 2-Iodo-Phenyl Methyl-Amides as Substrates for Radical Translocation Reactions, *Chemistry*, **2023**, *5*, 1233-1242.

[9] J. Pícha, M. Buděšínský, I. Hančlová, M. Šanda, P. Fiedler, V. Vaněk, J. Jiráček, Efficient synthesis of phosphonodepsipeptides derived from norleucine, *Tetrahedron*, **2009**, *65*, 6090.

[10] M. L. Han, J. J. Chen, H. Xu, Z. C. Huang, W. Huang, Y. W. Liu, X. Wang, M. Liu, Z. Q. Guo, H. X. Dai, Palladium/Norbornene-Catalyzed Decarbonylative Difunctionalization of Thioesters, *JACS Au.*, **2021**, *1*, 1877-1884.

Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra

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77.32
77.00
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39.73
21.13
14.26
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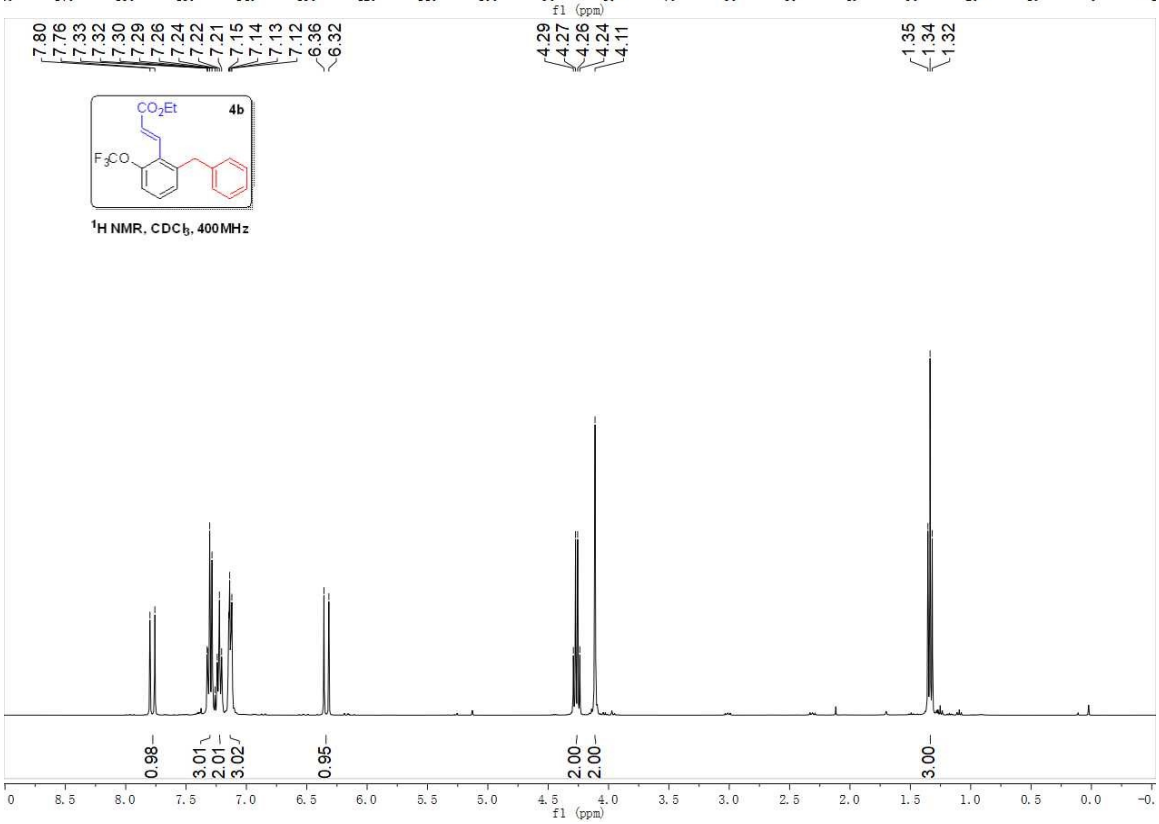
4a
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.12
6.36
6.32
4.29
4.27
4.26
4.24
4.11
1.35
1.34
1.32
CO2Et
4b
F3CO
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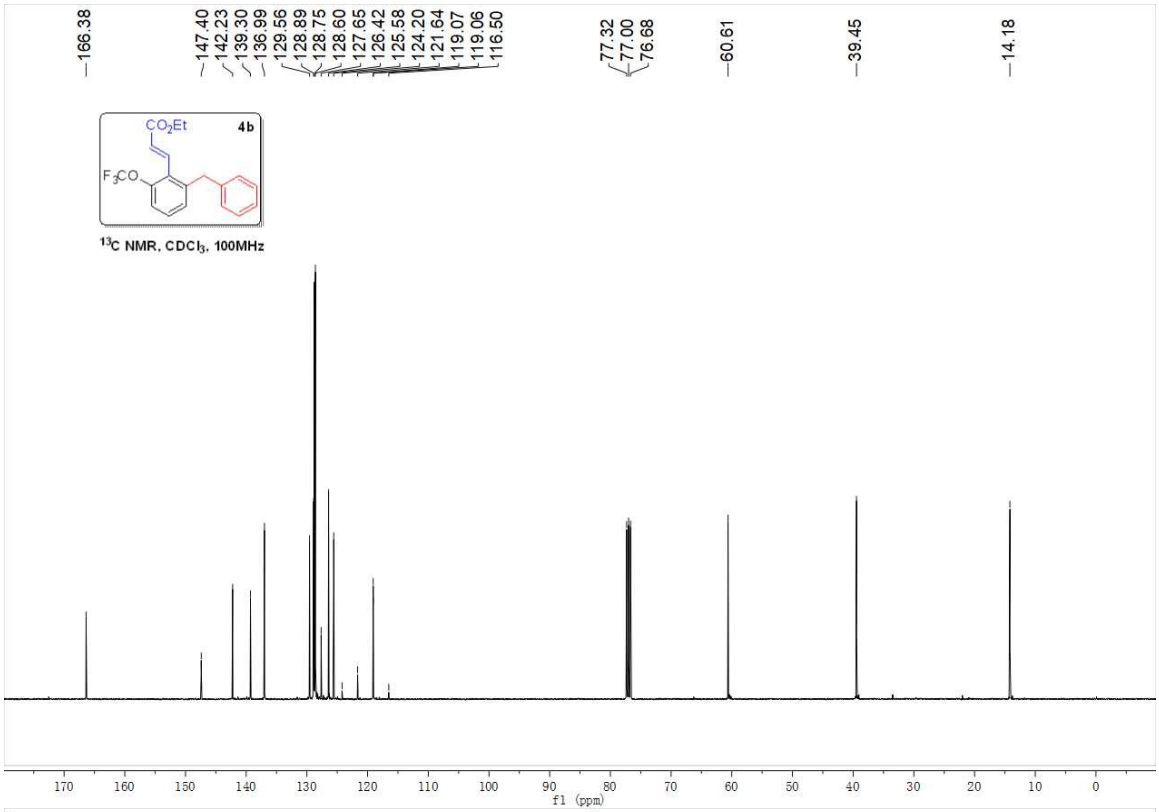
3.00
f1 (ppm)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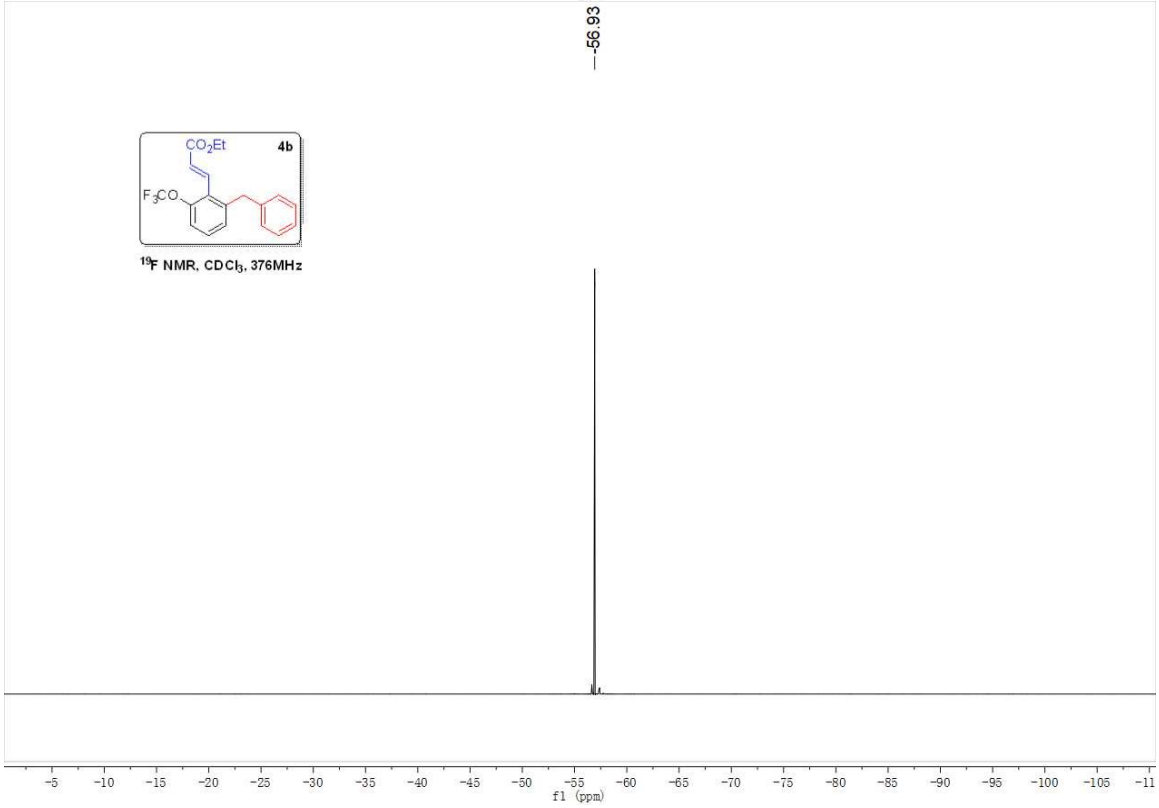
f1 (ppm)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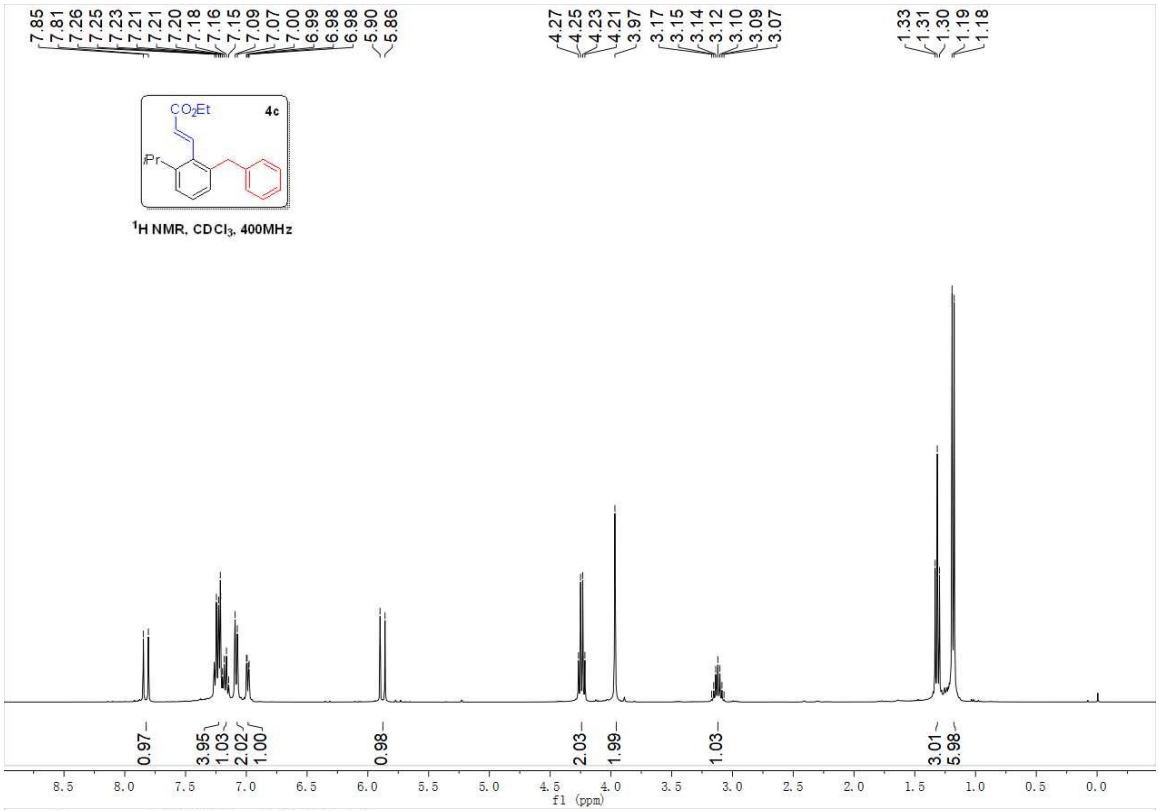

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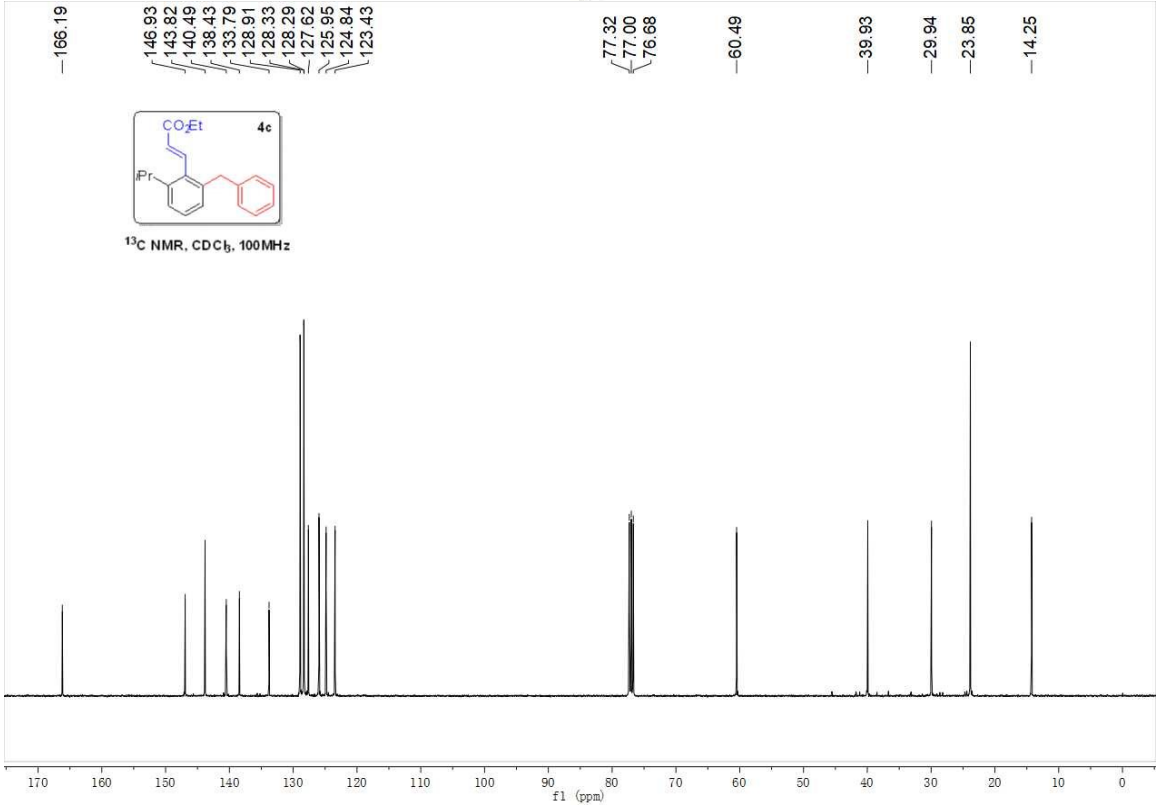

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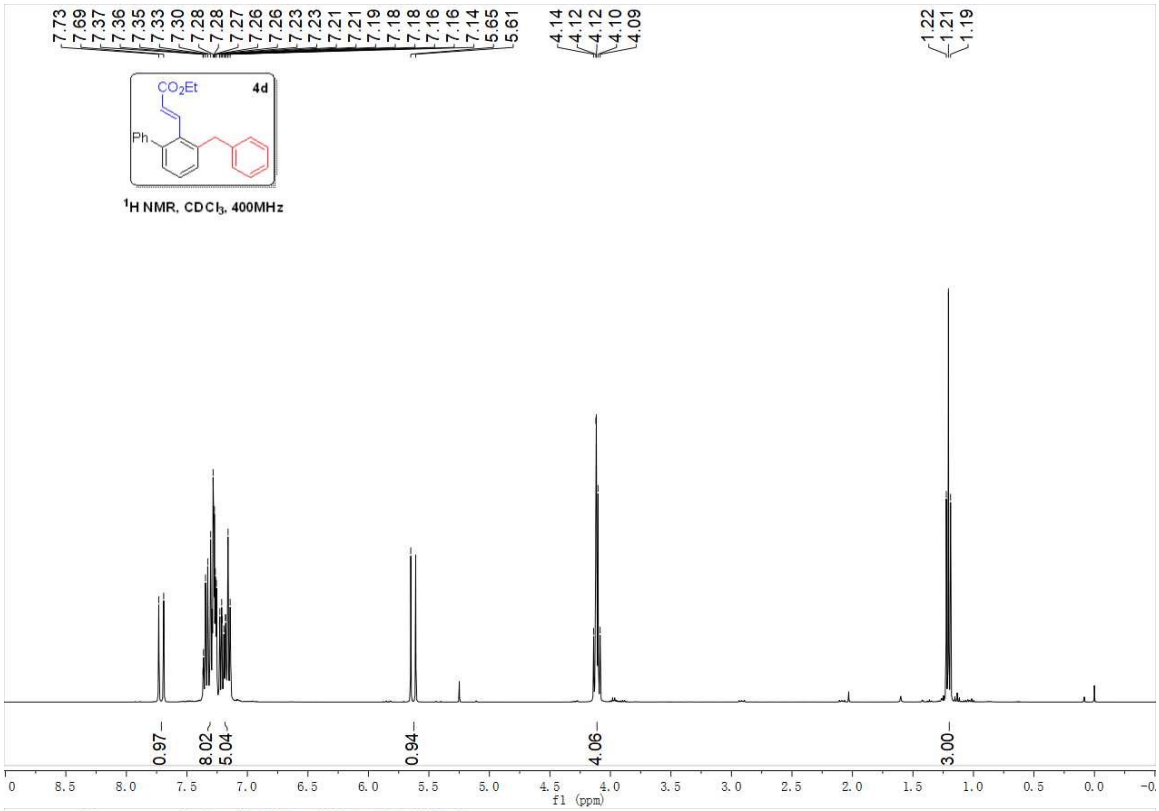
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7.16
7.16
7.14
5.65
5.61
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4.12
4.10
4.09
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1.21
1.19
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4d
Ph
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3.00
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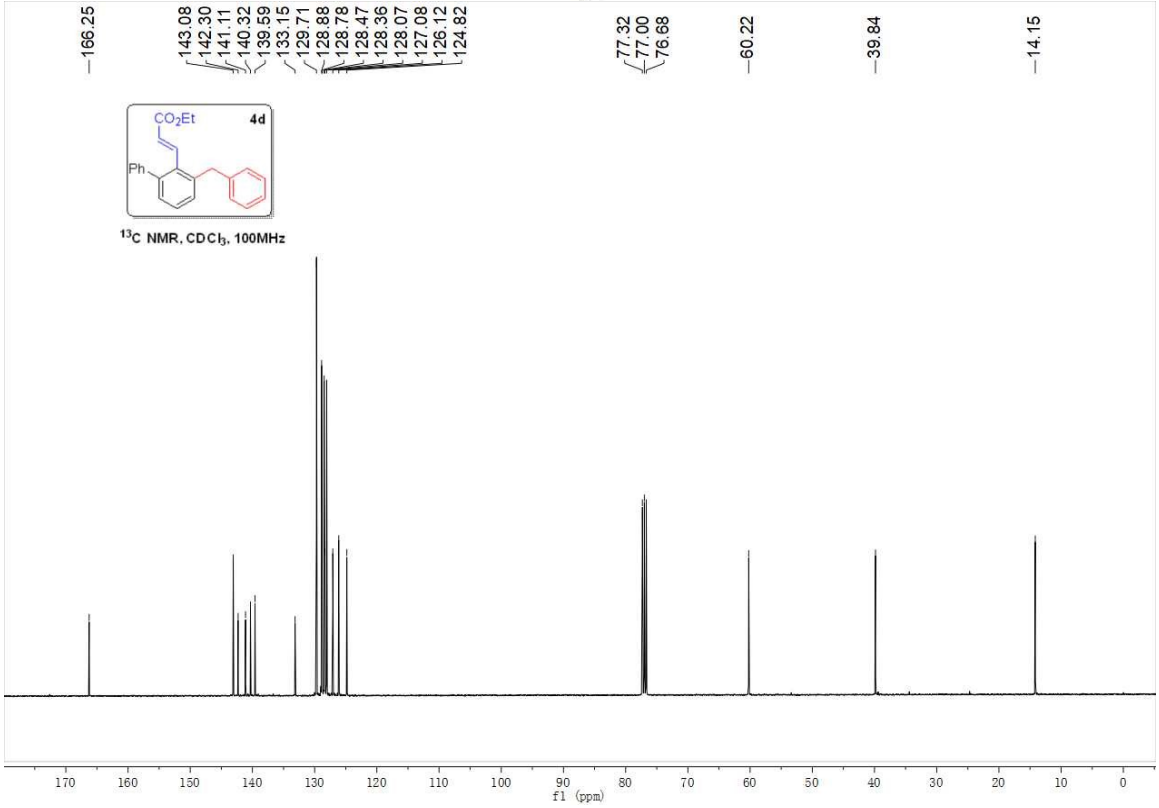
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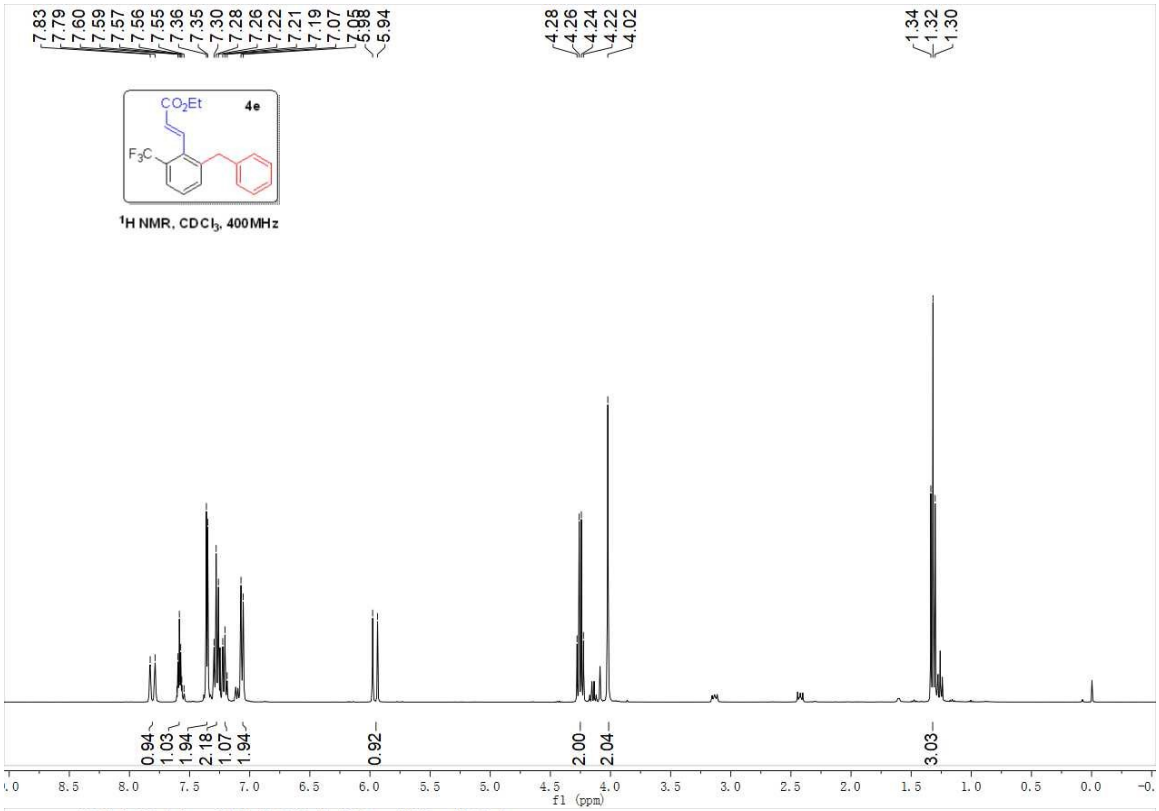
f1 (ppm)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5.94
4.28
4.26
4.24
4.22
4.02
1.34
1.32
1.30
CO2Et
4e
F3C
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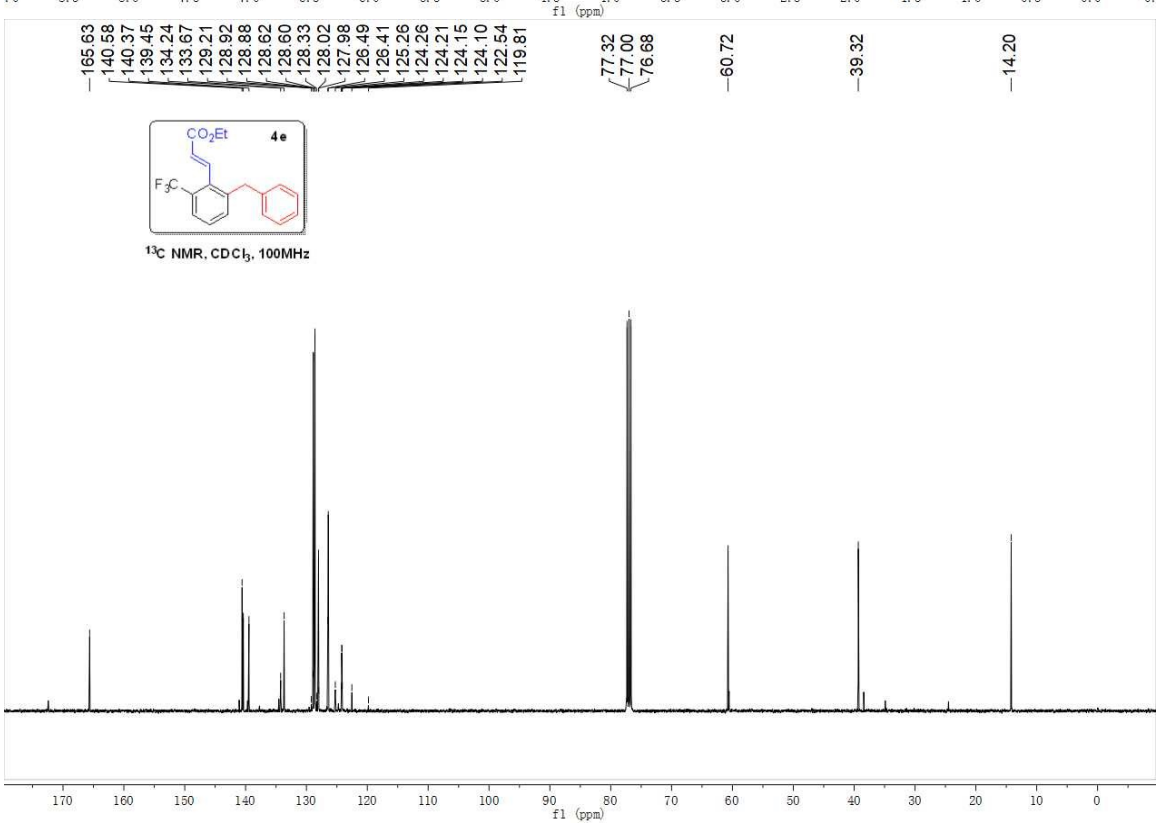
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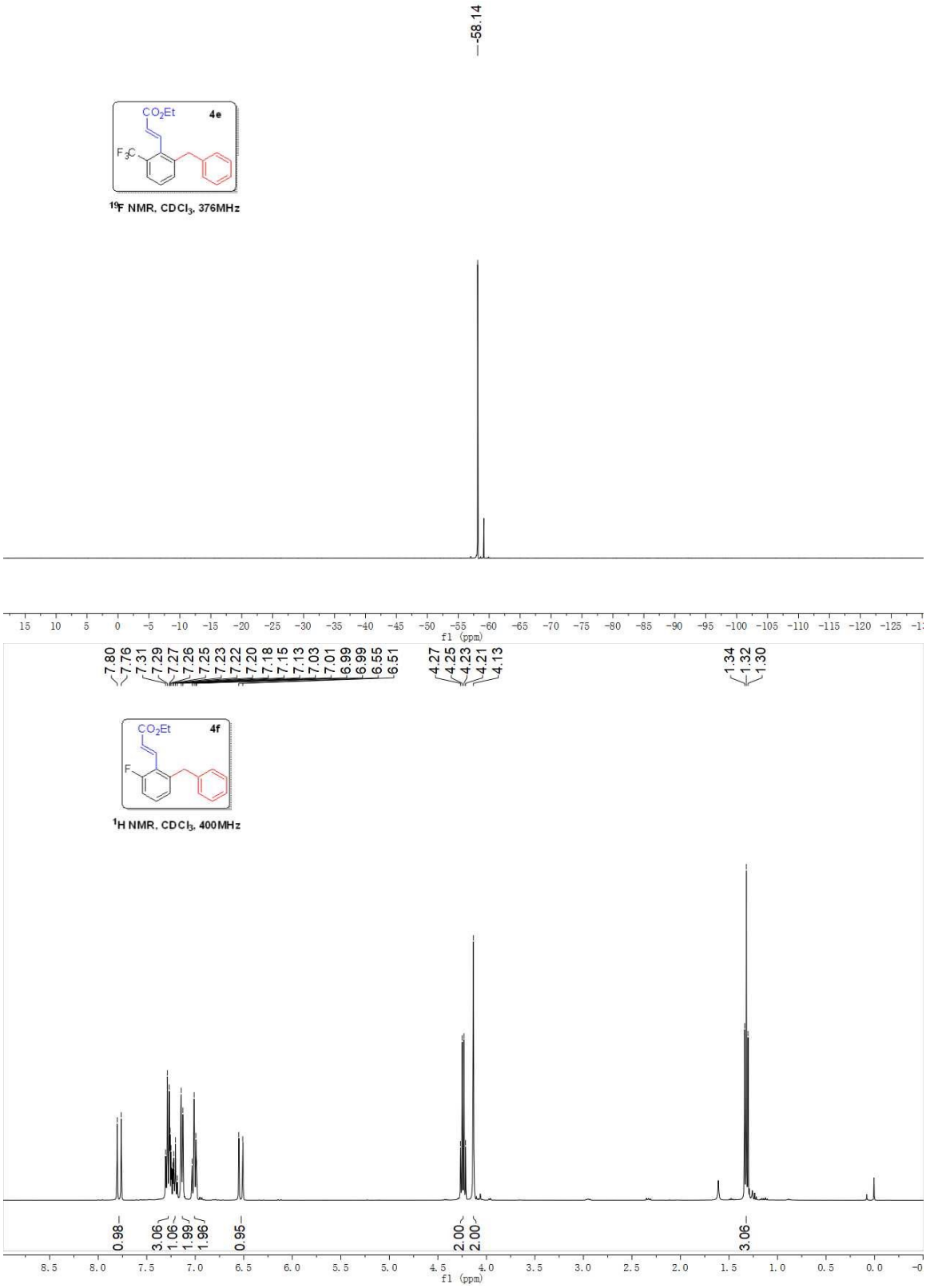
f1 (ppm)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7.15
7.13
7.03
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4.23
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1.30
4f
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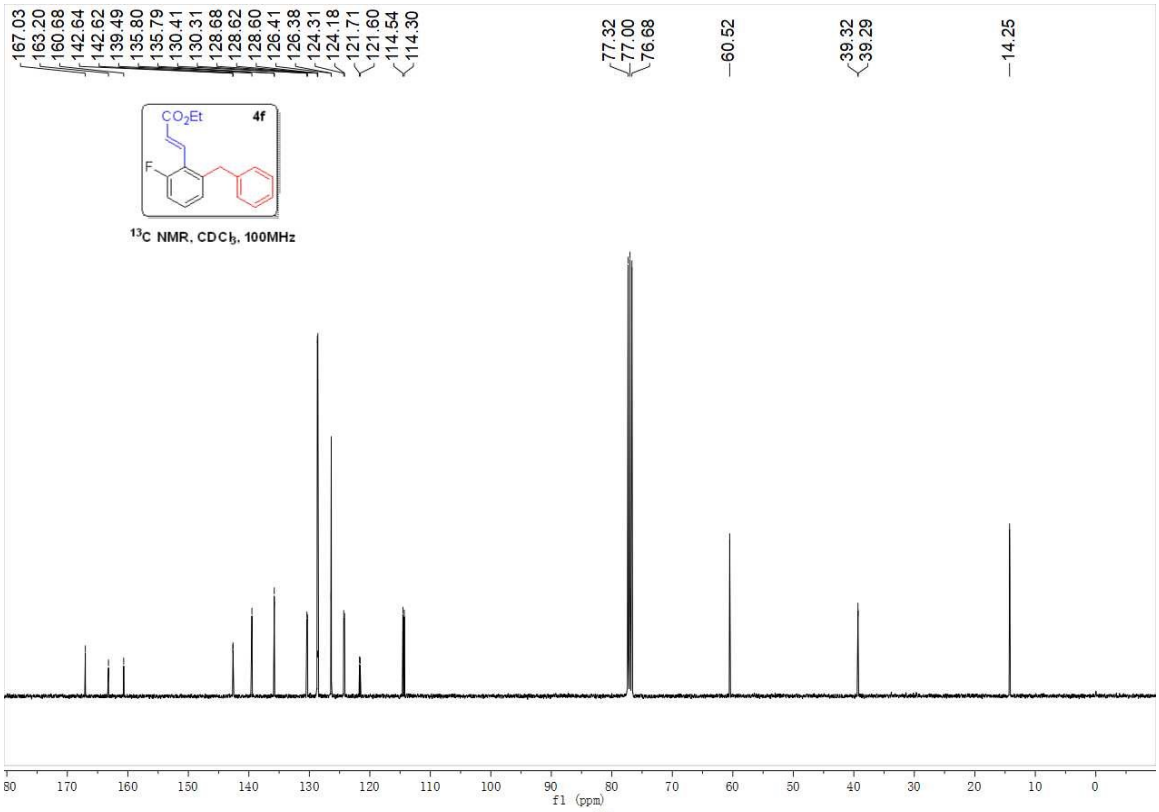
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4f
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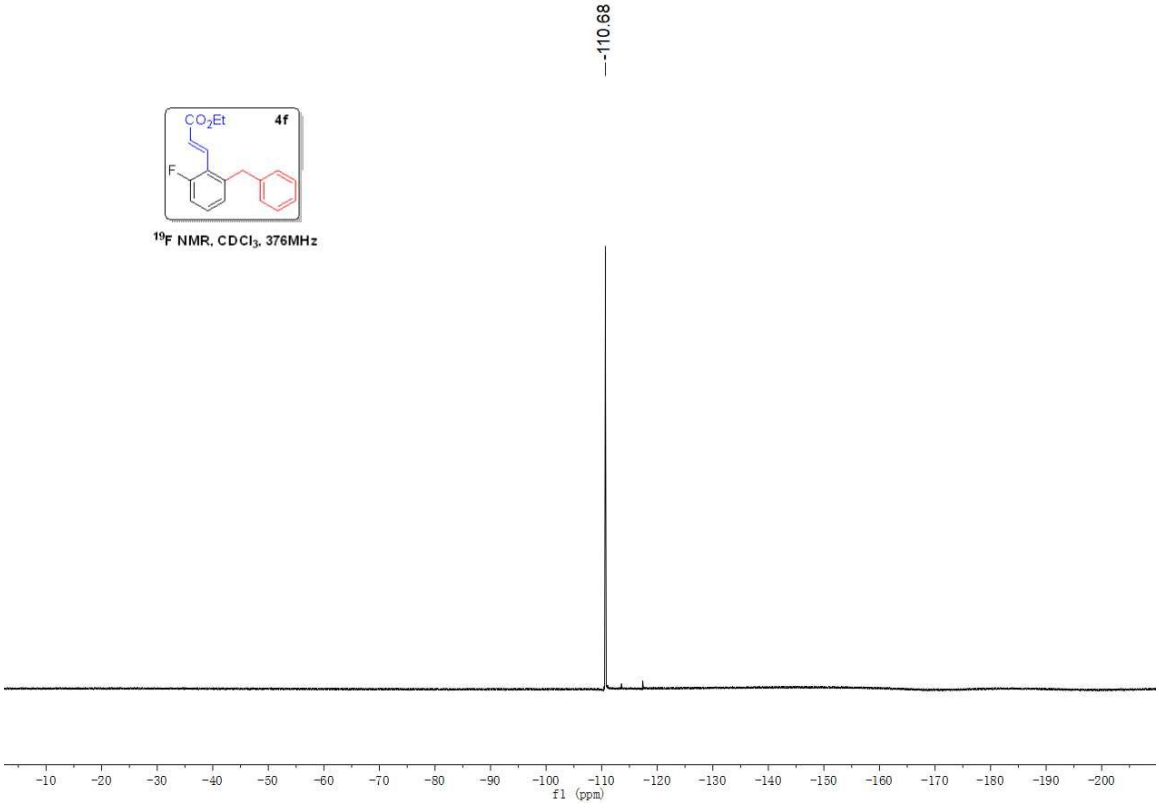
f1 (ppm)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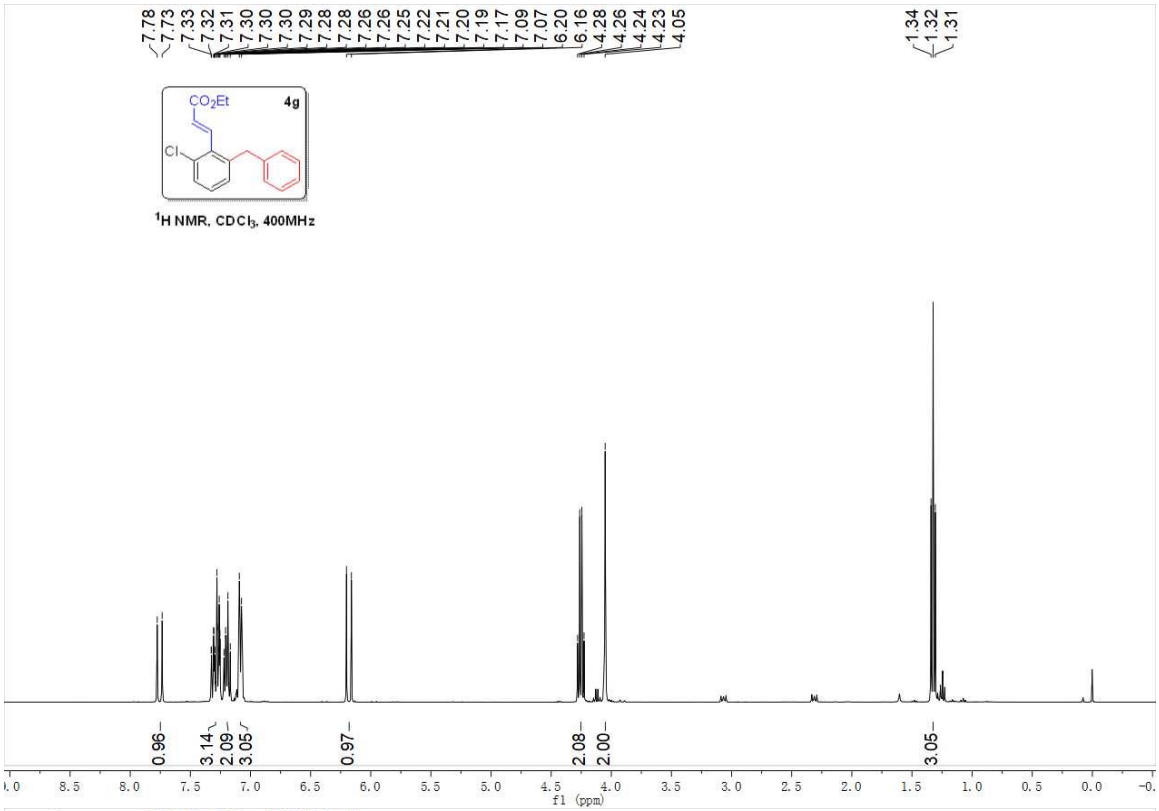
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7.20
7.19
7.17
7.09
7.07
6.20
6.16
4.28
4.26
4.24
4.23
4.05
1.34
1.32
1.31
CO2Et
4g
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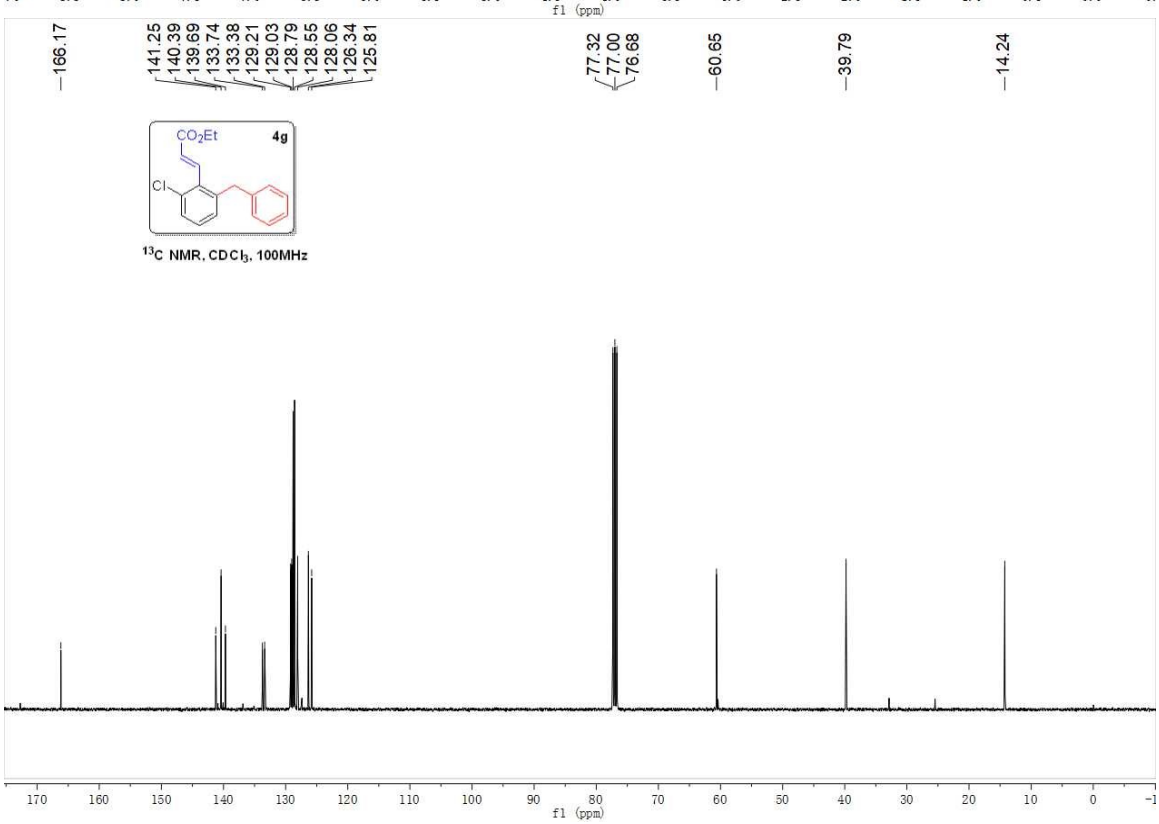
f1 (ppm)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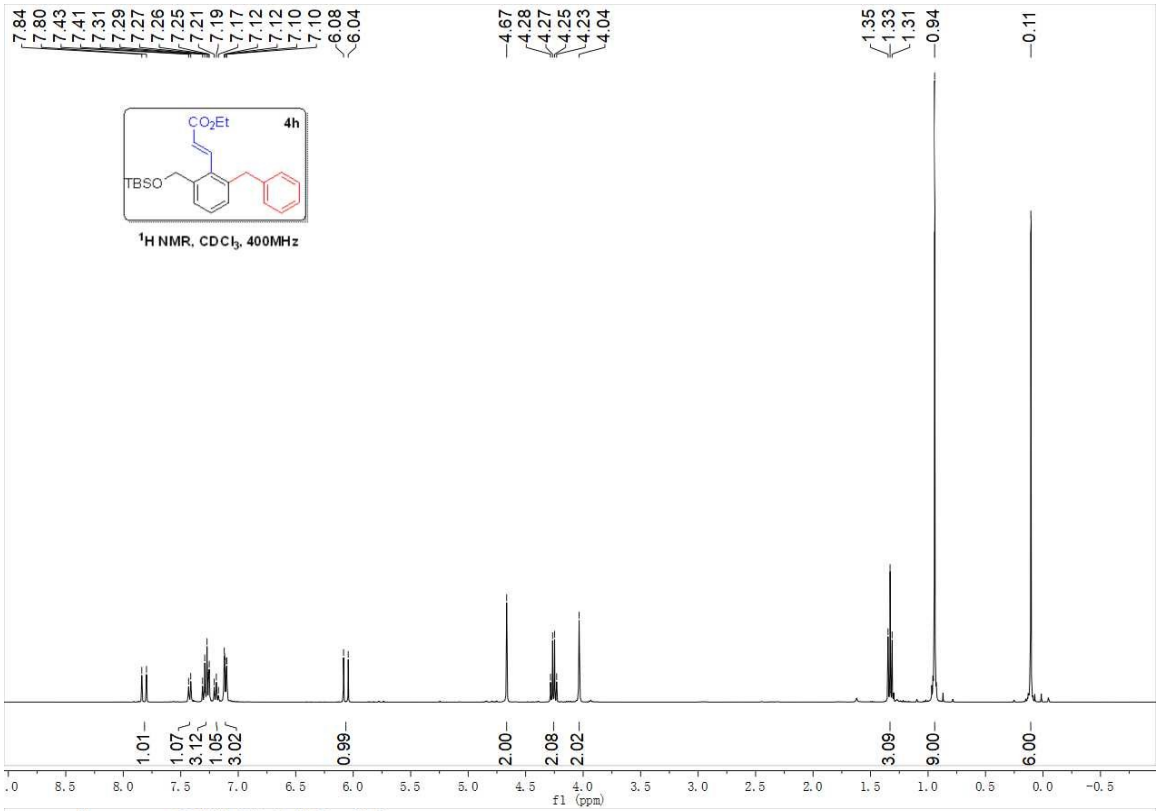
Cl
13C NMR, CDCl3, 100MHz
f1 (ppm)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CO2Et
4h
TBSO
1H NMR, CDCl3, 400MHz
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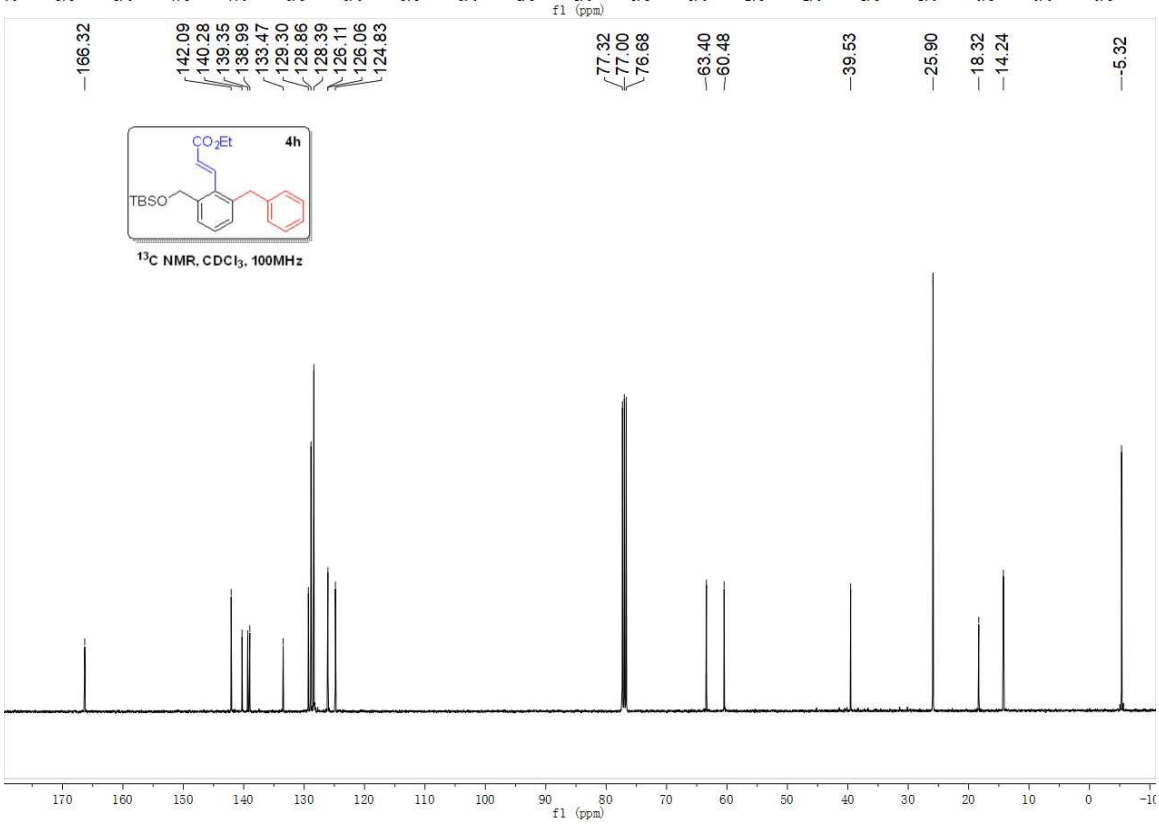
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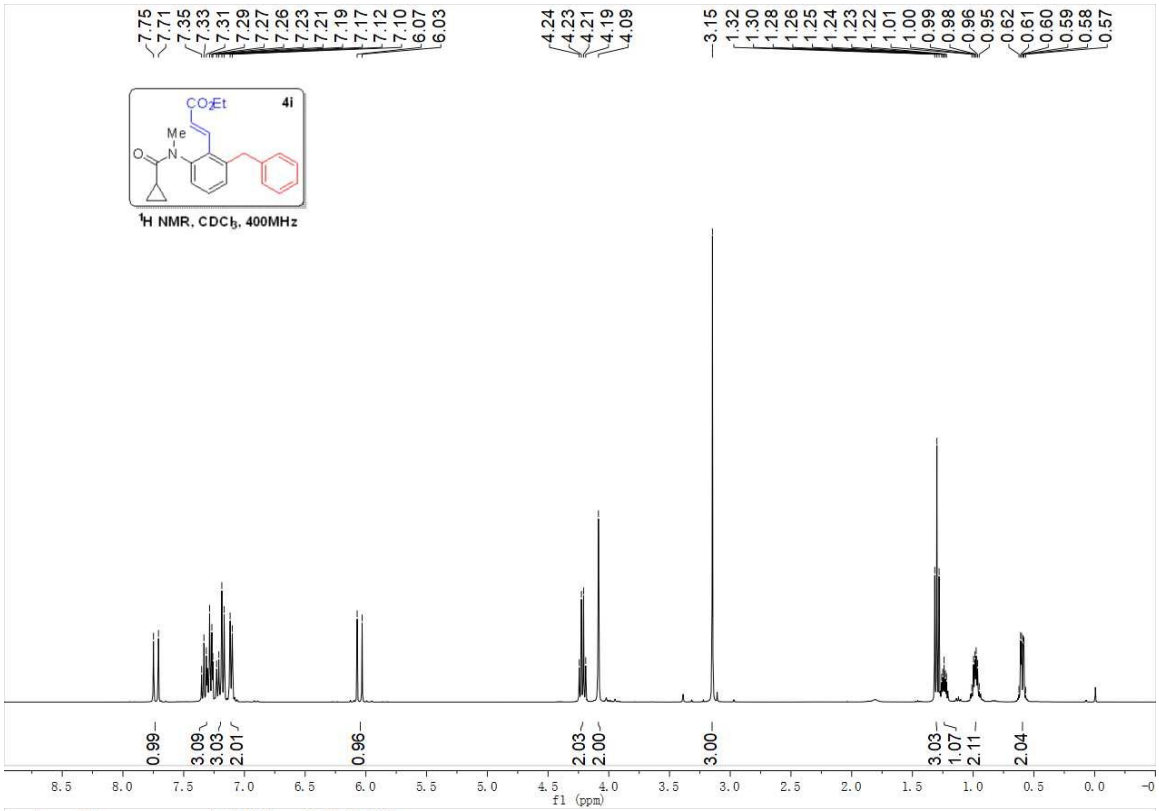
TBSO
13C NMR, CDCl3, 100MHz
f1 (ppm)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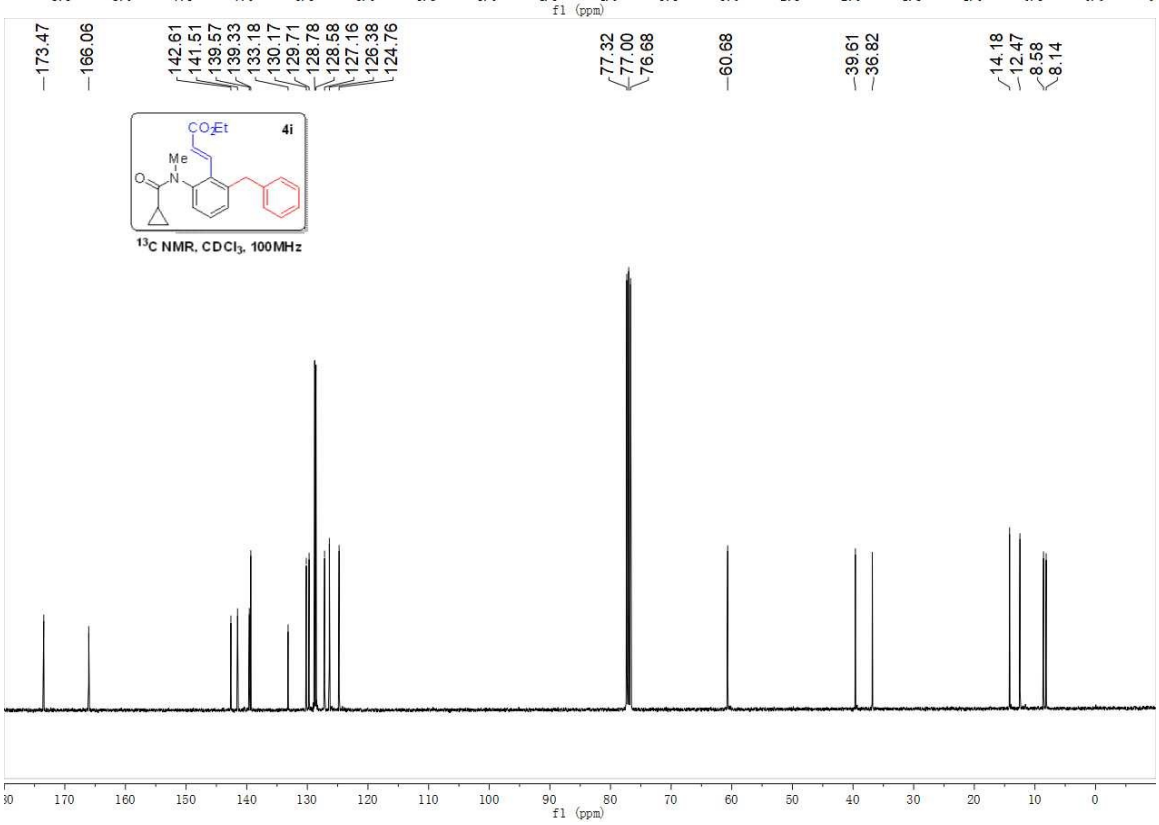
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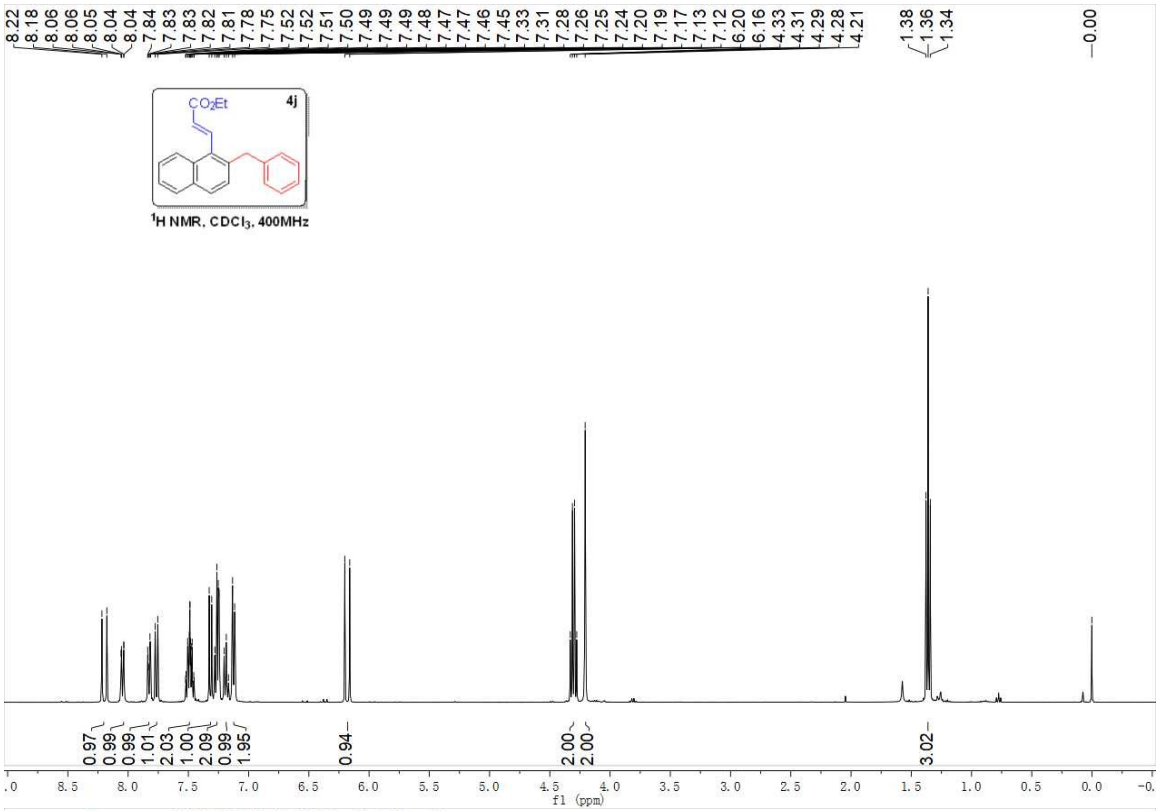
8.58
8.14
CO2Et
4i
Me
N
O
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.49
7.48
7.47
7.47
7.46
7.45
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7.31
7.28
7.26
7.25
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7.20
7.19
7.17
7.13
7.12
6.20
6.16
4.33
4.31
4.29
4.28
4.21
1.38
1.36
1.34
0.00
CO2Et
4j
1H NMR, CDCl3, 400MHz
0.97
0.99
0.99
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1.00
2.09
0.99
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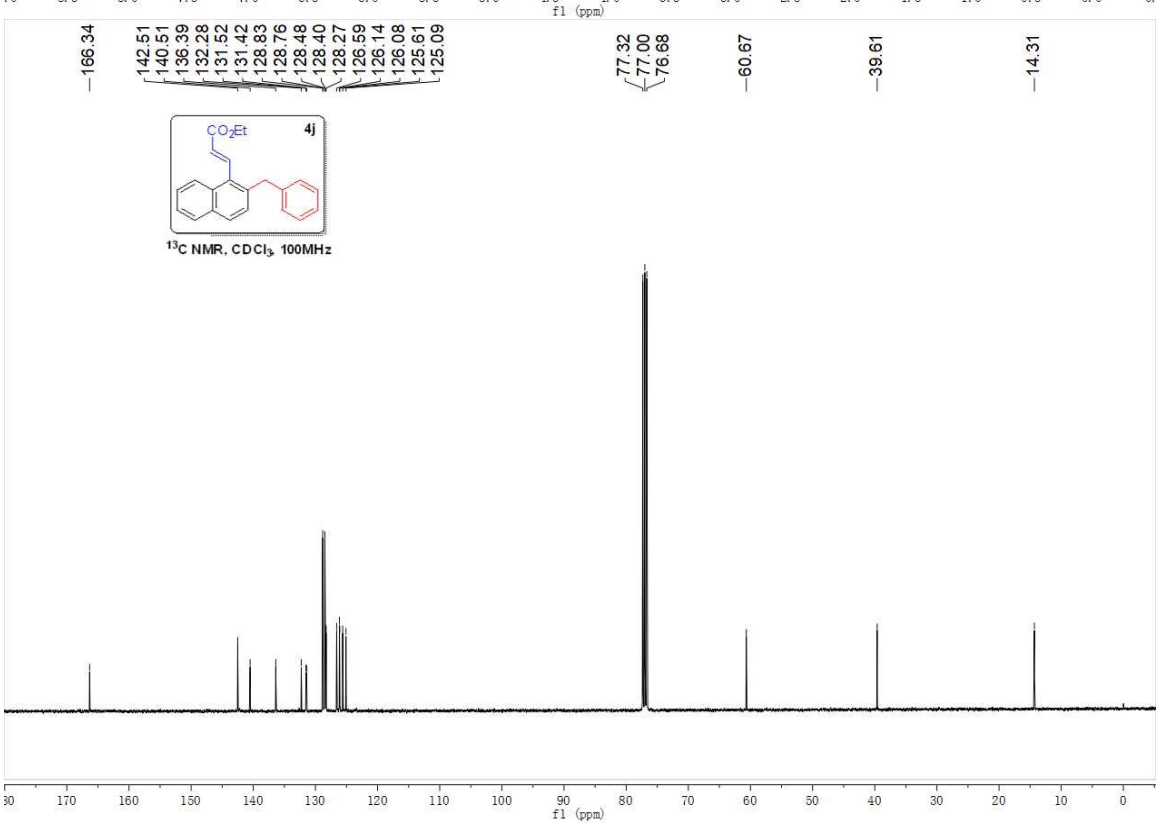
2.00
2.00
3.02
f1 (ppm)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126.59
126.14
126.08
125.61
125.09
77.32
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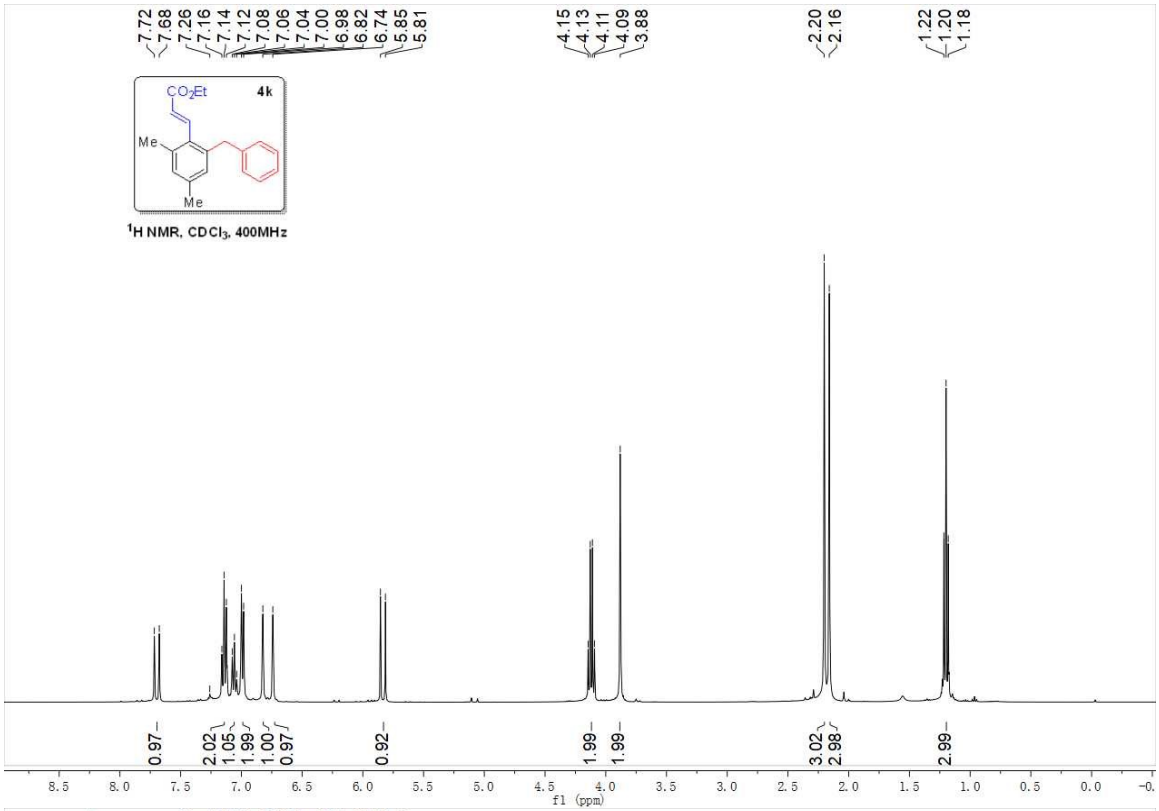
76.68
60.67
39.61
14.31
CO2Et
4j
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.06
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6.82
6.74
5.85
5.81
4.15
4.13
4.11
4.09
3.88
2.20
2.16
1.22
1.20
1.18
CO2Et
4k
Me
Me
1H NMR, CDCl3, 400MHz
0.97
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1.00
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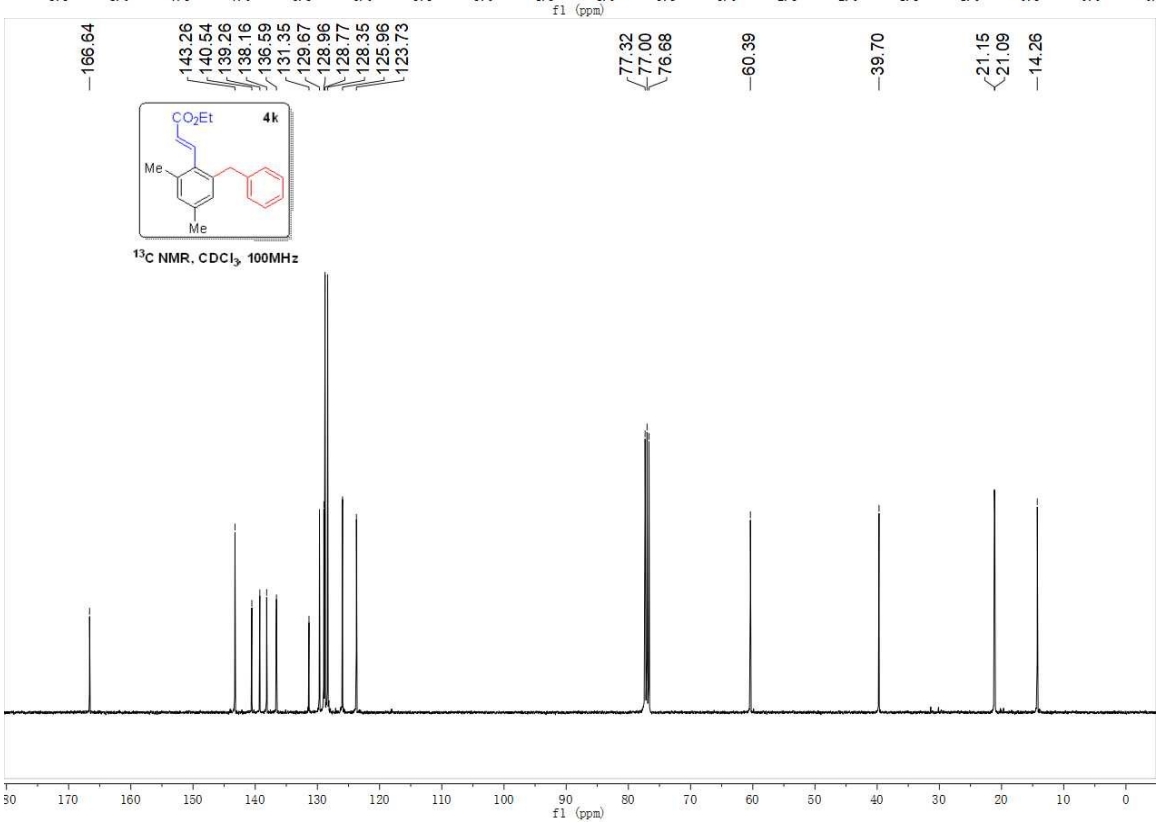
0.92
1.99
1.99
3.02
2.98
2.99
f1 (ppm)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128.35
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123.73
77.32
77.00
76.68
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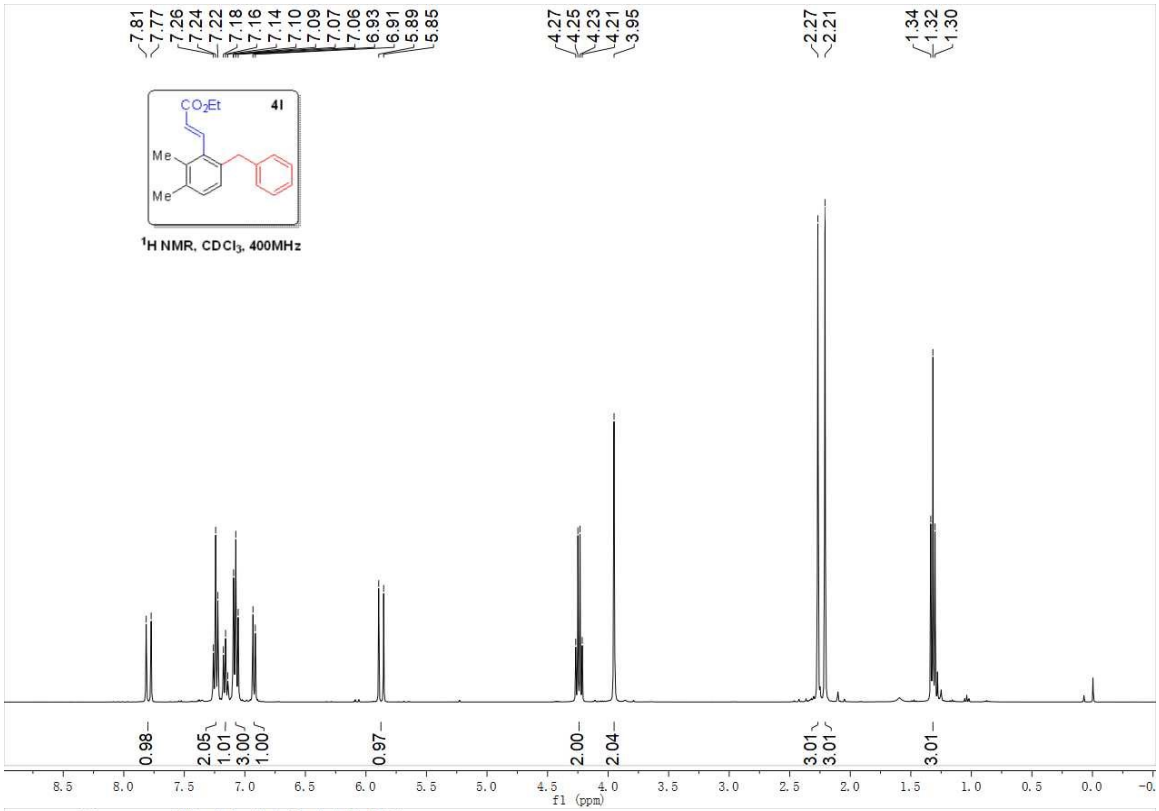
21.15
21.09
14.26
CO2Et
4k
Me
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.93
6.91
5.89
5.85
4.27
4.25
4.23
4.21
3.95
2.27
2.21
1.34
1.32
1.30
CO2Et
4l
Me
Me
1H NMR, CDCl3, 400MHz
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3.00
1.00
0.97
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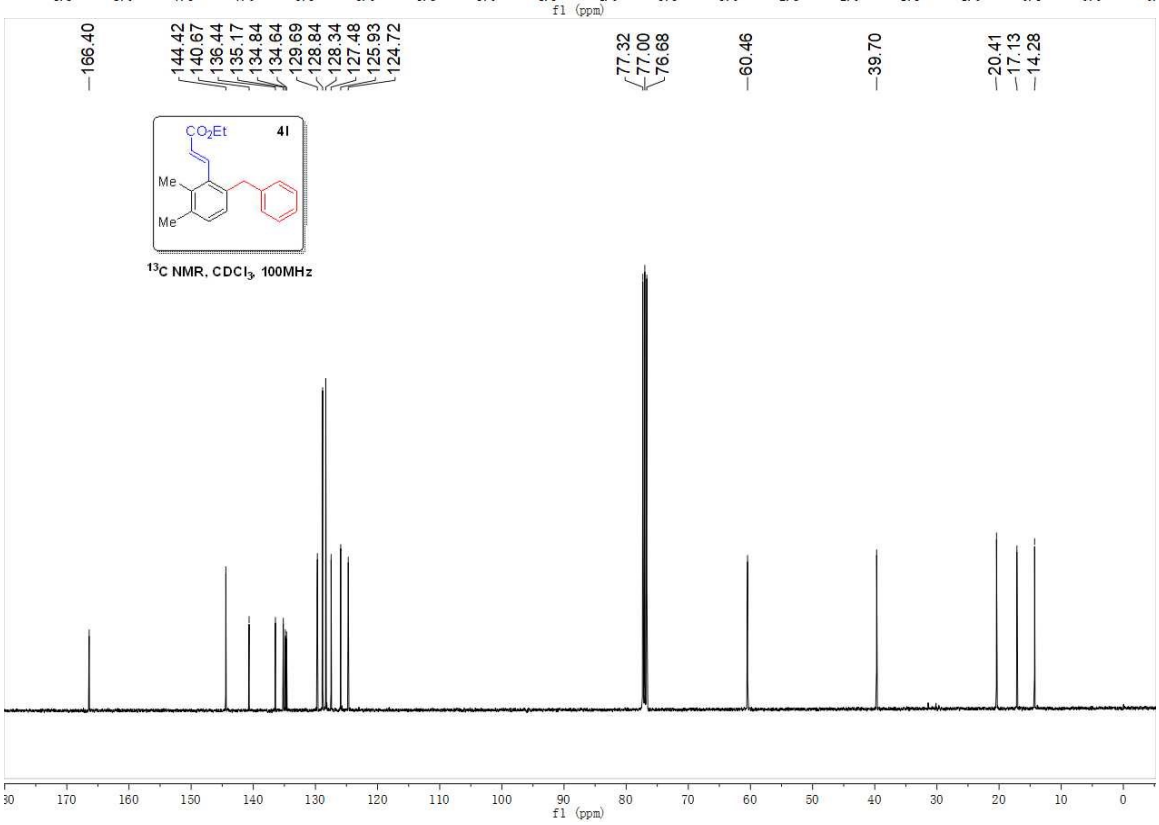
2.04
3.01
3.01
3.01
f1 (ppm)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125.93
124.72
77.32
77.00
76.68
60.46
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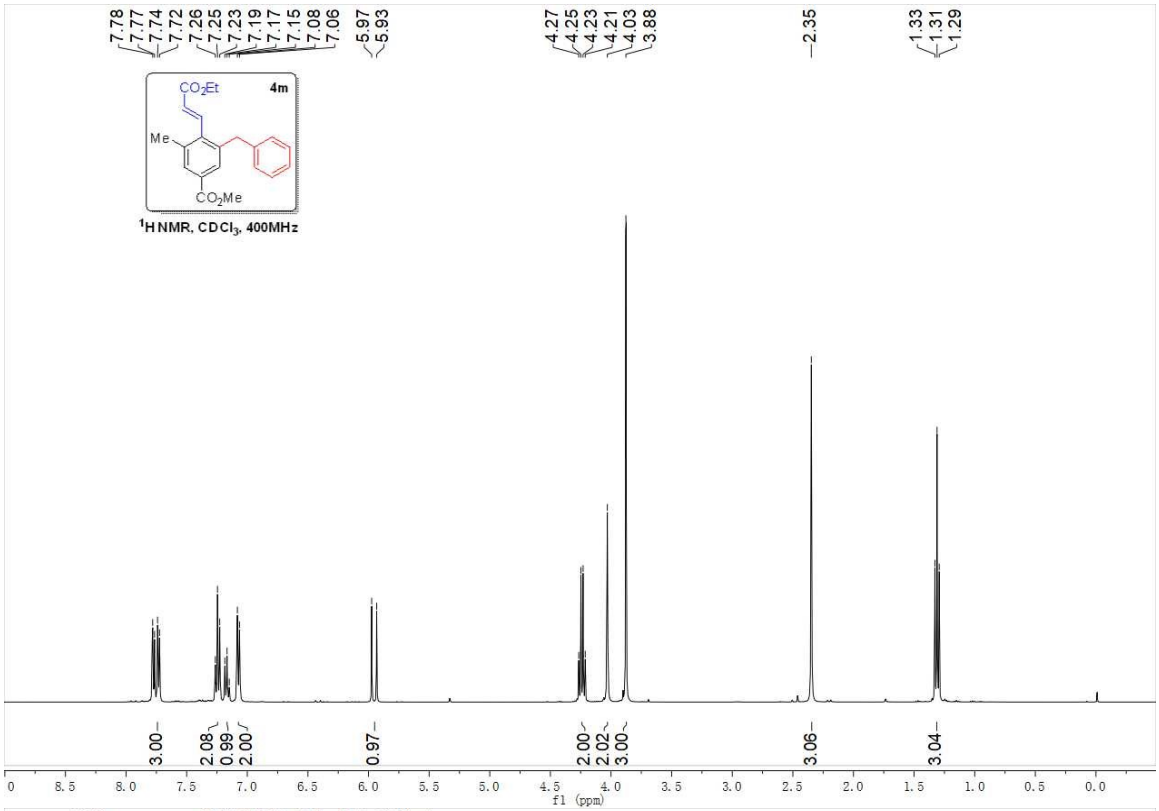
20.41
17.13
14.28
CO2Et
4l
Me
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.06
5.97
5.93
4.27
4.25
4.23
4.21
4.03
3.88
2.35
1.33
1.31
1.29
CO2Et
4m
Me
CO2Me
1H NMR, CDCl3, 400MHz
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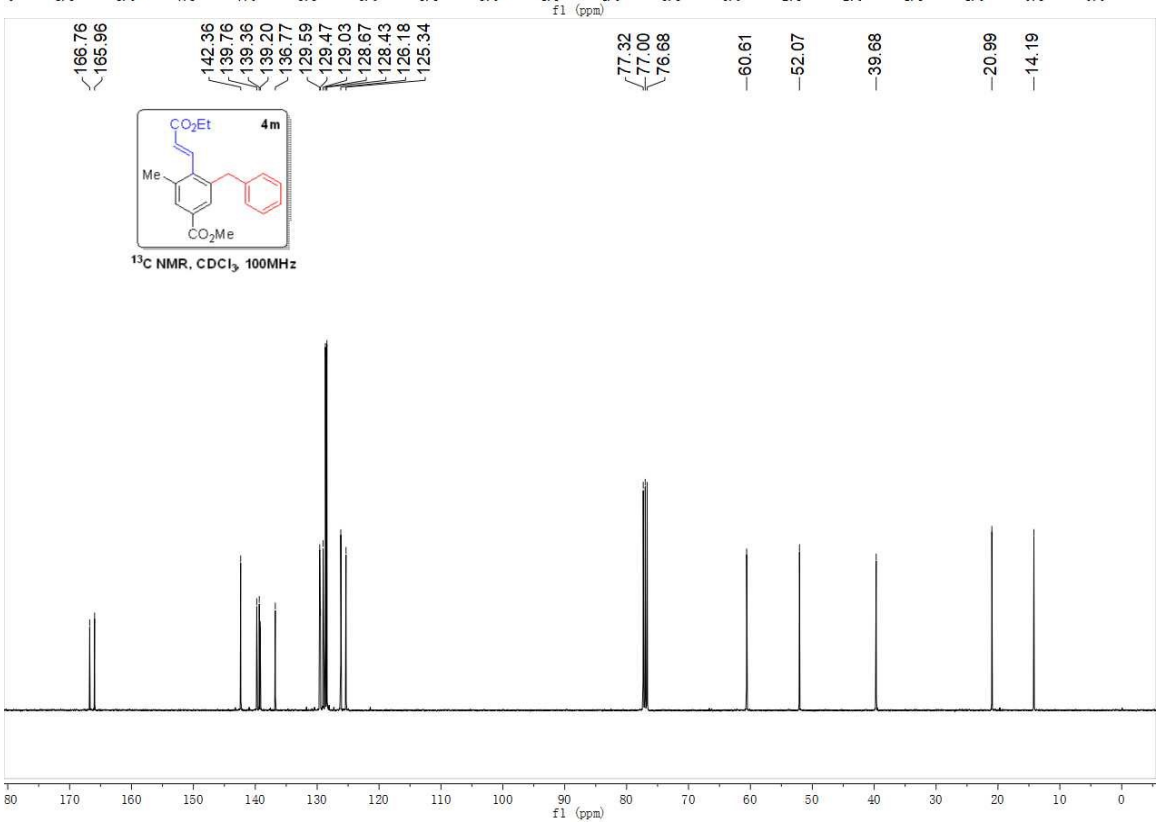
0.99
2.00
0.97
2.00
2.02
3.00
3.06
3.04
f1 (ppm)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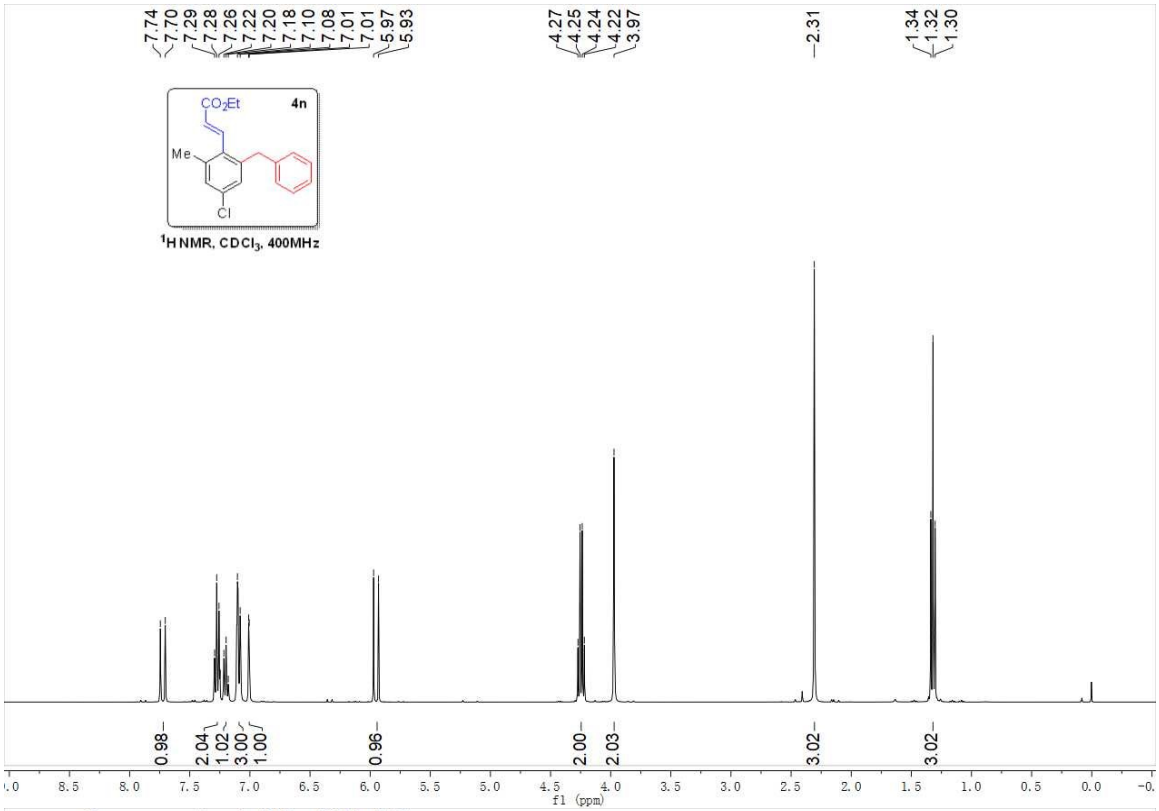
126.18
125.34
77.32
77.00
76.68
60.61
52.07
39.68
20.99
14.19
CO2Et
4m
Me
CO2Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.08
7.01
7.01
5.97
5.93
4.27
4.25
4.24
4.22
3.97
2.31
1.34
1.32
1.30
CO2Et
4n
Me
Cl
1H NMR, CDCl3, 400MHz
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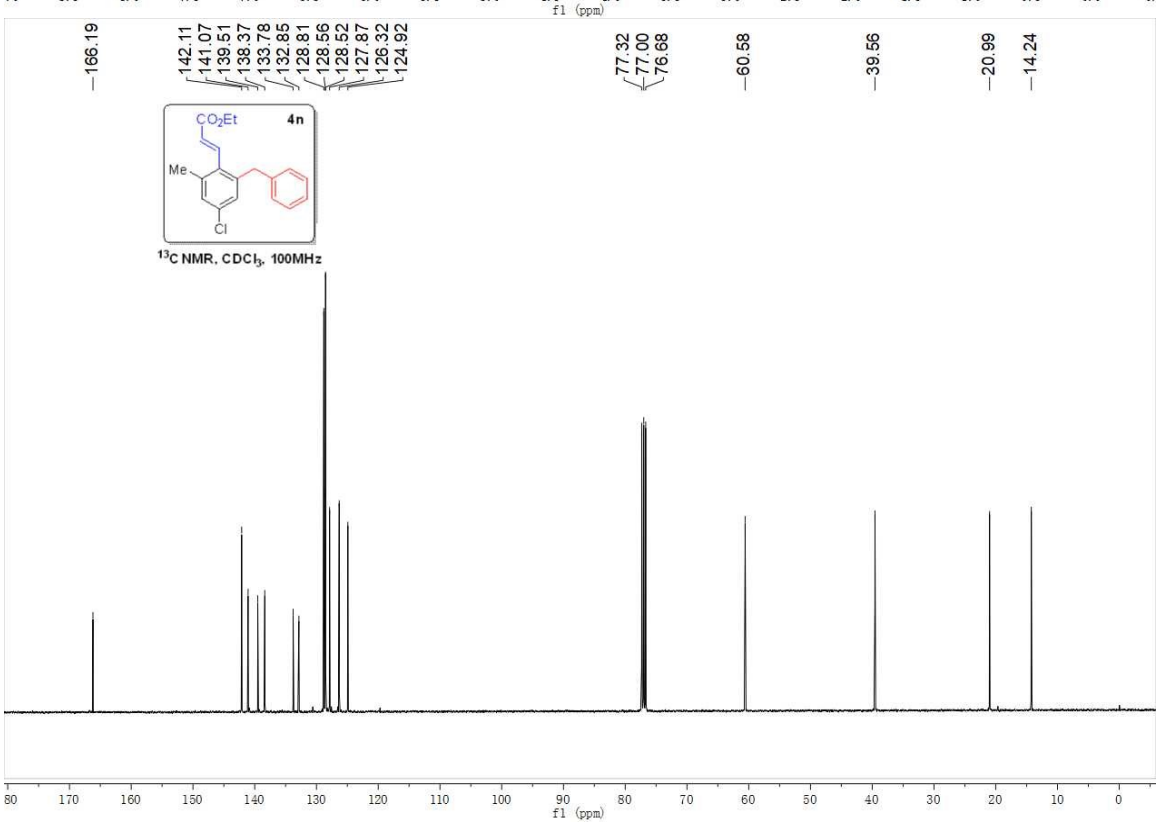
2.04
1.02
3.00
1.00
0.96
2.00
2.03
3.02
3.02
f1 (ppm)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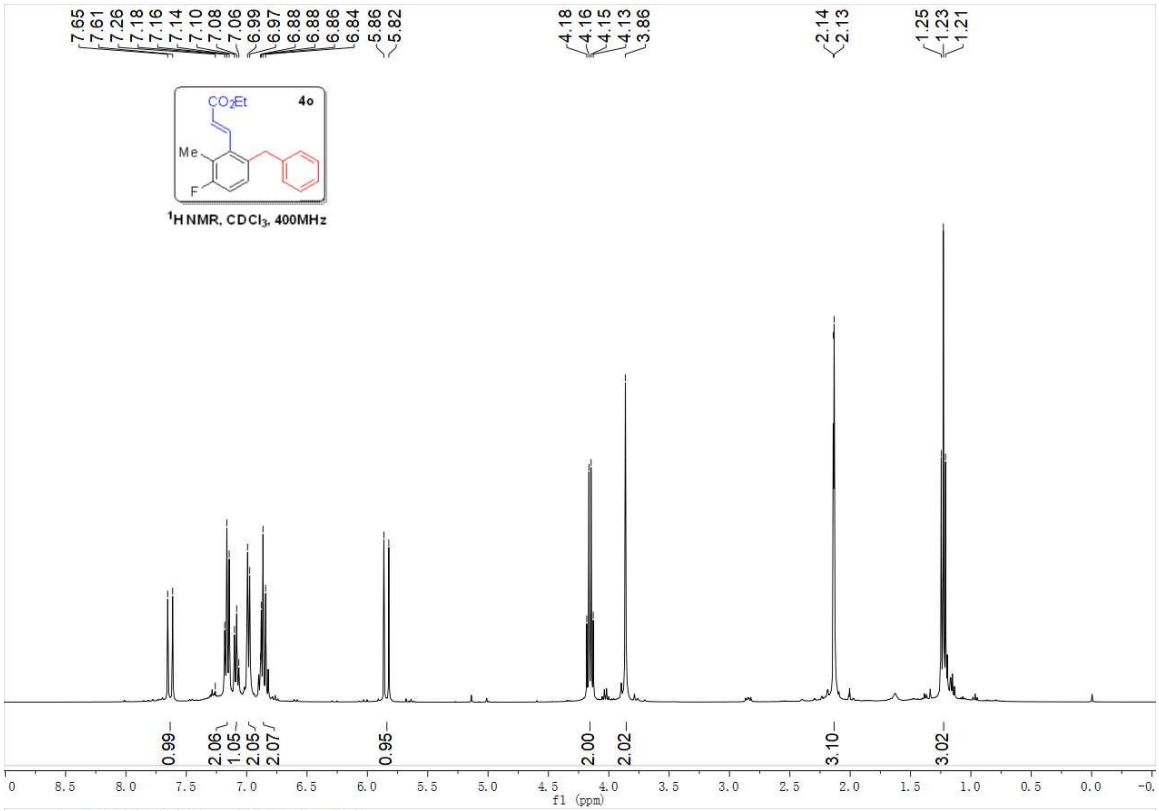
124.92
77.32
77.00
76.68
60.58
39.56
20.99
14.24
CO2Et
4n
Me
Cl
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.10
7.08
7.06
6.99
6.97
6.88
6.88
6.86
6.84
5.86
5.82
4.18
4.16
4.15
4.13
3.86
2.14
2.13
1.25
1.23
1.21
CO2Et
4o
Me
F
1H NMR, CDCl3, 400MHz
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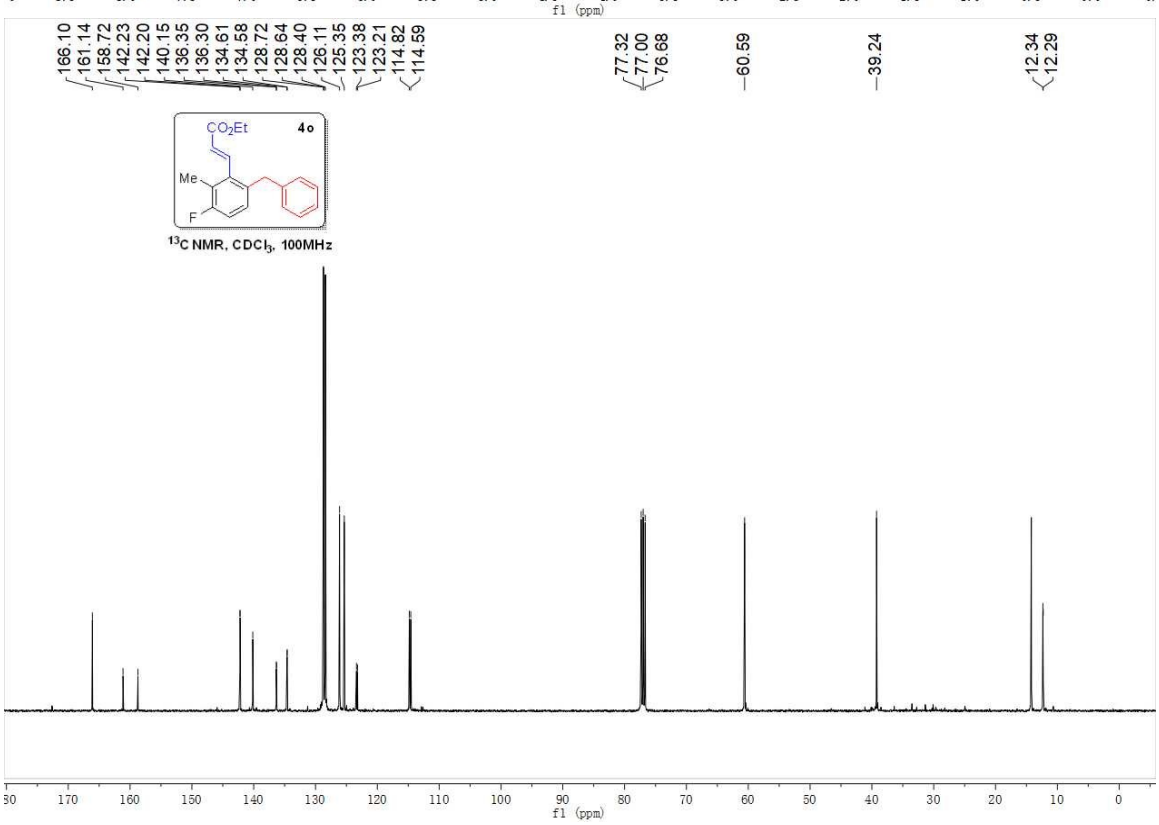
2.06
1.05
2.05
2.07
0.95
2.00
2.02
3.10
3.02
f1 (ppm)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128.72
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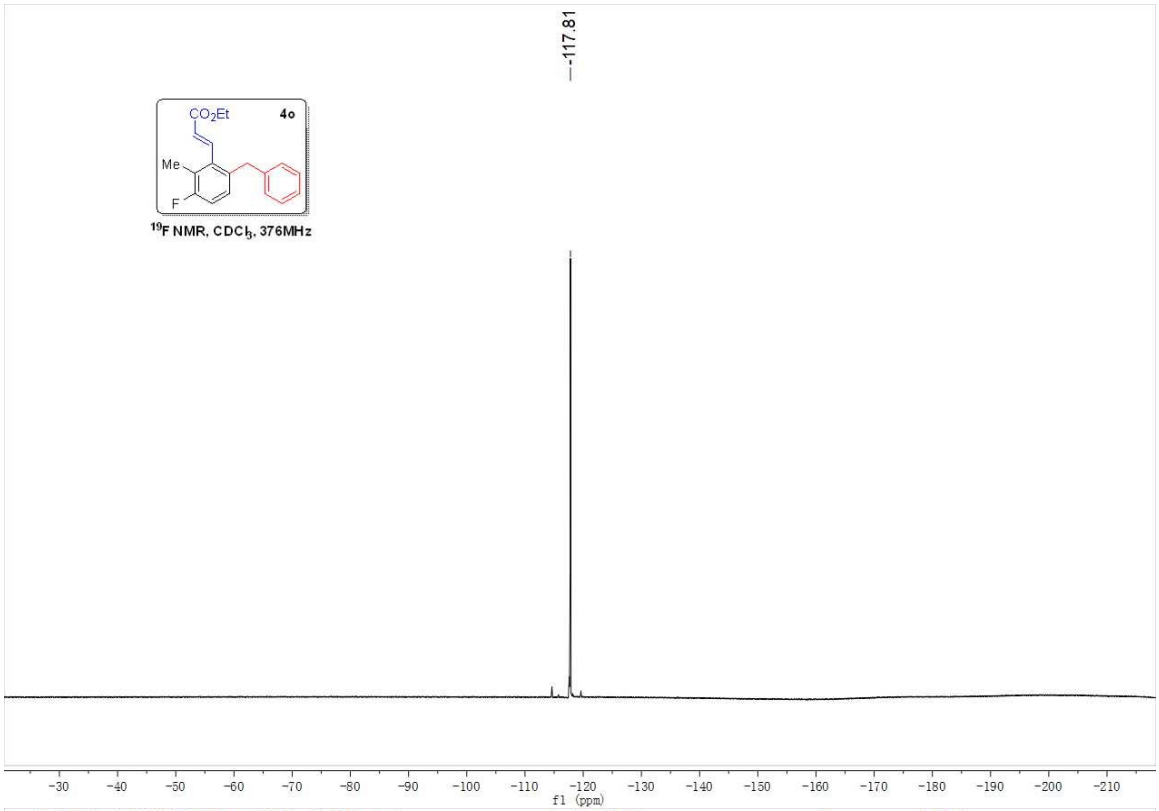
126.11
125.35
123.38
123.21
114.82
114.59
77.32
77.00
76.68
60.59
39.24
12.34
12.29
CO2Et
4o
Me
F
13C NMR, CDCl3, 100MHz
f1 (ppm)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4o
Me
F
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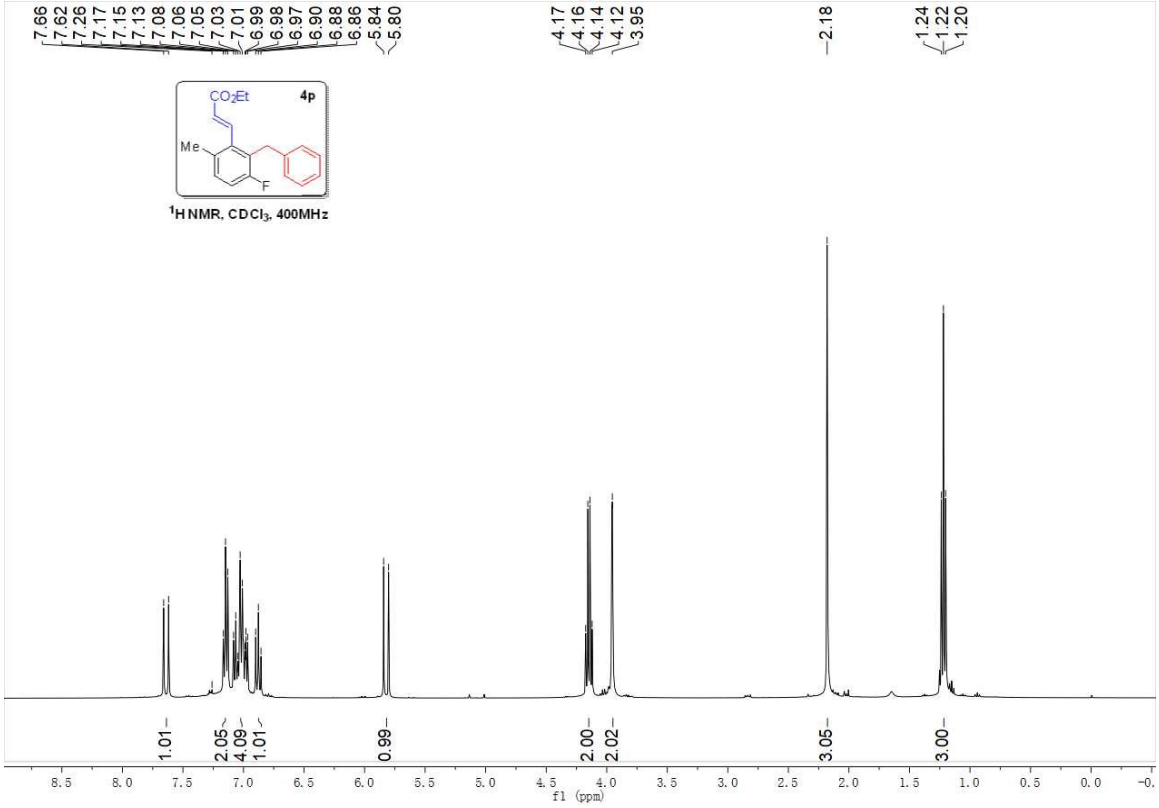
f1 (ppm)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7.06
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7.03
7.01
6.99
6.98
6.97
6.90
6.88
6.86
5.84
5.80
4.17
4.16
4.14
4.12
3.95
2.18
1.24
1.22
1.20
CO2Et
4p
Me
F
1H NMR, CDCl3, 400MHz
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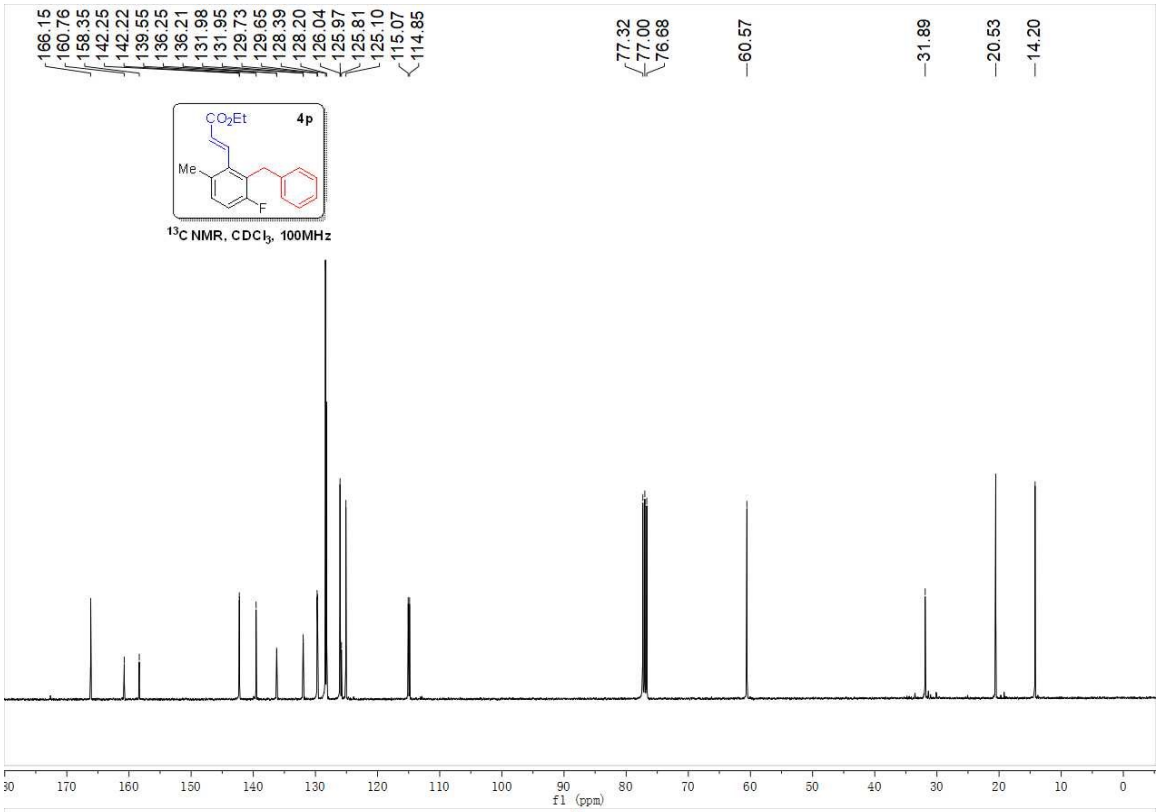
2.05
4.09
1.01
0.99
2.00
2.02
3.05
3.00
f1 (ppm)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128.39
128.20
126.04
125.97
125.81
125.10
115.07
114.85
77.32
77.00
76.68
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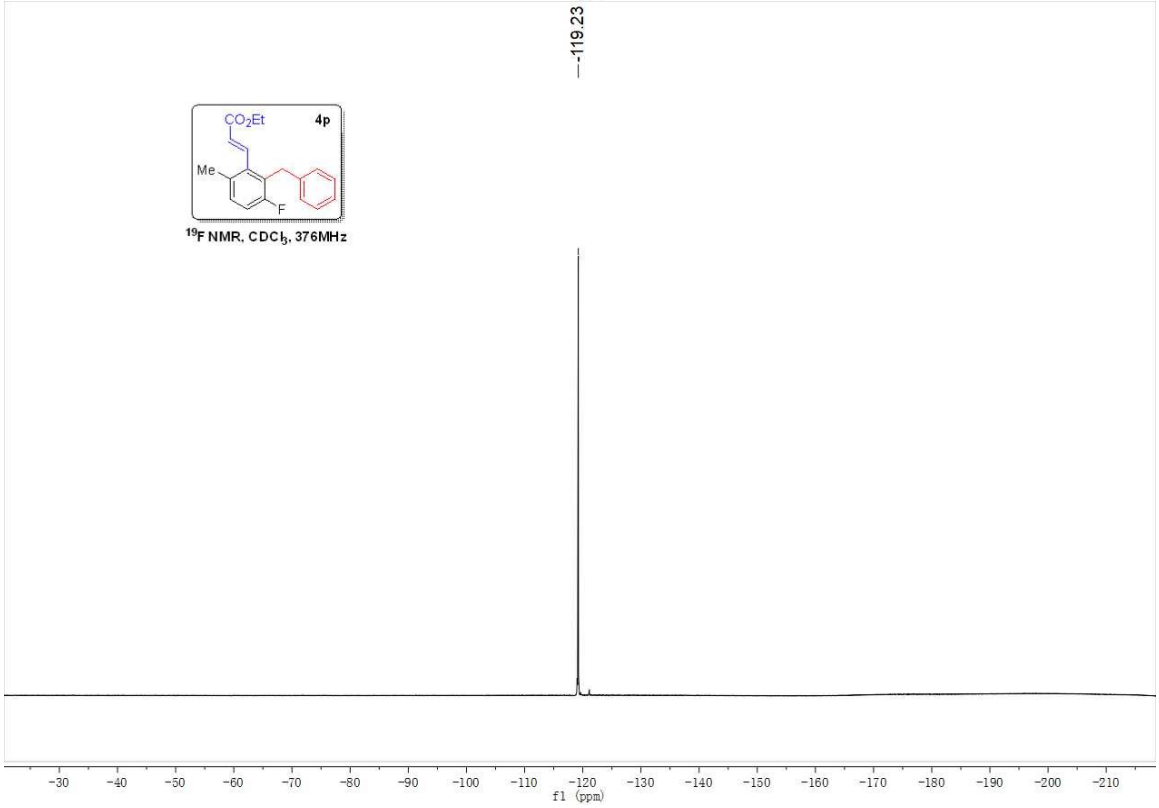
31.89
20.53
14.20
CO2Et
4p
Me
F
13C NMR, CDCl3, 100MHz
f1 (ppm)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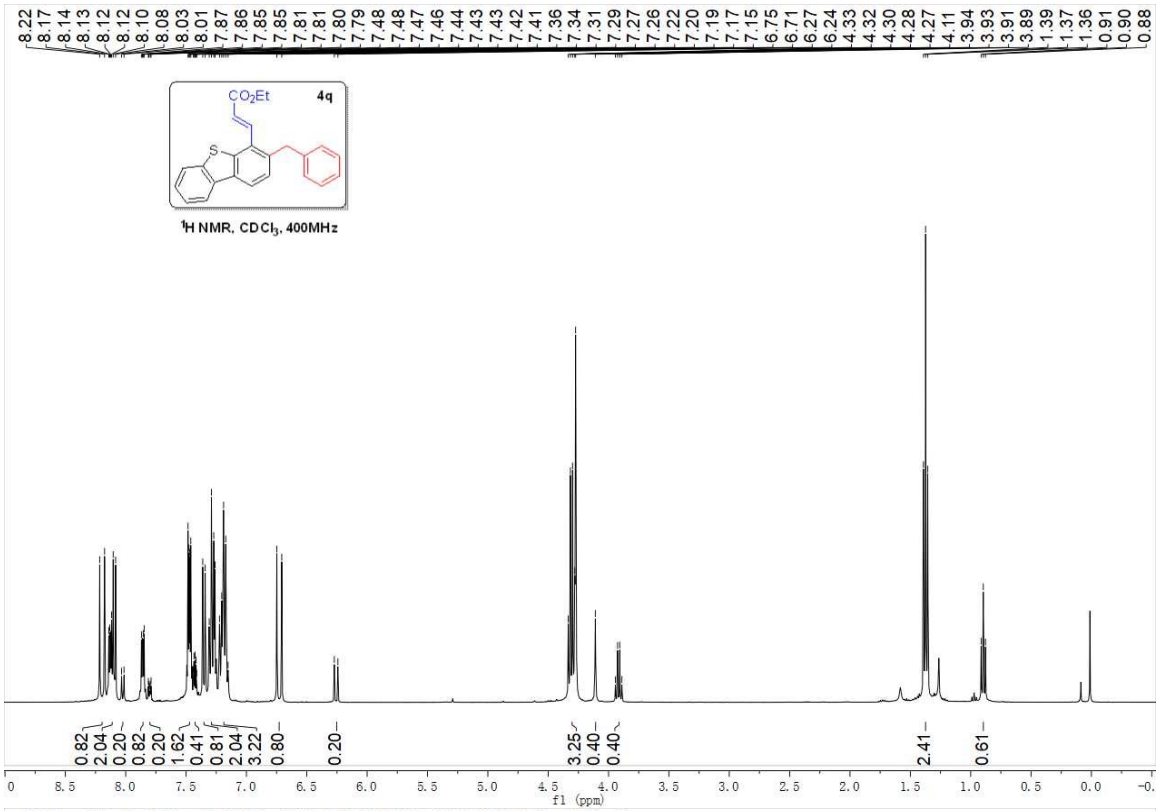
19F NMR, CDCl3, 376MHz
f1 (ppm)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CO2Et
4q
S
1H NMR, CDCl3, 400MHz
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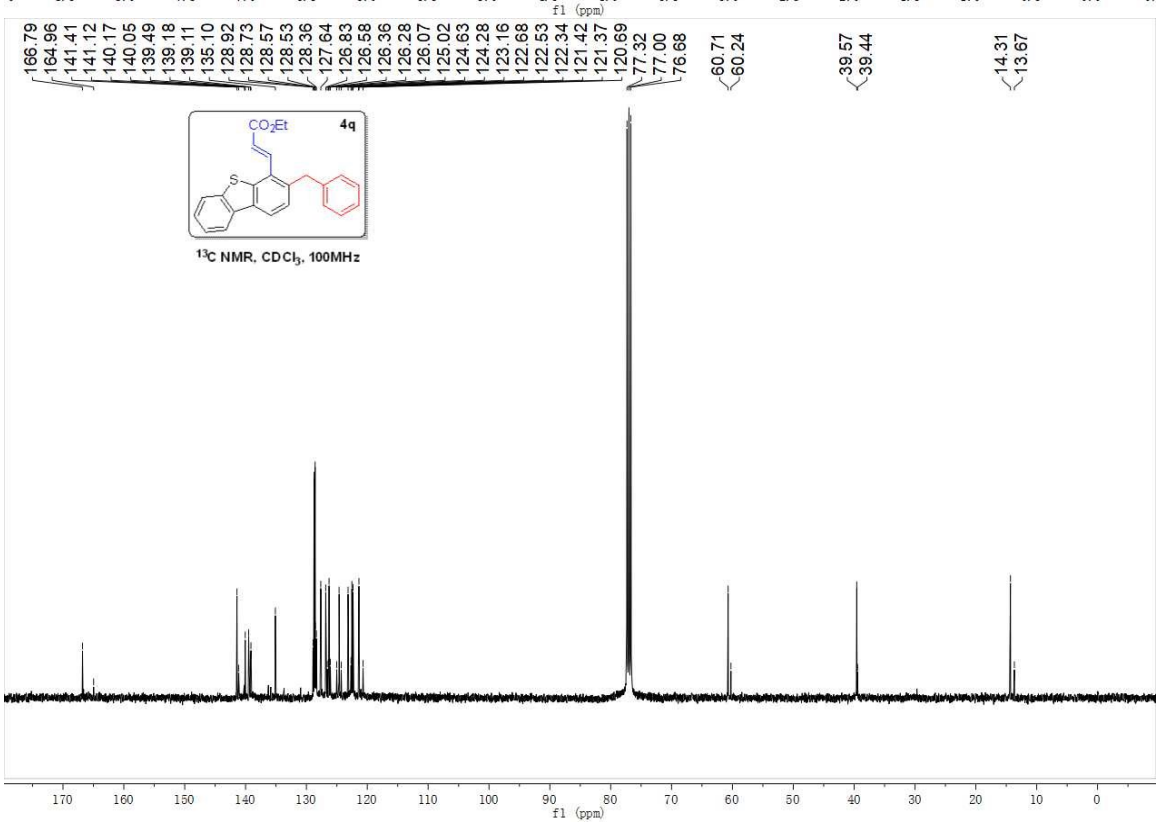
f1 (ppm)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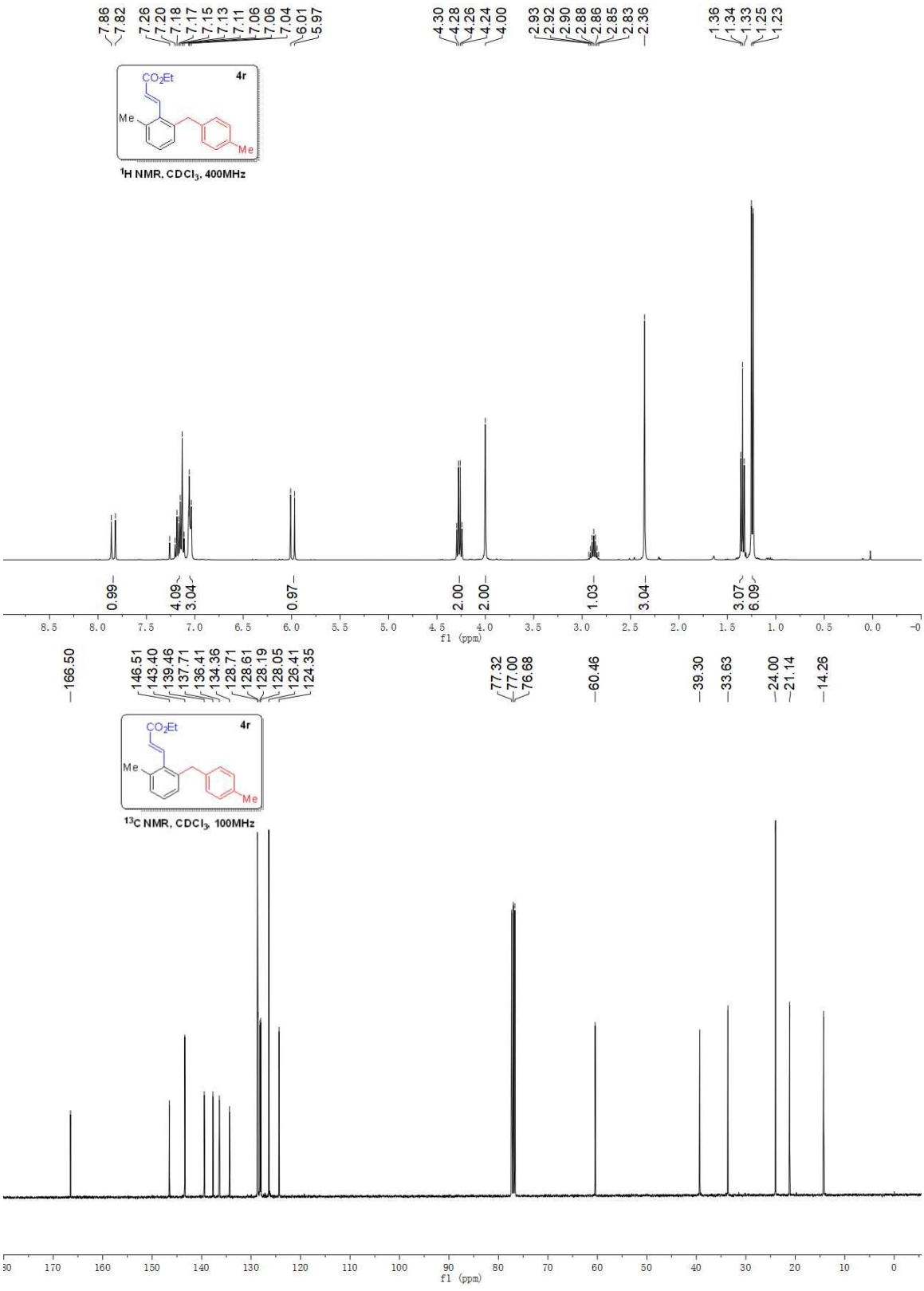
CO2Et
4q
S
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.06
7.04
6.01
5.97
4.30
4.28
4.26
4.24
4.00
2.93
2.92
2.90
2.88
2.86
2.85
2.83
2.36
1.36
1.34
1.33
1.25
1.23
CO2Et
4r
Me
Me
1H NMR, CDCl3, 400MHz
0.99
4.09
3.04
0.97
2.00
2.00
1.03
3.04
3.07
6.09
f1 (ppm)
166.50
146.51
143.40
139.46
137.71
136.41
134.36
128.71
128.61
128.19
128.05
126.41
124.35
77.32
77.00
76.68
60.46
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21.14
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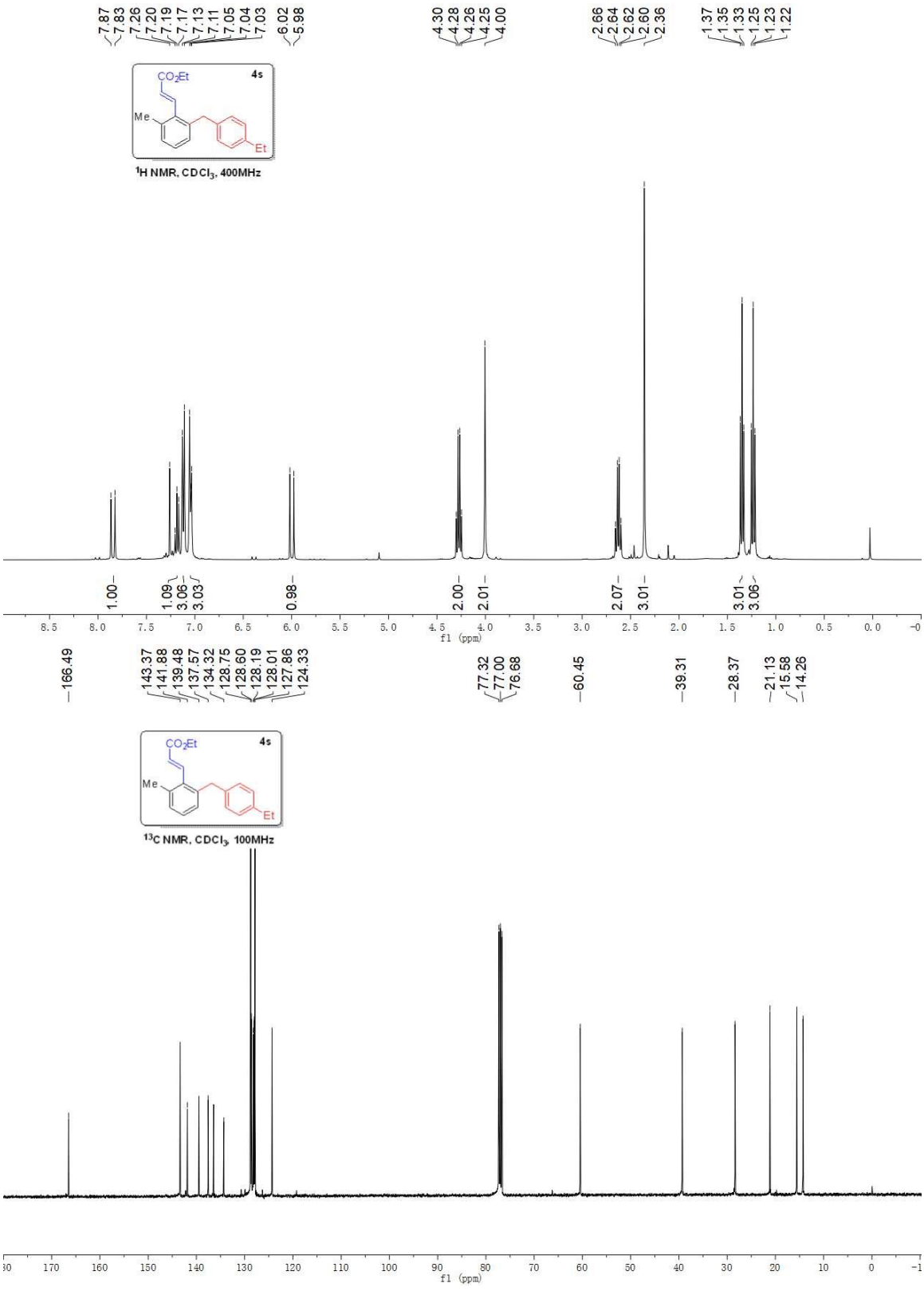
CO2Et
4r
Me
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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5.98
4.30
4.28
4.26
4.25
4.00
2.66
2.64
2.62
2.60
2.36
1.37
1.35
1.33
1.25
1.23
1.22
CO2Et
4s
Me
Et
1H NMR, CDCl3, 400MHz
1.00
1.09
3.08
3.03
0.98
2.00
2.01
2.07
3.01
3.01
3.06
f1 (ppm)
166.49
143.37
141.88
139.48
137.57
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124.33
77.32
77.00
76.68
60.45
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21.13
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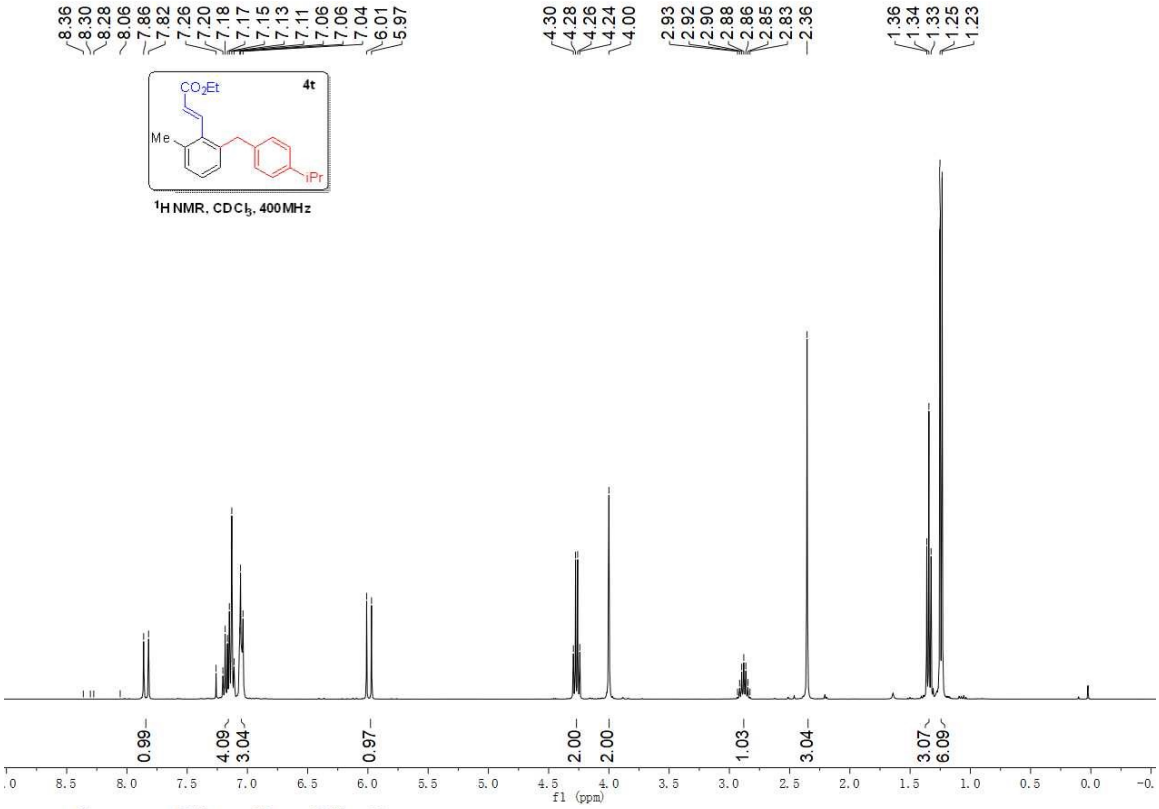
4s
Me
Et
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.06
7.06
7.04
6.01
5.97
4.30
4.28
4.26
4.24
4.00
2.93
2.92
2.90
2.88
2.86
2.85
2.83
2.36
1.36
1.34
1.33
1.25
1.23
CO2Et
4t
Me
iPr
1H NMR, CDCl3, 400MHz
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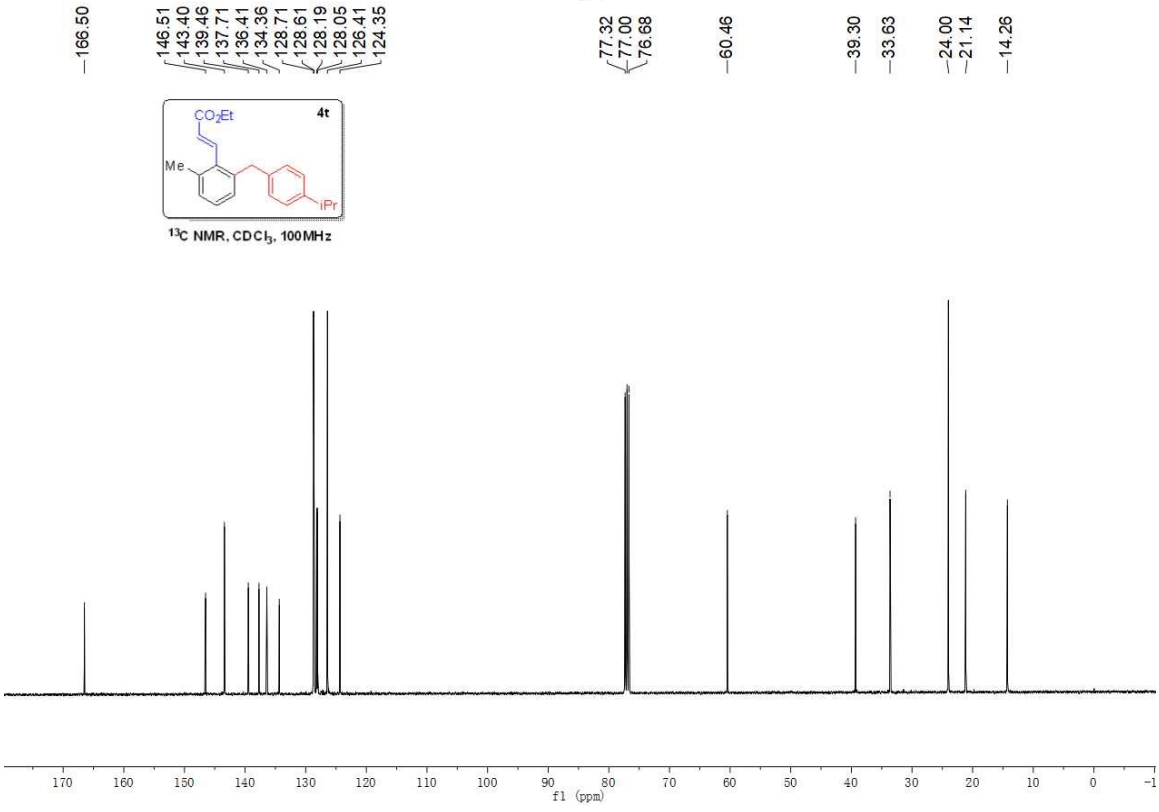
3.04
0.97
2.00
2.00
1.03
3.04
3.07
6.09
f1 (ppm)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124.35
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77.00
76.68
60.46
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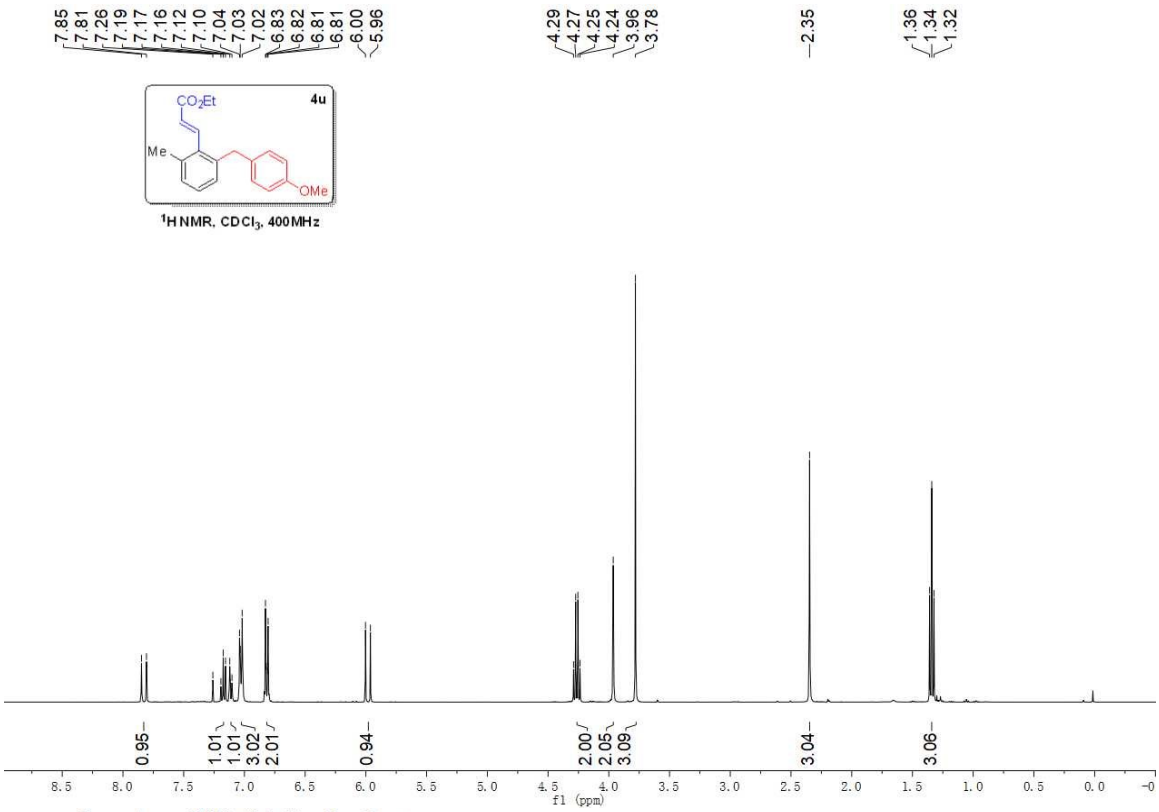
CO2Et
4t
Me
iPr
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.81
6.81
6.00
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4.27
4.25
4.24
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3.78
2.35
1.36
1.34
1.32
CO2Et
4u
Me
OMe
1H NMR, CDCl3, 400MHz
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2.01
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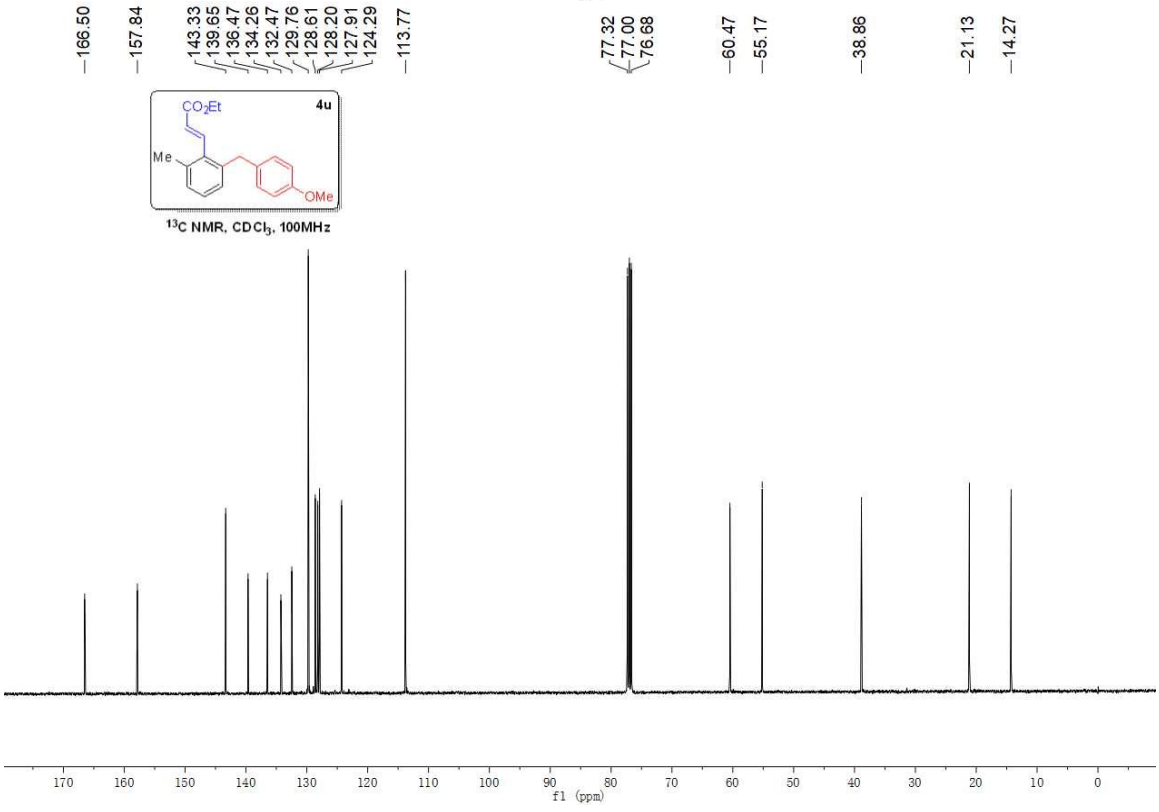
f1 (ppm)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77.32
77.00
76.68
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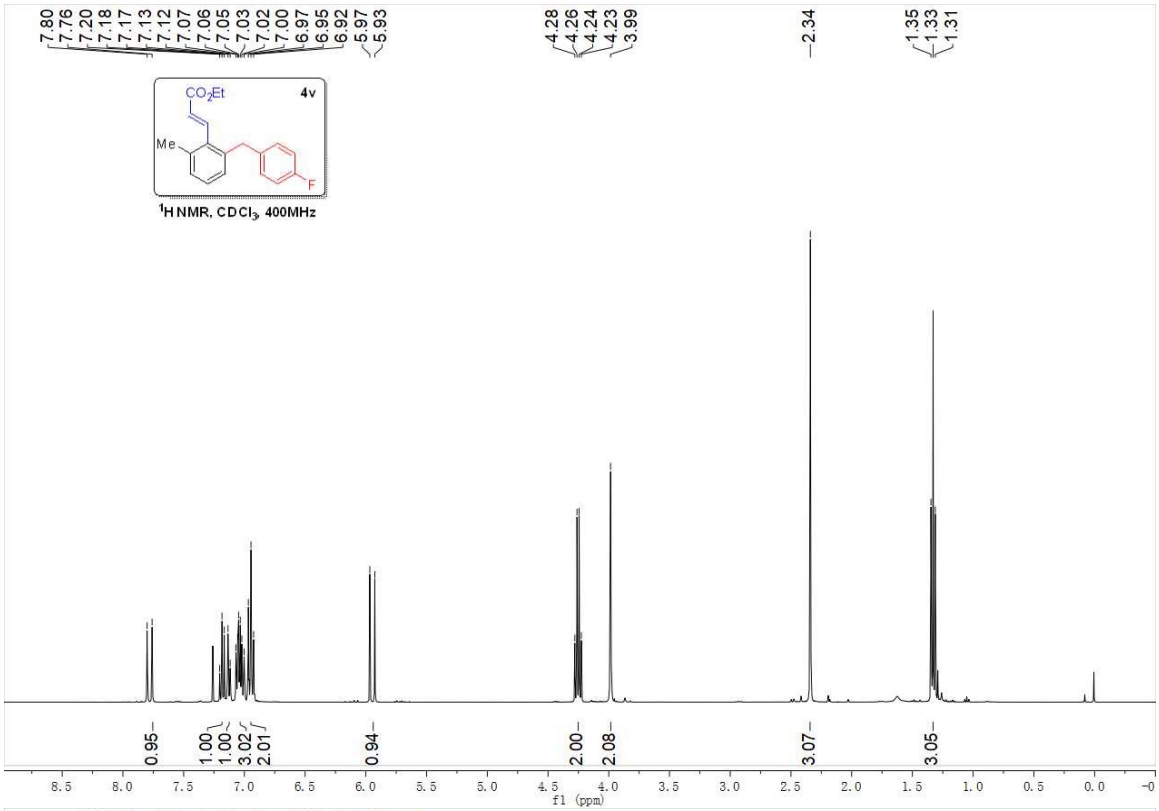
38.86
21.13
14.27
CO2Et
4u
Me
OMe
13C NMR, CDCl3, 100MHz
f1 (ppm)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4.23
3.99
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1.35
1.33
1.31
CO2Et
4v
Me
F
1H NMR, CDCl3, 400MHz
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1.00
3.02
2.01
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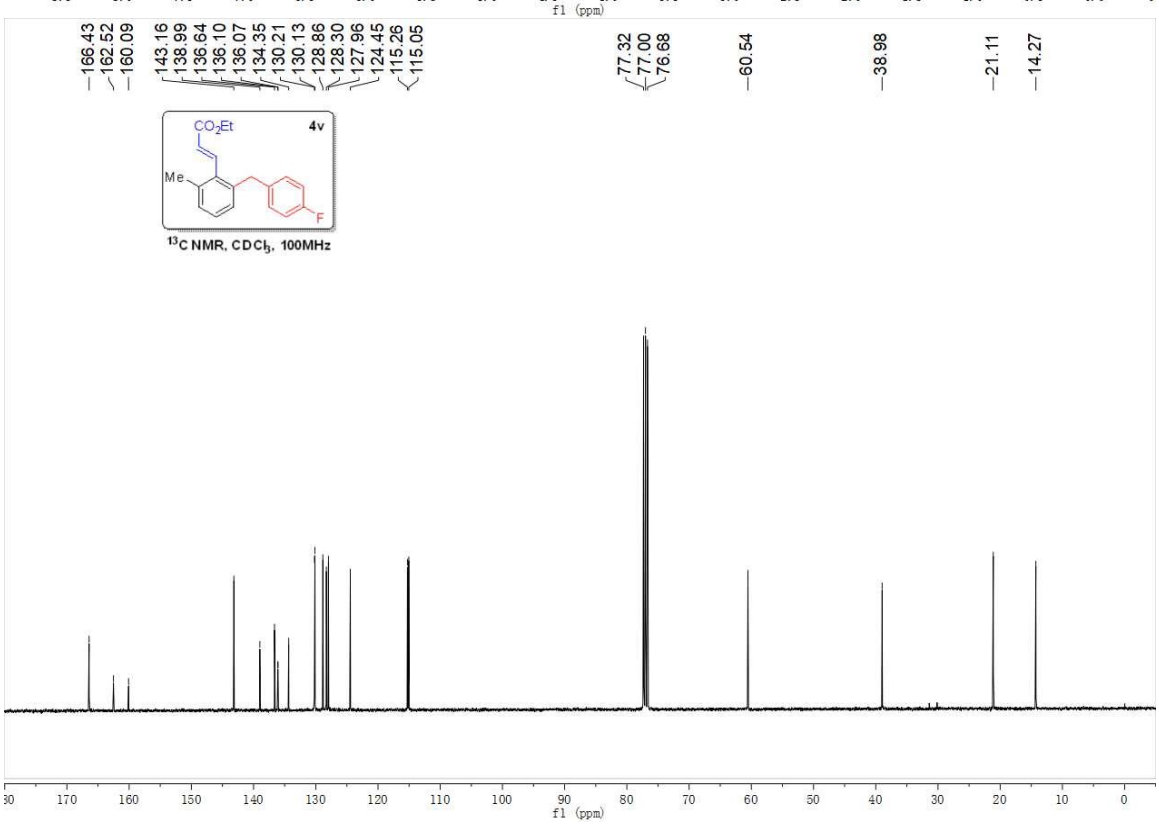
2.08
3.07
3.05
f1 (ppm)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124.45
115.26
115.05
77.32
77.00
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38.98
21.11
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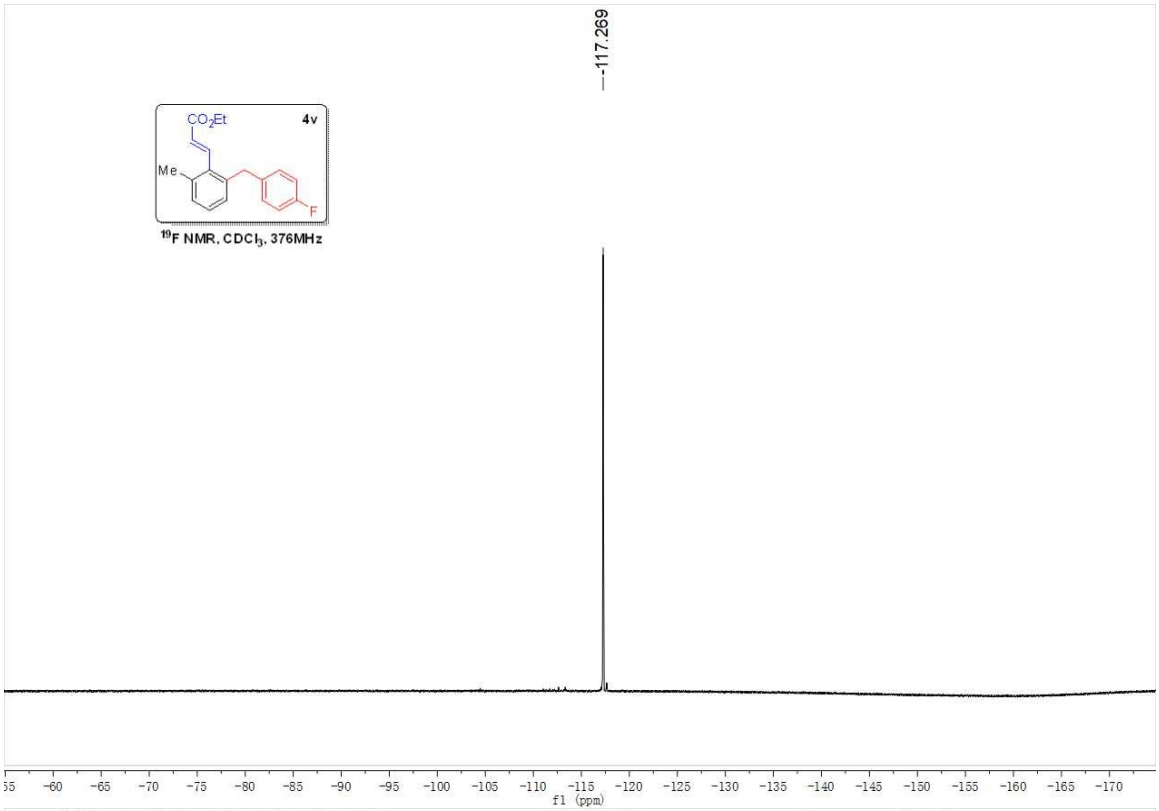
4v
Me
F
13C NMR, CDCl3, 100MHz
f1 (ppm)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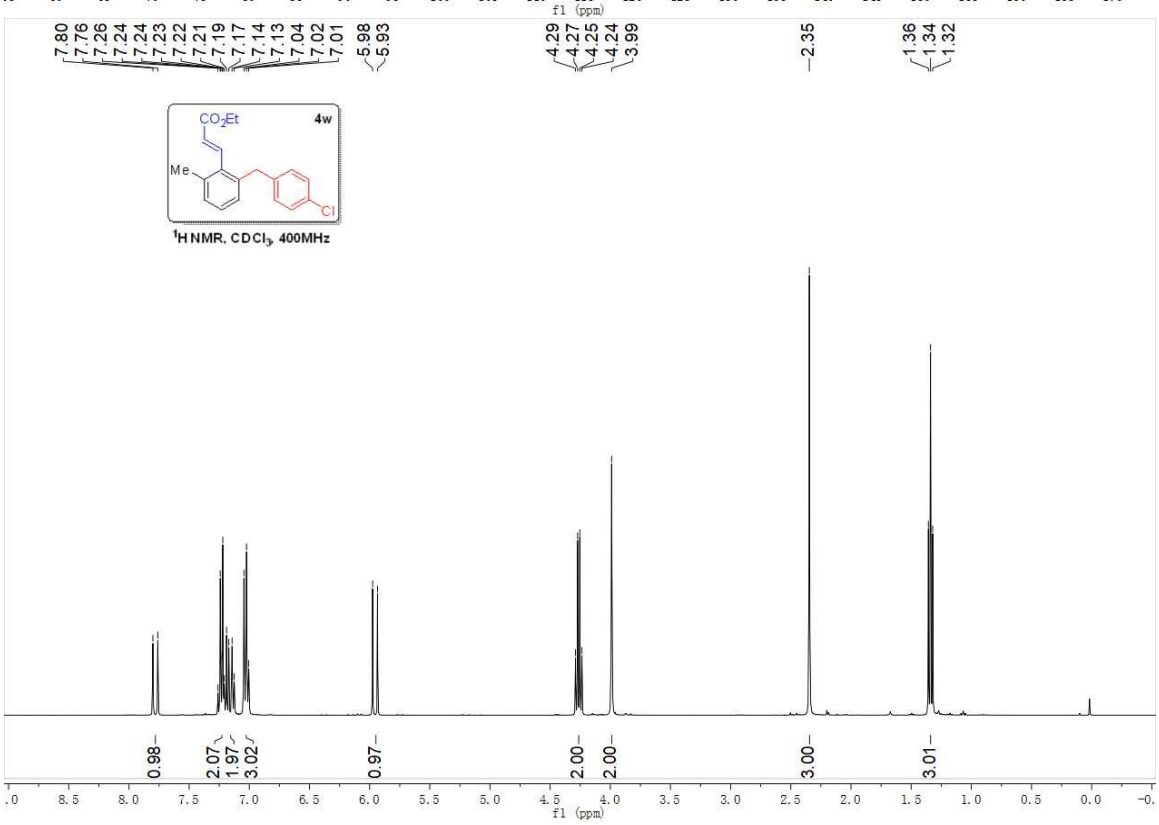
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7.13
7.04
7.02
7.01
5.98
5.93
4.29
4.27
4.25
4.24
3.99
2.35
1.36
1.34
1.32
4w
Me
Cl
^{1}H NMR, CDCl$_3$, 400MHz
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3.02
0.97
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2.00
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3.01
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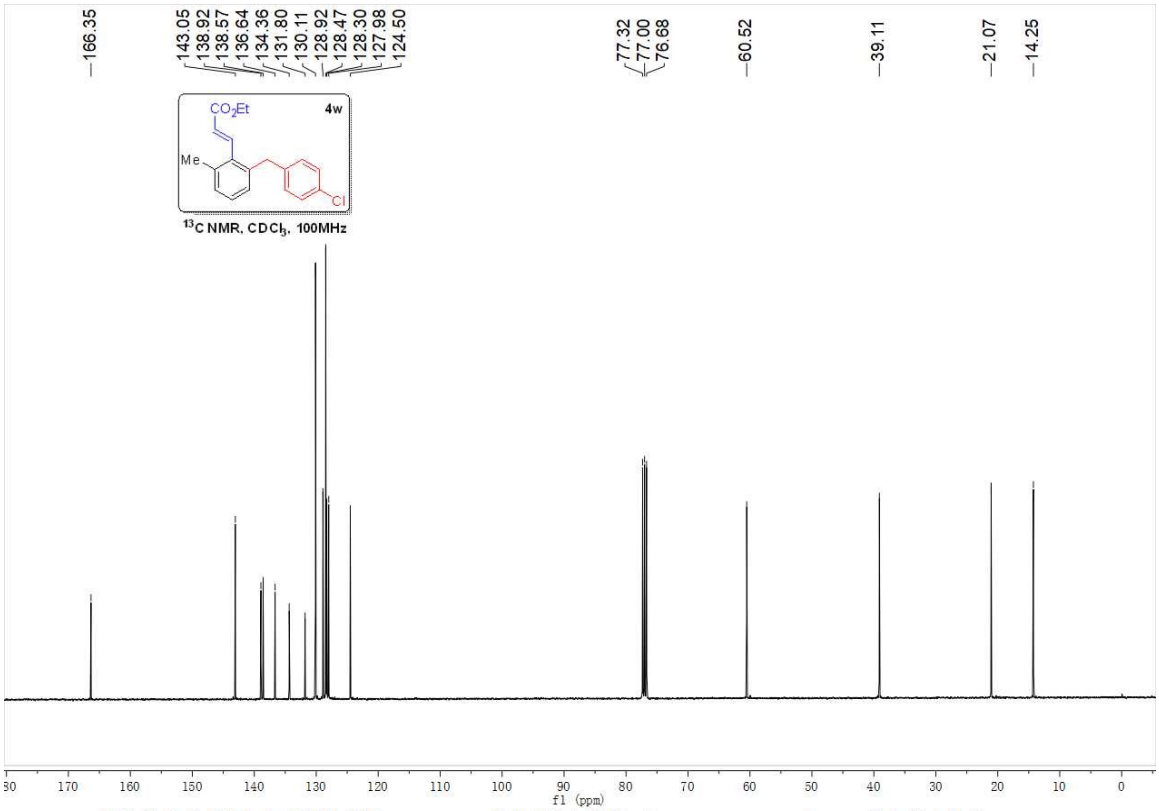
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77.00
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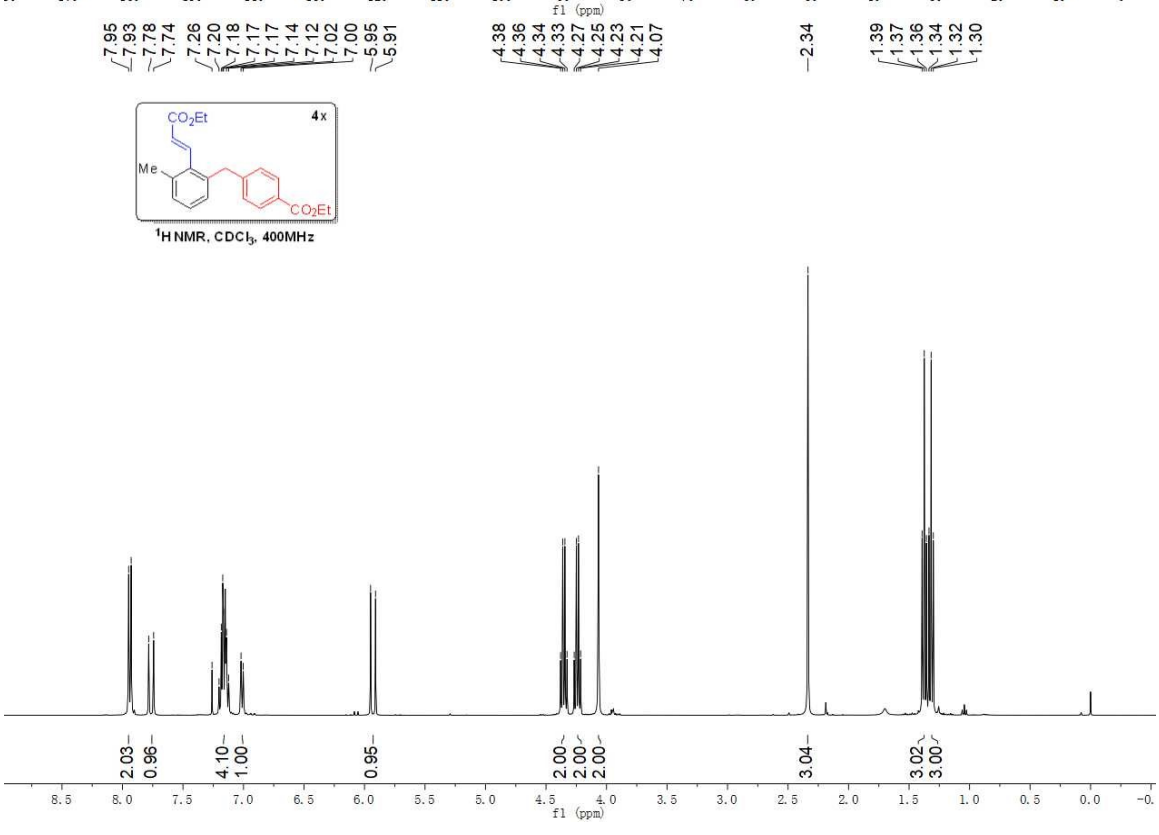
CO2Et
4w
Me
Cl
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.00
5.95
5.91
4.38
4.36
4.34
4.33
4.27
4.25
4.23
4.21
4.07
2.34
1.39
1.37
1.36
1.34
1.32
1.30
CO2Et
4x
Me
CO2Et
1H NMR, CDCl3, 400MHz
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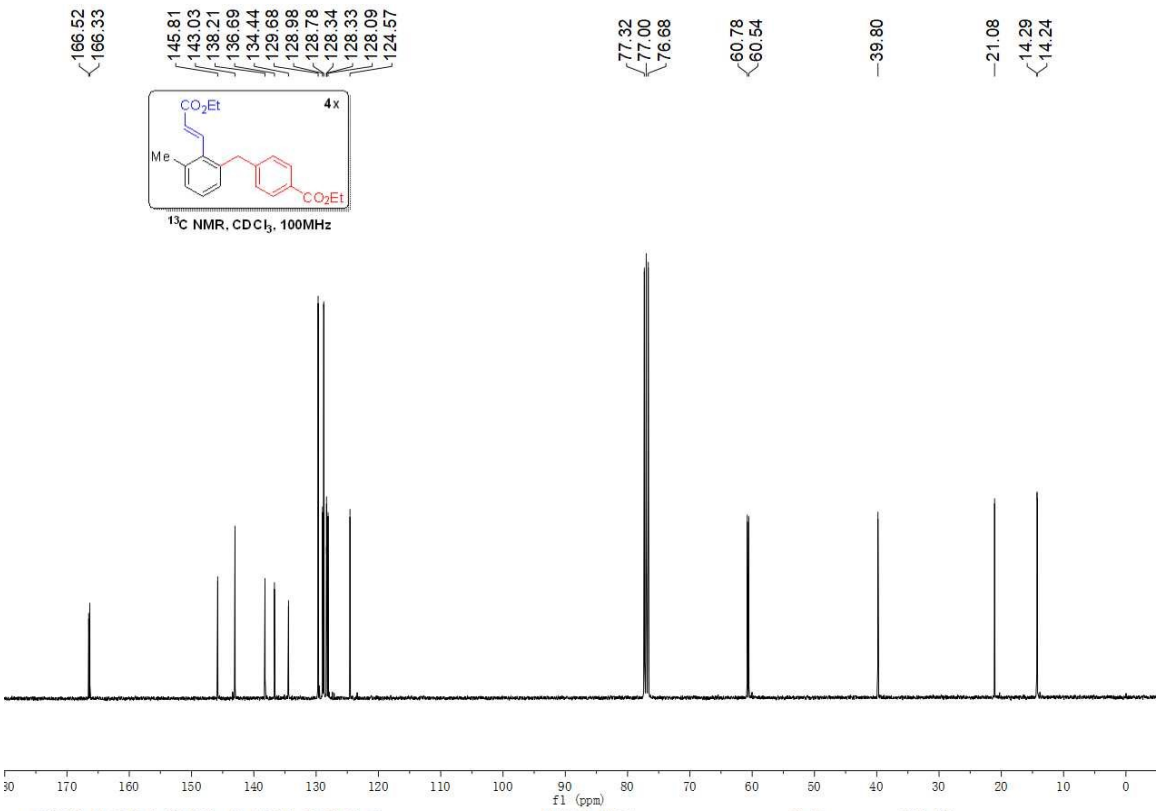
1.00
0.95
2.00
2.00
2.00
3.04
3.02
3.00
f1 (ppm)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77.32
77.00
76.68
60.78
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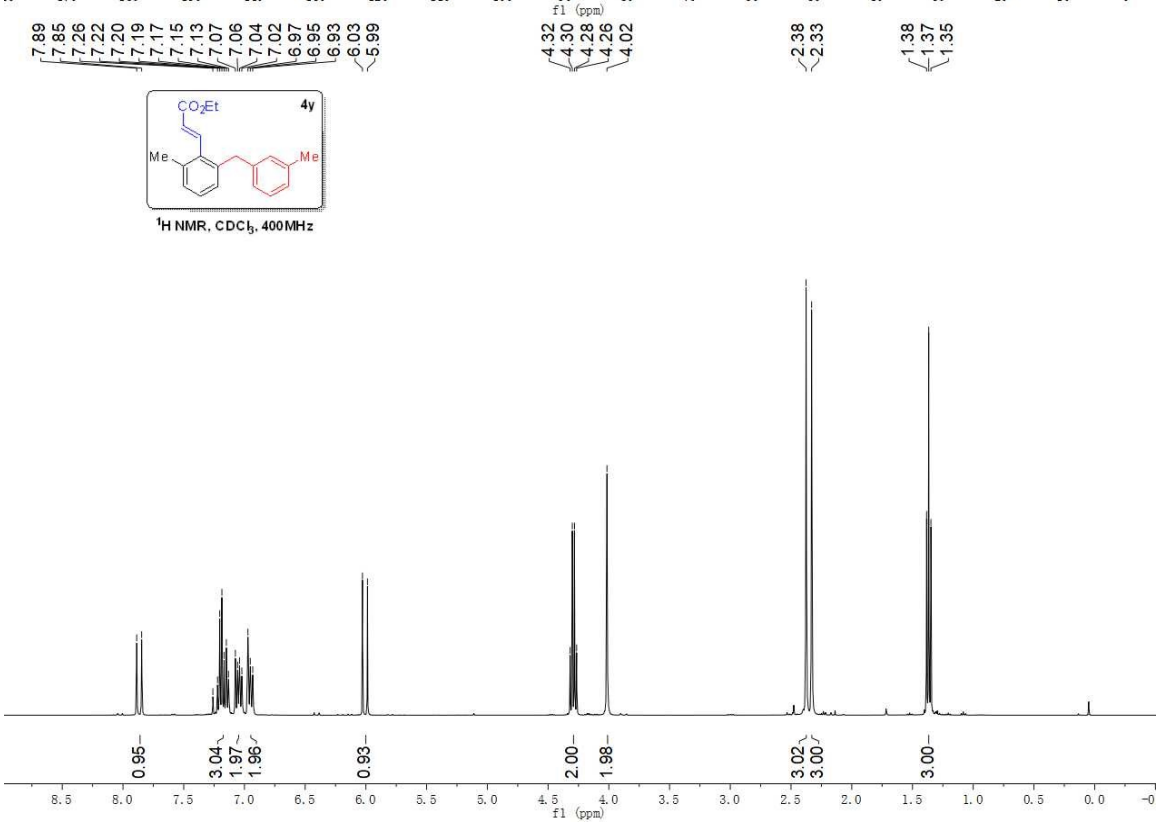
4x
Me
CO2Et
CO2Et
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.95
6.93
6.03
5.99
4.32
4.30
4.28
4.26
4.02
2.38
2.33
1.38
1.37
1.35
4y
Me
CO2Et
Me
1H NMR, CDCl3, 400MHz
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1.97
1.96
0.93
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3.02
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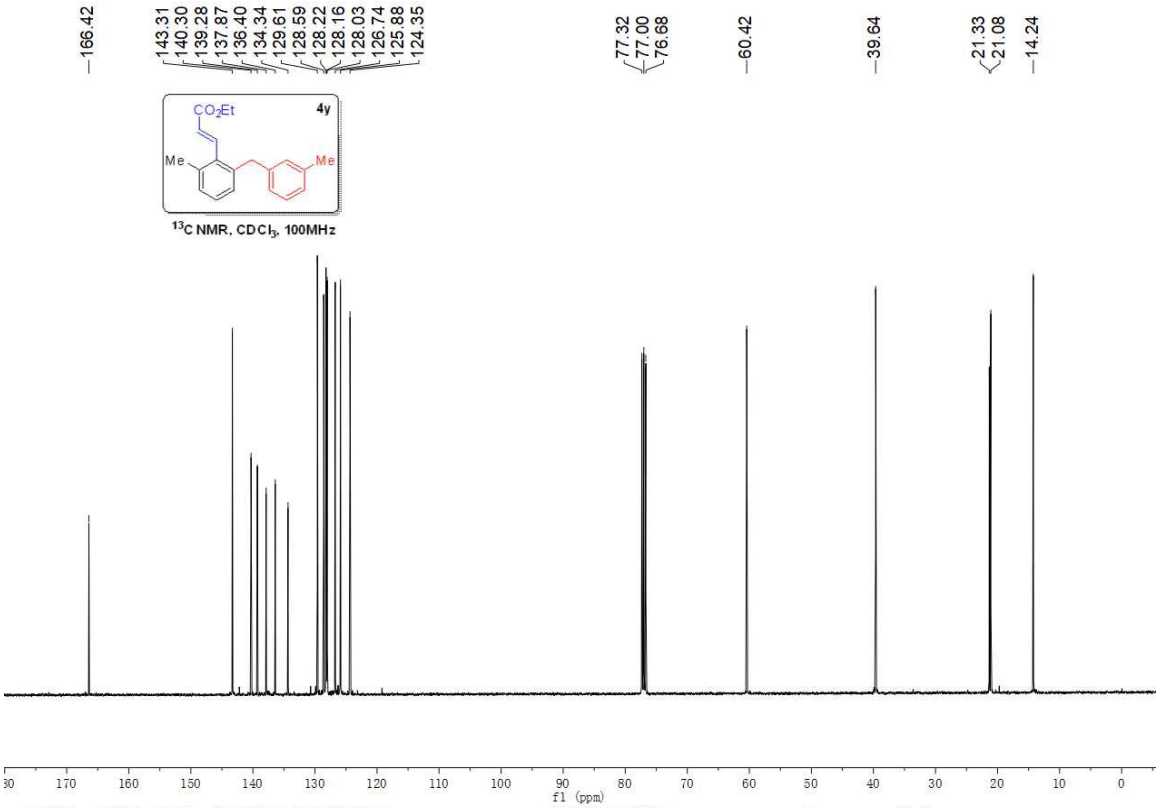
f1 (ppm)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125.88
124.35
77.32
77.00
76.68
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21.33
21.08
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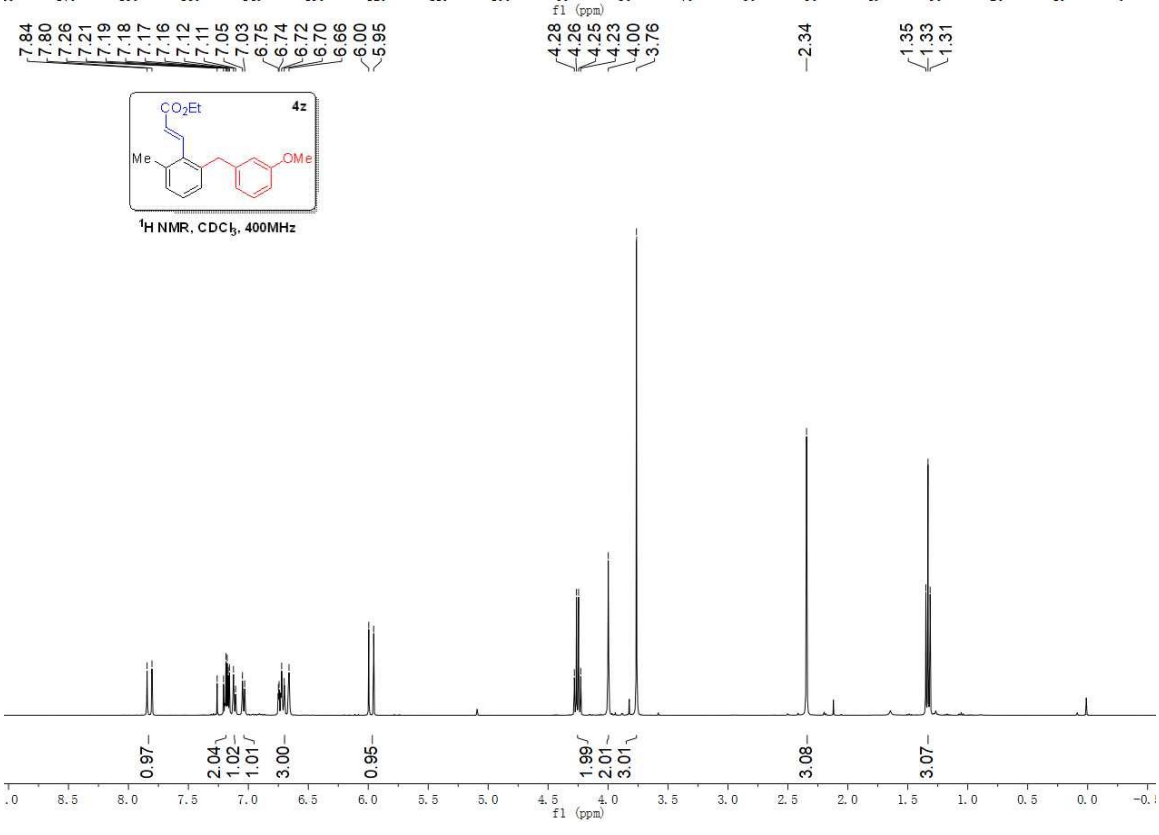
CO2Et
4y
Me
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.75
6.74
6.72
6.70
6.66
6.00
5.95
4.28
4.26
4.25
4.23
4.00
3.76
2.34
1.35
1.33
1.31
CO2Et
4z
Me
OMe
1H NMR, CDCl3, 400MHz
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1.01
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3.01
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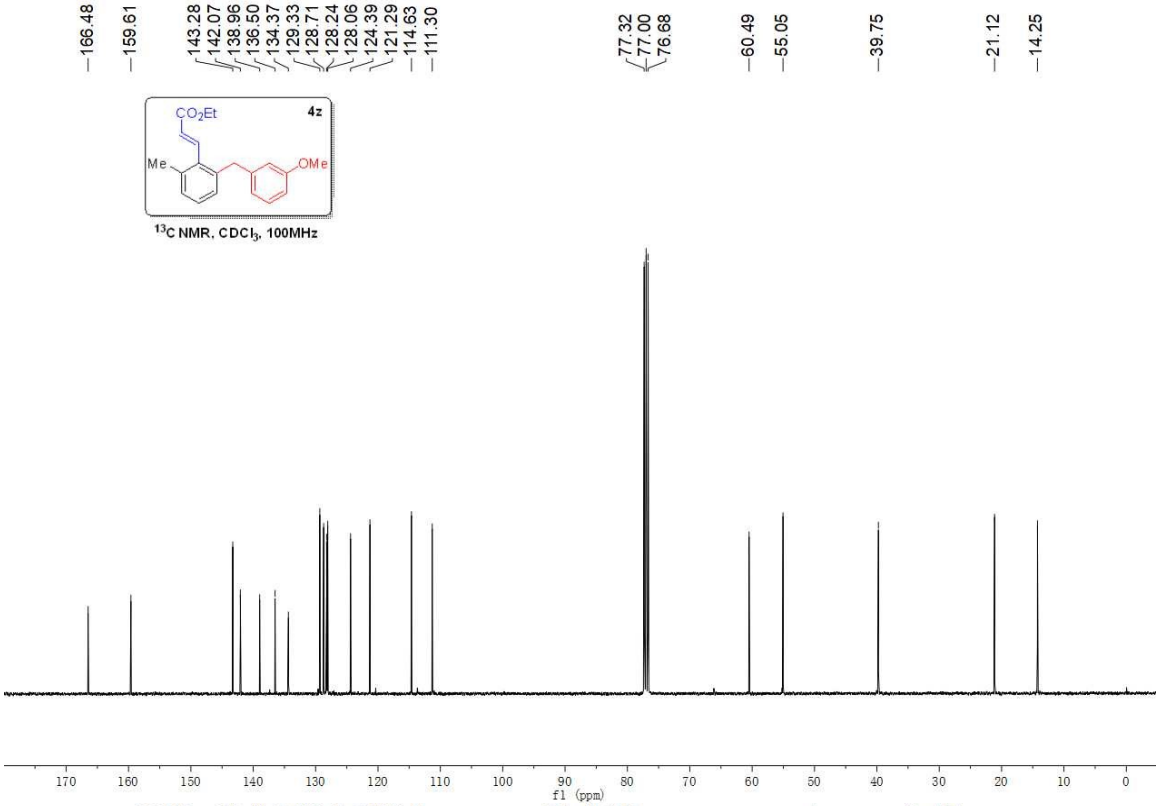
3.07
f1 (ppm)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77.32
77.00
76.68
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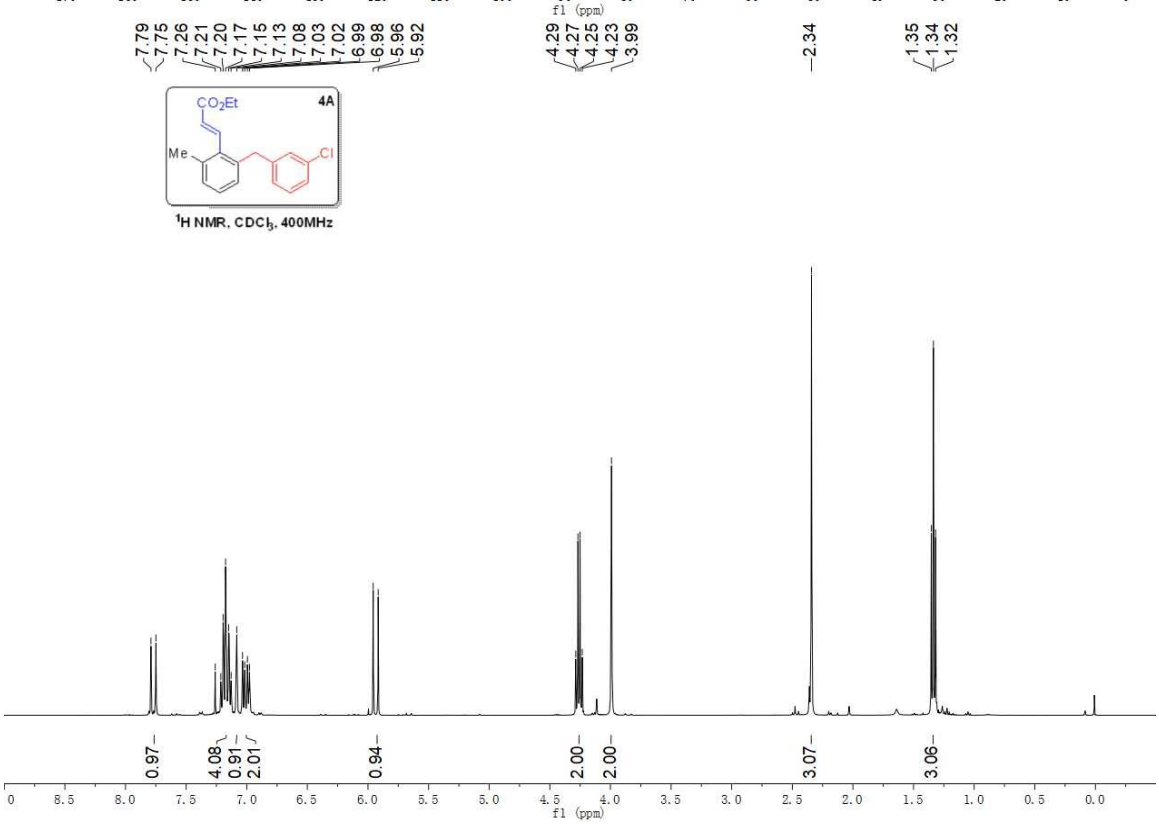
4z
CO2Et
Me
OMe
13C NMR, CDCl3, 100MHz
f1 (ppm)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4.27
4.25
4.23
3.99
2.34
1.35
1.34
1.32
4A
CO2Et
Me
Cl
1H NMR, CDCl3, 400MHz
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2.01
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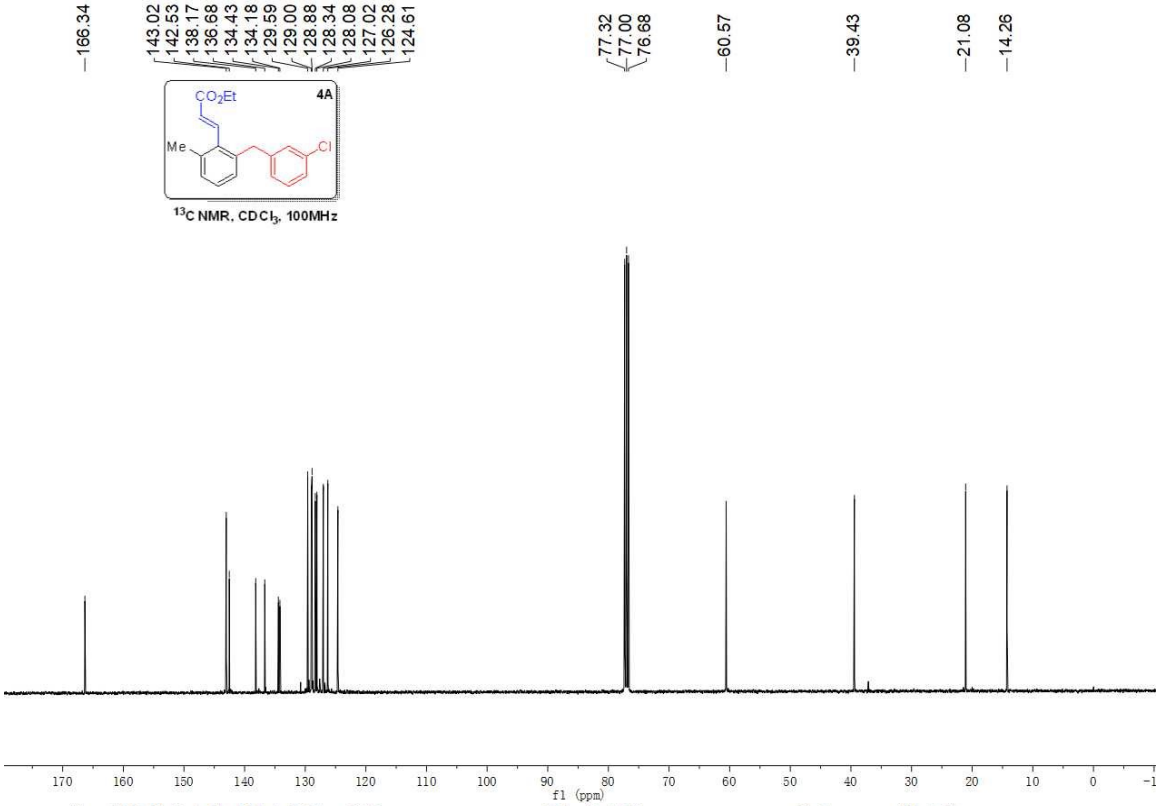
3.06
f1 (ppm)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126.28
124.61
77.32
77.00
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21.08
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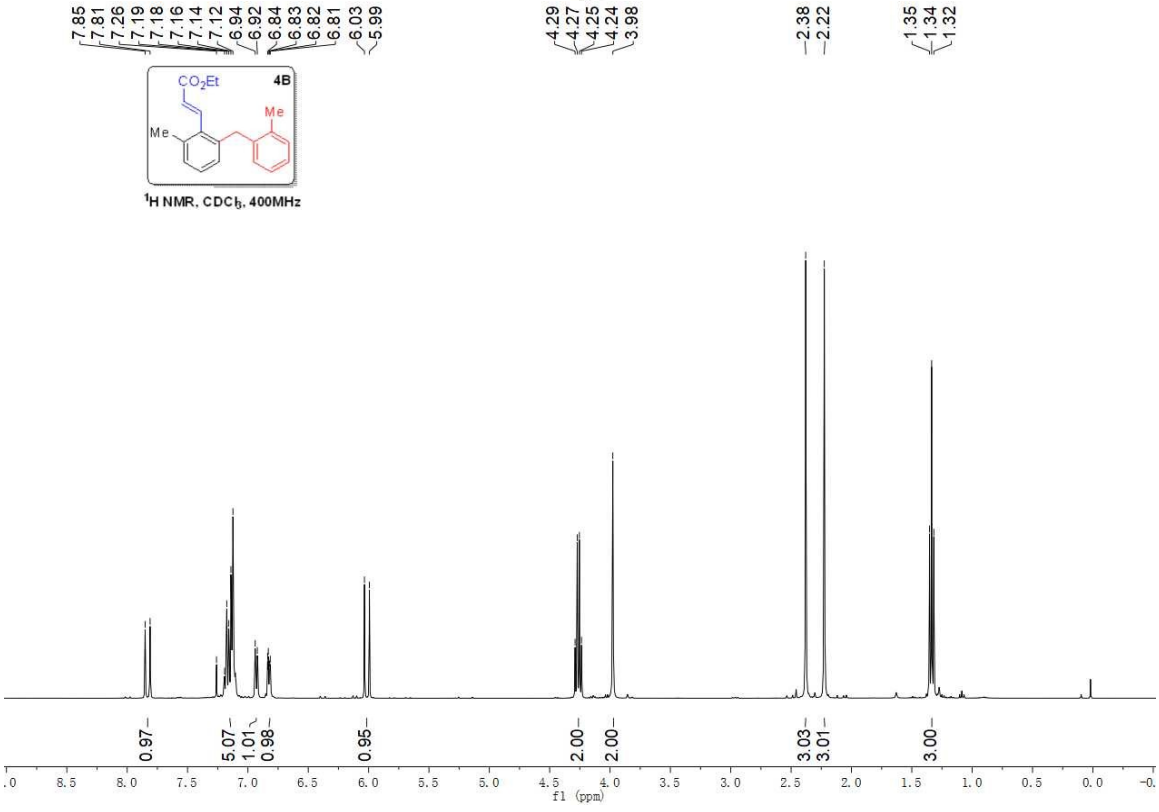
CO2Et
4A
Me
Cl
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.03
5.99
4.29
4.27
4.25
4.24
3.98
2.38
2.22
1.35
1.34
1.32
CO2Et
4B
Me
Me
1H NMR, CDCl3, 400MHz
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1.01
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3.03
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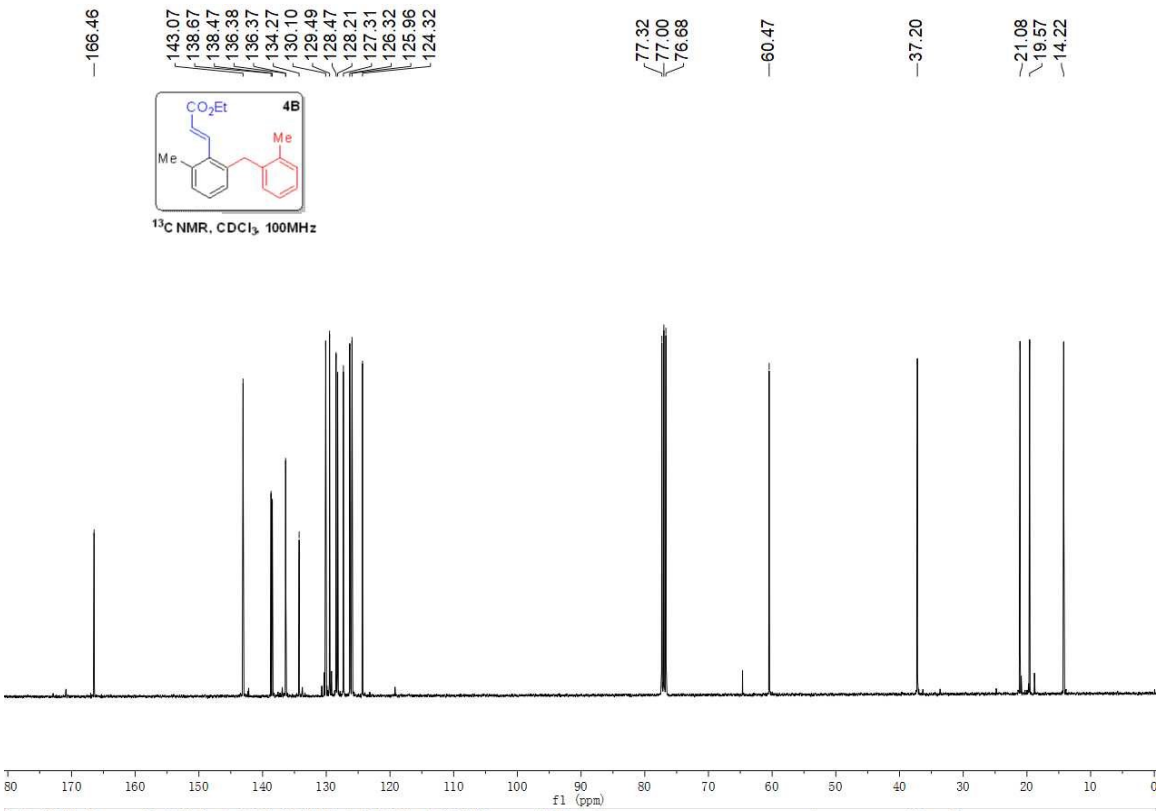
3.00
f1 (ppm)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125.96
124.32
77.32
77.00
76.68
60.47
37.20
21.08
19.57
14.22
CO2Et
4B
Me
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)
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7.97
7.95
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7.47
7.47
7.40
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7.36
7.26
7.15
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7.10
7.08
6.84
6.83
6.82
5.95
5.91
4.34
4.26
4.24
4.22
4.21
2.34
1.33
1.31
1.30
CO2Et
4C
Me
NO2
1H NMR, CDCl3, 400MHz
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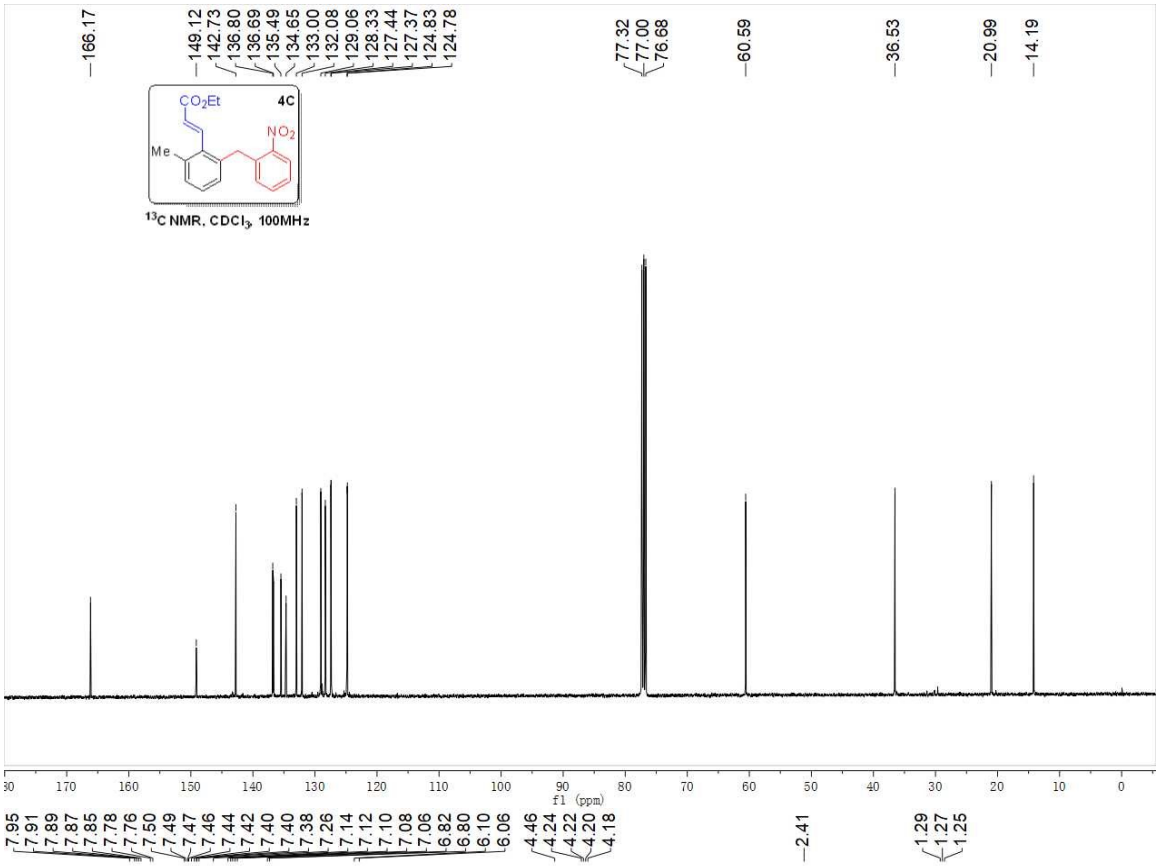
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77.32
77.00
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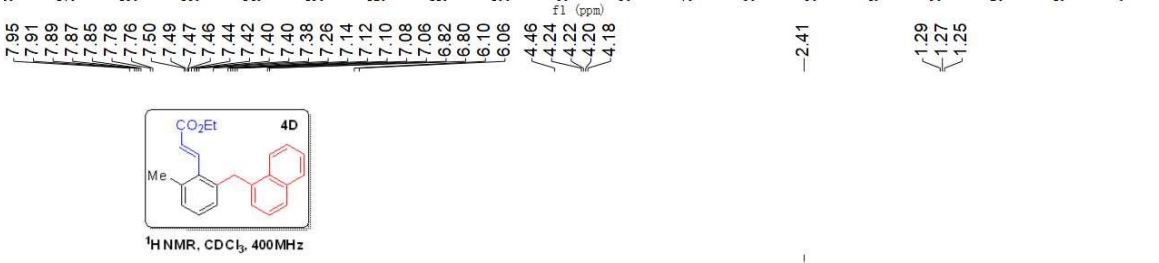
NO2
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.06
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4.18
2.41
1.29
1.27
1.25

CO2Et
4D
Me
1H NMR, CDCl3, 400MHz
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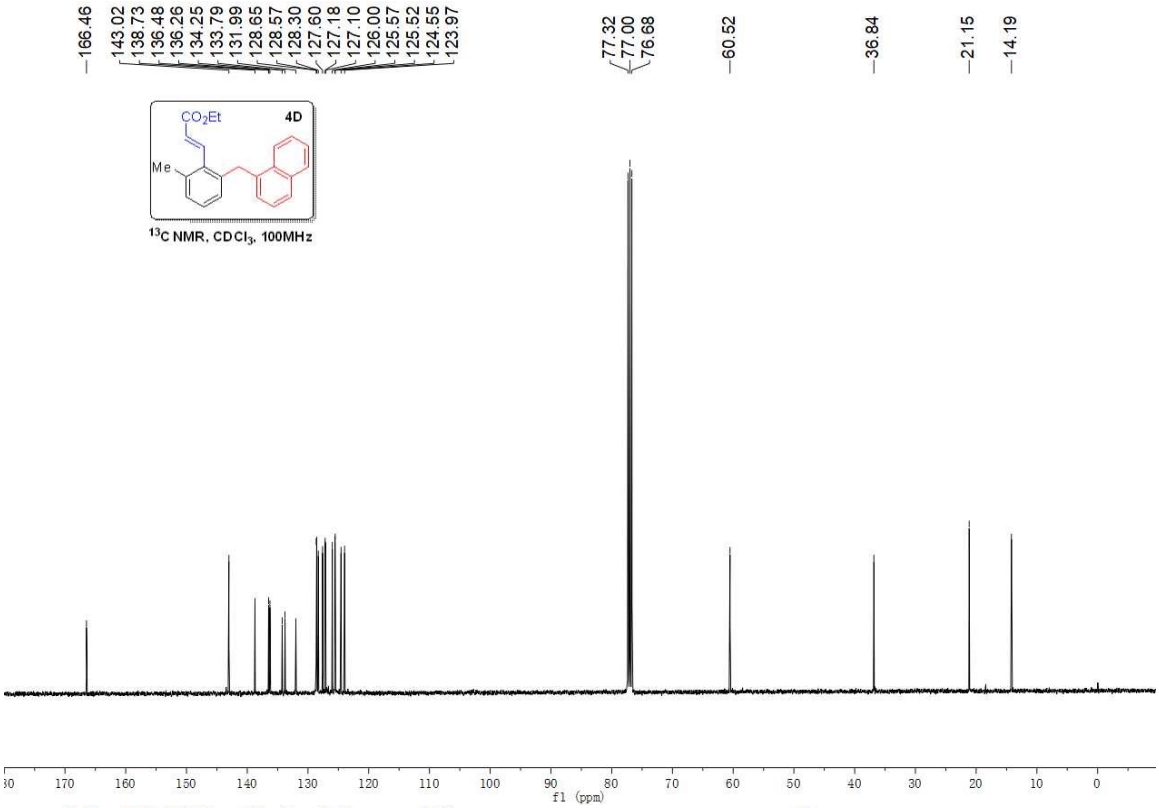
f1 (ppm)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123.97
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4D
Me
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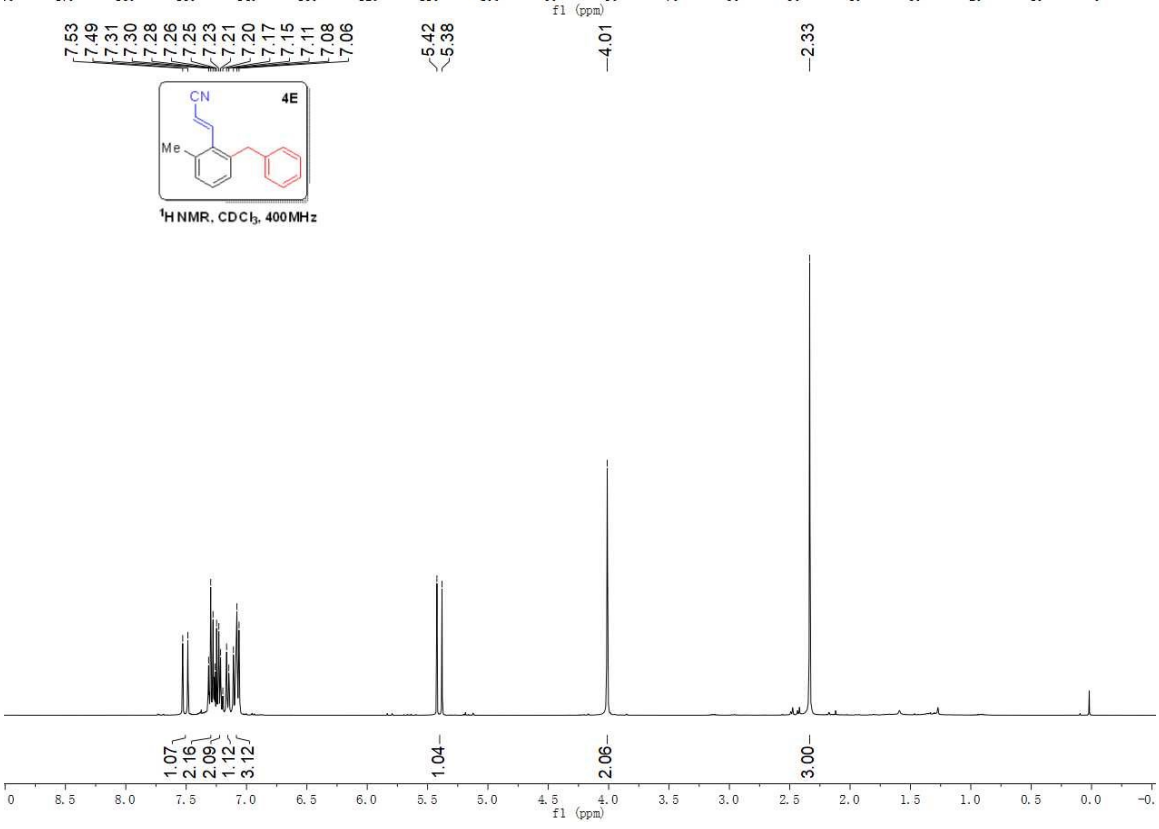
f1 (ppm)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7.08
7.06
5.42
5.38
4.01
2.33
CN
4E
Me
1H NMR, CDCl3, 400MHz
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2.16
2.09
1.12
3.12
1.04
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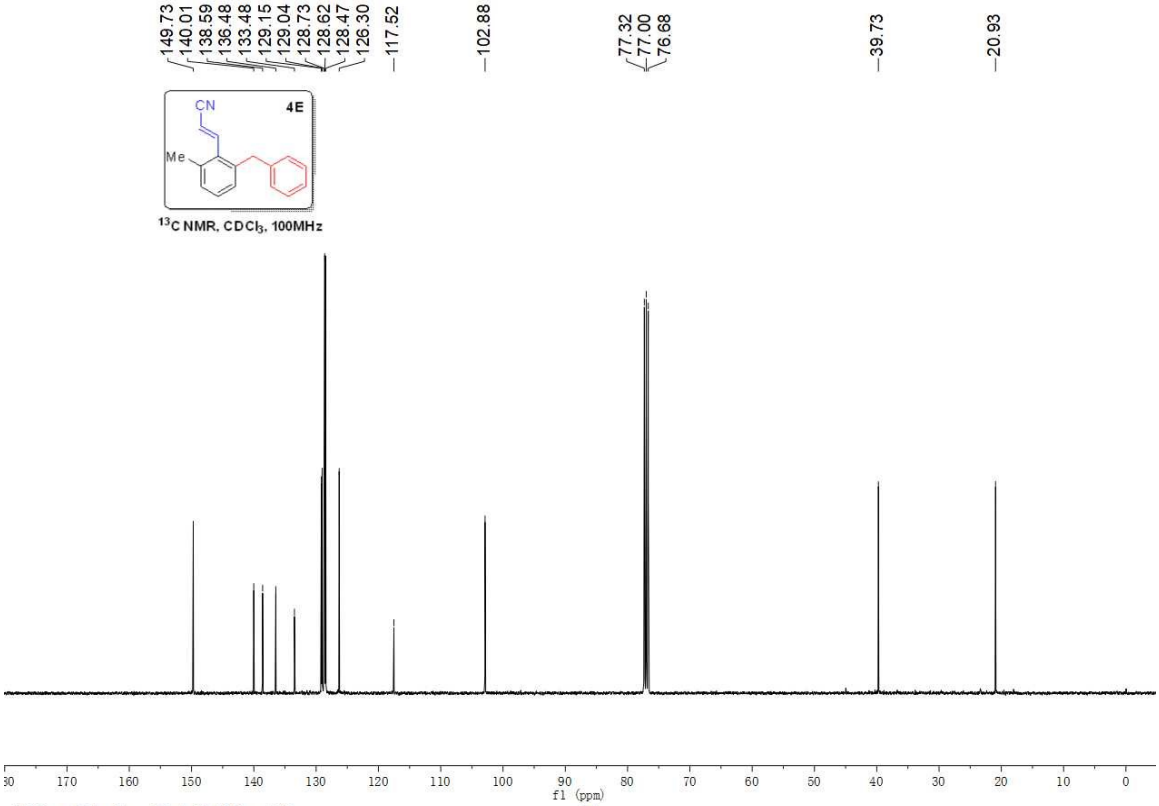
3.00
f1 (ppm)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77.00
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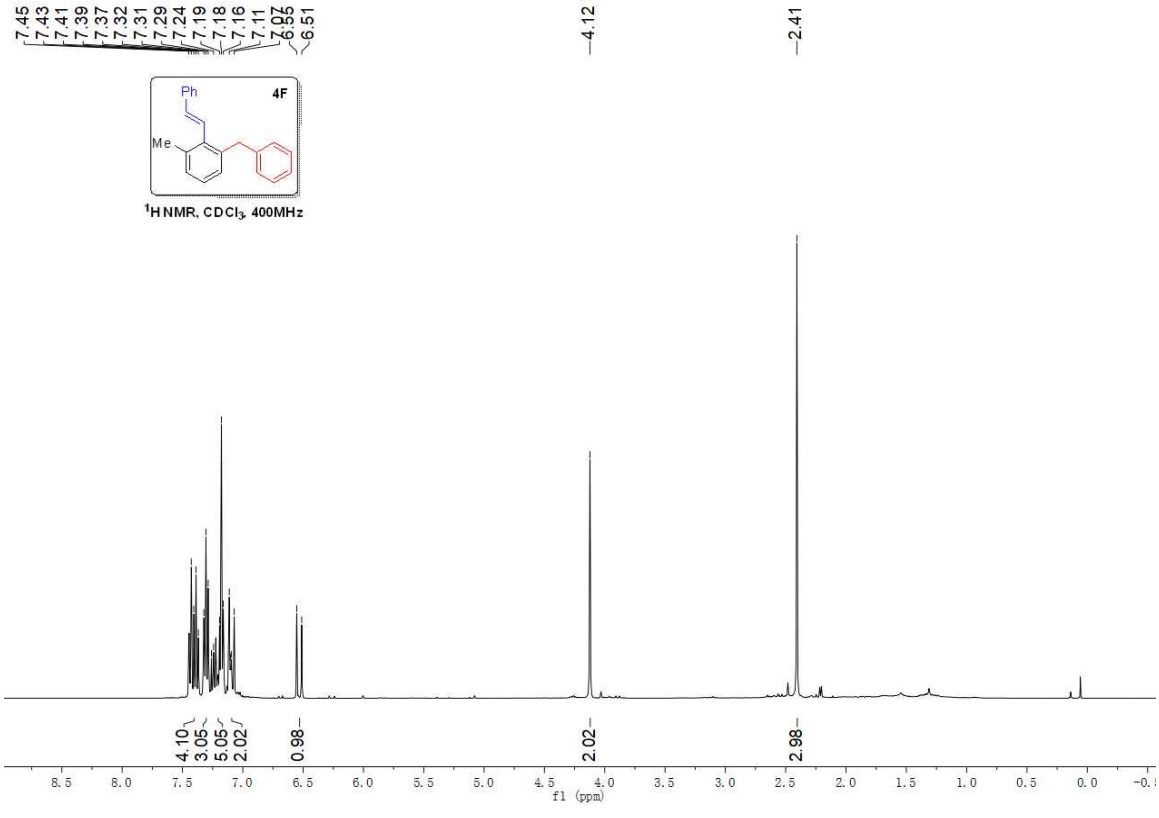
CN
4E
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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6.55
6.51
4.12
2.41
Ph
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Me
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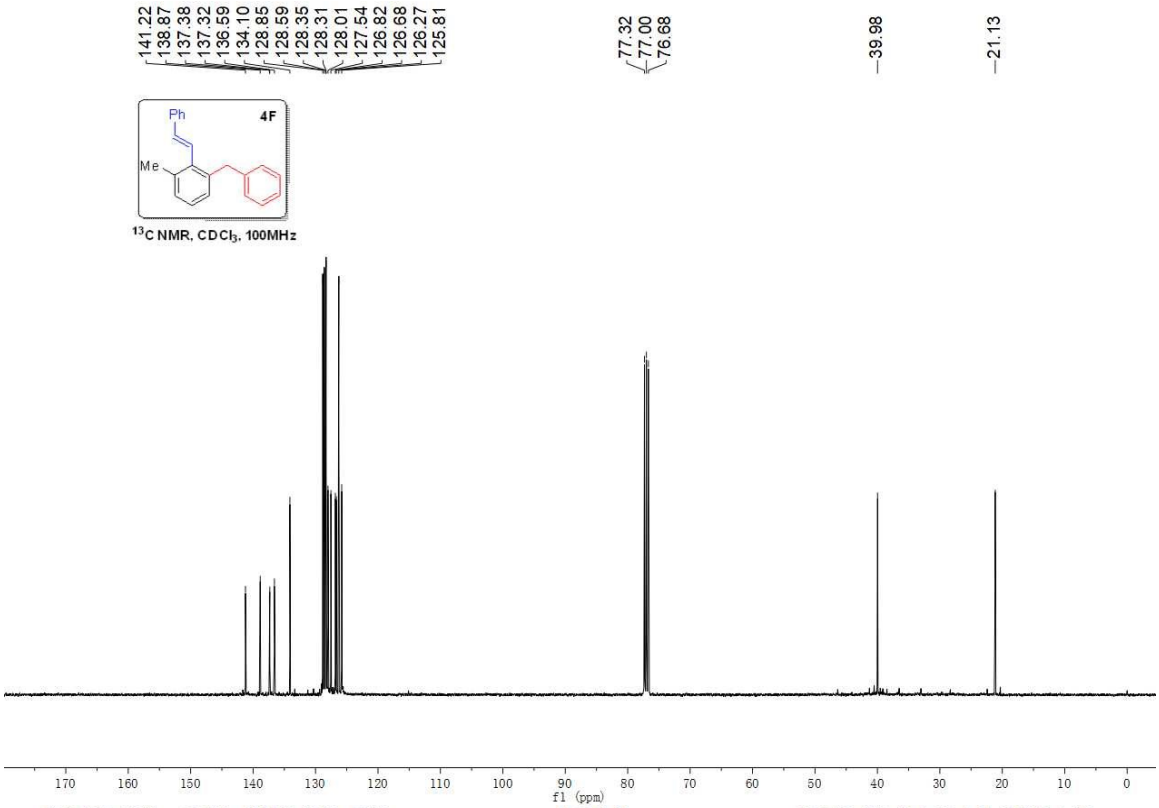
f1 (ppm)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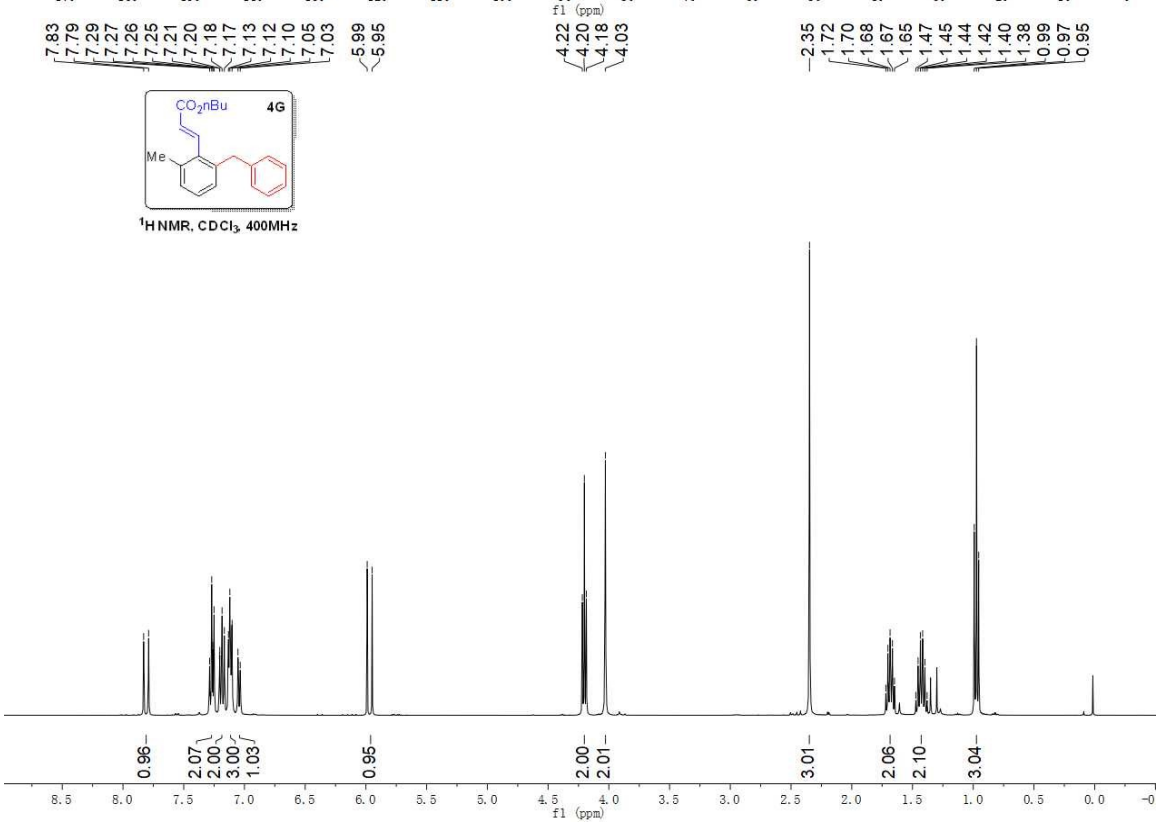
Ph
4F
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)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7.03
5.99
5.95
4.22
4.20
4.18
4.03
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1.70
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1.67
1.65
1.47
1.45
1.44
1.42
1.40
1.38
0.99
0.97
0.95
CO2nBu
4G
Me
1H NMR, CDCl3, 400MHz
0.96
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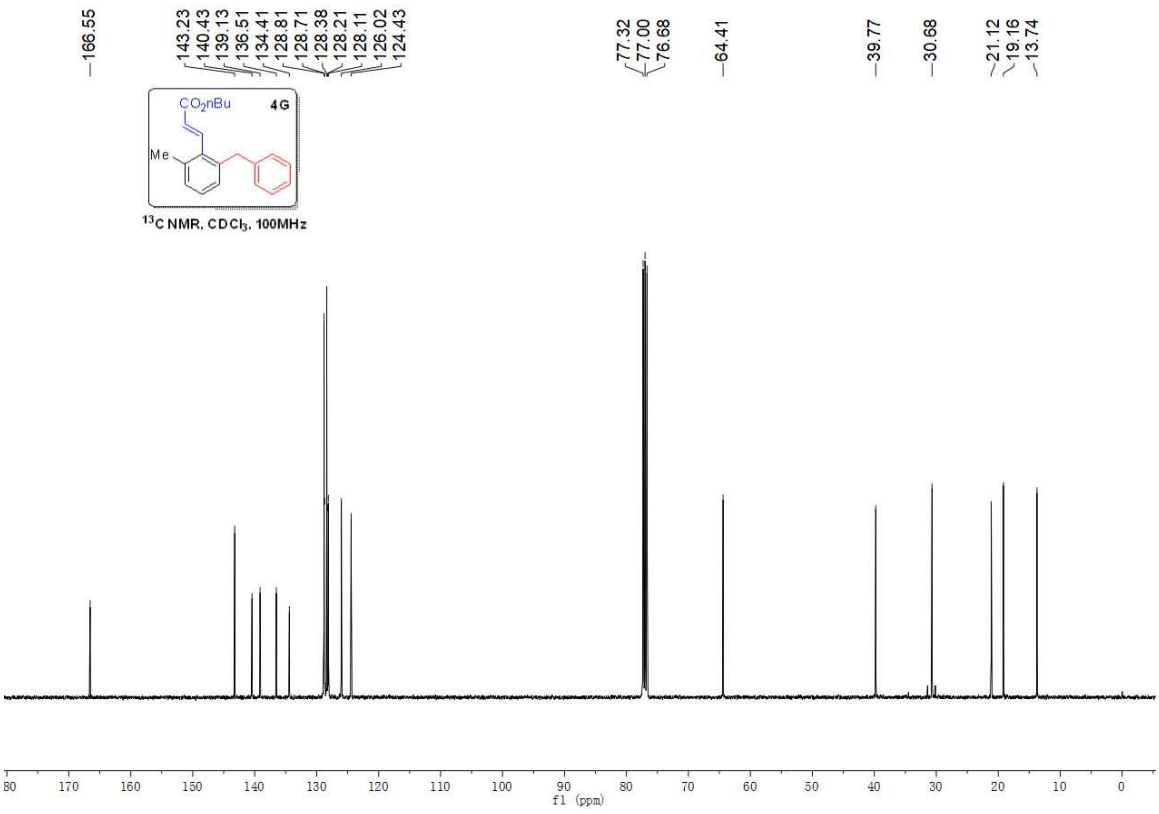
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CO2nBu
4G
Me
13C NMR, CDCl3, 100MHz
f1 (ppm)