

Supporting Information

Cu(II)-Catalyzed Esterification Reaction via Aerobic Oxidative

Cleavage of C(CO)–C(alkyl) Bonds

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1. General methods and materials

Part I. General Information

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, Aladdin Reagent Inc., Tianjin Guangfu Fine Chemical Research Institute. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification except for methanol and ethanol, which were distilled by the documented method prior to use. ^1H NMR spectra were recorded on a Bruker 400 spectrometer in CDCl_3 and CDCl_3 (7.26 ppm) was used as internal reference, ^{13}C NMR spectra were recorded at 100.6 MHz in CDCl_3 and CDCl_3 (77.0 ppm) was used as internal reference. GC-MS were recorded on a Thermo Finnigan Polaris Q equipment in EI mode. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-50, 30 mm $\times$ 0.25 mm) using a flame ionization detector.

Caution: Experiments using compressed oxygen are potentially dangerous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

Part II. General procedures for Cu-catalyzed oxidative esterification of ketones

A mixture of substrate (1 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34 mg, 20 mol%), LiBr (13 mg, 0.15 equiv) and 14 equiv EtOH were placed in a 25-mL stainless steel autoclave equipped with an inner glass tube in room temperature. O_2 (1 MPa) was subsequently introduced into the autoclave and the system was heated at the predetermined reaction temperature for 15 min to reach the equilibration. The mixture was stirred continuously for the desired reaction time. After cooling, products were then diluted by ethyl acetate and analyzed by gas chromatograph (Shimadzu GC-2014) equipped with a capillary column (RTX-50, 30 mm $\times$ 25 mm) using a flame ionization detector by comparison with the retention times of authentic samples. The residue was purified by column chromatography on silica gel (200–300 mesh, eluting with petroleum ether/ethyl acetate 30:1) to afford the desired product. The isolated products were further identified with NMR spectra and GC-MS, which are consistent with those reported in the literature.

2. Condition Screening and Mechanism Study

Table S1 The Evaluation of Metal Salts^a

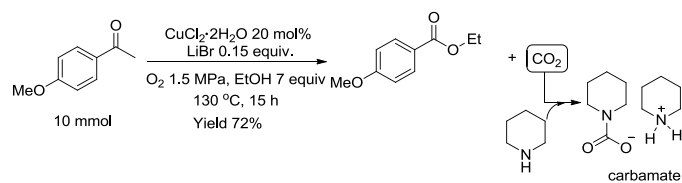
Entry	Catalyst (mol%)	Yield ^b (%)
1	CuCl ₂ · 2H ₂ O	59
2	CuBr ₂	49
3	CuCl ₂	46
4	CuCl	43
5	CuBr	30
6	Cu(acac) ₂	34
7	Cu(OTf) ₂	16
8	FeBr ₃	4
9	Fe(NO ₃) ₃	6
10	Fe(acac) ₃	4

^a Reaction conditions: **1a** (1 mmol, 150 mg), LiBr (0.3 equiv, 26 mg), EtOH (14 equiv, 645 mg), catalyst (20 mol%), O₂ 1MPa, 130 °C, 3 h. ^b Yields are determined by GC with 4-Acetylbiphenyl as internal standard.

To identify other products, we increased the reaction scale to 10 mmol. The generation of CO₂ was detected by limber–water test (Figure S1). In addition, CCU (Carbon capture and utilization) strategy with piperidine as the absorbent has also been used to confirm CO₂ (Figure S2).



Figure S1 limber–water test



(a)

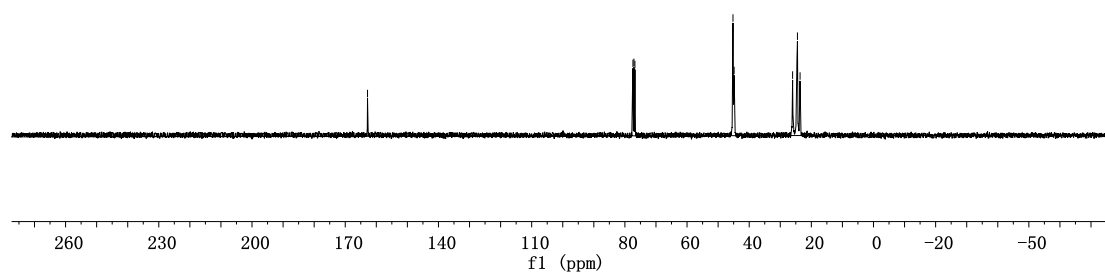
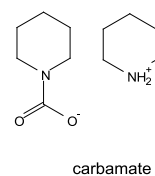


(b)

$^{13}\text{C NMR}(100.6 \text{ MHz, CDCl}_3)$

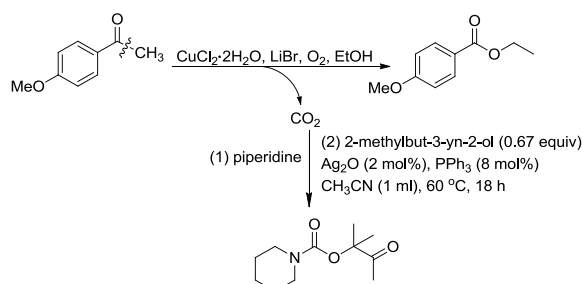
— 162.83

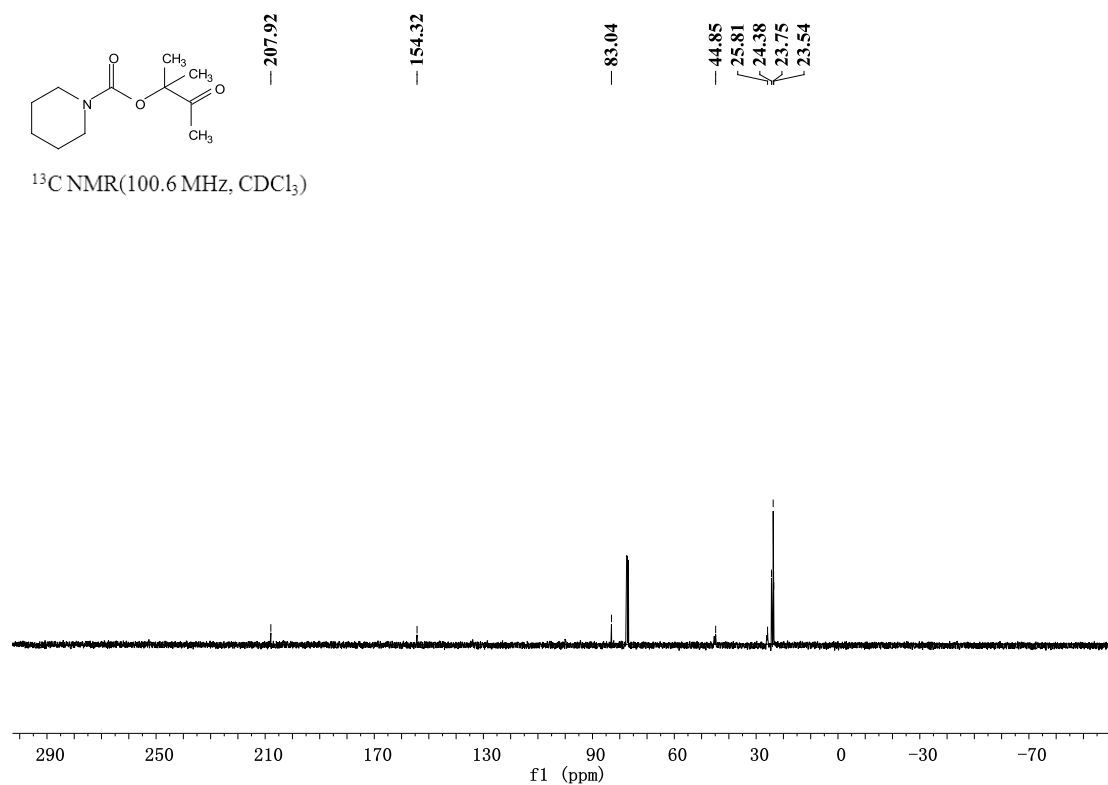
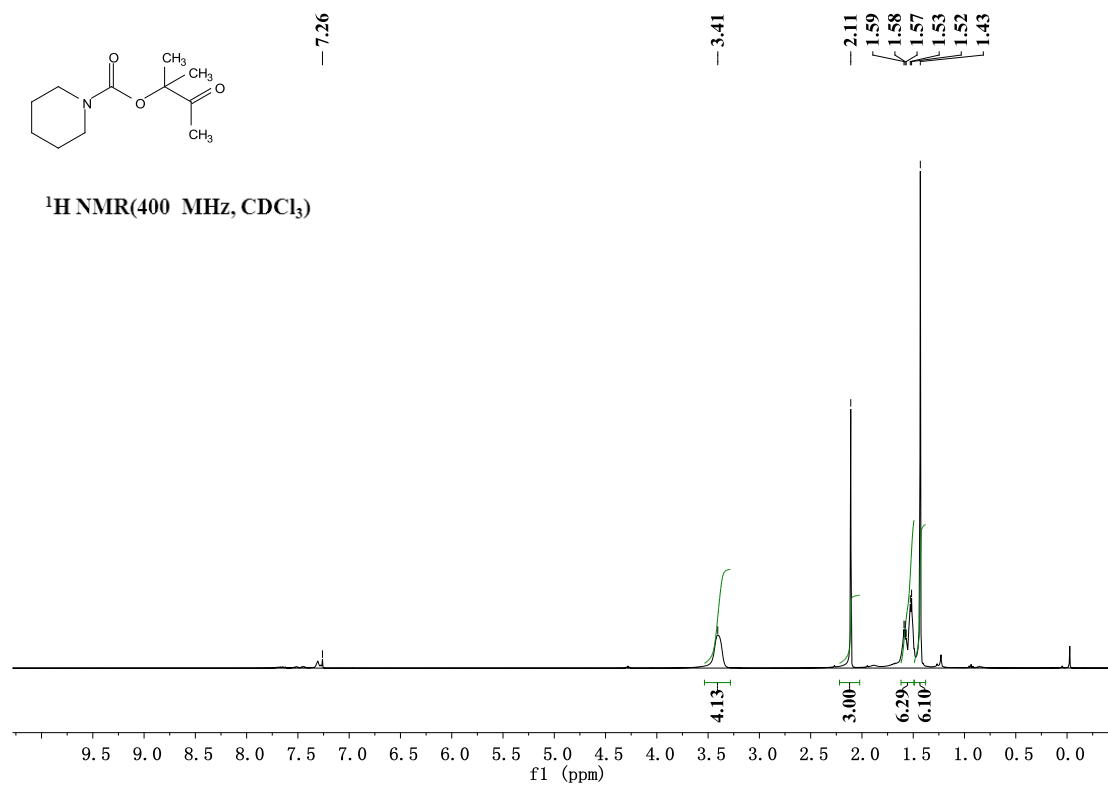
$\{ 77.41, 77.09, 76.77 \}$
 $\{ 45.22, 44.85 \}$
 $\{ 26.03, 24.47, 23.63 \}$



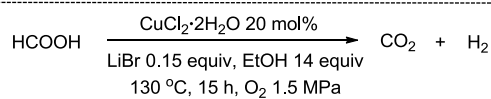
(c)

Figure S2 The formation of the carbamate between piperidine and CO_2 . (a): piperidine. (b) carbamate. (c): $^{13}\text{C NMR}$ of carbamate

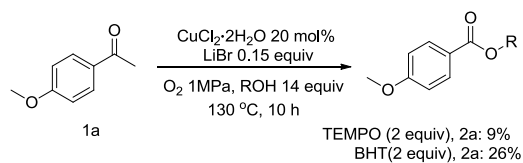




Scheme S1 β -oxopropylcarbamate synthesis upon CO_2 absorption by piperidine with 2-methylbut-3-yn-2-ol catalyzed by $\text{Ag}_2\text{O}/\text{PPh}_3$



Scheme S2 Decomposition of HCOOH under the standard conditions



Scheme S3 Radical Trapping Experiments

2,2-diethoxy-1-phenylethanone (**6f**) was detected by ^1H NMR when the conversion **6c** or **6d** to benzoate (**2k**) (Figure S3 and Figure S4). ^1H NMR (CDCl_3 , 400MHz): δ = 1.23 (t, 6H), 3.62-3.66 (m, 2H), 3.71-3.79 (m, 2H), 5.26 (s, 1H), 7.42-7.46 (m, 2H), 7.52-7.57 (m, 1H), 8.14 (d, 2H, $J=8.4\text{Hz}$). *Synlett*, **2014**, 25, 1591-159

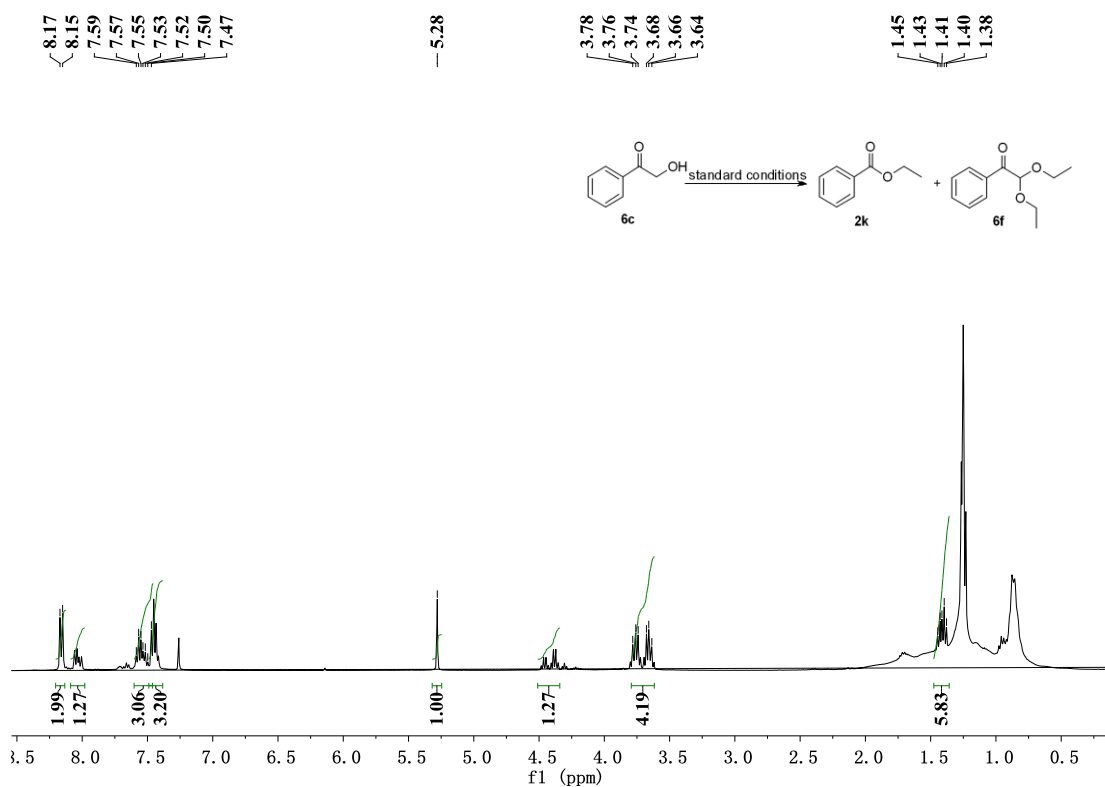


Figure S3 ^1H NMR spectra of the reaction mixture of compound **6c**.

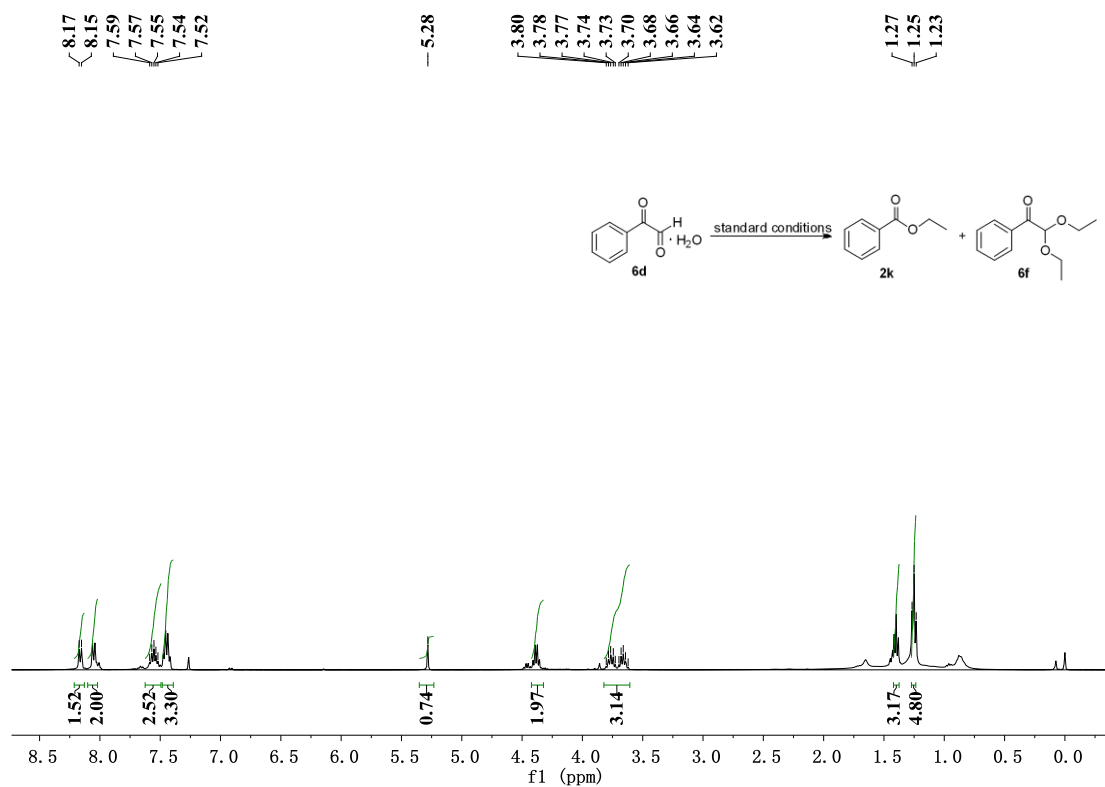
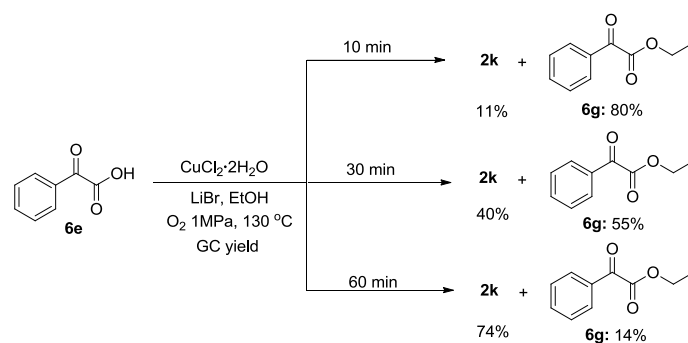
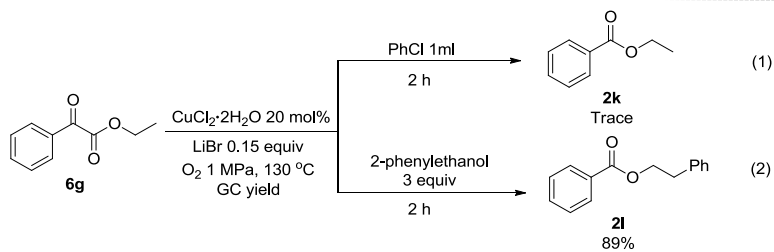


Figure S4 ¹H NMR spectra of the reaction mixture of compound 6d.



Scheme S4 Control experiments of intermediate 6e



Scheme S5. Reactions of intermediate 6g.

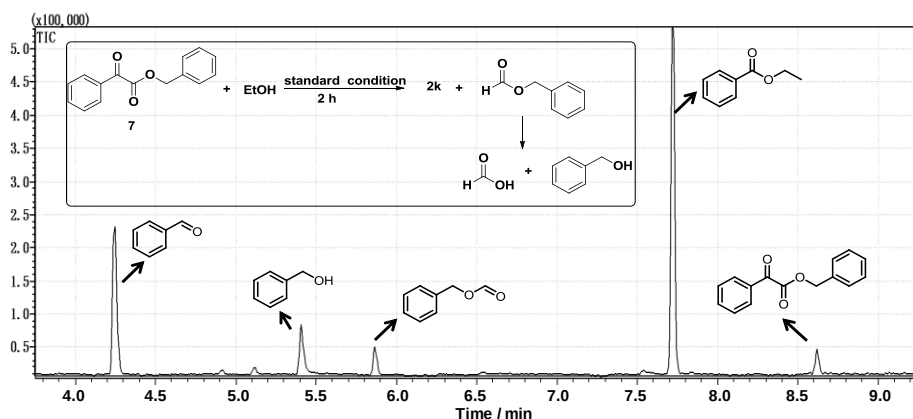
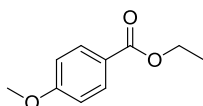


Figure S5. GC/MS chart (reaction conditions: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34 mg, 20 mol%), LiBr (13 mg, 0.15 equiv), O_2 1 MPa, 130°C).

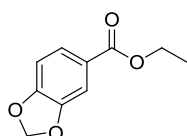
3. Characterization data for products

ethyl 4-methoxybenzoate (2a)¹



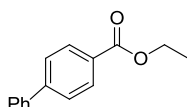
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.00 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.52, 163.36, 131.65, 123.07, 113.65, 60.75, 55.52, 14.50.

ethyl benzo[d][1,3]dioxole-5-carboxylate (2b)¹



^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.65 (d, J = 8.1 Hz, 1H), 7.47 (s, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.03 (s, 2H), 4.34 (q, J = 7.0 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.07, 151.56, 147.75, 125.31, 124.57, 109.56, 107.99, 101.85, 60.98, 14.44.

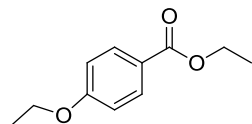
ethyl [1,1'-biphenyl]-4-carboxylate (2c)¹



^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.22 – 8.04 (m, 2H), 7.76 – 7.55 (m, 4H), 7.47 (t, J = 7.2 Hz, 2H), 7.43 – 7.37 (m, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz,

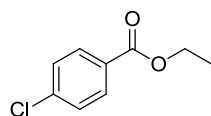
CDCl₃, ppm) δ = 166.55, 145.55, 140.08, 130.08, 129.27, 128.94, 128.13, 127.30, 127.03, 61.00, 14.39.

ethyl 4-ethoxybenzoate (2d)²



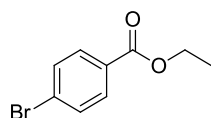
¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.97 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 7.2 Hz, 2H), 4.32 (q, J = 6.9 Hz, 2H), 4.15 – 3.94 (m, 2H), 1.52 – 1.26 (m, 6H). ¹³C NMR (100.6 MHz, CDCl₃, ppm) δ = 166.48, 162.71, 131.57, 122.73, 114.00, 63.69, 60.65, 14.74, 14.44.

ethyl 4-chlorobenzoate (2e)¹



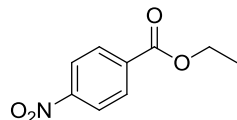
¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.99 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ¹³C NMR (100.6 MHz, CDCl₃, ppm) δ = 165.74, 139.23, 130.94, 128.94, 128.65, 61.21, 14.29.

ethyl 4-bromobenzoate (2f)³



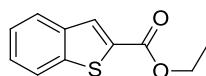
¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.90 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 4.37 (d, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ¹³C NMR (100.6 MHz, CDCl₃, ppm) δ = 165.88, 131.65, 131.09, 129.38, 127.91, 61.25, 14.30.

ethyl 4-nitrobenzoate (2g)¹



¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.33 – 8.16 (m, 4H), 4.43 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ¹³C NMR (100.6 MHz, CDCl₃, ppm) δ = 164.82, 150.59, 135.97, 130.79, 123.62, 62.09, 14.35.

ethyl benzo[b]thiophene-2-carboxylate (2h-a)

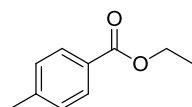


^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.06 (s, 1H), 7.86 (dd, J = 6.6, 5.7 Hz, 2H), 7.42 (dt, J = 15.0, 7.2 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 162.93, 142.27, 138.82, 133.96, 130.47, 126.95, 125.60, 124.96, 122.84, 61.68, 14.43.

ethyl benzofuran-2-carboxylate (2h-b)

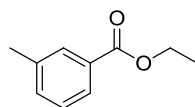
^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.53 (s, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 159.64, 155.71, 145.72, 127.58, 126.98, 123.77, 122.80, 113.81, 112.38, 61.54, 14.35.

ethyl 4-methylbenzoate (2i)¹



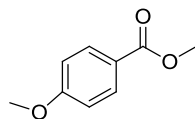
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.93 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.82, 143.51, 129.66, 129.12, 127.87, 60.85, 21.73, 14.45.

ethyl 3-methylbenzoate (2j)¹



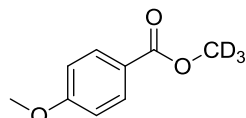
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 7.87 (d, J = 9.1 Hz, 2H), 7.35 (dt, J = 14.8, 7.5 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.89, 138.15, 133.65, 130.47, 130.13, 128.29, 126.74, 60.96, 21.34, 14.42.

methyl 4-methoxybenzoate (5a)¹



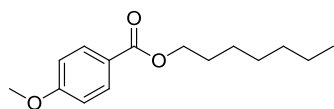
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.17 – 7.78 (m, 2H), 6.90 (d, J = 8.6 Hz, 3H), 3.87 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.96, 163.41, 131.68, 122.68, 113.69, 55.50, 51.95.

d-methyl 4-methoxybenzoate (5b)⁴



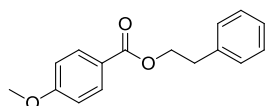
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.07 – 7.91 (m, 2H), 7.01 – 6.82 (m, 2H), 3.85 (d, J = 5.0 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 167.00, 163.42, 131.69, 122.70, 113.69, 55.51.

heptyl 4-methoxybenzoate (5c)⁵



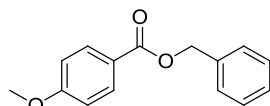
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.01 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 4.32 – 4.25 (m, 2H), 3.85 (s, 3H), 1.81 – 1.70 (m, 2H), 1.42 – 1.22 (m, 8H), 0.87 (d, J = 6.5 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.59, 163.34, 131.65, 123.08, 113.65, 64.97, 55.53, 31.88, 29.11, 28.90, 26.15, 22.74, 14.22.

phenethyl 4-methoxybenzoate (5d)⁶



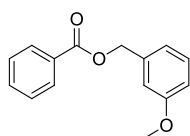
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.02 (d, J = 8.6 Hz, 2H), 7.41 – 7.21 (m, 5H), 6.95 (d, J = 8.5 Hz, 2H), 4.55 (t, J = 6.9 Hz, 2H), 3.88 (s, 3H), 3.11 (t, J = 6.9 Hz, 2H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.30, 163.37, 138.09, 131.62, 129.01, 128.56, 126.58, 122.75, 113.63, 65.23, 55.44, 35.34.

benzyl 4-methoxybenzoate (5e)⁷



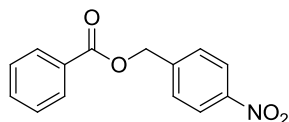
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.03 (d, J = 8.9 Hz, 2H), 7.62 – 7.28 (m, 5H), 6.90 (d, J = 8.8 Hz, 2H), 5.33 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.22, 163.45, 136.32, 131.78, 128.61, 128.19, 128.15, 122.53, 113.65, 66.43, 55.46.

3-methoxybenzyl benzoate (5f)⁶



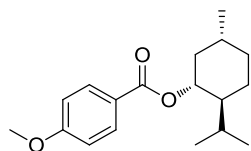
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.12 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.9 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.92 (dd, J = 8.2, 2.2 Hz, 1H), 5.38 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.49, 159.83, 137.65, 133.15, 130.15, 129.79, 129.75, 128.47, 120.40, 113.74, 113.70, 66.62, 55.33.

4-nitrobenzyl benzoate (5g)⁸



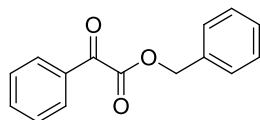
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.25 (d, J = 8.7 Hz, 2H), 8.13 – 8.03 (m, 2H), 7.60 (t, J = 7.3 Hz, 3H), 7.48 (t, J = 7.7 Hz, 2H), 5.46 (s, 2H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 166.25, 147.87, 143.49, 133.62, 129.88, 129.59, 128.71, 128.47, 124.03, 65.32.

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-methoxybenzoate (5h)⁹



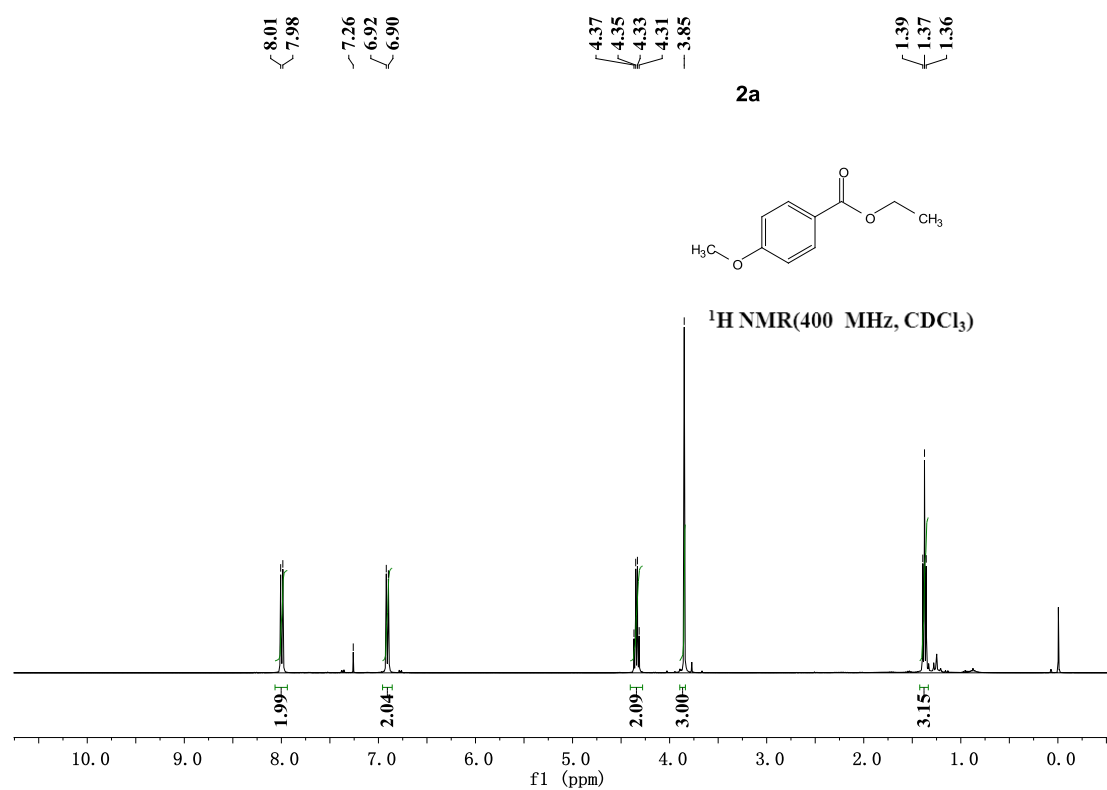
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.00 (d, J = 7.3 Hz, 2H), 6.92 (d, J = 7.4 Hz, 2H), 4.90 (td, J = 10.9, 3.4 Hz, 1H), 3.85 (s, 3H), 2.12 (d, J = 12.1 Hz, 1H), 2.00 – 1.93 (m, 1H), 1.72 (d, J = 11.0 Hz, 2H), 1.53 (t, J = 10.7 Hz, 2H), 1.15 – 1.03 (m, 2H), 0.95 – 0.89 (m, 7H), 0.79 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 163.31, 131.67, 123.44, 113.65, 74.56, 55.54, 47.44, 41.19, 34.48, 31.57, 26.64, 23.81, 22.19, 20.90, 16.70.

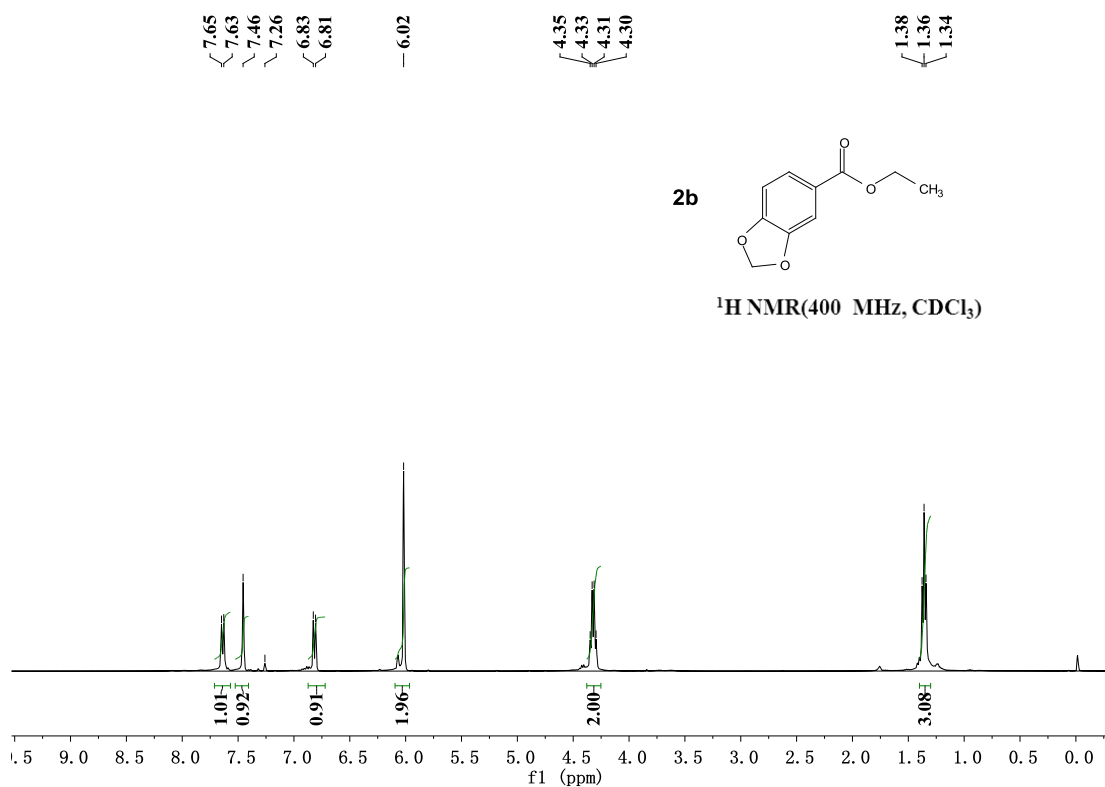
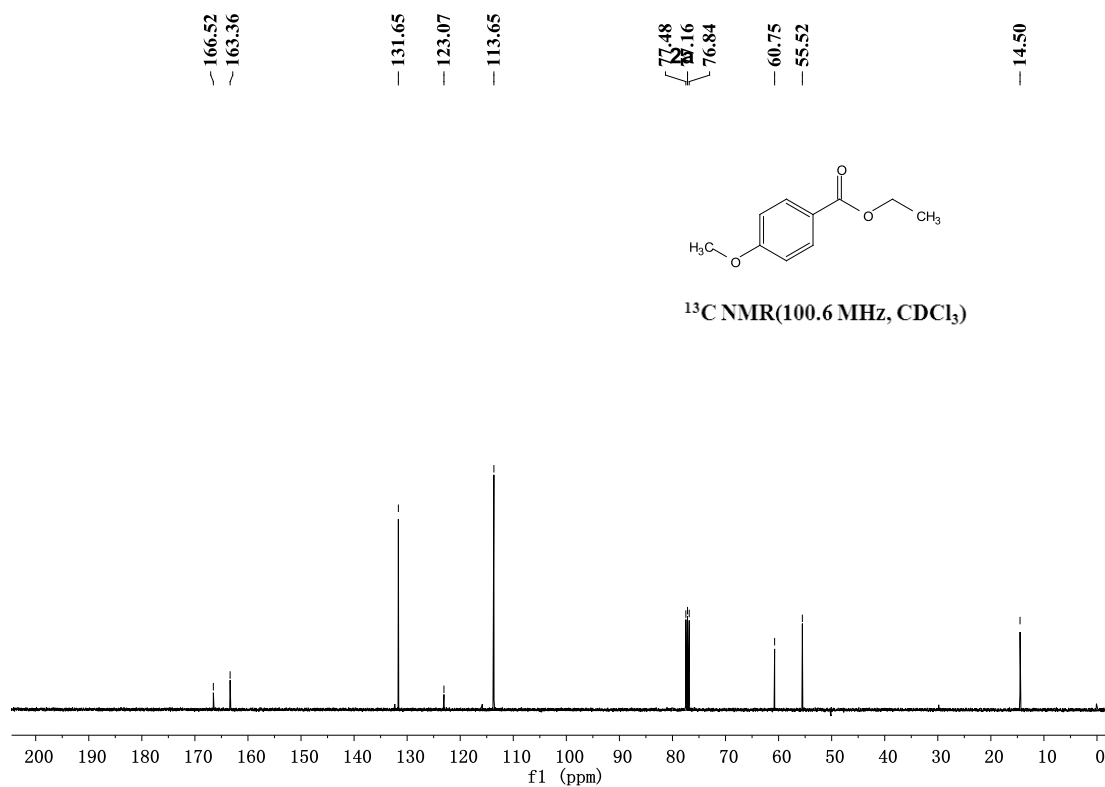
benzyl benzoylformate (7)⁶

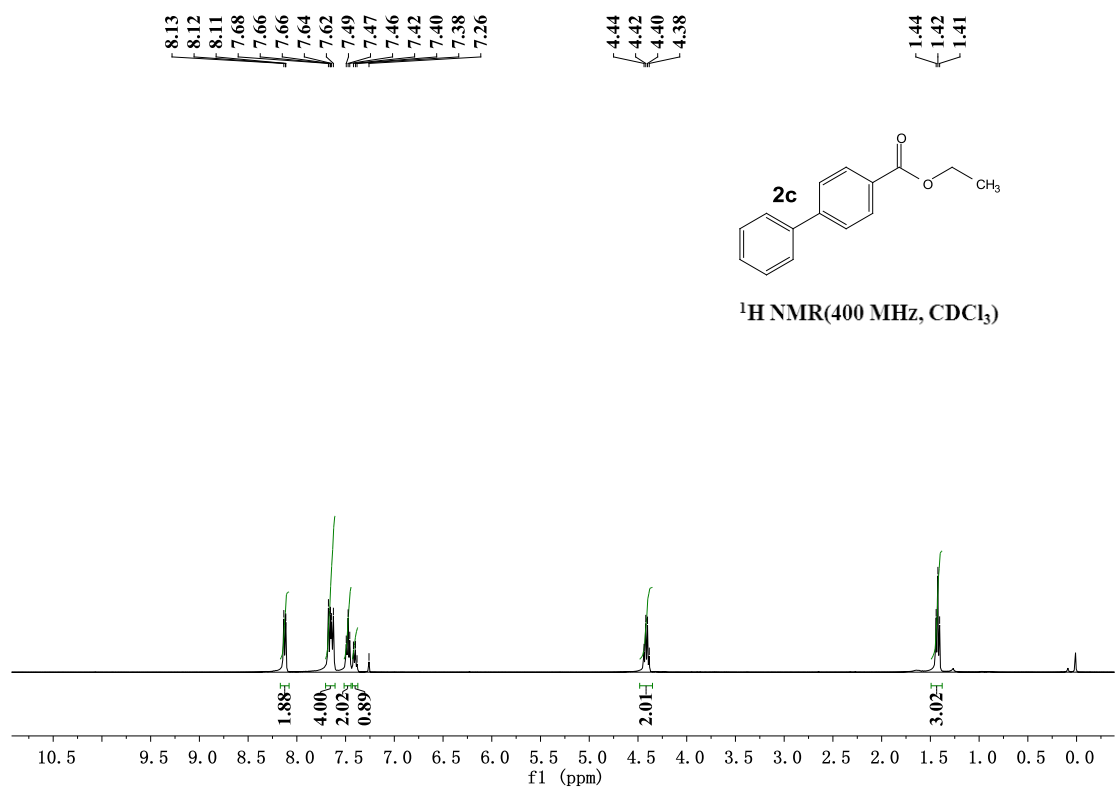
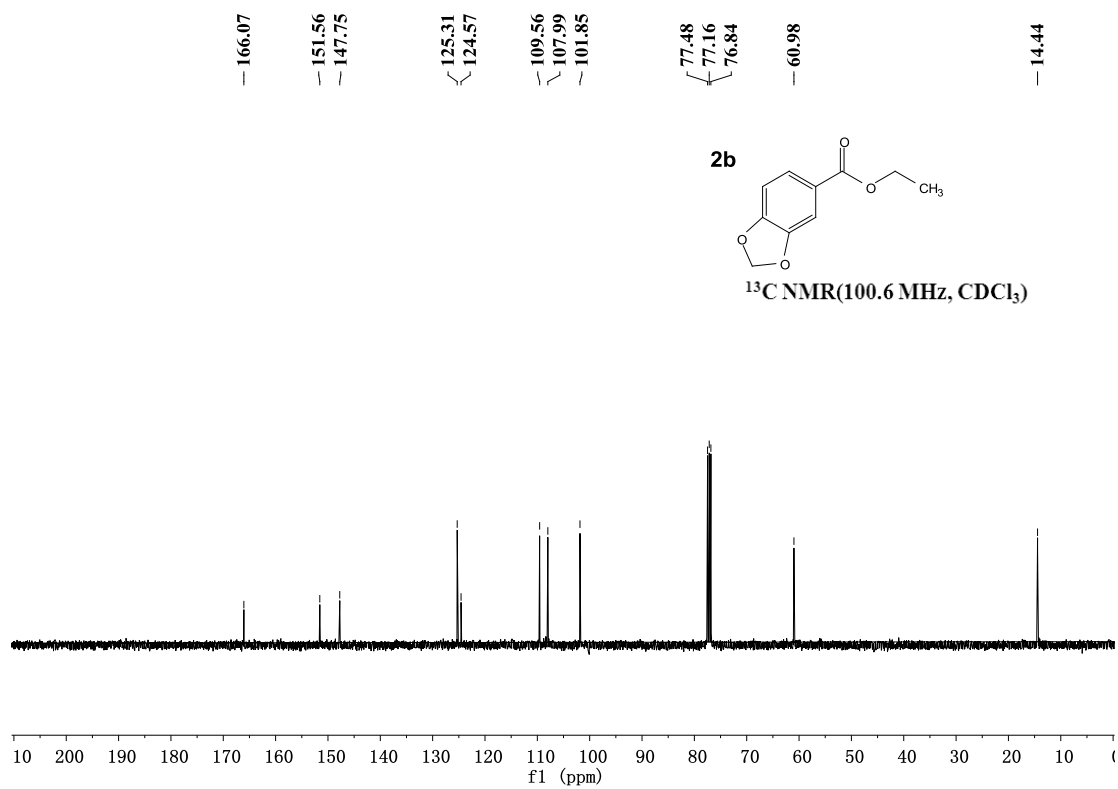


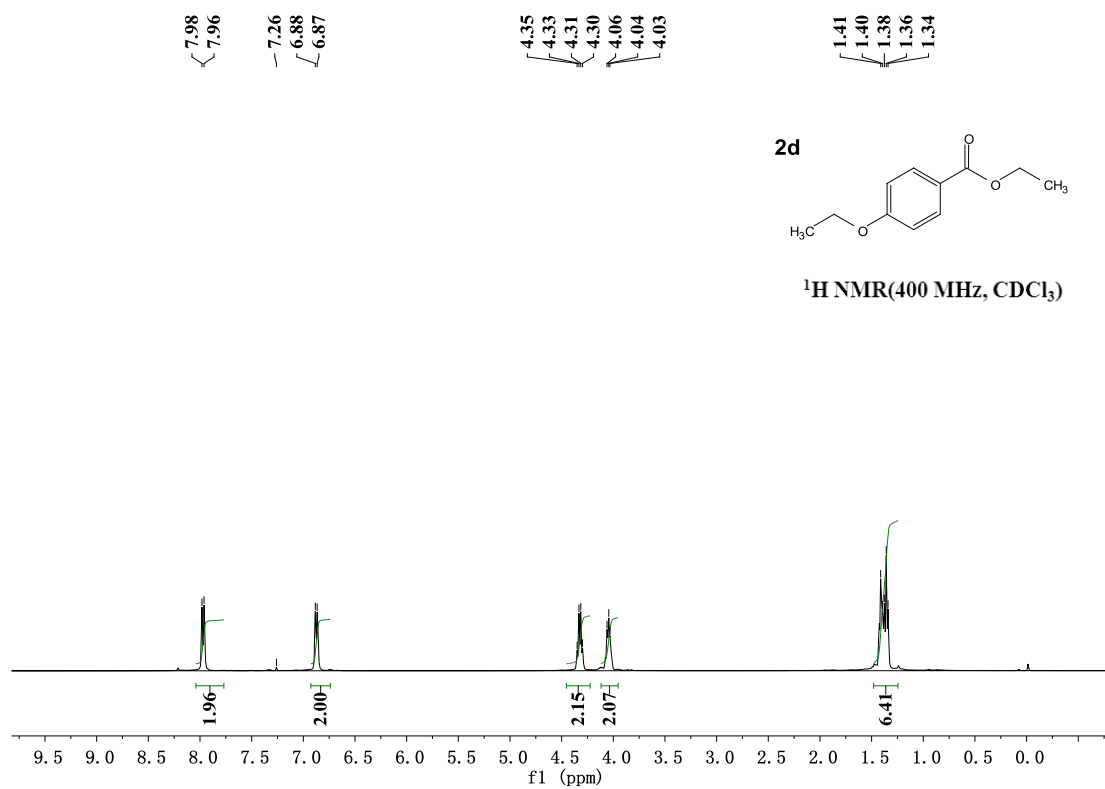
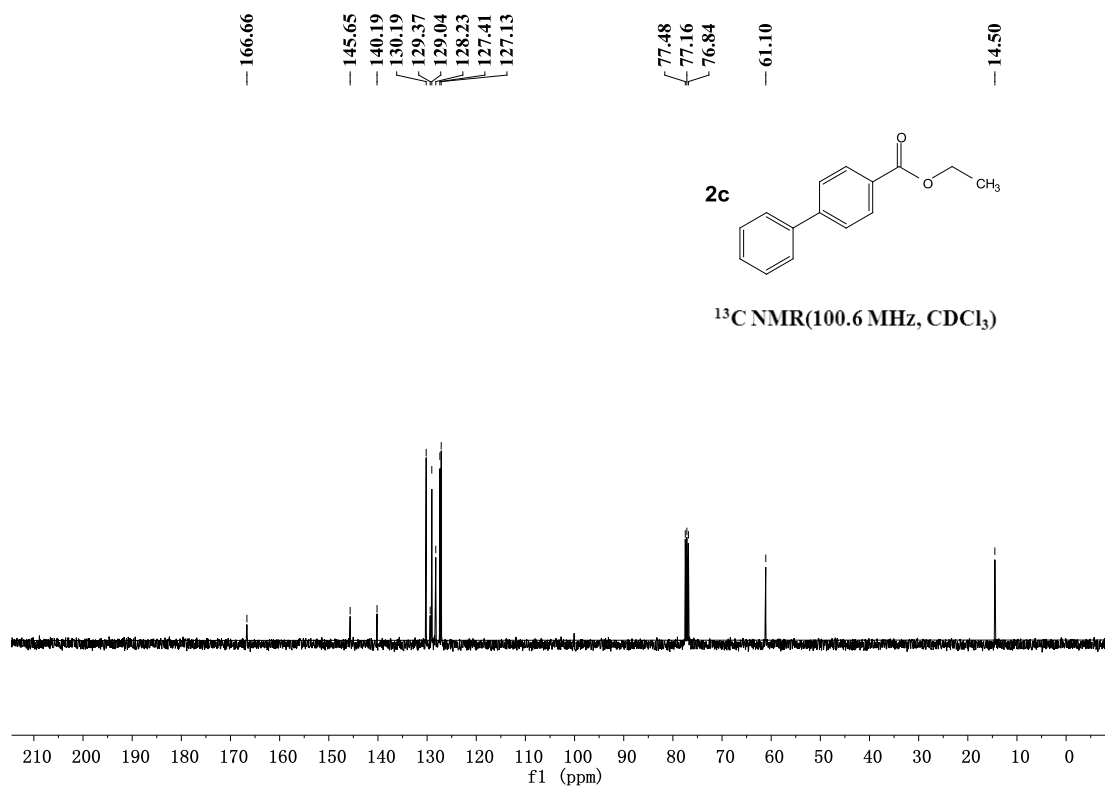
^1H NMR (400 MHz, CDCl_3 , ppm) δ = 8.12 – 7.88 (m, 2H), 7.76 – 7.35 (m, 8H), 5.45 (s, 2H). ^{13}C NMR (100.6 MHz, CDCl_3 , ppm) δ = 186.10, 163.69, 135.01, 134.57, 132.44, 130.06, 128.95, 128.86, 128.79, 128.66, 67.81.

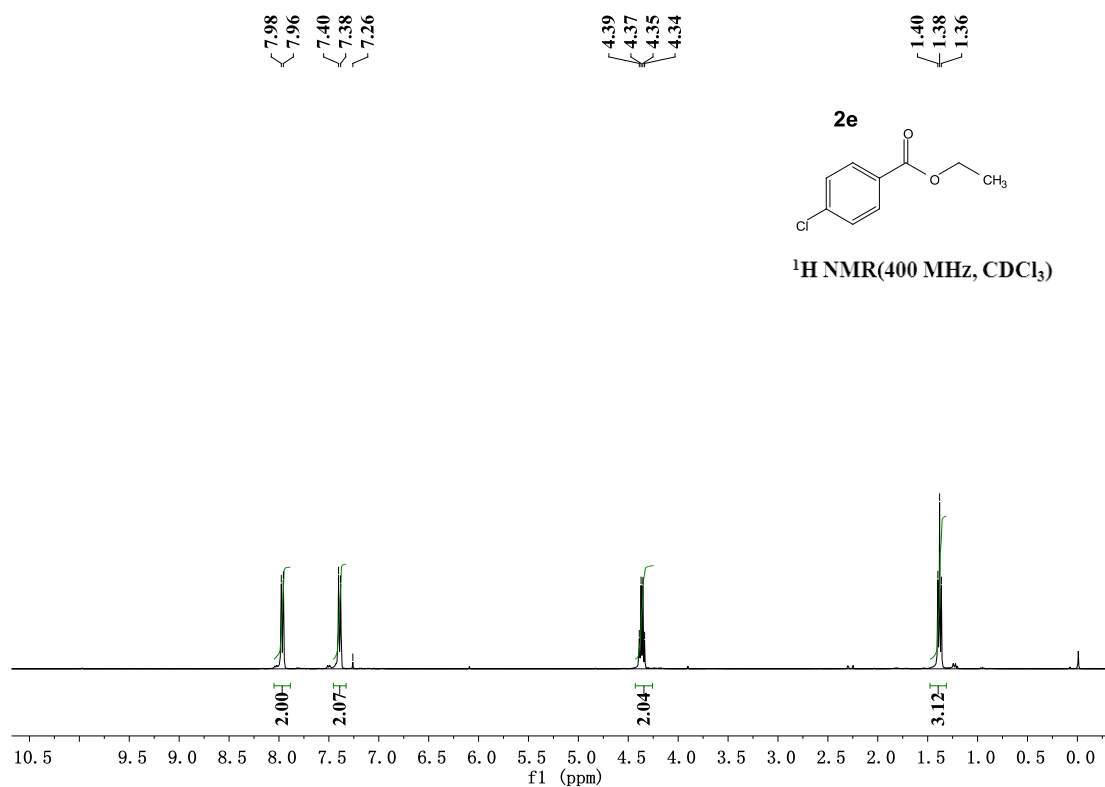
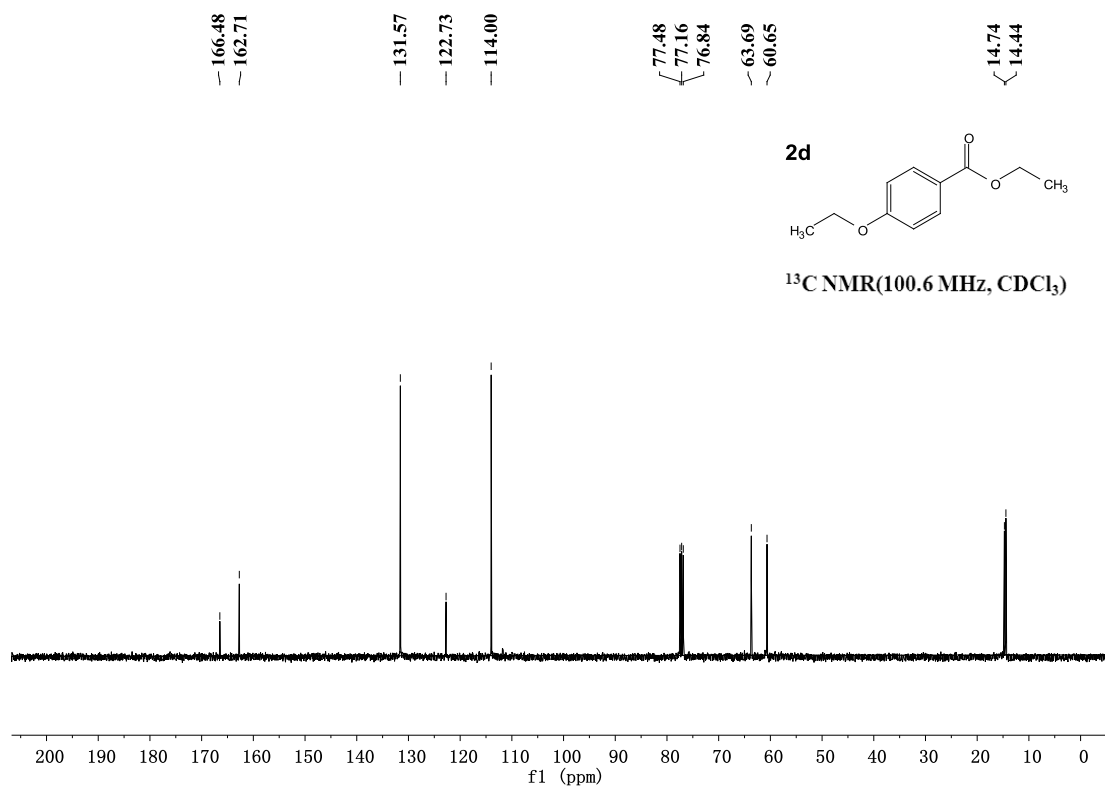
4. NMR and GC-MS Spectra Copies

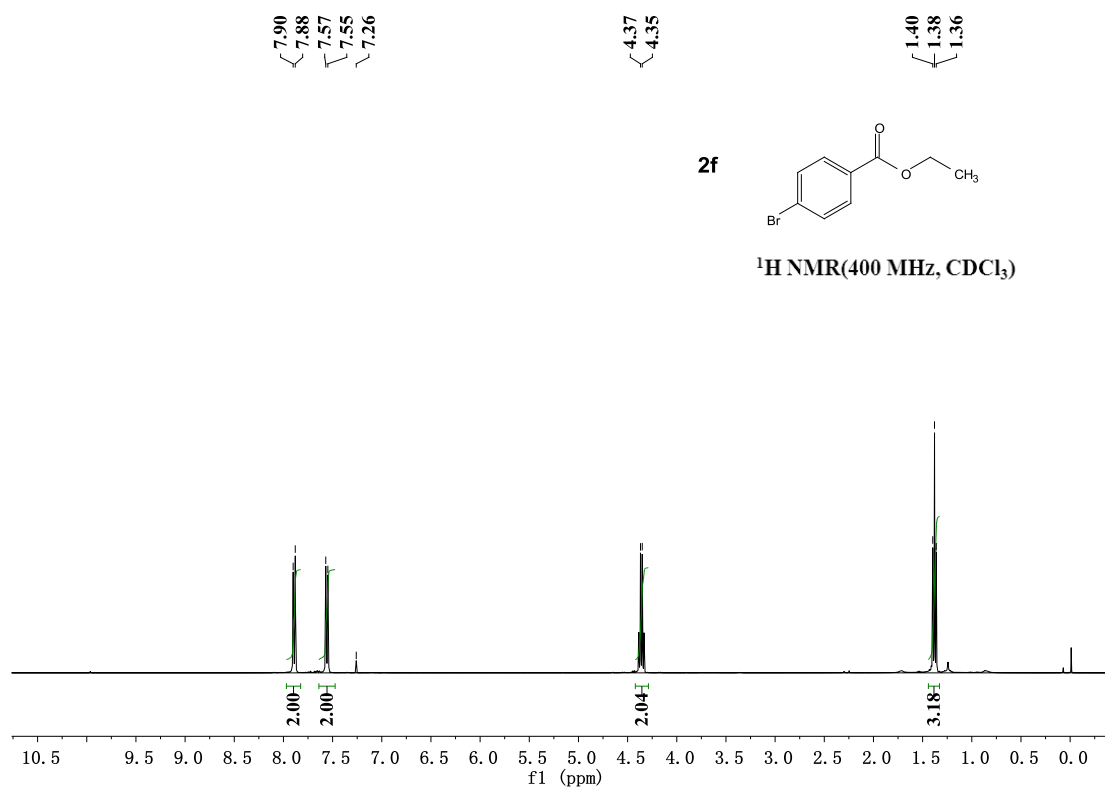
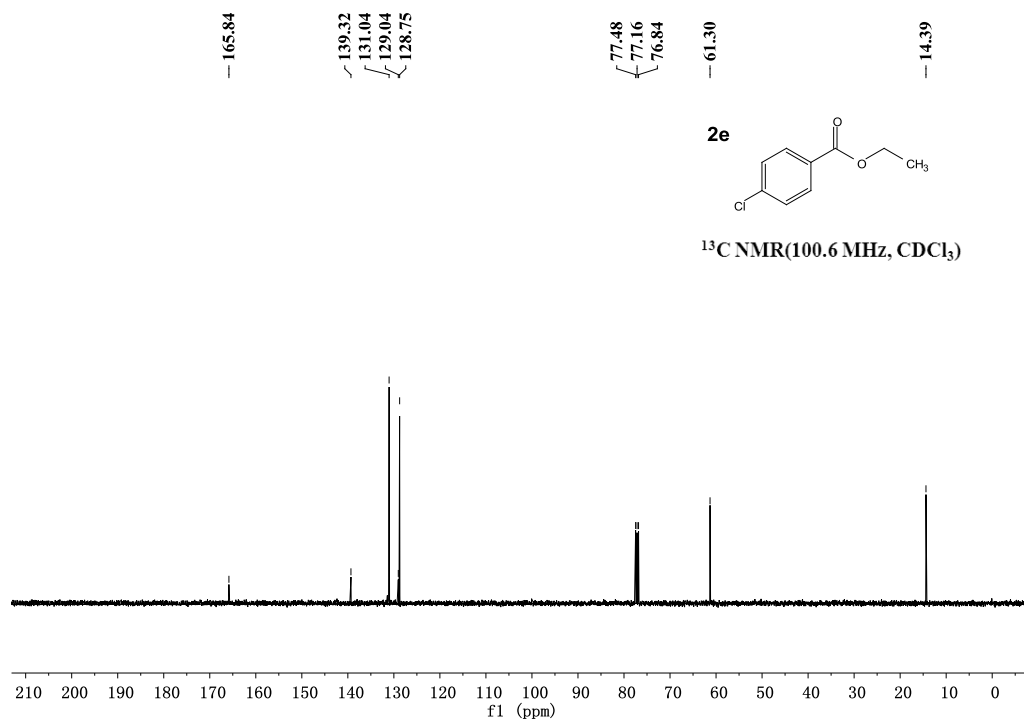


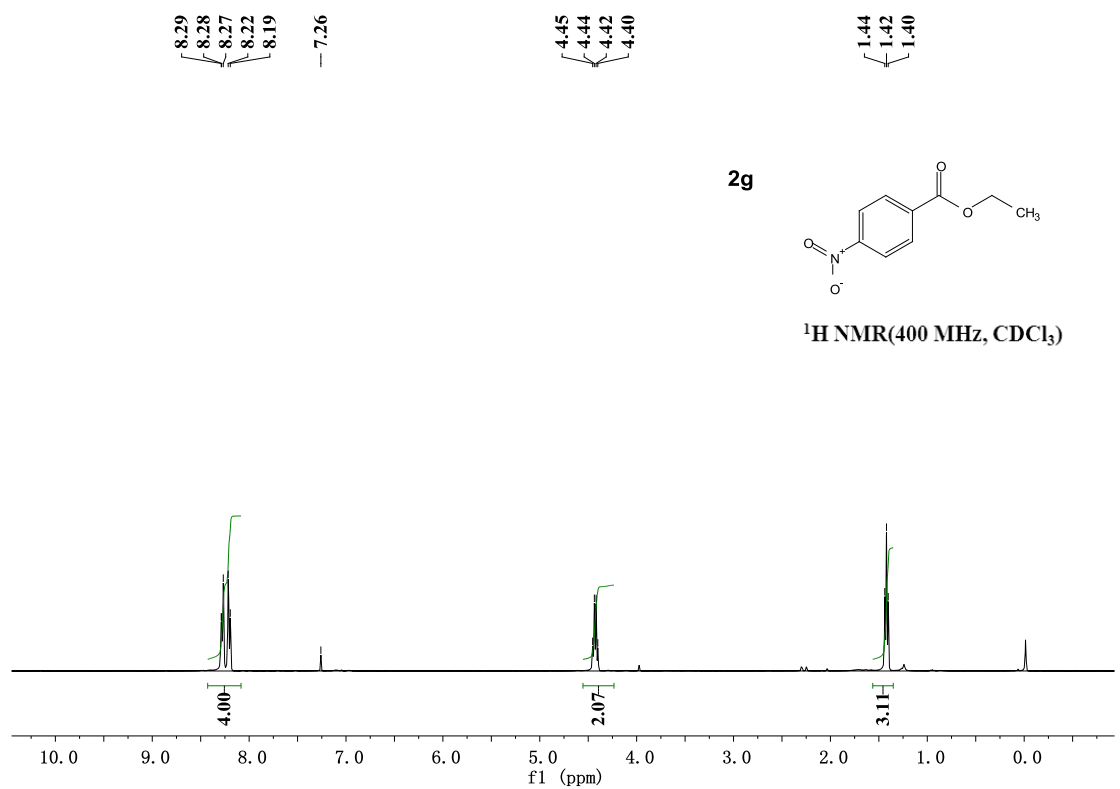
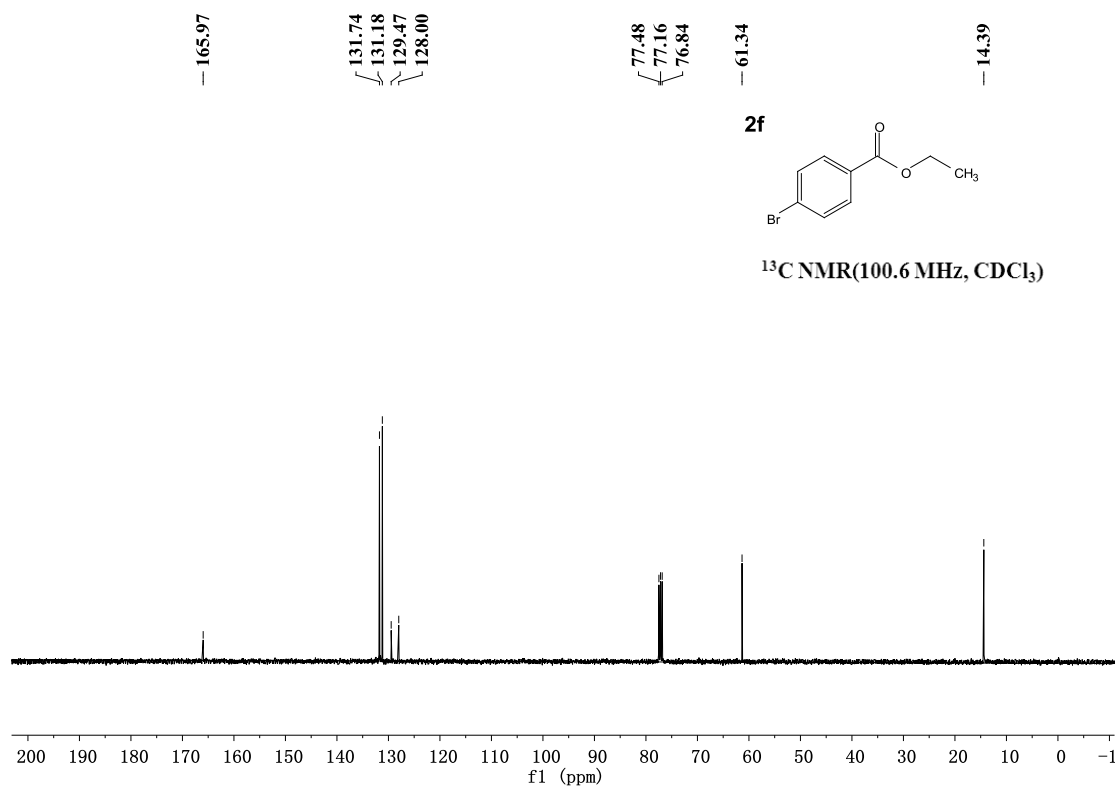


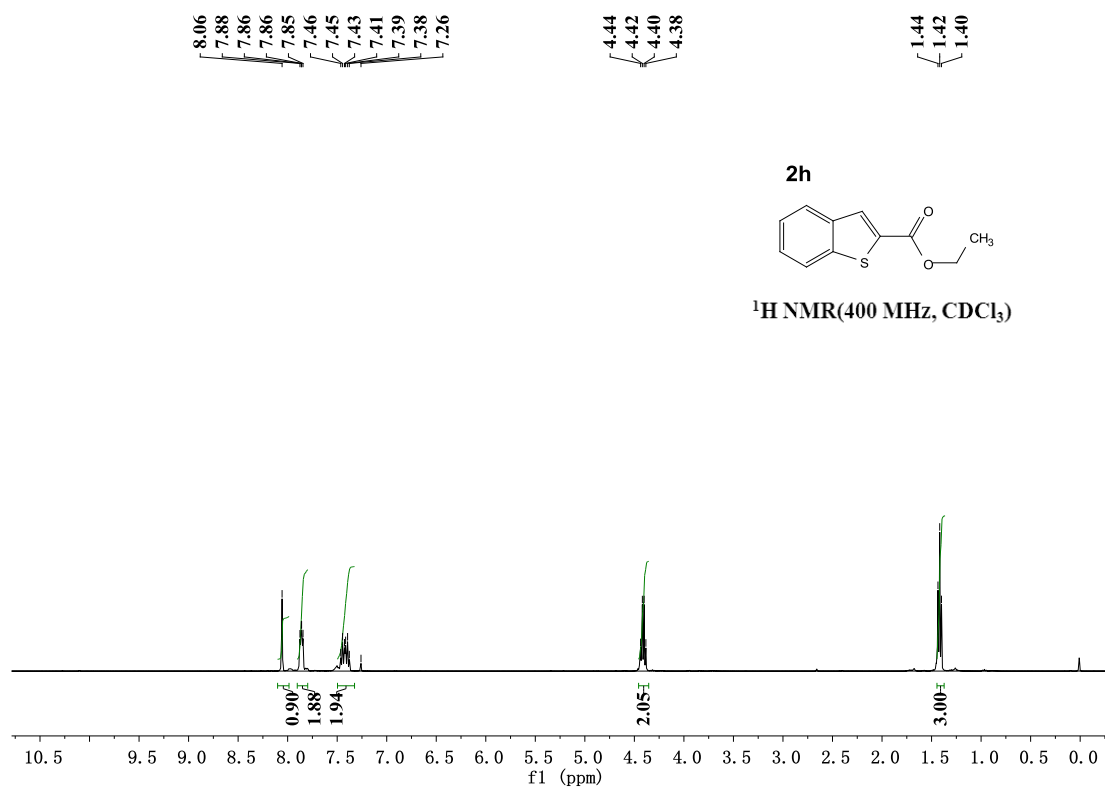
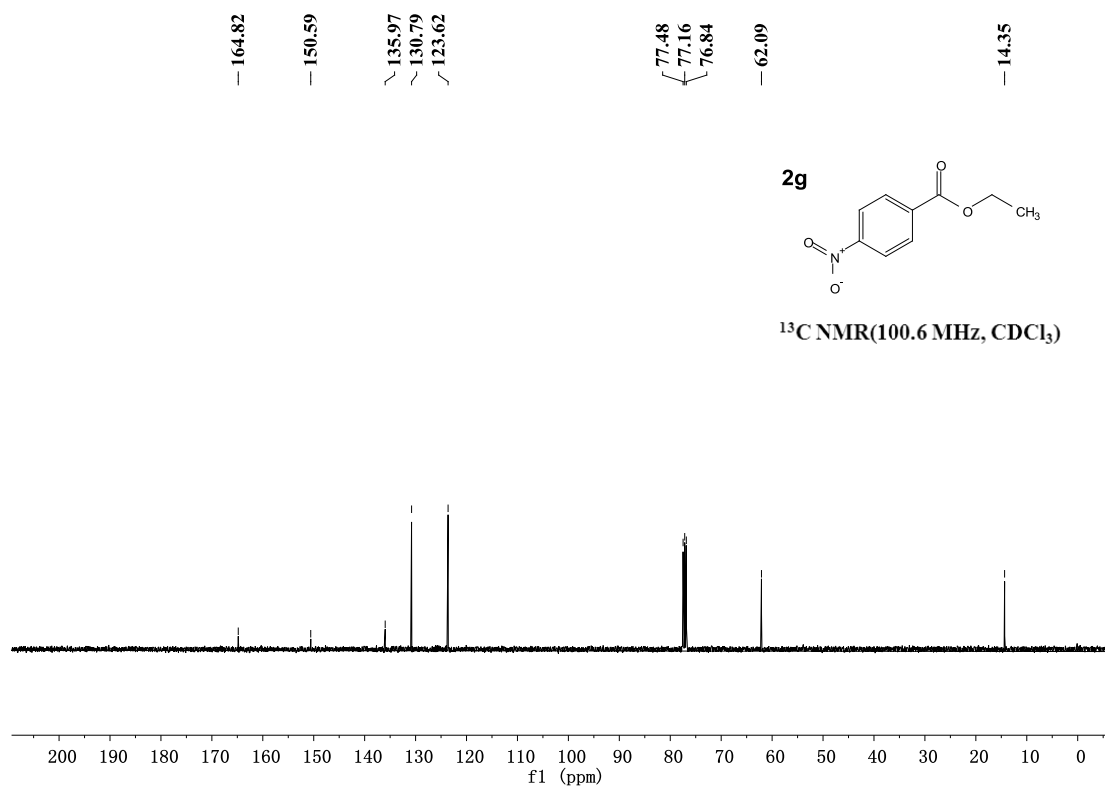


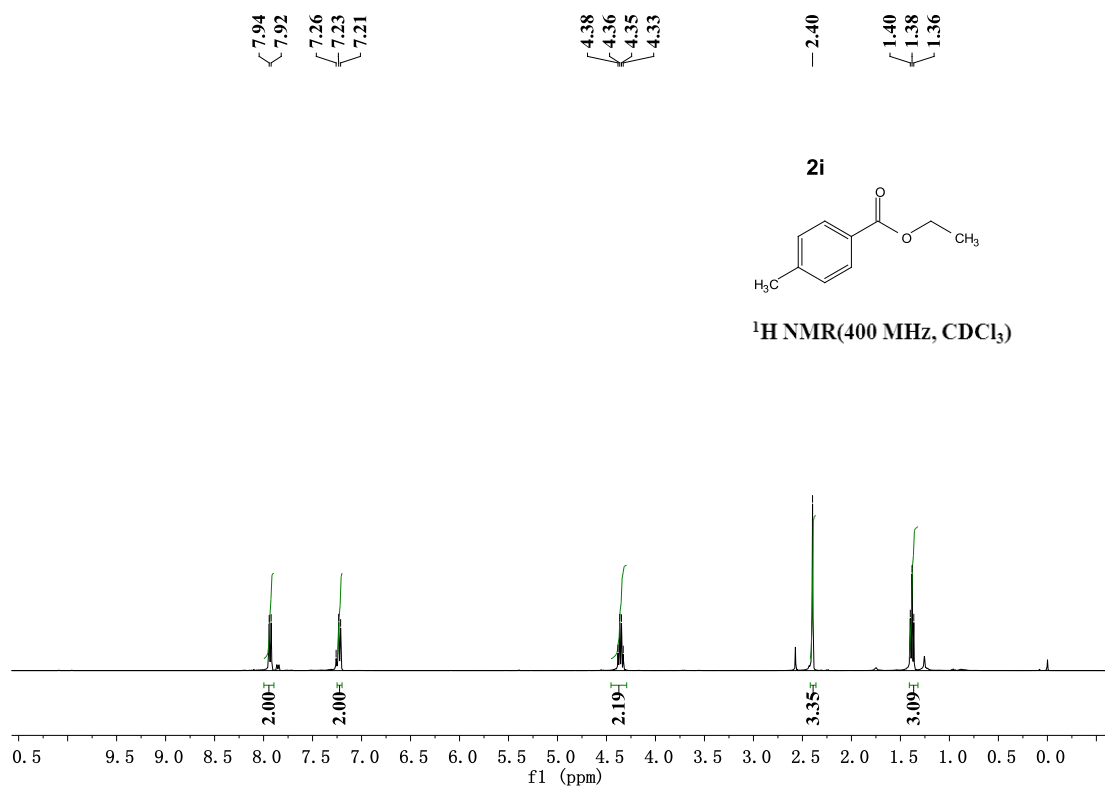
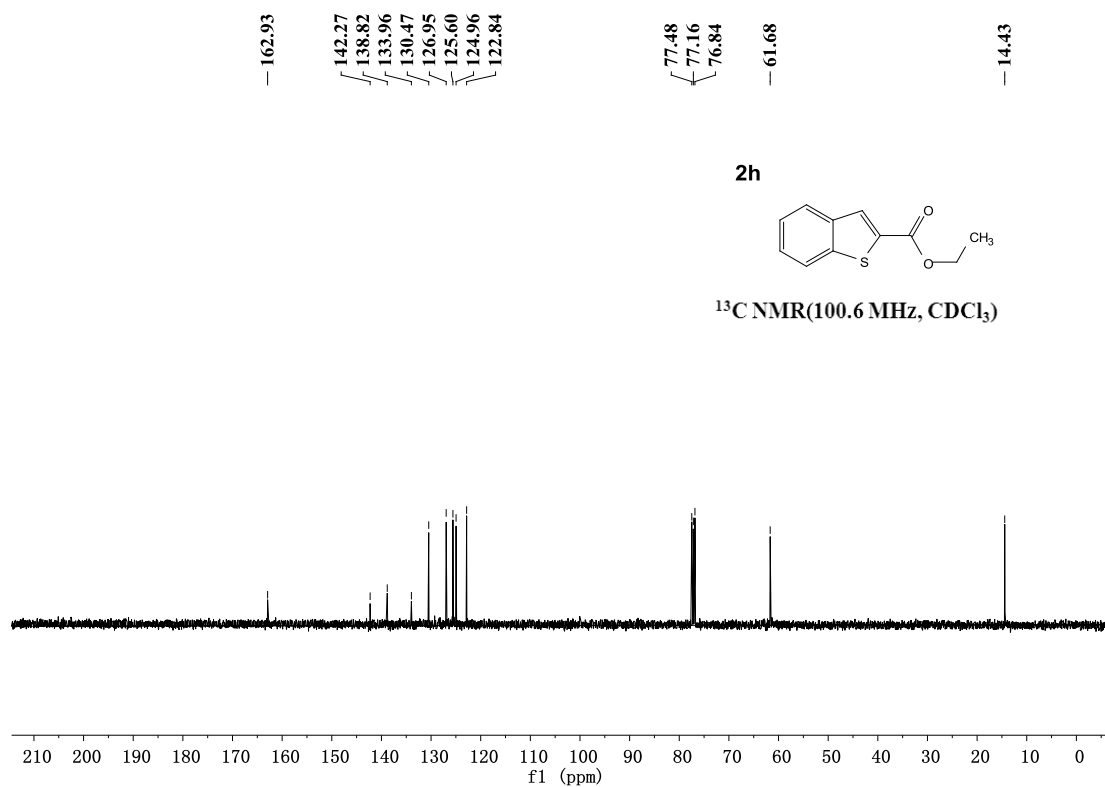


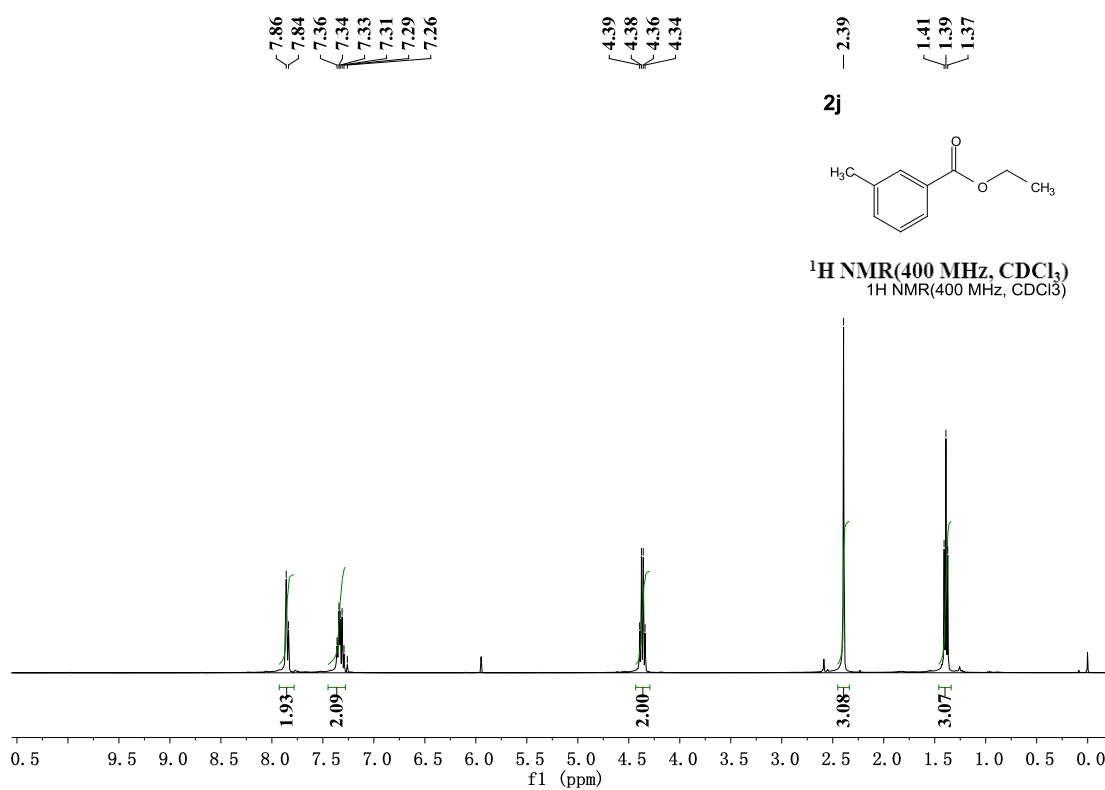
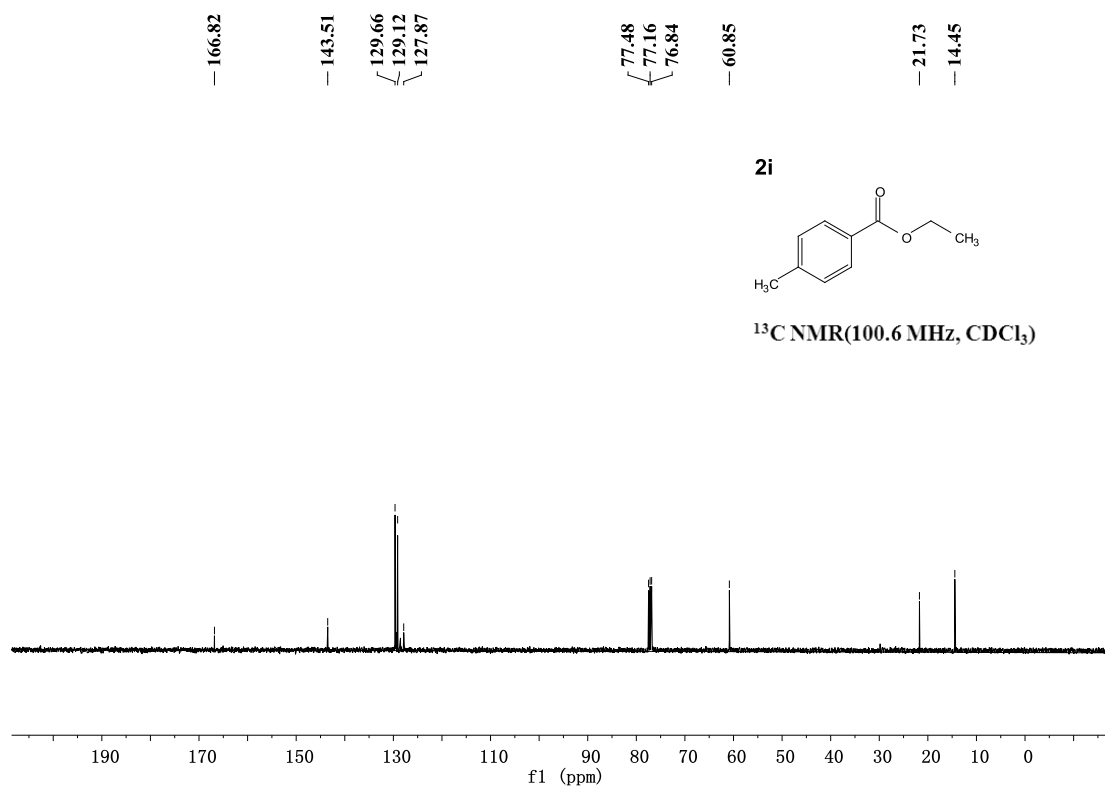


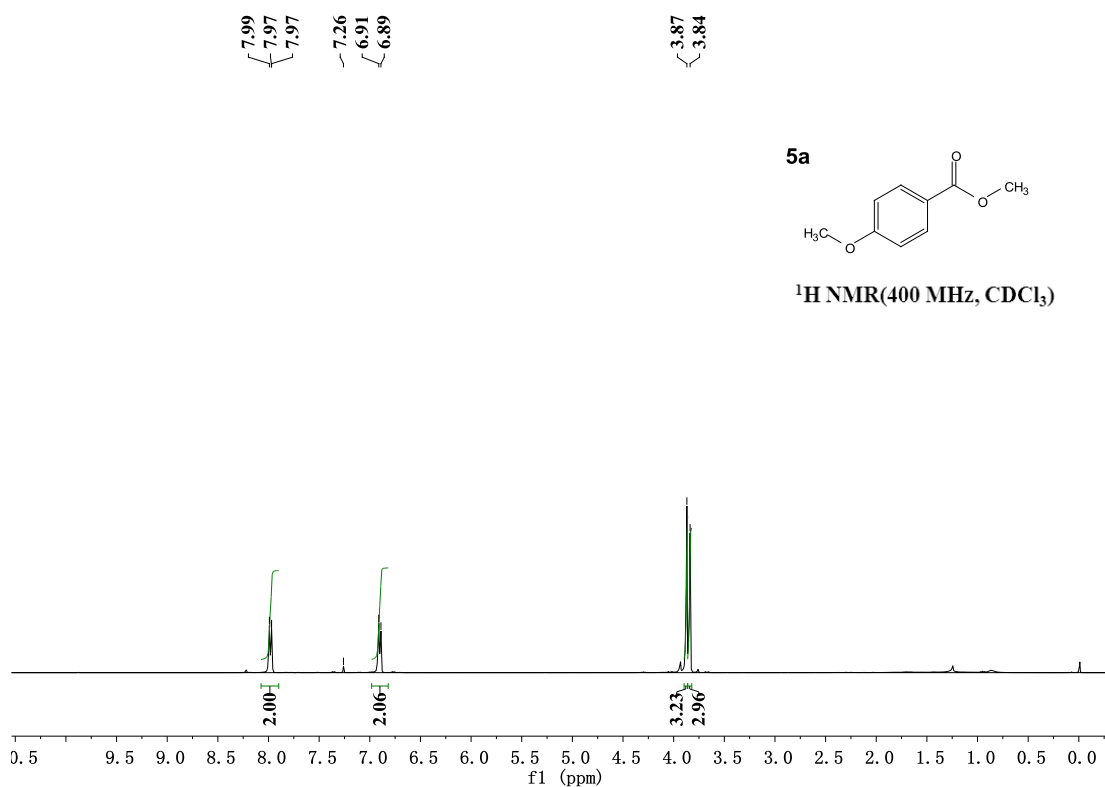
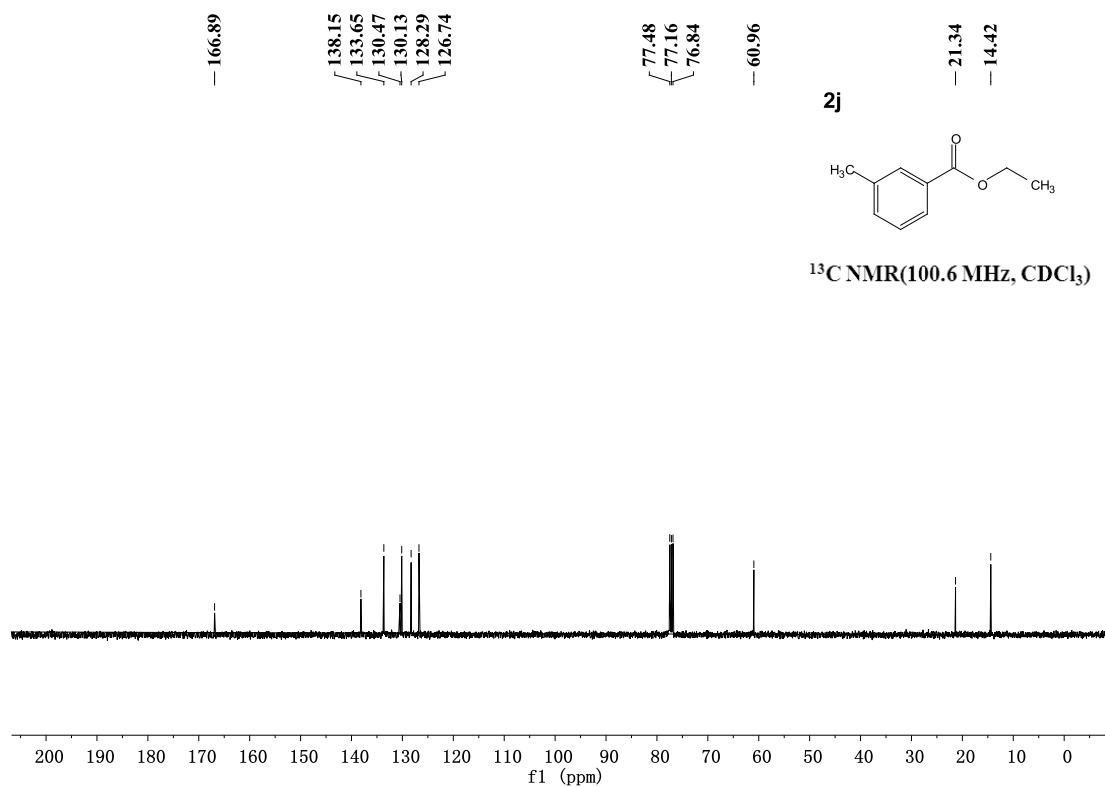


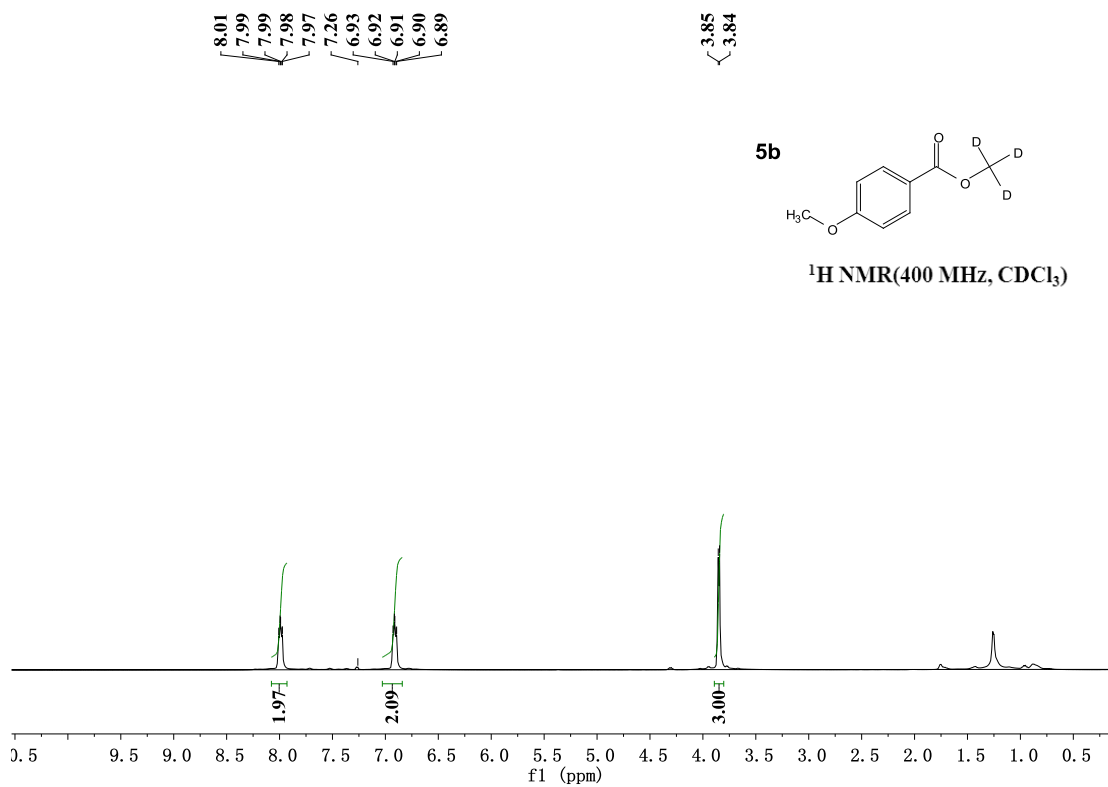
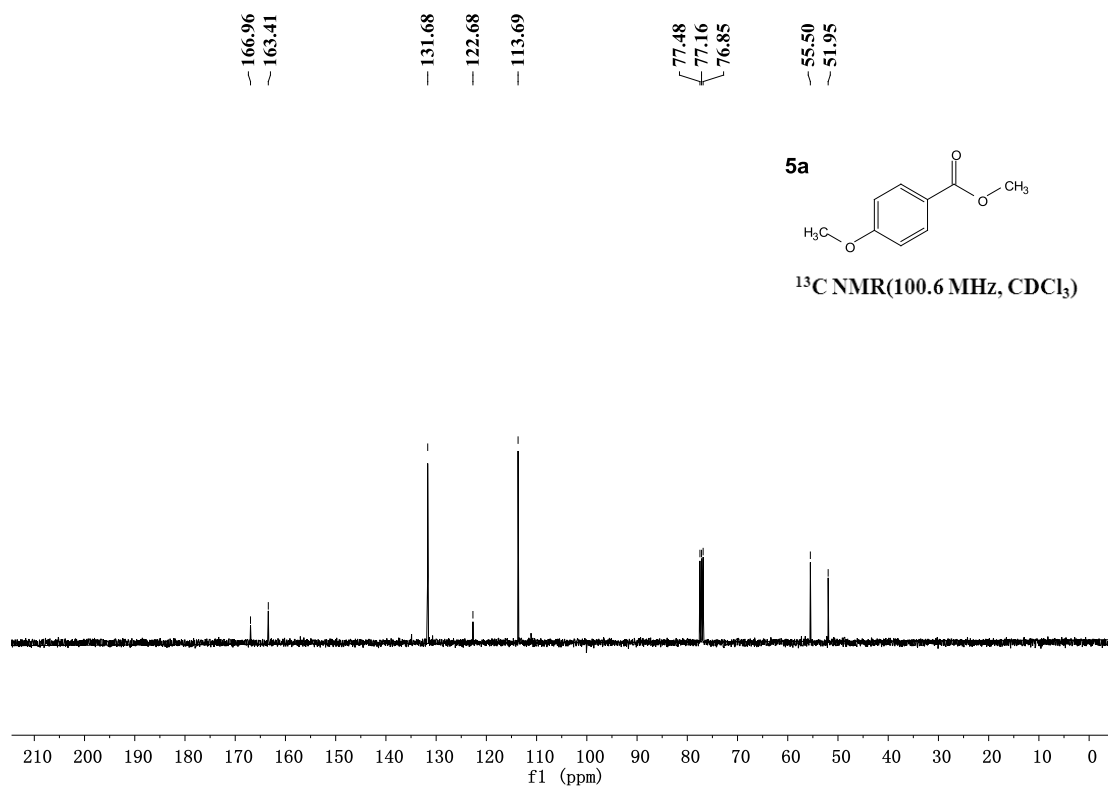


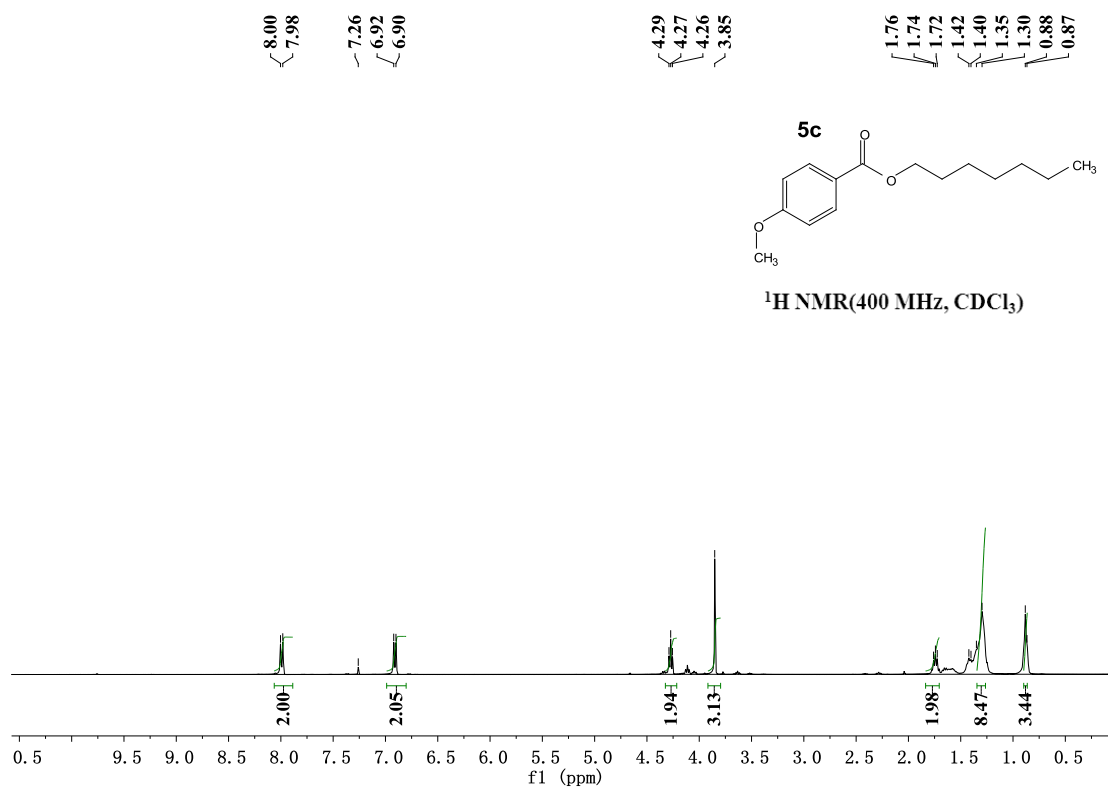
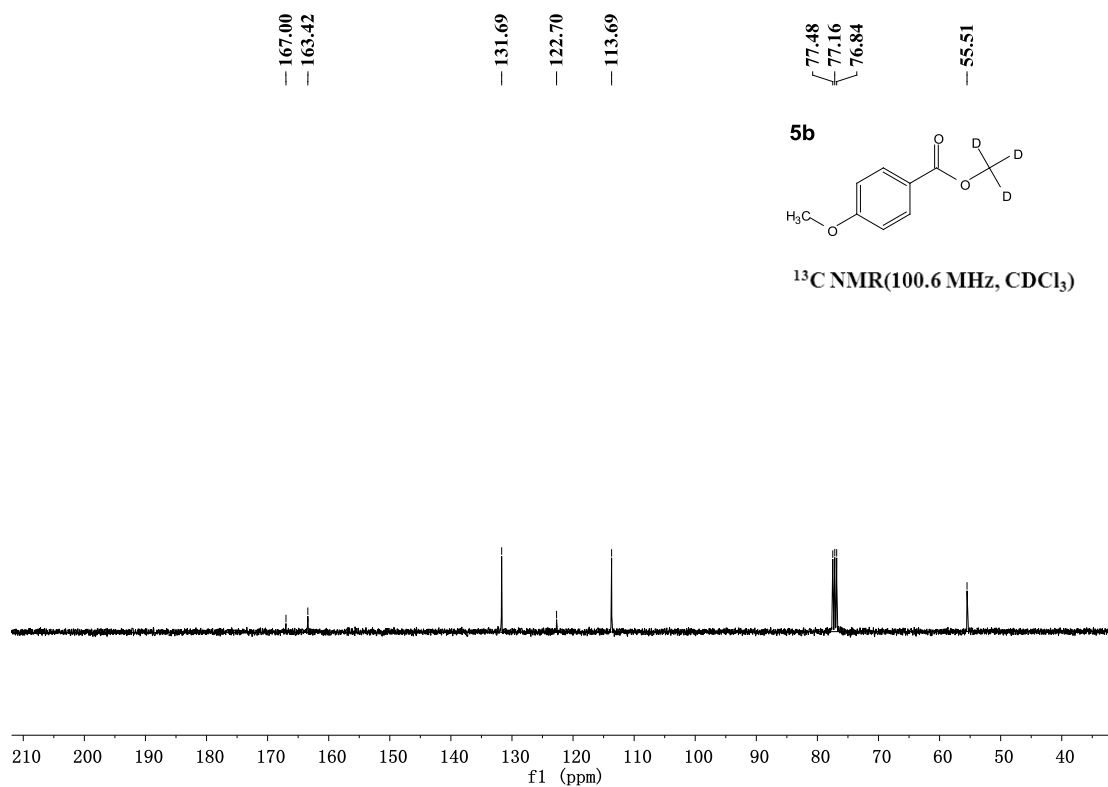


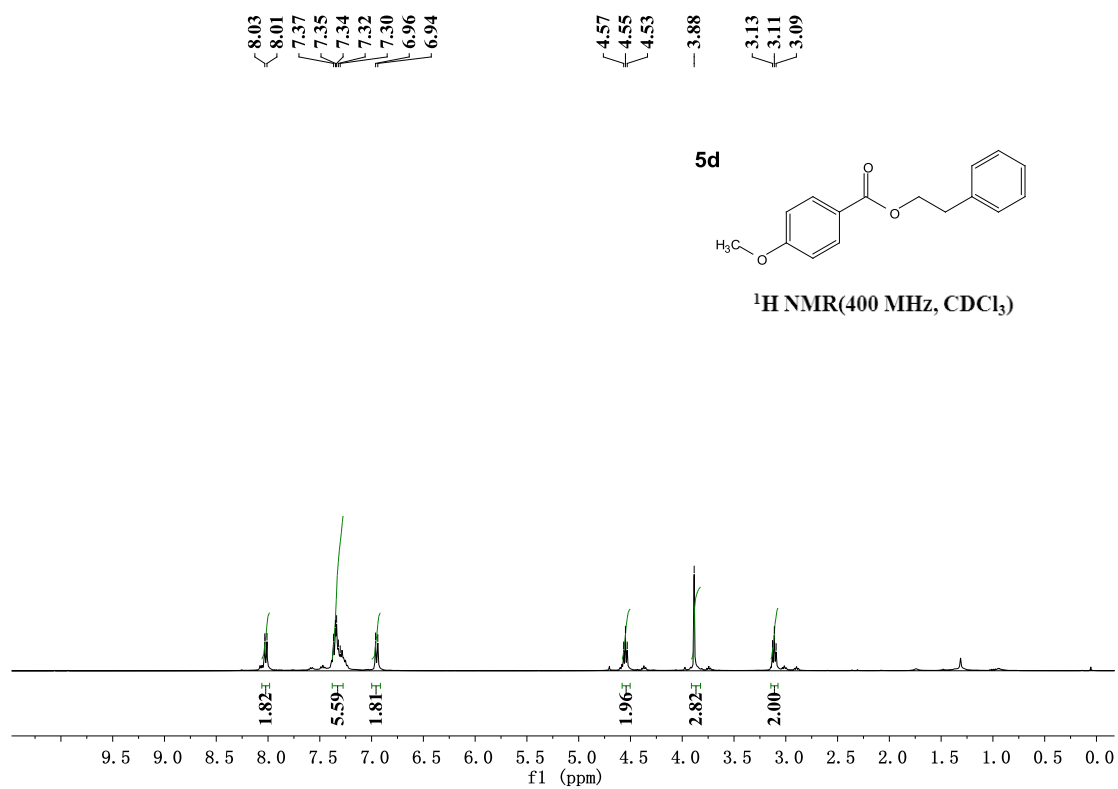
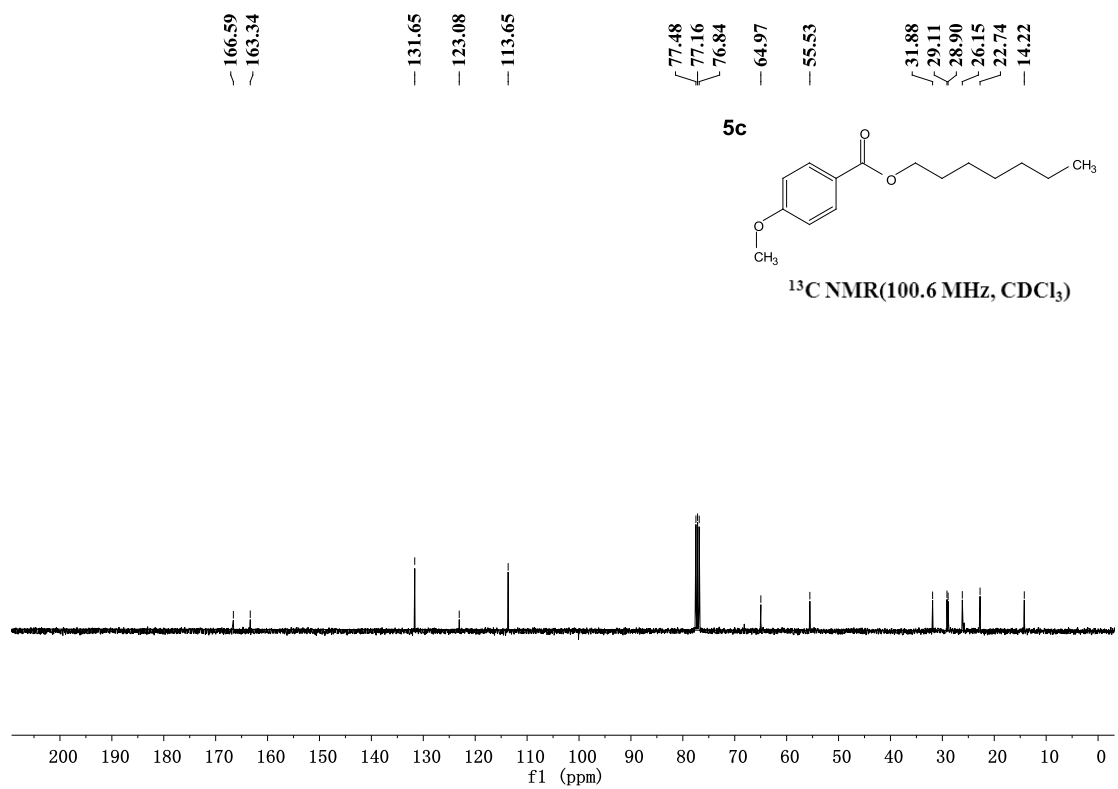






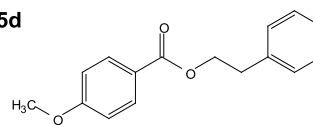




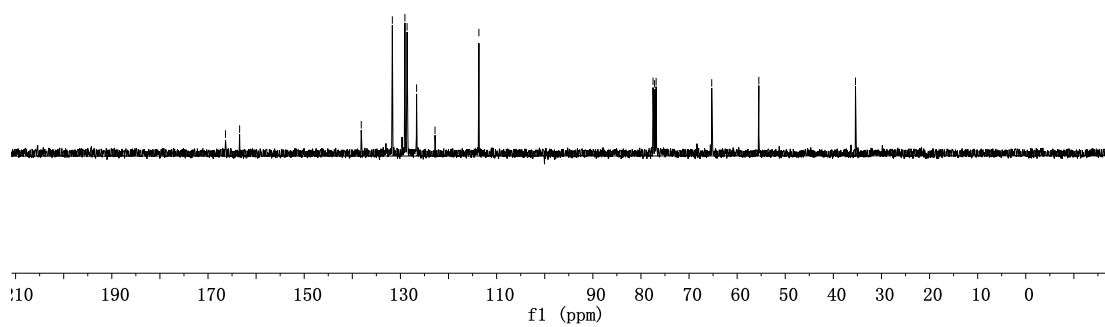


$\sim$ 166.36
 $\sim$ 163.43
 $\sim$ 138.14
 $\sim$ 131.68
 $\sim$ 129.07
 $\sim$ 128.61
 $\sim$ 126.64
 $\sim$ 122.81
 $\sim$ 113.69
77.48
77.16
76.84
— 65.28
— 55.49
— 35.40

5d

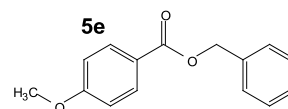


^{13}C NMR(100.6 MHz, CDCl_3)

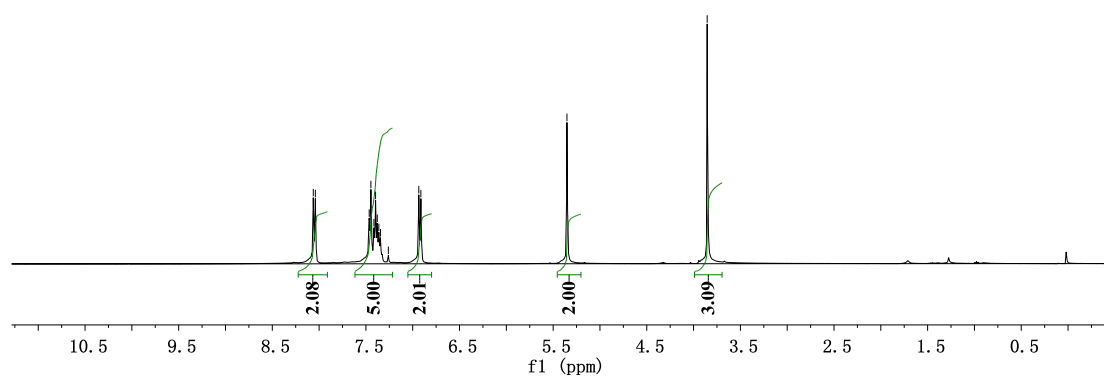


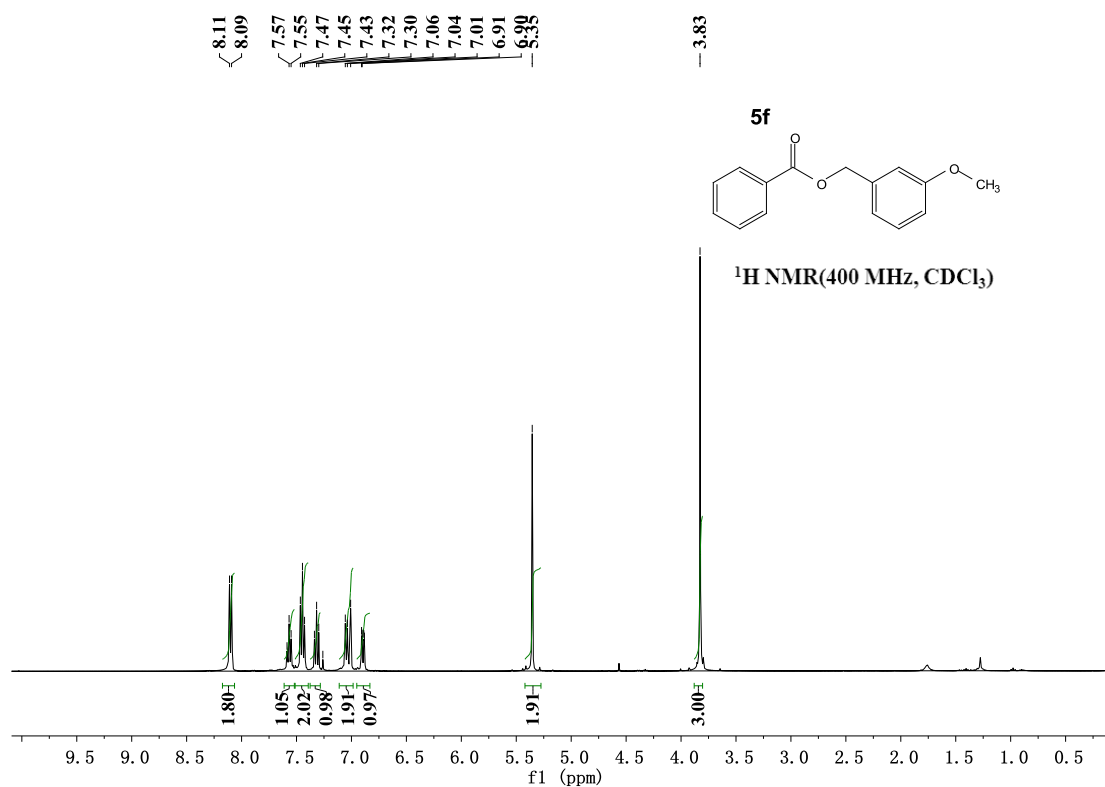
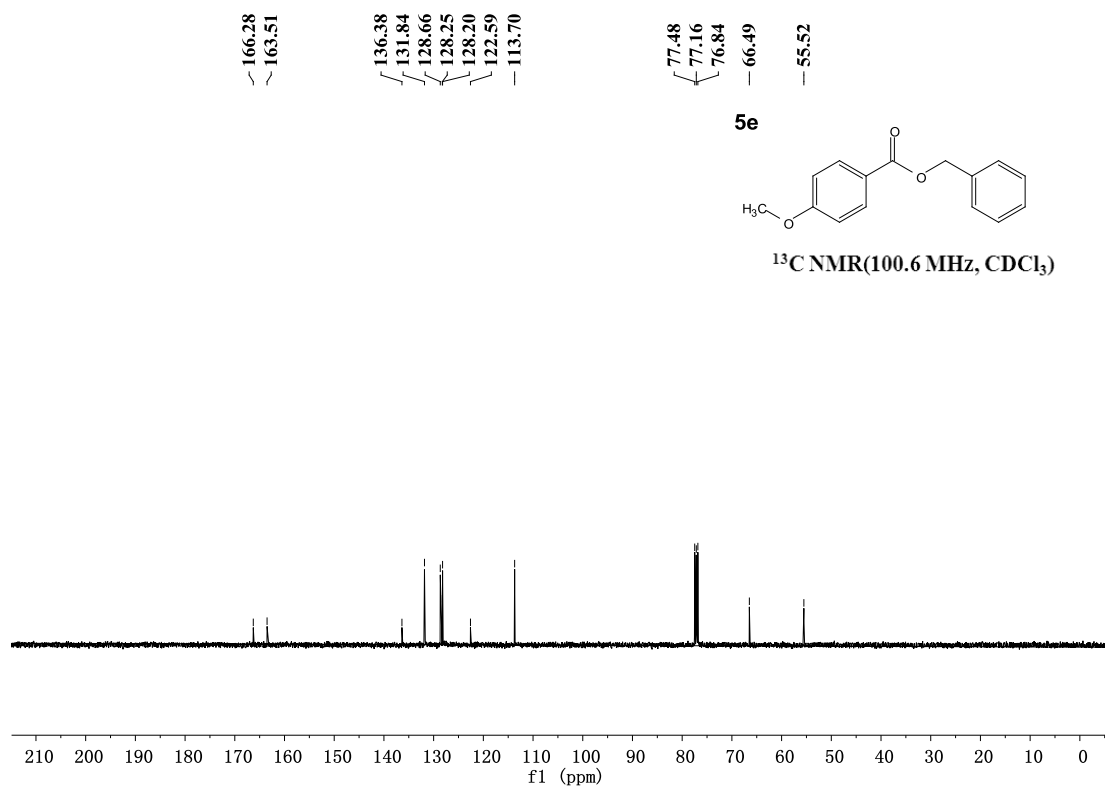
8.06
8.04
7.46
7.45
7.41
7.40
7.38
7.36
7.34
6.94
6.91
5.35
— 3.85

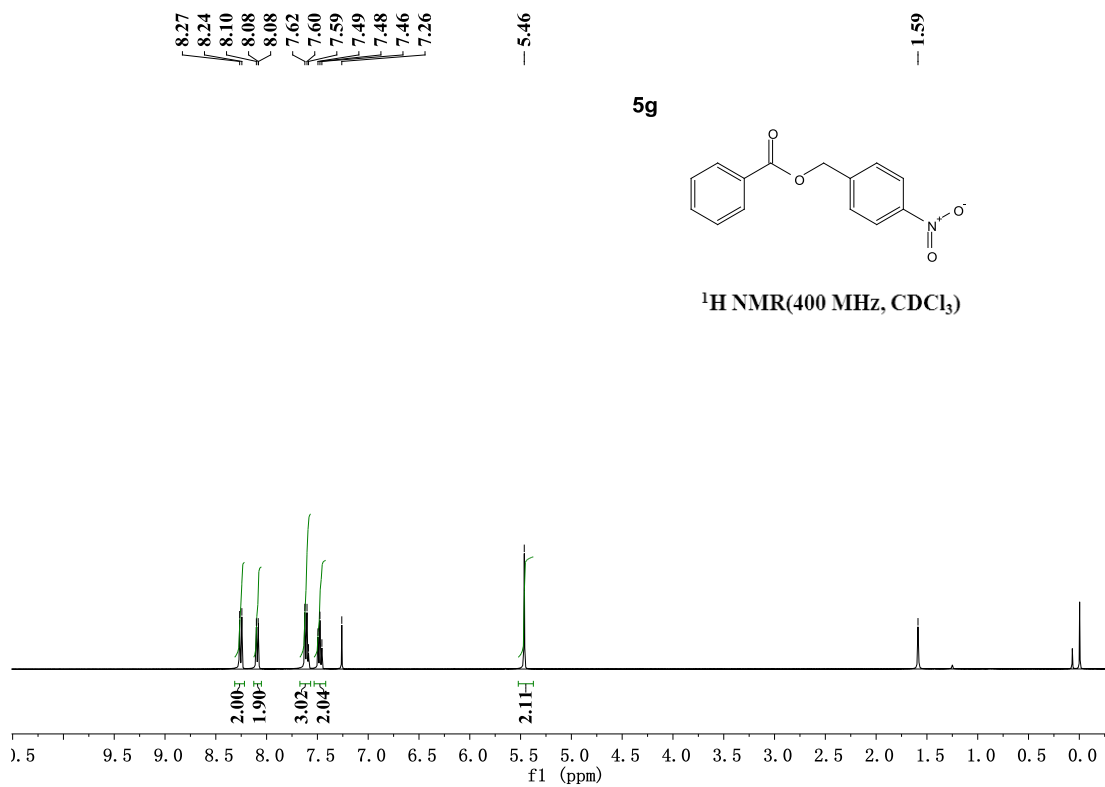
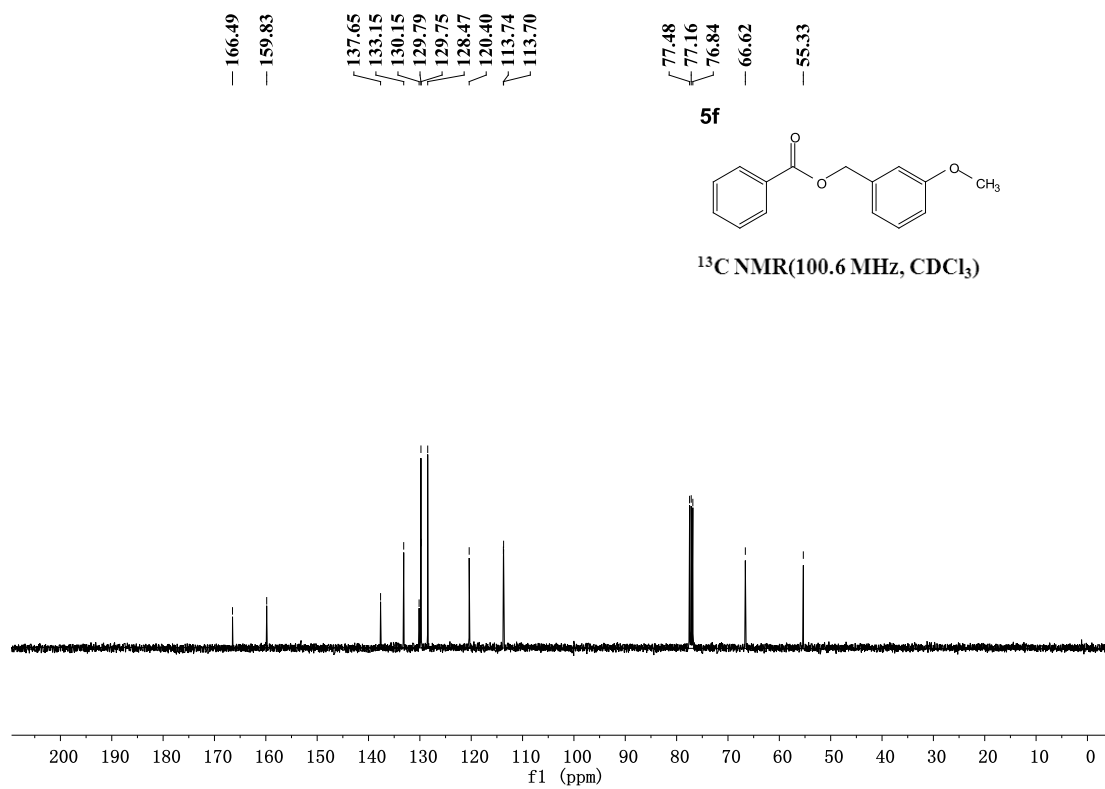
5e

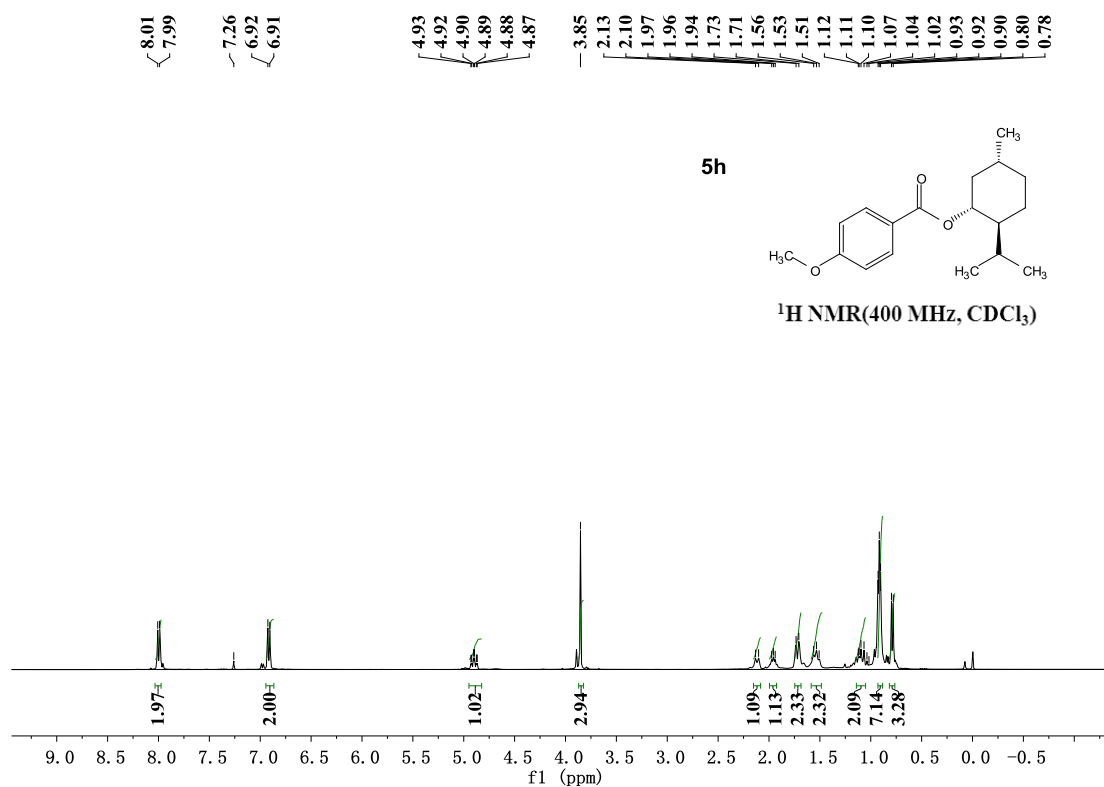
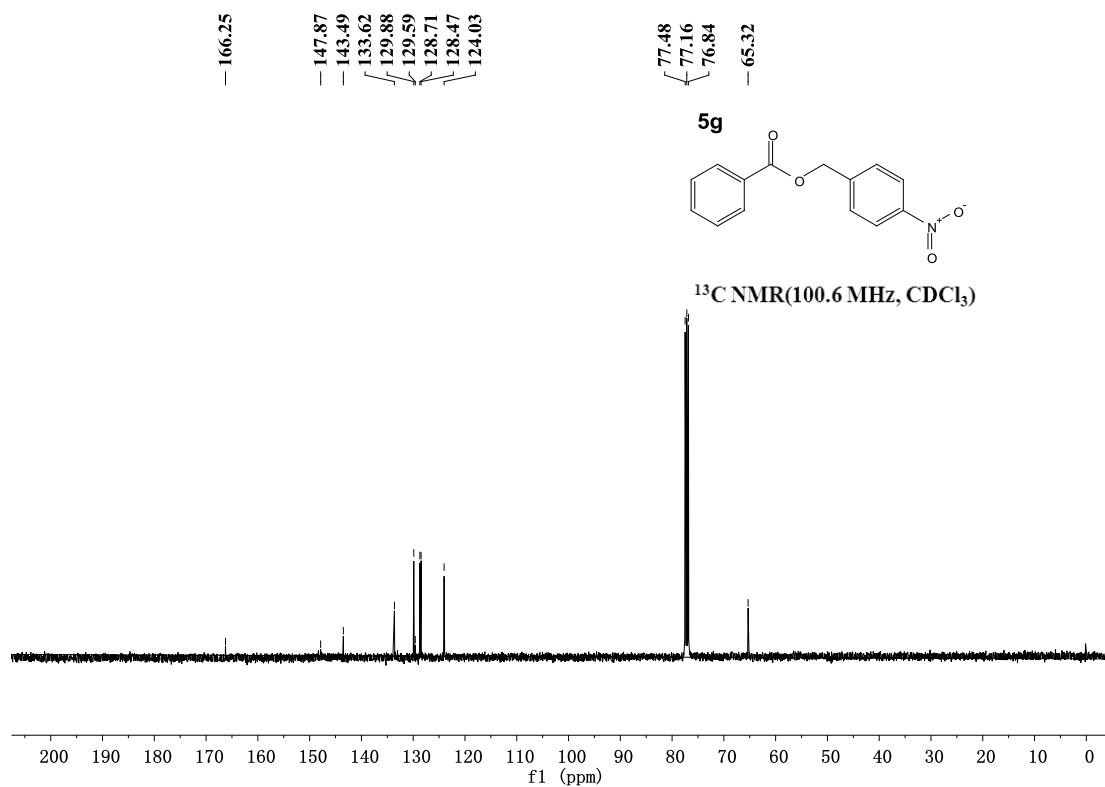


^1H NMR(400 MHz, CDCl_3)

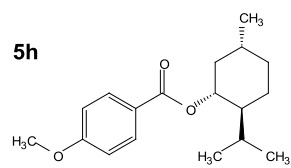




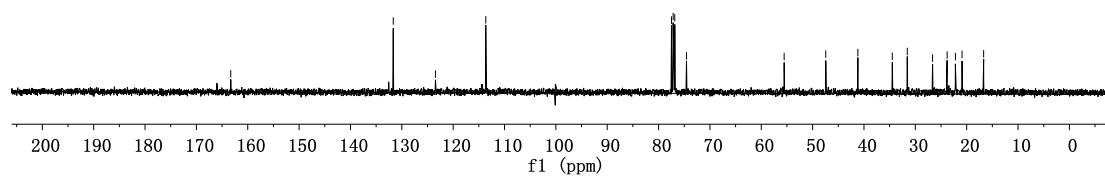




— 163.31
 — 131.67
 — 123.44
 — 113.65
 77.48
 77.16
 76.84
 74.56
 55.54
 47.44
 41.19
 34.48
 31.57
 26.64
 23.81
 22.19
 20.90
 16.70

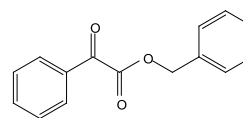


^{13}C NMR(100.6 MHz, CDCl_3)

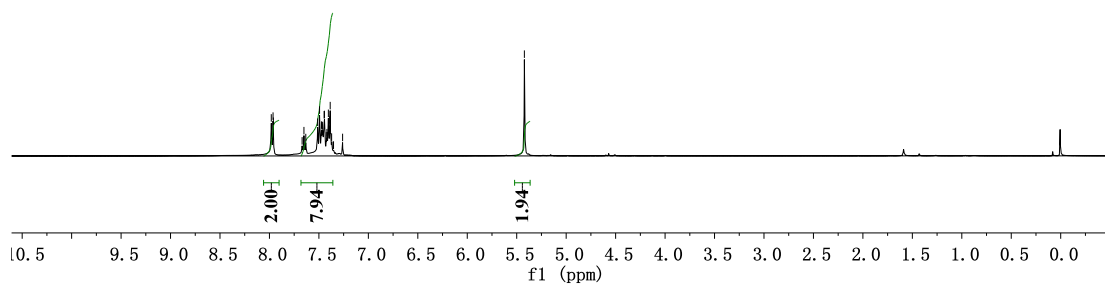


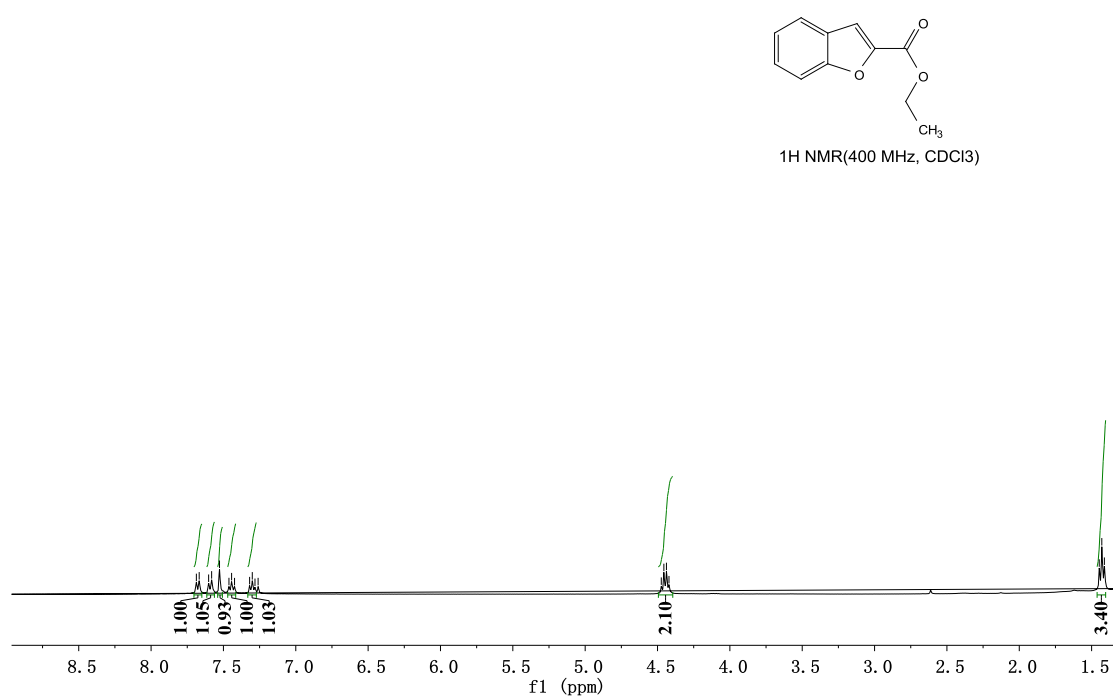
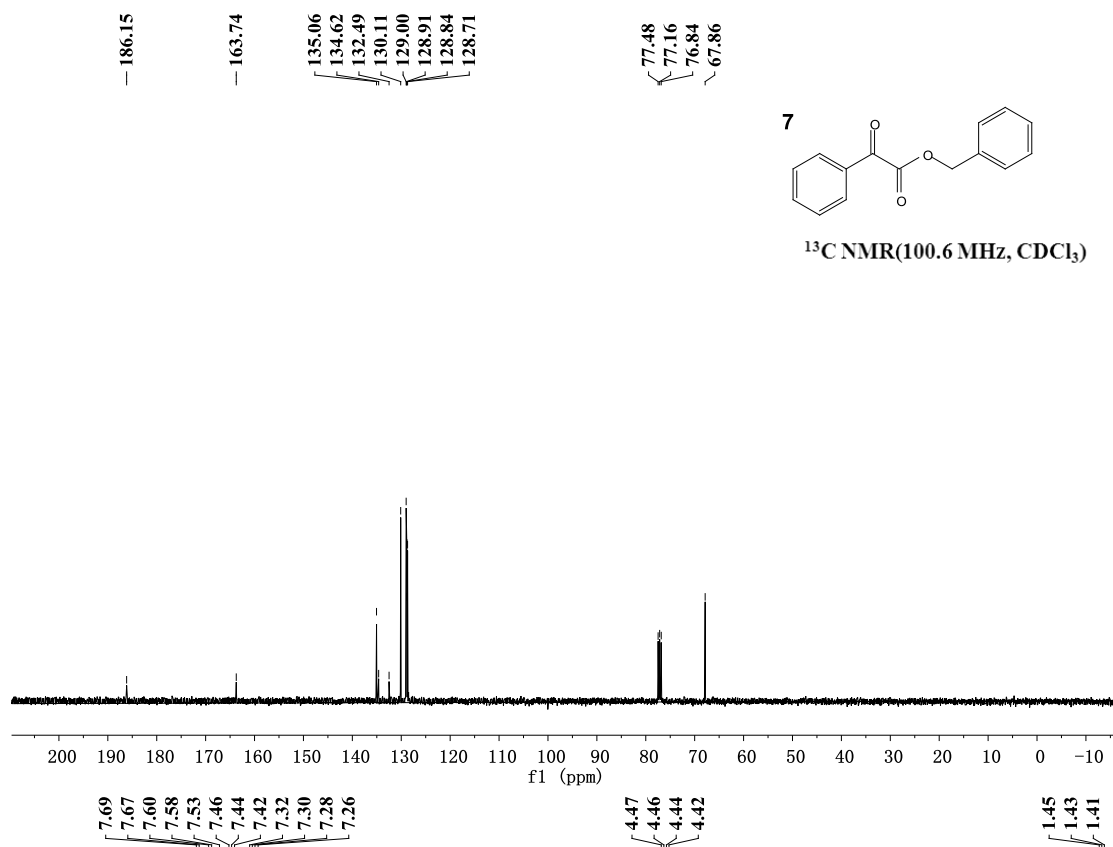
7.98
 7.96
 7.96
 7.67
 7.65
 7.63
 7.51
 7.49
 7.47
 7.47
 7.46
 7.45
 7.44
 7.43
 7.42
 7.41
 7.40
 7.39
 7.37
 7.35
 7.26
 5.42

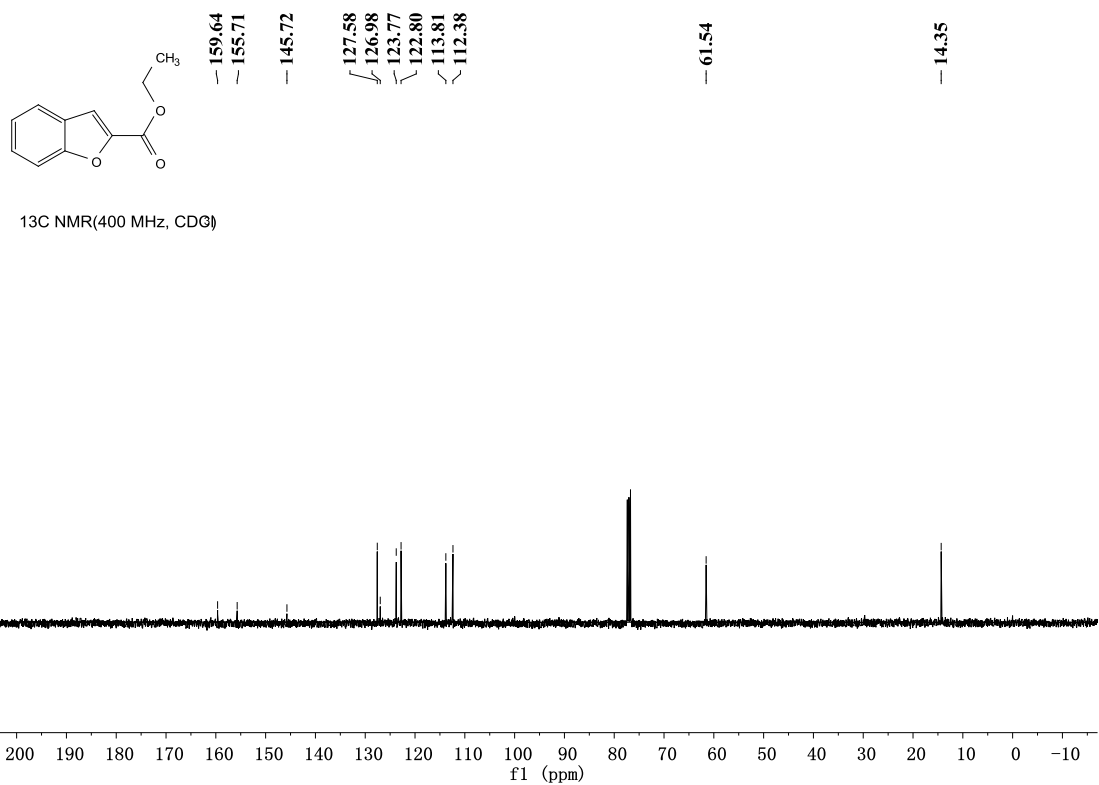
7



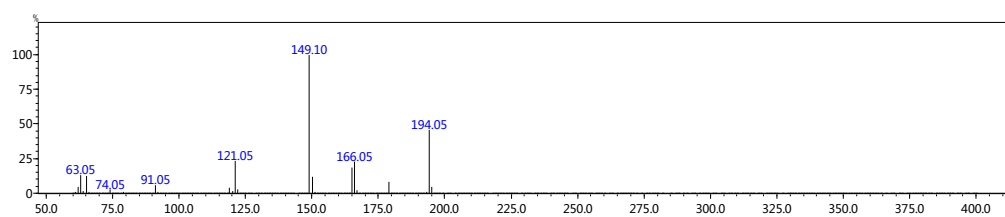
^1H NMR(400 MHz, CDCl_3)



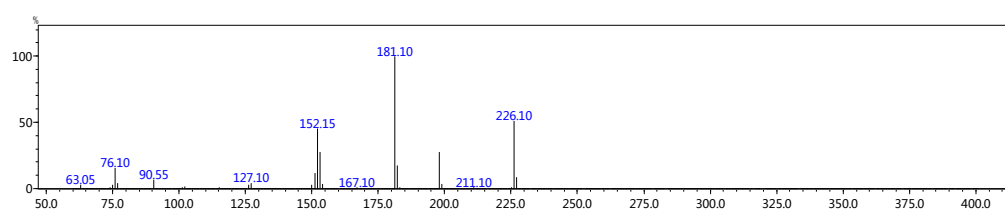




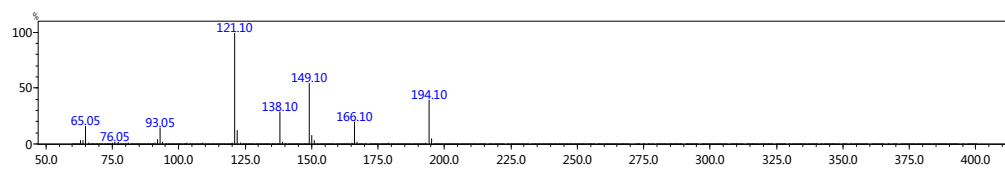
ethyl benzo[d][1,3]dioxole-5-carboxylate (2b)



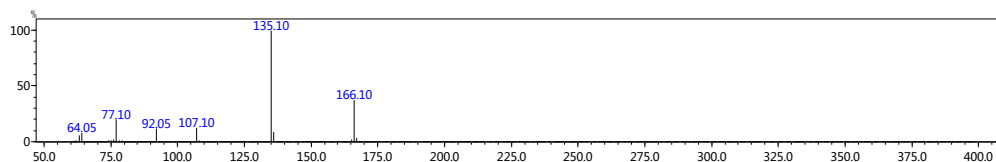
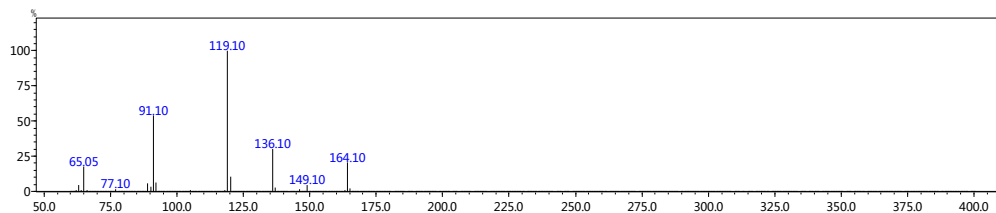
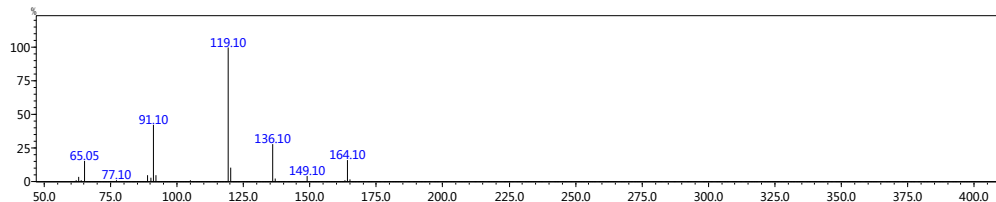
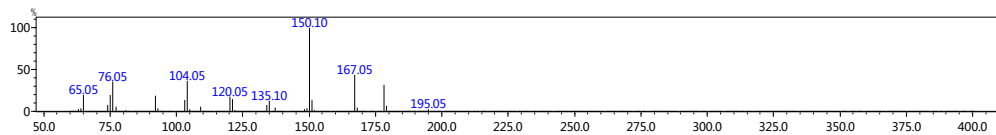
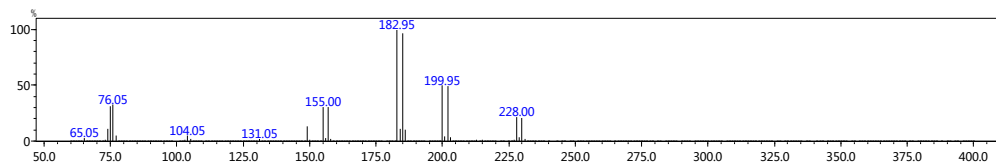
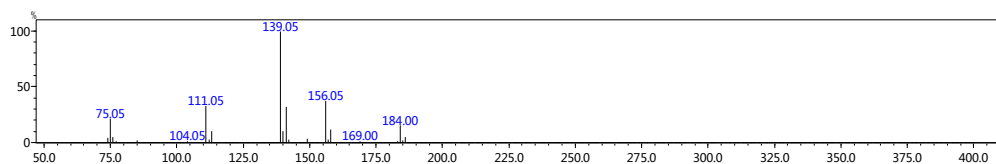
ethyl [1,1'-biphenyl]-4-carboxylate(2c)



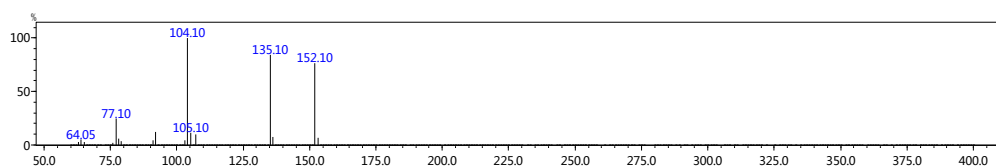
ethyl 4-ethoxybenzoate (2d)



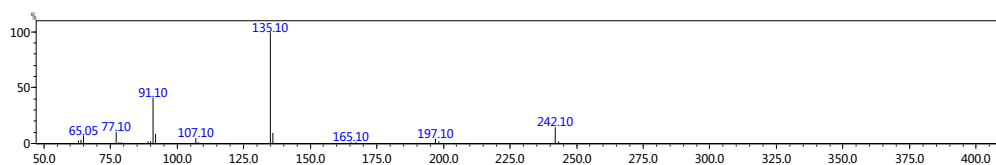
ethyl 4-chlorobenzoate (2e)



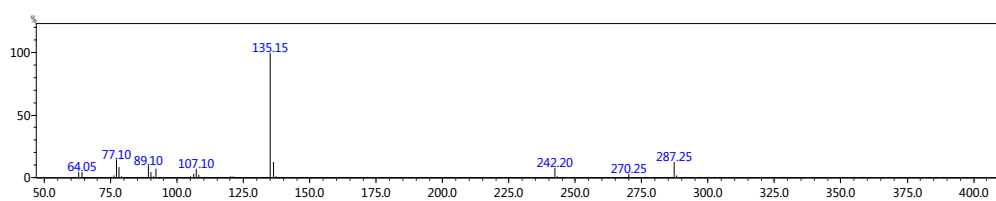
phenethyl 4-methoxybenzoate (5d)



benzyl 4-methoxybenzoate (5e)



4-nitrobenzyl benzoate (5g)



5. Reference

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