Supporting Information for

Photoinduced Reductive Reformatsky Reaction of α-Haloesters and Aldehydes or Ketones by Cooperative Dual-Metal Catalysis

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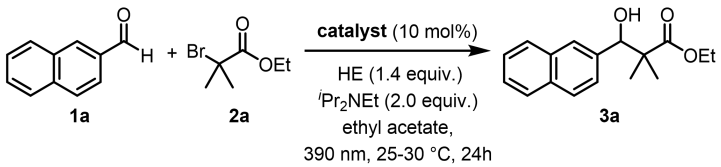
1. General Information

All moisture or air sensitive reactions were carried out under an argon atmosphere in oven-dried flasks. Except for commercially available ultradry solvents (DMF, DMSO, 1,4-dioxane, ethyl acetate, and CH_3CN), all solvents were purified by standard methods as indicated and were transferred under argon. Toluene and THF were distilled from sodium, while DCM was distilled from CaH_2. All other commercially available reagents were used as received without further purification unless otherwise noted. All reactions were monitored by thin-layer chromatography (TLC) on silica gel F_{254} plates using UV light as visualizing agent (if applicable). The products were purified by flash column chromatography on silica gel (200-300 meshes).

^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Bruker AVANCE^{III} 400 MHz, Bruker AVANCE^{III} HD 400 MHz or Bruker AVANCE NEO 600 MHz instrument. Chemical shifts were denoted in ppm (δ) and calibrated by using residual undeuterated solvent ($CHCl_3$ (7.27 ppm), tetramethylsilane (0.00 ppm)) as internal reference for ^1H NMR and the deuterated solvent ($CDCl_3$ (77.00 ppm) as internal standard for ^{13}C NMR. The following abbreviations were used to represent the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = double doublet, dt = double triplet, brs = broad singlet, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex^{II} mass spectrometer by means of the ESI technique. The FT-IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer using neat thin film technique with potassium bromide (KBr) salt plates.

2. Optimization of the Reaction Conditions

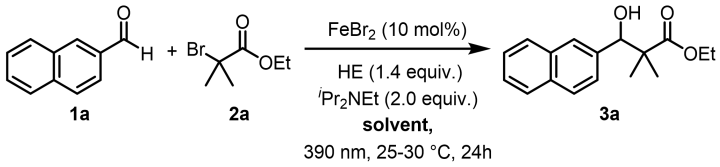
Table S1 Screening of iron catalysts[a]



entry	iron catalyst	conversion (%)	yield (%)[b]
1	$FeBr_3$	46	28
2	$Fe(OTf)_3$	60	22
3	$Fe(OAc)_2$	80	19
4	$FeBr_2$	40	36
5	$FeCl_2$	62	18
6	$FeCl_3$	65	17

[a]Unless otherwise noted: reactions were conducted with **1a** (0.20 mmol), **2a** (0.50 mmol), iron catalyst (10 mol%), HE (1.4 equiv.), and $^{i}Pr_2NEt$ (2.0 equiv.) in ethyl acetate (2.0 ml) at room temperature for 24 h under 40 W 390 nm light irradiation. [b]Yield determined by ^{1}H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

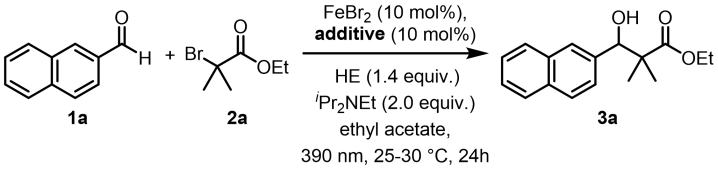
Table S2 Screening of solvents[a]



entry	solvent	conversion (%)	yield (%)[b]
1	THF	36	18
2	DCM	42	7
3	1,4-dioxane	18	9
4	CH_3CN	32	19
5	toluene	28	13
6	DMF	37	13
7	DMSO	38	21
8	EA	40	36

[a]Unless otherwise noted: reactions were conducted with **1a** (0.2 mmol), **2a** (0.5 mmol), $FeBr_2$ (10 mol%), HE (1.4 equiv.), and $^iPr_2NEt$ (2.0 equiv.) in solvent (2.0 ml) at room temperature for 24 h under 40 W 390 nm light irradiation. [b]Yield determined by ^1H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

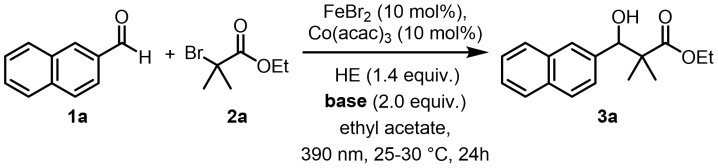
Table S3 Screening of additives[a]



entry	additive	conversion (%)	yield (%)[b]
1	$ZnBr_2$	58	24
2	$ZnCl_2$	46	17
3	LiI	49	38
4	LiBr	67	trace
5	LiCl	63	33
6	$MgCl_2$	81	33
7	$Co(acac)_3$	98	95 (93)[c]
8	CoI_2	42	30
9	$CoBr_2$	47	22

[a]Unless otherwise noted: reactions were conducted with **1a** (0.2 mmol), **2a** (0.5 mmol), $FeBr_2$ (10 mol), additive (10 mol%), HE (1.4 equiv.), and $^{i}Pr_2NEt$ (2.0 equiv.) in ethyl acetate (2.0 ml) at room temperature for 24 h under 40 W 390 nm light irradiation. [b]Yield determined by ^1H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield.

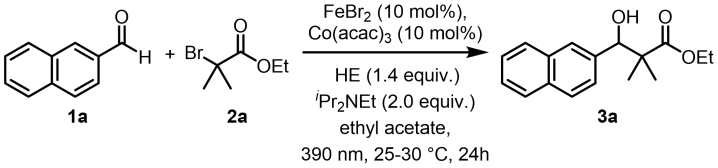
Table S4 Screening of bases[a]



entry	base	conversion (%)	yield (%)[b]
1	Et_3N	95	87
2	Et_2NH	68	55
3	2,6-lutidine	85	54
4	DBU	55	51
5	$NaHCO_3$	59	53
6	K_2CO_3	61	56
7	$^{i}Pr_2NEt$	98	95 (93)[c]
8	$^{i}Pr_2NEt$, 0.5 eq	67	60
9	$^{i}Pr_2NEt$, 1.0 eq	75	72
10	$^{i}Pr_2NEt$, 1.5 eq	86	82
11	$^{i}Pr_2NEt$, 2.5 eq	96	92

[a]Unless otherwise noted: reactions were conducted with **1a** (0.2 mmol), **2a** (0.5 mmol), $FeBr_2$ (10 mol), $Co(acac)_3$ (10 mmol%), HE (1.4 equiv.), and base (2.0 equiv.) in ethyl acetate (2.0 ml) at room temperature for 24 h under 40 W 390 nm light irradiation. [b]Yield determined by ^1H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S5 Control experiments[a]

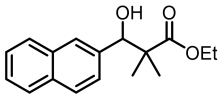


entry	variation	conversion (%)	yield (%)[b]
1	none	98	95 (93)[c]
2	without $FeBr_2$	11	7
3	without $Co(acac)_3$	40	36
4	without HE	0	0
5	without $^{i}Pr_2NEt$	59	42
6	without light	0	0
7	40W 427 nm LED	75	65
8	40W 440 nm LED	55	46
9	40W 450 nm LED	52	45
10	40W white LED	30	22

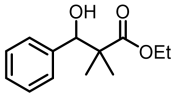
[a]Unless otherwise noted: reactions were conducted with **1a** (0.2 mmol), **2a** (0.5 mmol), $FeBr_2$ (10 mol), $Co(acac)_3$ (10 mol%), HE (1.4 equiv.), and $^{i}Pr_2NEt$ (2.0 equiv.) in ethyl acetate (2.0 ml) at room temperature for 24 h under 40 W 390 nm light irradiation. [b]Yield determined by ^{1}H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c]Isolated yield.

3. General Procedure for Reductive Reformatsky Reaction

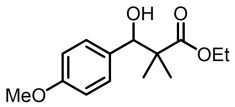
General procedure: Under an argon atmosphere, a 10 mL Schlenk tube was charged with **1** or **4** (0.2 mmol), **2** (0.5 mmol), $FeBr_2$ (0.02 mmol, 10 mol%), $Co(acac)_3$ (0.02 mmol, 10 mol%), HE (0.28 mmol, 1.4 equiv.), $^iPr_2NEt$ (0.4 mmol, 2.0 equiv.), and ethyl acetate (2 mL). Then, the reaction mixture was stirred at room temperature for 24 h under irradiation of 40 W 390 nm Kessil. The resulting mixture was concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel to afford the desired product **3**, **5** or **6**.



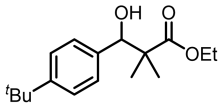
3a, 49.6 mg, 91% yield, white solid.
M.p. = 66-67 ºC
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 4H), 7.49 – 7.39 (m, 3H), 5.04 (d, *J* = 4.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.43 (d, *J* = 4.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 1.13 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 137.6, 132.9, 132.7, 128.0, 127.5, 127.2, 126.6, 125.9, 125.8, 125.7, 78.7, 60.9, 47.7, 23.1, 19.1, 14.0.
HRMS (ESI) calcd for [M+Na^+] : $C_{17}H_{20}NaO_3$, m/z: 295.1305, found: 295.1304 , Error: 0.3 ppm.
IR (KBr): 3491, 2980, 1717, 1365, 1262, 1175, 1054, 480.cm^{-1}



3b, 40.8 mg, 92% yield, colorless oil.
^{1}H NMR (600 MHz, CDCl3) δ 7.34 – 7.25 (m, 5H), 4.89 (d, J = 4.1 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.20 (d, *J* = 4.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 3H), 1.11 (s, 3H) ppm.
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 140.0, 127.7, 127.7, 78.7, 60.9, 47.5, 23.1, 19.0, 14.1.
HRMS (ESI) calcd for [M+Na^+]: $C_{13}H_{18}NaO_3$, m/z: 245.1148, found: 245.1140, Error: 3.2 ppm.
IR (KBr): 3498, 2981, 1717, 1470, 1387, 1132, 898, 704 cm^{-1}



3c, 37.0 mg, 82% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.1 Hz, 2H), 4.85 (d, *J* = 3.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.12 (d, *J* = 3.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.09 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.9, 159.1, 132.1, 128.8, 113.1, 78.3, 60.8, 55.20, 47.6, 23.1, 19.0, 14.1.
HRMS (ESI) calcd for [M+Na^+]: $C_{14}H_{20}NaO_4$, m/z: 275.1254, found: 275.1252, Error: 0.6 ppm.
IR (KBr): 3501, 2980, 2938, 2937, 1718, 1612, 1584, 1513,1249, 1132, 839 cm^{-1}



3d, 48.3 mg, 86% yield, white solid.

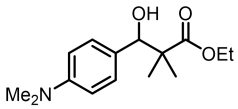
M.p. = 62-63 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.86 (d, *J* = 4.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.08 (d, *J* = 4.2 Hz, 1H), 1.31 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 150.5, 137.0, 127.3, 124.6, 78.5, 60.8, 47.5, 34.4, 31.3, 23.0, 19.0, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{17}H_{26}NaO_3$, m/z: 301.1774, found: 301.1761, Error: 4.5 ppm.

IR (KBr): 3499, 2965, 1719, 1131, 1109, 708, 576 cm^{-1}



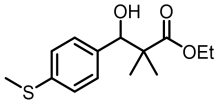
3e, 49.3 mg, 93% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.73 (d, *J* = 2.6 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.89 (d, *J* = 3.5 Hz, 1H), 2.85 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.06 (s, 3H), 1.00 (s, 3H)

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.9, 150.1, 128.4, 127.9, 111.7, 78.5, 60.7, 47.7, 40.5, 23.1, 18.9, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{23}NaO_3$, m/z: 228.1570, found: 288.1562, Error: 2.8 ppm.

IR (KBr): 3506, 2979, 2802, 1720, 1614, 1527, 1470, 1385, 1348, 1253, 544 cm^{-1}



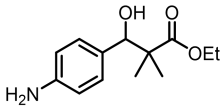
3f, 58.3 mg, 98%, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 4H), 4.84 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.27 (d, *J* = 4.1 Hz, 1H), 2.47 (d, *J* = 1.1 Hz, 3H), 1.26 (td, *J* = 7.1, 1.0 Hz, 3H), 1.12 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 137.6, 136.9, 128.1, 125.7, 78.1, 77.2, 77.0, 76.8, 60.8, 47.5, 22.9, 18.9, 15.7, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{20}NaO_3S$, m/z: 291.1020, found: 288.291.1025, Error: 1.9 ppm.

IR (KBr): 3485, 2980, 2922, 1716, 1493, 1131 cm^{-1}



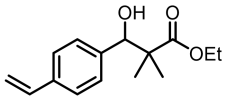
3g, 25.1 mg, 53% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.05 (m, 2H), 6.66 – 6.58 (m, 2H), 4.78 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.68 (d, *J* = 36.3 Hz, 2H), 3.22 – 2.79 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 145.2, 130.1, 128.7, 114.4, 78.5, 77.4, 77.0, 76.7, 60.8, 47.7, 23.1, 19.0, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{13}H_{19}NNaO_3$, m/z: 260.1248, found: 260.1257, Error: 3.6 ppm.

IR (KBr): 3421, 2972, 2922, 1711, 1621, 1048 cm^{-1}



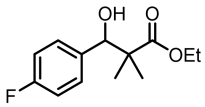
3h, 35.3 mg, 71% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 4.88 (d, *J* = 3.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.19 (d, *J* = 4.0 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 139.6, 137.0, 136.4, 127.9, 125.6, 113.8, 78.4, 60.9, 47.5, 23.1, 19.0, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{20}NaO_3$, m/z: 271.1305, found: 271.1292, Error: 4.8 ppm.

IR (KBr): 3479, 2981, 2937, 1715, 1608, 1132, 1053, 904 cm^{-1}



3i, 34.8 mg, 73% yield, colorless oil.

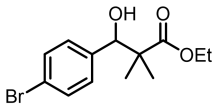
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.87 (d, *J* = 4.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.32 (d, *J* = 4.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 162.3(d, $J_{C\text{-}F}$ = 244.6 Hz), 135.7 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 114.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 77.9, 61.0, 47.5, 22.9, 19.0, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.93.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{13}H_{17}FNaO_3$, m/z: 263.1054, found: 263.1045, Error: 3.2 ppm.

IR (KBr): 3494, 2982, 2908, 1717, 1604, 1471, 812, 780, 578m^{-1}



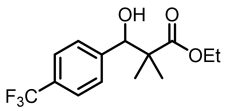
3j, 49.3 mg, 82% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.84 (d, *J* = 4.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.33 (d, *J* = 4.2 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 139.0, 130.8, 129.4, 121.6, 78.0, 61.0, 47.3, 22.9, 19.0, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{13}H_{17}BrNaO_3$, m/z: 323.0253, found: 323.0249, Error: 1.4 ppm.

IR (KBr): 3488, 2980, 2938, 1716, 1471, 1366, 867, 835 cm^{-1}



3k, 48.8 mg, 84% yield, white solid.

M.p. : 62-63 ºC

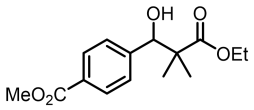
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 4.94 (d, *J* = 3.8 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.51 (d, *J* = 4.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 8.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 144.0, 129.8 (q, $J_{C\text{-}F}$ = 32.2 Hz), 128.1, 125.6, (q, $J_{C\text{-}F}$ = 3.8 Hz) 124.1 (q, $J_{C\text{-}F}$ = 270.3 Hz), 124.6, 124.6, 124.5, 122.8, 120.1, 78.0, 61.1, 47.4, 22.8, 19.0, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.54.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{17}F_3NaO_3$, m/z: 313.1022, found: 313.1018, Error: 1.3 ppm.

IR (KBr): 3480, 2983, 2940, 1715, 1327, 1126, 1068, 1017 cm^{-1}



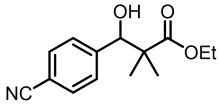
3l, 46.7 mg, 83% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.94 (d, *J* = 4.1 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.47 (d, *J* = 4.2 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 166.9, 145.2, 129.4, 128.9, 127.7, 78.2, 61.0, 52.0, 47.4, 22.8, 19.1, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{20}NaO_5$, m/z: 303.1203, found: 303.1192, Error: 3.5 ppm.

IR (KBr): 3498, 2982, 1722, 1469, 1282, 1116, 1019 cm^{-1}



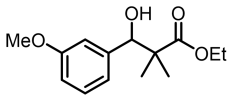
3m, 37.4 mg, 76% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 4.94 (d, *J* = 3.8 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.56 (d, *J* = 4.0 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 10.0 Hz, 6H

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.3, 145.4, 131.4, 128.4, 118.7, 111.4, 77.8, 61.1, 47.4, 22.7, 19.1, 14.0.

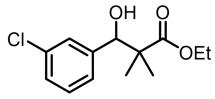
HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{17}NNaO_3$, m/z: 270.1101, found: 270.1100, Error: 0.2 ppm.

IR (KBr): 3484, 2982, 2939, 2229, 1717,1470, 1133, 1059, 851 cm^{-1}

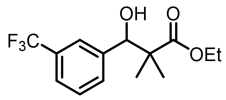


3n, 36.7 mg, 73% yield, colorless oil.

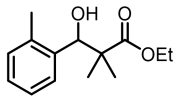
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 1H), 6.92 – 6.85 (m, 2H), 6.85 – 6.79 (m, 1H), 4.86 (d, *J* = 3.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.23 (d, *J* = 4.1 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 3H), 1.11 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 159.1, 141.7, 128.6, 120.1, 113.4, 113.0, 78.5, 60.9, 55.1, 47.5, 23.0, 19.1, 14.1.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{20}NaO_3$, m/z: 275.1254, found: 275.1247, Error: 2.6 ppm.
IR (KBr): 3481, 2981, 2939, 1717, 1603, 1467, 1259, 1132, 1094 cm^{-1}



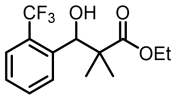
3o, 40.0 mg, 78% yield, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.28 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 4.84 (d, *J* = 4.3 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 4.4 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.11 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 142.1, 133.7, 128.9, 127.8, 127.7, 125.9, 78.0, 61.0, 47.4, 22.8, 19.1, 14.0.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{13}H_{17}ClNaO_3$, m/z: 279.0758, found: 279.0756, Error: 0.8 ppm.
IR (KBr): 3485, 2981, 2939, 1715, 1471, 1272, 1133, 783 cm^{-1}



3p, 50.0 mg, 83% yield, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (m, *J* = 28.1, 15.3, 7.7 Hz, 4H), 4.93 (d, *J* = 4.3 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.50 (d, *J* = 4.4 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.11 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 141.1, 131.1, 130.2 (q, $J_{C\text{-}F}$ = 32.3 Hz), 128.1, 125.0 (q, $J_{C\text{-}F}$ = 541.4 Hz), 124.5 (q, $J_{C\text{-}F}$ = 3.3 Hz), 124.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.2, 121.4, 78.1, 61.1, 47.5, 22.7, 19.2, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.62.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{17}F_3NaO_3$, m/z: 313.1022, found: 313.1015, Error: 2.2 ppm.
IR (KBr): 3487, 2984, 2942, 1716, 1471, 1367, 1164, 1128, 708 cm^{-1}



3q, 41.3 mg, 88% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.13 (d, *J* = 7.1 Hz, 1H), 5.24 (d, *J* = 4.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.26 (d, *J* = 4.4 Hz, 1H), 2.37 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.12 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 138.5, 135.9, 130.3, 127.6, 127.4, 125.6, 73.5, 60.9, 48.3, 23.2, 20.2, 18.9, 14.0.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{20}NaO_3$, m/z: 259.1305, found: 259.1298, Error: 2.5 ppm.
IR (KBr): 3499, 2981, 1718, 1470, 1252, 1134, 1040, 750 cm^{-1}



3r, 56.2 mg, 97% yield, colorless oil.

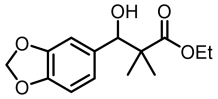
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 9.0 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 5.29 (d, *J* = 5.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.89 (d, *J* = 5.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 9.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 139.6, 131.6, 128.4 (d, $J_{C\text{-}F}$ = 113.2 Hz),128.5 (d, $J_{C\text{-}F}$ = 29.4 Hz), 125.9, 125.8 (q, $J_{C\text{-}F}$ = 5.9 Hz), 124.2 (q, $J_{C\text{-}F}$ = 27.5 Hz), 73.2, 61.2, 47.4, 24.1, 19.8, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -55.97.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{17}F_3NaO_3$, m/z: 313.1022, found: 313.1016, Error: 2.0 ppm.

IR (KBr): 3483, 2985, 1716, 1309, 1156, 1123, 1033, 772 cm^{-1}



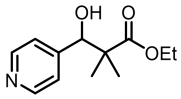
3s, 40.6 mg, 76% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.74 (s, 2H), 5.94 (s, 2H), 4.80 (d, *J* = 3.7 Hz, 1H), 4.17 (d, *J* = 7.1 Hz, 2H), 3.21 (d, *J* = 3.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 147.2, 146.9, 134.0, 121.1, 108.1, 107.4, 100.9, 78.4, 76.8, 60.8, 47.5, 23.0, 19.1, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{18}NaO_5$, m/z: 289.1046, found: 289.1042, Error: 1.4 ppm.

IR (KBr): 3488, 2981, 2938, 1716, 1488, 1443, 1248, 1132, 1039 cm^{-1}



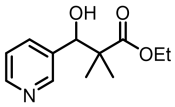
3t, 32.1 mg, 72% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.2 Hz, 2H), 7.25 (d, *J* = 5.4 Hz, 2H), 4.89 (s, 1H), 4.18 (d, *J* = 7.1 Hz, 2H), 4.07 – 3.91 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 7.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.3, 149.2, 149.1, 122.8, 76.8, 61.1, 47.3, 22.6, 19.2, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{12}H_{18}NNaO_3$, m/z: 224.1281, found: 224.1273, Error: 3.6 ppm.

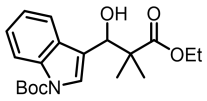
IR (KBr): 3421, 2981, 2939, 1723, 1603, 1258, 1131, 1061 cm^{-1}



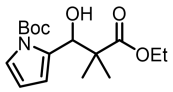
3u, 31.1 mg, 70% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 6.0, 2.6 Hz, 2H), 7.70 (dt, *J* = 7.9, 1.7 Hz, 1H), 7.25 (dd, *J* = 7.9, 4.8 Hz, 1H), 4.94 (s, 1H), 4.36 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15 (s, 3H), 1.09 (s, 3H).

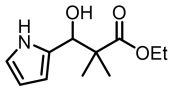
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 177.2, 148.9, 148.9, 148.7, 148.6, 136.0, 135.4, 122.8, 76.1, 76.1, 61.0, 47.5, 22.4, 22.4, 19.1, 14.0.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{12}H_{18}NNaO_3$, m/z: 224.1281, found: 224.1277, Error: 1.8 ppm.
IR (KBr): 3418, 2981, 2939, 1723, 1470, 1427, 1261, 1132, 1027 cm^{-1}



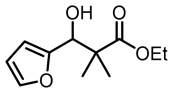
3v, 76.9 mg, 98% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 4.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.54 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 5.21 (d, *J* = 4.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.22 (d, *J* = 4.4 Hz, 1H), 1.67 (s, 9H), 1.31 – 1.26 (m, 6H), 1.20 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 149.6, 135.1, 129.9, 124.3, 124.0, 122.5, 120.3, 120.3, 115.1, 83.8, 72.6, 61.0, 47.9, 28.2, 23.2, 19.7, 14.1.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{20}H_{27}NNaO_5$, m/z: 384.1781, found: 384.1768, Error: 3.4 ppm.
IR (KBr): 3502, 2980, 2936, 1734, 1453, 1371, 1257, 1157, 1049 cm^{-1}



3w, 56.0 mg, 90% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 3.3, 1.7 Hz, 1H), 6.23 – 6.17 (m, 1H), 6.09 (t, *J* = 3.4 Hz, 1H), 5.41 (d, *J* = 7.2 Hz, 1H), 4.38 (d, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.60 (s, 9H), 1.26 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.3, 150.2, 134.7, 122.2, 113.2, 110.0, 84.4, 71.6, 60.6, 47.7, 27.9, 22.0, 21.9, 14.0.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{16}H_{25}NNaO_5$, m/z: 334.1625, found: 334.1611, Error: 4.3 ppm.
IR (KBr): 3483, 2982, 2939, 1717, 1502, 1366, 1132, 1024, 874 cm^{-1}



3x, 39.0 mg, 92% yield, light yellow oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (s, 1H), 6.73 (dd, *J* = 3.9, 2.5 Hz, 1H), 6.13 (dd, *J* = 5.8, 2.8 Hz, 1H), 6.02 (s, 1H), 4.84 (d, *J* = 5.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.16 (d, *J* = 5.1 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 3H), 1.12 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 178.2, 130.4, 117.2, 107.9, 107.0, 73.8, 61.0, 47.6, 23.0, 20.4, 14.1.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{17}NNaO_3$, m/z: 234.1011, found: 234.1089, Error: 5.2 ppm.
IR (KBr): 3746, 3421, 2980, 1711, 1265, 1148, 1027, 773 cm^{-1}



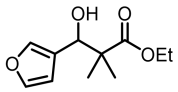
3y, 33.8 mg, 80% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.33 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 4.77 (d, *J* = 7.0 Hz, 1H), 4.20 (m, 2H), 3.45 (d, *J* = 7.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 154.0, 141.7, 110.1, 107.7, 73.4, 60.9, 46.9, 22.9, 20.2, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{16}NaO_4$, m/z: 235.0941, found: 235.0937, Error: 1.5 ppm.

IR (KBr): 3481, 2982, 2939, 1720, 1469, 1265, 1175, 1058, 736 cm^{-1}



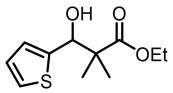
3z, 29.0 mg, 70% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.0 Hz, 2H), 6.35 (s, 1H), 4.79 (d, *J* = 5.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.20 (d, *J* = 5.3 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.17 (d, *J* = 6.5 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 142.6, 140.2, 124.9, 109.7, 72.3, 60.9, 47.1, 22.7, 19.8, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{16}NaO_4$, m/z: 235.0941, found: 235.0935, Error: 2.6 ppm.

IR (KBr): 3445, 2982, 2938, 1718, 1503, 1266, 1133, 1023 cm^{-1}



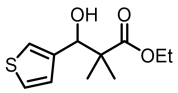
3aa, 39.0 mg, 85% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.00 – 6.88 (m, 2H), 5.09 (d, *J* = 5.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.47 (d, *J* = 5.3 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 7.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 143.7, 126.2, 125.6, 124.7, 76.7, 75.6, 61.0, 47.5, 22.8, 19.9, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{16}SNaO_3$, m/z: 251.0712, found: 251.0702, Error: 3.9 ppm.

IR (KBr): 3482, 2981, 2937, 1716, 1468, 1262, 1133, 1025, 698 cm^{-1}



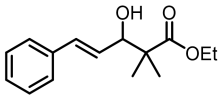
3ab, 36.6 mg, 81% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.16 (d, *J* = 2.7 Hz, 1H), 7.03 (d, *J* = 5.0 Hz, 1H), 4.96 (d, *J* = 4.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.26 (d, *J* = 4.8 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.16 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 141.7, 127.0, 124.9, 122.4, 75.4, 60.8, 47.4, 22.8, 19.5, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{16}SNaO_3$, m/z: 251.0712, found: 251.0710, Error: 0.8 ppm.

IR (KBr): 3498, 3106, 2981, 1716, 1469, 1261, 1132, 1051, 788 cm^{-1}



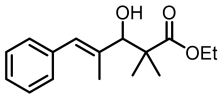
3ac, 43.1 mg, 87% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 7.0 Hz, 1H), 4.34 (t, *J* = 6.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.86 (d, *J* = 5.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.4, 136.6, 132.8, 128.5, 127.7, 127.5, 126.5, 77.8, 60.8, 47.0, 22.8, 20.1, 14.2.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{20}NaO_3$, m/z: 271.1305, found: 271.1296, Error: 3.3 ppm.

IR (KBr): 3485, 2979, 1718, 1267, 1174, 1071, 1027 cm^{-1}



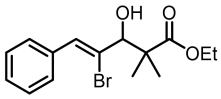
3ad, 39.8 mg, 76% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 10.2, 4.6 Hz, 2H), 7.29 – 7.19 (m, 3H), 6.47 (s, 1H), 4.25 (d, *J* = 5.8 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.42 (d, *J* = 5.9 Hz, 1H), 1.84 (d, *J* = 1.3 Hz, 3H), 1.29 (dd, *J* = 8.7, 5.6 Hz, 6H), 1.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 137.3, 137.1, 129.1, 129.1, 128.0, 126.5, 83.0, 61.0, 46.6, 24.0, 21.1, 14.7, 14.1.

HRMS (ESI) ccalcd for [M+Na$^+$]: $C_{16}H_{22}NaO_3$, m/z: 285.1461, found: 285.1453, Error: 2.9 ppm.

IR (KBr): 3483, 2980, 1717, 1469, 1253, 1132, 1025, 700 cm^{-1}



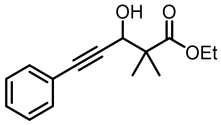
3ae, 52.9 mg, 81% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.01 (s, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 8.3 Hz, 1H), 1.39 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.0, 135.0, 131.3, 129.2, 128.2, 128.1, 126.1, 83.1, 61.3, 46.2, 24.7, 21.4, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{19}BrNaO_3$, m/z:349.0410, found:349.0404, Error: 1.7 ppm.

IR (KBr): 3471, 2980, 1718, 1469, 1259, 1174, 1025, 695 cm^{-1}



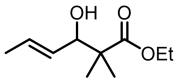
3af, 31.2 mg, 81% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 4.68 (d, *J* = 6.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.13 (d, *J* = 6.4 Hz, 1H), 1.37 (s, 3H), 1.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 131.7, 128.5, 128.2, 122.4, 87.2, 85.9, 77.3, 68.9, 61.0, 47.7, 22.7, 20.1, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{13}H_{18}NaO_3$, m/z: 269.1148, found: 269.1139, Error: 0.3ppm.

IR (KBr): 3460, 2980, 1719, 1490, 1254, 1134, 1051, 757 cm^{-1}



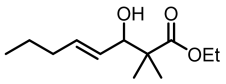
3ag, 28.6 mg, 76% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.67 (m, 1H), 5.48 (m, 1H), 4.19 – 4.13 (m, 2H), 4.12 – 4.06 (m, 1H), 2.70 (d, *J* = 5.8 Hz, 1H), 1.73 – 1.70 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 2.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 129.5, 129.1, 77.9, 60.6, 46.6, 22.6, 19.9, 17.8, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{10}H_{18}NaO_3$, m/z: 209.1148, found: 209.1144, Error: 1.9ppm.

IR (KBr): 3491, 2980, 1720, 1469, 1268, 1139, 1025 cm^{-1}



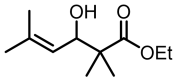
3ah, 39.8 mg, 88% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.69 (dd, *J* = 14.8, 7.3 Hz, 1H), 5.45 (dd, *J* = 15.3, 7.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.11 (d, *J* = 5.7 Hz, 1H), 2.68 (s, 1H), 2.03 (dt, *J* = 13.3, 6.7 Hz, 2H), 1.40 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 5.3 Hz, 6H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 134.7, 128.0, 77.9, 60.6, 46.7, 34.4, 22.6, 22.2, 20.0, 14.1, 13.6.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{12}H_{22}NaO_3$, m/z: 237.1461, found: 237.1457, Error: 2.0 ppm.

IR (KBr): 3498, 2964, 2934, 1730, 1467, 1265, 1142, 1026 cm^{-1}



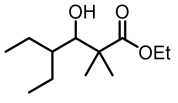
3ai, 30.3 mg, 78% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 – 5.15 (m, 1H), 4.41 (dd, *J* = 9.4, 5.2 Hz, 1H), 4.20 – 4.13 (m, 2H), 2.62 (d, *J* = 5.5 Hz, 1H), 1.75 (d, *J* = 1.0 Hz, 3H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 137.2, 123.1, 73.2, 60.6, 47.1, 26.0, 22.5, 19.7, 18.5, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{20}NaO_3$, m/z: 223.1305, found: 223.1298, Error: 2.9 ppm.

IR (KBr): 3486, 2979, 2934, 1721, 1469, 1260, 1130, 1026 cm^{-1}



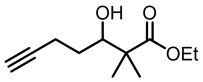
3aj, 30.4 mg, 70% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.15 (q, *J* = 7.1 Hz, 2H), 3.60 (dd, *J* = 8.2, 2.4 Hz, 1H), 2.74 (d, *J* = 8.3 Hz, 1H), 1.46 – 1.33 (m, 3H), 1.27 (dd, *J* = 12.6, 5.4 Hz, 7H), 1.19 – 1.13 (m, 4H), 0.89 (dt, *J* = 10.3, 7.4 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 178.1, 78.3, 60.7, 46.2, 42.7, 24.2, 23.9, 22.0, 21.9, 20.7, 14.0, 12.0, 11.6.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{12}H_{24}NaO_3$, m/z: 239.1618, found: 239.1606, Error: 4.8 ppm.

IR (KBr): 3505, 2965, 2936, 1725, 1464, 1262, 1140, 1025 cm^{-1}



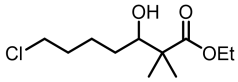
3ak, 22.9 mg, 62% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.1 Hz, 2H), 3.75 (dd, *J* = 10.7, 4.5 Hz, 1H), 2.72 (d, *J* = 6.4 Hz, 1H), 2.50 – 2.29 (m, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.75 – 1.65 (m, 1H), 1.57 – 1.47 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 84.2, 77.3, 75.4, 68.6, 60.8, 46.7, 30.6, 22.5, 20.3, 15.7, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{18}NaO_3$, m/z: 221.1148, found: 221.1150, Error: -1.0 ppm.

IR (KBr): 3391, 2959, 2922, 1646, 1464, 1260, 1090, 1030 cm^{-1}



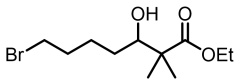
3al, 34.6 mg, 73% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 3.60 (dd, *J* = 9.2, 7.0 Hz, 1H), 3.57 – 3.52 (m, 2H), 2.58 (d, *J* = 6.8 Hz, 1H), 1.87 – 1.72 (m, 3H), 1.55 – 1.43 (m, 2H), 1.37 – 1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 76.4, 60.7, 46.9, 44.9, 32.5, 30.9, 24.1, 22.3, 20.4, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{21}ClNaO_3$, m/z: 259.1071, found: 259.1070, Error: 0.6 ppm.

IR (KBr): 3496, 2980, 2943, 1718, 1467, 1264, 1131, 1080, 1024 cm^{-1}



3am

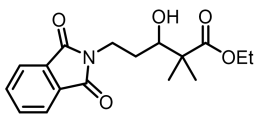
3am, 12.0 mg, 26 % yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 3.60 (ddd, *J* = 10.4, 6.9, 1.9 Hz, 1H), 3.49 – 3.36 (m, 2H), 2.55 (d, *J* = 6.8 Hz, 1H), 2.00 – 1.82 (m, 2H), 1.80 – 1.67 (m, 1H), 1.55 – 1.40 (m, 2H), 1.37 – 1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 77.3 (s), 77.0 (s), 76.7 (s), 76.4 (s), 60.7 (s), 46.9 (s), 33.7 (s), 32.7 (s), 30.8 (s), 25.4 (s), 22.4 (s), 20.4 (s), 14.2 (s).

HRMS (ESI) calcd for [M+Na$^+$]: $C_{11}H_{21}BrNaO_3$, m/z: 303.0562, found: 303.0566, Error: 1.5 ppm.

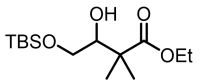
IR (KBr): 3444, 2979, 2933, 1715, 1266, 1173 cm^{-1}



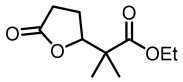
3an, 35.5 mg, 56% yield, white solid.

M.p. = 68-71 °C

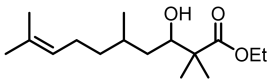
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.80 (m, 2H), 7.76 – 7.70 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.97 – 3.82 (m, 2H), 3.69 (dd, *J* = 10.9, 3.7 Hz, 1H), 3.10 (d, *J* = 6.0 Hz, 1H), 1.82 (m, *J* = 15.6, 8.8, 1.9 Hz, 1H), 1.74 – 1.62 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 1.15 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 168.7, 134.0, 132.0, 123.3, 73.6, 60.6, 46.8, 35.4, 30.5, 21.5, 20.7, 14.0.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{17}H_{21}NNaO_5$, m/z: 342.1312, found: 342.1280, Error: 0.9 ppm.
IR (KBr): 3514, 2980, 1771, 1710, 1396, 1173, 1206, 721 cm^{-1}



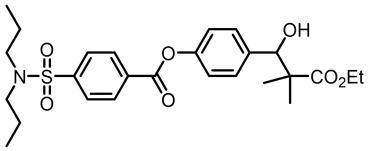
3ao, 31.3 mg, 54% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.08 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.66 (m, 1H), 3.62 (dd, *J* = 10.2, 3.3 Hz, 1H), 3.51 (dd, *J* = 10.2, 7.2 Hz, 1H), 2.89 (d, *J* = 4.7 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 3H), 1.13 (s, 3H), 0.83 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 176.7, 76.3, 63.8, 60.5, 45.0, 25.8, 21.6, 21.5, 18.3, 14.1.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{30}SiNaO_3$, m/z: 313.1806, found: 313.1796, Error: 3.2 ppm.
IR (KBr): 3468, 2955, 2931, 1729, 1637, 1255, 1112, 837 cm^{-1}



3ap, 21.5 mg, 53% yield, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (t, *J* = 7.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.60 – 2.51 (m, 2H), 2.27 (m, *J* = 13.4, 8.6, 7.5, 6.0 Hz, 1H), 2.09 – 1.93 (m, 1H), 1.29 – 1.24 (m, 6H), 1.20 (d, *J* = 6.0 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 174.8, 83.9, 61.0, 45.7, 28.6, 23.1, 21.3, 19.9, 14.1.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{10}H_{16}NaO_4$, m/z: 223.0941, found: 223.0940, Error: -1.6 ppm.
IR (KBr): 3446, 2983, 1779, 1727, 1471, 1266, 1148, 1007 cm^{-1}



3aq, 40.7 mg, 75% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.11 (dt, *J* = 12.0, 4.1 Hz, 1H), 4.16 (m, 2H), 3.74 – 3.67 (m, 1H), 2.35 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.08 – 1.87 (m, 2H), 1.76 – 1.66 (m, 4H), 1.60 (d, *J* = 2.9 Hz, 3H), 1.40 – 1.19 (m, 6H), 1.17 (dd, *J* = 9.2, 3.0 Hz, 6H), 1.08 (m, *J* = 18.7, 13.9, 10.3, 3.4 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 2H), 0.90 (d, *J* = 6.6 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 131.2, 124.8, 74.4, 60.6, 47.0, 38.8, 35.7, 29.3, 25.4, 22.1, 20.8, 20.5, 18.8, 17.6, 14.2.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{16}H_{30}NaO_3$, m/z: 293.2087, found: 293.2078, Error: 3.0 ppm.
IR (KBr): 3509, 2967, 2929, 1716, 1466, 1264, 1139, 1026 cm^{-1}



3ar, 62.1 mg, 61% yield, white solid.

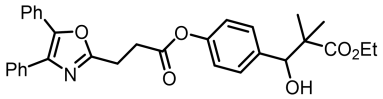
M.p. = 136-139 ºC

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.94 (d, *J* = 4.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.35 – 3.27 (m, 1H), 3.15 – 3.11 (m, 4H), 1.60 – 1.53 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 0.89 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 163.8, 150.0, 144.9, 138.1, 132.77, 130.7, 128.9, 127.1, 120.7, 78.0, 61.0, 49.9, 47.5, 23.0, 21.9, 19.0, 14.1, 11.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{26}H_{35}NSNaO_7$, m/z: 528.2026, found: 528.2038, Error: -2.3 ppm.

IR (KBr): 3455, 2972, 1737, 1506, 1398, 1073, 1016, cm^{-1}



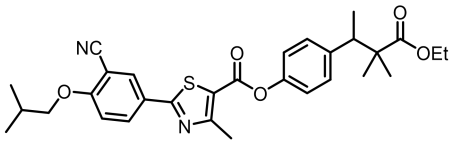
3as, 83.0 mg, 86% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.29 (m, 8H), 7.06 (d, *J* = 8.3 Hz, 2H), 4.89 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.29 (t, *J* = 7.3 Hz, 3H), 3.15 (t, *J* = 7.3 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 170.5, 161.4, 150.0, 145.5, 137.7, 135.1, 132.3, 128.8, 128.7, 128.6, 128.5, 128.5, 128.1, 127.8, 126.5, 120.7, 78.0, 60.9, 60.4, 47.5, 31.2, 23.4, 22.9, 18.9, 14.1, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{31}H_{31}NNaO_6$, m/z: 536.2044, found: 536.2049, Error: -1.0 ppm.

IR (KBr): 3467, 2980, 2936, 1759, 1720, 1201, 1166,1136 cm^{-1}



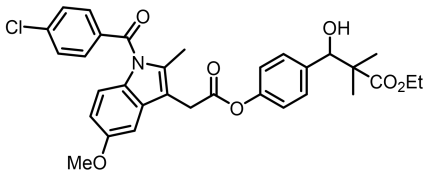
3at, 99.8 mg, 86% yield, yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.88 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 3.83 (s, 3H), 3.23 (s, 1H), 2.45 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 169.2, 168.3, 156.1, 150.1, 139.3, 137.7, 136.2, 133.8, 131.2, 130.8, 130.5, 129.1, 128.7, 120.6, 115.0, 112.0, 111.8, 101.2, 78.0, 61.0, 55.7, 47.5, 30.5, 23.0, 18.9, 14.1, 13.4.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{32}H_{32}ClNNaO_7$, m/z: 600.1760, found: 600.1744, Error: 2.6 ppm.

IR (KBr): 3488, 1754, 1684, 1594, 1321, 1165, 926 cm^{-1}



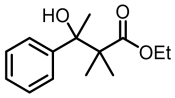
3au, 99.8 mg, 86% yield, yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.88 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 3.83 (s, 3H), 3.23 (s, 1H), 2.45 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.11 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 169.2, 168.3, 156.1, 150.1, 139.3, 137.7, 136.2, 133.8, 131.2, 130.8, 130.5, 129.1, 128.7, 120.6, 115.0, 112.0, 111.8, 101.2, 78.0, 61.0, 55.7, 47.5, 30.5, 23.0, 18.9, 14.1, 13.4.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{32}H_{32}ClNNaO_7$, m/z: 600.1760, found: 600.1744, Error: 2.6 ppm.

IR (KBr): 3488, 1754, 1684, 1594, 1321, 1165, 926 cm^{-1}



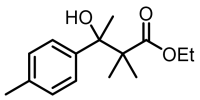
5a, 31.4 mg, 67% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.31 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.26 – 7.23 (m, 1H), 4.52 (s, 1H), 4.15 (m, 2H), 1.61 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 4.8 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 178.6, 143.4, 127.2, 127.2, 126.9, 77.2, 61.1, 50.1, 24.9, 21.8, 21.6, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{14}H_{20}NaO_3$, m/z: 259.1305, found: 259.1294, Error: 4.3 ppm.

IR (KBr): 3453, 2981, 2937, 1691, 1636, 1273, 1146, 1028, 703 cm^{-1}



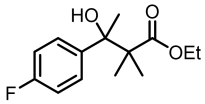
5b, 27.5 mg, 55% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.47 (s, 1H), 4.18 – 4.11 (m, 2H), 2.33 (s, 3H), 1.59 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 2.1 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 178.6, 140.4, 136.4, 127.9, 127.1, 76.8, 61.1, 50.1, 25.0, 21.8, 21.6, 20.9, 14.0.

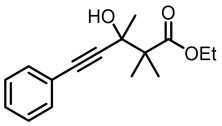
HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{22}NaO_3$, m/z: 273.1461, found: 273.1454, Error: 2.5 ppm.

IR (KBr): 3478, 2981, 2938, 1693, 1468, 1369, 1272, 1146, 1092 cm^{-1}

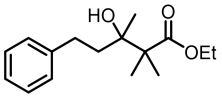


5c, 20.7 mg, 41% yield, colorless oil.

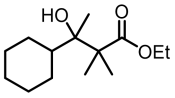
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.03 – 6.95 (m, 2H), 4.60 (s, 1H), 4.20 – 4.12 (m, 2H), 1.60 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 2.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 163.1, 160.6, 139.1 (d, $J_{C\text{-}F}$ = 3.1 Hz) 129.0 (d, $J_{C\text{-}F}$ = 7.9 Hz), 114.0,(d, $J_{C\text{-}F}$ = 21.1 Hz), 76.7, 61.1, 50.0, 25.1, 21.7, 21.6, 14.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.50 .
HRMS (ESI) calcd for [M+Na^+]: $C_{14}H_{19}FNaO_3$, m/z: 277.1210, found: 277.1208, Error: 0.8 ppm.
IR (KBr): 3465, 2983, 2939, 1692, 1601, 1509, 1146, 1084 cm^{-1}



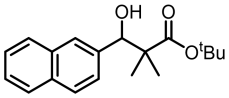
5d, 32.8 mg, 63% yield, colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.29 (d, *J* = 3.7 Hz, 3H), 4.56 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.54 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.8, 131.6, 128.2, 128.2, 122.7, 91.4, 83.6, 72.3, 61.2, 50.3, 24.3, 21.9, 20.5, 14.1.
HRMS (ESI) calcd for [M+Na^+]: $C_{16}H_{20}NaO_3$, m/z: 283.1305, found: 283.1296, Error: 3.1 ppm.
IR (KBr): 3453, 2985, 1637, 1468, 1386, 1126, 756 cm^{-1}



5e, 22.2 mg, 42% yield, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 4.22 – 4.12 (m, 2H), 3.89 (s, 1H), 2.87 (m, 1H), 2.67 (m, 1H), 1.82 – 1.65 (m, 2H), 1.27 (dd, *J* = 9.9, 4.3 Hz, 6H), 1.21 (d, *J* = 3.1 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 143.0, 128.4, 128.4, 125.7, 75.0, 61.0, 50.2, 39.5, 30.0, 21.4, 21.1, 20.9, 14.1.
HRMS (ESI) calcd for [M+Na^+]: $C_{16}H_{24}NaO_3$, m/z: 287.1618, found: 287.1610, Error: 2.6 ppm.
IR (KBr): 3472, 3025, 2981, 1693, 1601, 1271, 1136, 1094, 1021 cm^{-1}



5f, 21.6 mg, 50% yield, colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.1 Hz, 2H), 3.35 (s, 1H), 1.72 – 1.60 (m, 3H), 1.51 (d, *J* = 11.4 Hz, 4H), 1.44 – 1.35 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (s, 1H), 1.21 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 74.0, 60.8, 50.0, 31.6, 25.8, 21.6, 20.8, 14.1.
HRMS (ESI) calcd for [M+Na^+]: $C_{12}H_{22}NaO_3$, m/z: 237.1461, found: 237.1457, Error: -4.2 ppm.
IR (KBr): 3484, 2933, 2853, 1720, 1695, 1266, 1173, 1133, 1022 cm^{-1}



6a, 54.1 mg, 90% yield, white solid.

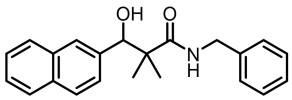
M.p. = 63 - 66 ºC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.70 (m, 4H), 7.52 – 7.39 (m, 3H), 4.98 (d, *J* = 4.2 Hz, 1H), 3.63 (t, *J* = 3.9 Hz, 1H), 1.46 (s, 9H), 1.12 (d, *J* = 3.3 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.2, 137.9, 132.9, 132.8, 128.0, 127.5, 127.1, 126.7, 125.9, 125.9, 125.8, 81.1, 78.9, 48.0, 27.9, 23.4, 19.4.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{19}H_{24}NaO_3$, m/z: 323.1618, found: 323.1610, Error: 2.5 ppm.

IR (KBr): 3467, 3057, 2977, 2933, 1711, 1390, 1254, 1130, 1053 cm^{-1}



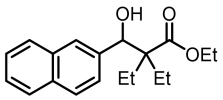
6b, 51.2 mg, 77% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.76 – 7.69 (m, 2H), 7.51 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.24 (dd, *J* = 6.7, 3.9 Hz, 3H), 7.13 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.24 (s, 1H), 4.83 (s, 1H), 4.64 (s, 1H), 4.42 (m, 2H), 1.30 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 177.6, 138.3, 137.8, 133.0, 132.9, 128.7, 128.1, 127.6, 127.5, 127.5, 127.4, 126.6, 126.0, 125.9, 125.6, 80.2, 46.4, 43.5, 24.5, 20.8.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{22}H_{23}NNaO_2$, m/z: 356.1621, found: 356.1624, Error: -0.7 ppm.

IR (KBr): 3347, 3059, 2972, 1638, 1533, 1050, 785 cm^{-1}



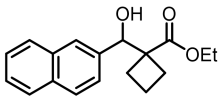
6c, 31.7 mg, 53% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.74 (m, 3H), 7.71 (s, 1H), 7.45 (dt, *J* = 6.8 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.24 – 4.12 (m, 2H), 3.94 (dd, *J* = 5.9, 2.8 Hz, 1H), 1.85 – 1.77 (m, 2H), 1.71 (m, 1H), 1.44 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.95 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 176.9, 138.2, 132.4, 132.9, 128.0, 127.5, 127.4, 126.3, 126.0, 125.8, 125.2, 76.8, 60.7, 54.8, 25.8, 23.7, 14.1, 9.1, 8.8.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{19}H_{24}NaO_3$, m/z: 323.1618, found: 323.1603, Error: 4.5 ppm.

IR (KBr): 3493, 3057, 2972, 2881, 1715, 1459, 1227, 1123, 1031 cm^{-1}



6d, 38.6 mg, 65% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 3H), 7.75 (s, 1H), 7.51 – 7.42 (m, 3H), 5.07 (d, *J* = 6.2 Hz, 1H), 4.18 – 4.06 (m, 2H), 3.42 (d, *J* = 6.7 Hz, 1H), 2.52 – 2.43 (m, 2H), 2.38 – 2.29 (m, 2H), 1.89 (m, 1H), 1.76 – 1.68 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 176.3, 138.3, 133.0, 132.9, 128.0, 127.7, 127.6, 126.0, 125.8, 125.5, 124.7, 77.2, 60.9, 52.6, 28.0, 26.8, 15.7, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{18}H_{20}NaO_3$, m/z: 307.1305, found: 307.1299, Error: 2.0 ppm.

IR (KBr): 3472, 2980, 2948, 1713, 1205, 1155, 1102, 748 cm^{-1}

6e, 38.6 mg, 65% yield, colorless oil.

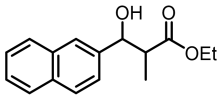
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.83 (dd, *J* = 11.6, 5.8 Hz, 3H), 7.58 – 7.45 (m, 3H), 5.32 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.94 (d, *J* = 4.5 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5 (t, $J_{C\text{-}F}$ = 31.6 Hz), 133.6, 132.9, 131.8, 128.2, 128.2, 127.7, 127.4, 126.7, 126.4, 124.8, 113.9, (dd, $J_{C\text{-}F}$ = 252.7, 252.8 Hz), 73.9, (dd, $J_{C\text{-}F}$ = 24.2, 24.6 Hz) 63.2, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4, -200.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{14}F_2NaO_3$, m/z: 303.0803, found: 303.0798, Error: 1.7 ppm.

IR (KBr): 3476, 1757, 1306, 1073, 858, 798, 479 cm^{-1}



6f, 55.8 mg, 90% yield, colorless oil.

Major:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.8, 6.1 Hz, 4H), 7.51 – 7.40 (m, 3H), 5.27 (d, *J* = 3.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.17 (s, 1H), 2.88 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 138.8, 133.2, 132.8, 128.0, 127.9, 127.6, 126.1, 125.8, 124.9, 124.0, 73.6, 60.8, 46.2, 14.1, 10.7.

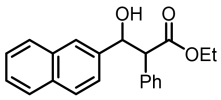
Minor:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.8, 4.7 Hz, 3H), 7.78 (s, 1H), 7.53 – 7.43 (m, 3H), 4.92 (d, *J* = 6.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.18 (d, *J* = 3.3 Hz, 1H), 2.91 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 139.0, 133.2, 133.1, 128.4, 128.0, 127.7, 126.2, 126.0, 125.9, 124.2, 76.5, 60.8, 47.0, 14.6, 14.1.

HRMS (ESI) calcd for [M+Na]$^+$ $C_{16}H_{18}NaO_3$, m/z:281.1148, found: 281.1145, Error 1.1 ppm.

IR (KBr): 3467, 2980, 2937, 1715, 1260, 1186, 1030, 818, 478 cm^{-1}



6g, 43.8 mg, 68% yield, colorless oil.

Major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 4H), 7.46 (m, 3H), 7.40 – 7.28 (m, 5H), 5.46 (d, *J* = 7.4 Hz, 1H), 4.05 – 3.89 (m, 3H), 2.72 (d, *J* = 1.5 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 138.2, 134.7, 133.1, 133.1, 129.2, 128.6, 128.1, 128.0, 127.9, 127.6, 126.0, 126.0, 124.5, 75.2, 61.0, 59.6, 13.8.

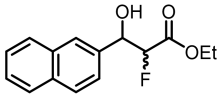
Minor: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.2, 4.9 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.57 (s, 1H), 7.45 – 7.36 (m, 2H), 7.24 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.21 – 6.94 (m, 5H), 5.34 (dd, *J* = 9.0, 2.5

Hz, 1H), 4.29 – 4.10 (m, 2H), 3.98 (d, *J* = 9.1 Hz, 1H), 3.32 (d, *J* = 3.5 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 138.3, 135.3, 133.0, 132.9, 128.5, 128.5, 128.0, 127.8, 127.6, 127.5, 126.0, 125.9, 125.8, 124.4, 61.3, 59.8, 14.0.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{21}H_{20}NaO_3$, m/z: 343.1305, found: 343.1299, Error: 1.7 ppm.

IR (KBr): 3449, 2926, 1727, 1600, 1152, 1028, 859, 747 cm^{-1}



6h, 34.4 mg, 66% yield, yellow oil.

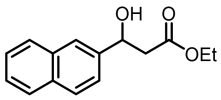
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (m, 4.0 Hz, 10H), 7.53 – 7.45 (m, 7H), 5.34 – 5.25 (m, 3H), 5.16 (dd, *J* = 15.3, 4.3 Hz, 1H), 5.08 (dd, *J* = 15.0, 4.3 Hz, 1H), 4.25 – 4.11 (m, 6H), 3.09 (s, 1H), 2.94 (d, *J* = 4.7 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 4H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 167.8 (d, $J_{C\text{-}F}$ = 22.9 Hz), 135.4 , 135.1 , 133.4 (d, $J_{C\text{-}F}$ = 10.7 Hz), 133.1 (d, *J* = 4.5 Hz), 128.5 , 128.3 , 128.1(d, $J_{C\text{-}F}$ = 3.2 Hz), 127.7 (s), 126.55 – 126.2 (m), 125.8, 124.3, 124.1, 92.2, 91.7, 90.9, 90.4, 74.1, 74.0 (d, $J_{C\text{-}F}$ = 12.6 Hz), 73.8, 61.9 (d, $J_{C\text{-}F}$ = 18.4 Hz), 14.0 (d, $J_{C\text{-}F}$ = 1.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -197.15, -202.72.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{15}FNaO_3$, m/z: 285.0897, found: 285.0898, Error: -0.3 ppm.

IR (KBr): 3448, 2923, 2852, 1742, 1627, 1097, 1062, 749 cm^{-1}



6i, 24.7 mg, 51% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 4H), 7.48 (dt, *J* = 5.2, 1.8 Hz, 3H), 5.33 – 5.26 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.44 (d, *J* = 2.8 Hz, 1H), 2.88 – 2.75 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

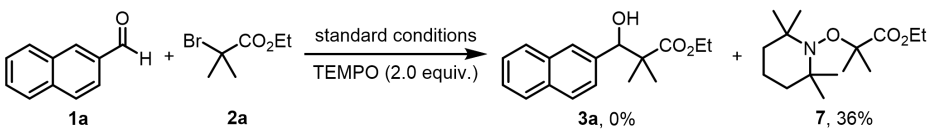
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 139.9, 133.2, 133.0, 128.3, 128.0, 127.7, 126.2, 126.0, 124.4, 123.7, 70.4, 60.9, 43.3, 14.1.

HRMS (ESI) calcd for [M+Na$^+$]: $C_{15}H_{16}NaO_3$, m/z: 267.0992, found: 267.0992, Error: 0.0 ppm.

IR (KBr): 3446, 2980, 2925, 1724, 1633, 1173, 1036, 747 cm^{-1}

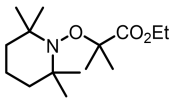
4. Mechanistic Studies

4.1 Radical capture experiment



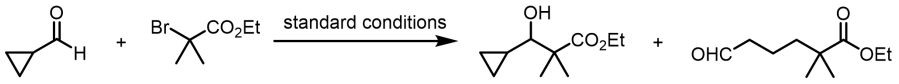
Under an argon atmosphere, a 10 mL Schlenk tube was charged with **1a** (0.2 mmol), **2a** (0.5 mmol), $FeBr_2$ (0.02 mmol, 10 mol%), $Co(acac)_3$ (0.02 mmol, 10 mol%), HE (0.28 mmol, 1.4 equiv.), ^{i}Pr$_2$NEt (0.4 mmol, 2.0 equiv.), TEMPO (0.4 mmol, 2.0 equiv.), and ethyl acetate (2 mL).

Then, the reaction mixture was stirred at room temperature for 24 h under irradiation of 40 W 390 nm Kessil. The resulting mixture was concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel to afford the desired product **7**.

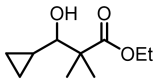


7, 20.2 mg, 36% yield, colorless oil.
^{1}H NMR (400 MHz, CDCl3) δ 4.17 (q, *J* = 7.1 Hz, 2H), 1.55 – 1.43 (m, 10H), 1.41 (t, *J* = 8.3 Hz, 1H), 1.28 (m, 4H), 1.15 (s, 6H), 1.00 (s, 6H).
^{13}C NMR (100 MHz, CDCl3) δ 176.1, 81.0, 77.3, 60.5, 59.5, 40.6, 33.4, 24.4, 20.4, 17.0, 14.1.
HRMS (ESI) calcd for [M+H$^+$]: $C_{15}H_{30}NO_3$, m/z: 271.2220, found: 271.2208, Error: 4.4 ppm.
IR (KBr): 3444, 2976, 2933, 1733, 1635, 1359, 1160, 1136, 1028 cm^{-1}

4.2 Radical clock experiment

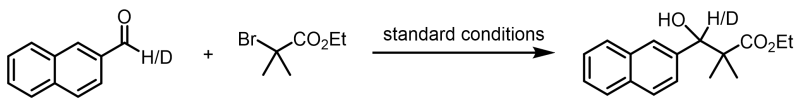


Under an argon atmosphere, a 10 mL Schlenk tube was charged with **1as** (0.2 mmol), **2a** (0.5 mmol), $FeBr_2$ (0.02 mmol, 10 mol%), $Co(acac)_3$ (0.02 mmol, 10 mol%), HE (0.28 mmol, 1.4 equiv.), ^{i}Pr$_2$NEt (0.4 mmol, 2.0 equiv.), and ethyl acetate (2 mL). Then, the reaction mixture was stirred at room temperature for 24 h under irradiation of 40 W 390 nm Kessil. The resulting mixture was concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel to afford the desired product **3as**.



3as, 35.4 mg, 95% yield, colorless oil.
^{1}H NMR (600 MHz, CDCl3) δ 4.19 – 4.13 (m, 2H), 3.00 (dd, *J* = 8.6, 4.9 Hz, 1H), 2.44 (d, *J* = 5.2 Hz, 1H), 1.28 (t, *J* = 3.5 Hz, 6H), 1.26 (s, 3H), 0.93 (m, 1H), 0.57 (m, 1H), 0.50 (m, 1H), 0.36 – 0.29 (m, 2H).
^{13}C NMR (150 MHz, CDCl3) δ 177.6, 80.8, 60.6, 47.7, 22.6, 20.6, 14.1, 13.1, 4.4, 1.6.
HRMS (ESI) calcd for [M+Na$^+$]: $C_{10}H_{18}NaO_3$, m/z: 209.1148, found: 209.1153, Error -2.3 ppm.
IR (KBr): 3374, 1637, 1112, 674 cm^{-1}

4.3 Secondary isotope effect[1]



Under an argon atmosphere, a 10 mL Schlenk tube was charged with **1a** (0.1 mmol), **1a-D** (0.1 mmol), **2a** (0.5 mmol), $FeBr_2$ (0.02 mmol, 10 mol%), $Co(acac)_3$ (0.02 mmol, 10 mol%), HE (0.28

mmol, 1.4 equiv.), $^{i}Pr_2NEt$ (0.4 mmol, 2.0 equiv.), and ethyl acetate (2 mL). Then, the reaction mixture was stirred at room temperature for 24 h under irradiation of 40 W 390 nm Kessil. The resulting mixture was concentrated in vacuum, and the residue was purified by flash column chromatography on silica gel to afford the desired product **3a** and **3a-D.**

4.4 Switching light experiment

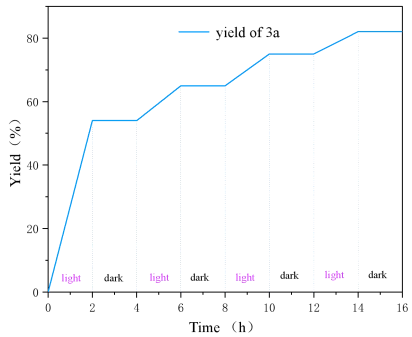


Figure S1 Switching light experiment.

4.5 Stern-Volmer fluorescence quenching experiment[2]

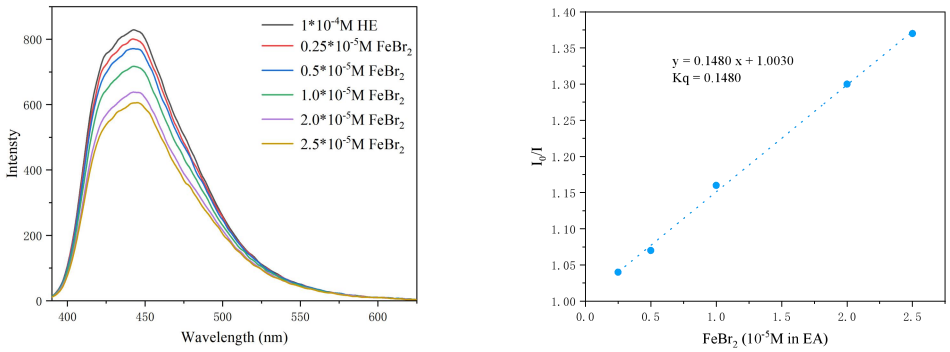


Figure S2 The excited Hantzsch ester quenched by $FeBr_2$ in ethyl acetate.

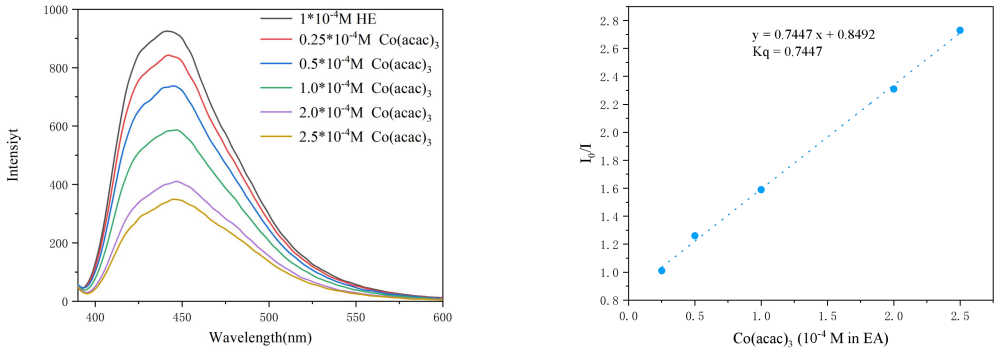


Figure S3 The excited Hantzsch ester quenched by $Co(acac)_3$ in ethyl acetate.

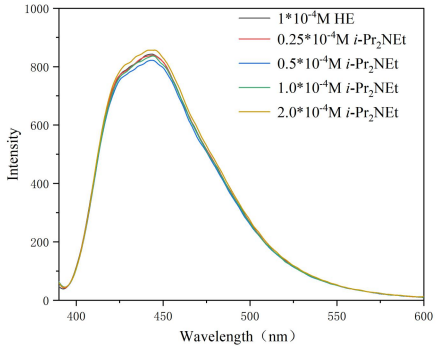


Figure S4 The excited Hantzsch ester not quenched by *i*-Pr$_2$NEt in ethyl acetate.

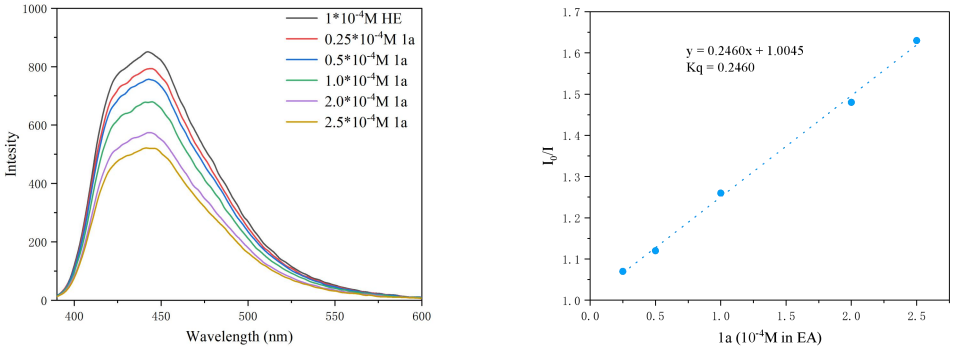


Figure S5 The excited Hantzsch ester quenched by aldehyde **1a** in ethyl acetate.

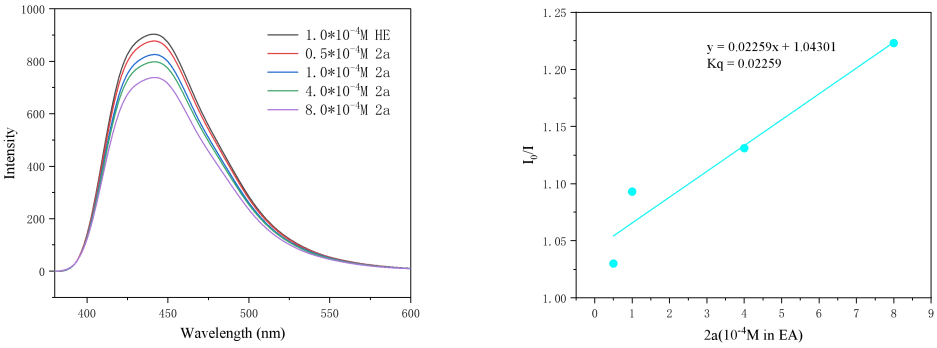


Figure S6 The excited Hantzsch ester quenched by α-bromoester **2a** in ethyl acetate.

Table S6 Quenching of the excited Hansch ester with each component of the reaction

entry	component	Kq
1	$FeBr_2$	0.1480
2	$Co(acac)_3$	0.7447
3	**1a**	0.2460
4	**2a**	0.0226

4.6 Cyclic Voltammetry Data

Cyclic voltammetry experiments were performed in anhydrous degassed CH_3CN with analyte (1 mM) and $[(n\text{-}Bu)_4N]^+[PF_6]^-$ (100 mM) using a glassy carbon working electrode, platinum wire counter electrode, a saturated calomel electrode as reference electrode with a scan rate of 50 mV/s. Data were analyzed by subtracting the electrolyte solution background current prior to identifying the maximum current (C_p).

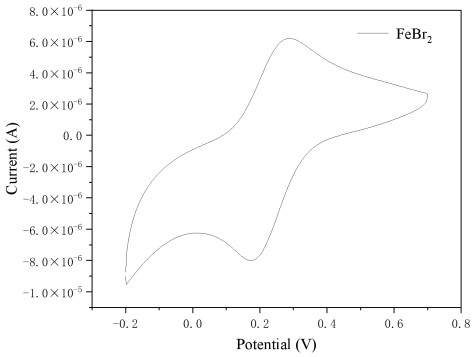


Figure S7 Oxidation potential of $FeBr_2$

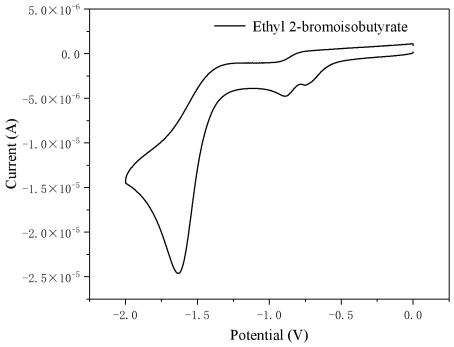
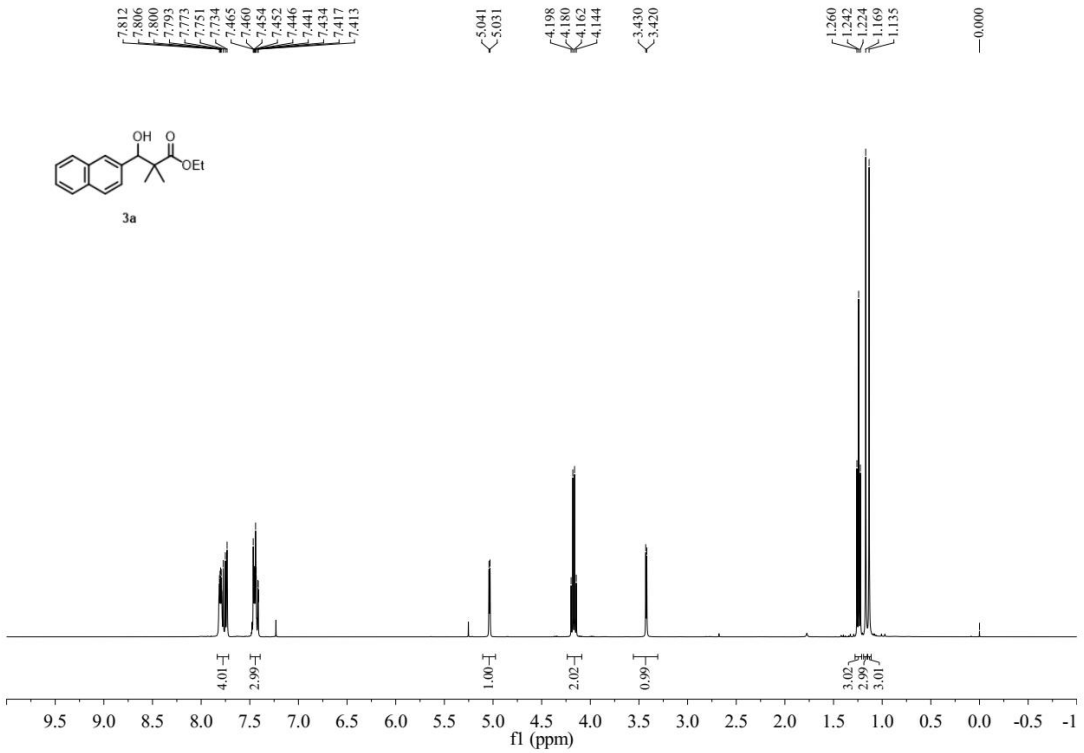


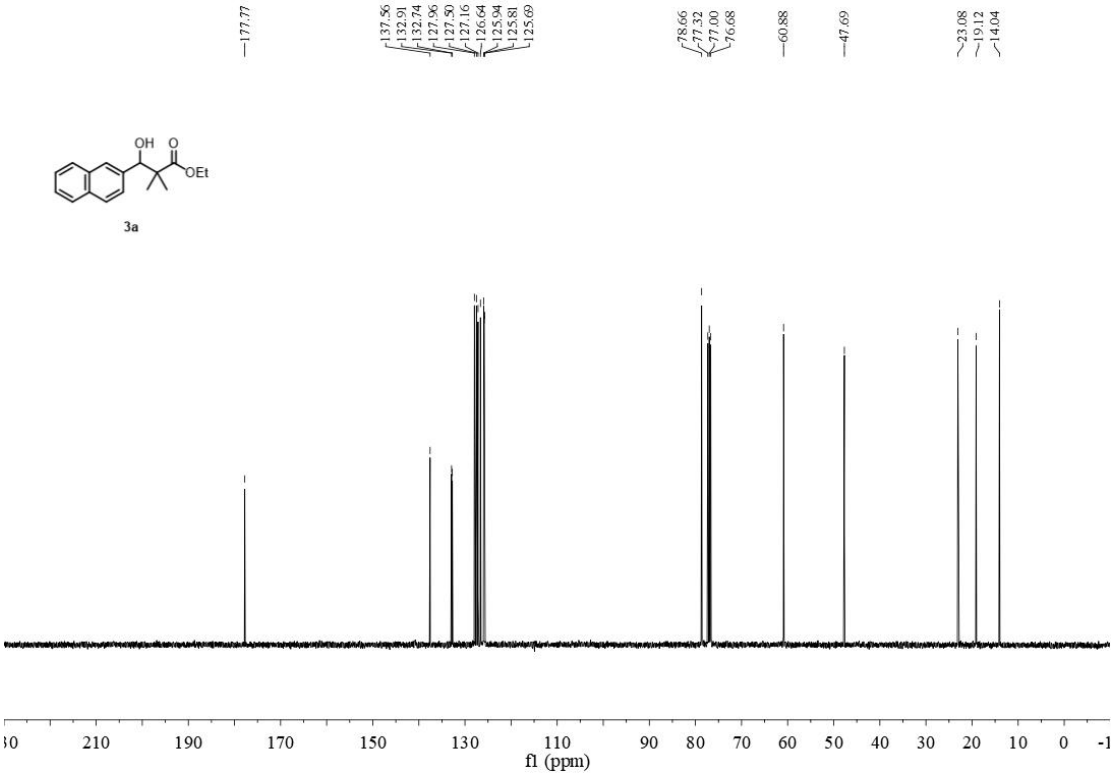
Figure S8 Reduction potential of α-bromo ethyl isobutyrate **2a**

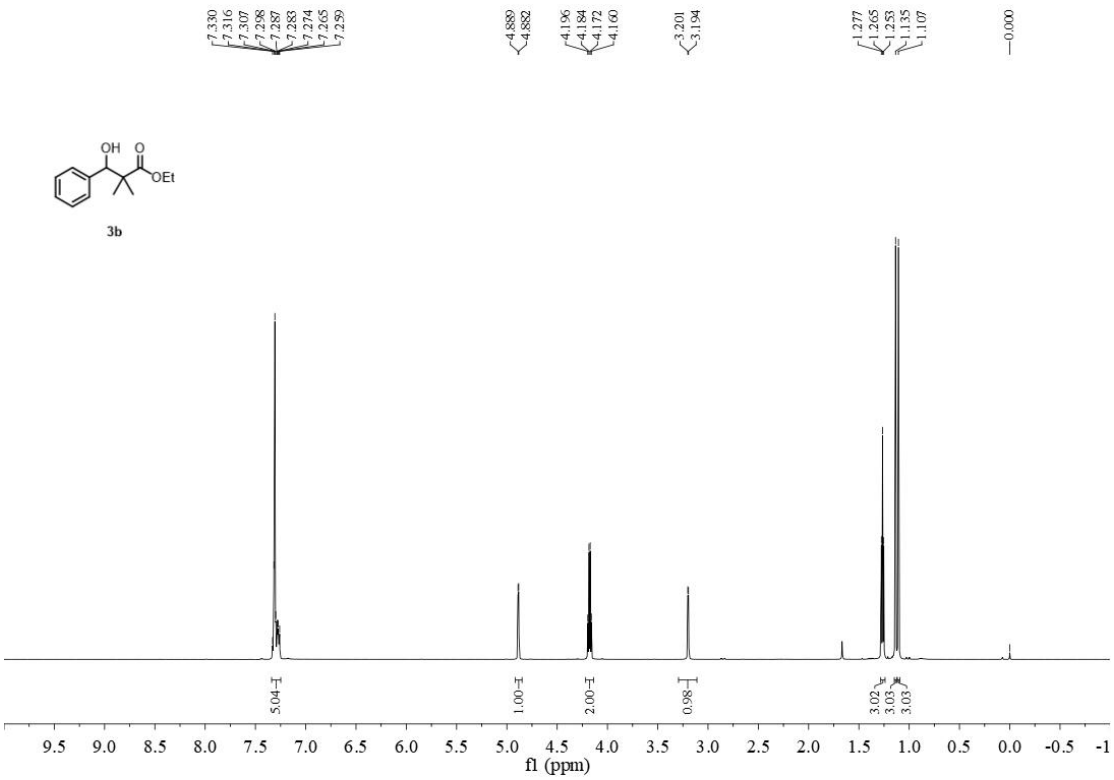
5. References

1. X. Jiang, H. Jiang, Q. Yang, Y. Cheng, L.-Q. Lu, J. A. Tunge and W.-J. Xiao, *J. Am. Chem. Soc.*, 2022, **144**, 8347-8354.
2. K. Cui, Y.-L. Li, G. Li and J.-B. Xia, *J. Am. Chem. Soc.*, 2022, **144**, 23001-23009.

6. Copies of NMR Spectra



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7.265
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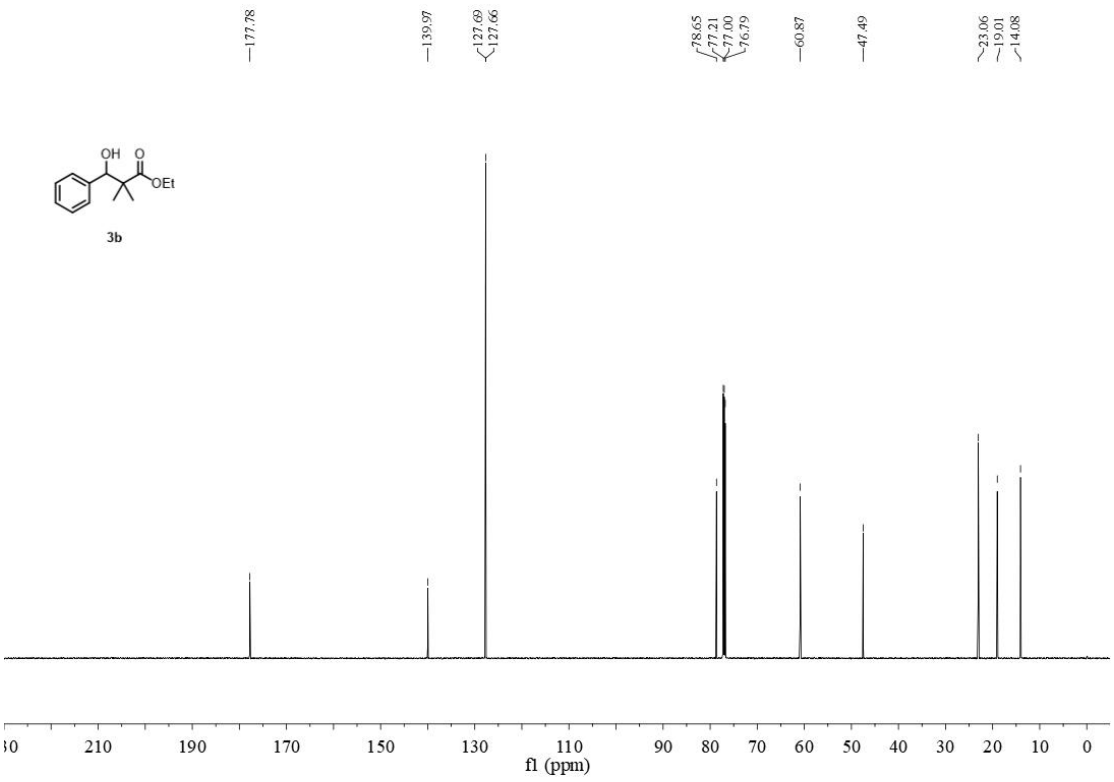
4.184
4.172
4.160
3.201
3.194
1.277
1.265
1.253
1.135
1.107
0.000
OH
O
OEt
3b
5.04
1.00
2.00
0.98
3.02
3.03
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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O
OEt
3b
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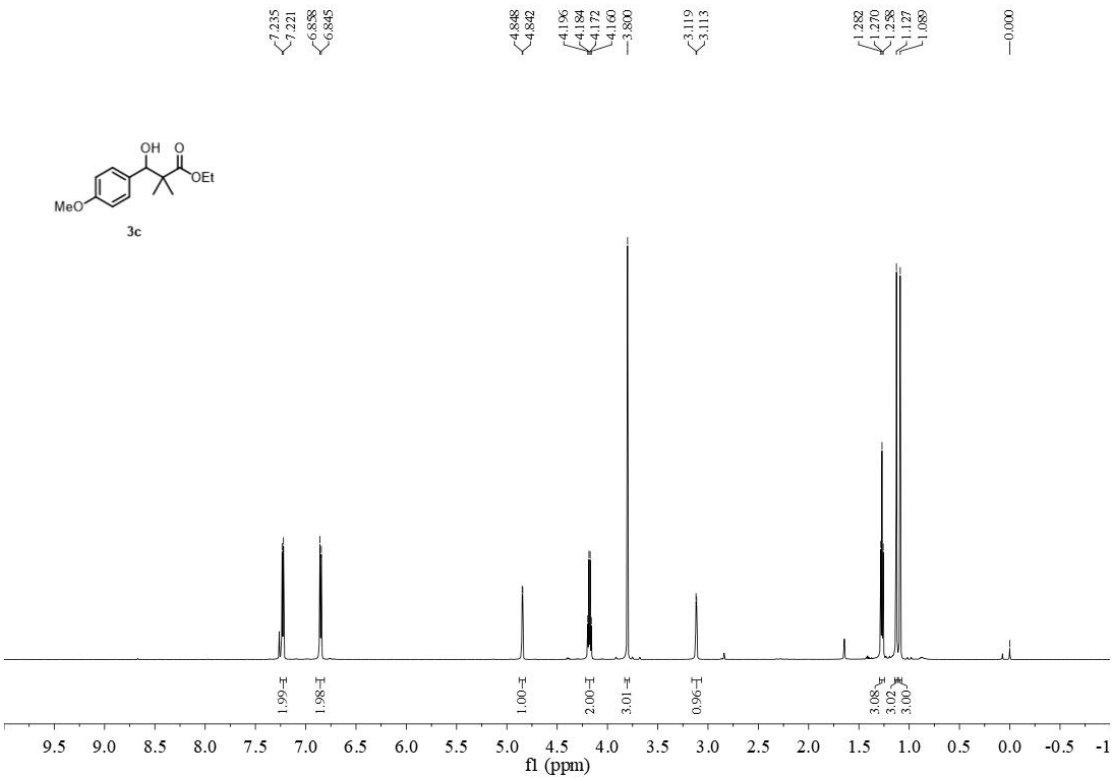
f1 (ppm)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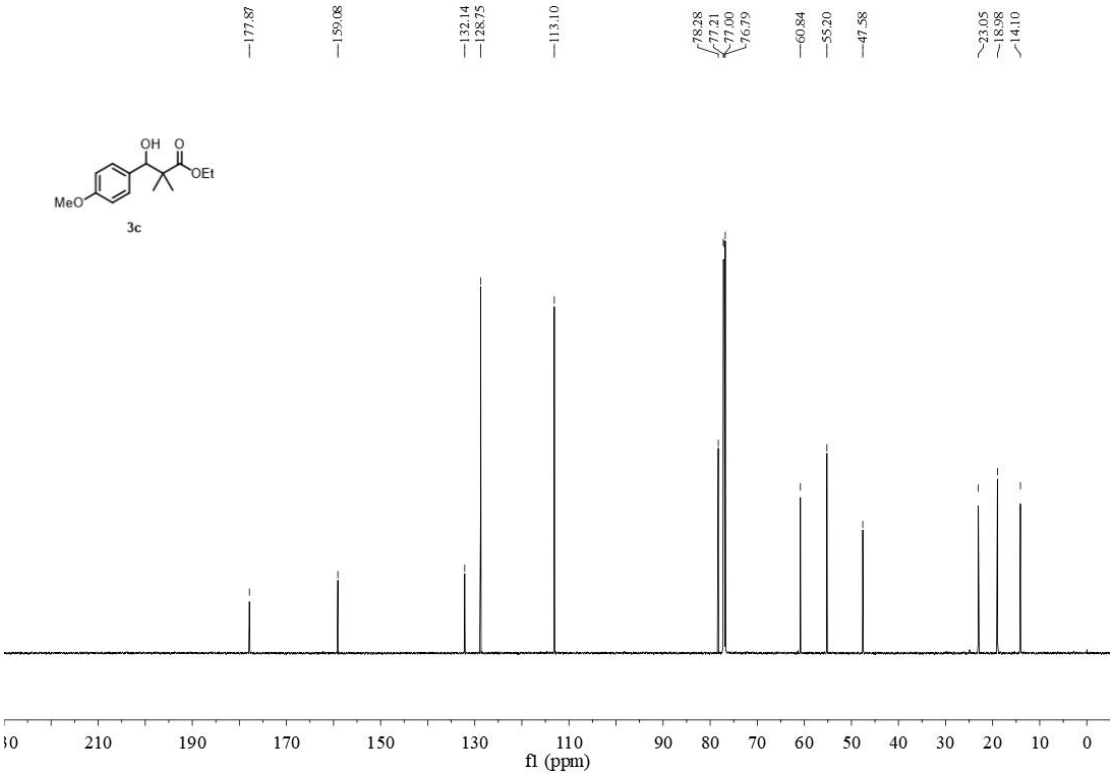
1.270
1.258
1.127
1.089
0.000
OH
O
OEt
MeO
3c
1.99
1.98
1.00
2.00
3.01
0.96
3.08
3.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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60.84
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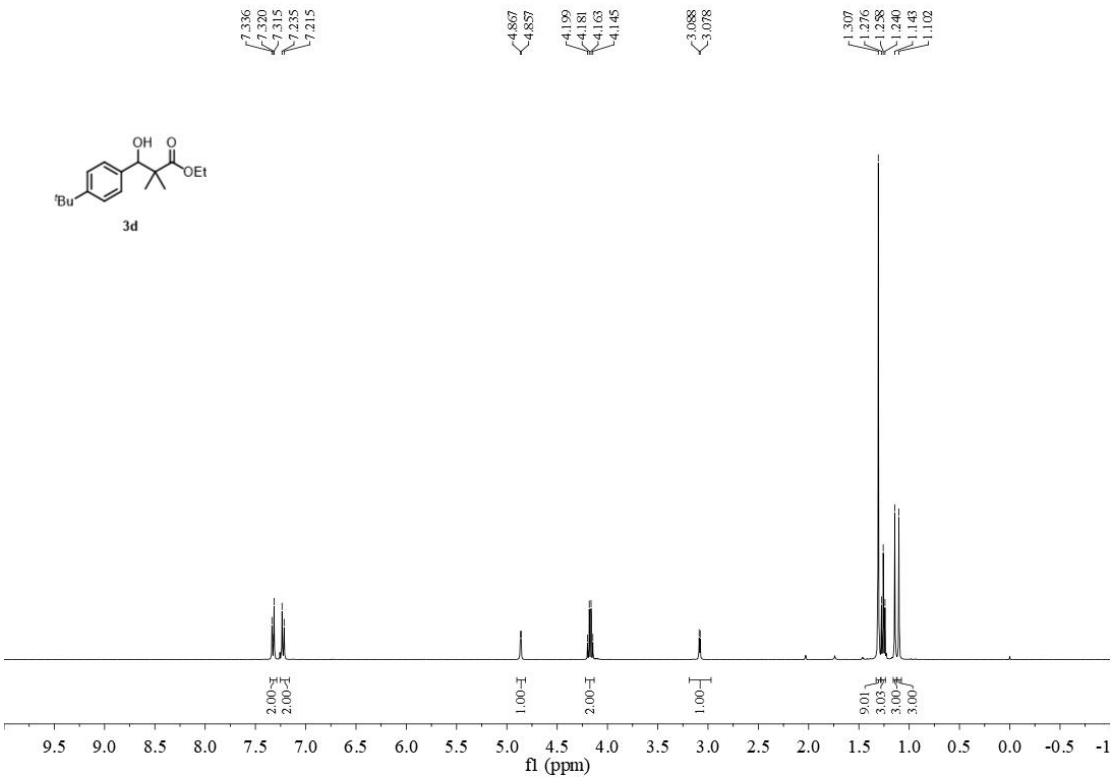
14.10
OH
O
OEt
MeO
3c
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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1.00
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3.00
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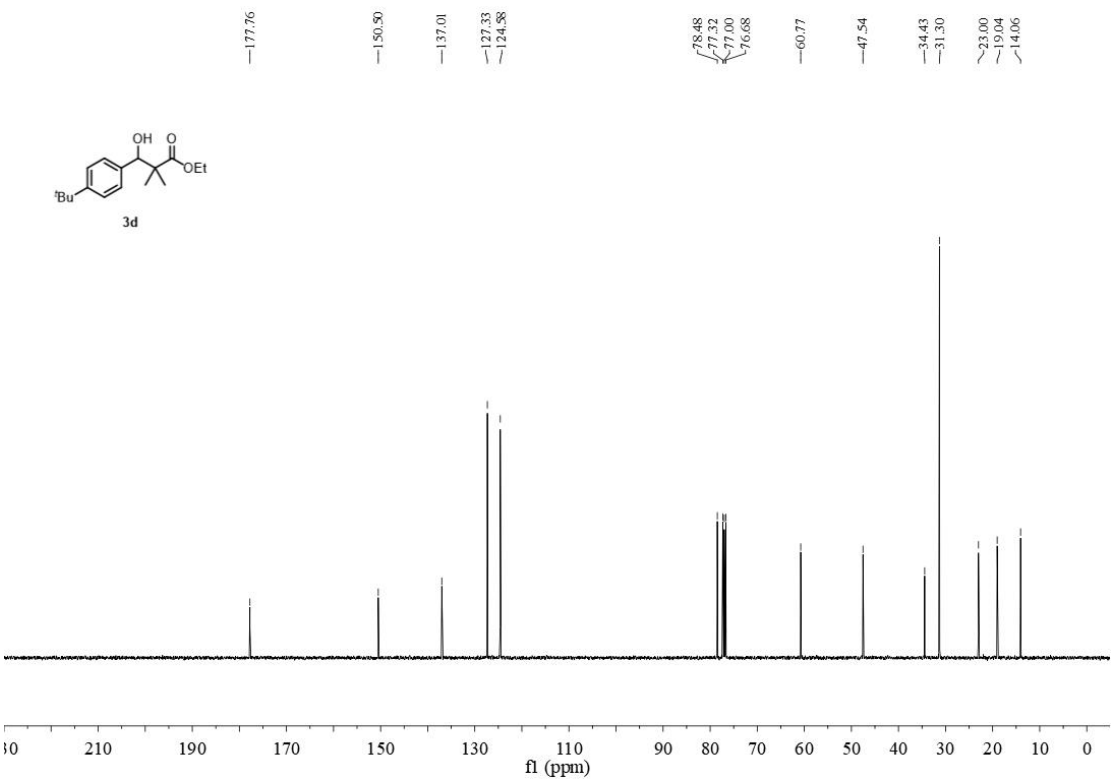
f1 (ppm)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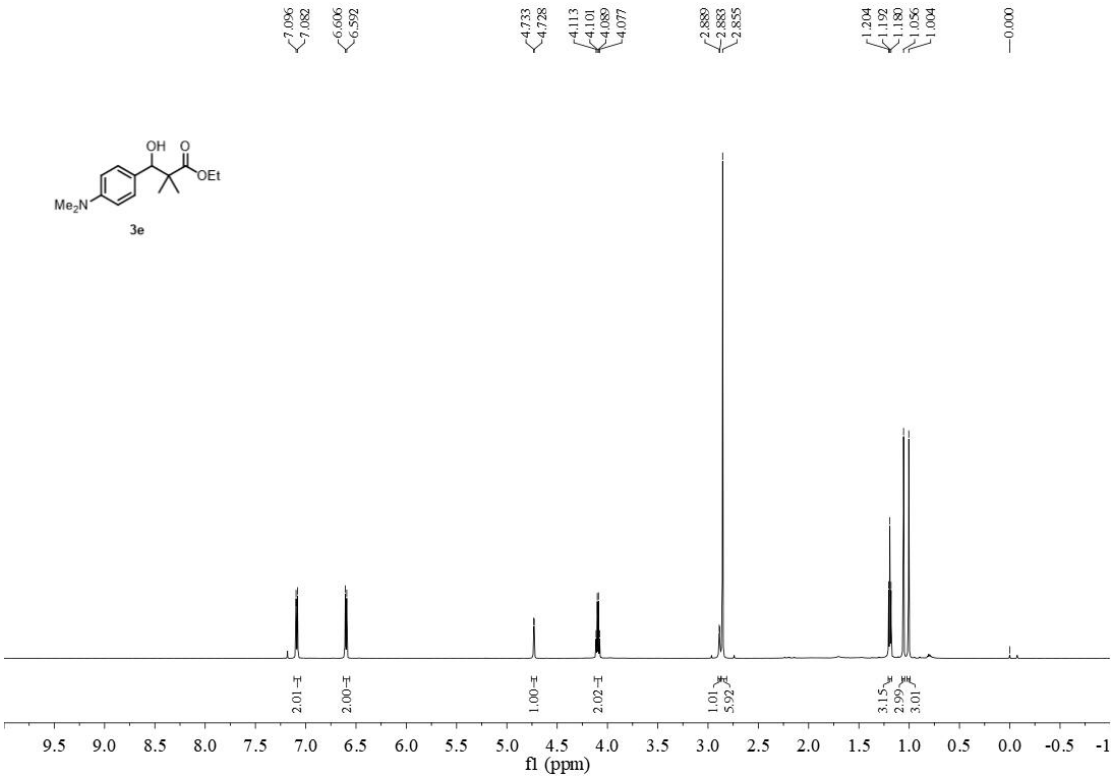
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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2.00
1.00
2.02
1.01
5.92
3.15
2.99
3.01
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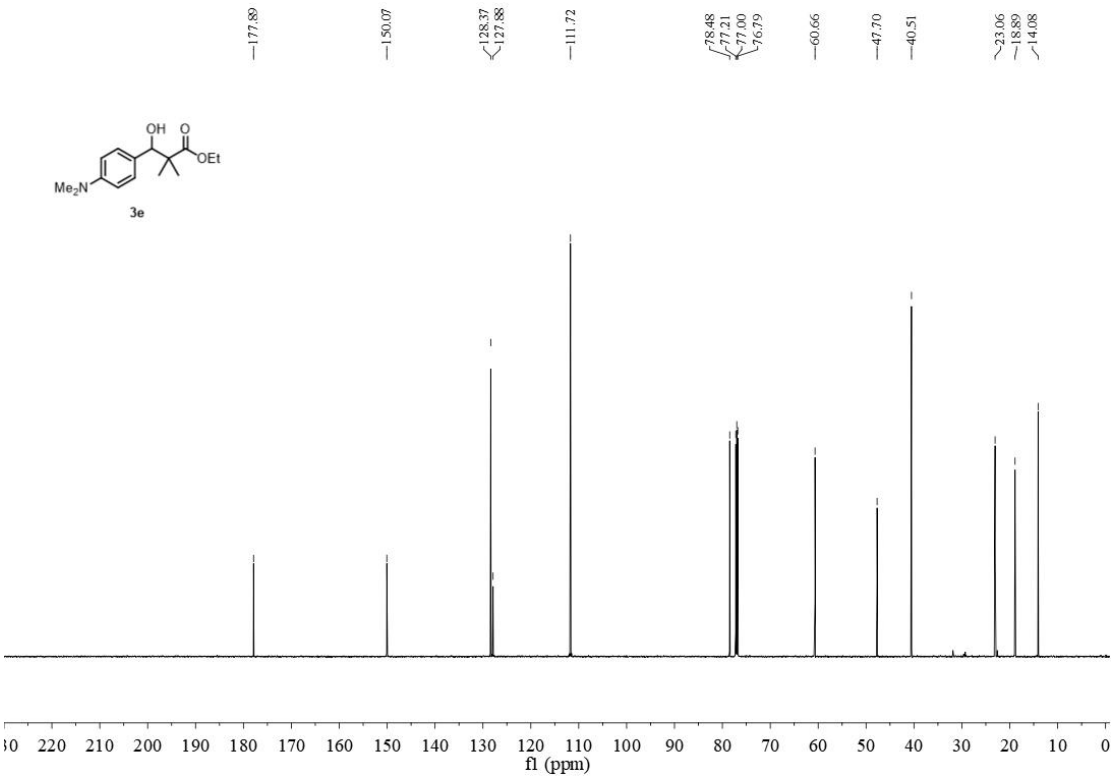
f1 (ppm)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77.21
77.00
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47.70
40.51
23.06
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14.08
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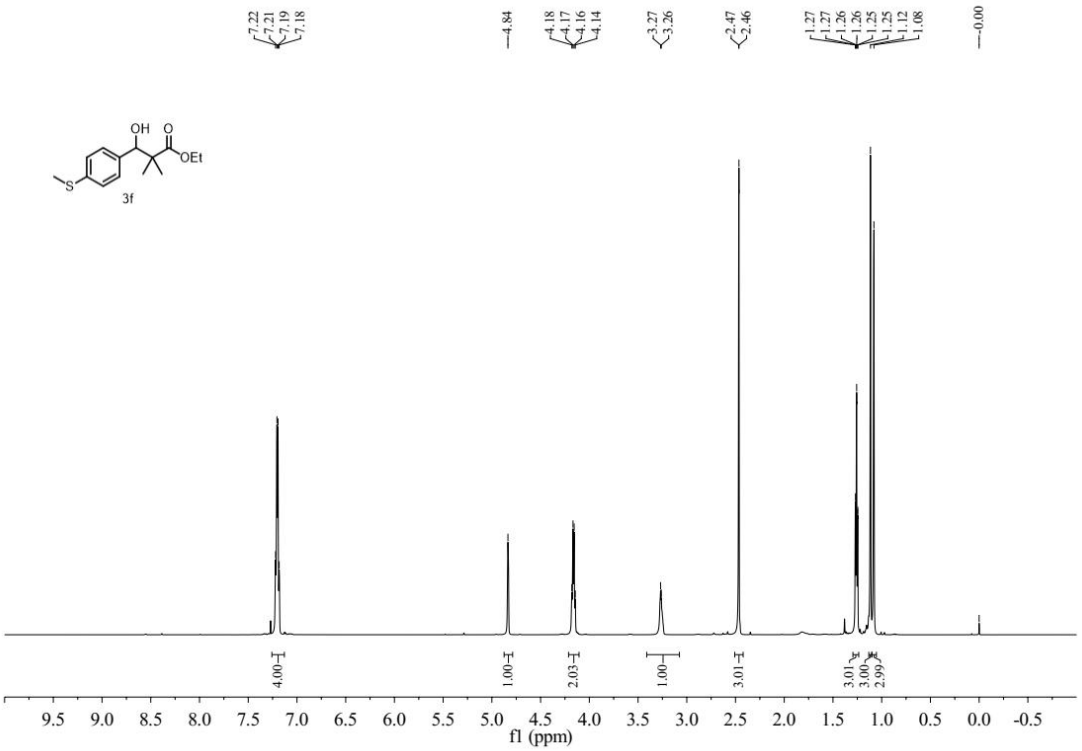
3e
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3f
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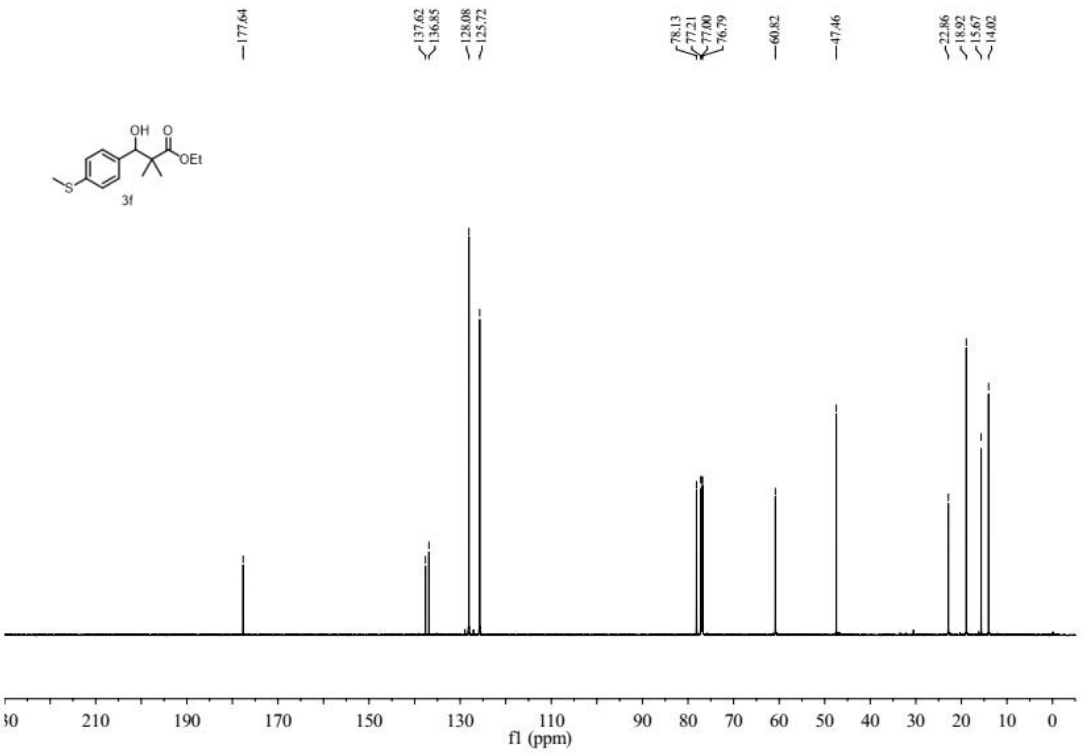
1.00
3.01
3.01
3.00
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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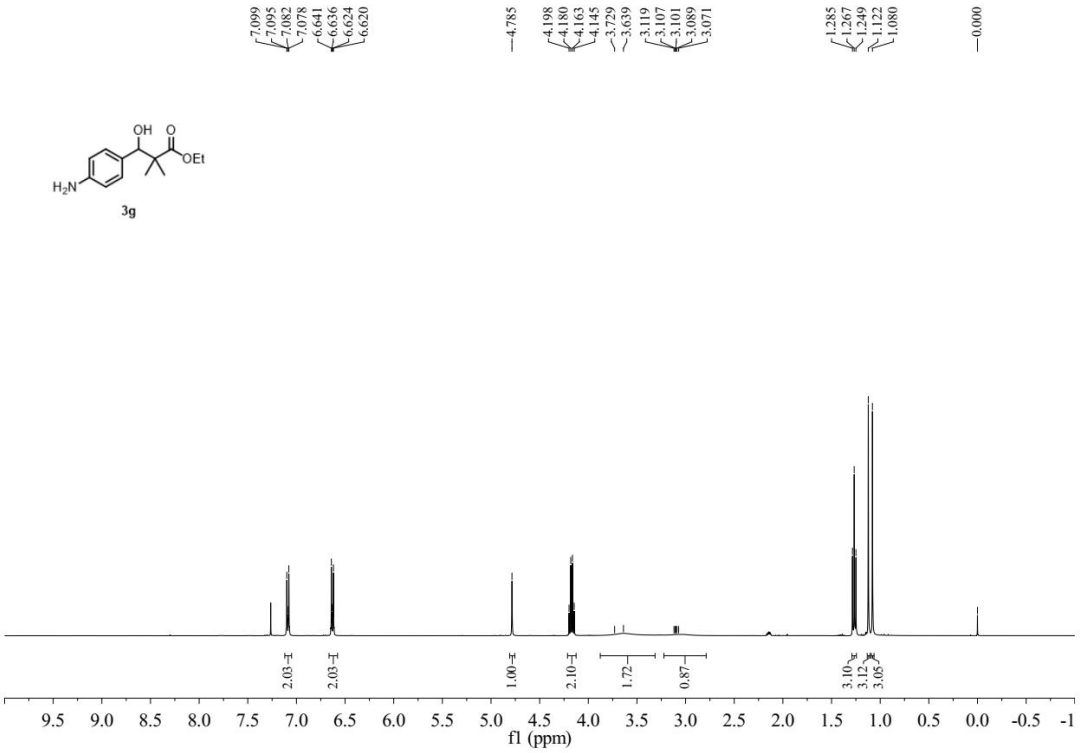
f1 (ppm)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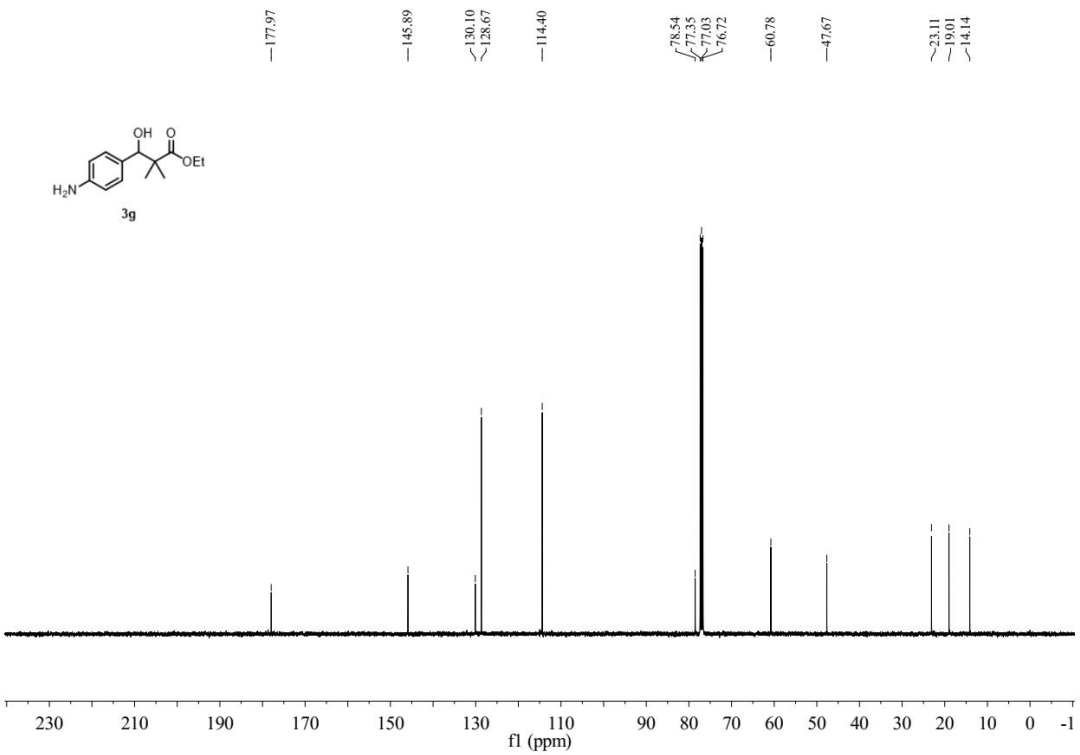
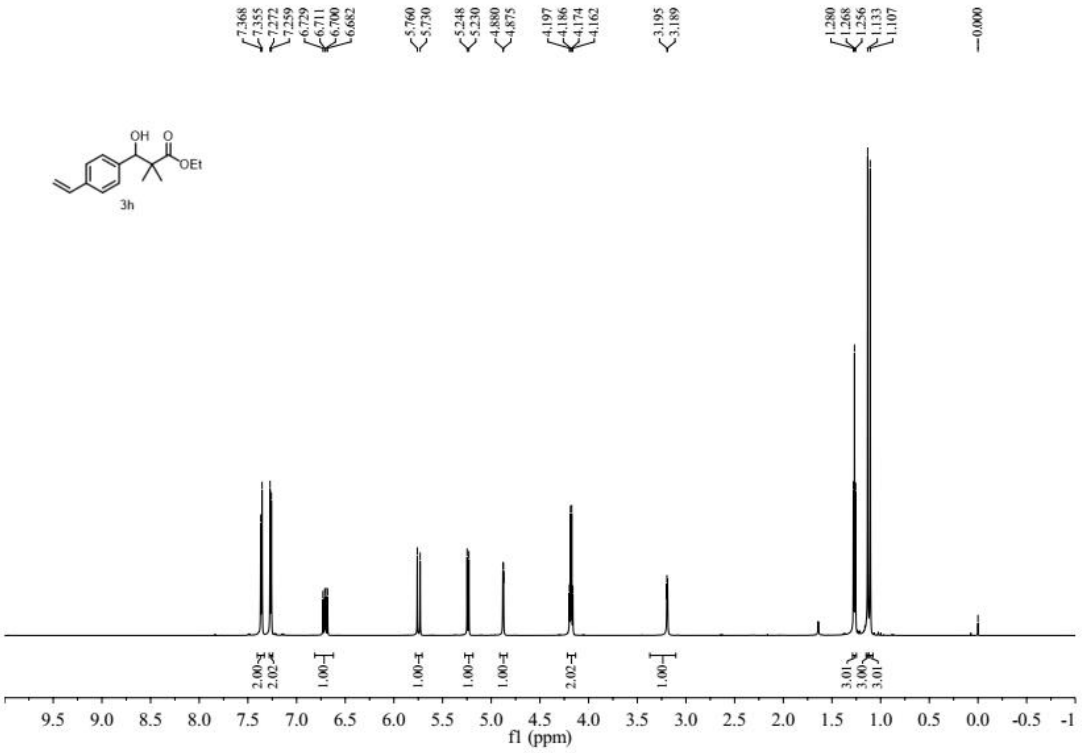
2.10
1.72
0.87
3.10
3.12
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.97
145.89
130.10
128.67
114.40
78.54
77.35
77.03
76.72
60.78
47.67
23.11
19.01
14.14
OH
O
OEt
H2N
3g
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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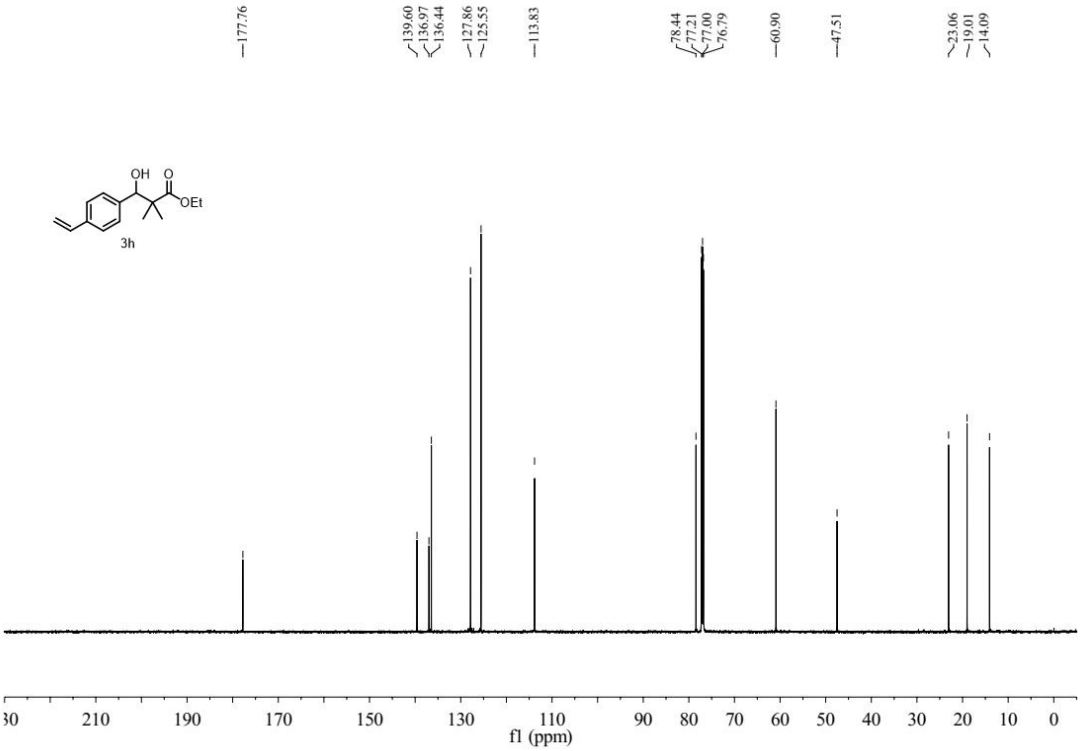
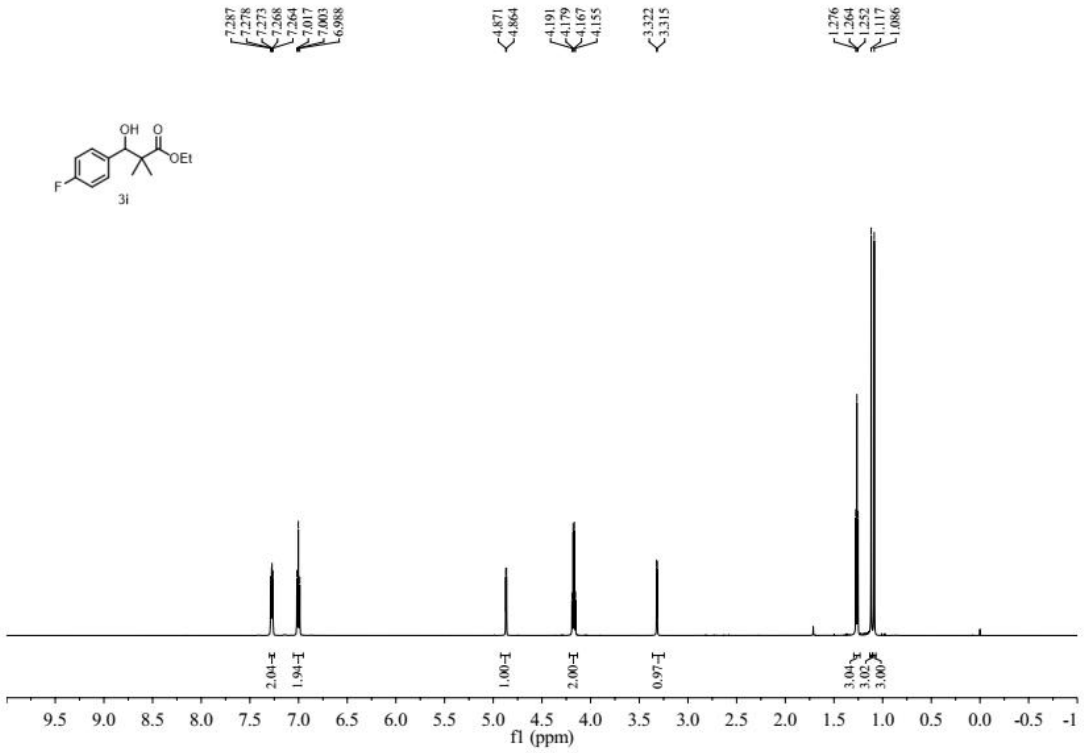
7.355
7.272
7.259
6.729
6.711
6.700
6.682
5.760
5.730
5.248
5.230
4.880
4.875
4.197
4.186
4.174
4.162
3.195
3.189
1.280
1.268
1.256
1.133
1.107
0.000
OH
O
OEt
3h
2.00
2.02
1.00
1.00
1.00
1.00
2.02
1.00
3.01
3.00
3.01
f1 (ppm)


177.76
139.60
136.97
136.44
127.86
125.55
113.83
78.44
77.21
77.00
76.79
60.90
47.51
23.06
19.01
14.09
OH
O
OEt
3h
f1 (ppm)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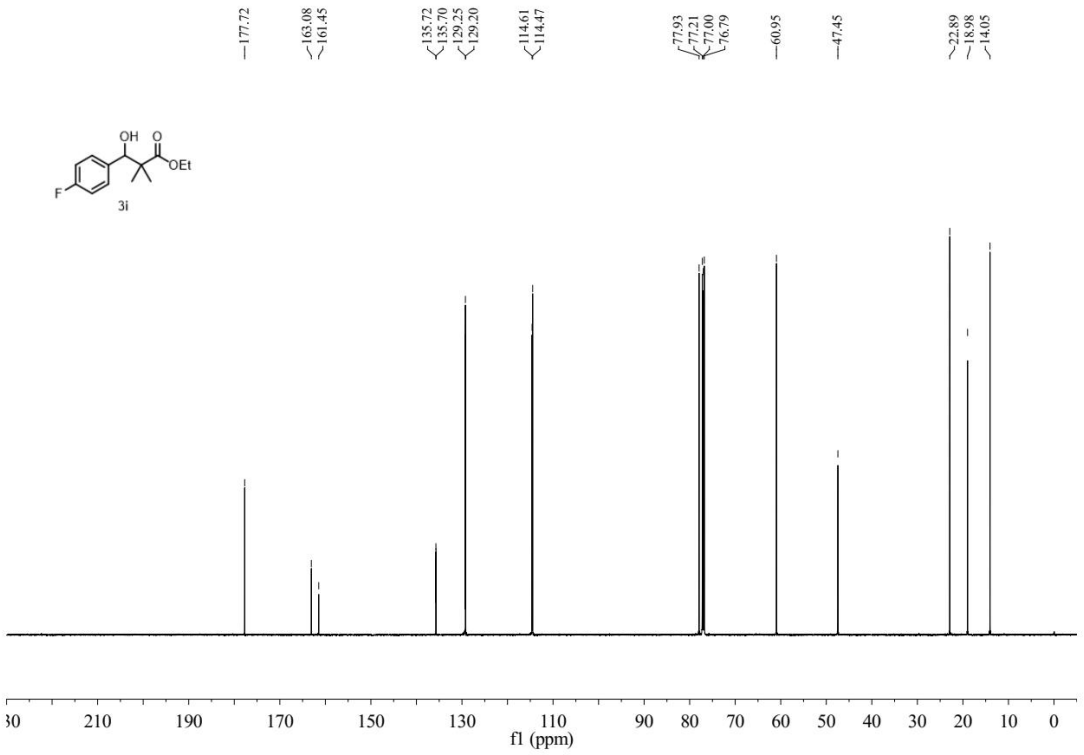
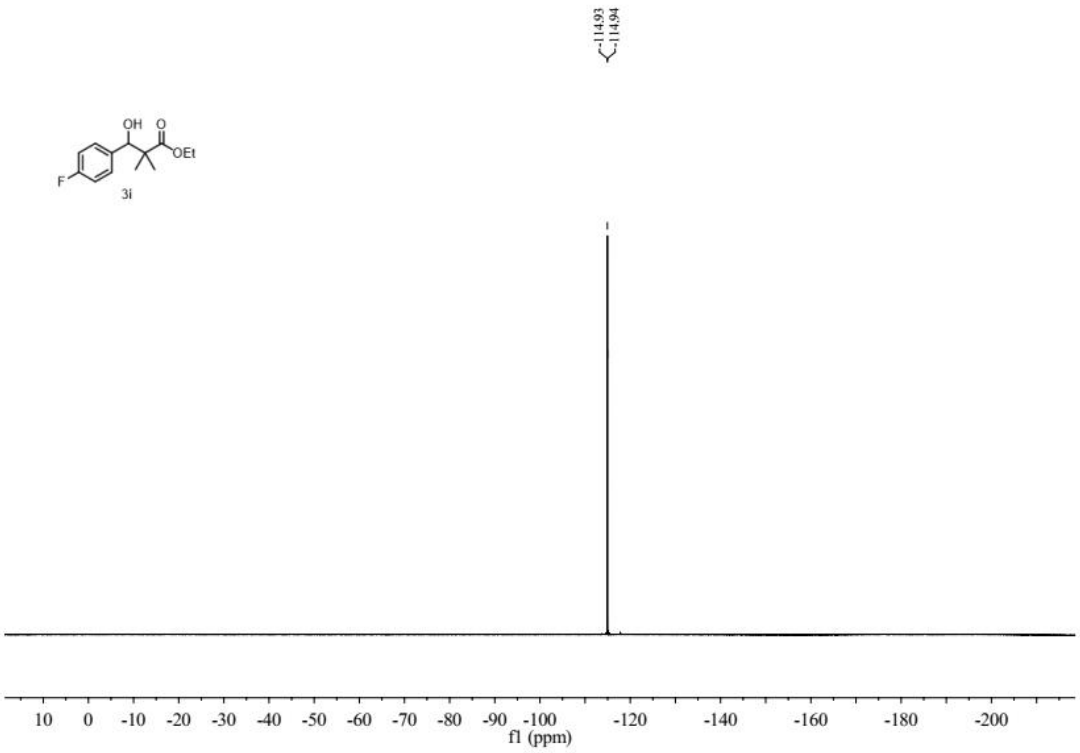
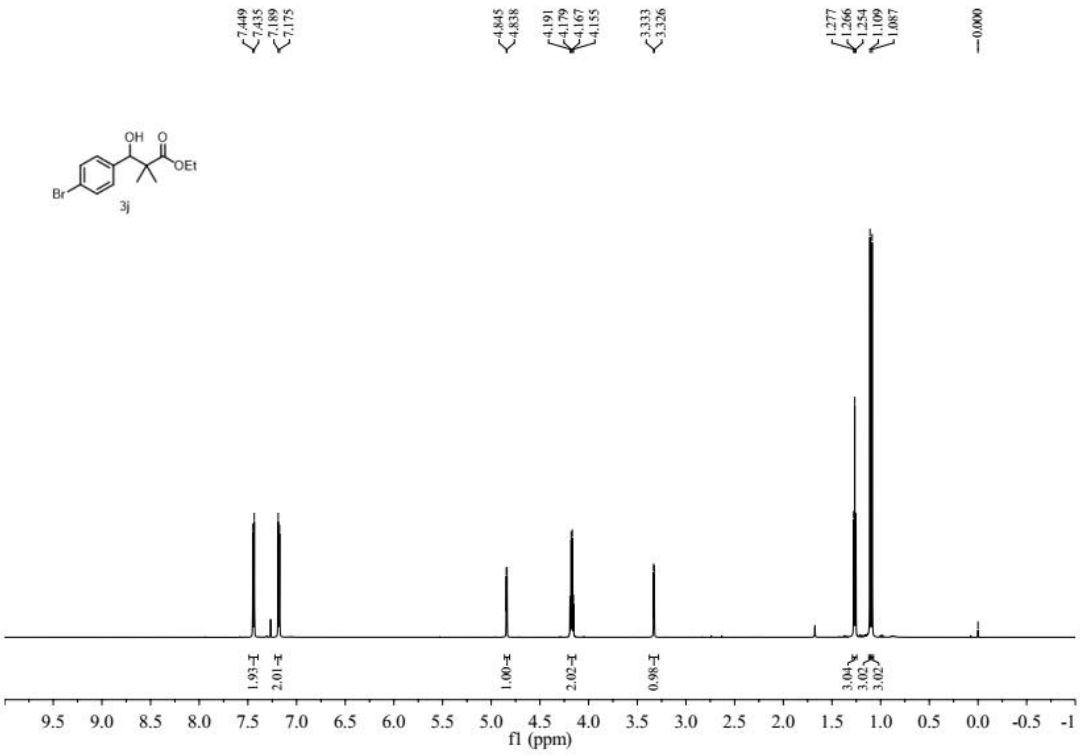
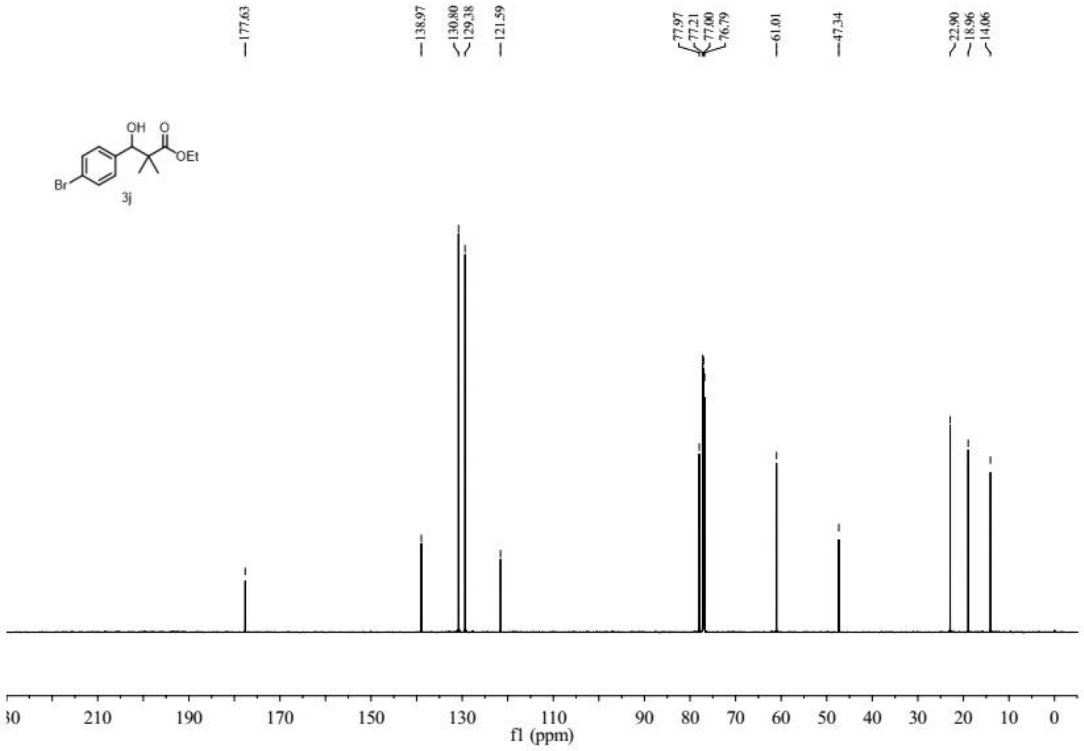
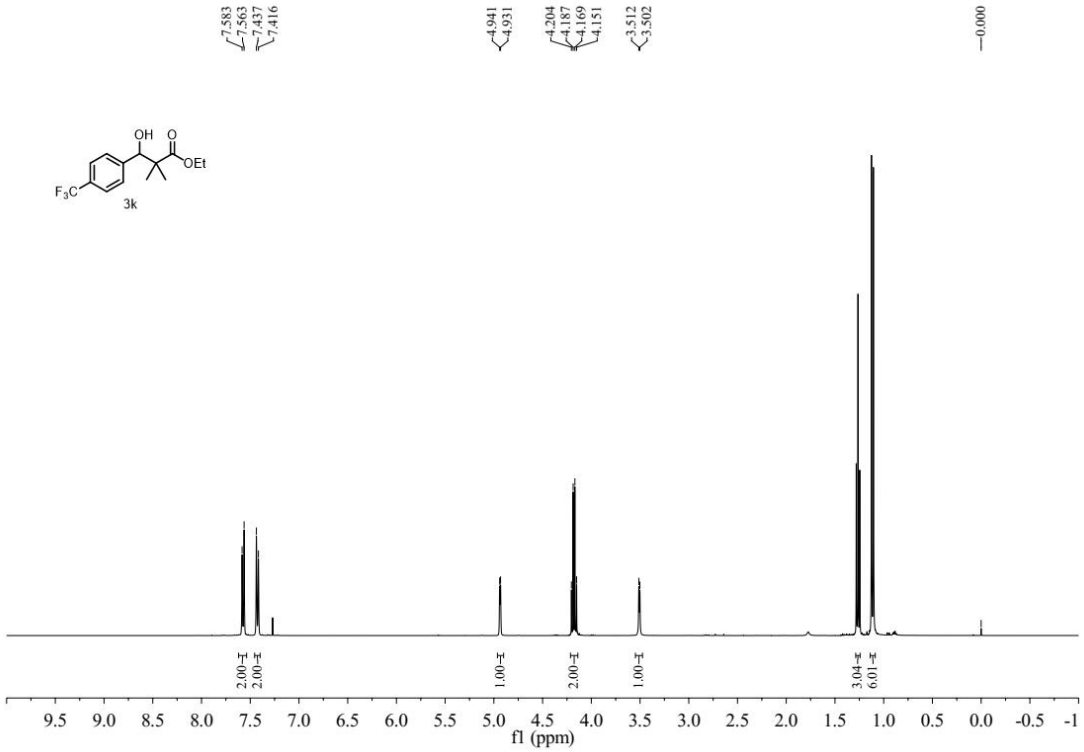
7.278
7.273
7.268
7.264
7.017
7.003
6.988
4.871
4.864
4.191
4.179
4.167
4.155
3.322
3.315
1.276
1.264
1.252
1.117
1.086
OH
O
OEt
F
3i
2.04
1.94
1.00
2.00
0.97
3.04
3.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

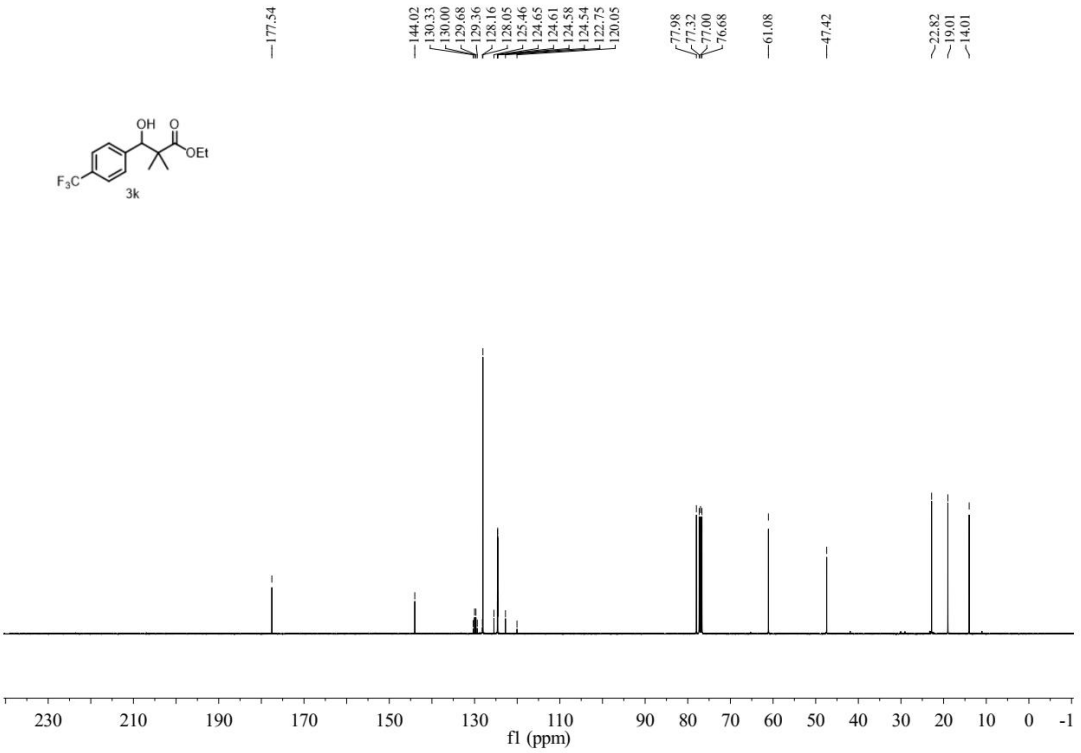

177.72
163.08
161.45
135.72
135.70
129.25
129.20
114.61
114.47
77.93
77.21
77.00
76.79
60.95
47.45
22.89
18.98
14.05
OH
O
OEt
F
3i
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

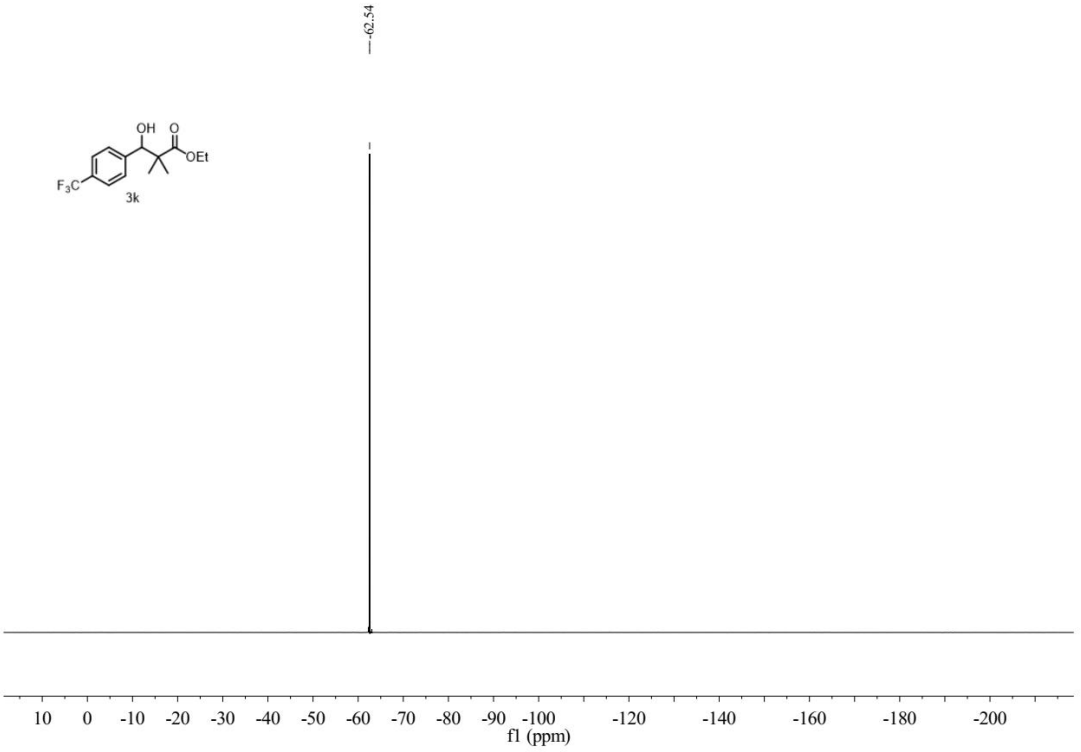

-114.93
-114.94
OH
O
OEt
F
3i
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.449
7.435
7.189
7.175
4.845
4.838
4.191
4.179
4.167
4.155
3.333
3.326
1.277
1.266
1.254
1.109
1.087
0.000
OH
O
OEt
Br
3j
1.93
2.01
1.00
2.02
0.98
3.04
3.02
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.63
138.97
130.80
129.38
121.59
77.97
77.21
77.00
76.79
61.01
47.34
22.90
18.96
14.06
OH
O
OEt
Br
3j
fl (ppm)


7.583
7.563
7.437
7.416
4.941
4.931
4.204
4.187
4.169
4.151
3.512
3.502
0.000
OH
O
OEt
F3C
3k
2.00
2.00
1.00
2.00
1.00
3.04
6.01
fl (ppm)


177.54
144.02
130.33
130.00
129.68
129.36
128.16
128.05
125.46
124.65
124.61
124.58
124.54
122.75
120.05
77.98
77.32
77.00
76.68
61.08
47.42
22.82
19.01
14.01
OH
O
OEt
F3C
3k
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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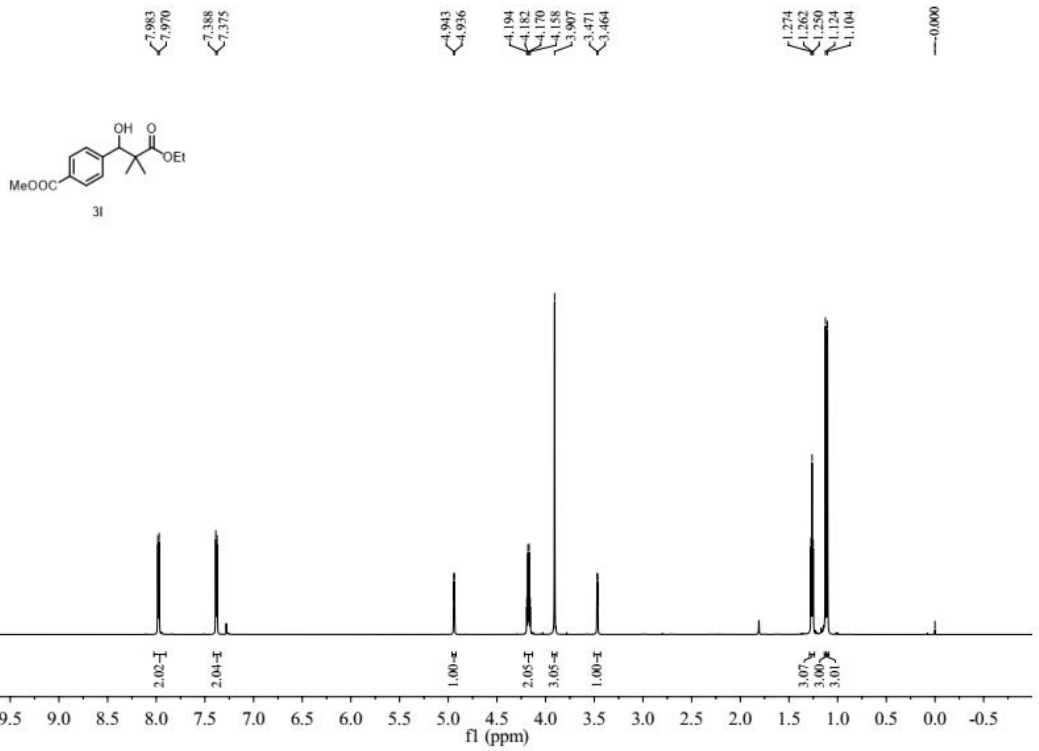
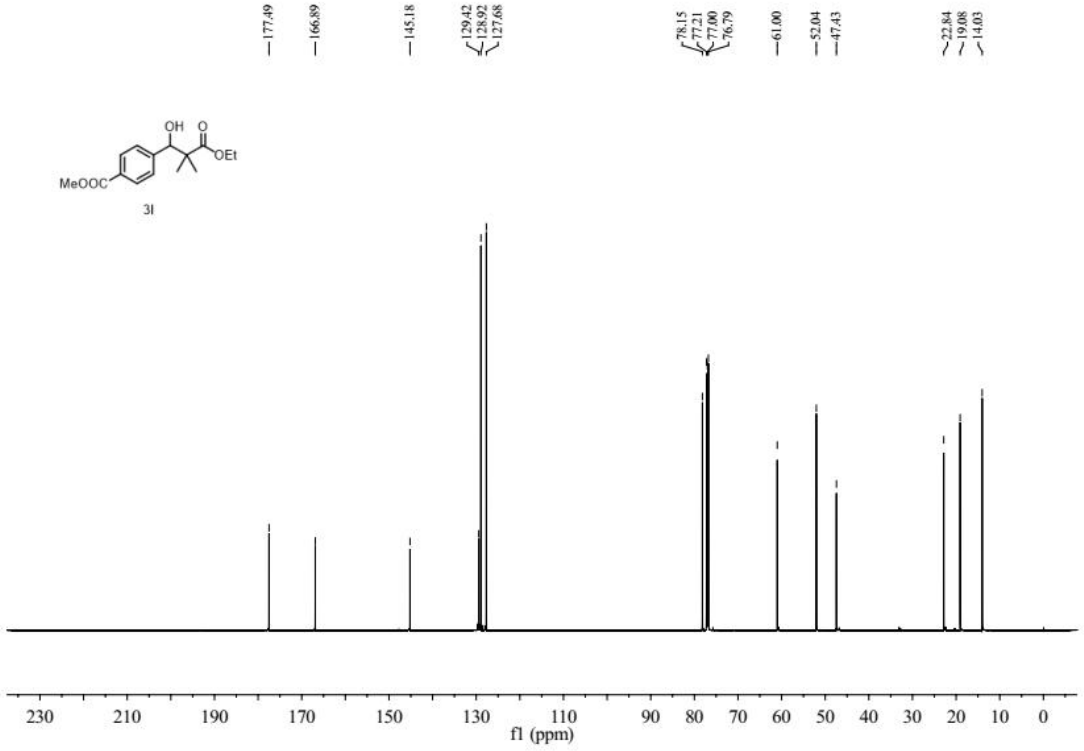
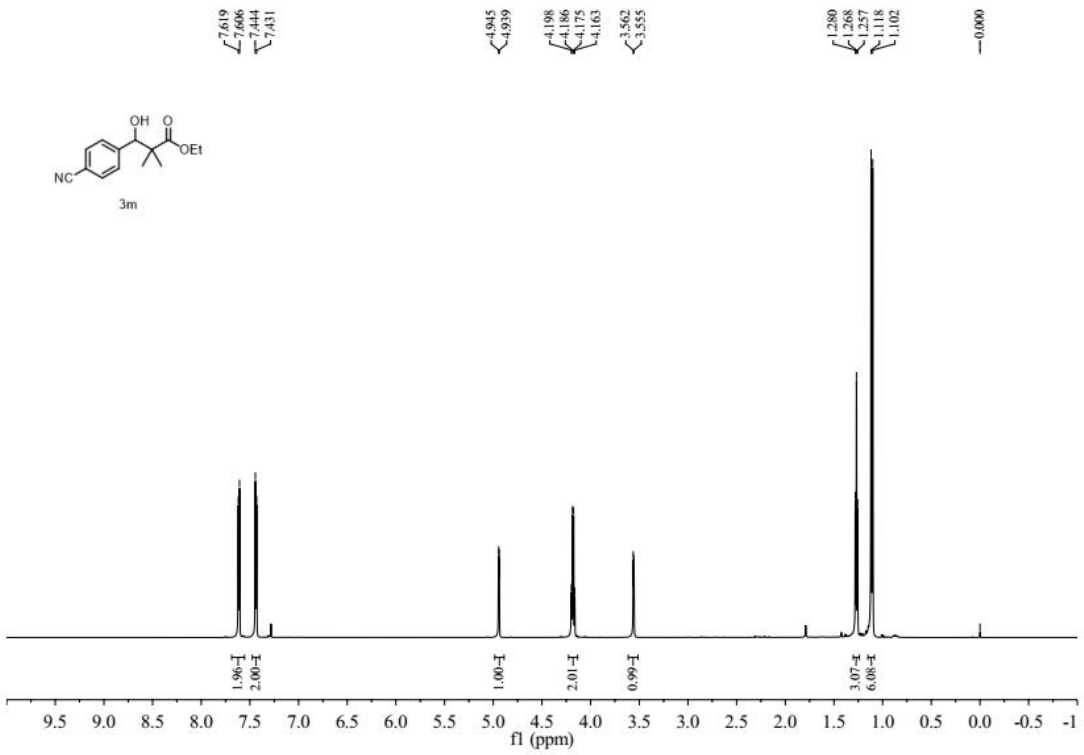
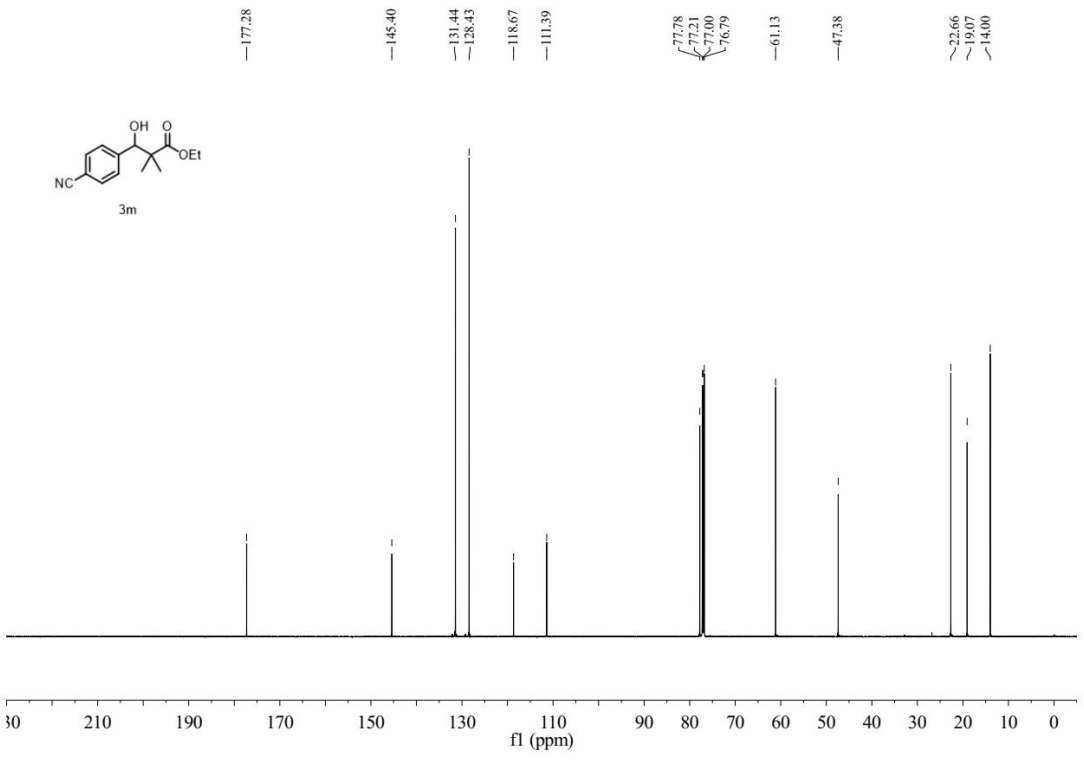
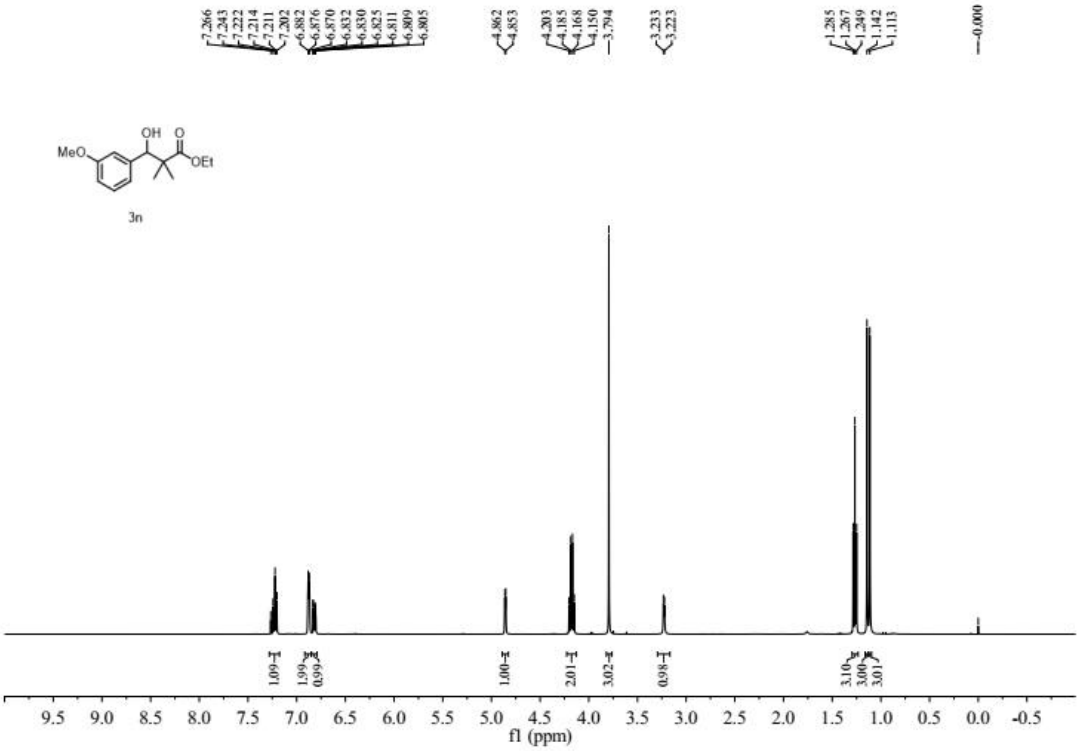
OH
O
OEt
F3C
3k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

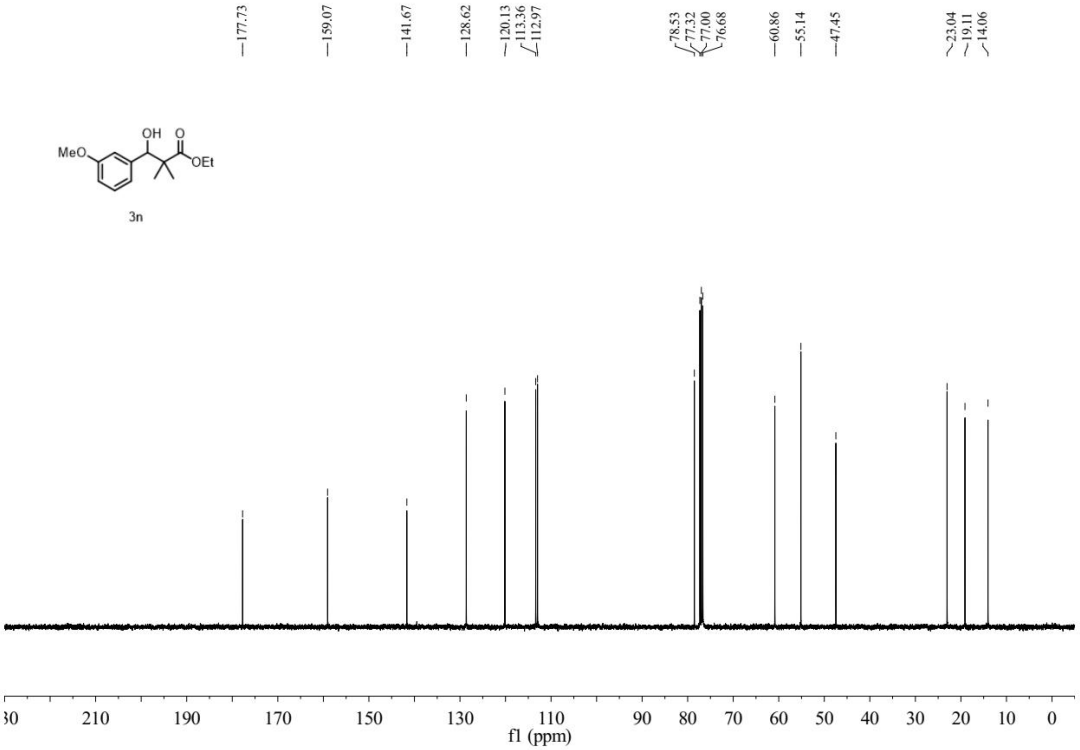

7.983
7.970
7.388
7.375
4.943
4.936
4.194
4.182
4.170
4.158
3.907
3.471
3.464
1.274
1.262
1.250
1.124
1.104
0.000
OH
O
OEt
MeOOC
3l
2.02
2.04
1.00
2.05
3.05
1.00
3.07
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

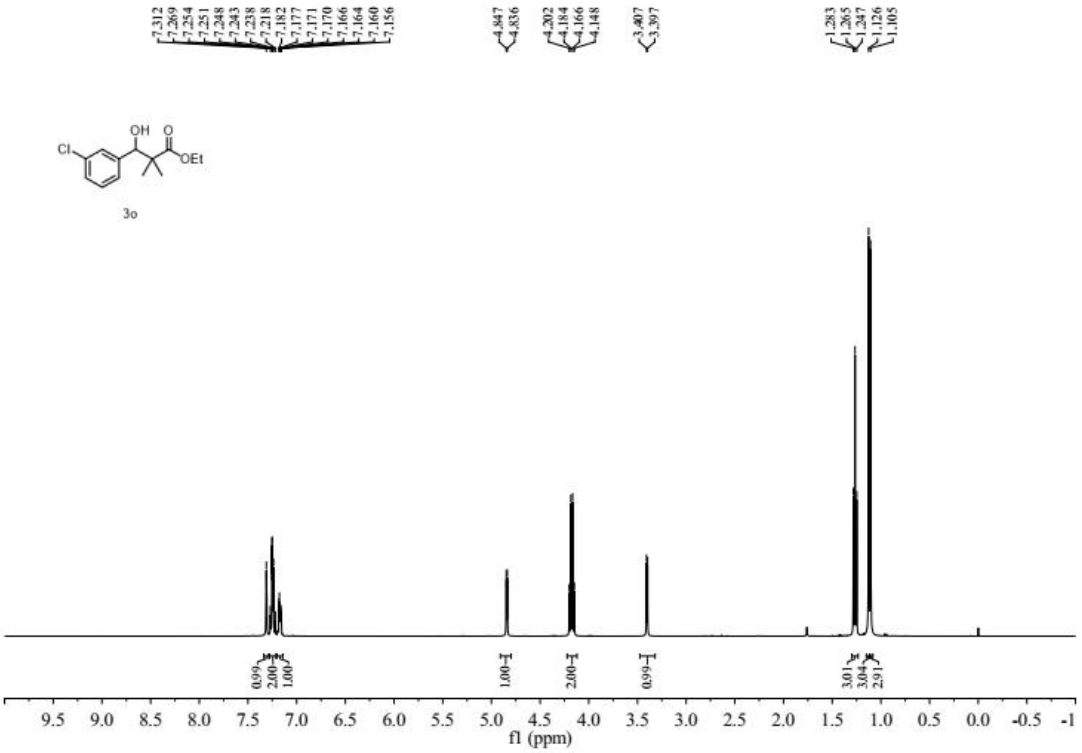

177.49
166.89
145.18
129.42
128.92
127.68
78.15
77.21
77.00
76.79
61.00
52.04
47.43
22.84
19.08
14.03
OH
O
OEt
MeOOC
3l
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

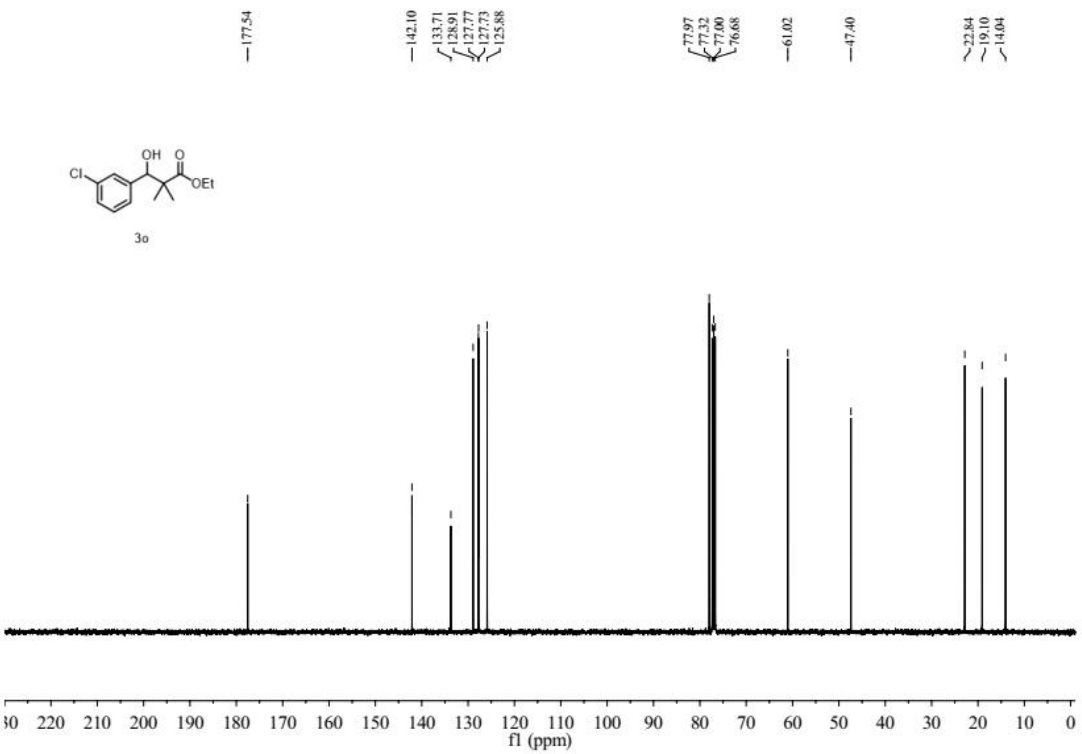

7.619
7.606
7.444
7.431
4.945
4.939
4.198
4.186
4.175
4.163
3.562
3.555
1.280
1.268
1.257
1.118
1.102
0.000
OH
O
OEt
NC
3m
1.96
2.00
1.00
2.01
0.99
3.07
6.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

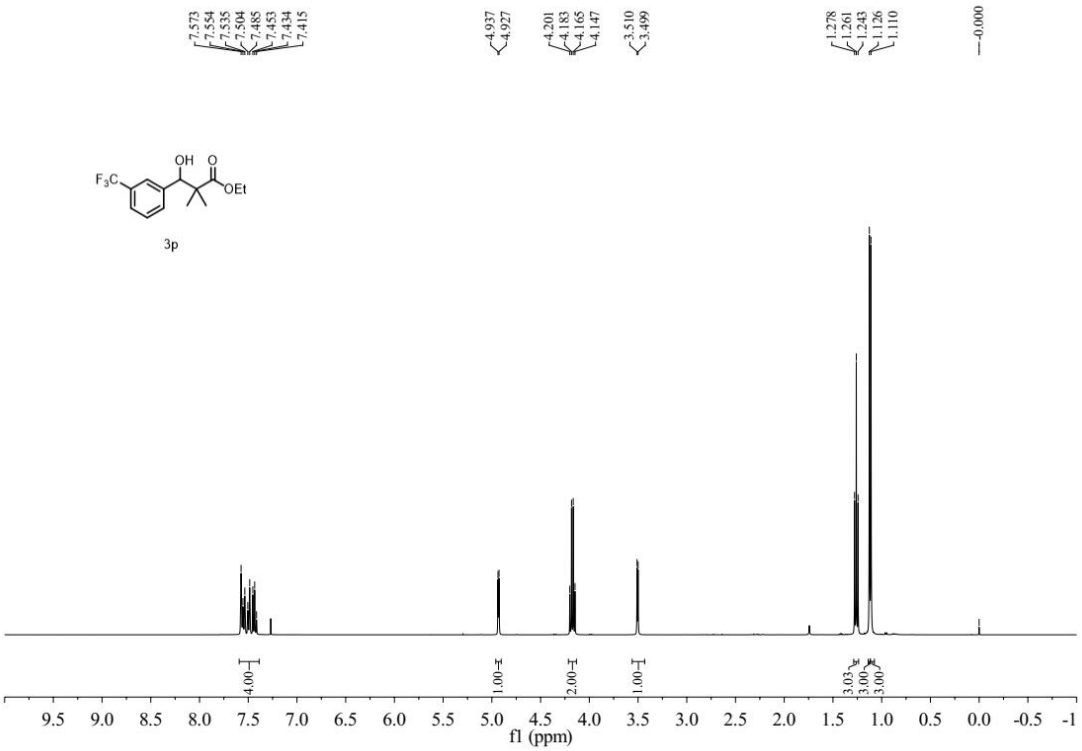

177.28
145.40
131.44
128.43
118.67
111.39
77.78
77.21
77.00
76.79
61.13
47.38
22.66
19.07
14.00
OH
O
OEt
NC
3m
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

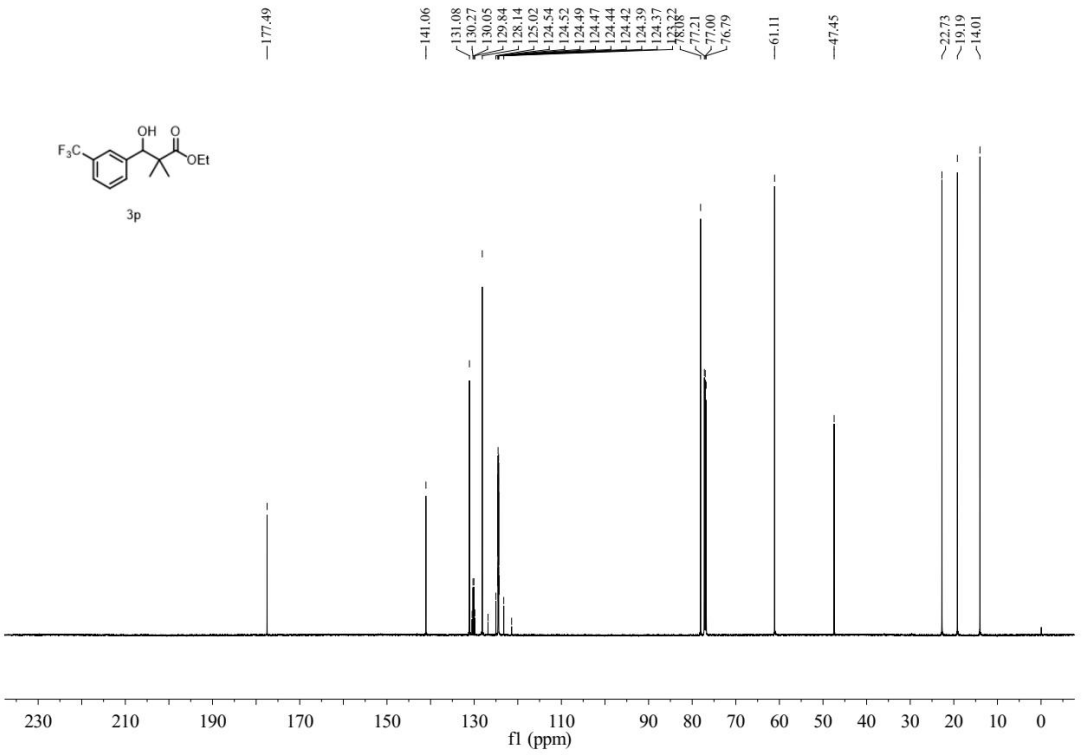

7.266
7.243
7.222
7.214
7.211
7.202
6.882
6.876
6.870
6.832
6.830
6.825
6.811
6.809
6.805
4.862
4.853
4.203
4.185
4.168
4.150
3.794
3.233
3.223
1.285
1.267
1.249
1.142
1.113
0.000
OH
O
MeO
OEt
3n
1.09
1.99
0.99
1.00
2.01
3.02
0.98
3.10
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

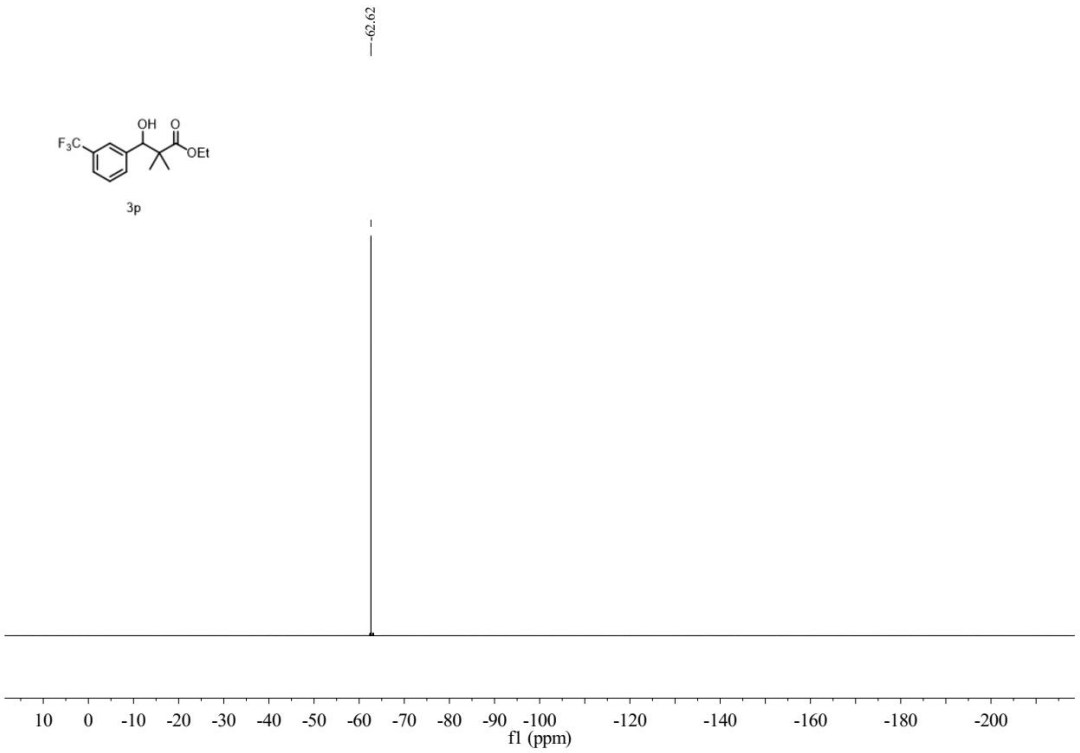

177.73
159.07
141.67
128.62
120.13
113.36
112.97
78.53
77.32
77.00
76.68
60.86
55.14
47.45
23.04
19.11
14.06
OH
O
MeO
OEt
3n
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

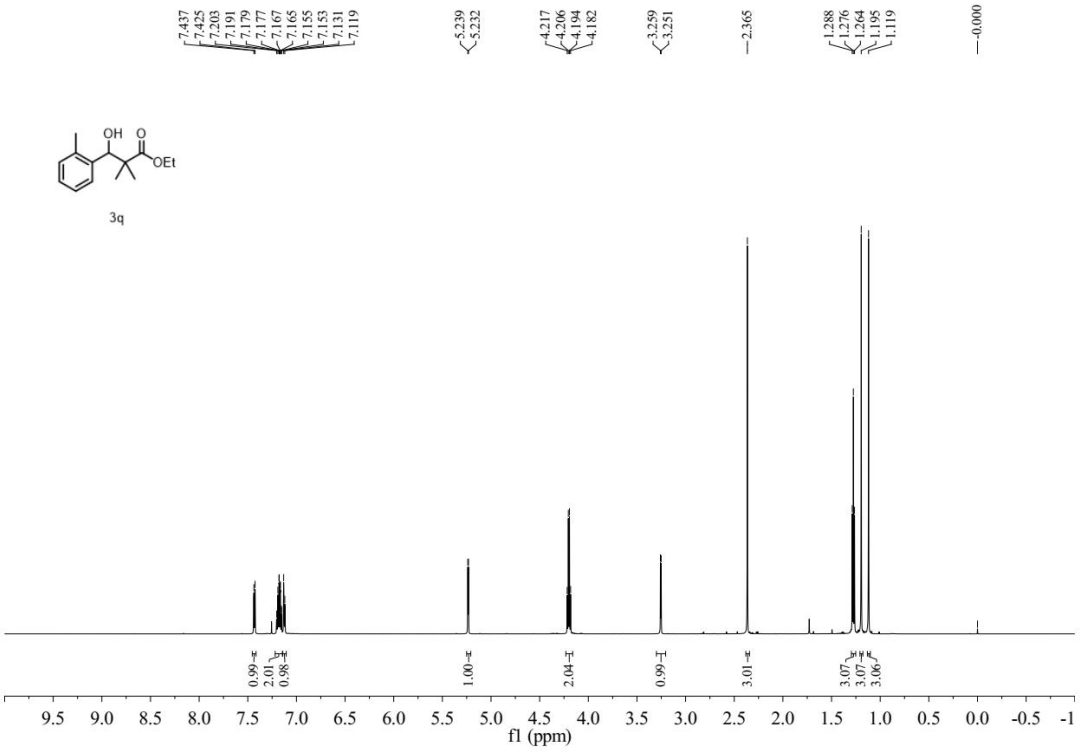

7.312
7.269
7.254
7.251
7.248
7.243
7.238
7.218
7.182
7.177
7.171
7.170
7.166
7.164
7.160
7.156
4.847
4.836
4.202
4.184
4.166
4.148
3.407
3.397
1.283
1.265
1.247
1.126
1.105
OH
O
Cl
OEt
3o
0.99
2.00
1.00
1.00
2.00
0.99
3.01
3.04
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

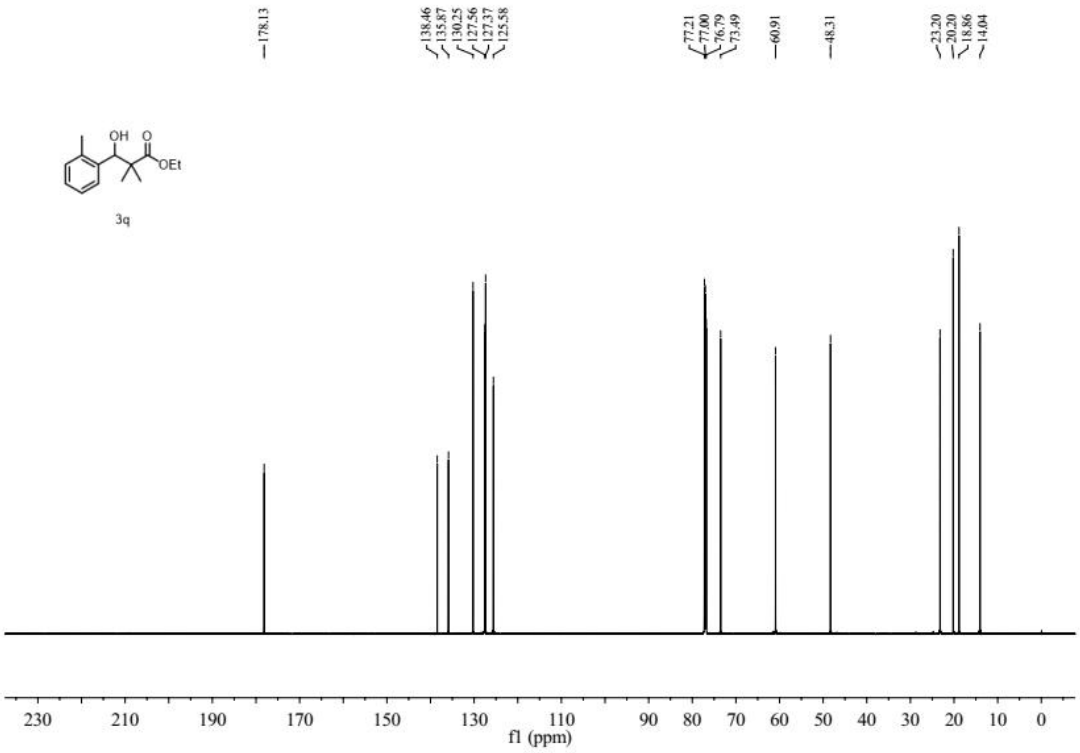

177.54
142.10
133.71
128.91
127.77
127.73
125.88
77.97
77.32
77.00
76.68
61.02
47.40
22.84
19.10
14.04
OH
O
Cl
OEt
3o
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.573
7.554
7.535
7.504
7.485
7.453
7.434
7.415
4.937
4.927
4.201
4.183
4.165
4.147
3.510
3.499
1.278
1.261
1.243
1.126
1.110
-0.000
OH
O
F3C
OEt
3p
4.00
1.00
2.00
1.00
3.03
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.49
141.06
131.08
130.27
130.05
129.84
128.14
125.02
124.54
124.52
124.49
124.47
124.44
124.42
124.39
124.37
78.08
77.21
77.00
76.79
61.11
47.45
22.73
19.19
14.01
OH
O
F3C
OEt
3p
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.62
OH
O
F3C
OEt
3p
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.437
7.425
7.203
7.191
7.179
7.177
7.167
7.165
7.155
7.153
7.131
7.119
5.239
5.232
4.217
4.206
4.194
4.182
3.259
3.251
2.365
1.288
1.276
1.264
1.195
1.119
0.000
OH
O
OEt
3q
0.99
2.01
0.98
1.00
2.04
0.99
3.01
3.07
3.07
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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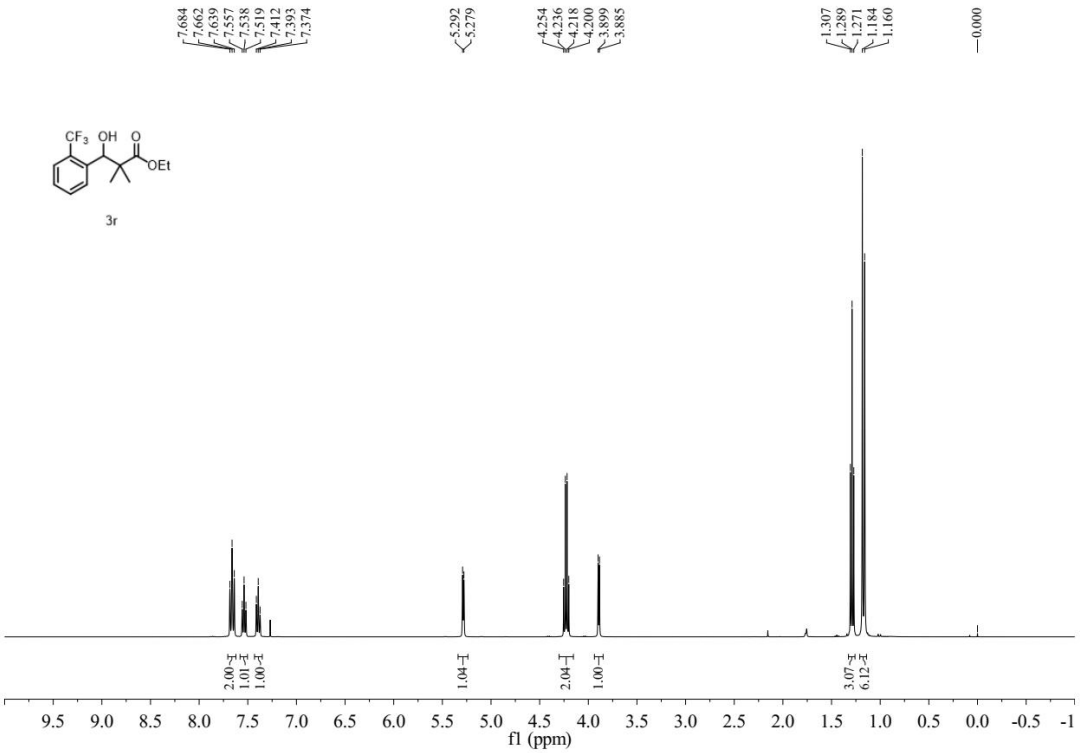
138.46
135.87
130.25
127.56
127.37
125.58
77.21
77.00
76.79
73.49
60.91
48.31
23.20
20.20
18.86
14.04
OH
O
OEt
3q
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.684
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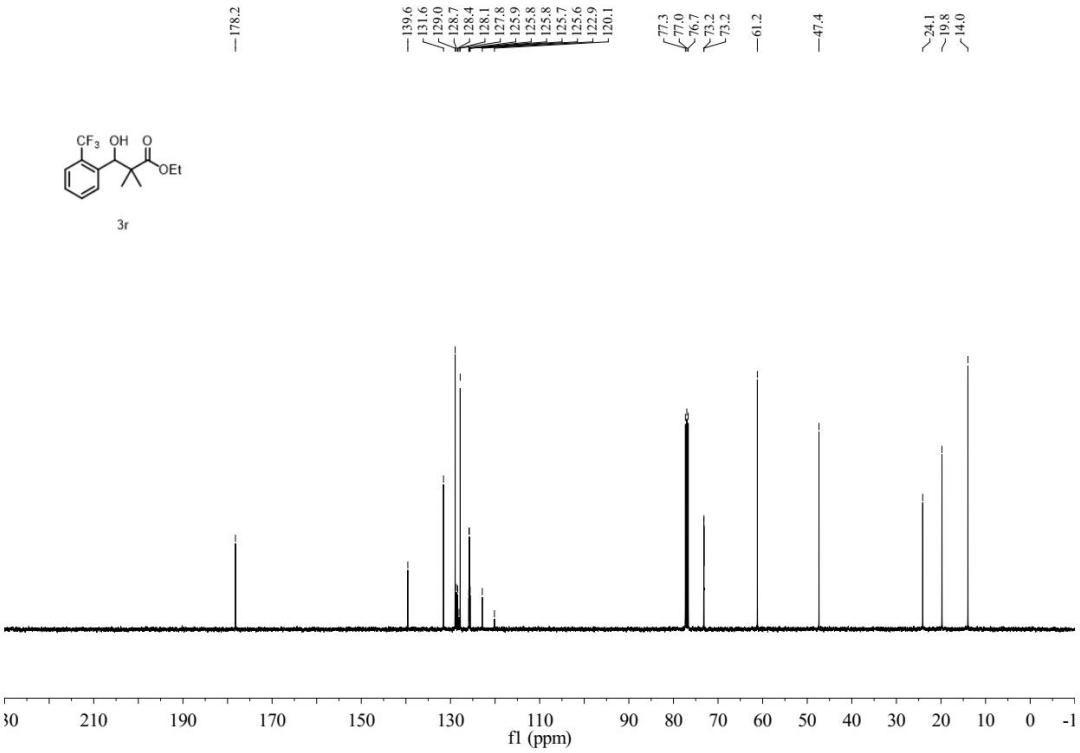
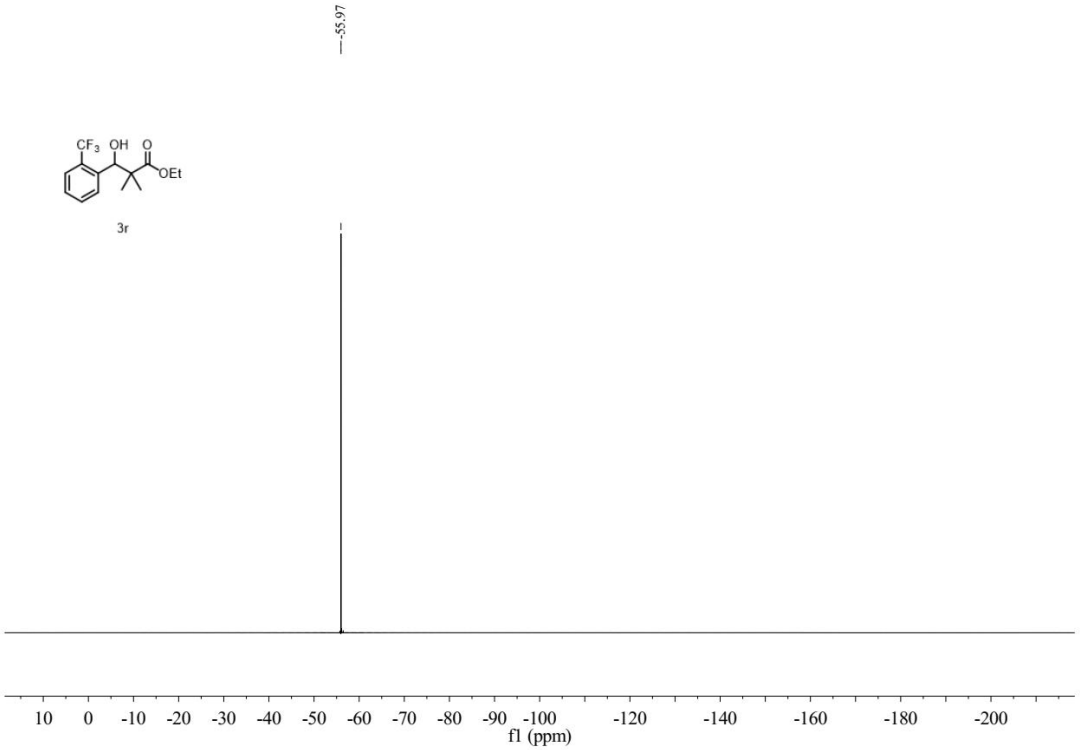
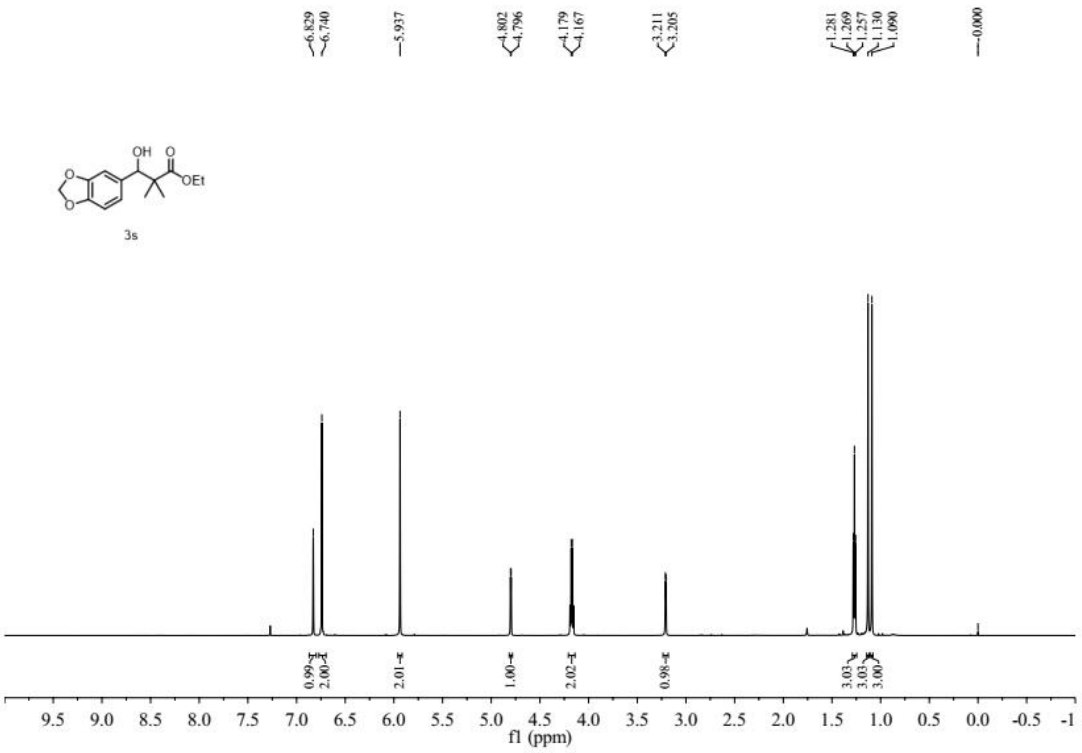
7.557
7.538
7.519
7.412
7.393
7.374
5.292
5.279
4.254
4.236
4.218
4.200
3.899
3.885
1.307
1.289
1.271
1.184
1.160
0.000
CF3
OH
O
OEt
3r
2.00
1.01
1.00
1.04
2.04
1.00
3.07
6.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


178.2
139.6
131.6
129.0
128.7
128.4
128.1
127.8
125.9
125.8
125.8
125.7
125.6
122.9
120.1
77.3
77.0
76.7
73.2
73.2
61.2
47.4
24.1
19.8
14.0
CF3 OH O
OEt
3r
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-55.97
CF3 OH O
OEt
3r
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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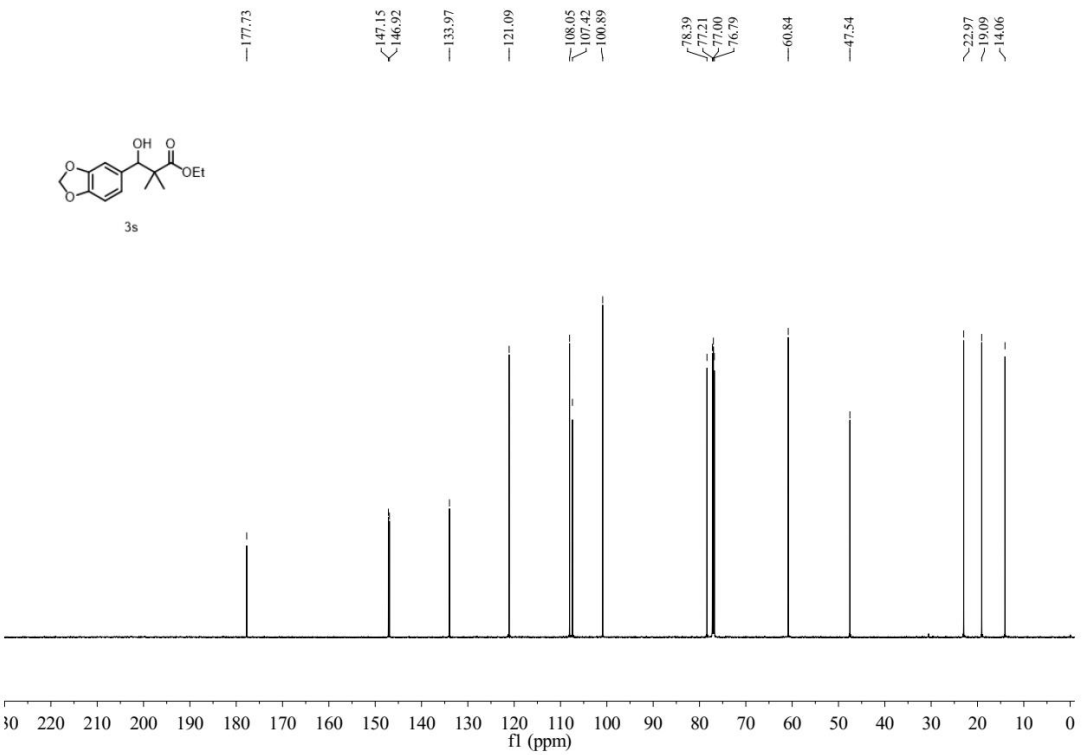
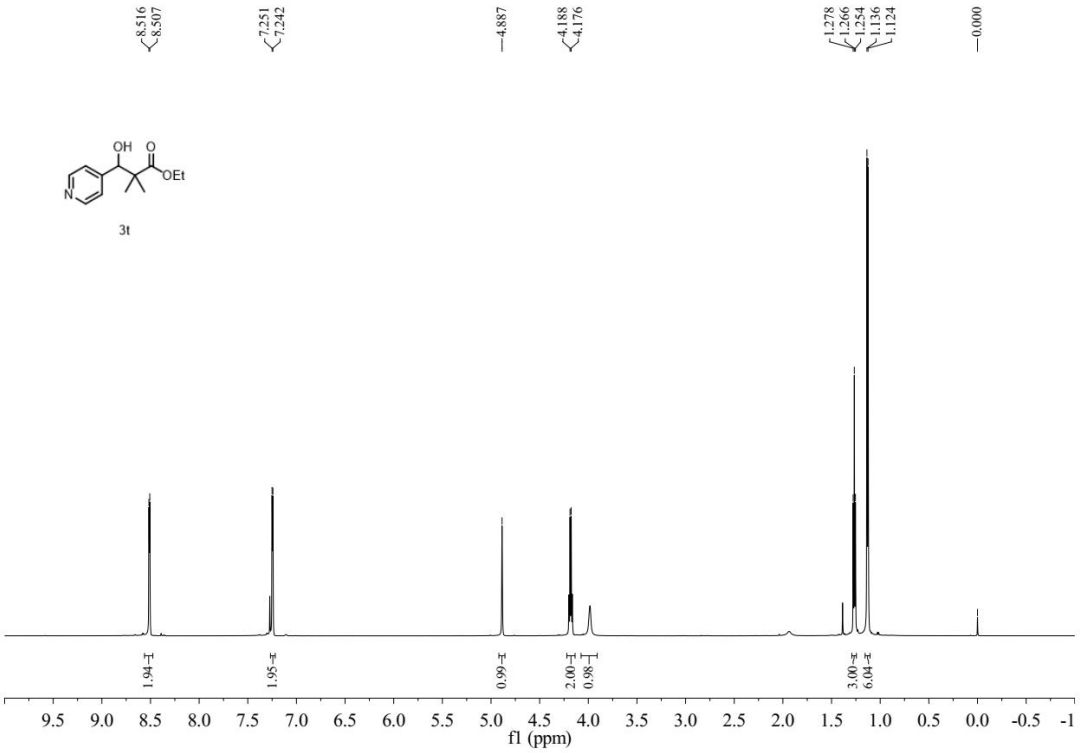
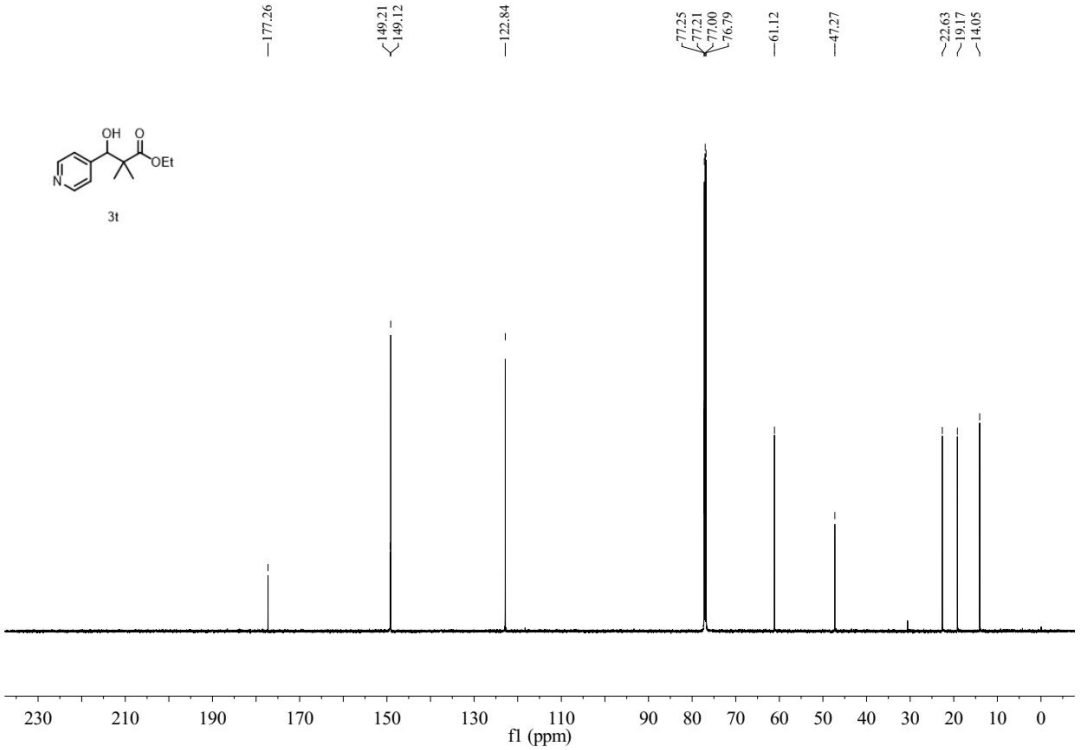
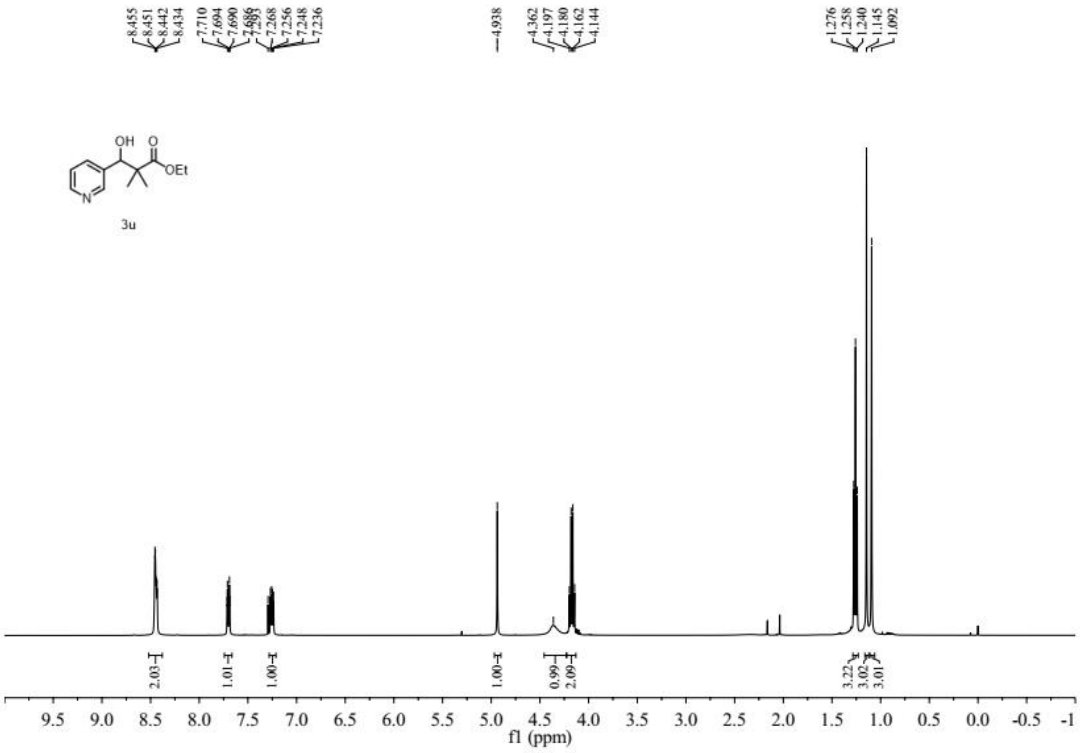
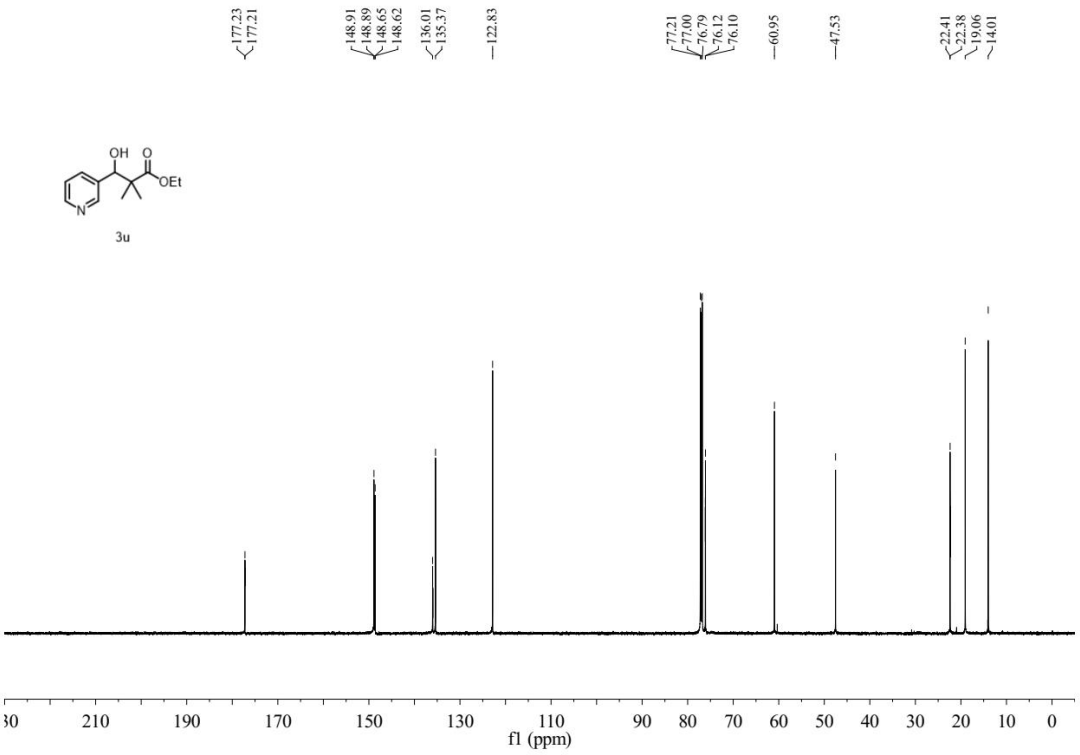
6.740
5.937
4.802
4.796
4.179
4.167
3.211
3.205
1.281
1.269
1.257
1.130
1.090
0.000
OH
O
OEt
3s
0.99
2.00
2.01
1.00
2.02
0.98
3.03
3.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

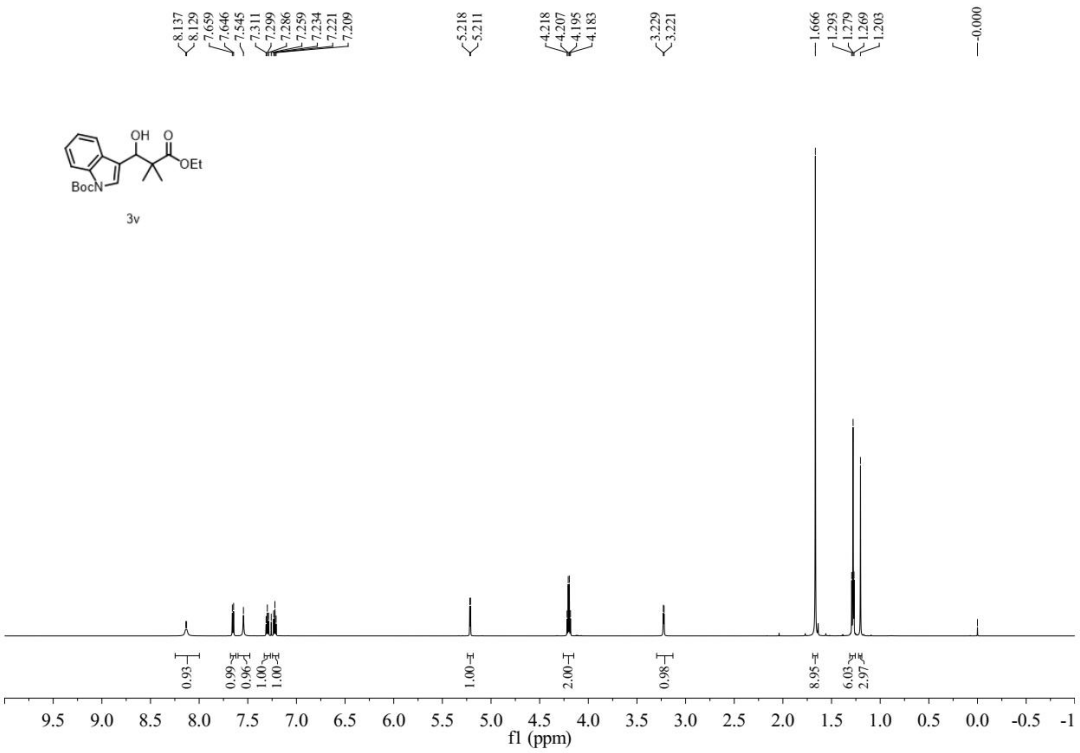

177.73
147.15
146.92
133.97
121.09
108.05
107.42
100.89
78.39
77.21
77.00
76.79
60.84
47.54
22.97
19.09
14.06
OH
O
OEt
3s
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

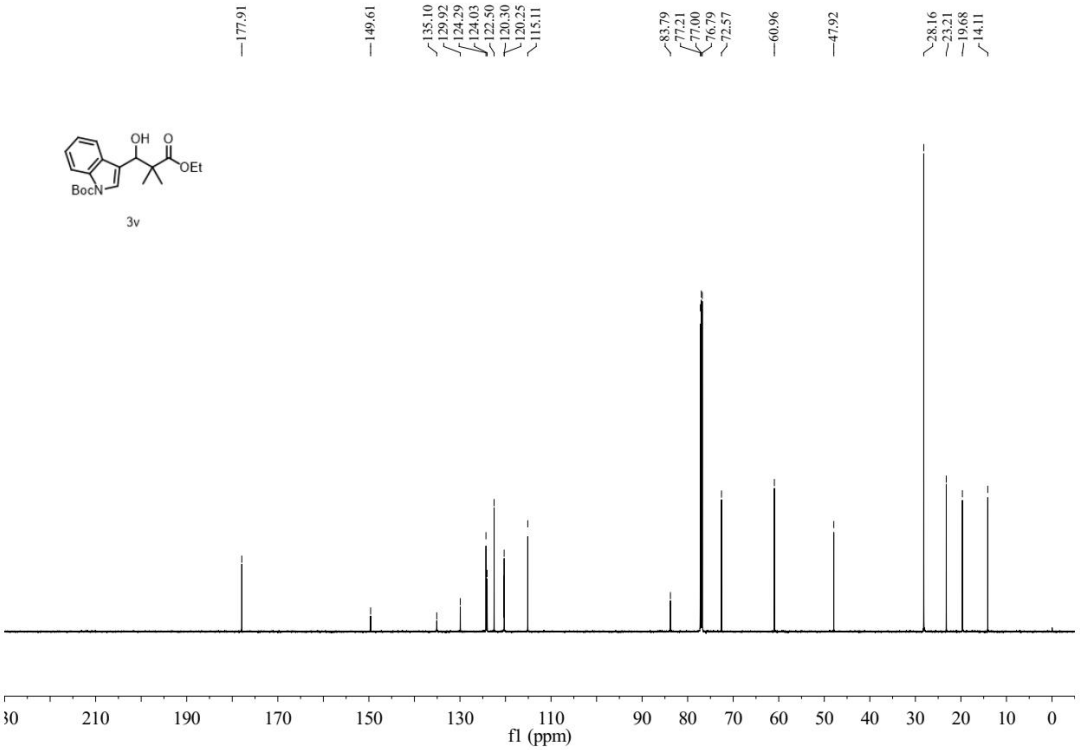

8.516
8.507
7.251
7.242
4.887
4.188
4.176
1.278
1.266
1.254
1.136
1.124
0.000
OH
O
OEt
N
3t
1.94
1.95
0.99
2.00
0.98
3.00
6.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.26
149.21
149.12
122.84
77.25
77.21
77.00
76.79
61.12
47.27
22.63
19.17
14.05
OH
O
OEt
N
3t
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.455
8.451
8.442
8.434
7.710
7.694
7.690
7.686
7.268
7.256
7.248
7.236
4.938
4.362
4.197
4.180
4.162
4.144
1.276
1.258
1.240
1.145
1.092
OH
O
OEt
N
3u
2.03
1.01
1.00
1.00
0.99
2.09
3.22
3.02
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.23
177.21
148.91
148.89
148.65
148.62
136.01
135.37
122.83
77.21
77.00
76.79
76.12
76.10
60.95
47.53
22.41
22.38
19.06
14.01
OH
O
OEt
N
3u
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.137
8.129
7.659
7.646
7.545
7.311
7.299
7.286
7.259
7.234
7.221
7.209
5.218
5.211
4.218
4.207
4.195
4.183
3.229
3.221
1.666
1.293
1.279
1.269
1.203
0.000
OH
O
OEt
BocN
3v
0.93
0.99
0.96
1.00
1.00
1.00
2.00
0.98
8.95
6.03
2.97
fl (ppm)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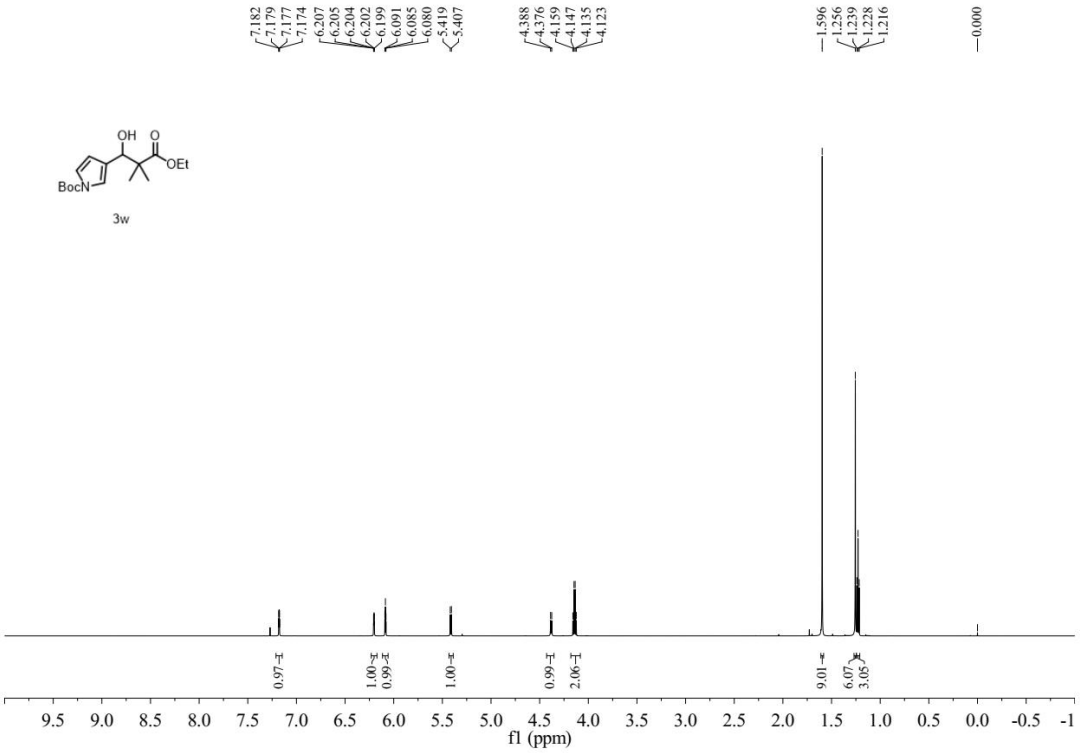
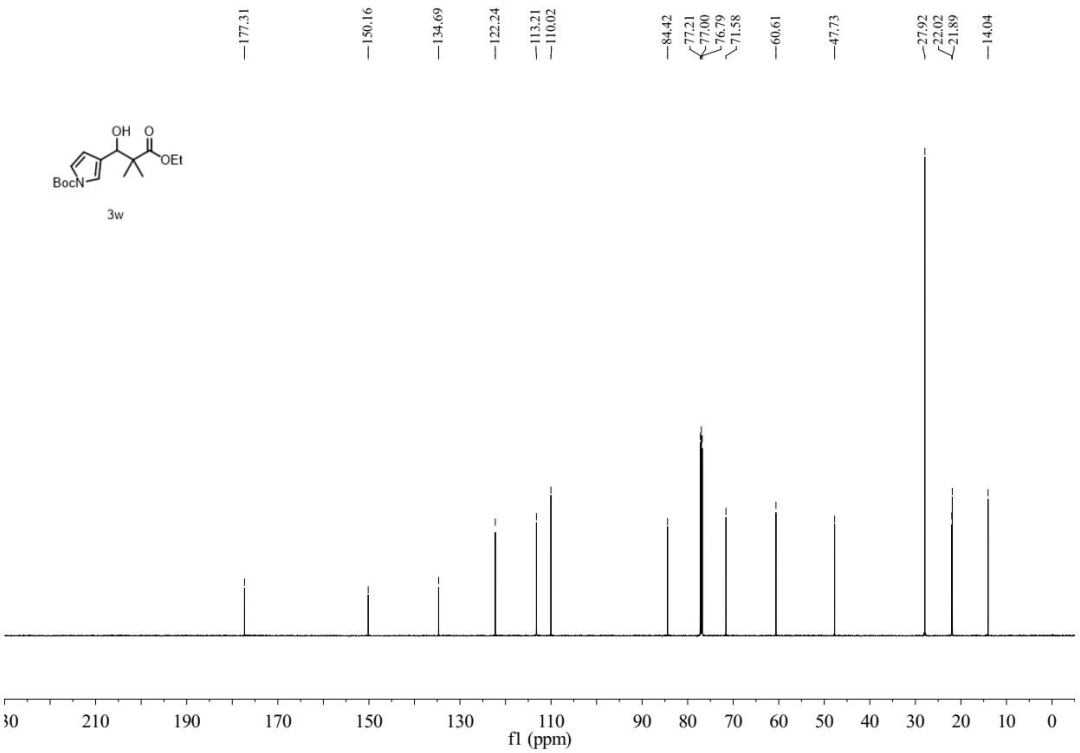
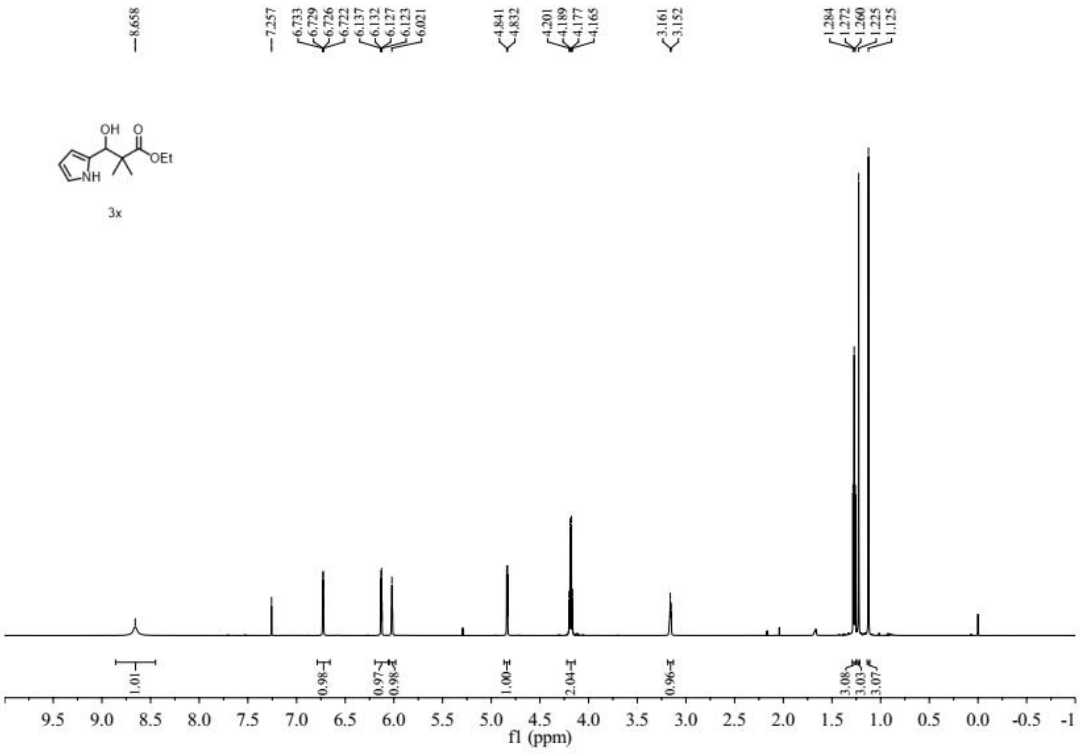
149.61
135.10
129.92
124.29
124.03
122.50
120.30
120.25
115.11
83.79
77.21
77.00
76.79
72.57
60.96
47.92
28.16
23.21
19.68
14.11
OH
O
OEt
BocN
3v
fl (ppm)


7.182
7.179
7.177
7.174
6.207
6.205
6.204
6.202
6.199
6.091
6.085
6.080
5.419
5.407
4.388
4.376
4.159
4.147
4.135
4.123
1.596
1.256
1.239
1.228
1.216
0.000
OH
O
OEt
BocN
3w
0.97
1.00
0.99
1.00
0.99
2.06
9.01
6.07
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.31
150.16
134.69
122.24
113.21
110.02
84.42
77.21
77.00
76.79
71.58
60.61
47.73
27.92
22.02
21.89
14.04
OH
O
OEt
BocN
3w
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.257
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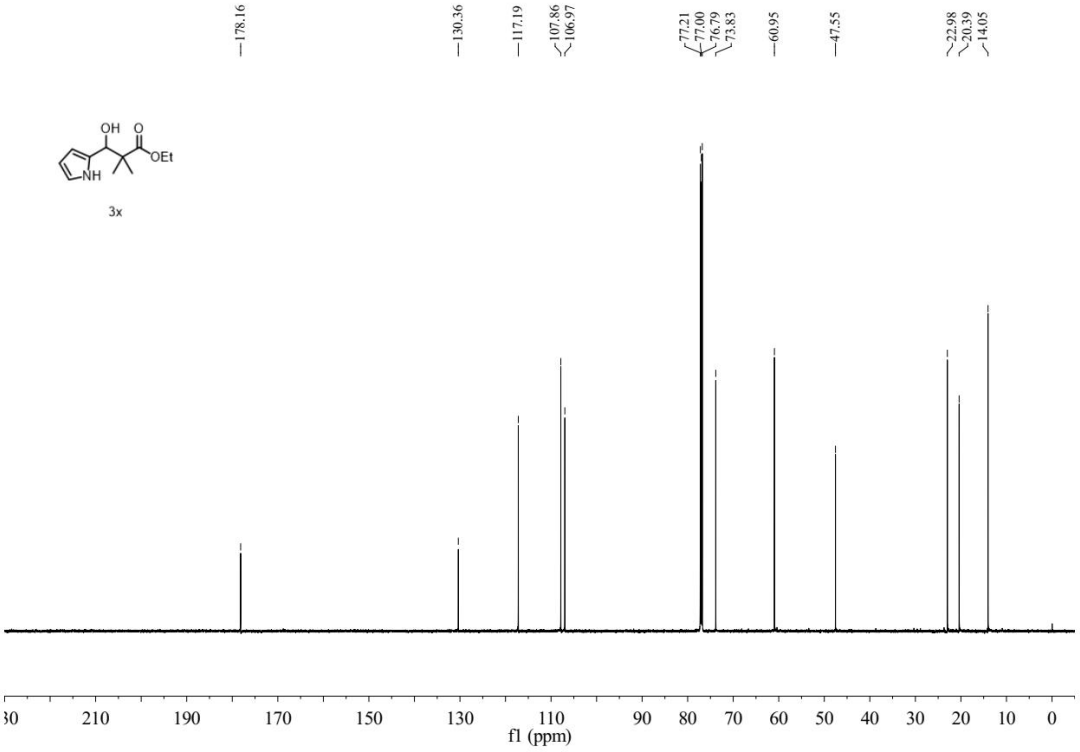
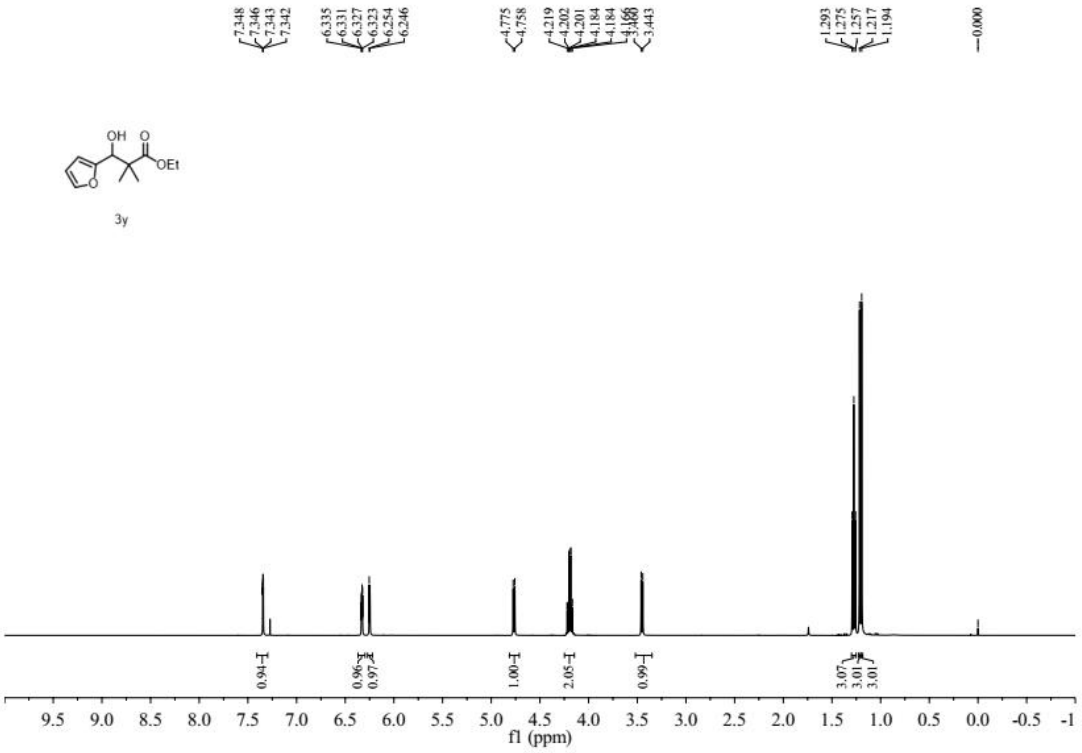
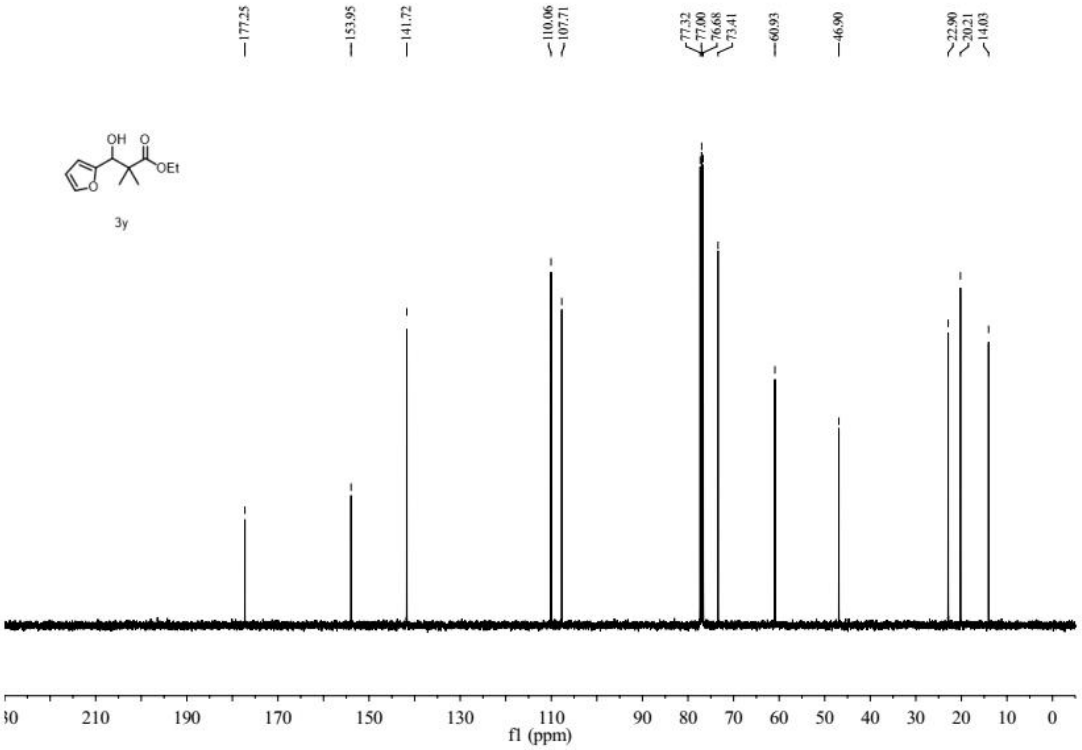
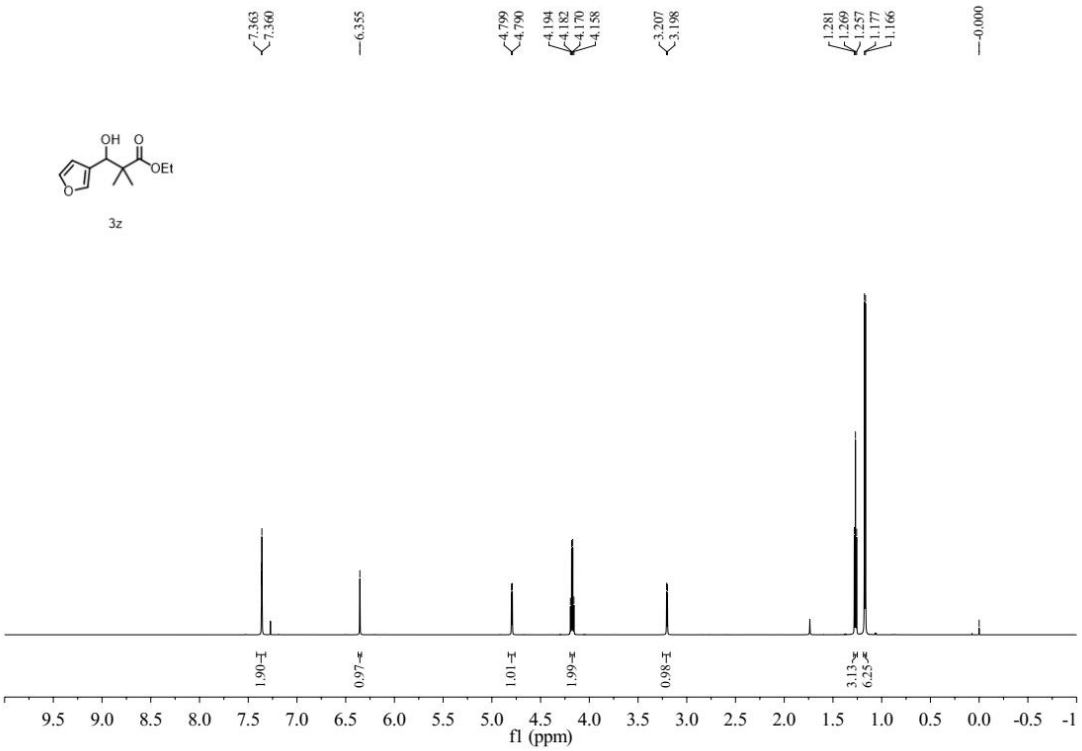
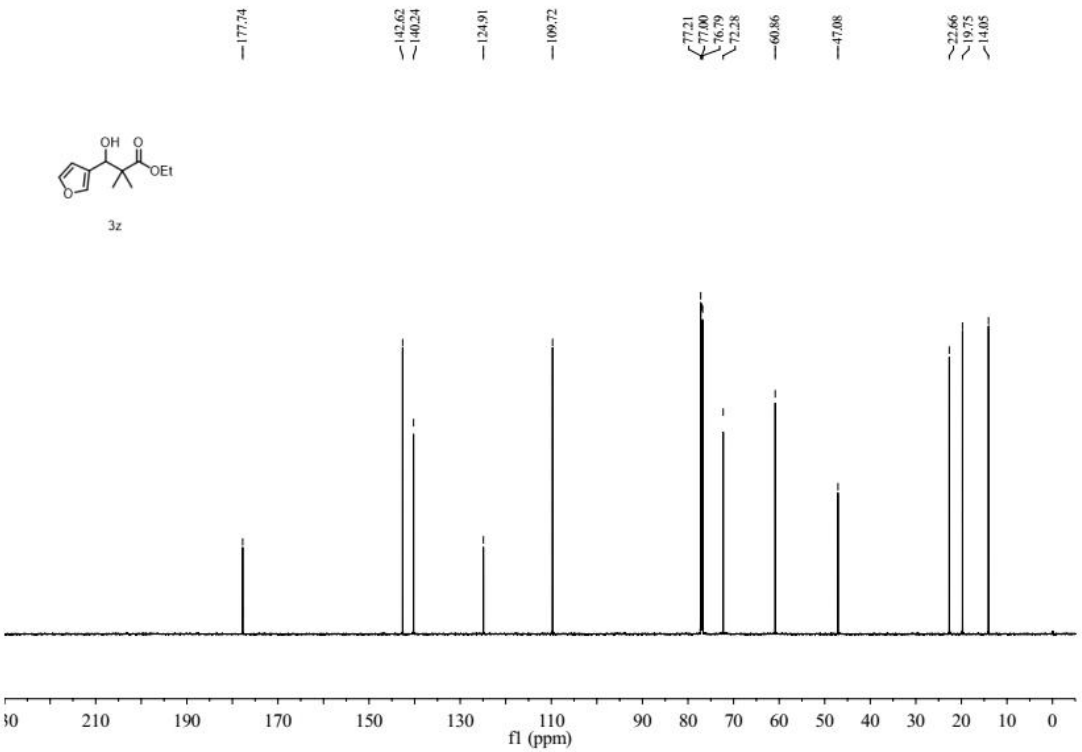
6.729
6.726
6.722
6.137
6.132
6.127
6.123
6.021
4.841
4.832
4.201
4.189
4.177
4.165
3.161
3.152
1.284
1.272
1.260
1.225
1.125
OH
O
OEt
NH
3x
1.01
0.98
0.97
0.98
1.00
2.04
0.96
3.08
3.03
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


178.16
130.36
117.19
107.86
106.97
77.21
77.00
76.79
73.83
60.95
47.55
22.98
20.39
14.05
OH
O
OEt
NH
3x
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.348
7.346
7.343
7.342
6.335
6.331
6.327
6.323
6.254
6.246
4.775
4.758
4.219
4.202
4.201
4.184
4.184
3.443
1.293
1.275
1.257
1.217
1.194
0.000
OH
O
OEt
3y
0.94
0.96
0.97
1.00
2.05
0.99
3.07
3.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.25
153.95
141.72
110.06
107.71
77.32
77.00
76.68
73.41
60.93
46.90
22.90
20.21
14.03
OH
O
OEt
3y
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.363
7.360
6.355
4.799
4.790
4.194
4.182
4.170
4.158
3.207
3.198
1.281
1.269
1.257
1.177
1.166
0.000
OH
O
OEt
3z
1.90
0.97
1.01
1.99
0.98
3.13
6.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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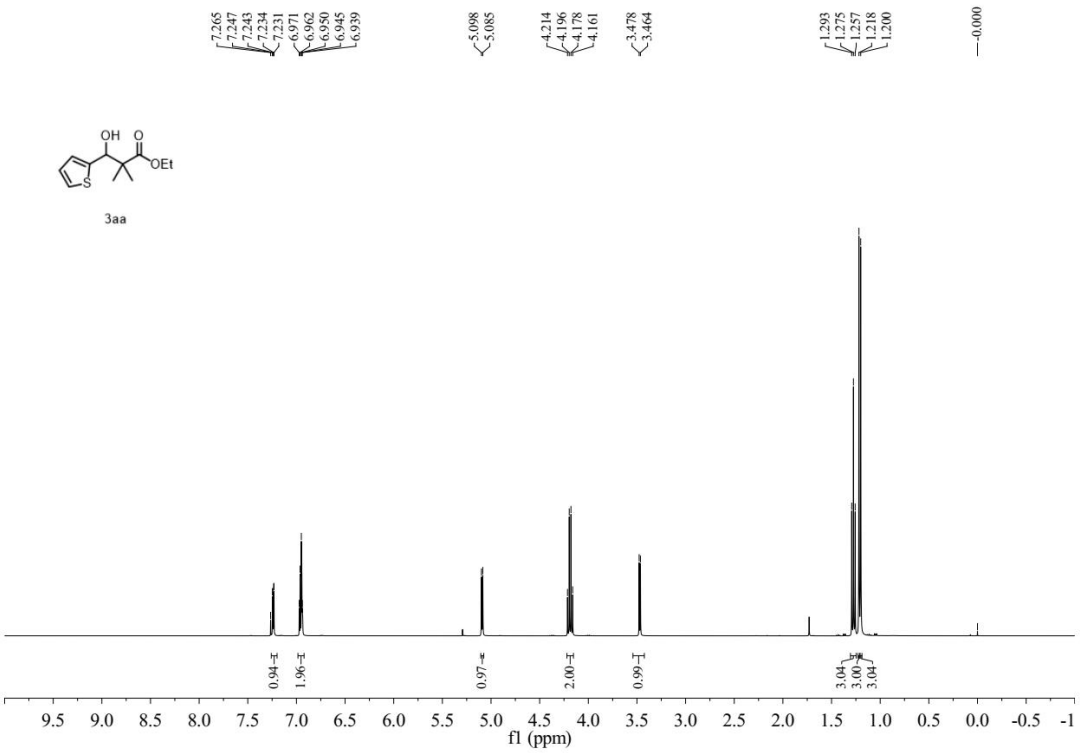
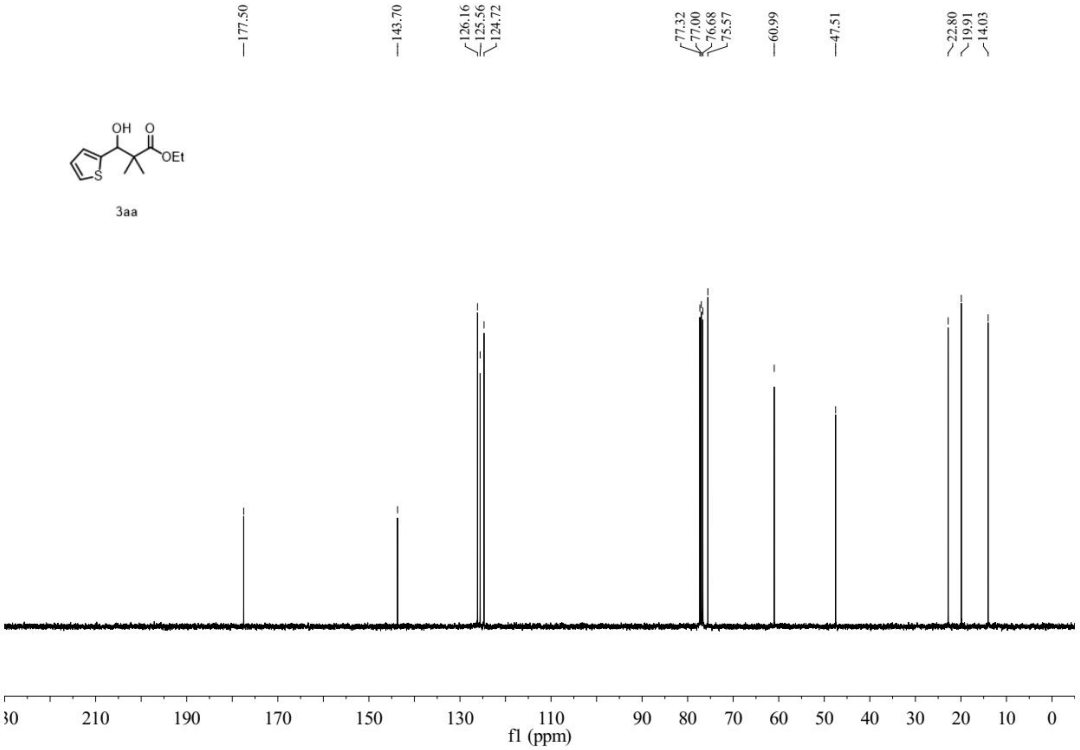
142.62
140.24
124.91
109.72
77.21
77.00
76.79
72.28
60.86
47.08
22.66
19.75
14.05
OH
O
OEt
3z
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.265
7.247
7.243
7.234
7.231
6.971
6.962
6.950
6.945
6.939
5.098
5.085
4.214
4.196
4.178
4.161
3.478
3.464
1.293
1.275
1.257
1.218
1.200
0.000
OH
O
OEt
S
3aa
0.94
1.96
0.97
2.00
0.99
3.04
3.00
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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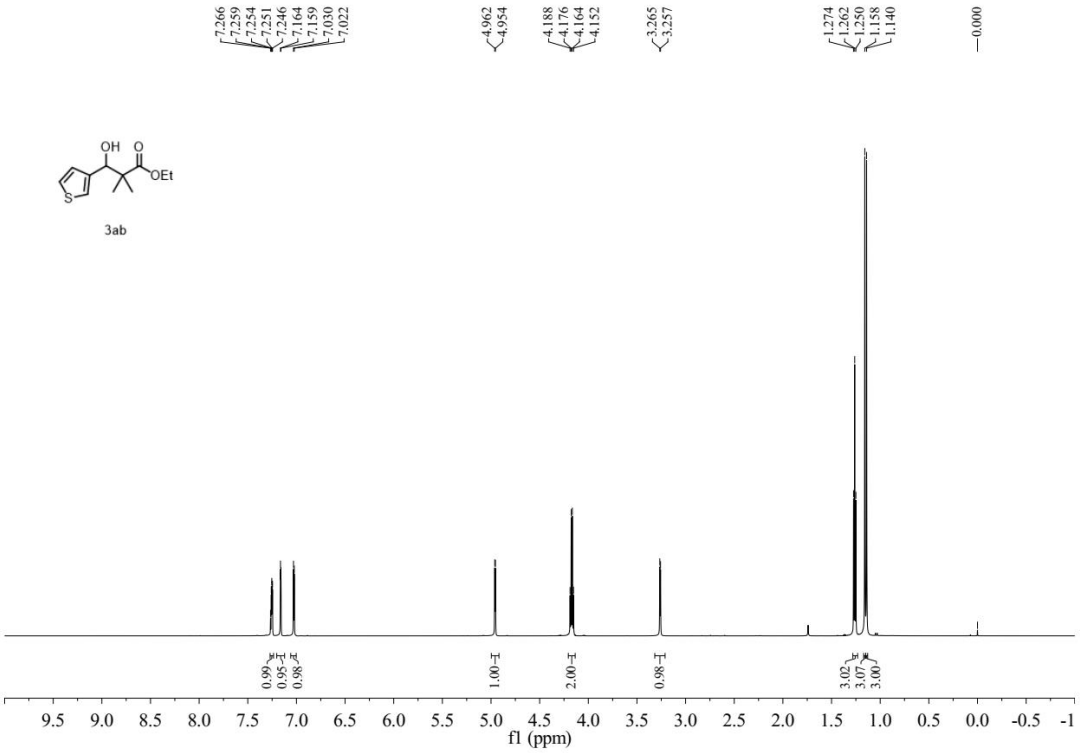
143.70
126.16
125.56
124.72
77.32
77.00
76.68
75.57
60.99
47.51
22.80
19.91
14.03
OH
O
OEt
S
3aa
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.259
7.254
7.251
7.246
7.164
7.159
7.030
7.022
4.962
4.954
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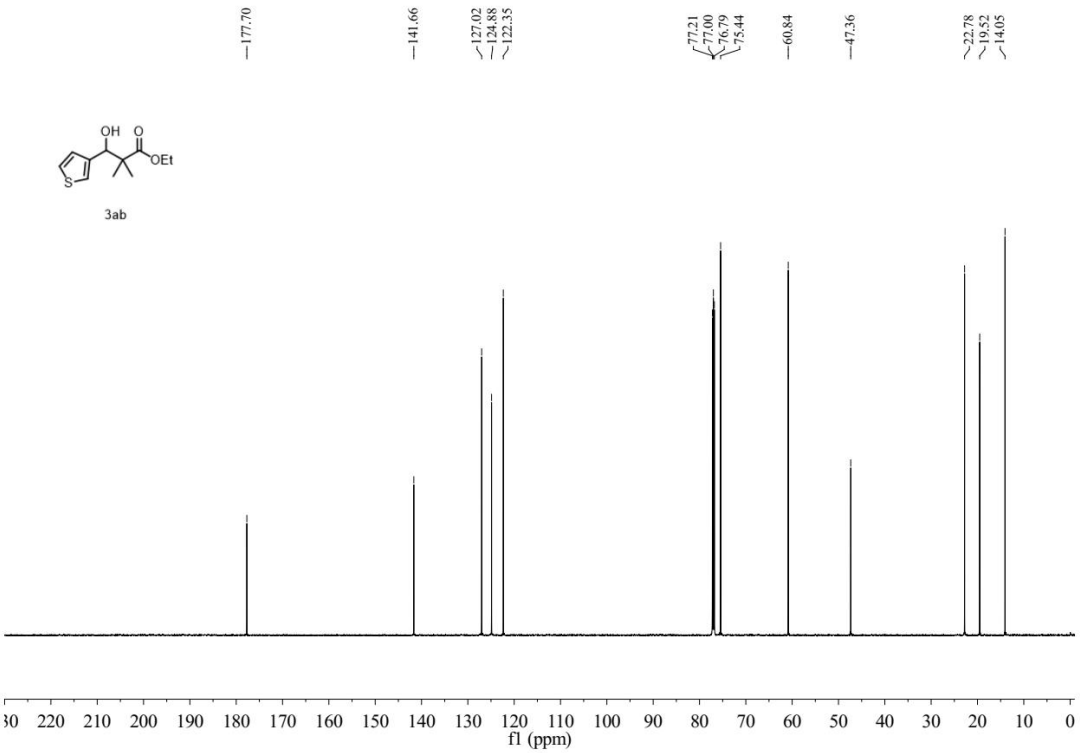
4.176
4.164
4.152
3.265
3.257
1.274
1.262
1.250
1.158
1.140
0.000
OH
O
OEt
S
3ab
0.99
0.95
0.98
1.00
2.00
0.98
3.02
3.07
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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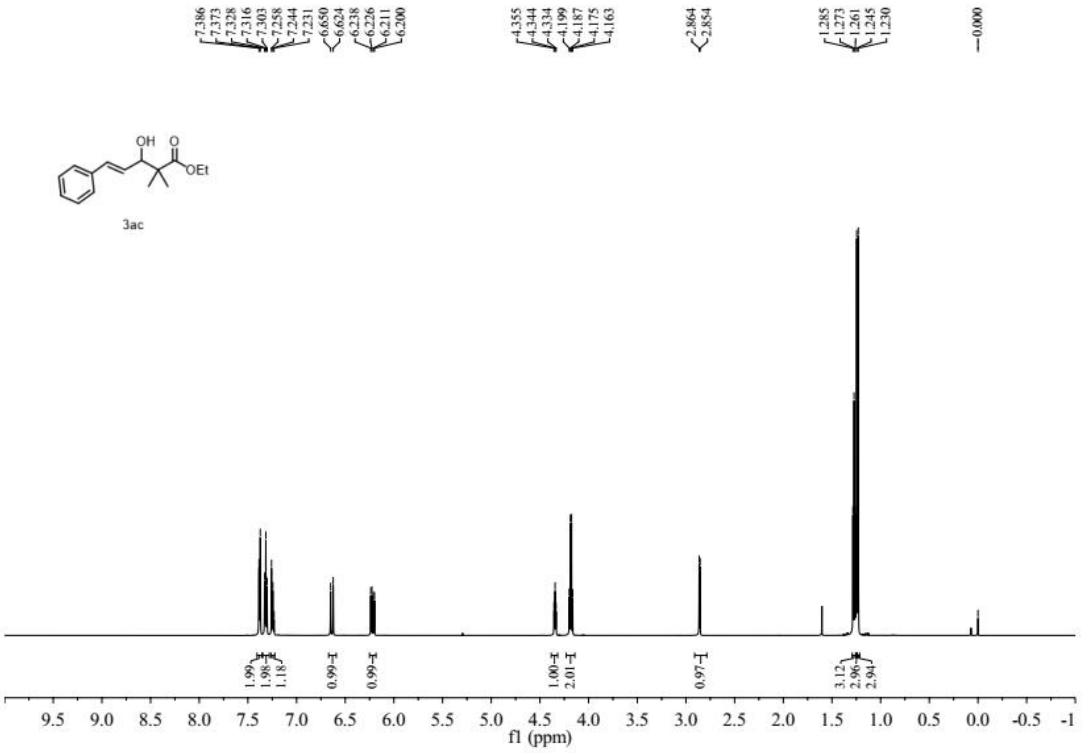
141.66
127.02
124.88
122.35
77.21
77.00
76.79
75.44
60.84
47.36
22.78
19.52
14.05
OH
O
OEt
S
3ab
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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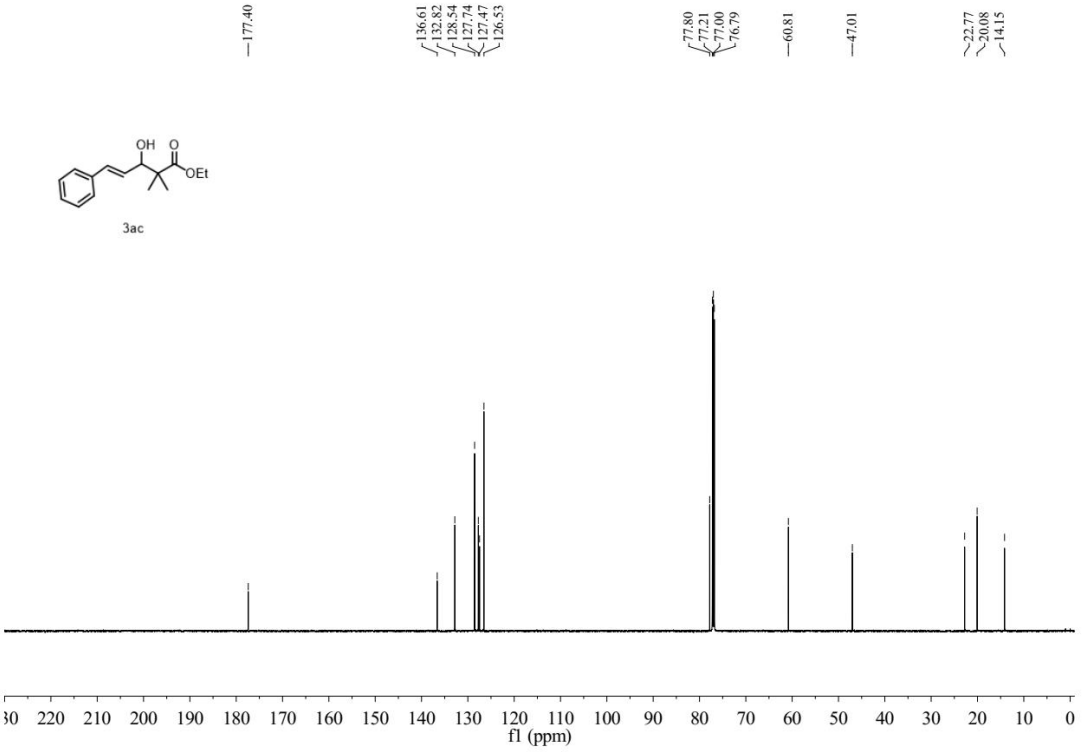
7.258
7.244
7.231
6.650
6.624
6.238
6.226
6.211
6.200
4.355
4.344
4.334
4.199
4.187
4.175
4.163
2.864
2.854
1.285
1.273
1.261
1.245
1.230
0.000
OH
O
OEt
3ac
1.99
1.98
1.18
0.99
0.99
1.00
2.01
0.97
3.12
2.96
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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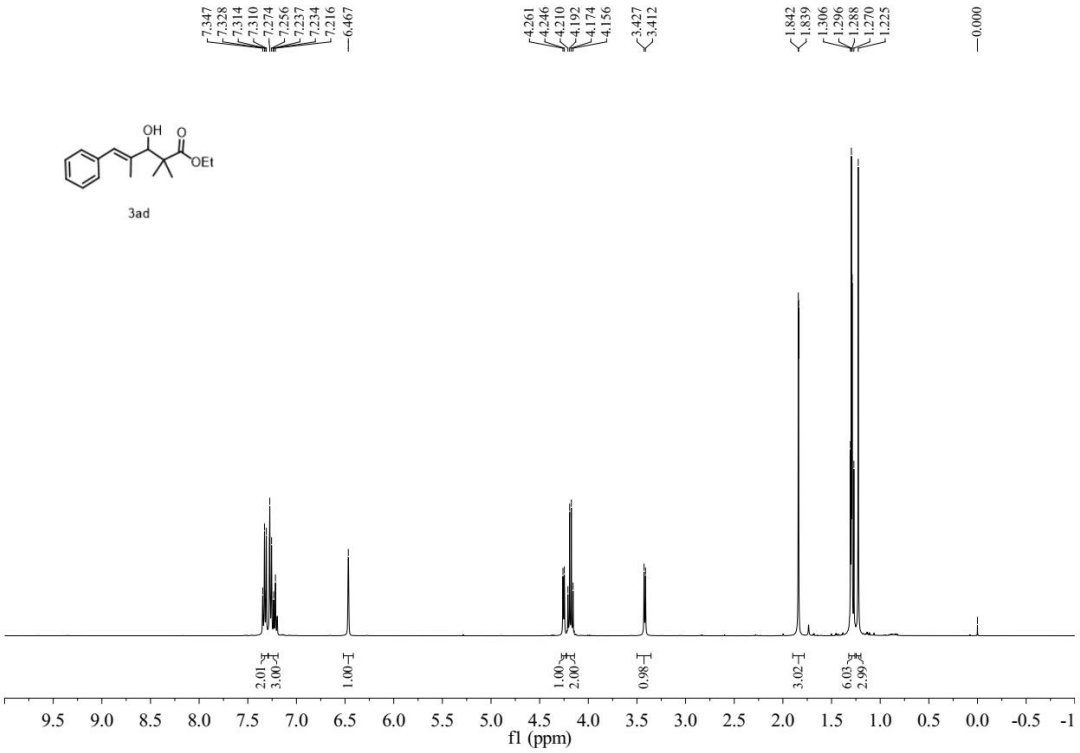
127.74
127.47
126.53
77.80
77.21
77.00
76.79
60.81
47.01
22.77
20.08
14.15
OH
O
OEt
3ac
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.347
7.328
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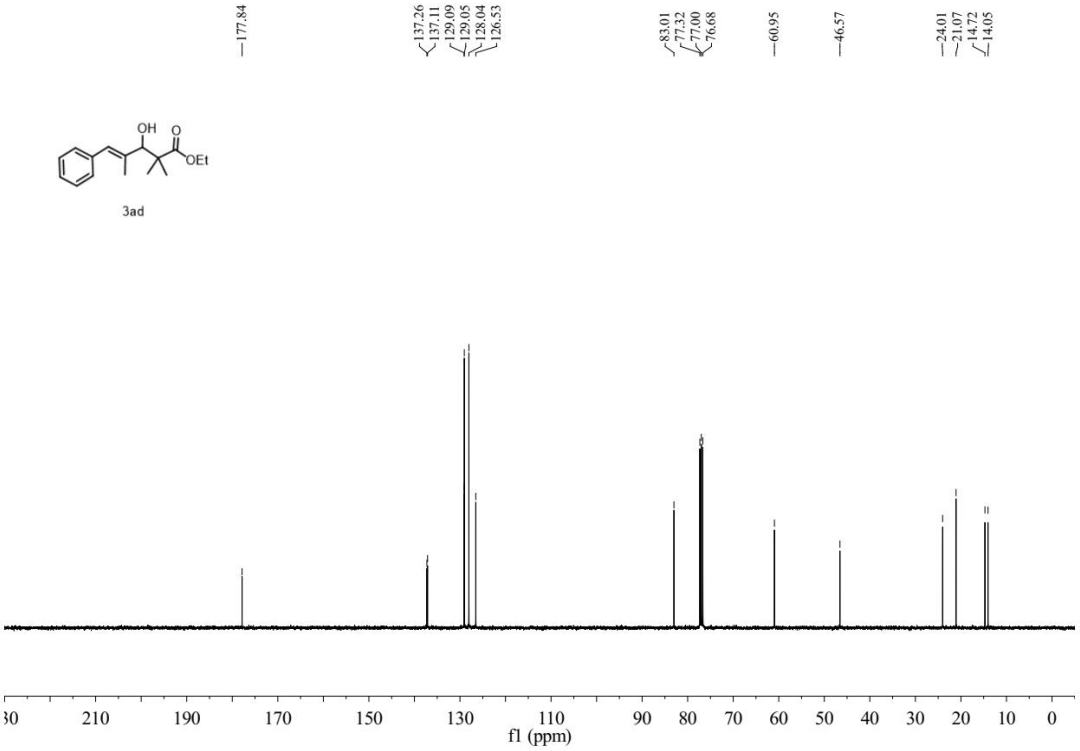
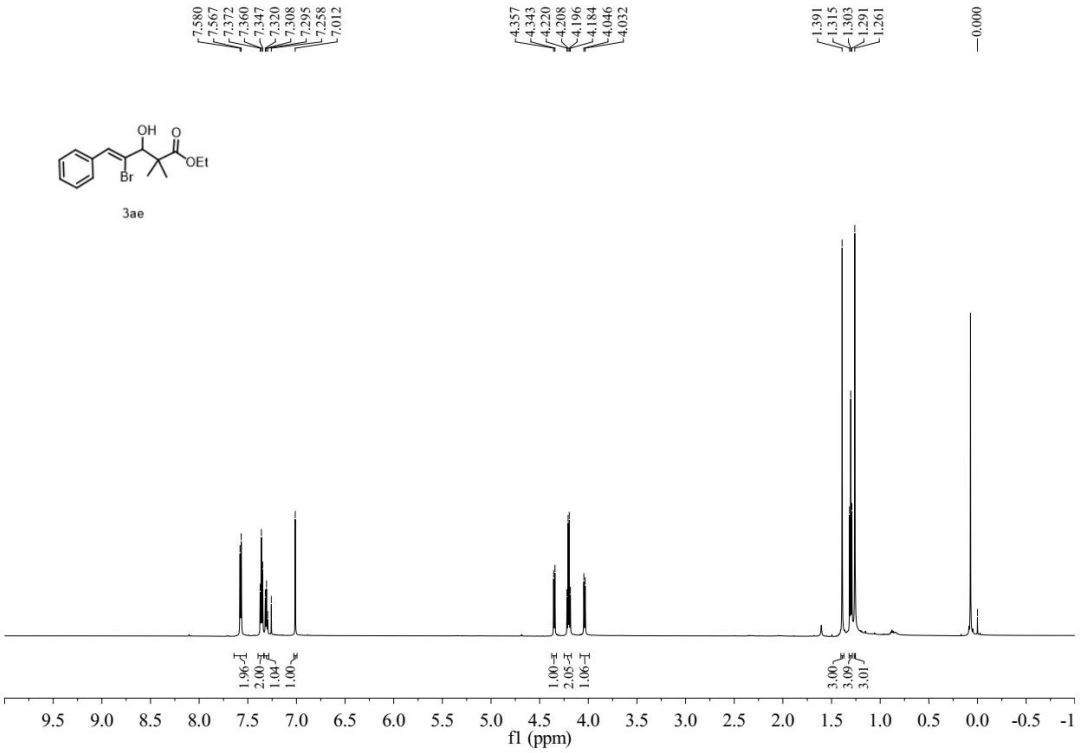
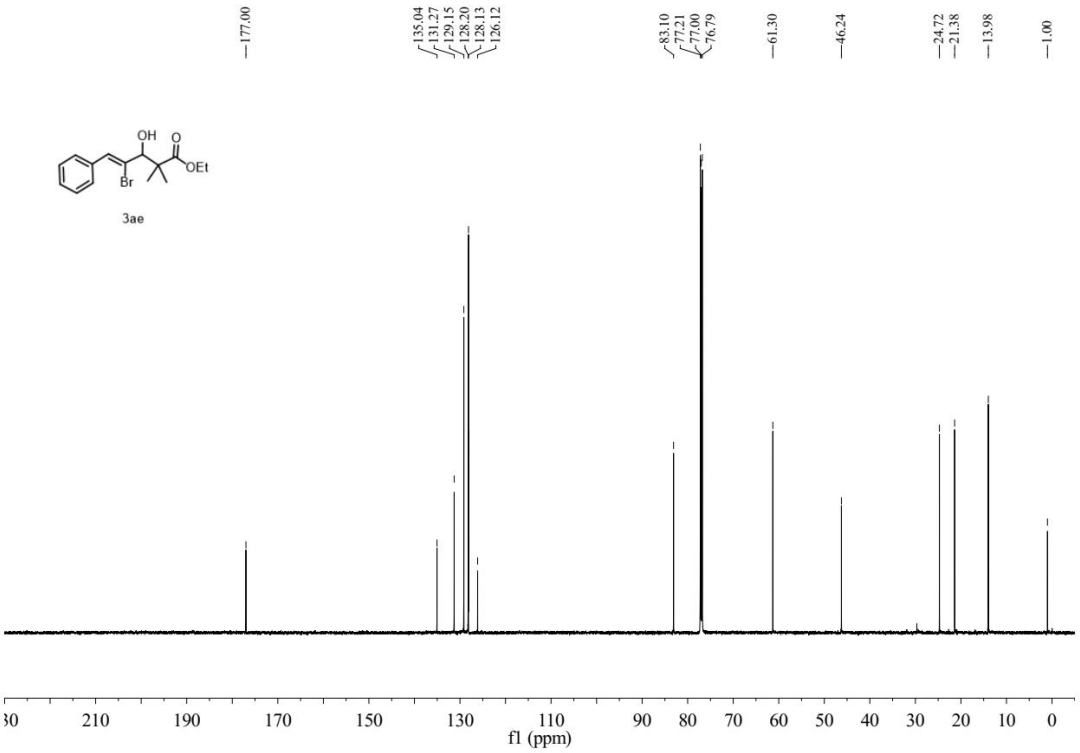
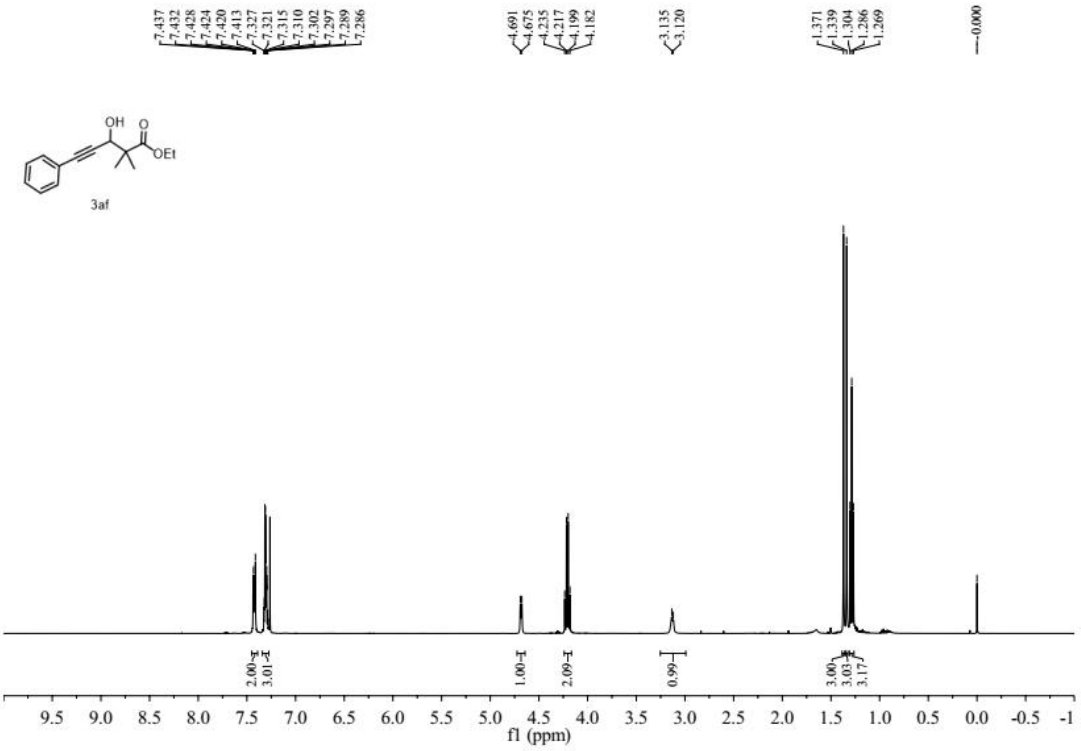
7.310
7.274
7.256
7.237
7.234
7.216
6.467
4.261
4.246
4.210
4.192
4.174
4.156
3.427
3.412
1.842
1.839
1.306
1.296
1.288
1.270
1.225
0.000
OH
O
OEt
3ad
2.01
3.00
1.00
1.00
2.00
0.98
3.02
6.03
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.84
137.26
137.11
129.09
129.05
128.04
126.53
83.01
77.32
77.00
76.68
60.95
46.57
24.01
21.07
14.72
14.05
OH
O
OEt
3ad
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.580
7.567
7.372
7.360
7.347
7.320
7.308
7.295
7.258
7.012
4.357
4.343
4.220
4.208
4.196
4.184
4.046
4.032
1.391
1.315
1.303
1.291
1.261
0.000
OH
O
OEt
Br
3ae
1.96
2.00
1.04
1.00
1.00
2.05
1.06
3.00
3.09
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


177.00
135.04
131.27
129.15
128.20
128.13
126.12
83.10
77.21
77.00
76.79
61.30
46.24
24.72
21.38
13.98
1.00
OH
O
OEt
Br
3ae
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.428
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7.420
7.413
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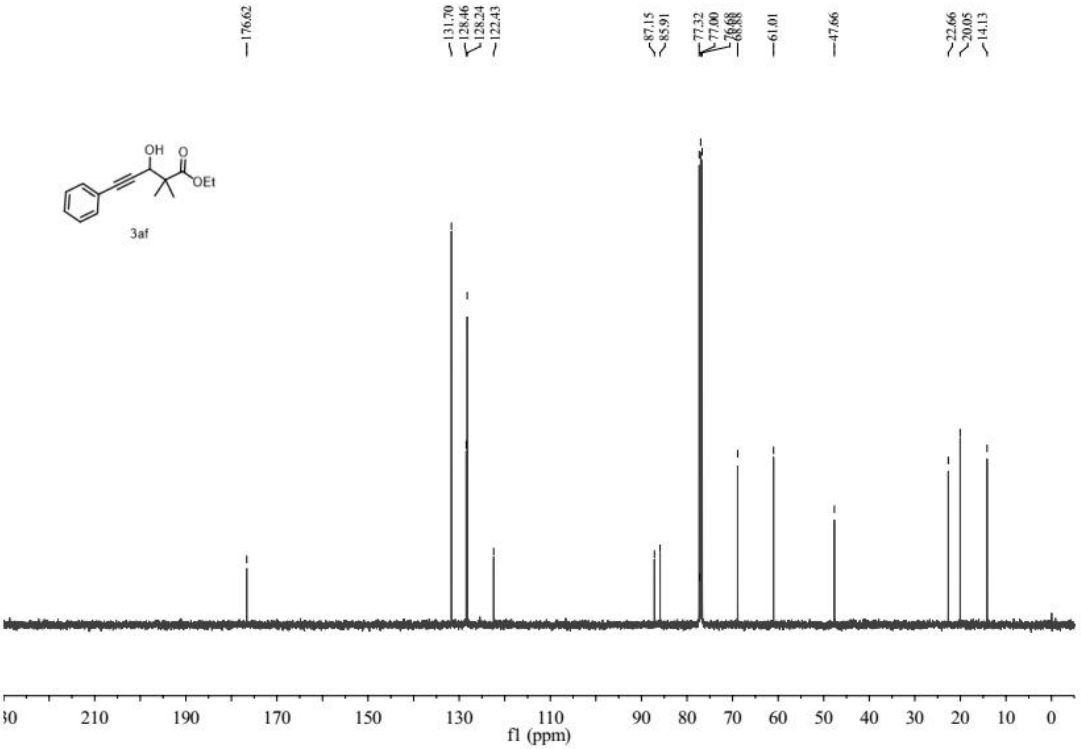
7.321
7.315
7.310
7.302
7.297
7.289
7.286
4.691
4.675
4.235
4.217
4.199
4.182
3.135
3.120
1.371
1.339
1.304
1.286
1.269
0.000
OH
O
OEt
3af
2.00
3.01
1.00
2.09
0.99
3.00
3.03
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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128.46
128.24
122.43
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85.91
77.32
77.00
76.68
69.88
61.01
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22.66
20.05
14.13
OH
O
OEt
3af
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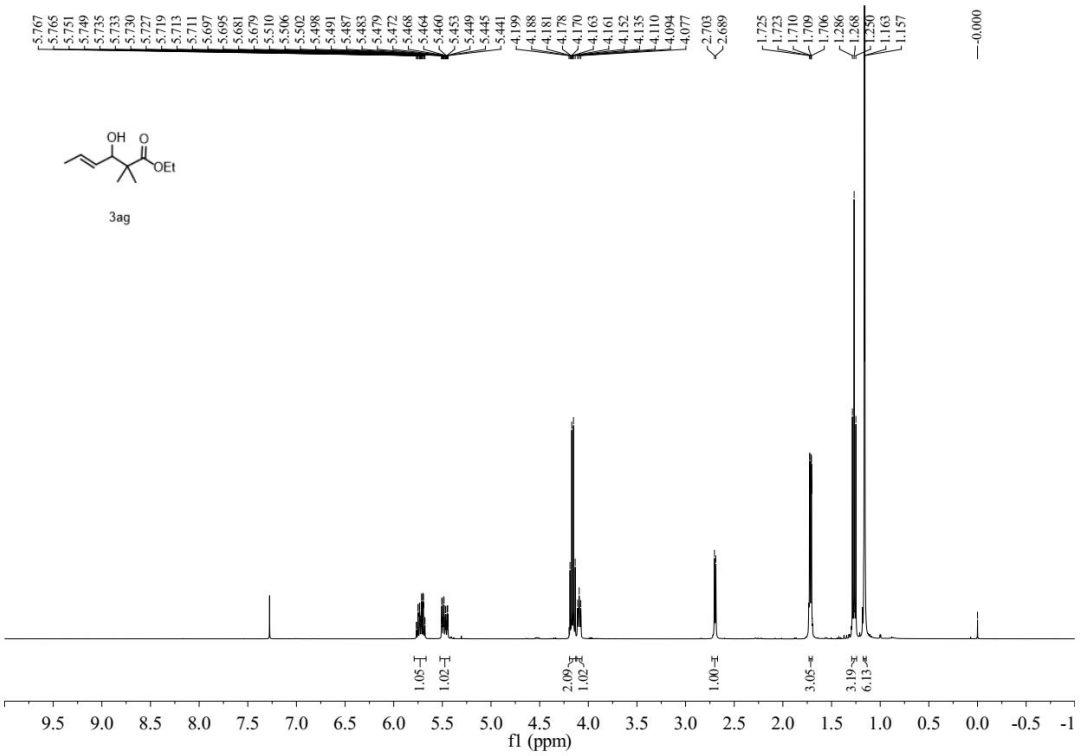
f1 (ppm)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5.727
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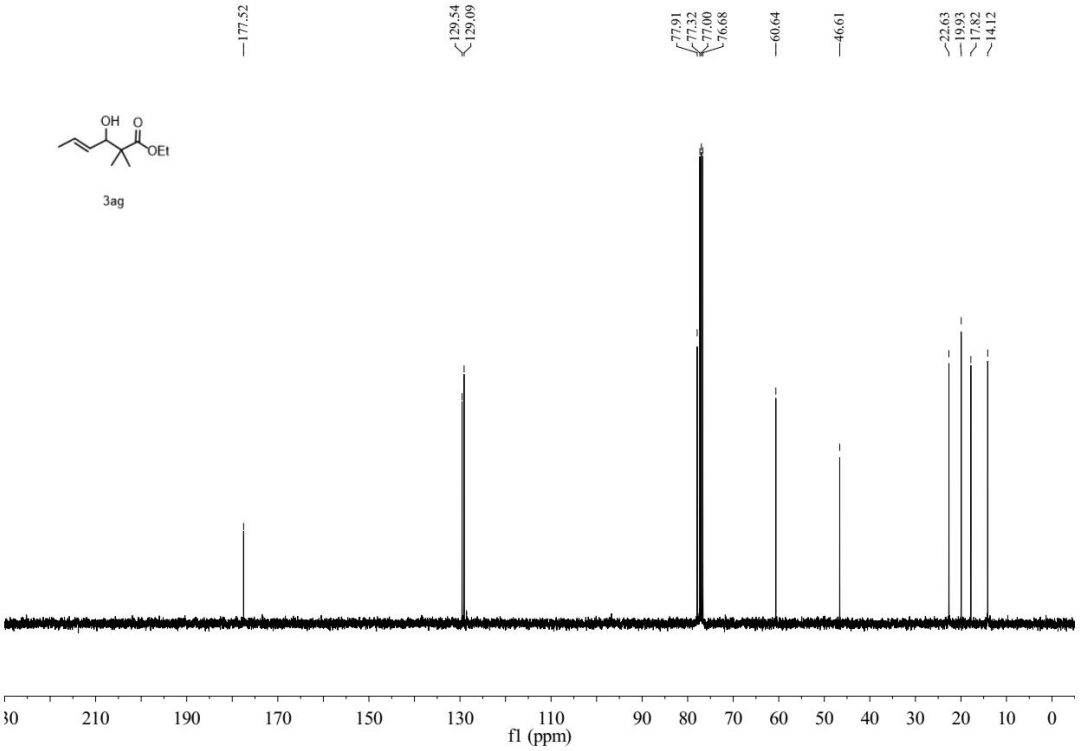
5.713
5.711
5.697
5.695
5.681
5.679
5.510
5.506
5.502
5.498
5.491
5.487
5.483
5.479
5.472
5.468
5.464
5.460
5.453
5.449
5.445
5.441
4.199
4.188
4.181
4.178
4.170
4.163
4.161
4.152
4.135
4.110
4.094
4.077
2.703
2.689
1.725
1.723
1.710
1.709
1.706
1.286
1.268
1.250
1.163
1.157
0.000
OH
O
OEt
3ag
1.05
1.02
2.09
1.02
1.00
3.05
3.19
6.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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129.54
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77.00
76.68
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46.61
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17.82
14.12
OH
O
OEt
3ag
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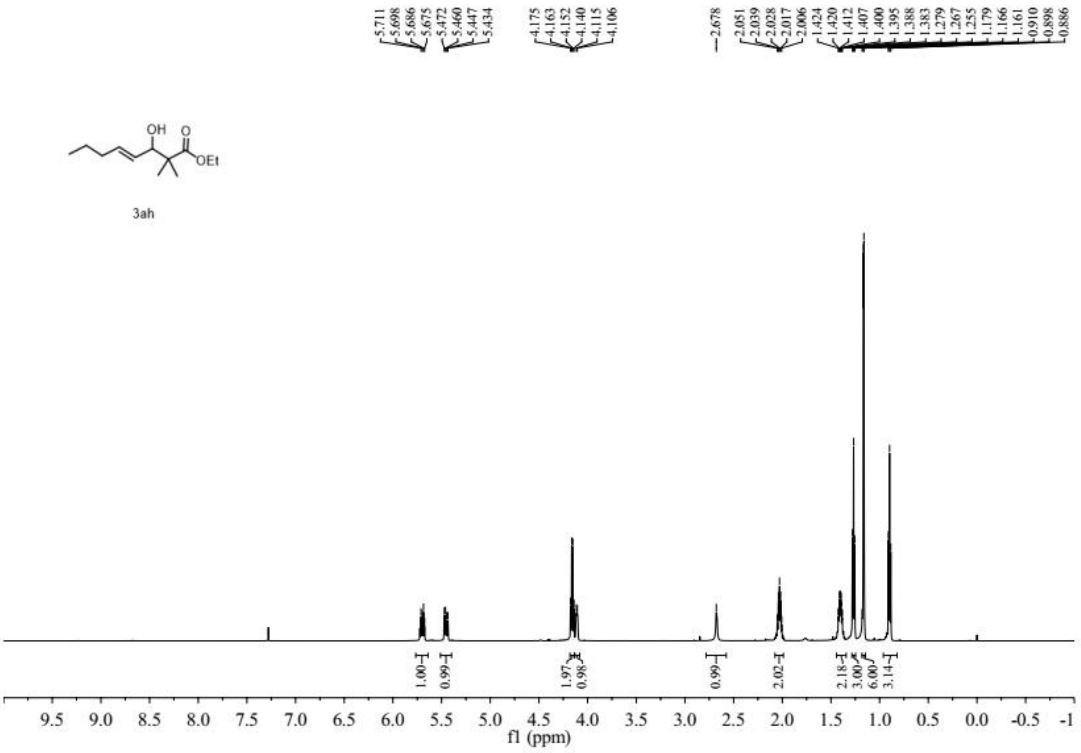
f1 (ppm)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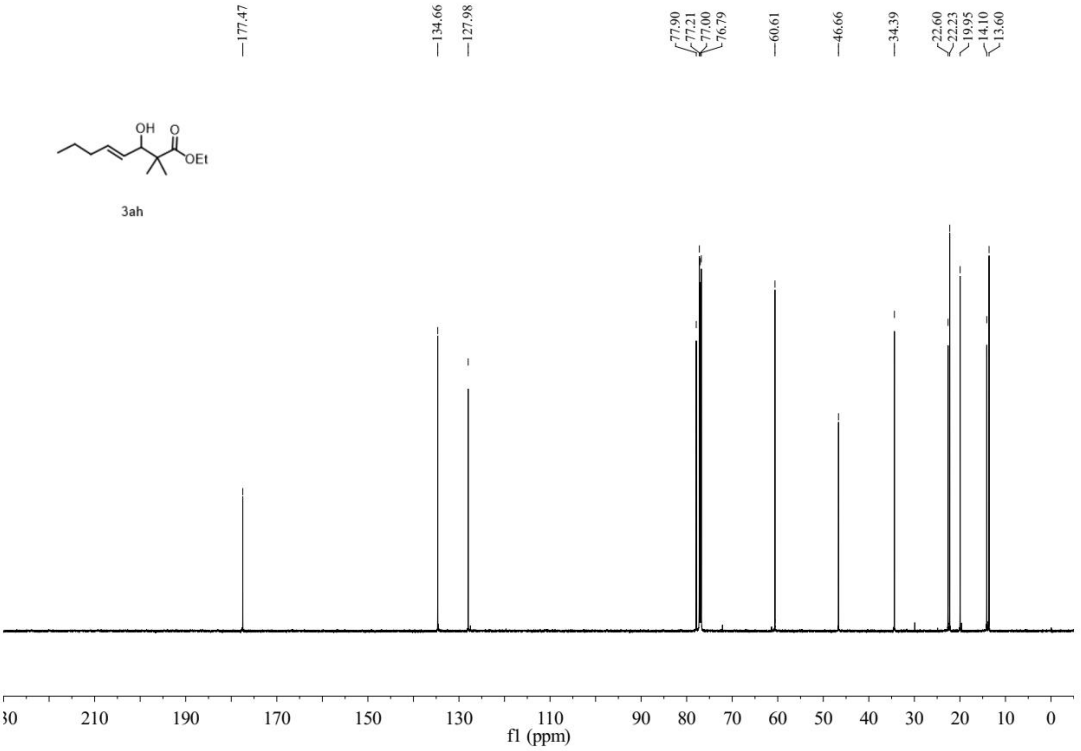
5.686
5.675
5.472
5.460
5.447
5.434
4.175
4.163
4.152
4.140
4.115
4.106
2.678
2.051
2.039
2.028
2.017
2.006
1.424
1.420
1.412
1.407
1.400
1.395
1.388
1.383
1.279
1.267
1.255
1.179
1.166
1.161
0.910
0.898
0.886
OH
O
OEt
3ah
1.00
0.99
1.97
0.98
0.99
2.02
2.18
3.00
6.00
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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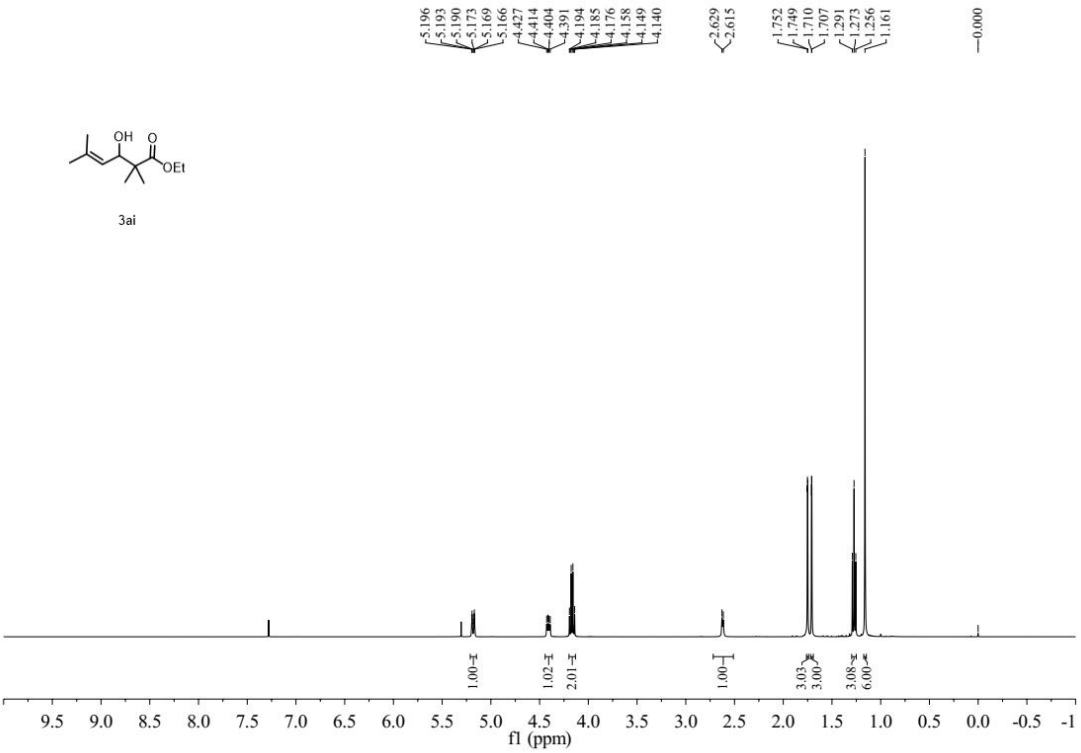
77.00
76.79
60.61
46.66
34.39
22.60
22.23
19.95
14.10
13.60
OH
O
OEt
3ah
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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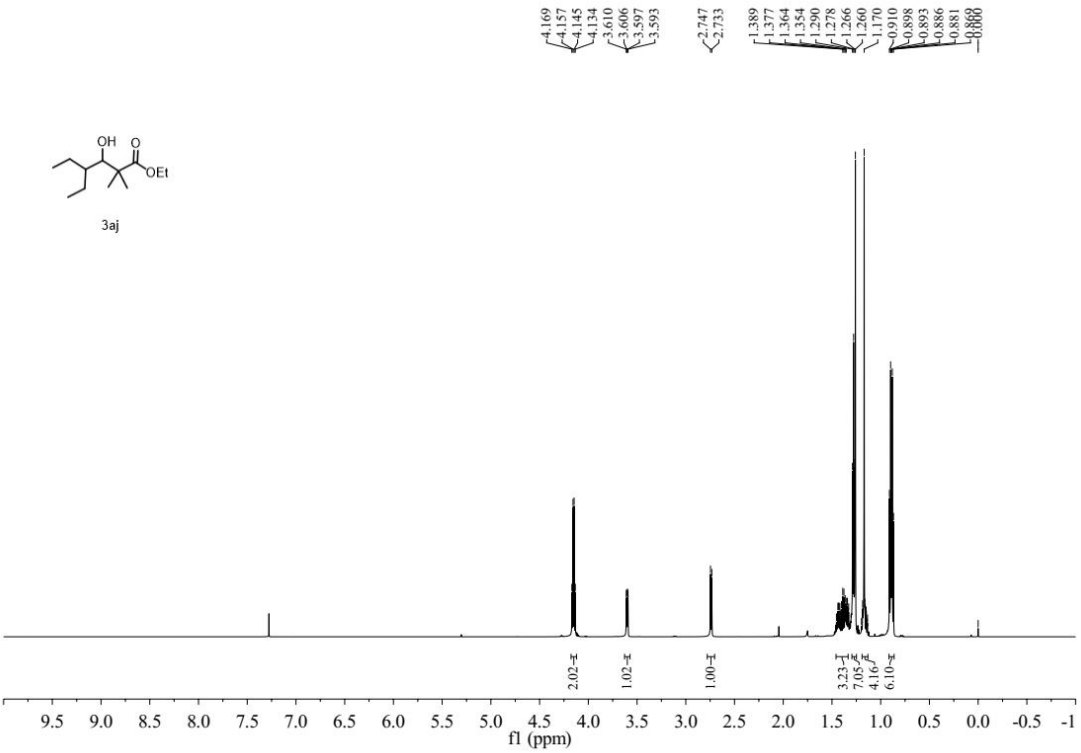
5.193
5.190
5.173
5.169
5.166
4.427
4.414
4.404
4.391
4.194
4.185
4.176
4.158
4.149
4.140
2.629
2.615
1.752
1.749
1.710
1.707
1.291
1.273
1.256
1.161
0.000
OH
O
OEt
3ai
1.00
1.02
2.01
1.00
3.03
3.00
3.08
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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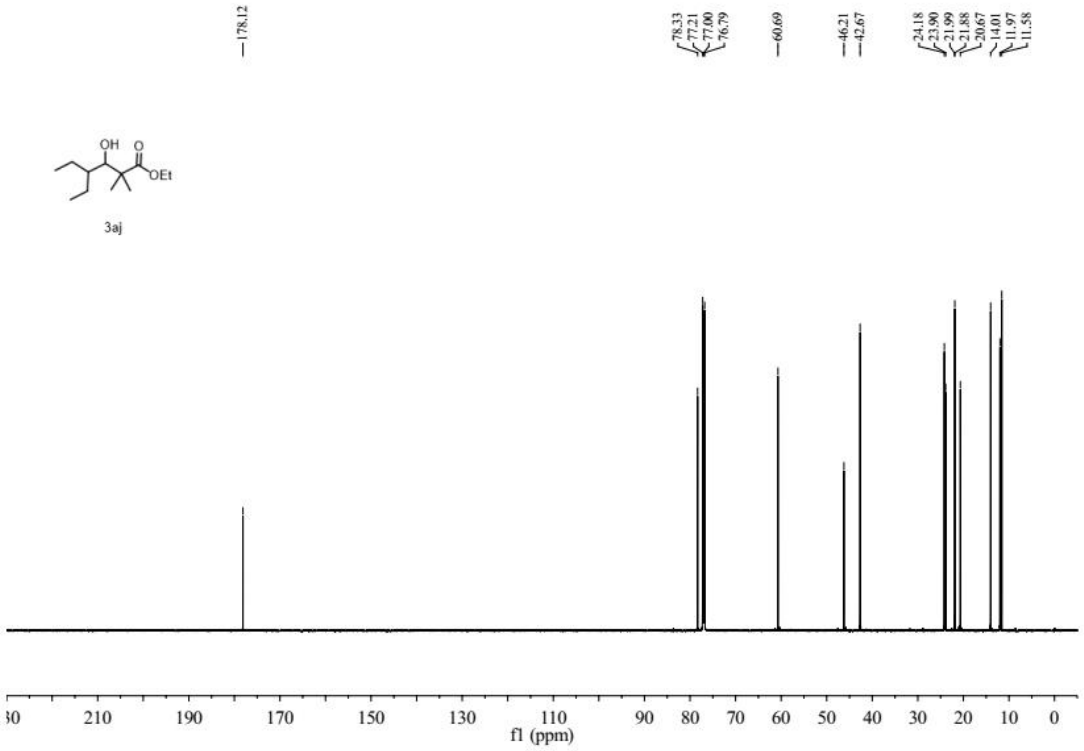
4.157
4.145
4.134
3.610
3.606
3.597
3.593
2.747
2.733
1.389
1.377
1.364
1.354
1.290
1.278
1.266
1.260
1.170
0.910
0.898
0.893
0.886
0.881
0.868
0.000
OH
O
OEt
3aj
2.02
1.02
1.00
3.23
7.05
4.16
6.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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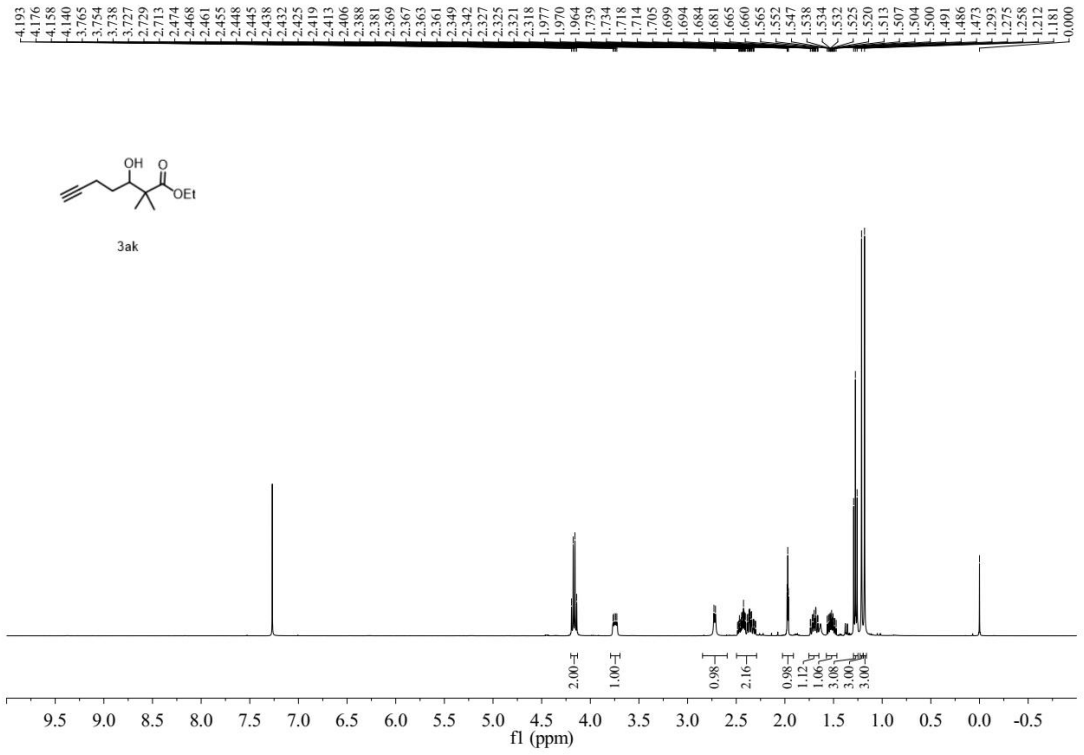
77.21
77.00
76.79
60.69
46.21
42.67
24.18
23.90
21.99
21.88
20.67
14.01
11.97
11.58
OH
O
OEt
3aj
fl (ppm)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4.140
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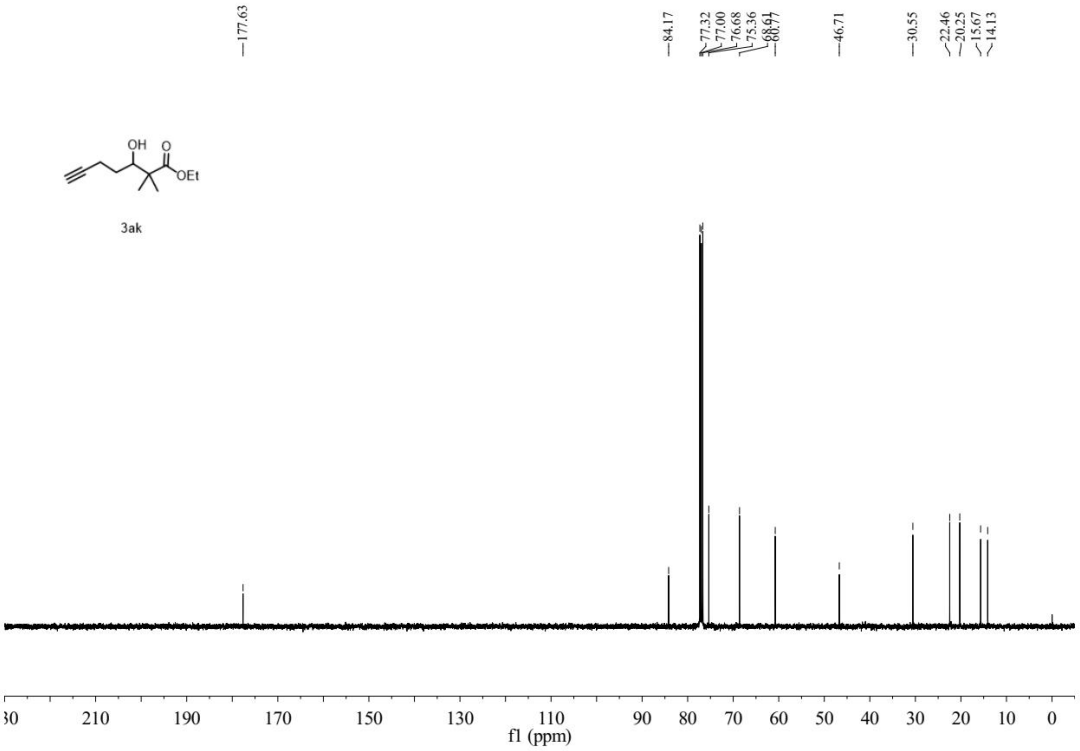
3.754
3.738
3.727
2.729
2.713
2.474
2.468
2.461
2.455
2.448
2.445
2.438
2.432
2.425
2.419
2.413
2.406
2.388
2.381
2.369
2.367
2.363
2.361
2.349
2.342
2.327
2.325
2.321
2.318
1.977
1.970
1.964
1.739
1.734
1.718
1.714
1.705
1.699
1.694
1.684
1.681
1.665
1.660
1.565
1.552
1.547
1.538
1.534
1.532
1.525
1.520
1.513
1.507
1.504
1.500
1.491
1.486
1.473
1.293
1.275
1.258
1.212
1.181
0.000
OH
O
OEt
3ak
2.00
1.00
0.98
2.16
0.98
1.12
1.06
3.08
3.00
3.00
fl (ppm)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77.32
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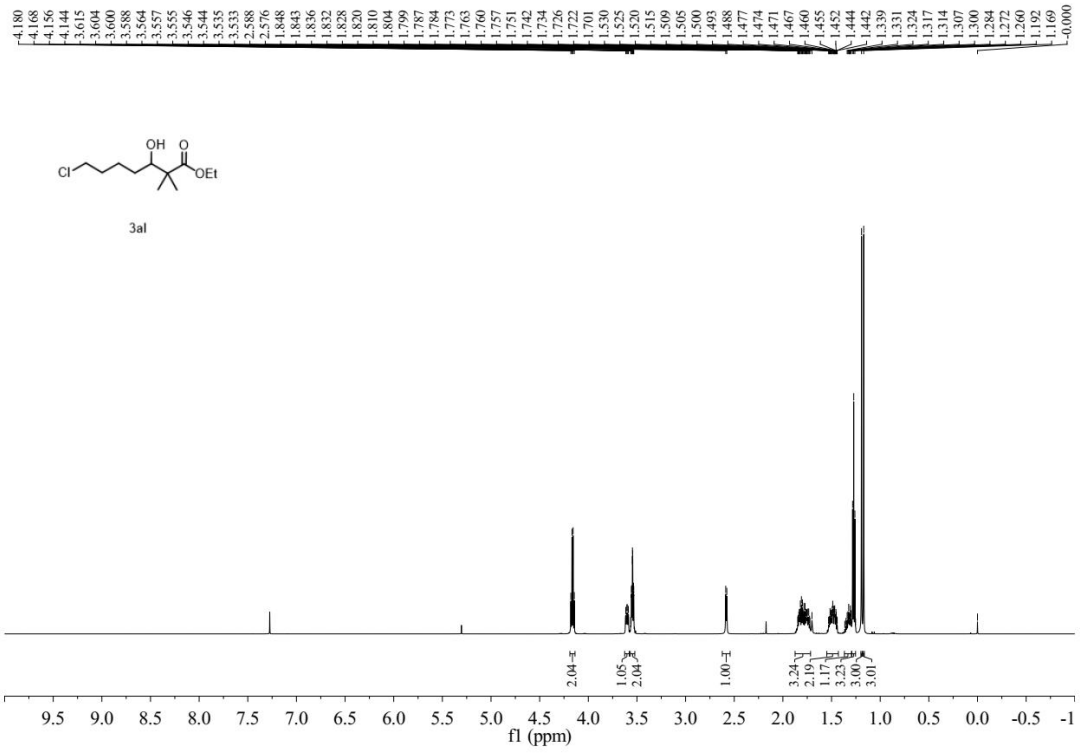
75.36
68.61
68.47
46.71
30.55
22.46
20.25
15.67
14.13
OH
O
OEt
3ak
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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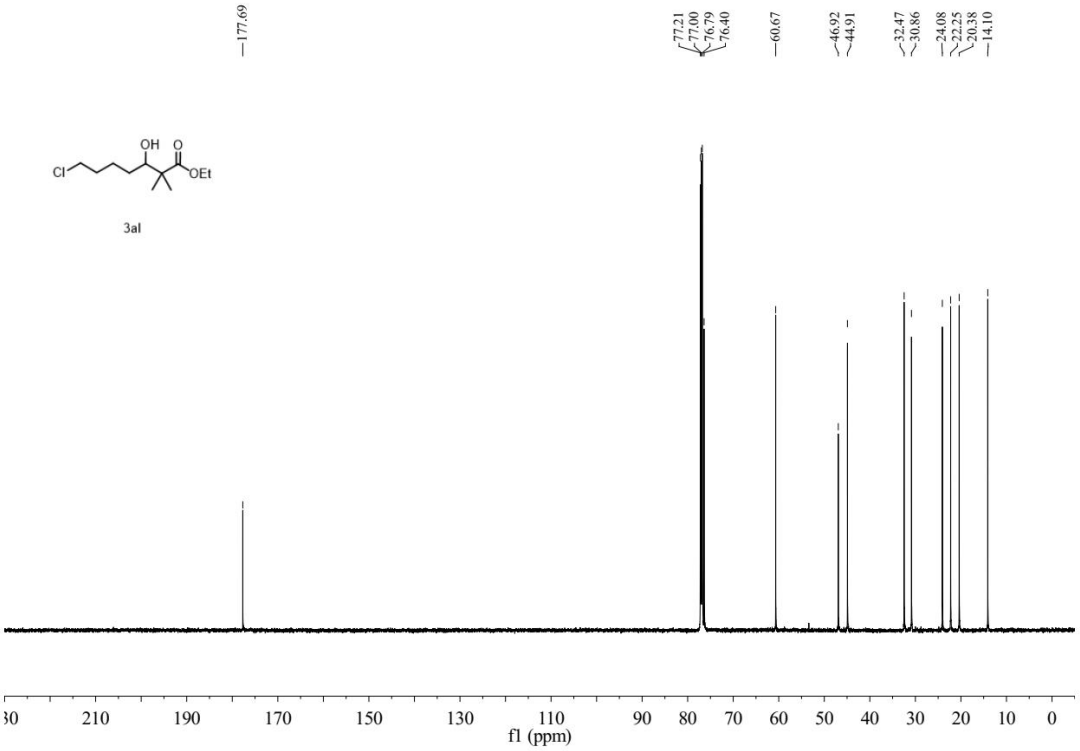
3.604
3.600
3.588
3.564
3.557
3.555
3.546
3.544
3.535
3.533
2.588
2.576
1.848
1.843
1.836
1.832
1.828
1.820
1.810
1.804
1.799
1.787
1.784
1.773
1.763
1.760
1.757
1.751
1.742
1.734
1.726
1.722
1.701
1.530
1.525
1.520
1.515
1.509
1.505
1.500
1.493
1.488
1.477
1.474
1.471
1.467
1.460
1.455
1.452
1.444
1.442
1.339
1.331
1.324
1.317
1.314
1.307
1.300
1.284
1.272
1.260
1.192
1.169
-0.000
OH
O
Cl
OEt
3al
2.04
1.05
2.04
1.00
3.24
2.19
1.17
3.23
3.00
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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76.40
60.67
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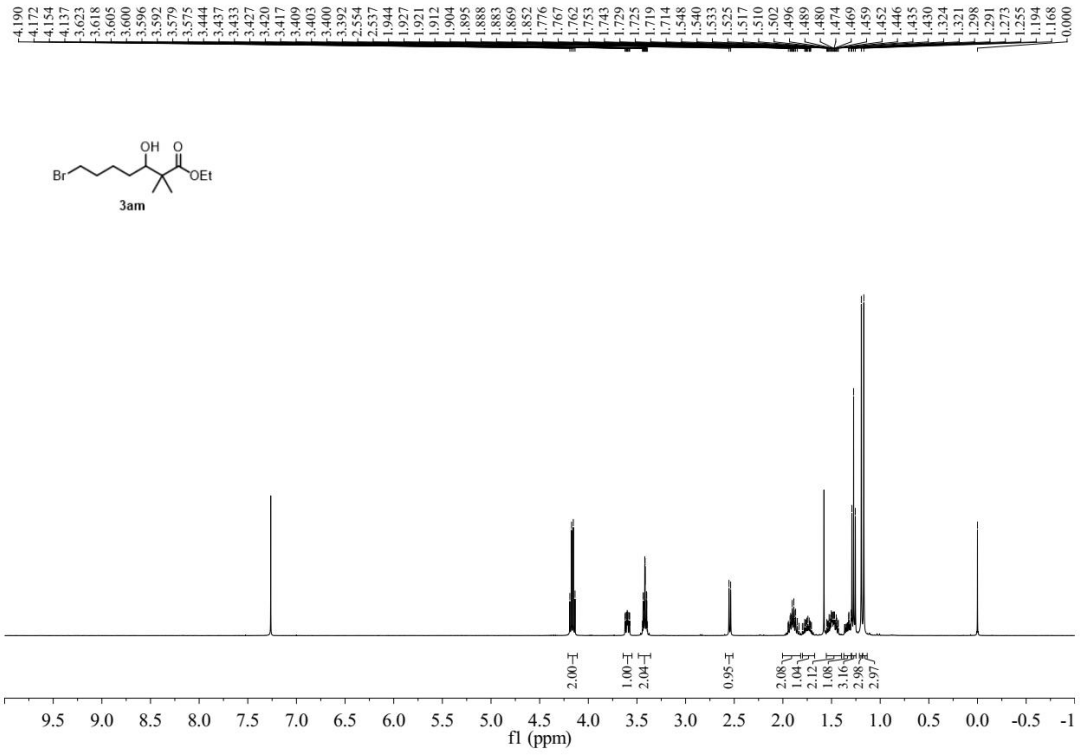
44.91
32.47
30.86
24.08
22.25
20.38
14.10
OH
O
Cl
OEt
3al
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.154
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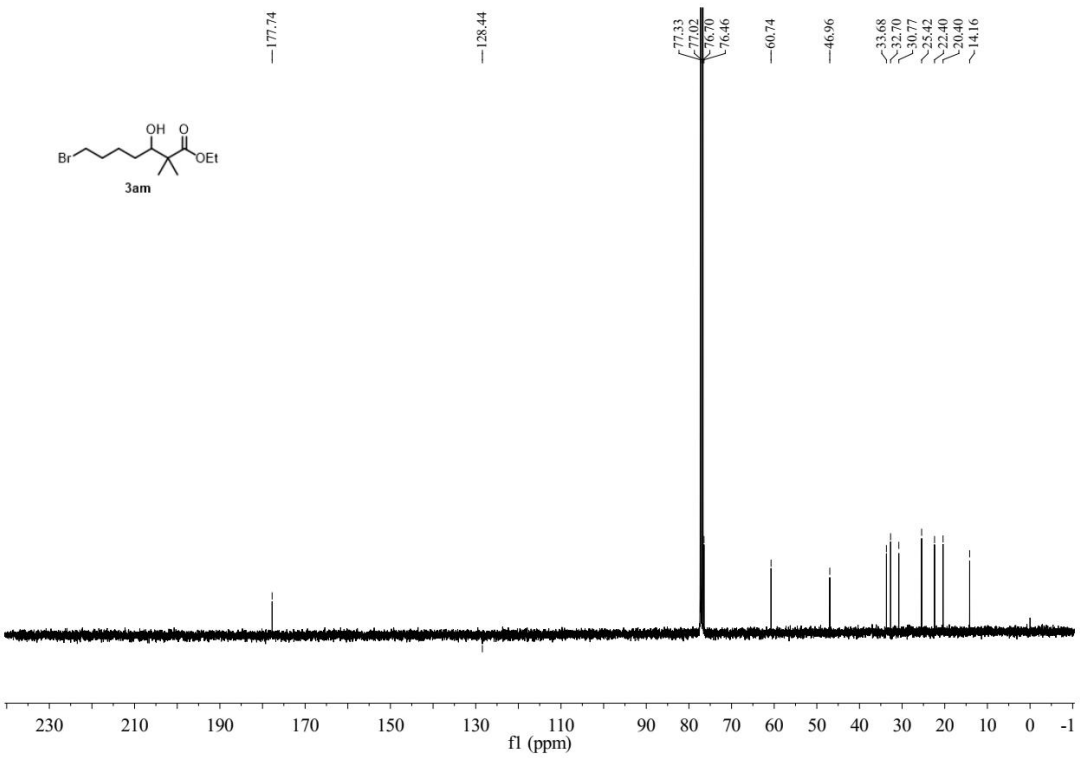
3.618
3.605
3.600
3.596
3.592
3.579
3.575
3.444
3.437
3.433
3.427
3.420
3.417
3.409
3.403
3.400
3.392
2.554
2.537
1.944
1.927
1.921
1.912
1.904
1.895
1.888
1.883
1.869
1.852
1.776
1.767
1.762
1.753
1.743
1.729
1.725
1.719
1.714
1.548
1.540
1.533
1.525
1.517
1.510
1.502
1.496
1.489
1.480
1.474
1.469
1.459
1.452
1.446
1.435
1.430
1.324
1.321
1.298
1.291
1.273
1.255
1.194
1.168
0.000
OH
O
Br
OEt
3am
2.00
1.00
2.04
0.95
2.08
1.04
2.12
1.08
3.16
2.98
2.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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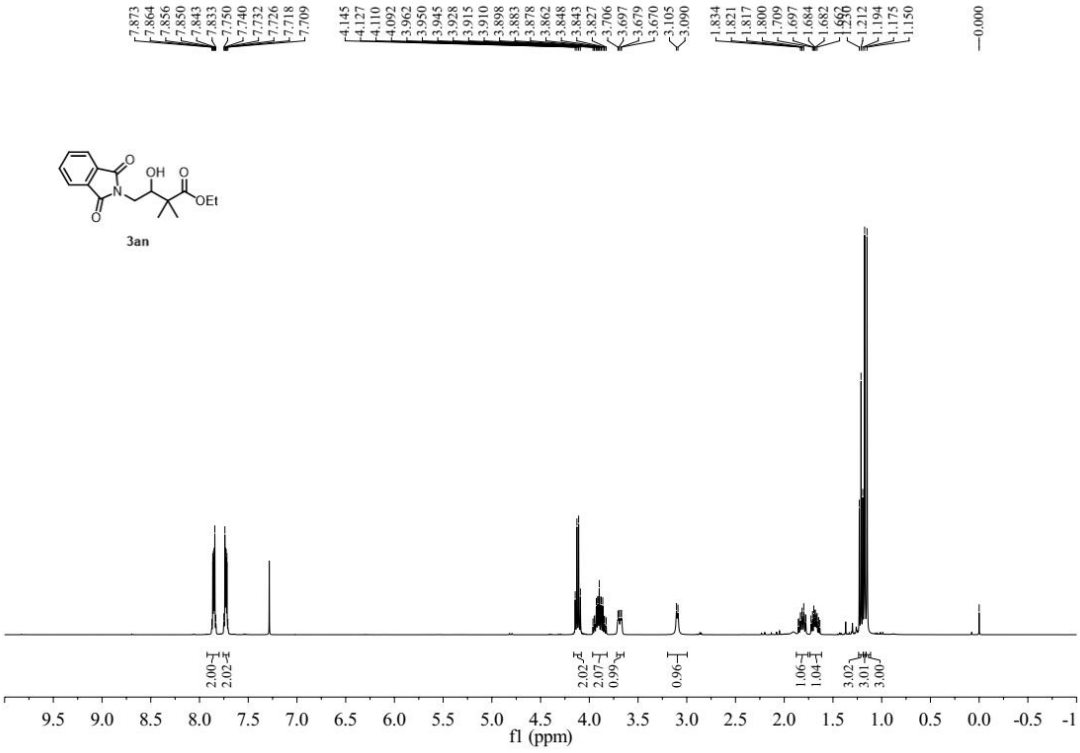
128.44
77.33
77.02
76.70
76.46
60.74
46.96
33.68
32.70
30.77
25.42
22.40
20.40
14.16
OH
O
Br
OEt
3am
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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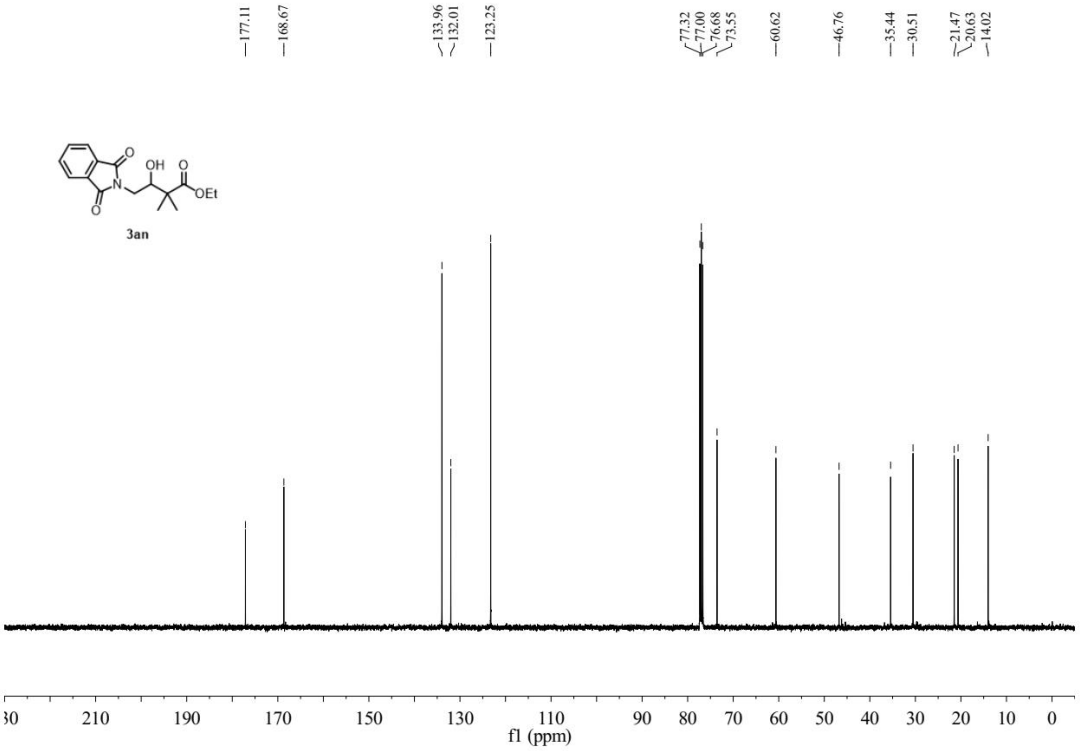
7.732
7.726
7.718
7.709
4.145
4.127
4.110
4.092
3.962
3.950
3.945
3.928
3.915
3.910
3.898
3.883
3.878
3.862
3.848
3.843
3.827
3.706
3.697
3.679
3.670
3.105
3.090
1.834
1.821
1.817
1.800
1.709
1.697
1.684
1.682
1.212
1.194
1.175
1.150
0.000
O
OH
O
N
OEt
O
3an
2.00
2.02
2.02
2.07
0.99
0.96
1.06
1.04
3.02
3.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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132.01
123.25
77.32
77.00
76.68
73.55
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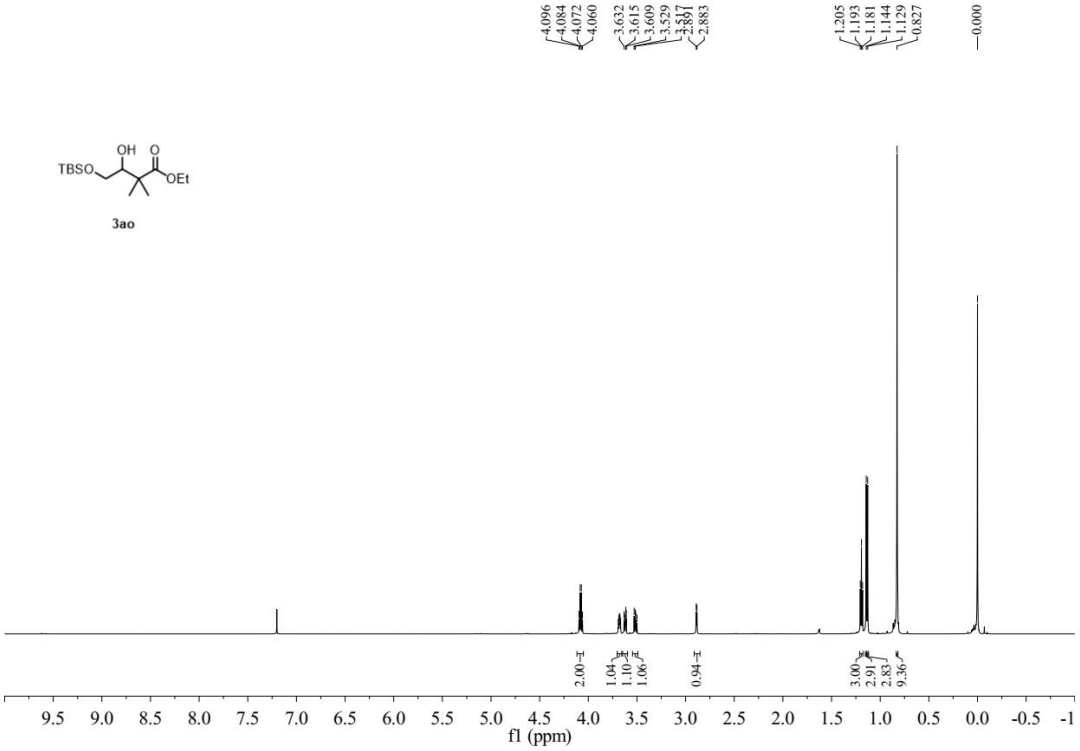
35.44
30.51
21.47
20.63
14.02
OH
O
OEt
3an
f1 (ppm)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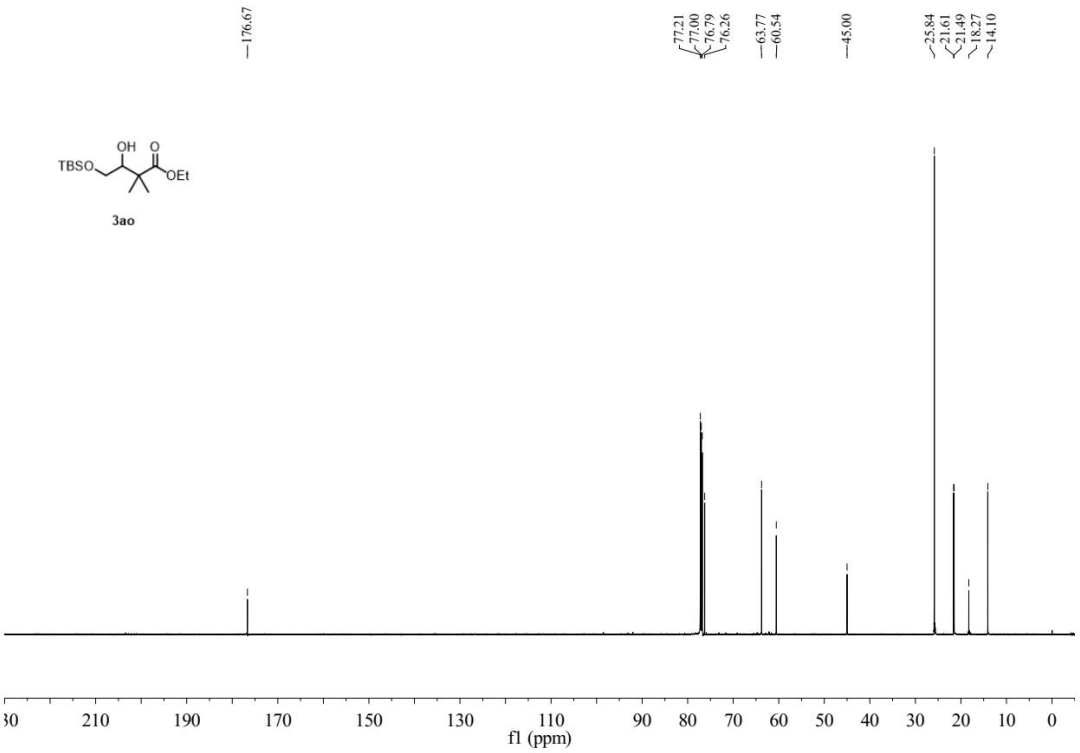
4.060
3.632
3.615
3.609
3.529
3.517
2.891
2.883
1.205
1.193
1.181
1.144
1.129
0.827
0.000
TBSO
OH
O
OEt
3ao
2.00
1.04
1.10
1.06
0.94
3.00
2.91
2.83
9.36
f1 (ppm)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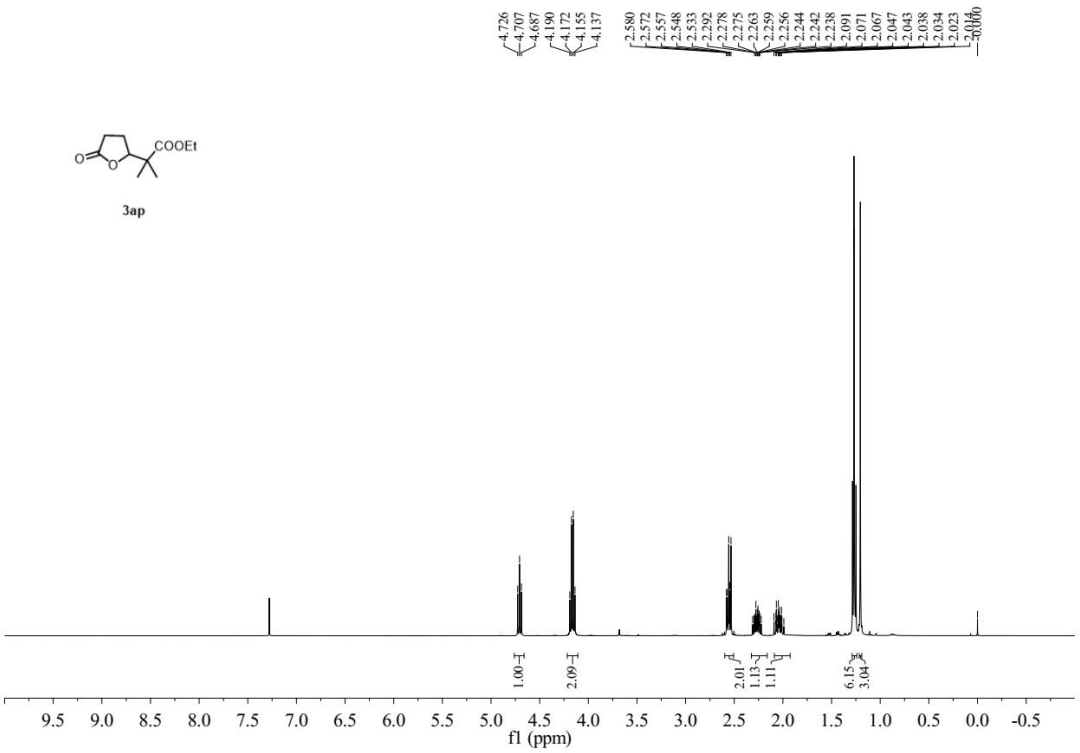
76.79
76.26
63.77
60.54
45.00
25.84
21.61
21.49
18.27
14.10
OH
O
TBSO
OEt
3ao
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.172
4.155
4.137
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2.572
2.557
2.548
2.533
2.292
2.278
2.275
2.263
2.259
2.256
2.244
2.242
2.238
2.091
2.071
2.067
2.047
2.043
2.038
2.034
2.023
COOEt
O
O
3ap
1.00
2.09
2.01
1.13
1.11
6.15
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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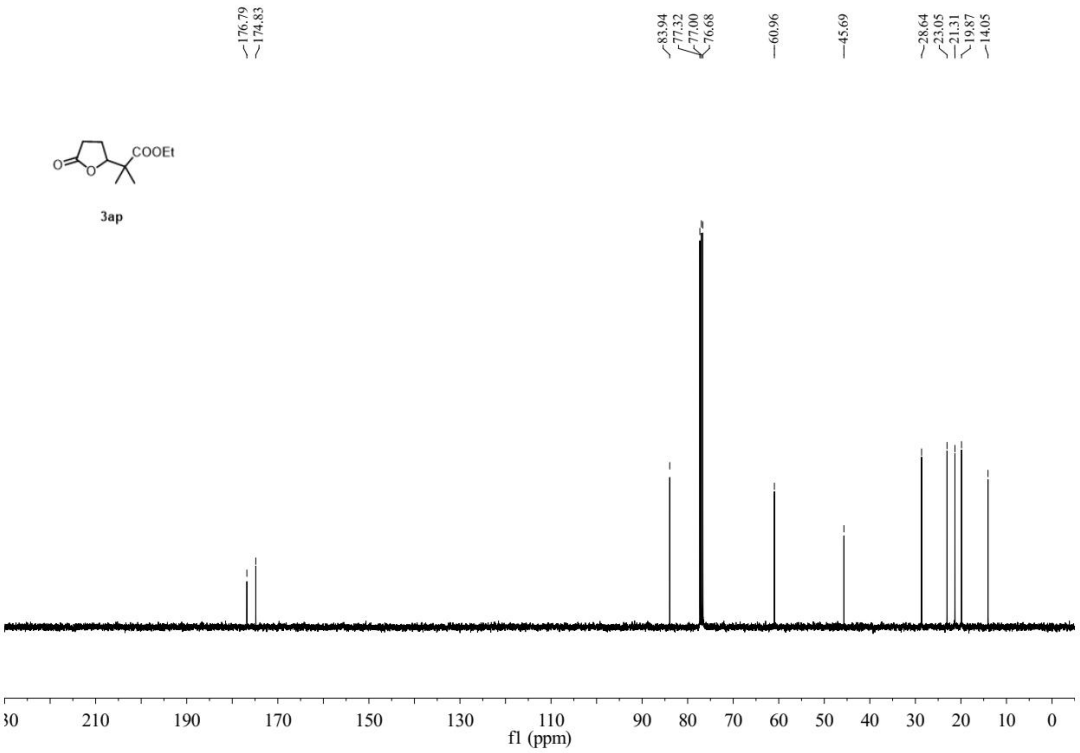
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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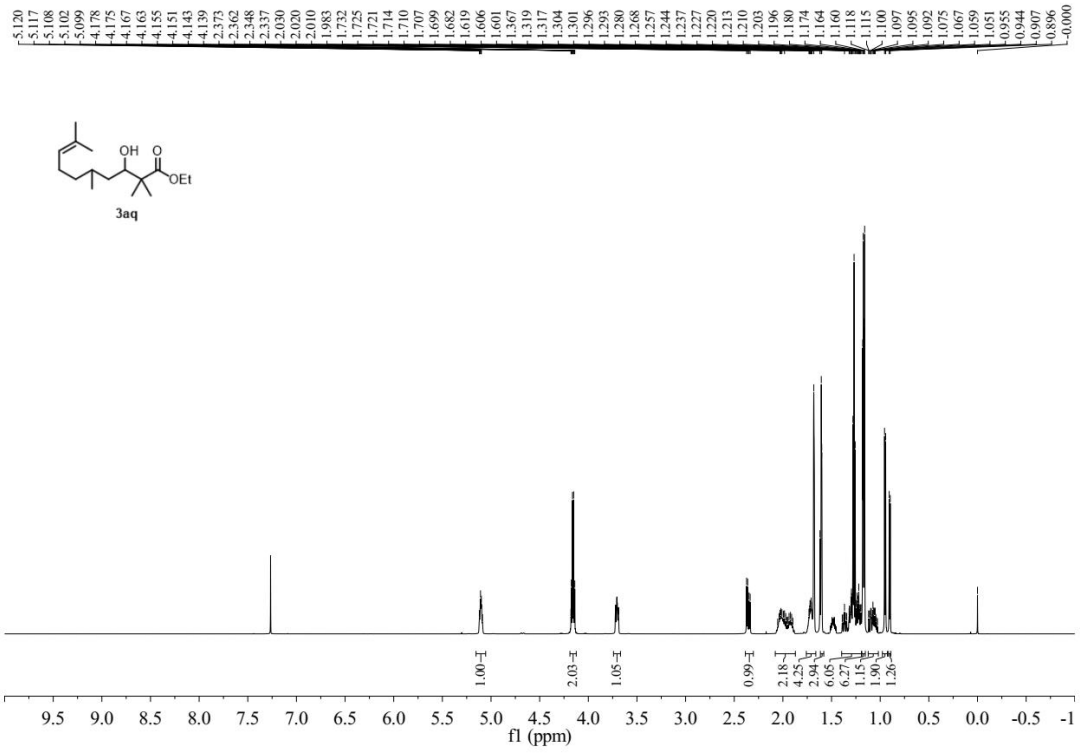
77.00
76.68
60.96
45.69
28.64
23.05
21.31
19.87
14.05
COOEt
O
O
3ap
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.117
5.108
5.102
5.099
4.178
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4.167
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4.155
4.151
4.143
4.139
2.373
2.362
2.348
2.337
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2.020
2.010
1.983
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1.257
1.244
1.237
1.227
1.220
1.213
1.210
1.203
1.196
1.180
1.174
1.164
1.160
1.118
1.115
1.100
1.097
1.095
1.092
1.075
1.067
1.059
1.051
0.955
0.944
0.907
0.896
0.000
OH
O
OEt
3aq
1.00
2.03
1.05
0.99
2.18
4.25
2.94
6.05
6.27
1.15
1.90
1.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
1.5
1.0
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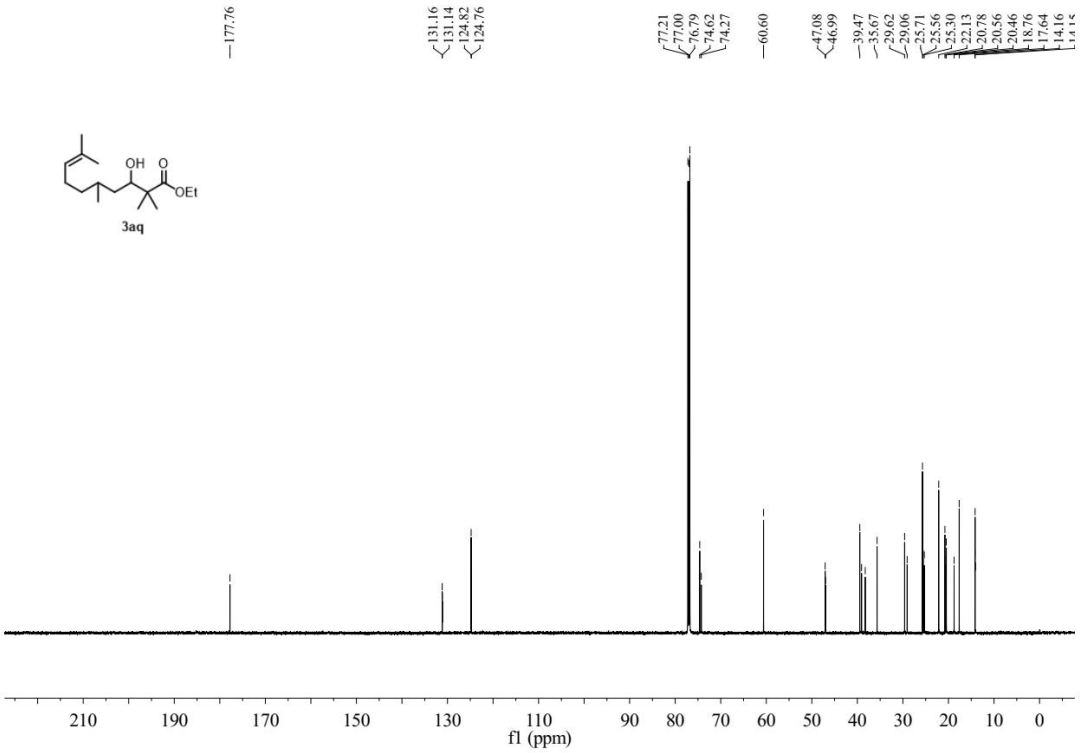
0.0
-0.5
-1
f1 (ppm)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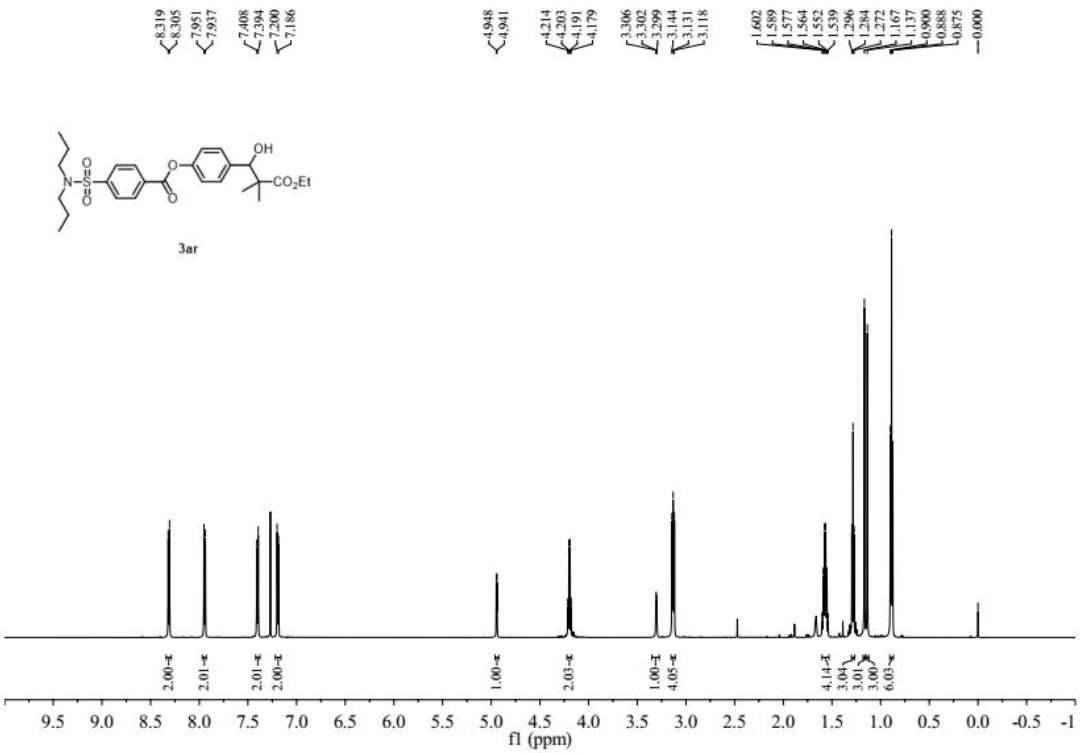
131.16
131.14
124.82
124.76
77.21
77.00
76.79
74.62
74.27
60.60
47.08
46.99
39.47
35.67
29.62
29.06
25.71
25.56
25.30
22.13
20.78
20.56
20.46
18.76
17.64
14.16
OH
O
OEt
3aq
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.305
7.951
7.937
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7.394
7.200
7.186
4.948
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4.214
4.203
4.191
4.179
3.306
3.302
3.299
3.144
3.131
3.118
1.602
1.589
1.577
1.564
1.552
1.539
1.296
1.284
1.272
1.167
1.137
0.900
0.888
0.875
0.000
OH
CO2Et
3ar
2.00
2.01
2.01
2.00
1.00
2.03
1.00
4.05
4.14
3.04
3.01
3.00
6.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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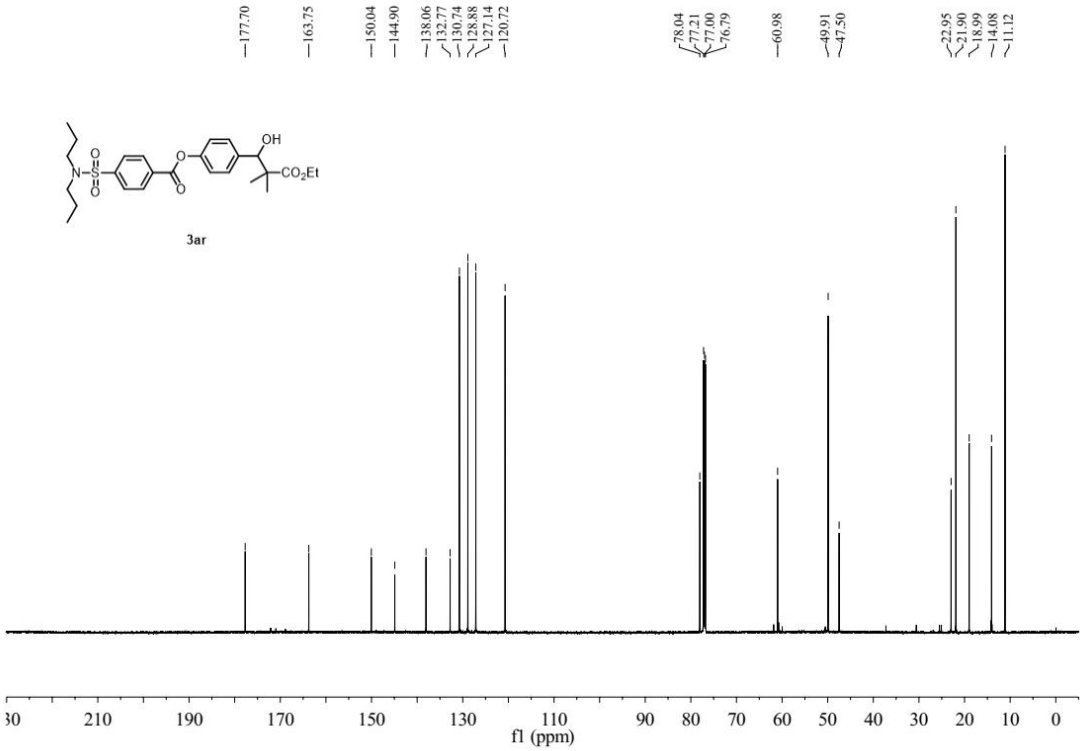
-1
f1 (ppm)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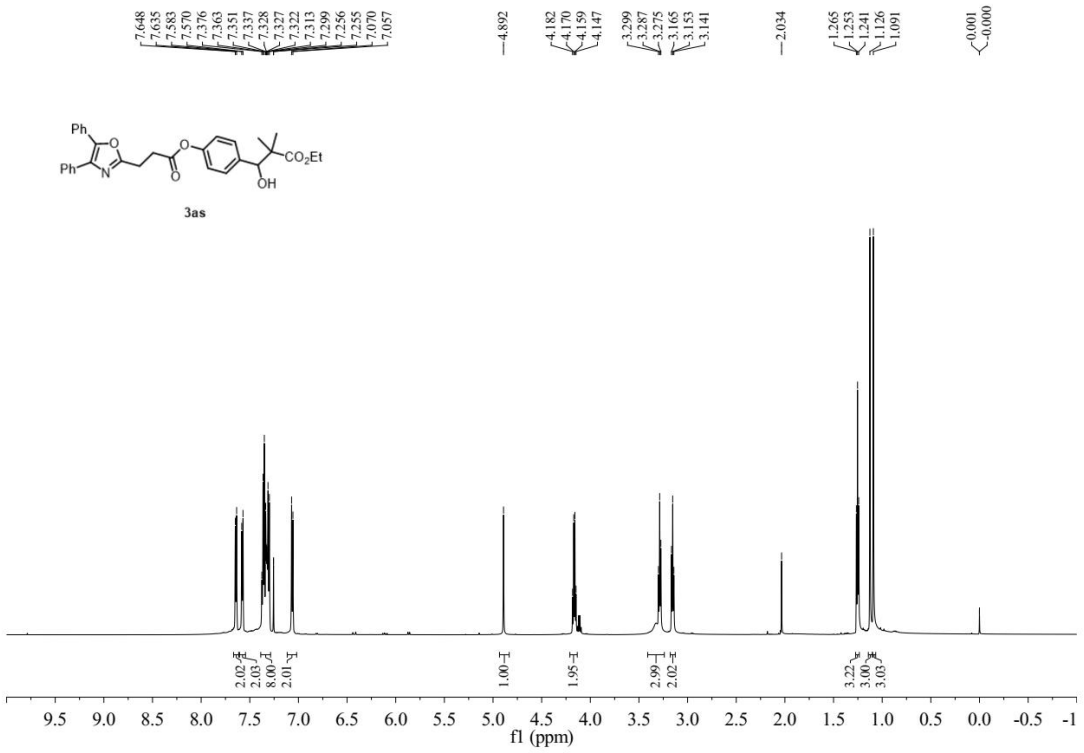
128.88
127.14
120.72
78.04
77.21
77.00
76.79
60.98
49.91
47.50
22.95
21.90
18.99
14.08
11.12
OH
CO2Et
3ar
f1 (ppm)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7.635
7.583
7.570
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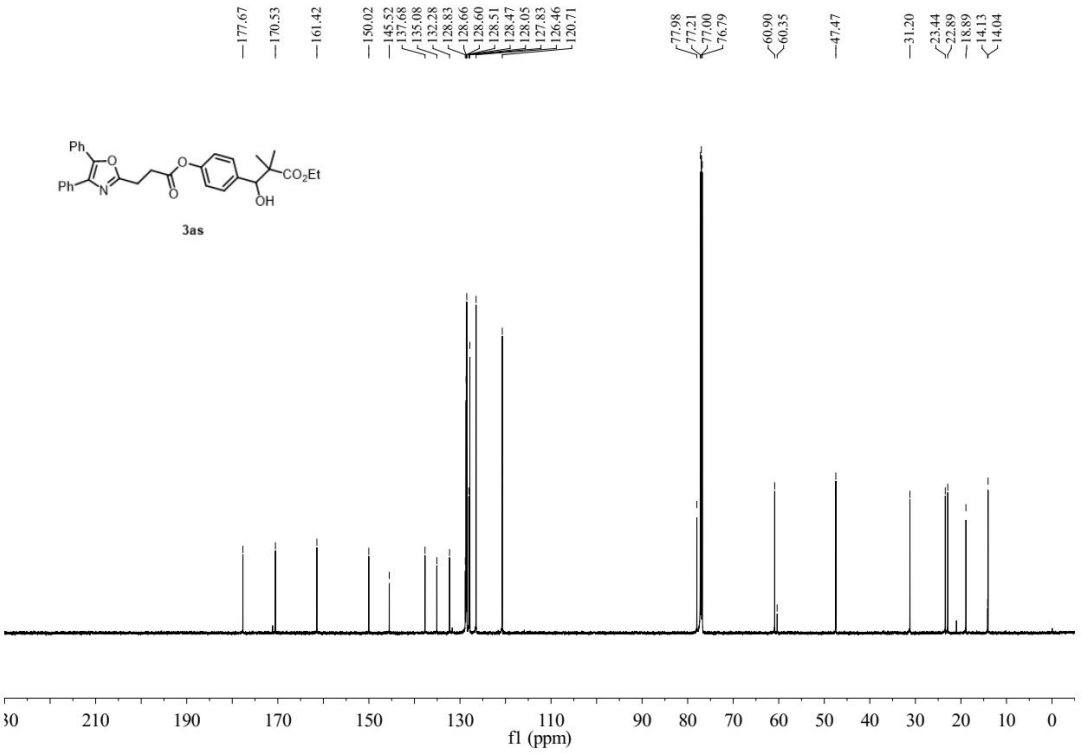
7.363
7.351
7.337
7.328
7.327
7.322
7.313
7.299
7.256
7.255
7.070
7.057
4.892
4.182
4.170
4.159
4.147
3.299
3.287
3.275
3.165
3.153
3.141
2.034
1.265
1.253
1.241
1.126
1.091
0.001
-0.000
Ph
Ph
CO2Et
OH
3as
2.02
2.03
8.00
2.01
1.00
1.95
2.99
2.02
3.22
3.00
3.03
f1 (ppm)


177.67
170.53
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145.52
137.68
135.08
132.28
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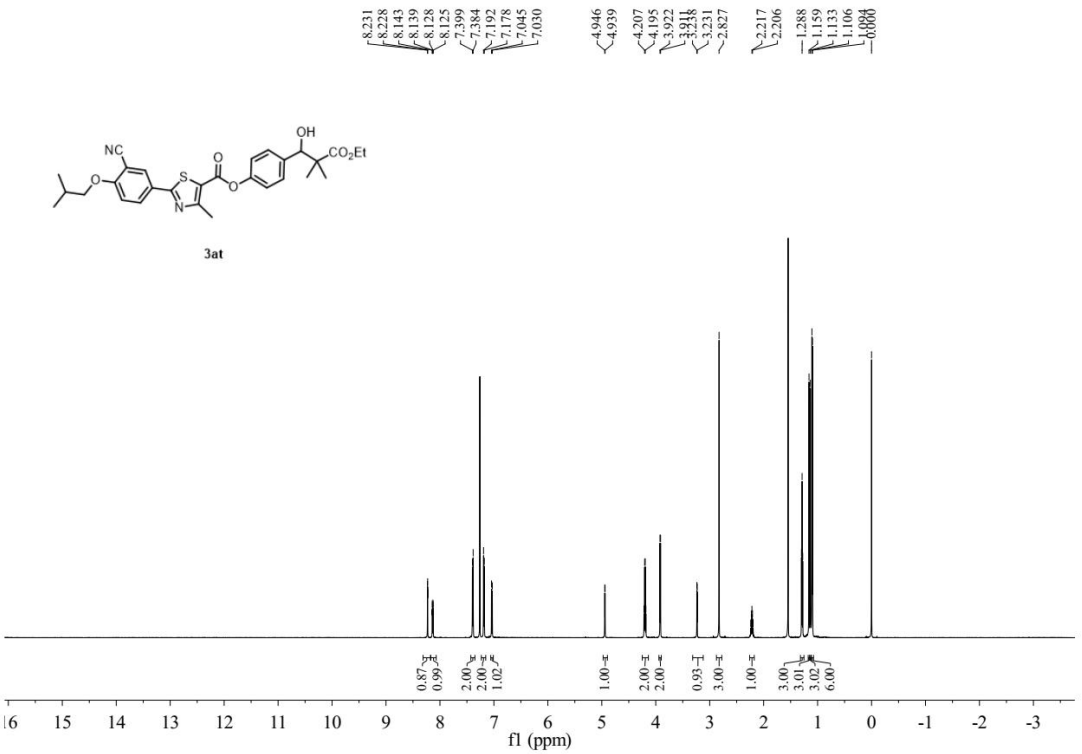
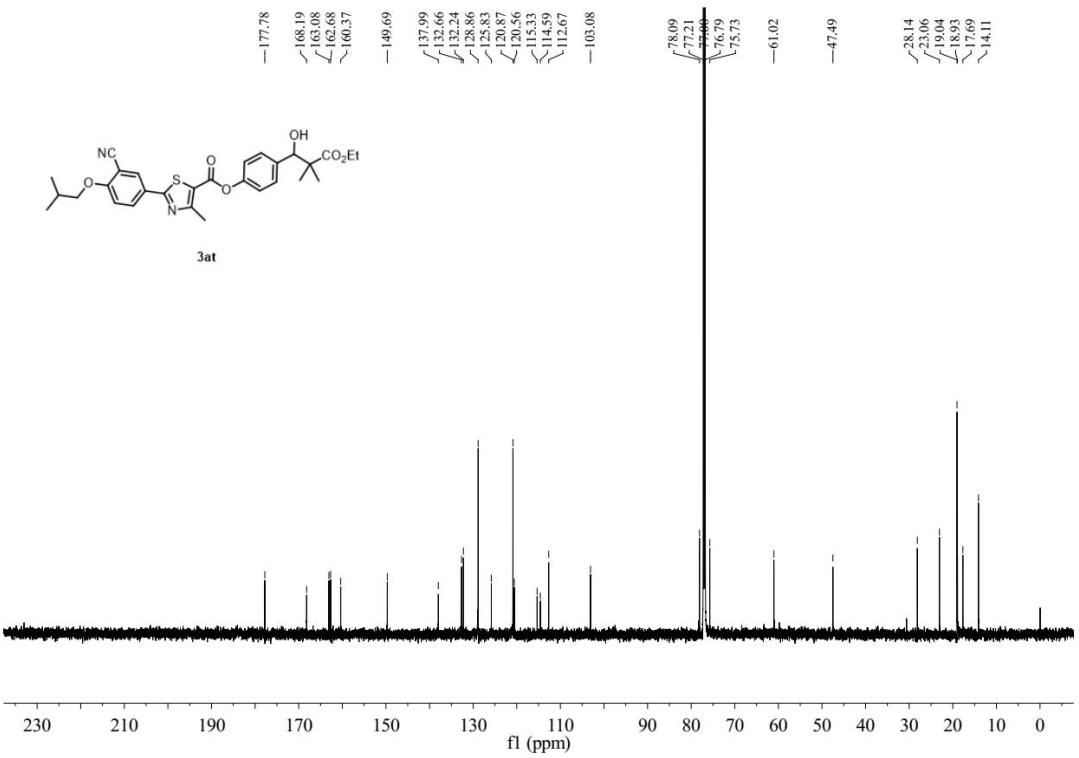
128.66
128.60
128.51
128.47
128.05
127.83
126.46
120.71
77.98
77.21
77.00
76.79
60.90
60.35
47.47
31.20
23.44
22.89
18.89
14.13
14.04
Ph
Ph
O
N
O
O
CO2Et
OH
3as
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.231
8.228
8.143
8.139
8.128
8.125
7.399
7.384
7.192
7.178
7.045
7.030
4.946
4.939
4.207
4.195
3.922
3.231
2.827
2.217
2.206
1.288
1.159
1.133
1.106
NC
S
N
O
O
OH
CO2Et
3at
0.87
0.99
2.00
2.00
1.02
1.00
2.00
2.00
0.93
3.00
1.00
3.00
3.01
3.02
6.00
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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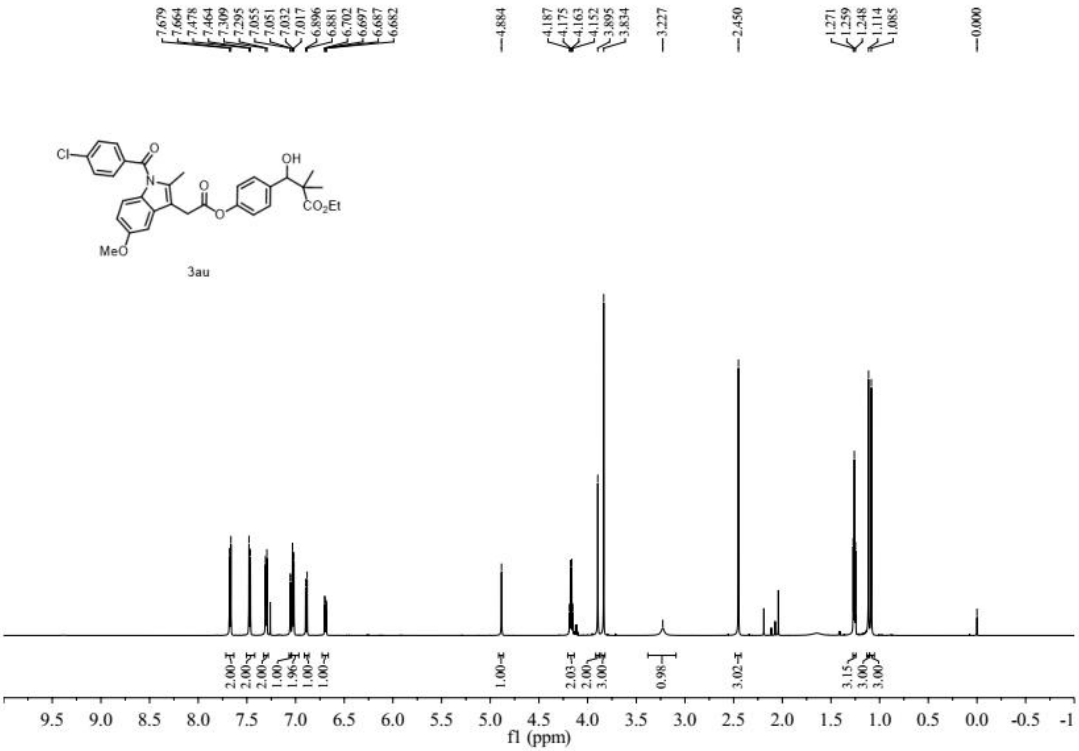
168.19
163.08
162.68
160.37
149.69
137.99
132.66
132.24
128.86
125.83
120.87
120.56
115.33
114.59
112.67
103.08
78.09
77.21
76.79
75.73
61.02
47.49
28.14
23.06
19.04
18.93
17.69
14.11
NC
O
S
N
O
O
OH
CO2Et
3at
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.664
7.478
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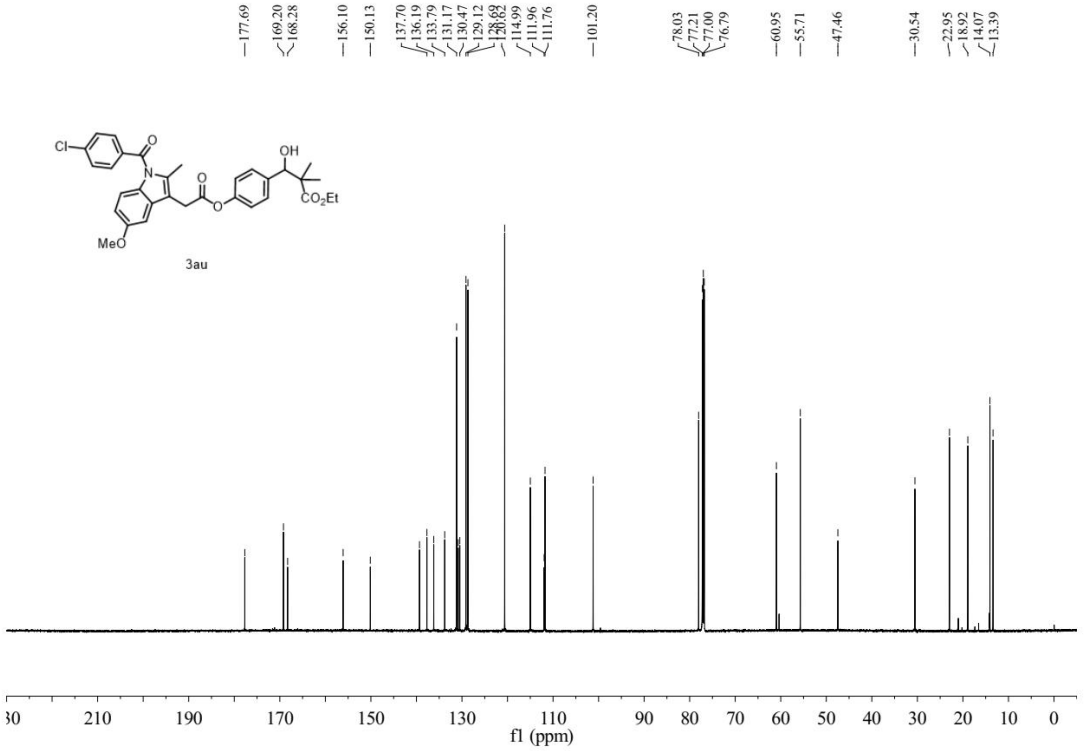
7.309
7.295
7.055
7.051
7.032
7.017
6.896
6.881
6.702
6.697
6.687
6.682
4.884
4.187
4.175
4.163
4.152
3.895
3.834
3.227
2.450
1.271
1.259
1.248
1.114
1.085
0.000
Cl
O
N
O
O
OH
CO2Et
MeO
3au
2.00
2.00
2.00
1.00
1.96
1.00
1.00
1.00
2.03
2.00
3.00
0.98
3.02
3.15
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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168.28
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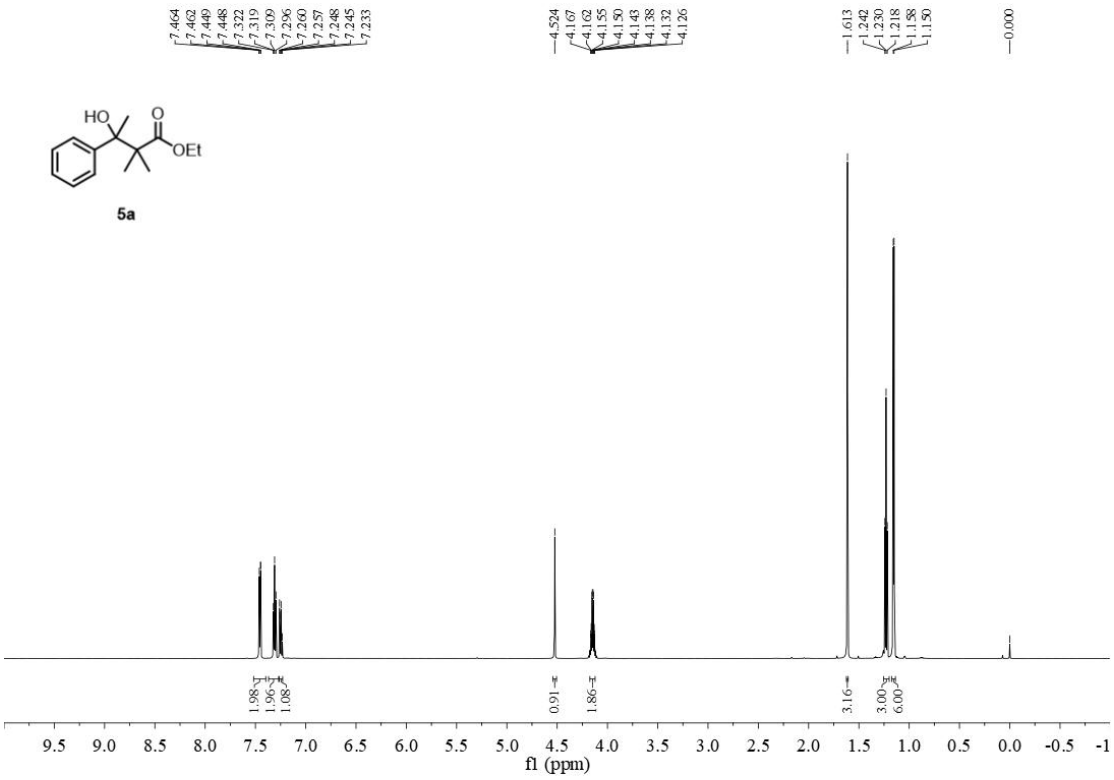
150.13
137.70
136.19
133.79
131.17
130.47
129.12
114.99
111.96
111.76
101.20
78.03
77.21
77.00
76.79
60.95
55.71
47.46
30.54
22.95
18.92
14.07
13.39
Cl
O
N
O
O
OH
CO2Et
MeO
3au
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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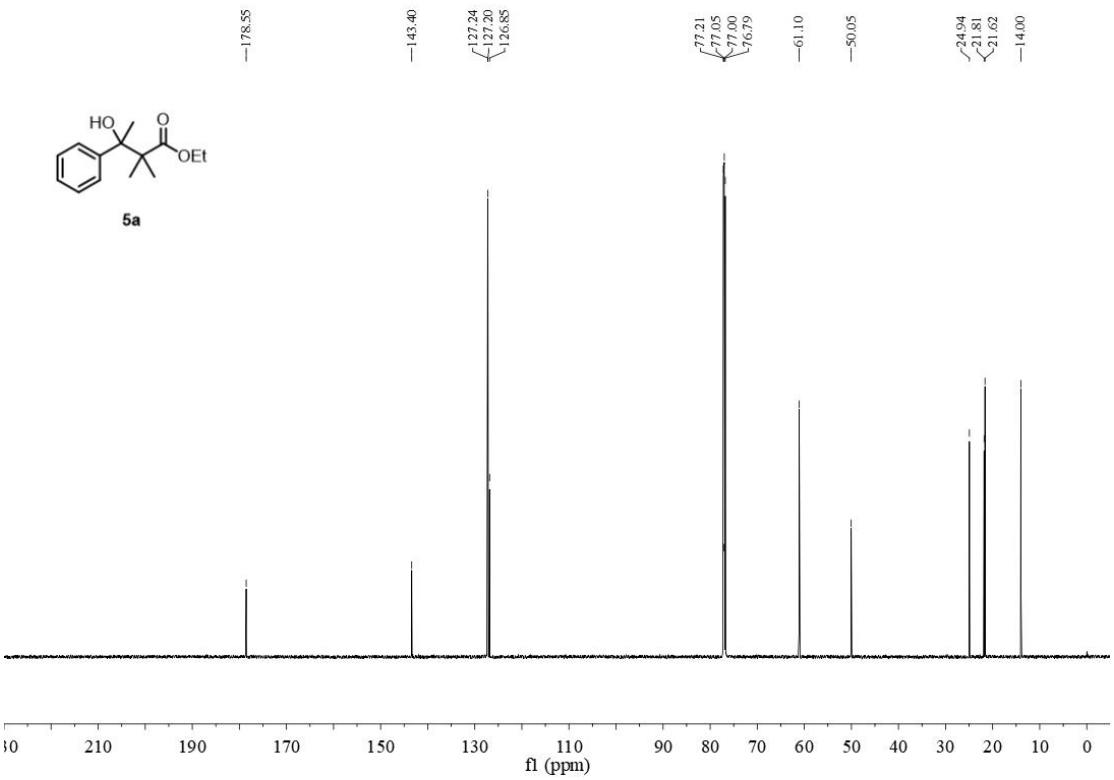
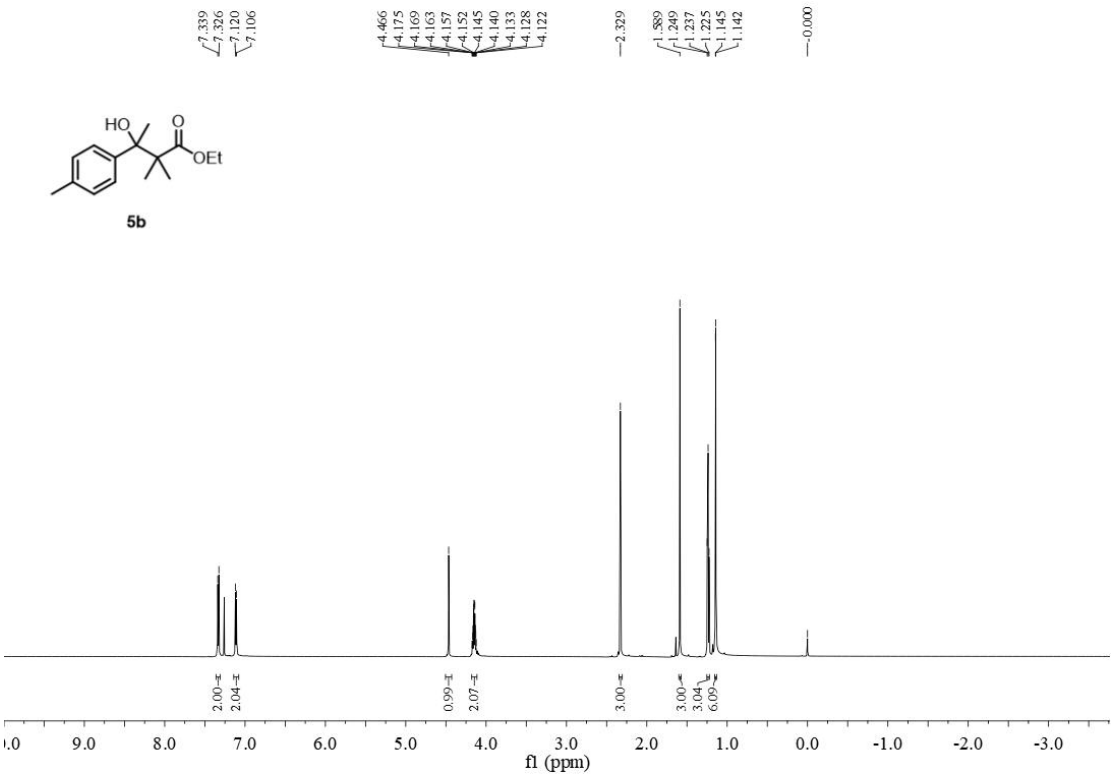
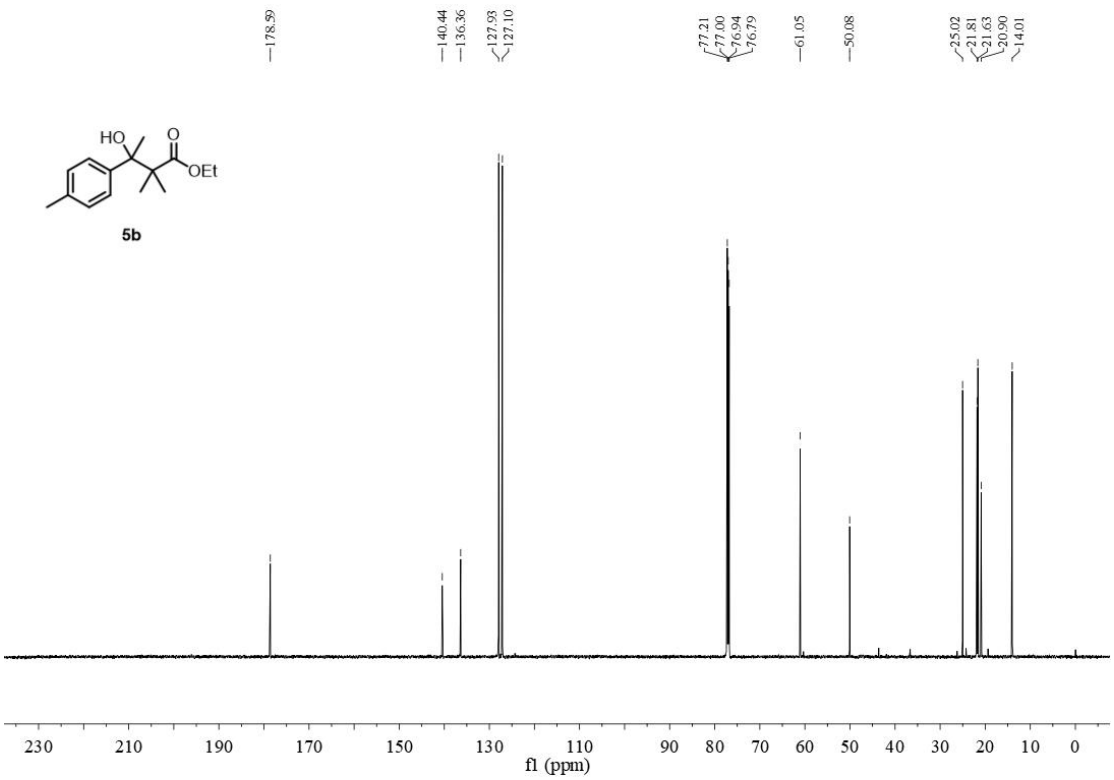
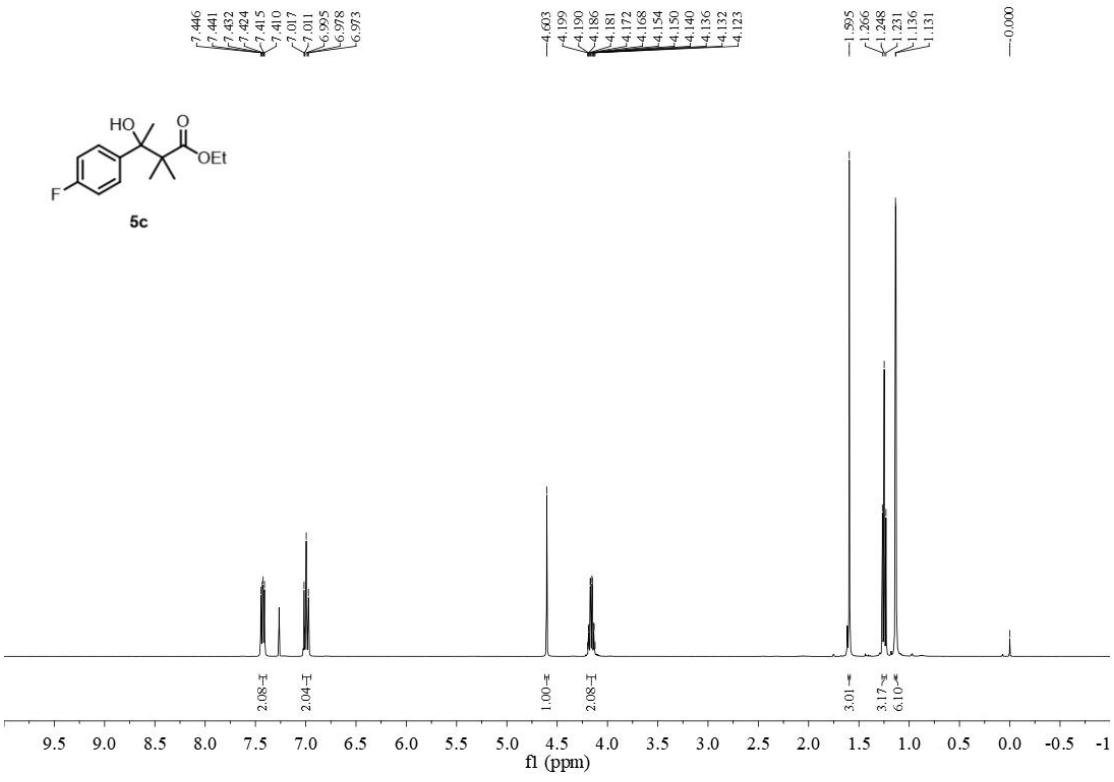
7.462
7.449
7.448
7.322
7.319
7.309
7.296
7.260
7.257
7.248
7.245
7.233
4.524
4.167
4.162
4.155
4.150
4.143
4.138
4.132
4.126
1.613
1.242
1.230
1.218
1.158
1.150
0.000
HO
O
OEt
5a
1.98
1.96
1.08
0.91
1.86
3.16
3.00
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


178.55
143.40
127.24
127.20
126.85
77.21
77.05
77.00
76.79
61.10
50.05
24.94
21.81
21.62
14.00
HO
O
OEt
5a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.339
7.326
7.120
7.106
4.466
4.175
4.169
4.163
4.157
4.152
4.145
4.140
4.133
4.128
4.122
2.329
1.589
1.249
1.237
1.225
1.145
1.142
0.000
HO
O
OEt
5b
2.00
2.04
0.99
2.07
3.00
3.00
3.04
6.09
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
f1 (ppm)


178.89
140.44
136.36
127.93
127.10
77.21
77.00
76.94
76.79
61.05
50.08
25.02
21.81
21.63
20.90
14.01
HO
O
OEt
5b
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.446
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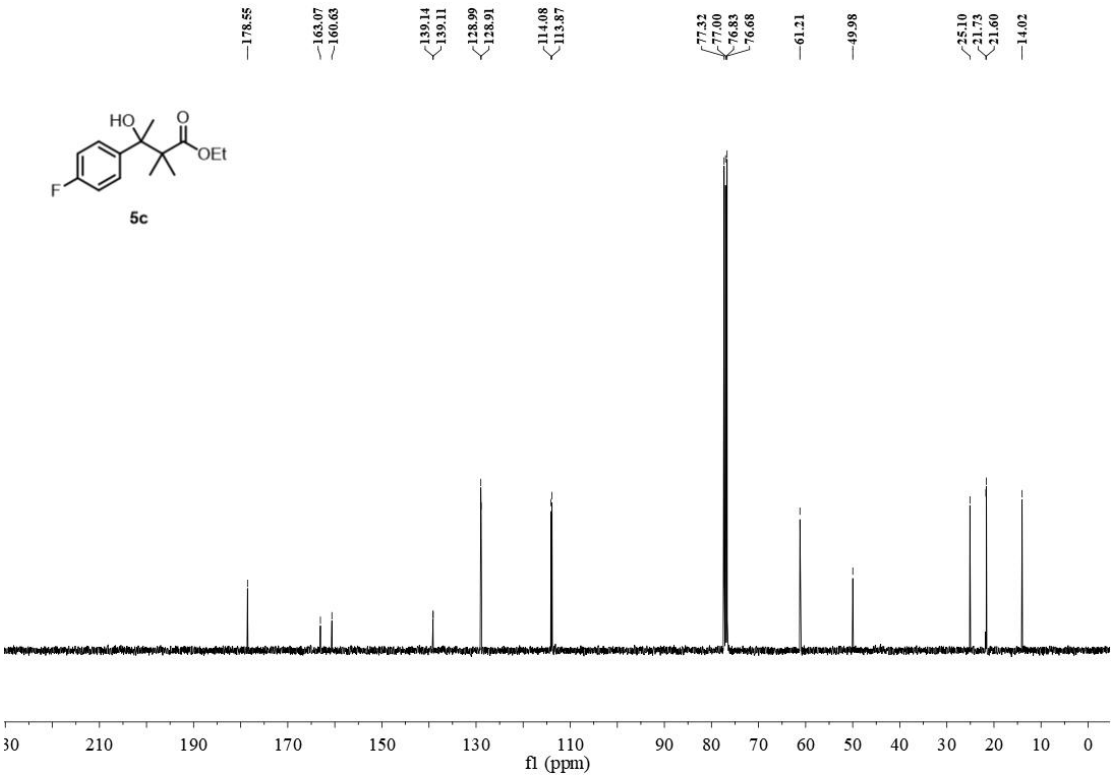
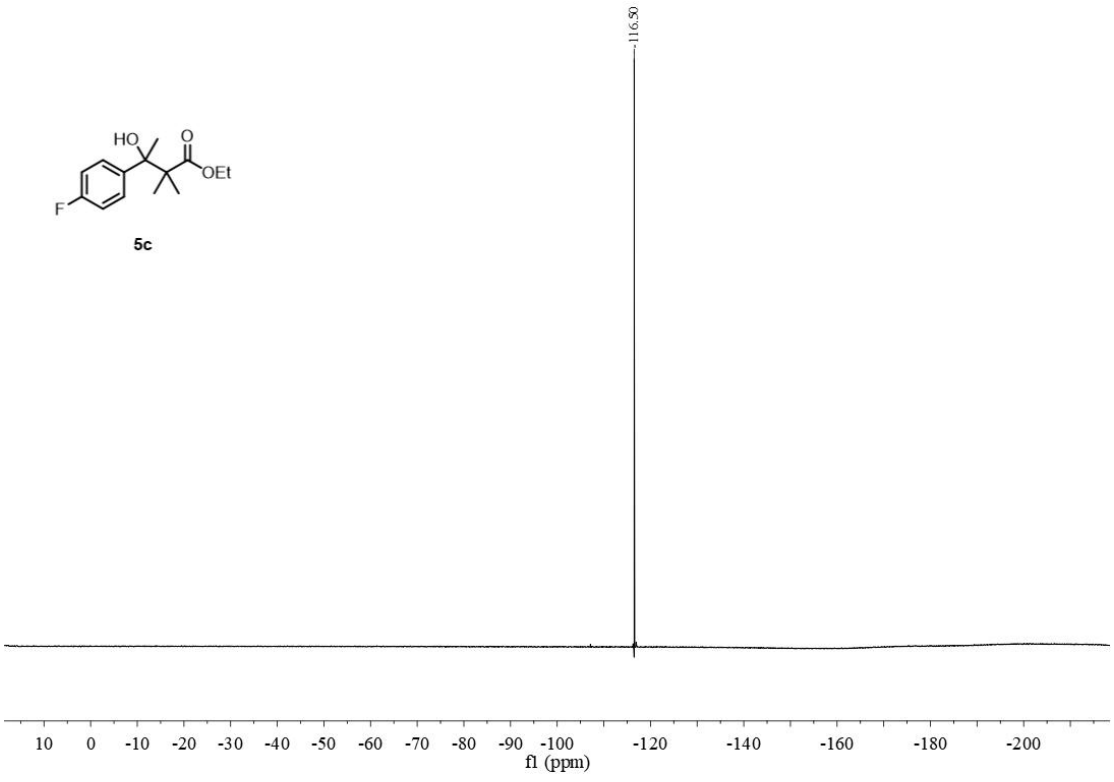
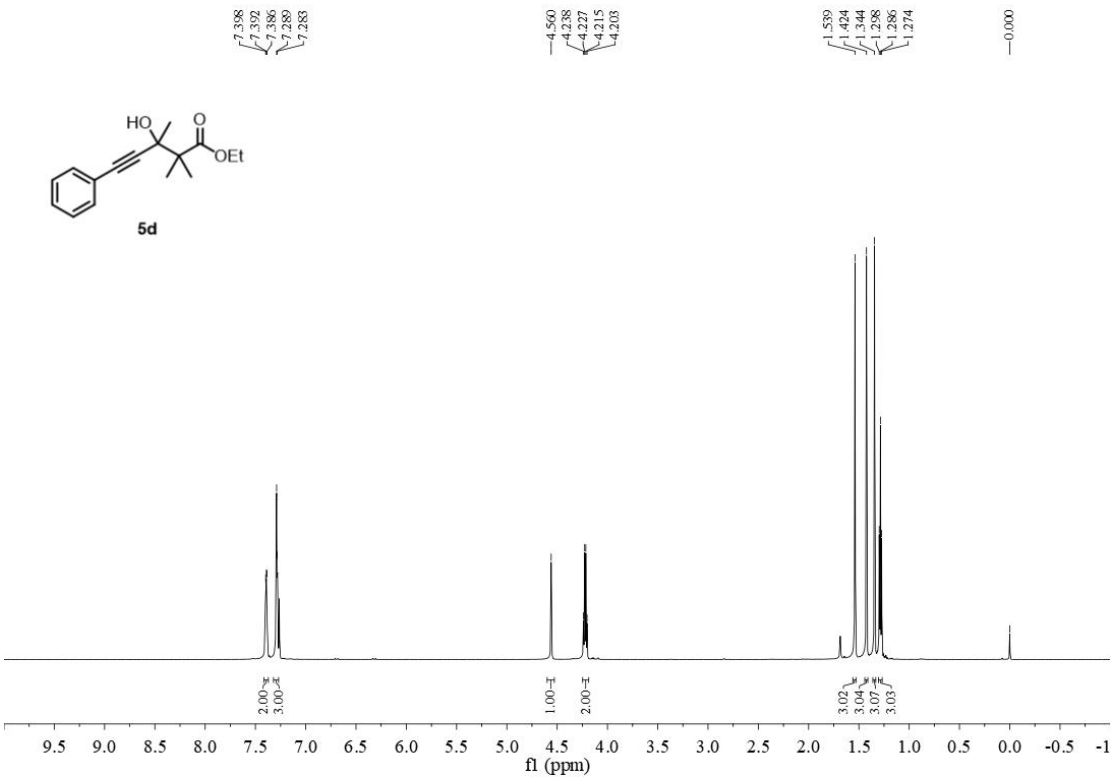
7.432
7.424
7.415
7.410
7.017
7.011
6.995
6.978
6.973
4.603
4.199
4.190
4.186
4.181
4.172
4.168
4.154
4.150
4.140
4.136
4.132
4.123
1.595
1.266
1.248
1.231
1.136
1.131
0.000
HO
O
OEt
F
5c
2.08
2.04
1.00
2.08
3.01
3.17
6.10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


178.55
163.07
160.63
139.14
139.11
128.99
128.91
114.08
113.87
77.32
77.00
76.83
76.68
61.21
49.98
25.10
21.73
21.60
14.02
HO
O
OEt
F
5c
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


116.90
HO
O
OEt
F
5c
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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7.392
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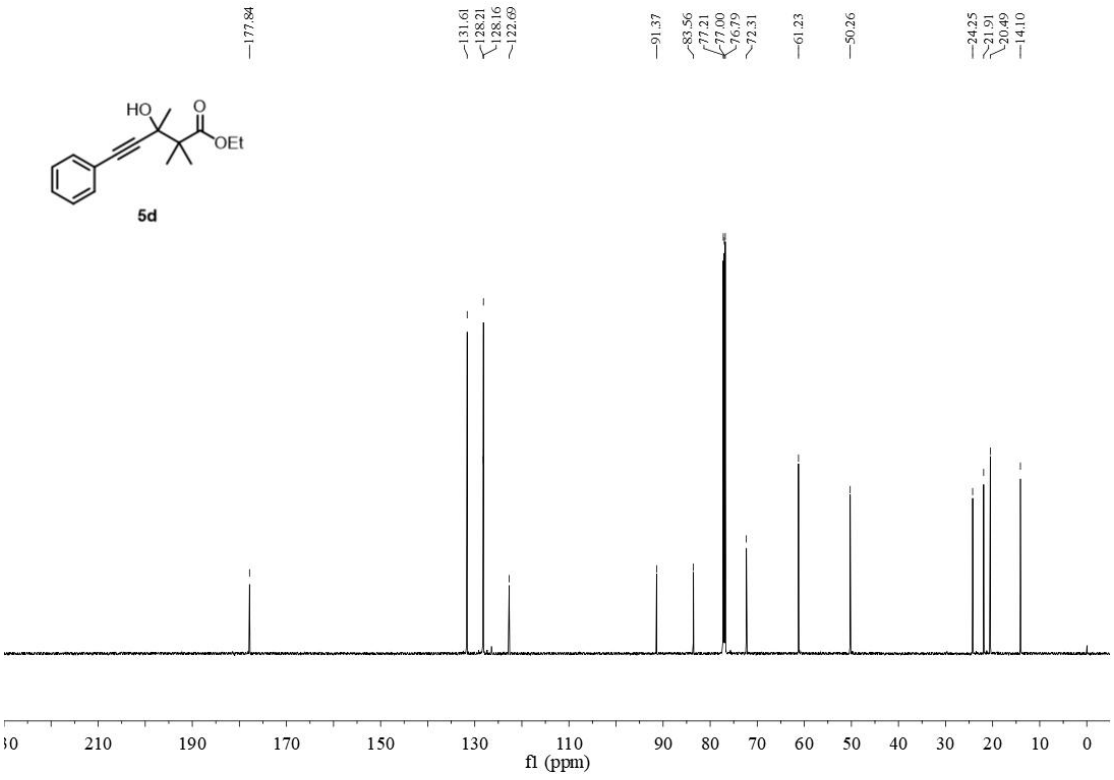
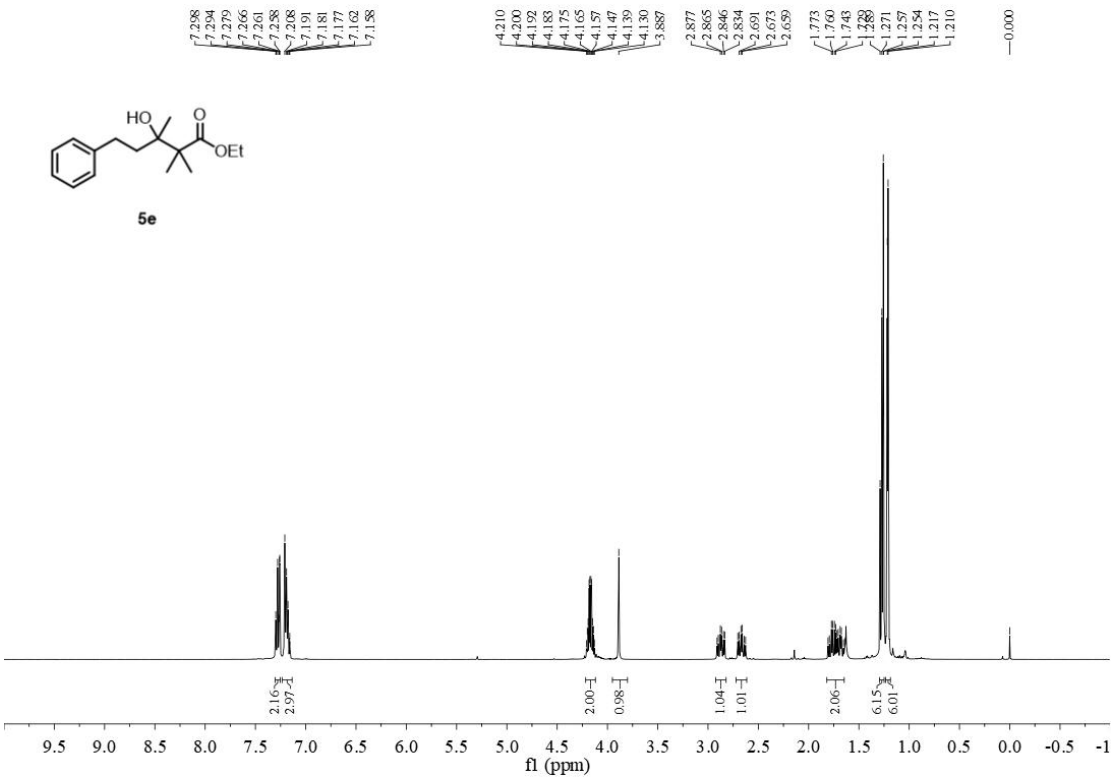
7.289
7.283
4.560
4.238
4.227
4.215
4.203
1.539
1.424
1.344
1.298
1.286
1.274
0.000
HO
O
OEt
5d
2.00
3.00
1.00
2.00
3.02
3.04
3.07
3.03
fl (ppm)


177.84
131.61
128.21
128.16
122.69
91.37
83.56
77.21
77.00
76.79
72.31
61.23
50.26
24.25
21.91
20.49
14.10
HO
O
OEt
5d
fl (ppm)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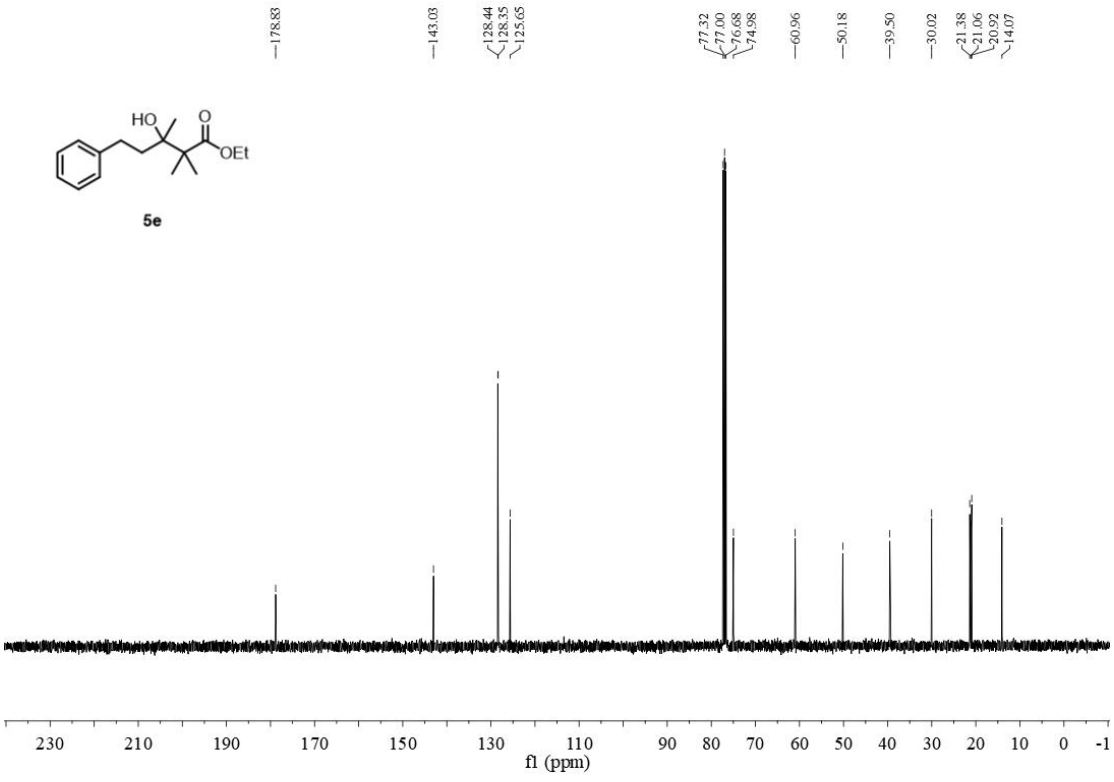
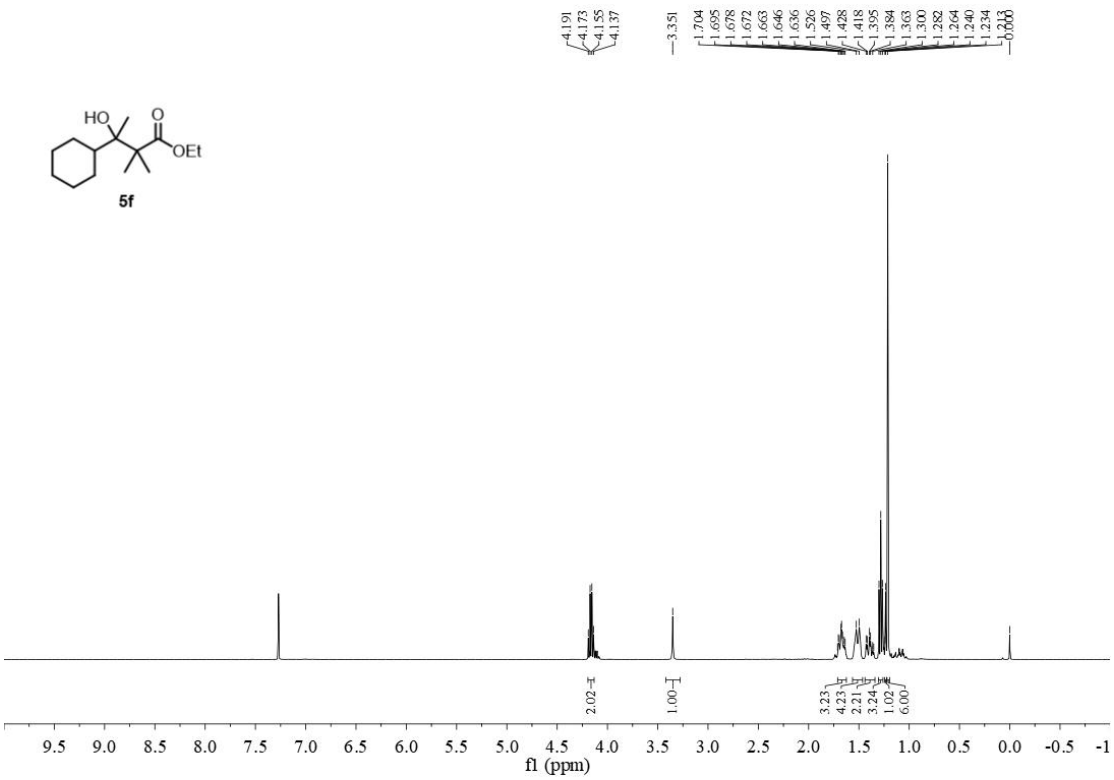
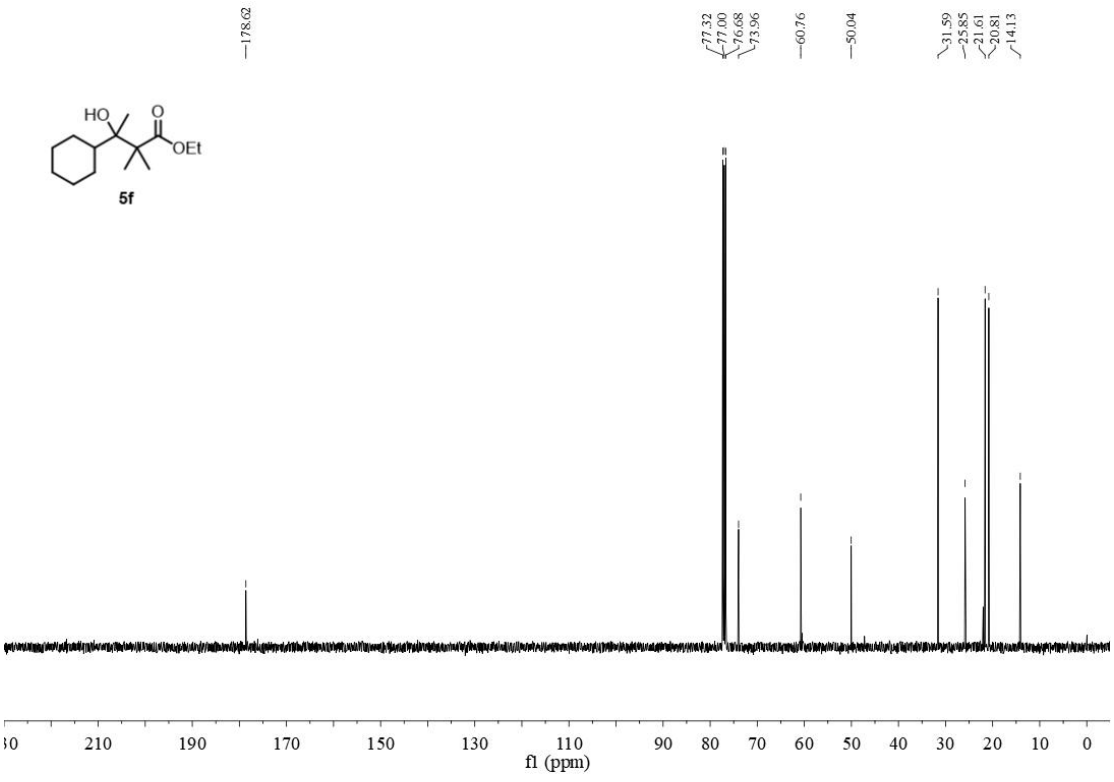
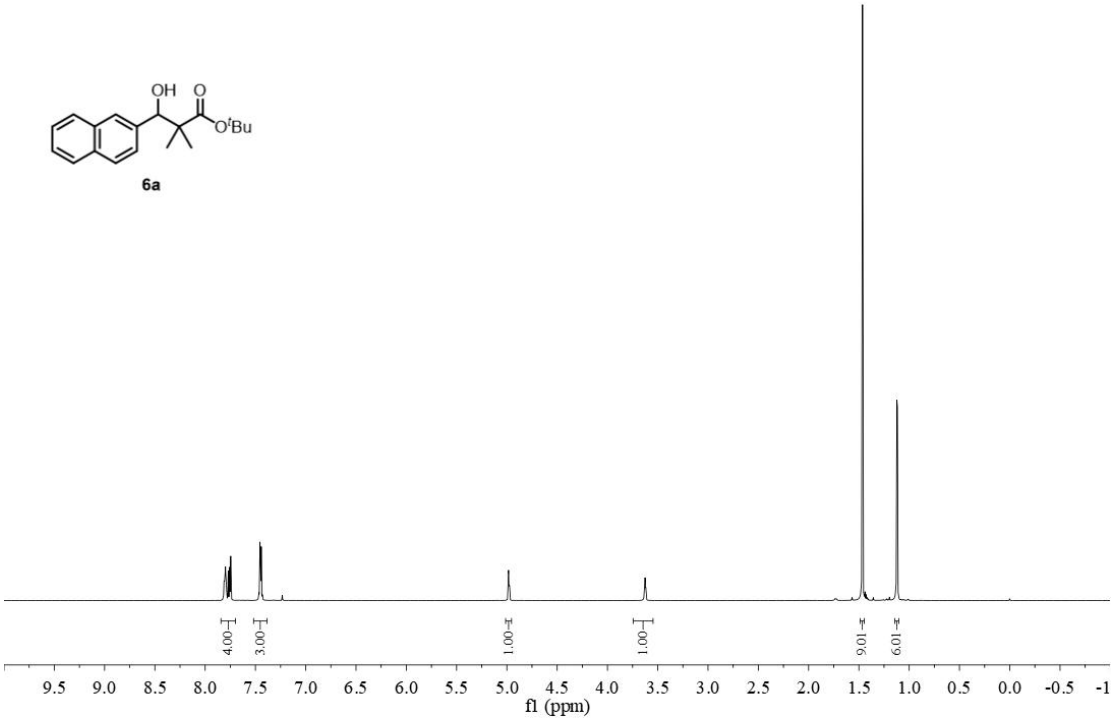
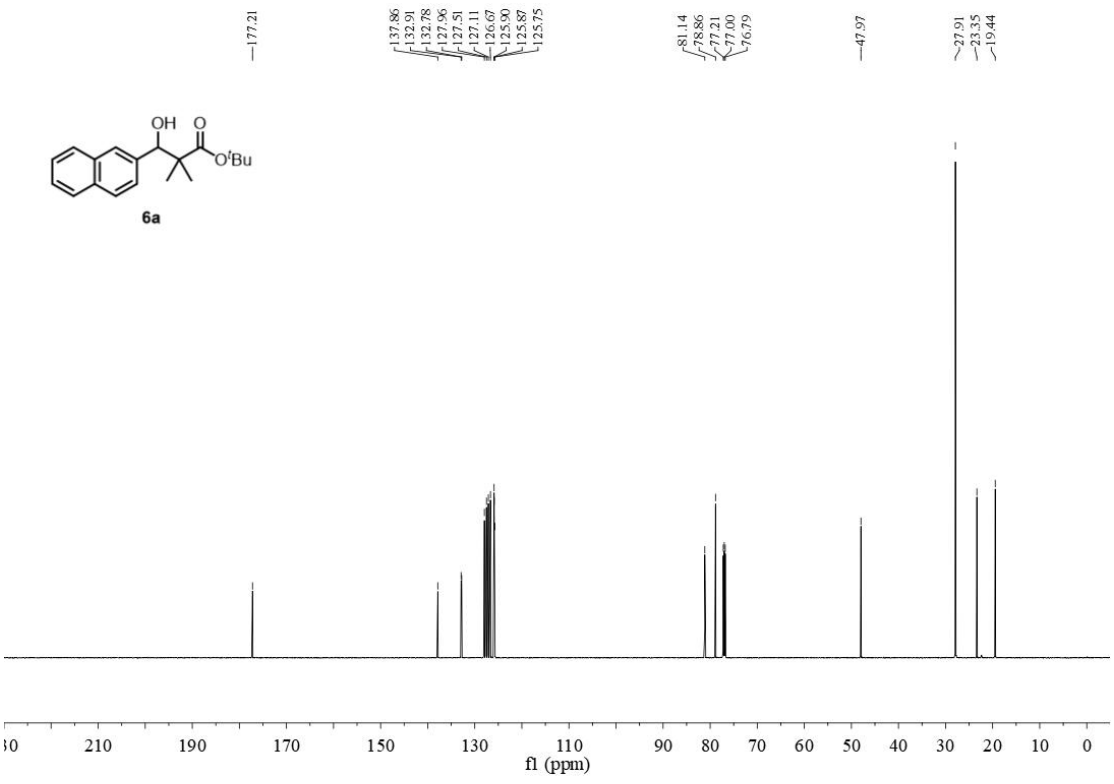
7.294
7.279
7.266
7.261
7.258
7.208
7.191
7.181
7.177
7.162
7.158
4.210
4.200
4.192
4.183
4.175
4.165
4.157
4.147
4.139
4.130
3.887
2.877
2.865
2.846
2.834
2.691
2.673
2.659
1.773
1.760
1.743
1.271
1.257
1.254
1.217
1.210
0.000
HO
O
OEt
5e
2.16
2.97
2.00
0.98
1.04
1.01
2.06
6.15
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


178.83
143.03
128.44
128.35
125.65
77.32
77.00
76.68
74.98
60.96
50.18
39.50
30.02
21.38
21.06
20.92
14.07
HO
O
OEt
5e
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


4.191
4.173
4.155
4.137
3.351
1.704
1.695
1.678
1.672
1.663
1.646
1.636
1.526
1.497
1.428
1.418
1.395
1.384
1.363
1.300
1.282
1.264
1.240
1.234
0.000
HO
O
OEt
5f
2.02
1.00
3.23
4.23
2.21
3.24
1.02
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


178.62
77.32
77.00
76.68
73.96
60.76
50.04
31.59
25.85
21.61
20.81
14.13
HO
O
OEt
5f
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
O
O'Bu
6a
4.00
3.00
1.00
1.00
9.01
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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132.91
132.78
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126.67
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125.87
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81.14
78.86
77.21
77.00
76.79
47.97
27.91
23.35
19.44
OH
O
O'Bu
6a
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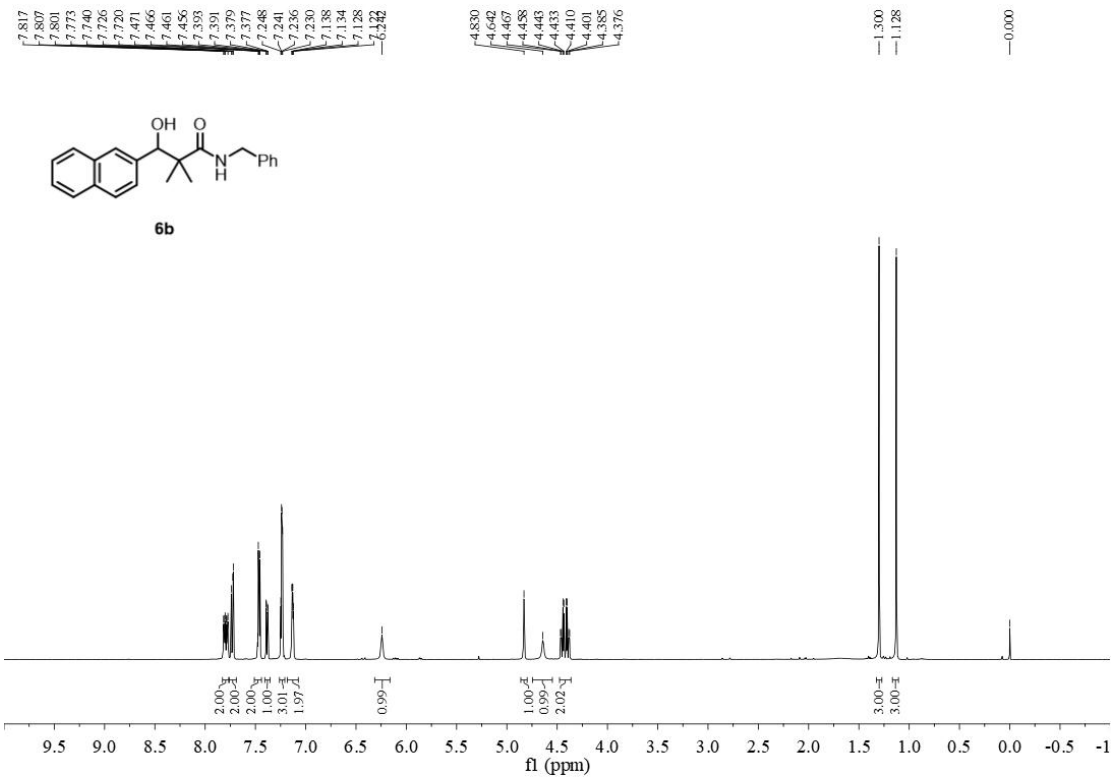
f1 (ppm)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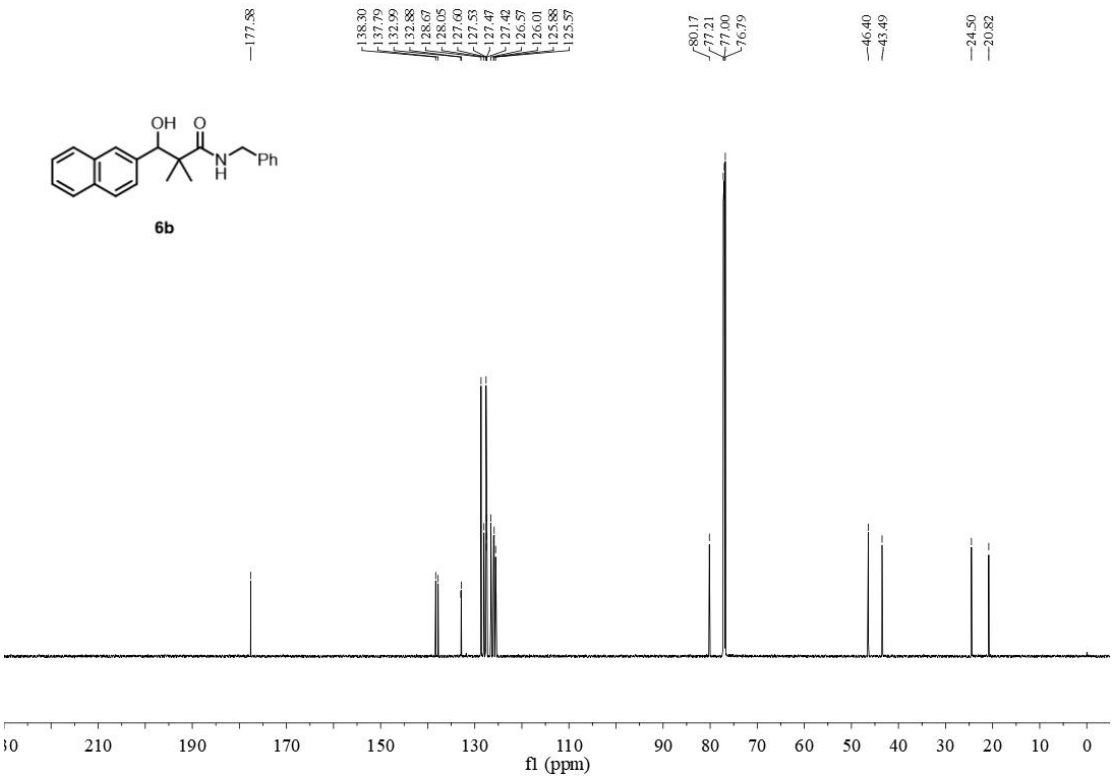
7.456
7.393
7.391
7.379
7.377
7.248
7.241
7.236
7.230
7.138
7.134
7.128
6.242
4.830
4.642
4.467
4.458
4.443
4.433
4.410
4.401
4.385
4.376
1.300
1.128
0.000
OH
O
N
H
Ph
6b
2.00
2.00
2.00
1.00
3.01
1.97
0.99
1.00
0.99
2.02
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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127.60
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127.47
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126.01
125.88
125.57
80.17
77.21
77.00
76.79
46.40
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20.82
OH
O
N
H
Ph
6b
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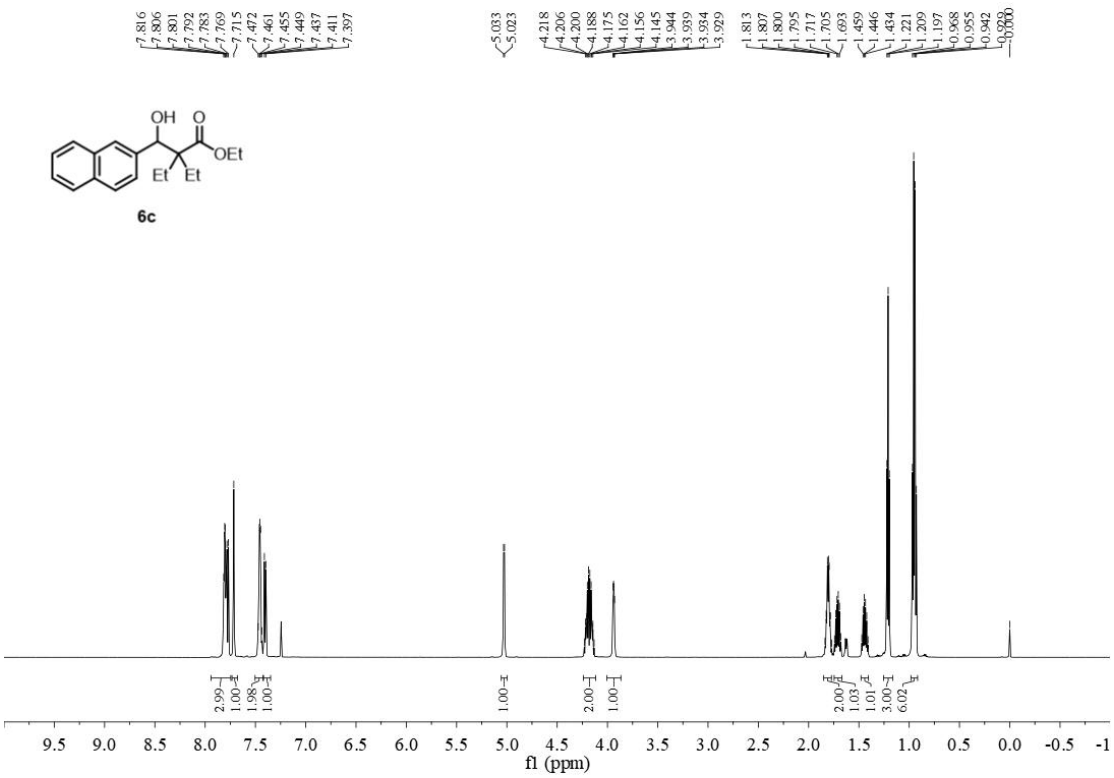
f1 (ppm)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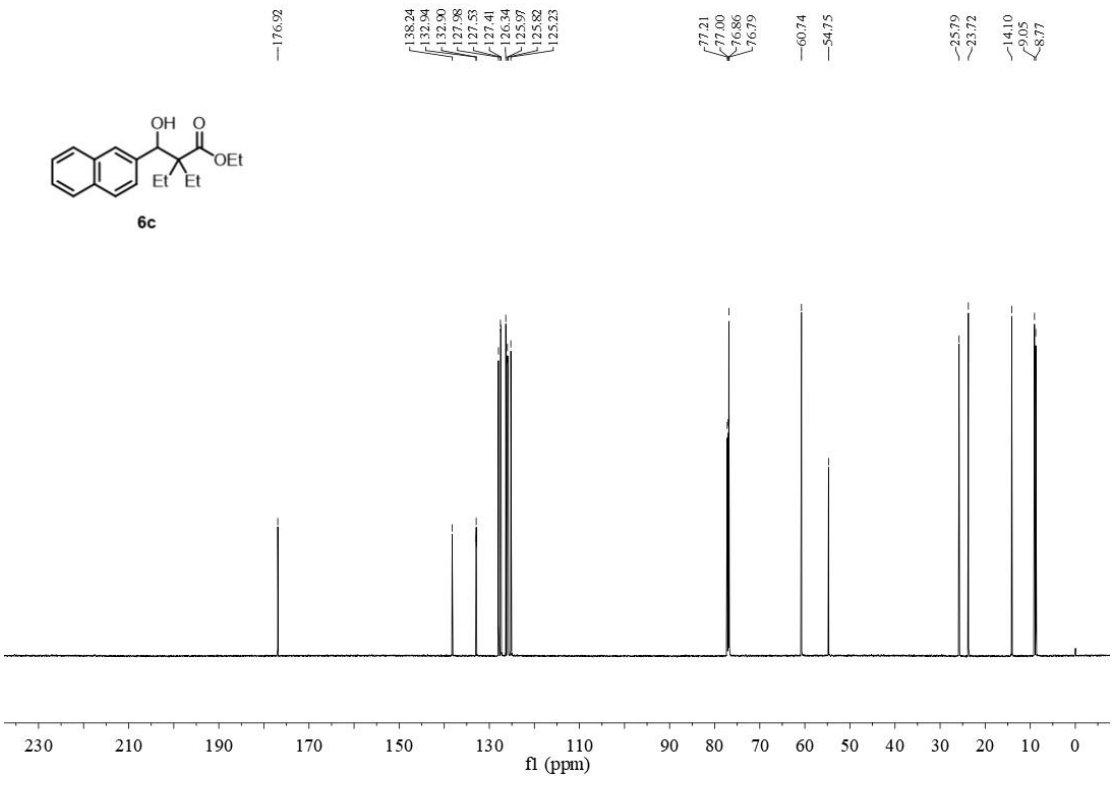
7.449
7.437
7.411
7.397
5.033
5.023
4.218
4.206
4.200
4.188
4.175
4.162
4.156
4.145
3.944
3.939
3.934
3.929
1.813
1.807
1.800
1.795
1.717
1.705
1.693
1.459
1.446
1.434
1.221
1.209
1.197
0.968
0.955
0.942
0.000
OH
O
OEt
Et
Et
6c
2.99
1.00
1.98
1.00
1.00
2.00
1.00
2.00
1.03
1.01
3.00
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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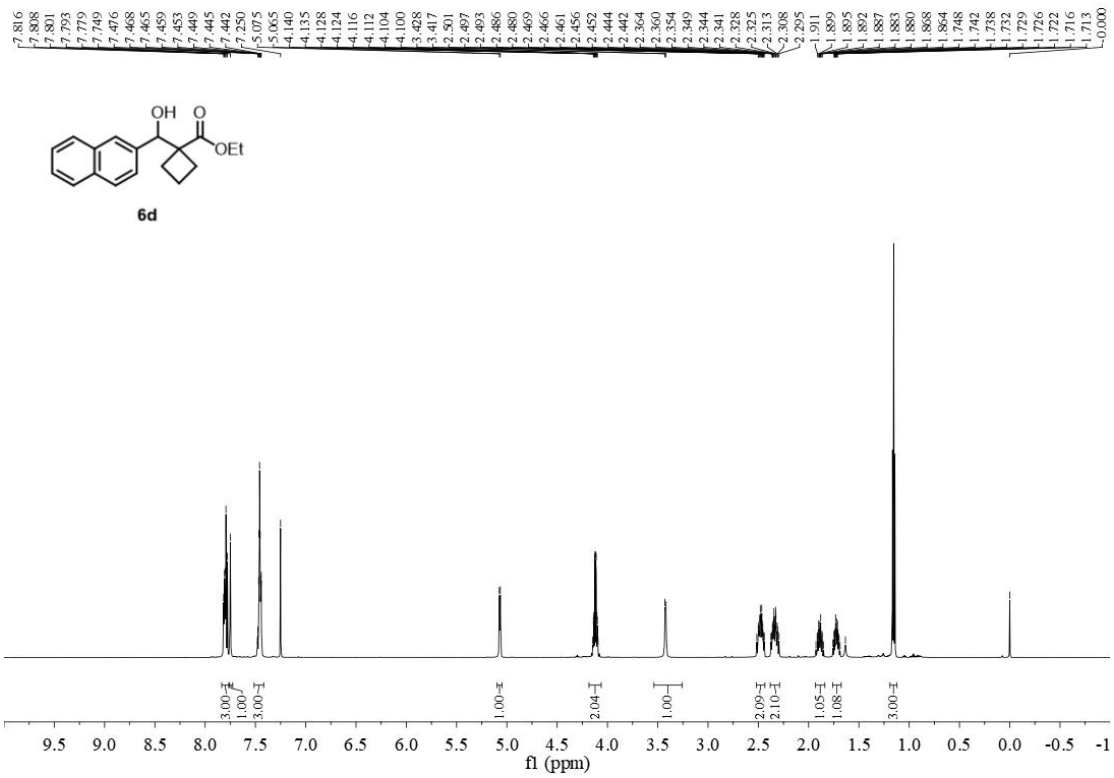
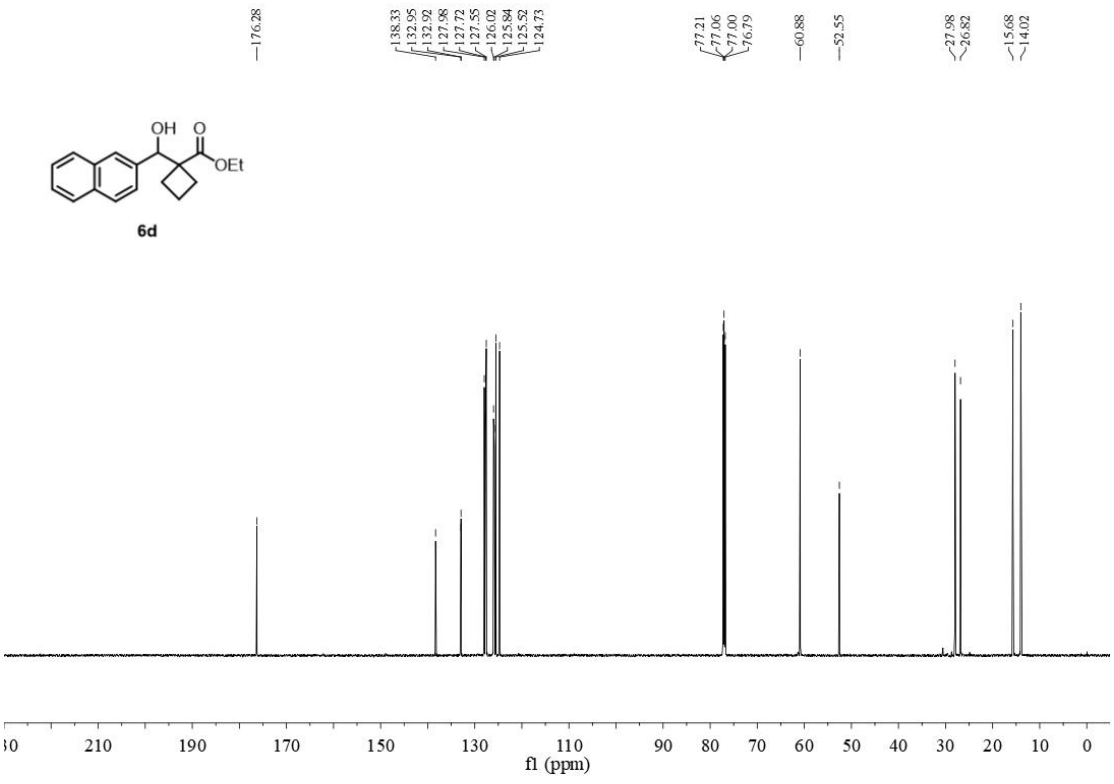
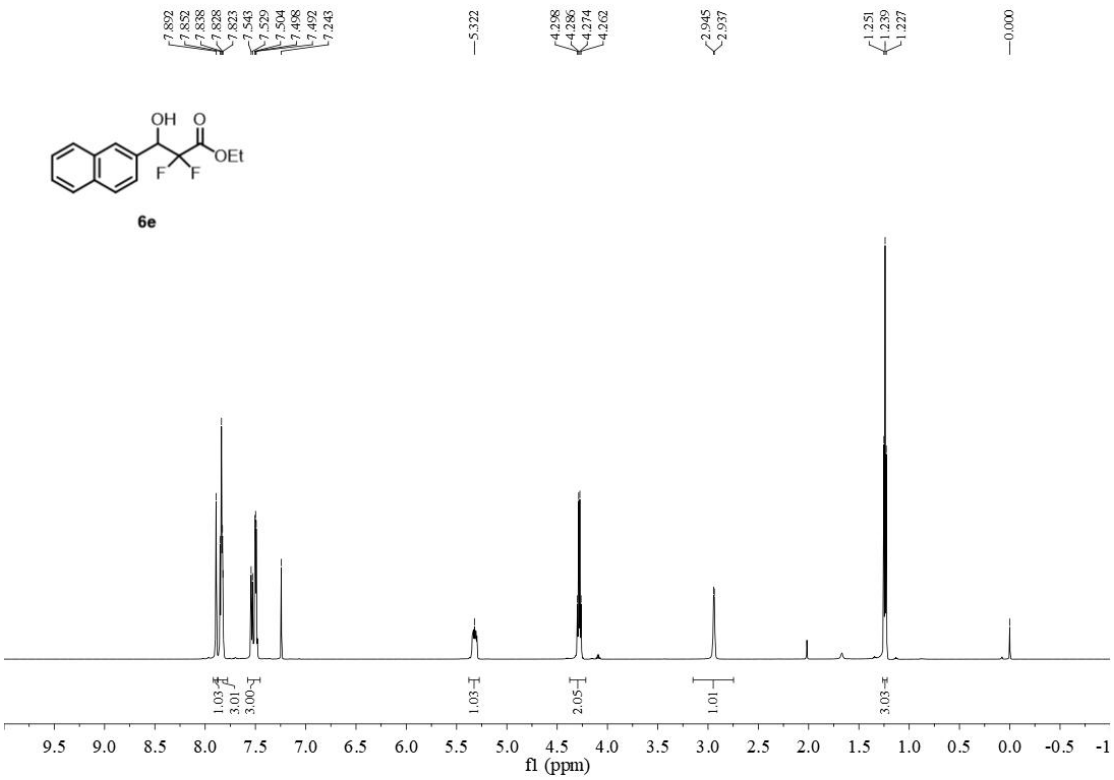
125.82
125.23
77.21
77.00
76.86
76.79
60.74
54.75
25.79
23.72
14.10
9.05
8.77
OH
O
OEt
Et
Et
6c
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
O
OEt
6d
fl (ppm)


OH
O
OEt
6d
fl (ppm)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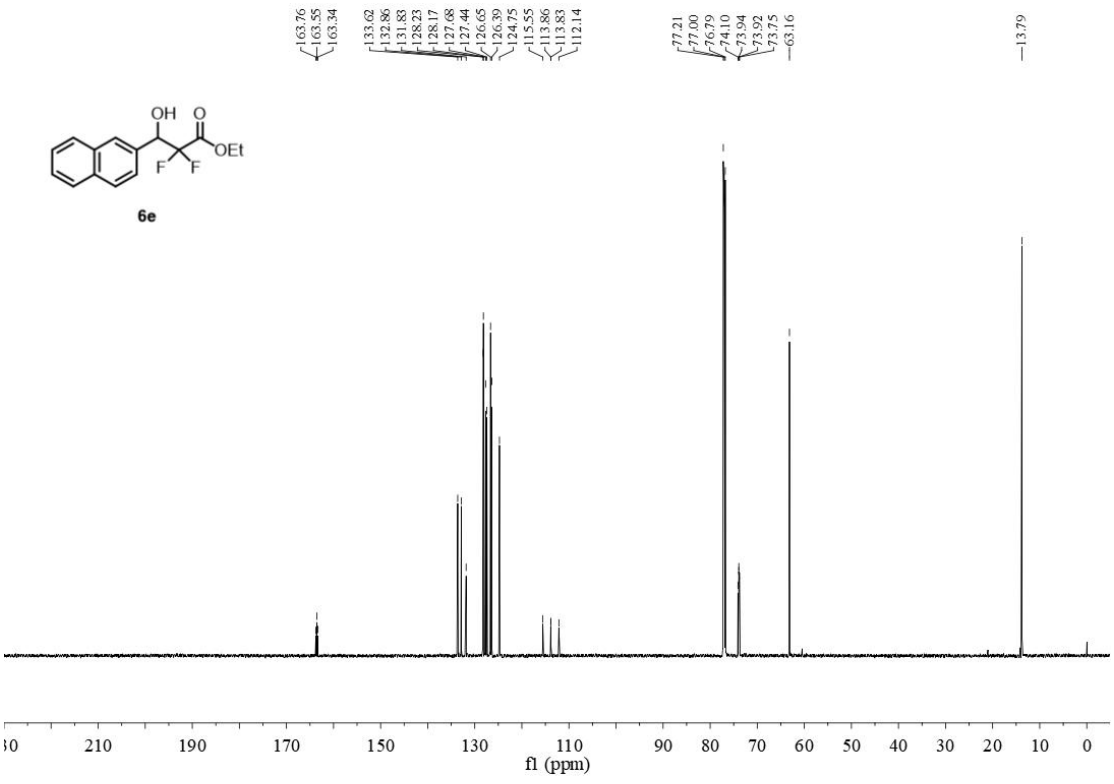
7.529
7.504
7.498
7.492
7.243
5.322
4.298
4.286
4.274
4.262
2.945
2.937
1.251
1.239
1.227
0.000
OH
O
OEt
F
F
6e
1.03
3.01
3.00
1.03
2.05
1.01
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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163.34
133.62
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131.83
128.23
128.17
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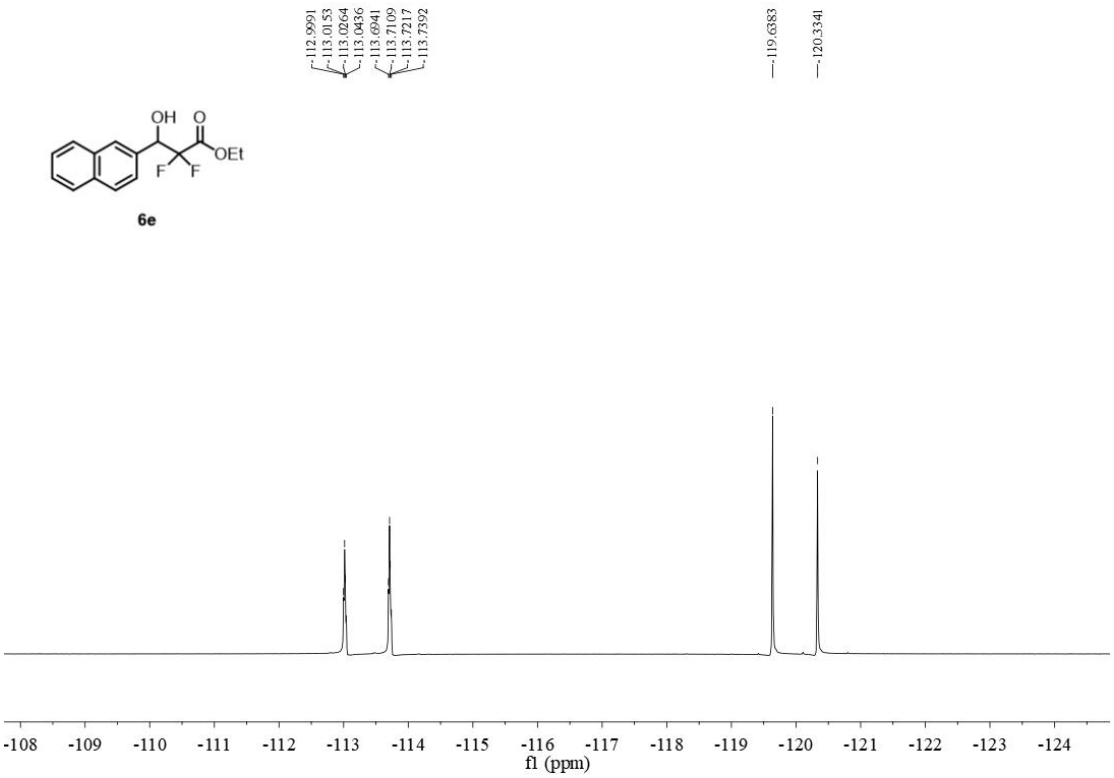
127.44
126.65
126.39
124.75
115.55
113.86
113.83
112.14
77.21
77.00
76.79
74.10
73.94
73.92
73.75
63.16
13.79
OH
O
OEt
F
F
6e
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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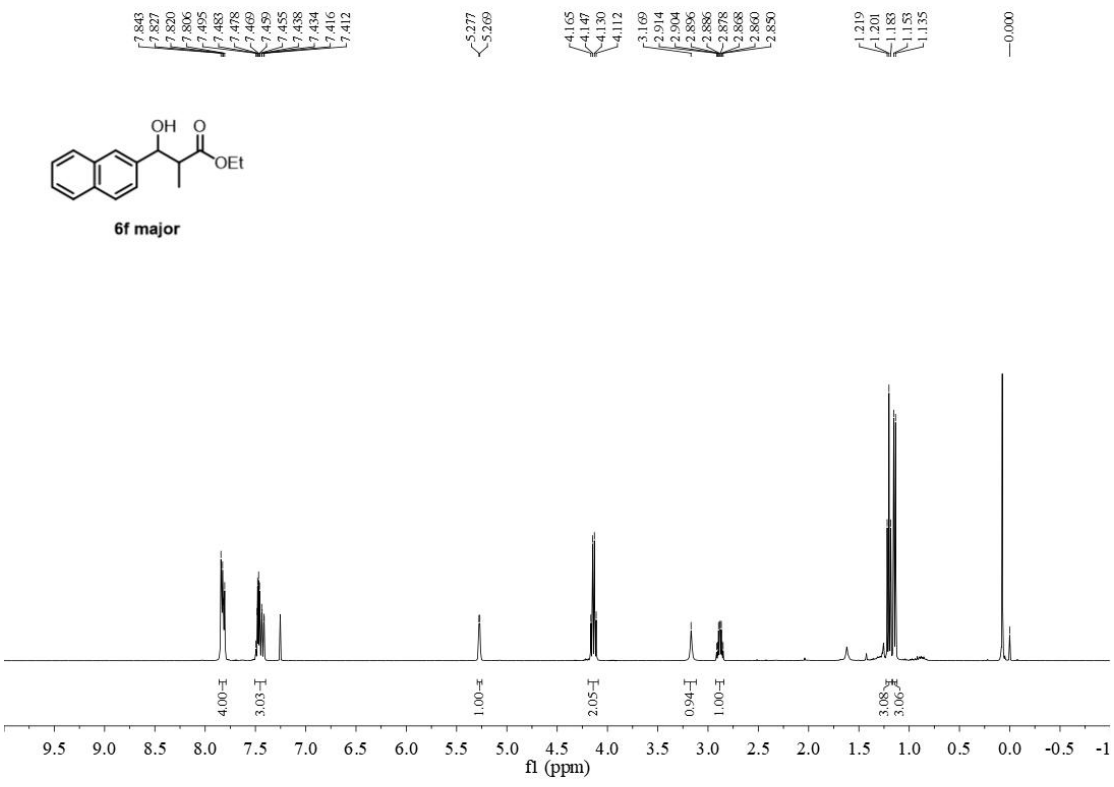
113.0264
113.0436
113.6941
113.7109
113.7217
113.7392
119.6383
120.3341
OH
O
OEt
F
F
6e
-108
-109
-110
-111
-112
-113
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
f1 (ppm)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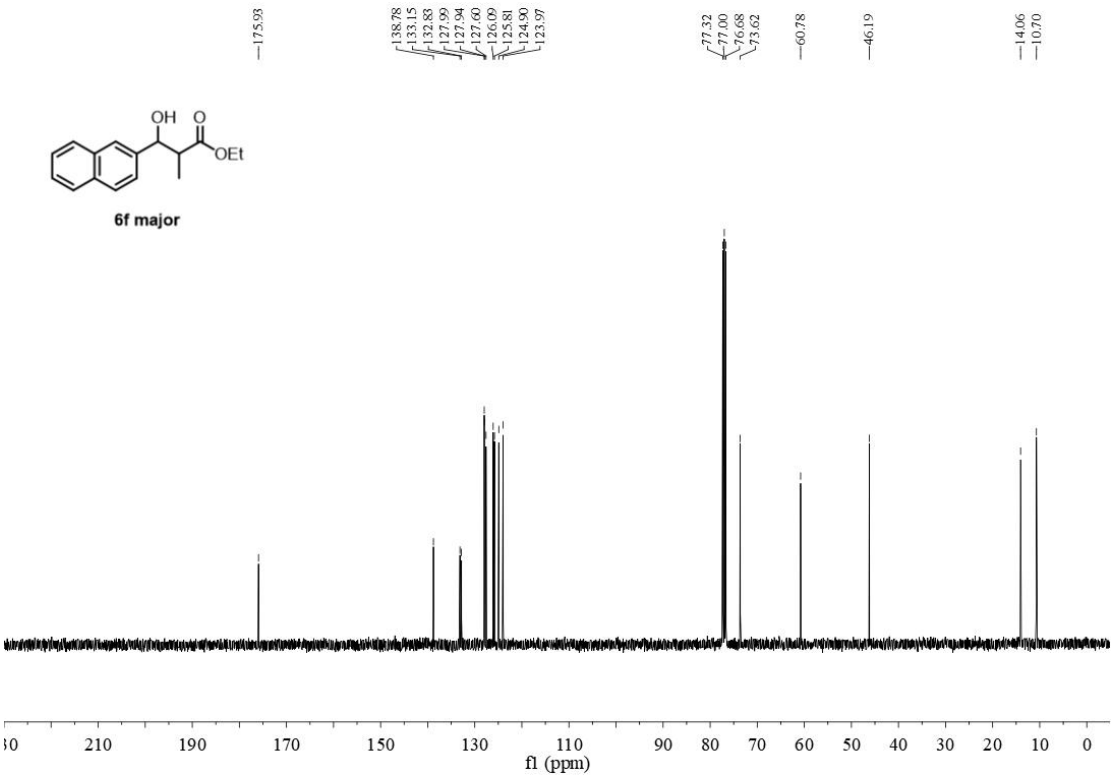
7.483
7.478
7.469
7.459
7.455
7.438
7.434
7.416
7.412
5.277
5.269
4.165
4.147
4.130
4.112
3.169
2.914
2.904
2.896
2.886
2.878
2.868
2.860
2.850
1.219
1.201
1.183
1.153
1.135
0.000
OH
O
OEt
6f major
4.00
3.03
1.00
2.05
0.94
1.00
3.08
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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127.94
127.60
126.09
125.81
124.90
123.97
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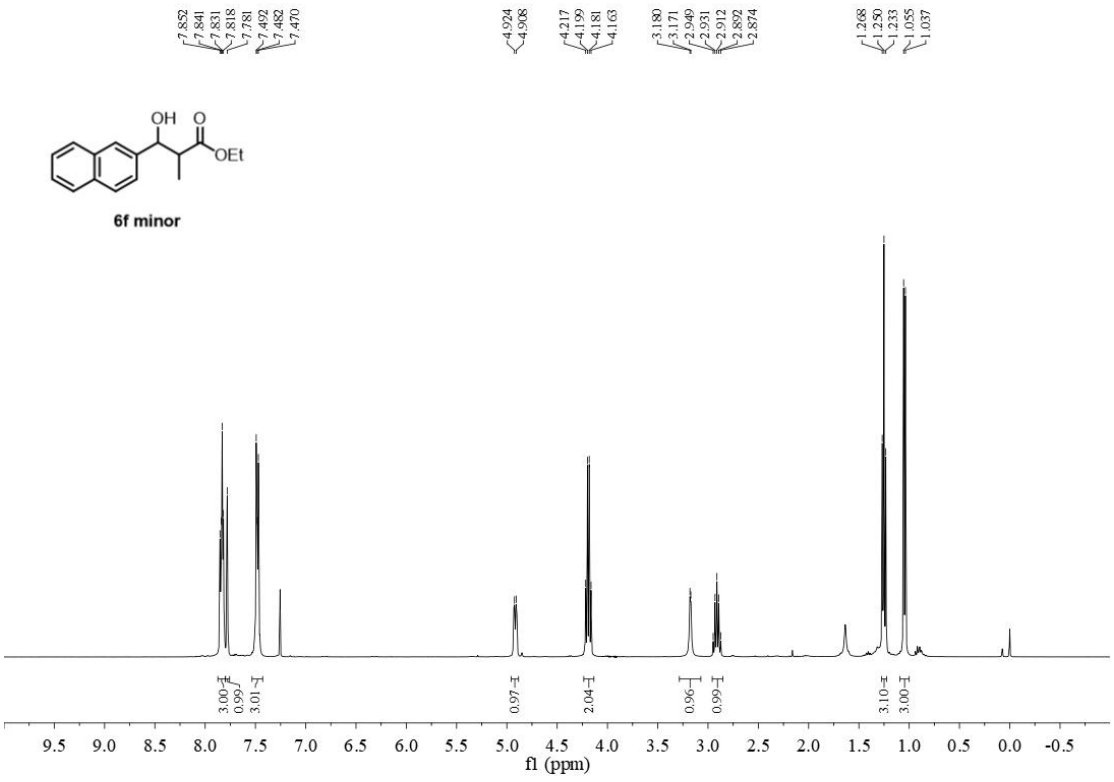
77.00
76.68
73.62
60.78
46.19
14.06
10.70
OH
O
OEt
6f major
f1 (ppm)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7.470
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4.908
4.217
4.199
4.181
4.163
3.180
3.171
2.949
2.931
2.912
2.892
2.874
1.268
1.250
1.233
1.055
1.037
OH
O
OEt
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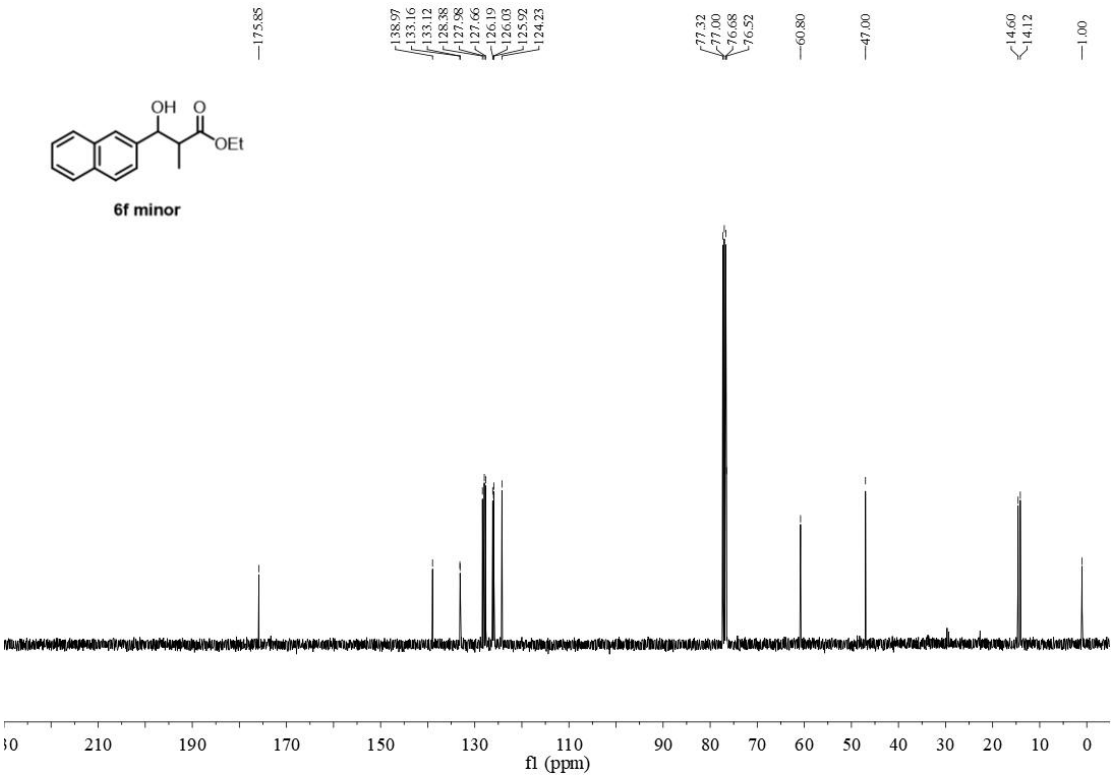
0.99
3.01
0.97
2.04
0.96
0.99
3.10
3.00
f1 (ppm)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127.98
127.66
126.19
126.03
125.92
124.23
77.32
77.00
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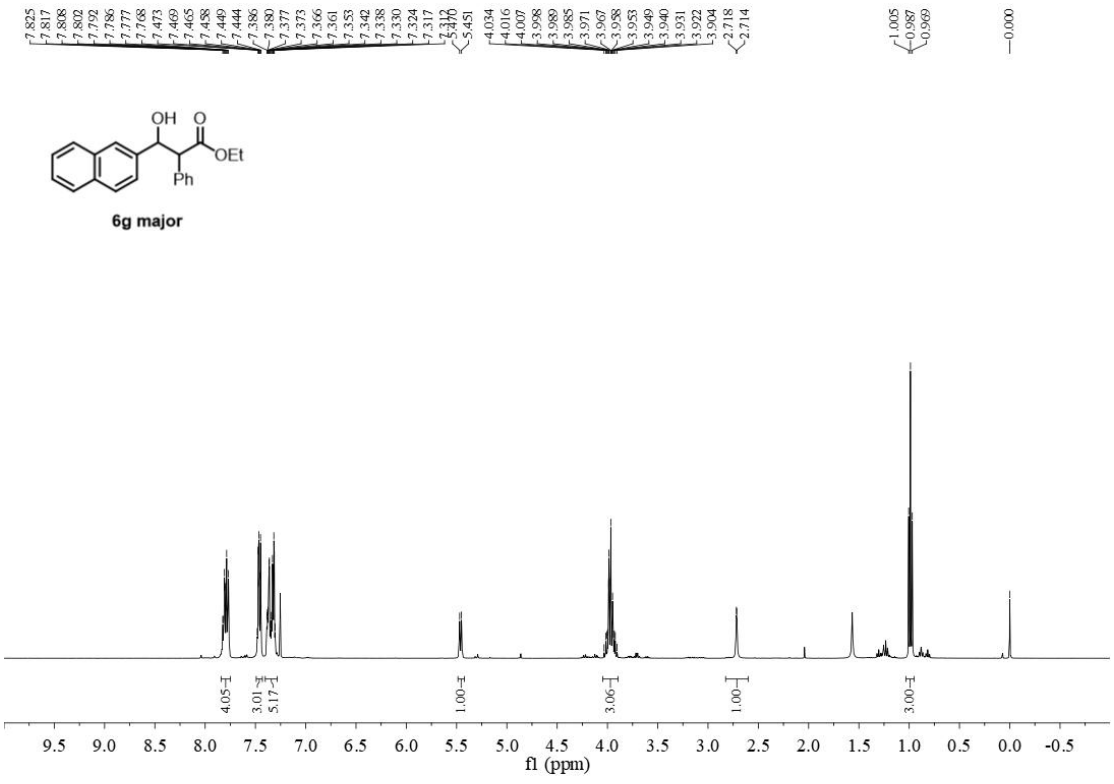
76.52
60.80
47.00
14.60
14.12
1.00
OH
O
OEt
6f minor
fl (ppm)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7.444
7.386
7.380
7.377
7.373
7.366
7.361
7.353
7.342
7.338
7.330
7.324
7.317
5.470
5.451
4.034
4.016
4.007
3.998
3.989
3.985
3.971
3.967
3.958
3.953
3.949
3.940
3.931
3.922
3.904
2.718
2.714
1.005
0.987
0.969
0.000
OH
O
OEt
Ph
6g major
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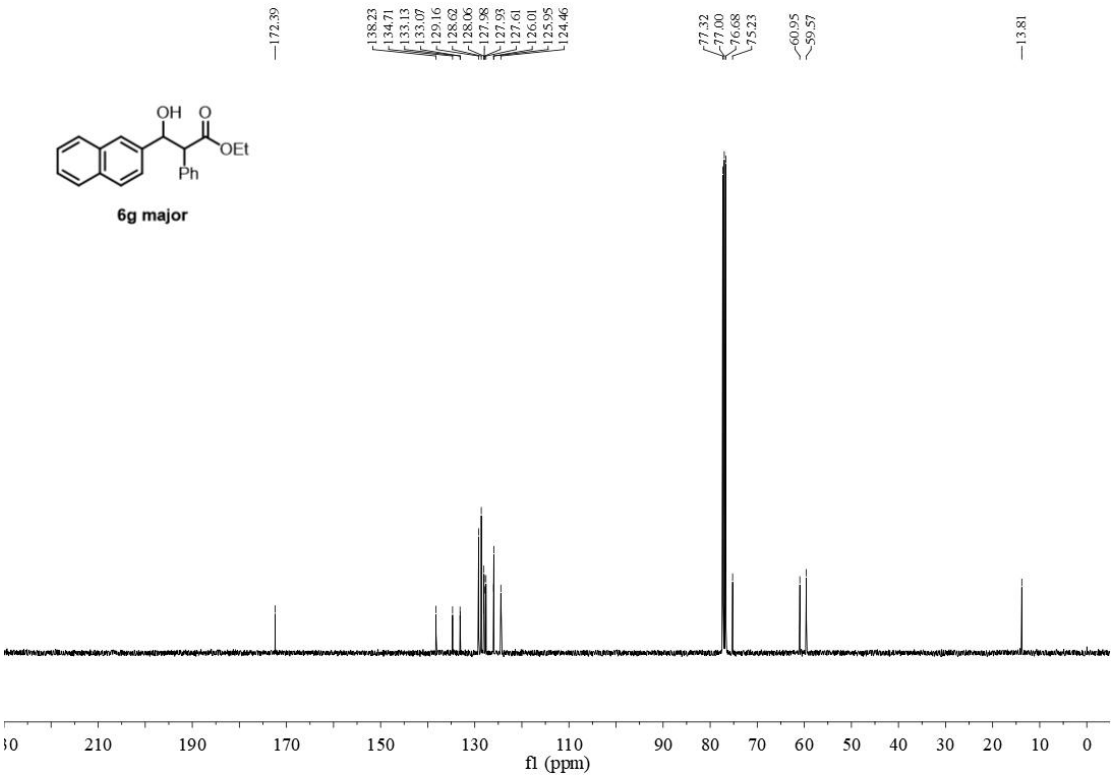
3.01
5.17
1.00
3.06
1.00
3.00
fl (ppm)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127.93
127.61
126.01
125.95
124.46
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75.23
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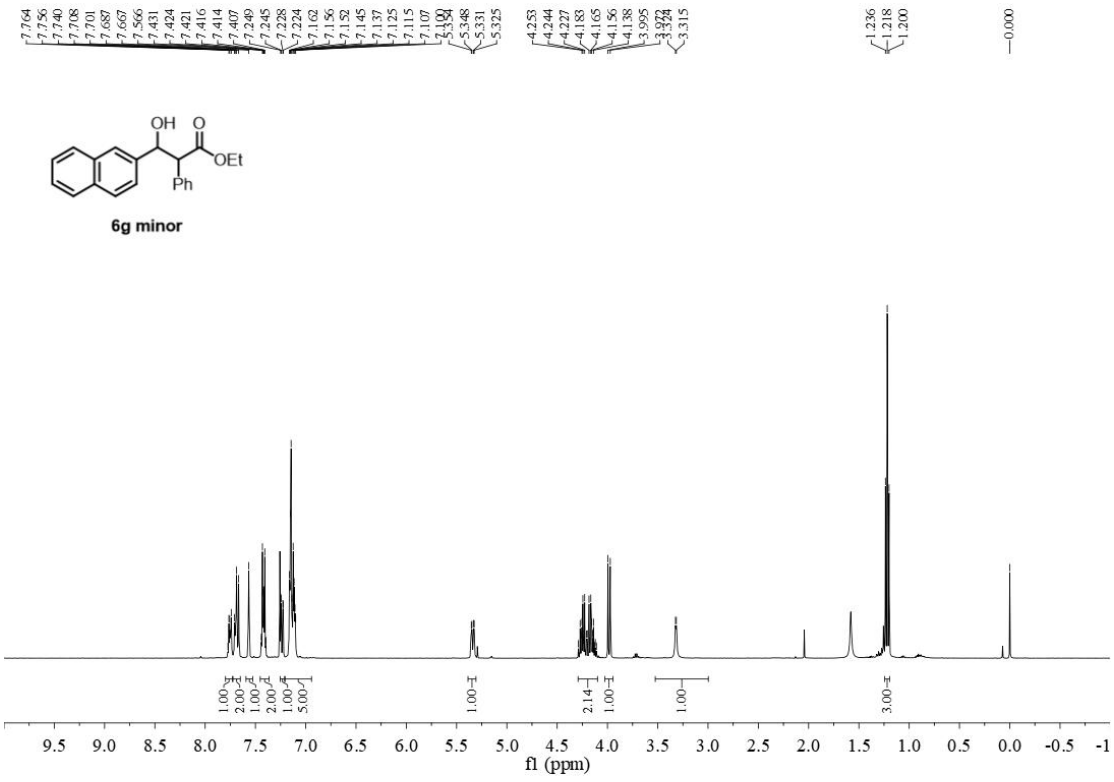
13.81
OH
O
OEt
Ph
6g major
f1 (ppm)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7.414
7.407
7.249
7.245
7.228
7.224
7.162
7.156
7.152
7.145
7.137
7.125
7.115
7.107
5.348
5.331
5.325
4.253
4.244
4.227
4.183
4.165
4.156
4.138
3.995
3.972
3.324
3.315
1.236
1.218
1.200
0.000
OH
O
OEt
Ph
6g minor
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2.00
1.00
5.00
1.00
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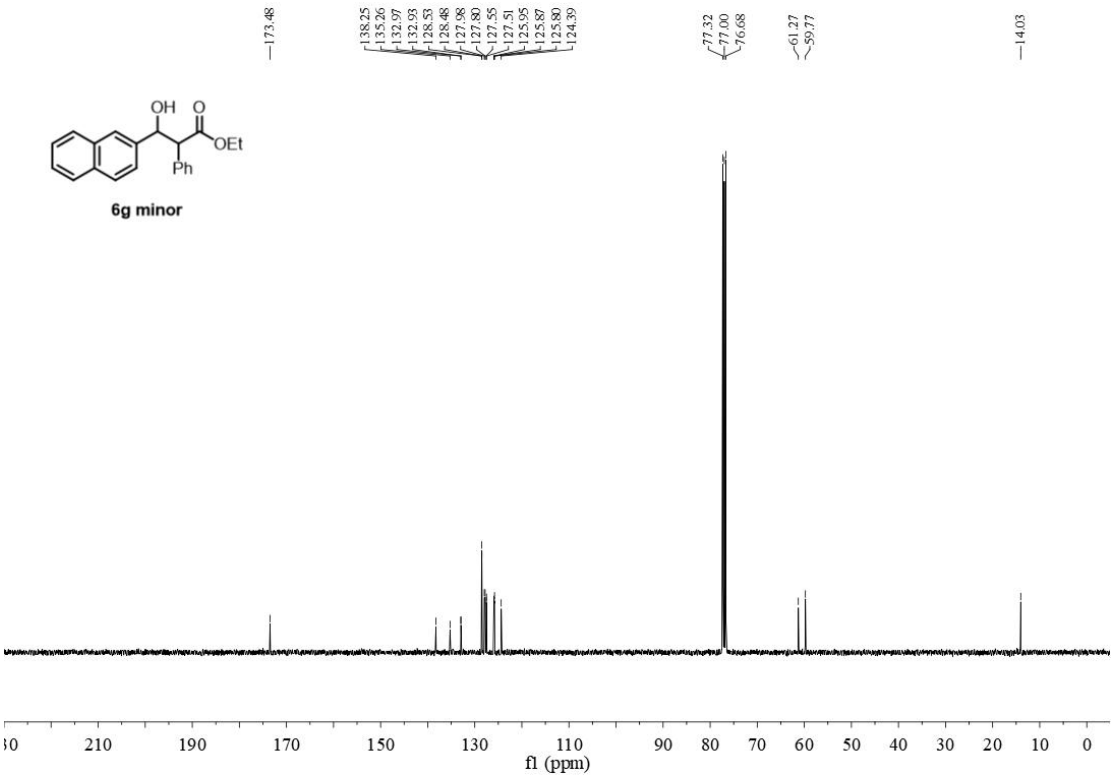
1.00
1.00
3.00
f1 (ppm)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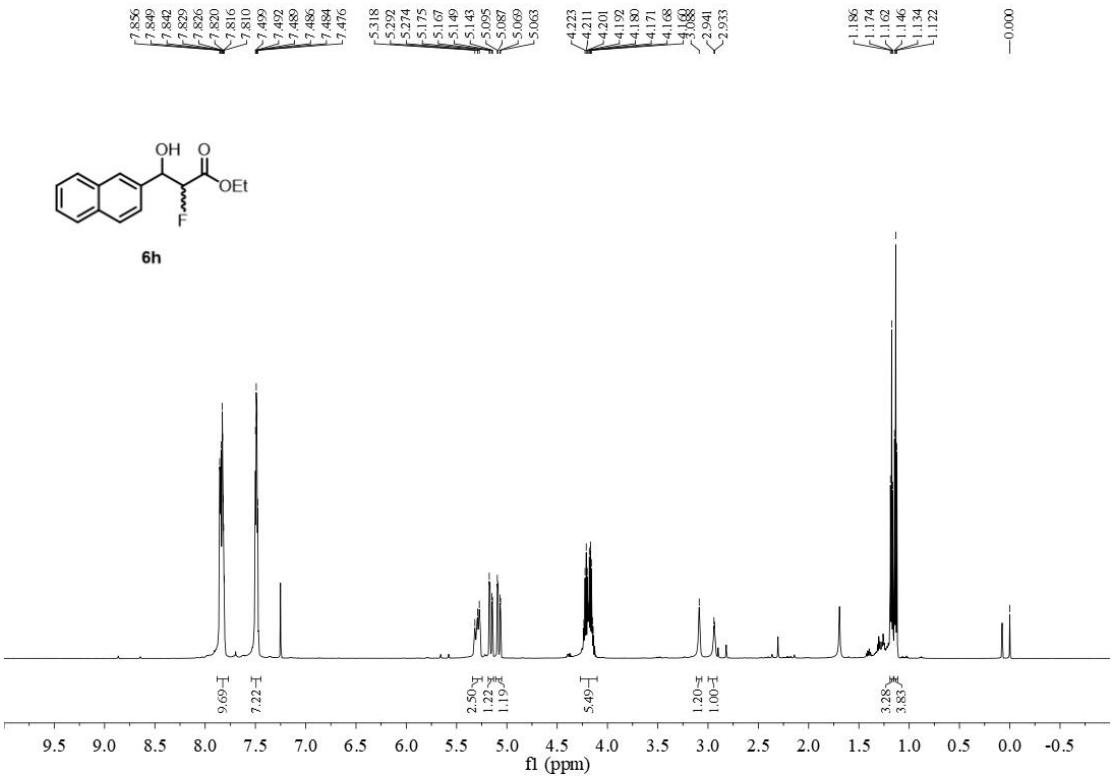
127.51
125.95
125.87
125.80
124.39
77.32
77.00
76.68
61.27
59.77
14.03
OH
O
OEt
Ph
6g minor
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.484
7.476
5.318
5.292
5.274
5.175
5.167
5.149
5.143
5.095
5.087
5.069
5.063
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4.211
4.201
4.192
4.180
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4.168
3.088
2.941
2.933
1.186
1.174
1.162
1.146
1.134
1.122
0.000
OH
O
OEt
F
6h
9.69
7.22
2.50
1.22
1.19
5.49
1.20
1.00
3.28
3.83
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
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1.5
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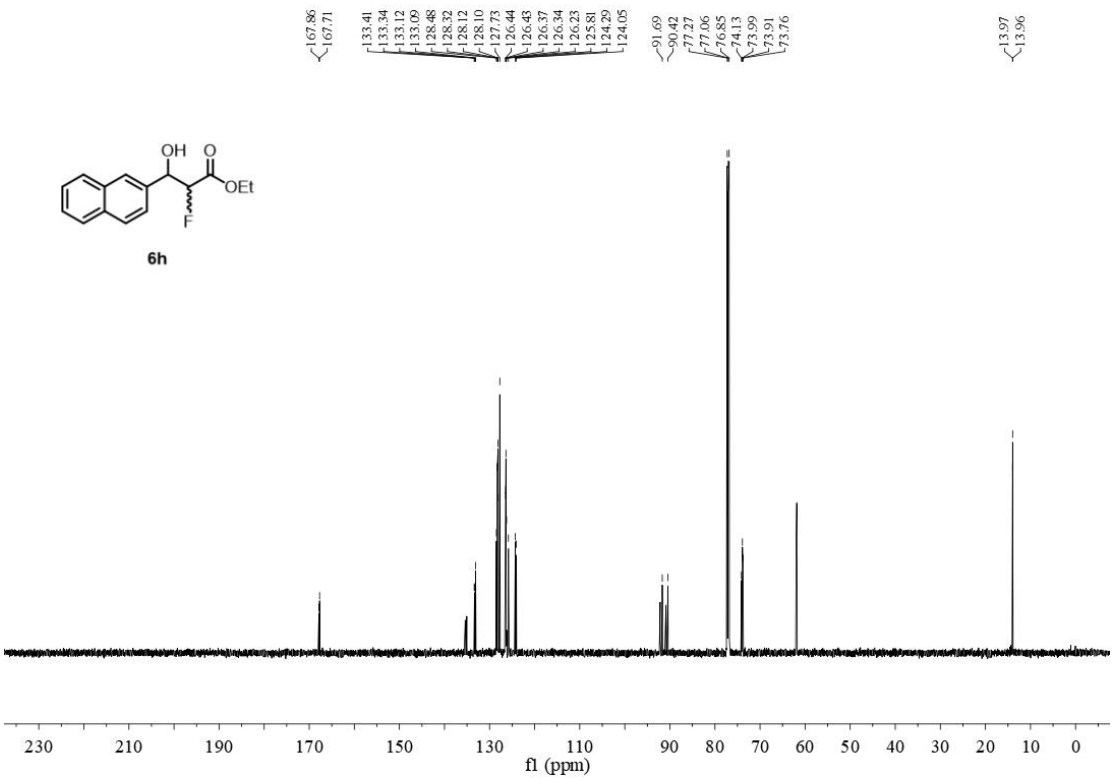
-0.5
f1 (ppm)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128.10
127.73
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126.43
126.37
126.34
126.23
125.81
124.29
124.05
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90.42
77.27
77.06
76.85
74.13
73.99
73.91
73.76
13.97
13.96
OH
O
OEt
F
6h
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170
150
130
110
90
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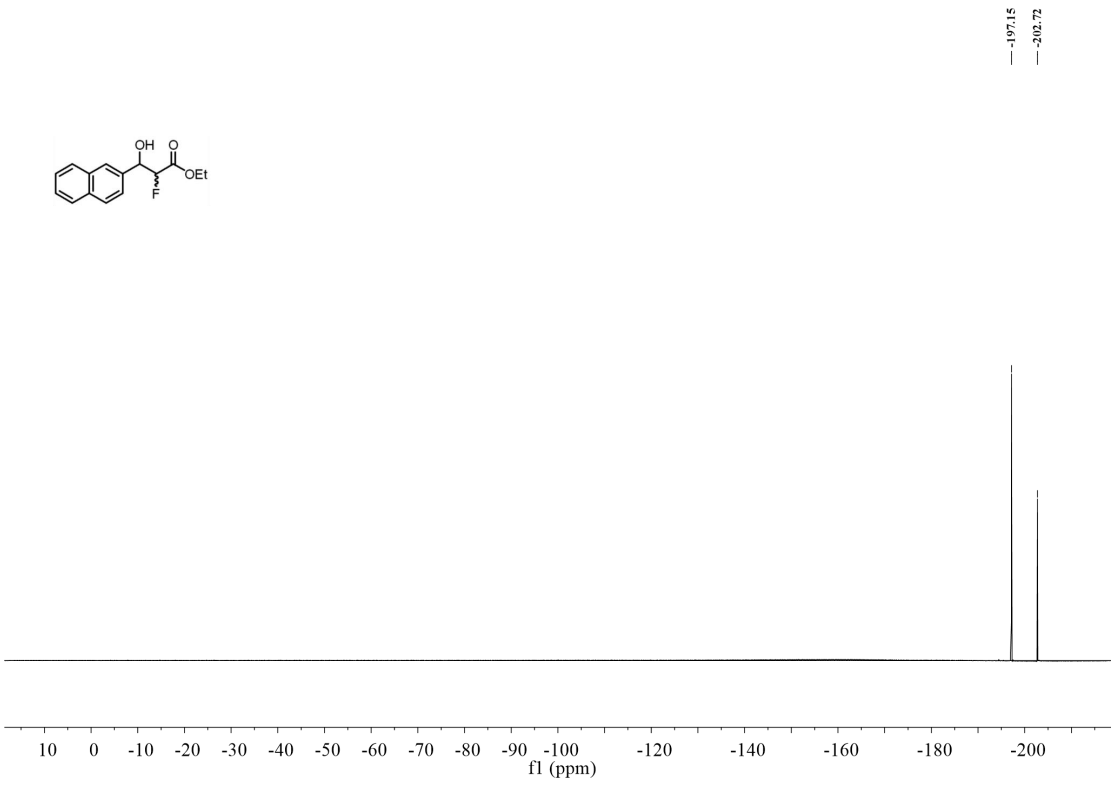
70
60
50
40
30
20
10
0
f1 (ppm)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OH
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OEt
F
10
0
-10
-20
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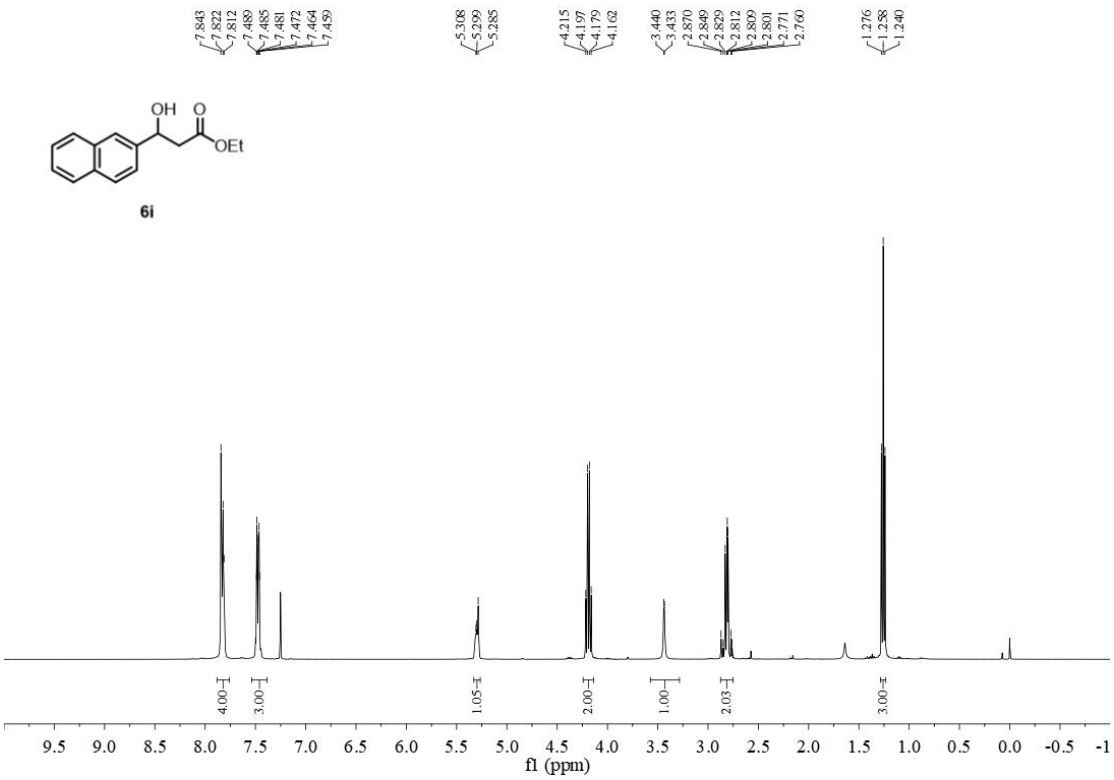
-120
-140
-160
-180
-200
f1 (ppm)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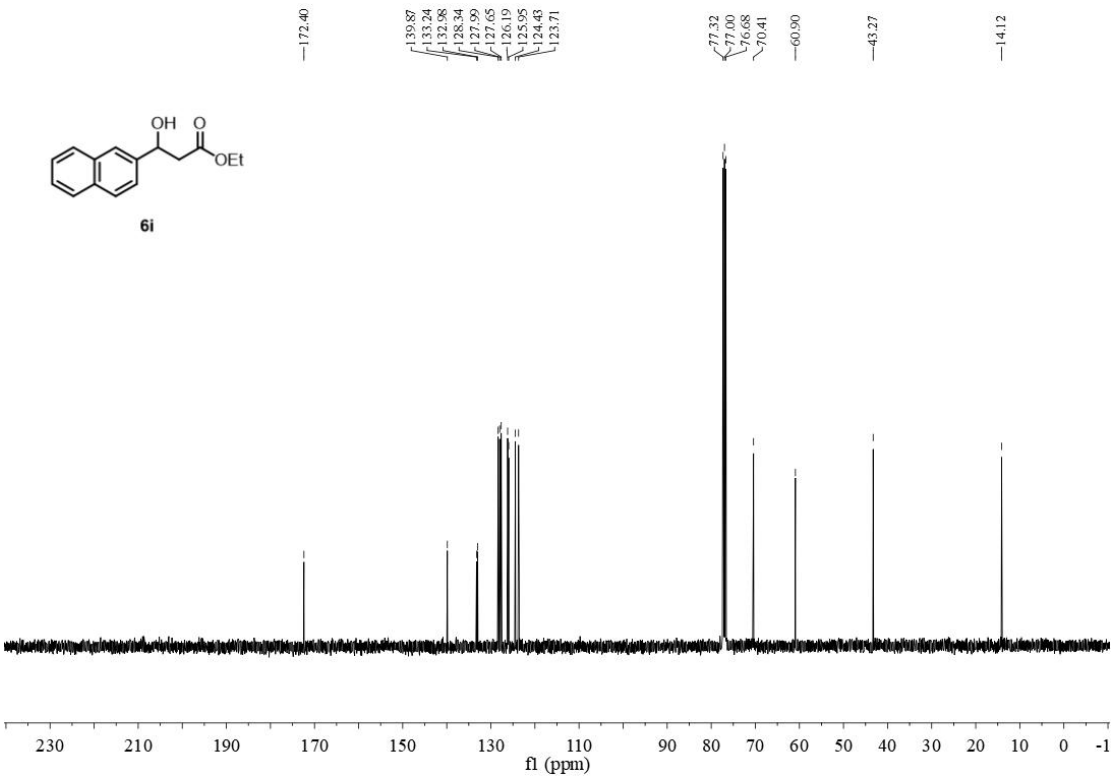
4.215
4.197
4.179
4.162
3.440
3.433
2.870
2.849
2.829
2.812
2.809
2.801
2.771
2.760
1.276
1.258
1.240
OH
O
OEt
6i
4.00
3.00
1.05
2.00
1.00
2.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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123.71
77.32
77.00
76.68
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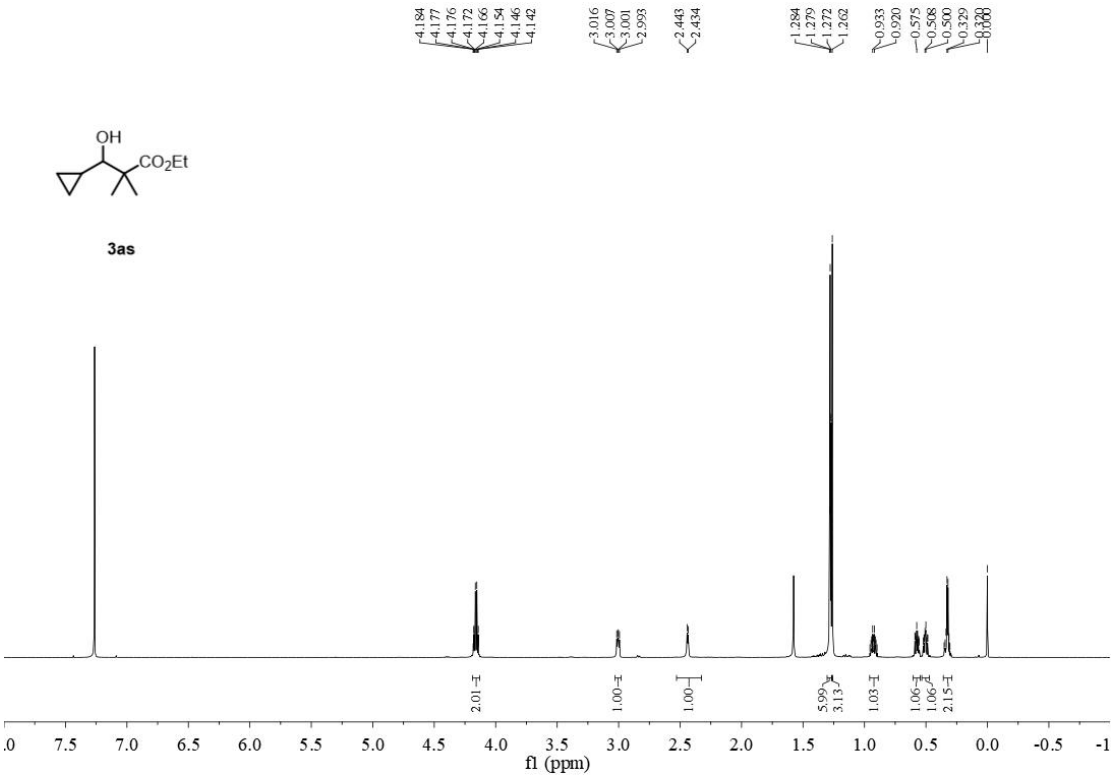
60.90
43.27
14.12
OH
O
OEt
6i
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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3.007
3.001
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2.443
2.434
1.284
1.279
1.272
1.262
0.933
0.920
0.575
0.508
0.500
0.329
0.320
0.000
OH
CO2Et
3as
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1.00
1.00
5.99
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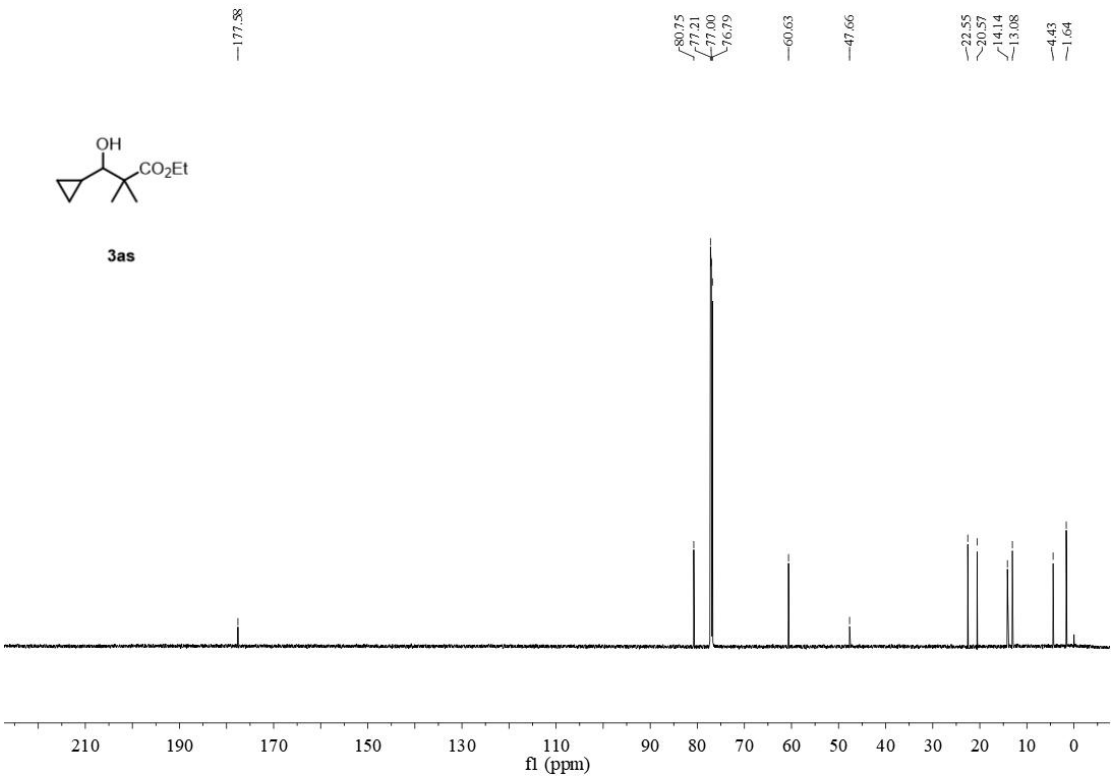
1.06
1.06
2.15
f1 (ppm)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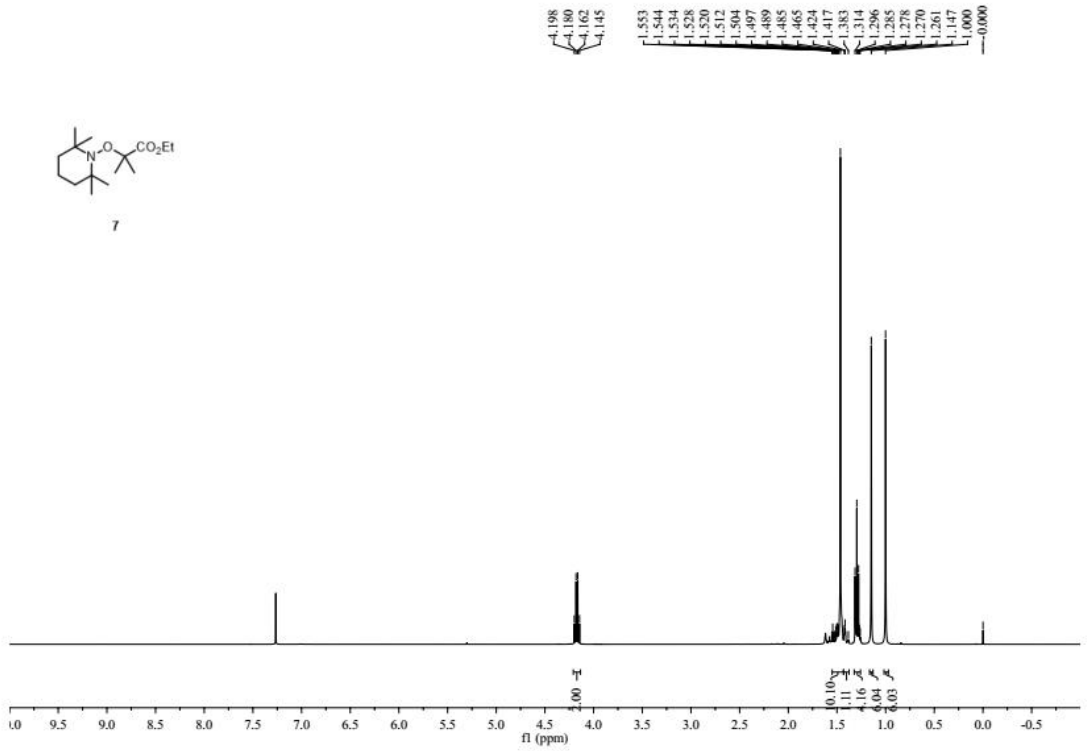
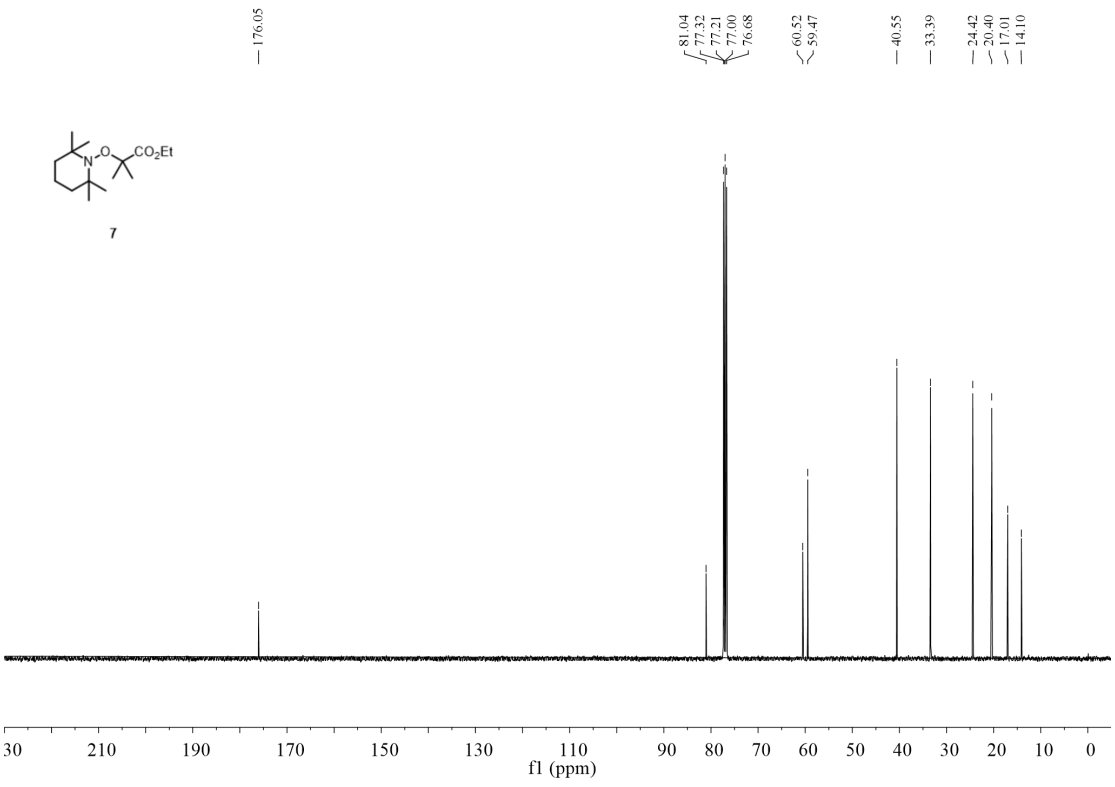
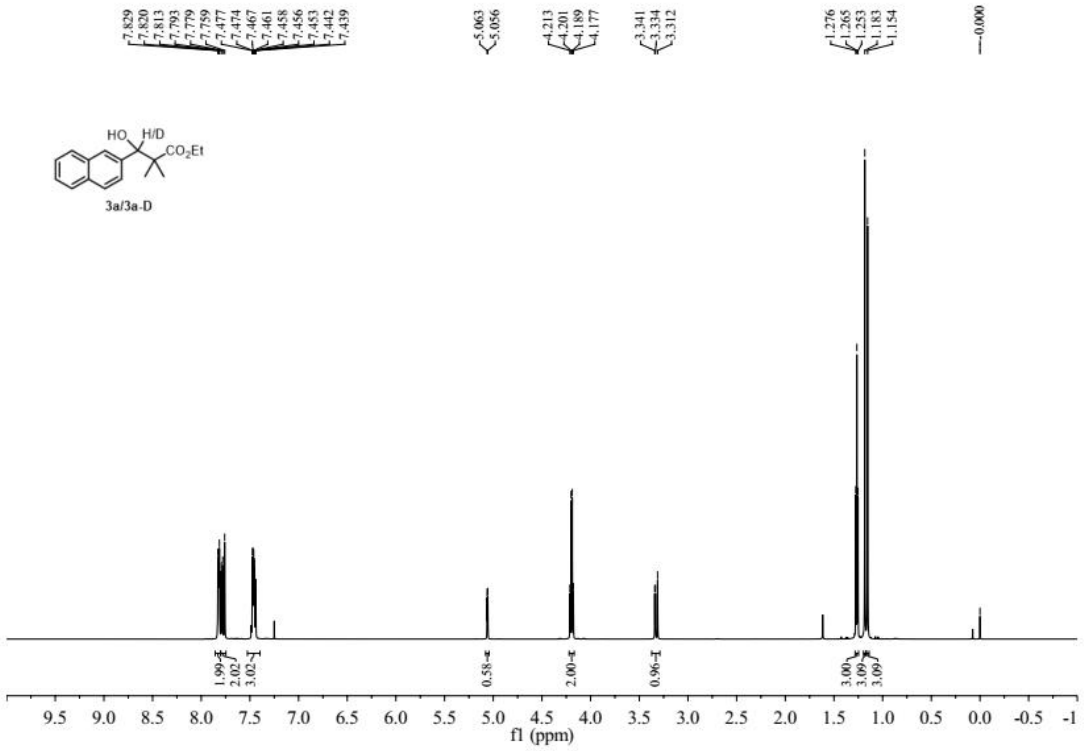
47.66
22.55
20.57
14.14
13.08
4.43
1.64
OH
CO2Et
3as
f1 (ppm)


4.198
4.180
4.162
4.145
1.553
1.544
1.534
1.528
1.520
1.512
1.504
1.497
1.489
1.485
1.465
1.424
1.417
1.383
1.314
1.296
1.285
1.278
1.270
1.261
1.147
1.000
0.000
CO2Et
7
1.00
10.10
1.11
4.16
6.04
6.03
f1 (ppm)


176.05
81.04
77.32
77.21
77.00
76.68
60.52
59.47
40.55
33.39
24.42
20.40
17.01
14.10
CO2Et
7
f1 (ppm)


7.829
7.820
7.813
7.793
7.779
7.759
7.477
7.474
7.467
7.461
7.458
7.456
7.453
7.442
7.439
5.063
5.056
4.213
4.201
4.189
4.177
3.341
3.334
3.312
1.276
1.265
1.253
1.183
1.154
0.000
HO
H/D
CO2Et
3a/3a-D
1.99
2.02
3.02
0.58
2.00
0.96
3.00
3.09
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)