Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Three-Component Carboacylation of Alkenes *via* Cooperative Nickelaphotoredox Catalysis

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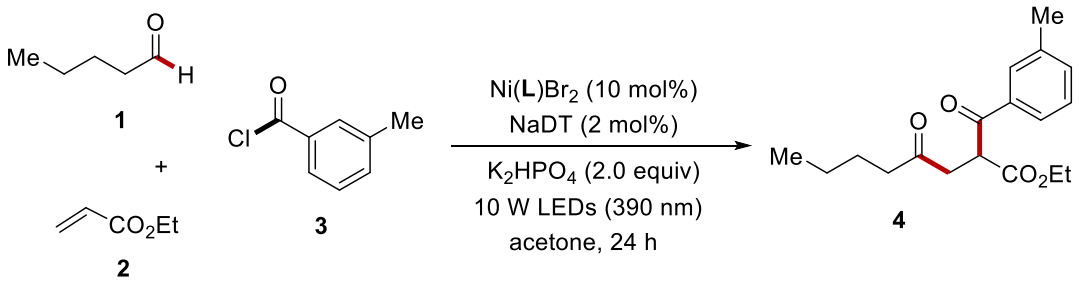
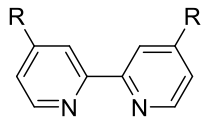
1. General Experimental Details

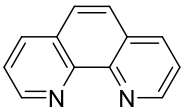
Catalytic reactions were performed under a N_2 atmosphere in pre-dried glassware using a Kessil PR160L photoreactor with 390 nm irradiation. The reaction temperature was measured by digital thermometer PCE-T 390, which was in the range of 30 to 32 °C (Room temperature: 22 to 25 °C). Methanol, dichloromethane, ethyl acetate, *n*-hexane and *n*-pentane were distilled prior to use. **44´** was synthesized following the procedures from literature examples.[1] Sodium decatungstate (NaDT) was synthesized following the procedure from literature example.[2] Other chemicals were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, TCI, or BLD Pharmatech GmbH) and used without further purification. Reactions were monitored by thin layer chromatography (TLC), using Merck silica gel 60 F254 glass plates (0.25 mm thick). Chromatography was carried out on Merck silica gel 60 (40–63 μm). Data for ^{1}H NMR are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p= quintet, m = multiplet, dd =doublet of doublets, ddd= doublet of double doublets, dt = doublet of triplets), coupling constants (J) were reported in Hertz (Hz). EI-MS was recorded on *Jeol AccuTOF* at 70 eV; ESI-MS was recorded on Bruker Daltonik *micrOTOF* and *maXis*. The ratios of mass to charge (*m/z*) are reported and the intensity relative to the base peak (I = 100) is given in parenthesis. All IR spectra were recorded on a Bruker FT-IR Alpha-P device.

2. Optimization of the Reaction Condition

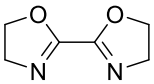




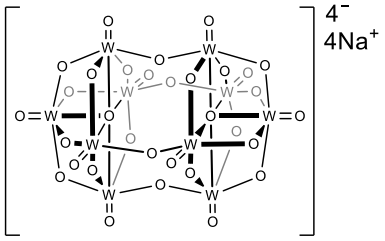
R = H (**L1**)
R = OMe (**L2**)
R = *t*Bu (**L3**)
R = CO_2Me (**L4**)



L5



L6

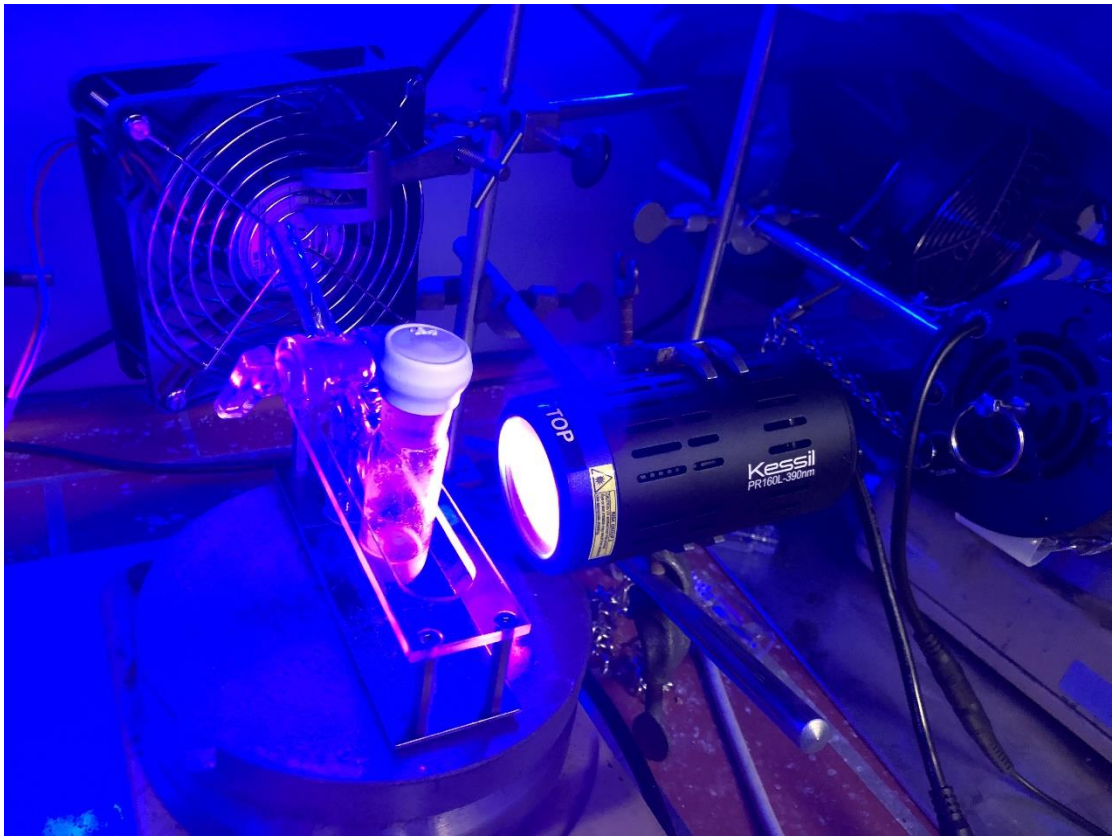


NaDT

Entry	**1** (equiv)	**2** (equiv)	**3** (equiv)	**L** (10 mol%)	Base (equiv)	Solvent (mL)	Yield (%)[b]
1	5	2	1	**L1**	K_2HPO_4 (2.0)	Acetone (1.0)	26
2	5	2	1	**L2**	K_2HPO_4 (2.0)	Acetone (1.0)	36
3	5	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	76 (71)[c]
4	5	2	1	**L4**	K_2HPO_4 (2.0)	Acetone (1.0)	15
5	5	2	1	**L5**	K_2HPO_4 (2.0)	Acetone (1.0)	0
6	5	2	1	**L6**	K_2HPO_4 (2.0)	Acetone (1.0)	0
7	5	2	1	**L3**	KH_2PO_4 (2.0)	Acetone (1.0)	17
8	5	2	1	**L3**	K_3PO_4 (2.0)	Acetone (1.0)	42
9	5	2	1	**L3**	Na_2HPO_4 (2.0)	Acetone (1.0)	27
10	5	2	1	**L3**	K_2CO_3 (2.0)	Acetone (1.0)	trace
11	5	2	1	**L3**	$KHCO_3$ (2.0)	Acetone (1.0)	trace
12	5	2	1	**L3**	K_2HPO_4 (2.0)	MeCN (1.0)	11
13	5	2	1	**L3**	K_2HPO_4 (2.0)	DCM (1.0)	trace
14	5	2	1	**L3**	K_2HPO_4 (2.0)	DMSO (1.0)	0
15	5	2	1	**L3**	K_2HPO_4 (2.0)	$PhCF_3$ (1.0)	trace
16	8	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	77
17	4	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	70
18	5	3	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	64
19	5	1	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	59
20	5	1	2	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	66

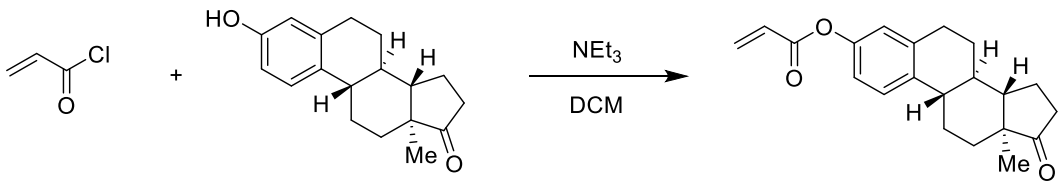
21	5	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (2.0)	72
22	5	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (0.5)	75
23[d]	5	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	59
24[e]	5	2	1	**L3**	K_2HPO_4 (2.0)	Acetone (1.0)	0

[a] Reaction conditions: **1** (1 mmol), **2** (0.4 mmol), **3** (0.2 mmol), Ni(**L3**)Br_2 (10 mol%), NaDT (2 mol%), K_2HPO_4 (0.4 mmol) in acetone (0.2 M) at 30 °C under irradiation of LEDs (10 W, λ = 390 nm) for 24 hours; [b] GC yield with *n*-dodecane as internal standard; [c] isolated yield; [d] using TBADT as a photocatalyst; [e] absence of NaDT, Ni or Light



Supplementary Figure S1. Set-up of experiments.

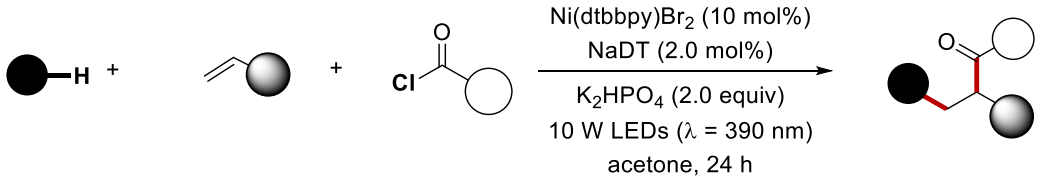
3. General Procedure for Synthesis of Starting Material 44´



Estrone (2 mmol) and NEt_3 (2 equiv.) was dissolved in DCM (5 mL). The solution

was cooled to 0 °C. Then acryloyl chloride (2 equiv.) in DCM (5 mL) was added. The solution was stirred at room temperature for 12 h. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel afforded the desired products **44´** white soild (421 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28 (dd, J = 8.5, 1.1 Hz, 1H), 6.92 – 6.82 (m, 2H), 6.57 (dd, J = 17.3, 1.3 Hz, 1H), 6.37 – 6.23 (m, 1H), 5.97 (dd, J = 10.4, 1.3 Hz, 1H), 2.90 (dd, J = 9.2, 4.5 Hz, 2H), 2.54 – 2.33 (m, 2H), 2.33 – 2.22 (m, 1H), 2.16 – 1.90 (m, 4H), 1.66 – 1.41 (m, 6H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 220.7 (C_q), 164.8 (C_q), 148.4 (C_q), 138.0 (C_q), 137.4 (C_q), 132.3 (C_q), 128.0 (CH), 126.4 (CH), 121.5 (CH), 118.6 (CH_2), 50.4 (CH), 47.9 (C_q), 44.1 (CH), 37.9 (CH), 35.8 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 26.3 (CH_2), 25.7 (CH_2), 21.5 (CH_2), 13.8 (CH_3).

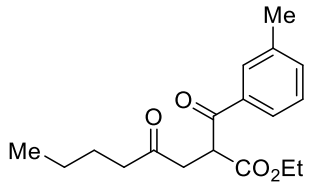
4. General Procedures



In an oven-dried tube, sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acyl chloride (0.20 mmol, 1.0 equiv.), aldehyde/alkane (1.0-2.0 mmol, 5.0-10 equiv.), alkene (0.40 mmol, 2.0 equiv.), and K_2HPO_4 (69.6 mg, 2.0 equiv.) were dissolved in acetone (1.0 mL). The reaction mixture was stirred and irradiated using a 10-W 390-nm LED lamp under N_2 for 24 h. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel afforded the desired products **4-52**, **56-58**.

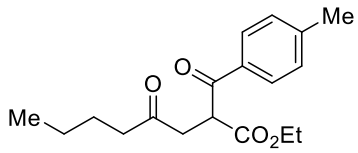
5. Characterization Data of Products

Ethyl 2-(3-methylbenzoyl)-4-oxooctanoate (4)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **4** as colorless oil (43.0 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.98 – 7.62 (m, 2H), 7.42 – 7.25 (m, 2H), 4.84 (dd, J = 7.4, 6.5 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.11 (dd, J = 18.1, 7.4 Hz, 1H), 3.03 (dd, J = 18.1, 6.5 Hz, 1H), 2.42 (t, J = 7.5 Hz, 2H), 2.34 (d, J = 0.7 Hz, 3H), 1.68 – 1.45 (m, 3H), 1.34 – 1.20 (m, 2H), 1.09 (t, J = 7.1 Hz, 3H), 0.83 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 194.9 (C_q), 169.4 (C_q), 138.5 (C_q), 136.0 (C_q), 134.4 (CH), 129.3 (CH), 128.5 (CH), 126.1 (CH), 61.6 (CH_2), 48.8 (CH), 42.4 (CH_2), 41.4 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 21.3 (CH_3), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2854, 1735, 1684, 1447, 1180, 1156, 1124, 1081, 876, 749 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 327 (100) $[M+Na]^+$, 305 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{25}O_4$ $[M+H]^+$: 305.1747, found: 305.1747.

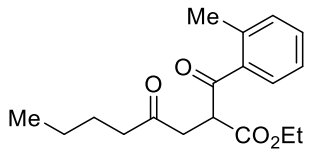
Ethyl 2-(4-methylbenzoyl)-4-oxooctanoate (5)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **5** as colorless oil (40.1 mg, 66%

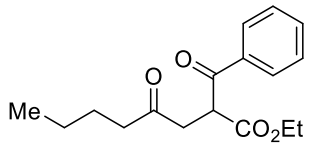
yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.2 Hz, 2H), 7.22 – 7.19 (m, 2H), 4.83 (t, J = 6.9 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.14 – 2.98 (m, 2H), 2.42 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 1.53 – 1.47 (m, 2H), 1.23 (dd, J = 8.5, 6.3 Hz, 2H), 1.09 (t, J = 7.1 Hz, 3H), 0.81 (d, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 194.3 (C_q), 169.4 (C_q), 144.5 (C_q), 133.5 (C_q), 129.4 (CH), 129.0 (CH), 61.6 (CH_2), 48.6 (CH), 42.5 (CH_2), 41.4 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 21.7 (CH_3), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2960, 1746, 1564, 1502, 1176, 1144, 1114, 1070, 926, 546 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 327 (100) $[M+Na]^+$, 305 (20) $[M+H]^+$. HR-MS (ESI) $C_{18}H_{25}O_4$ $[M+H]^+$: 305.1747, found: 305.1739.

Ethyl 2-(2-methylbenzoyl)-4-oxooctanoate (6)



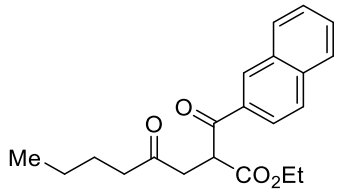
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 2-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **6** as colorless oil (24.3 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.6 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.30 – 7.25 (m, 2H), 4.80 (dd, J = 8.1, 5.8 Hz, 1H), 4.18 – 3.98 (m, 2H), 3.25 (dd, J = 18.1, 8.1 Hz, 1H), 3.05 (dd, J = 18.1, 5.8 Hz, 1H), 2.51 (t, J = 7.4 Hz, 2H), 2.47 (s, 3H), 1.61 – 1.58 (m, 2H), 1.37 – 1.27 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 198.1 (C_q), 169.3 (C_q), 138.6 (C_q), 137.1 (C_q), 131.7 (CH), 131.6 (CH), 128.7 (CH), 125.6 (CH), 61.5 (CH_2), 51.4 (CH), 42.3 (CH_2), 41.2 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 20.8 (CH_3), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2964, 1698, 1660, 1537, 1458, 1275, 1220, 1145, 963, 842 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 327 (100) $[M+Na]^+$, 305 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{25}O_4$ $[M+H]^+$: 305.1747, found: 305.1738.

Ehyl 2-benzoyl-4-oxooctanoate (7)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), benzoyl chloride (28.0 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **7** as colorless oil (40.6 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.02 – 7.97 (m, 2H), 7.63 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 4.89 (dd, *J* = 7.5, 6.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.18 (dd, *J* = 18.1, 7.5 Hz, 1H), 3.09 (dd, *J* = 18.1, 6.3 Hz, 1H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.58 – 1.49 (m, 2H), 1.35 – 1.24 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 194.8 (C_q), 169.3 (C_q), 136.0 (C_q), 133.5 (CH), 128.8 (CH), 128.6 (CH), 61.7 (CH_2), 48.7 (CH), 42.4 (CH_2), 41.4 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2929, 1758, 1737, 1714, 1680, 1493, 1322, 1223, 1153, 749 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 313 (100) $[M+Na]^+$, 291 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found: 291.1588.

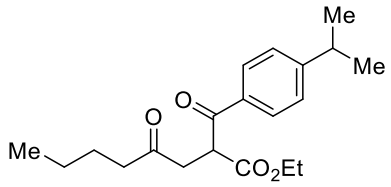
Ethyl 2-(2-naphthoyl)-4-oxooctanoate (8)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 2-naphthoyl chloride (38 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **8** as colorless oil (51.0 mg, 75%

yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.58 (d, J = 1.8 Hz, 1H), 8.04 – 8.01 (m, 1H), 8.00 – 7.94 (m, 1H), 7.92 – 7.83 (m, 2H), 7.59 – 7.55 (m, 2H), 5.07 (dd, J = 7.3, 6.5 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.23 (dd, J = 18.1, 7.3 Hz, 1H), 3.16 (dd, J = 18.1, 6.5 Hz, 1H), 2.50 (t, J = 7.5 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.36 – 1.27 (m, 2H), 1.12 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 194.6 (C_q), 169.3 (C_q), 135.8 (C_q), 133.3 (C_q), 132.5 (C_q), 130.9 (CH), 129.8 (CH), 128.8 (CH), 128.5 (CH), 127.7 (CH), 126.8 (CH), 124.2 (CH), 61.7 (CH_2), 48.8 (CH), 42.4 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 1738, 1714, 1687, 1593, 1497, 1264, 1026, 905, 729, 649 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 363 (100) $[M+Na]^+$, 341 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{21}H_{25}O_4$ $[M+H]^+$: 341.1747, found: 341.1741.

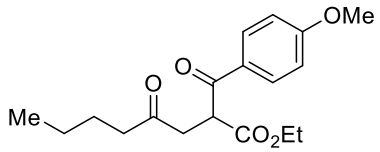
Ethyl 2-(4-isopropylbenzoyl)-4-oxooctanoate (9)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-isopropylbenzoyl chloride (36.4 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol, 5.0 equiv.), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **9** as colorless oil (46.5 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 4.90 (t, J = 6.9 Hz, 1H), 4.13 (q, J = 7.1, 2H), 3.18 – 3.08 (m, 2H), 3.00 – 2.92 (m, 1H), 2.50 – 2.47 (m, 2H), 1.60 – 1.55 (m, 2H), 1.35 – 1.29 (m, 2H), 1.27 (d, J = 0.6 Hz, 3H), 1.26 (d, J = 0.6 Hz, 3H), 1.16 (t, J = 7.1, 3H), 0.91 – 0.87 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 194.4 (C_q), 169.5 (C_q), 155.2 (C_q), 133.8 (C_q), 129.2 (CH), 126.8 (CH), 61.7 (CH_2), 48.7 (CH), 42.5 (CH_2), 41.5 (CH_2), 34.3 (CH), 25.8 (CH_2), 23.6 (CH_2), 22.3 (CH_3), 14.0 (CH_3), 13.8 (CH_3). **IR** (ATR): 3030, 1736, 1683, 1606, 1484,1351, 1231, 1183, 1096, 738 cm^{-1}. **MS** (ESI) *m/z* (relative

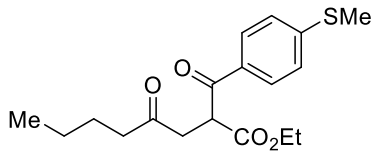
intensity): 355 (100) $[M+Na]^+$, 333 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{20}H_{29}O_4$ $[M+H]^+$: 333.2060, found: 333.2057.

Ethyl 2-(4-methoxybenzoyl)-4-oxooctanoate (10)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methoxybenzoyl chloride (34.0 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to obtain **10** as colorless oil (39.6 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 4.85 (t, J = 6.9 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.10 (dd, J = 6.9, 3.2 Hz, 2H), 2.46 (dd, J = 7.9, 7.0 Hz, 2H), 1.59 – 1.50 (m, 2H), 1.32 – 1.23 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.1 (C_q), 193.0 (C_q), 169.4 (C_q), 163.9 (C_q), 131.3 (CH), 128.9 (C_q), 113.8 (CH), 61.6 (CH_2), 55.5 (CH_3), 48.4 (CH), 42.4 (CH_2), 41.4 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2966, 2670, 1737, 1713, 1685, 1530, 1275, 1151, 1024, 417 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 343 (100) $[M+Na]^+$, 321 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{25}O_5$ $[M+H]^+$: 321.1697, found: 321.1690.

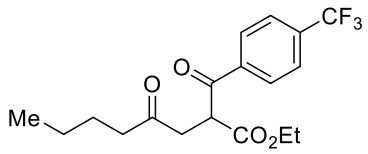
Ethyl 2-(4-(methylthio)benzoyl)-4-oxooctanoate (11)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-(methylthio)benzoyl chloride (37.3 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg,

0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **11** as colorless oil (40.3 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.88 (t, *J* = 6.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.26 – 3.06 (m, 2H), 2.54 (s, 3H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.62 – 1.56 (m, 2H), 1.33 (d, *J* = 7.5 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.1 (C_q), 193.6 (C_q), 169.3 (C_q), 146.8 (C_q), 132.2 (C_q), 129.3 (CH), 125.0 (CH), 61.7 (CH_2), 48.5 (CH), 42.5 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 14.7 (CH_3), 14.0 (CH_3), 13.8 (CH_3). **IR** (ATR): 2958, 2935, 1738, 1689, 1530, 1405, 1367, 1263, 854, 749 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 359 (100) $[M+Na]^+$, 337 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{25}O_4S$ $[M+H]^+$: 337.1468, found: 337.1469.

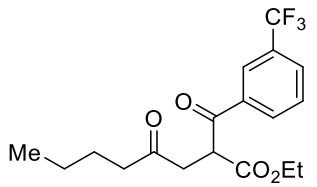
Ethyl 4-oxo-2-(4-(trifluoromethyl)benzoyl)octanoate (12)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-(trifluoromethyl)benzoyl chloride (41.6 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **12** as colorless oil (37.2 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 – 8.09 (m, 2H), 7.75 – 7.71 (m, 2H), 4.86 (dd, *J* = 8.6, 5.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.29 (dd, *J* = 18.3, 8.6 Hz, 1H), 3.09 (dd, *J* = 18.3, 5.3 Hz, 1H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.31 – 1.25 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = δ 207.9 (C_q), 194.1 (C_q), 168.7 (C_q), 139.0 (C_q), 134.7 (q, $^2J_{C\text{-}F}$ = 32.8 Hz, C_q), 129.1 (CH), 125.7 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, CH), 123.5 (q, $^1J_{C\text{-}F}$ = 272.7 Hz, C_q). 62.0 (CH_2), 48.8 (CH), 42.3 (CH_2), 41.6 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **^{19}F NMR** (377 MHz, $CDCl_3$): δ = -63.2. **IR** (ATR): 2959, 2934, 1738, 1686,

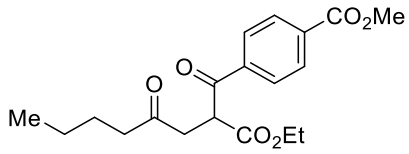
1586, 1397, 1367, 1266, 1070, 1009, 947 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 381 (100) $[M+Na]^+$, 359 (15) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{22}F_3O_4$ $[M+H]^+$: 359.1465, found: 359.1463.

Ethyl 4-oxo-2-(3-(trifluoromethyl)benzoyl)octanoate (13)



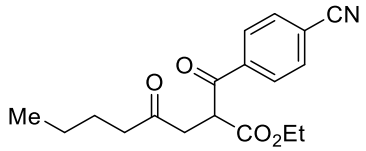
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-(trifluoromethyl)benzoyl chloride (41.6 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol, 2.0 equiv.) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **13** as colorless oil (36.5 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 – 8.27 (m, 1H), 8.21 – 8.19 (m, 1H), 7.85 – 7.79 (m, 1H), 7.63 – 7.58 (m, 1H), 4.87 (dd, *J* = 8.6, 5.3 Hz, 1H), 4.16 – 4.06 (q, *J* = 7.1 Hz, 2H), 3.30 (dd, *J* = 18.3, 8.6 Hz, 1H), 3.10 (dd, *J* = 18.3, 5.3 Hz, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.53 (m, 2H), 1.29 (dd, *J* = 7.5, 2.0 Hz, 2H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 193.5 (C_q), 168.6 (C_q), 136.8 (C_q), 132.0 (CH), 129.8 (q, $^2J_{C\text{-}F}$ = 3.6 Hz, CH), 129.3 (C_q), 127.04 (d, $^1J_{C\text{-}F}$ = 208.3 Hz, C_q), 125.7 (q, $^2J_{C\text{-}F}$ = 3.8 Hz, CH), 122 (CH), 62.0 (CH_2), 48.7 (CH), 42.3 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.8 (CH_3), 13.8 (CH_3). **^{19}F NMR** (377 MHz, $CDCl_3$): δ = -62.8. **IR** (ATR): 2960, 2934, 2871, 1738, 1680, 1415, 1367, 1056, 850, 414 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 381 (100) $[M+Na]^+$, 359 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{22}F_3O_4$ $[M+H]^+$: 359.1465, found: 359.1465.

Methyl-4-(2-(ethoxycarbonyl)-4-oxooctanoyl)benzoate (14)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), methyl 4-(chlorocarbonyl)benzoate (39.6 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **14** as colorless oil (32.0 mg, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 4.92 (dd, *J* = 8.2, 5.6 Hz, 1H), 4.21 – 4.11 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.30 (dd, *J* = 18.2, 8.2 Hz, 1H), 3.13 (dd, *J* = 18.2, 5.6 Hz, 1H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.33 – 1.26 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 194.5 (C_q), 168.9 (C_q), 166.2 (C_q), 139.5 (C_q), 134.2 (C_q), 129.9 (CH), 128.7 (CH), 61.9 (CH_2), 52.5 (CH), 48.9 (CH_3), 42.3 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 1735, 1678, 1563, 1151, 1155, 1057, 1038, 873, 599, 417 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 371 (100) $[M+Na]^+$, 349 (5) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{25}O_6$ $[M+H]^+$: 349.1646, found: 349.1650.

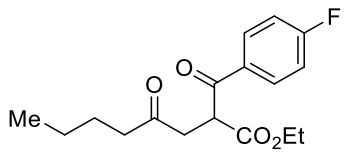
Ethyl-2-(4-cyanobenzoyl)-4-oxooctanoate (15)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-cyanobenzoyl chloride (33.0 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to obtain **15** as colorless oil (26.4 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.14 – 8.09 (m, 2H), 7.81 – 7.76 (m, 2H), 4.84

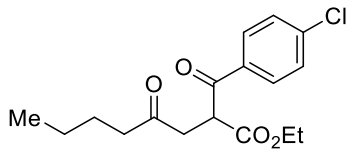
(dd, J = 9.0, 5.0 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.34 (dd, J = 18.3, 9.0 Hz, 1H), 3.11 (dd, J = 18.3, 5.0 Hz, 1H), 2.48 (t, J = 7.4 Hz, 2H), 1.58 – 1.52 (m, 2H), 1.33 – 1.27 (m, 2H), 1.14 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 193.8 (C_q), 168.5 (C_q), 139.5 (C_q), 132.5 (CH), 129.2 (CH), 117.9 (C_q), 116.6 (C_q), 62.1 (CH_2), 48.7 (CH), 42.2 (CH_2), 41.63 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2958, 1737, 1679, 1562, 1511, 1257, 1155, 872, 599, 419 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (100) $[M+Na]^+$, 316 (5) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{22}NO_4$ $[M+H]^+$: 316.1543, found: 316.1538.

Ethyl 2-(4-fluorobenzoyl)-4-oxooctanoate (16)



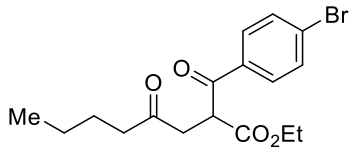
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-fluorobenzoyl chloride (31.6 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **16** as colorless oil (42.5 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.09 – 8.04 (m, 2H), 7.15 (t, J = 8.6 Hz, 2H), 4.86 (dd, J = 7.9, 5.8 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.23 (dd, J = 18.2, 7.9 Hz, 1H), 3.10 (dd, J = 18.2, 5.8 Hz, 1H), 2.51 – 2.49 (m, 2H), 1.59 – 1.54 (m, 2H), 1.34 – 1.28 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 193.1 (C_q), 169.0 (C_q), 166.0 (d, $^1J_{C\text{-}F}$ = 255.8 Hz, C_q), 132.5 (C_q), 131.6 (d, $^2J_{C\text{-}F}$ = 9.4 Hz, CH), 115.8 (d, $^2J_{C\text{-}F}$ = 21.9 Hz, CH), 61.8 (CH_2), 48.6 (CH), 42.4 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **^{19}F NMR** (377 MHz, $CDCl_3$): δ = -104.3. **IR** (ATR): 1736, 1681, 1606, 1483, 1350, 1231, 1057, 1183, 1096, 738 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 331 (100) $[M+Na]^+$, 309 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{22}O_4$ $[M+H]^+$: 309.1497, found: 309.1503.

Ethyl 2-(4-chlorobenzoyl)-4-oxooctanoate (17)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-chlorobenzoyl chloride (35.0 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **17** as colorless oil (41.4 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.99 – 7.95 (m, 2H), 7.49 – 7.42 (m, 2H), 4.84 (dd, *J* = 8.1, 5.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.23 (dd, *J* = 18.2, 8.1 Hz, 1H), 3.10 (dd, *J* = 18.2, 5.7 Hz, 1H), 2.51 – 2.46 (m, 2H), 1.57 – 1.54 (m, 2H), 1.32 – 1.27 (m, 2H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 193.6 (C_q), 168.9 (C_q), 140.1 (C_q), 134.5 (C_q), 130.3 (CH), 129.0 (CH), 61.8 (CH_2), 48.6 (CH), 42.3 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR):1736, 1716, 1681, 1603, 1585, 1367, 1278, 1018, 781, 690 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 347 (100) $[M+Na]^+$, 327 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{22}O_4{}^{35}Cl$ $[M+H]^+$: 325.1201, found: 325.1198.

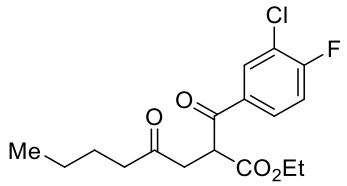
Ethyl 2-(4-bromobenzoyl)-4-oxooctanoate (18)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-bromobenzoyl chloride (43.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **18** as colorless oil (39.7 mg, 54% yield).**^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 – 7.83 (m, 2H), 7.68 – 7.57 (m, 2H), 4.84 (dd, *J* = 8.1, 5.7 Hz, 1H), 4.11 (t, *J* = 7.1 Hz, 2H), 3.24 (dd, *J* = 18.2, 8.1 Hz, 1H), 3.10 (dd, *J* = 18.2, 5.7 Hz, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.58 – 1.55 (m, 2H), 1.32 – 1.27 (m,

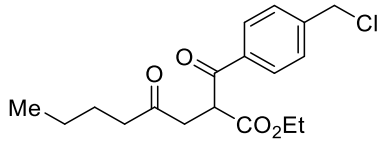
2H), 1.15 (t, J = 7.1 Hz, 3H), 0.91 – 0.88 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 193.8 (C_q), 168.9 (C_q), 134.9 (C_q), 132.0 (CH), 130.4 (CH), 128.9 (C_q), 61.9 (CH_2), 48.6 (CH), 42.3 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 3005, 2785, 2670, 1778, 1692, 1275, 1259, 756, 749, 411 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 391 (100) $[M+Na]^+$, 369 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{22}O_4{}^{79}Br$ $[M+H]^+$: 369.0696, found: 369.0695.

Ethyl 2-(3-chloro-4-fluorobenzoyl)-4-oxooctanoate (19)



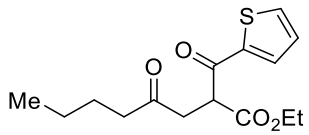
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-chloro-4-fluorobenzoyl chloride (38.6 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **19** as colorless oil (49.9 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.11 (dd, J = 7.0, 2.2 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.26 – 7.22 (m, 1H), 4.80 (dd, J = 8.5, 5.4 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.28 (dd, J = 18.3, 8.5 Hz, 1H), 3.10 (dd, J = 18.3, 5.4 Hz, 1H), 2.48 (t, J = 7.5 Hz, 2H), 1.59 – 1.54 (m, 2H), 1.33 – 1.27 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 192.3 (C_q), 168.6 (C_q), 161.3 (d, J = 258.0 Hz) (C_q), 133.4 (d, $^1J_{C\text{-}F}$ = 3.6 Hz, C_q), 131.8 (d, $^3J_{C\text{-}F}$ = 1.4 Hz, CH), 129.3 (d, $^3J_{C\text{-}F}$ = 8.6 Hz, CH), 122.0 (d, $^2J_{C\text{-}F}$ = 18.2 Hz, C_q), 116.8 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, CH), 61.9 (CH_2), 48.5 (CH), 42.2 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **^{19}F NMR** (377 MHz, $CDCl_3$): δ = -106.8. **IR** (ATR): 2958, 2932, 1738, 1715, 1688, 1368, 1305, 1260, 1129, 1022 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 365 (100) $[M+Na]^+$, 343 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{21}{}^{35}ClFO_4$ $[M+H]^+$: 343.1107, found: 343.1105.

Ethyl 2-(4-(chloromethyl)benzoyl)-4-oxooctanoate (20)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-(chloromethyl)benzoyl chloride (37.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **20** as colorless oil (43.2 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.4 Hz, 2H), 7.53 – 7.46 (m, 2H), 4.89 (dd, J = 7.8, 6.0 Hz, 1H), 4.61 (s, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.22 (dd, J = 18.2, 7.8 Hz, 1H), 3.14 – 3.05 (dd, J = 18.2, 6.0 Hz, 1H), 2.48 (t, J = 7.5 Hz, 2H), 1.59 – 1.54 (m, 2H), 1.33 – 1.28 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H), 0.91 – 0.87 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 194.1 (C_q), 169.1 (C_q), 142.8 (C_q), 135.9 (C_q), 129.3 (CH), 128.7 (CH), 61.7 (CH_2), 48.7 (CH), 45.2 (CH_2), 42.3 (CH_2), 41.4 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 3052, 1730, 1679, 1606, 1448, 1368, 1183, 1144, 1025, 876 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 361 (100) $[M+Na]^+$, 339 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{24}{}^{35}ClO_4$ $[M+H]^+$: 339.1358, found: 339.1363.

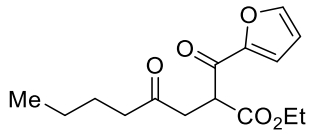
Ethyl 4-oxo-2-(thiophene-2-carbonyl)octanoate (21)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), thiophene-2-carbonyl chloride (29.3 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **21** as colorless oil (32.5 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.23 (dd, J = 2.9, 1.3 Hz, 1H), 7.58 (dd, J = 5.1, 1.3 Hz, 1H), 7.32 (dd, J = 5.1, 2.9 Hz, 1H), 4.71 (dd, J = 7.3, 6.6 Hz, 1H), 4.13 (q,

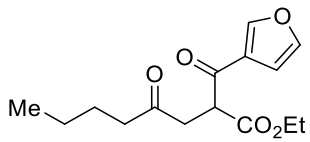
J = 7.1 Hz, 2H), 3.16 (dd, *J* = 18.2, 7.3 Hz, 1H), 3.10 (dd, *J* = 18.2, 6.6 Hz, 1H), 2.52 – 2.44 (m, 2H), 1.61 – 1.52 (m, 2H), 1.33 – 1.25 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 188.3 (C_q), 169.0 (C_q), 141.0 (C_q), 133.8 (CH), 127.3 (CH), 126.4 (CH), 61.7 (CH_2), 50.5 (CH), 42.4 (CH_2), 41.2 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.8 (CH_3). **IR** (ATR): 2958, 1756, 1714, 1681, 1588, 1492, 1272, 1162, 1024, 752 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 319 (100) $[M+Na]^+$, 297 (5) $[M+H]^+$. **HR-MS** (ESI) $C_{15}H_{21}O_4S$ $[M+H]^+$: 297.1155, found: 297.1152.

Ethyl 2-(furan-2-carbonyl)-4-oxooctanoate (22)



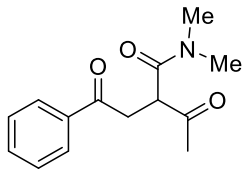
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), furan-2-carbonyl chloride (26.0 mg, 0.20 mmol, 1.0 equiv.), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **22** as colorless oil (32.5 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.36 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.71 (dd, *J* = 7.5, 6.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.19 (dd, *J* = 18.1, 7.5 Hz, 1H), 3.10 (dd, *J* = 18.1, 6.5 Hz, 1H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.37 – 1.29 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.7 (C_q), 183.0 (C_q), 168.9 (C_q), 151.8 (C_q), 147.1 (CH), 118.8 (CH), 112.6 (CH), 61.7 (CH_2), 49.0 (CH), 42.3 (CH_2), 40.7 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 13.9 (CH_3), 13.7 (CH_3). **IR** (ATR): 1737, 1717, 1684, 1602, 1495, 1369, 1271, 1031, 700, 411 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 303 (100) $[M+Na]^+$, 281 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{15}H_{21}O_5$ $[M+H]^+$: 281.1384, found: 281.1386.

Ethyl 2-(furan-3-carbonyl)-4-oxooctanoate (23)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), furan-3-carbonyl chloride (29.3 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **23** as colorless oil (27.4 mg, 49% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.64 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.36 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.71 (dd, *J* = 7.5, 6.5 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.18 (dd, *J* = 18.1, 7.5 Hz, 1H), 3.10 (dd, *J* = 18.1, 6.5 Hz, 1H), 2.50 (t, *J* = 7.4 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.37 – 1.29 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.0 (C_q), 188.5 (C_q), 168.8 (C_q), 148.7 (CH), 144.3 (CH), 126.9 (C_q), 109.0 (CH), 61.8 (CH_2), 51.3 (CH), 42.4 (CH_2), 40.9 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 14.0 (CH_3), 13.8 (CH_3). **IR** (ATR): 2958, 1737, 1685, 1597, 1448, 1269, 1156, 1024, 946, 689 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 303 (100) $[M+Na]^+$, 281 (5) $[M+H]^+$. **HR-MS** (ESI) $C_{15}H_{21}O_5$ $[M+H]^+$: 281.1384, found: 281.1375.

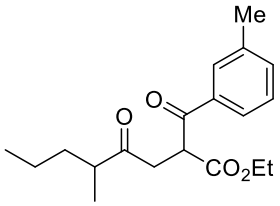
2-acetyl-*N*,*N*-dimethyl-4-oxo-4-phenylbutanamide (24)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), dimethylcarbamic chloride (21.4 mg, 0.20 mmol), benzaldehyde (106 mg, 1.0 mmol), but-3-en-2-one (28.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 3/1) to obtain **24** as colorless oil (8.4 mg, 17% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 – 7.94 (m, 2H), 7.60 – 7.52 (m, 1H), 7.47

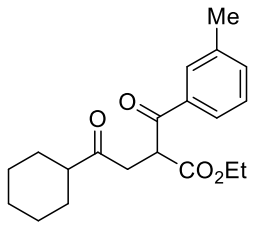
– 7.41 (m, 2H), 4.40 (t, J = 6.6 Hz, 1H), 3.58 (d, J = 6.5 Hz, 2H), 3.23 (s, 3H), 3.00 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 202.7 (C_q), 197.5 (C_q), 169.1 (C_q), 136.1 (C_q), 133.4 (CH), 128.6 (CH), 128.1 (CH), 51.87 (CH), 37.9 (CH_3), 37.7 (CH_2), 36.0 (CH_3), 28.0 (CH_3). **IR** (ATR): 2950, 1873, 1771, 1620, 1560, 1328, 1276, 1016, 965, 553 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 270 (100) $[M+Na]^+$, 248 (5) $[M+H]^+$. **HR-MS** (ESI) $C_{14}H_{18}NO_3$ $[M+H]^+$: 248.1281, found: 248.1282.

Ethyl 5-methyl-2-(3-methylbenzoyl)-4-oxooctanoate (25)



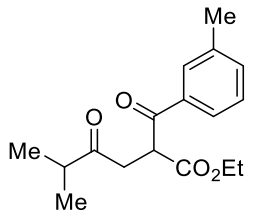
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 2-methylpentanal (86.2 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **25** as colorless oil (45.8 mg, 72% yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 – 7.78 (m, 2H), 7.41 – 7.33 (m, 2H), 4.90 (dd, J = 7.5, 6.3 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.28 – 3.08 (m, 2H), 2.65 – 2.56 (m, 1H), 2.41 (s, 3H), 1.71 – 1.62 (m, 1H), 1.36 – 1.26 (m, 3H), 1.16 (t, J = 7.1 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 0.92 – 0.87 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 211.6 (C_q), 195.0 (C_q), 169.4 (C_q), 138.5 (C_q), 136.1 (C_q), 134.3 (CH), 129.3 (CH), 128.5 (CH), 126.1 (CH), 61.6 (CH_2), 48.6 (CH), 46.0 (CH), 40.2 (CH_2), 35.1 (CH_2), 21.3 (CH_2), 20.3 (CH_3), 16.2 (CH_3), 14.0 (CH_3), 13.9 (CH_3). **IR** (ATR): 2745, 1647, 1566, 1462, 1403, 1288, 1054, 973, 889, 750 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 341 (100) $[M+Na]^+$, 319 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{27}O_4$ $[M+H]^+$: 319.1904, found: 319.1902.

Ethyl 4-cyclohexyl-2-(3-methylbenzoyl)-4-oxobutanoate (26)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), cyclohexanecarbaldehyde (112 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **26** as colorless oil (42.2 mg, 64% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 – 7.79 (m, 2H), 7.42 – 7.32 (m, 2H), 4.90 (dd, J = 7.4, 6.4 Hz, 1H), 4.12 (q, J = 7.1, 2H), 3.21 (dd, J = 18.1, 7.4 Hz, 1H), 3.13 (dd, J = 18.2, 6.4 Hz, 1H), 2.46 – 2.38 (m, 1H), 2.41 (s, 3H), 1.94 – 1.85 (m, 2H), 1.82 – 1.71 (m, 2H), 1.69 – 1.63 (m, 1H), 1.40 – 1.19 (m, 5H), 1.15 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 210.8 (C_q), 195.0 (C_q), 169.4 (C_q), 138.5 (C_q), 136.0 (C_q), 134.3 (CH), 129.3 (CH), 128.5 (CH), 126.1 (CH), 61.6 (CH_2), 50.6 (CH), 48.7 (CH), 39.6 (CH_2), 28.4 (CH_2), 25.8 (CH_2), 25.5 (CH_2), 21.3 (CH_3), 13.9 (CH_3). **IR** (ATR): 3005, 1744, 1714, 1684, 1560, 1264, 1105, 732, 702, 558 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 353 (100) $[M+Na]^+$, 331 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{20}H_{27}O_4$ $[M+H]^+$: 331.1904, found: 331.1902.

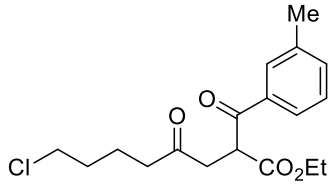
Ethyl-5-methyl-2-(3-methylbenzoyl)-4-oxohexanoate (27)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), isobutyraldehyde (72.1 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column

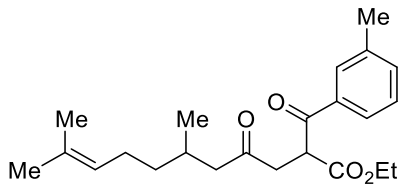
chromatography (*n*-hexane/EtOAc = 10/1) to obtain **27** as colorless oil (35.4 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 5.5 Hz, 2H), 7.42 – 7.32 (m, 2H), 4.91 (t, J = 6.9 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.31 – 3.08 (m, 2H), 2.69 – 2.65 (m, 1H), 2.41 (s, 3H), 1.18 – 1.12 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 211.5 (C_q), 195.0 (C_q), 169.4 (C_q), 138.5 (C_q), 136.0 (C_q), 134.3 (CH), 129.3 (CH), 128.5 (CH), 126.1 (CH), 61.6 (CH_2), 48.7 (CH), 40.8 (CH), 39.4 (CH_2), 21.3 (CH_3), 18.1 (CH_3), 13.9 (CH_3). **IR** (ATR): 1738, 1714, 1685, 1264, 1153, 908, 733, 701, 649, 452 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 313 (100) $[M+Na]^+$, 291 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{23}O_4$ $[M+H]^+$: 291.1591, found 291.1593.

Ethyl 8-chloro-2-(3-methylbenzoyl)-4-oxooctanoate (28)



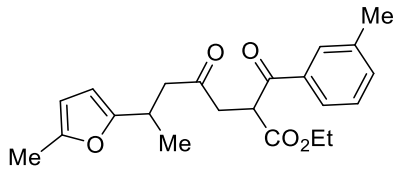
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 5-chloropentanal (120 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **28** as colorless oil (50.0 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 – 7.75 (m, 2H), 7.43 – 7.32 (m, 2H), 4.90 (dd, J = 7.5, 6.4 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.18 (dd, J = 18.0, 7.5 Hz, 1H), 3.08 (dd, J = 18.0, 6.4 Hz, 1H), 3.23 – 3.03 (m, 2H), 2.55 (t, J = 6.8 Hz, 2H), 2.41 (t, J = 0.7 Hz, 3H), 1.81 – 1.69 (m, 4H), 1.15 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.1 (C_q), 194.8 (C_q), 169.3 (C_q), 138.5 (C_q), 135.9 (C_q), 134.4 (CH), 129.3 (CH), 128.5 (CH), 126.1 (CH), 61.7 (CH_2), 48.8 (CH), 44.5 (CH_2), 41.6 (CH_2), 41.4 (CH_2), 31.8 (CH_2), 21.3 (CH_3), 20.9 (CH_2), 13.9 (CH_3). **IR** (ATR): 2959, 1737, 1685, 1589, 1466, 1266, 1153, 1092, 1012, 530 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 361 (100) $[M+Na]^+$, 339 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{24}{}^{35}ClO_4$ $[M+H]^+$: 339.1358, found 339.1361.

Ethyl 6,10-dimethyl-2-(3-methylbenzoyl)-4-oxoundec-9-enoate (29)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), citronellal (154 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **29** as colorless oil (48.4 mg, 65% yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.88 – 7.77 (m, 2H), 7.43 – 7.32 (m, 2H), 5.18 – 5.06 (m, 1H), 4.92 – 4.88 (m, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.19 – 3.04 (m, 2H), 2.51-2.45 (m, 1H), 2.41 (s, 3H), 2.32 – 2.24 (m, 1H), 2.02 – 1.96 (m, 4H), 1.67 (s, 3H), 1.59 (s, 3H), 1.36 – 1.19 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H), 0.91 – 0.89 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.7 (C_q), 194.9 (C_q), 169.3 (C_q), 138.5 (C_q), 136.0 (C_q), 134.3 (CH), 131.5 (C_q), 129.3 (CH), 128.5 (CH), 126.1 (CH), 124.2 (CH), 61.6 (CH_2), 50.1 (CH_2), 48.7 (CH), 42.0 (CH_2), 36.9 (CH_2), 29.0 (CH), 25.4 (CH_2), 21.3 (CH_3), 19.6 (CH_3), 17.6 (CH_3), 13.9 (CH_3). **IR** (ATR): 2972, 1737, 1712, 1684, 1597, 1508, 1268, 1234, 1158, 850 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 395 (100) $[M+Na]^+$, 373 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{23}H_{33}O_4$ $[M+H]^+$: 373.2373, found: 373.2365.

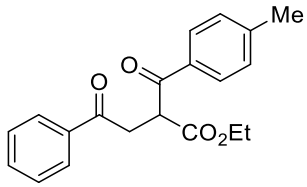
Ethyl 2-(3-methylbenzoyl)-6-(5-methylfuran-2-yl)-4-oxoheptanoate (30)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 3-(5-methylfuran-2-yl)butanal (152 mg, 1.0 mmol), ethyl acrylate

(40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **30** as colorless oil (43.6 mg, 59% yield, d.r. = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.82 (m, 2H), 7.41 – 7.34 (m, 2H), 5.84 – 5.81 (m, 2H), 4.92 – 4.88 (m, 1H), 4.19 – 4.09 (m, 2H), 3.36 – 3.32 (m, 1H), 3.21 – 3.05 (m, 2H), 2.69 – 2.61 (m, 2H), 2.41 (s, 3H), 2.24 (s, 3H) 1.27 – 1.13 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 206.3 (C_q), 194.9 (C_q), 169.3 (C_q), 157.0 (C_q), 150.5 (C_q), 138.5 (C_q), 136.0 (C_q), 134.4 (CH), 134.4 (CH), 134.3 (CH), 129.5 (CH), 129.4 (CH), 128.8 (CH), 128.62 (CH), 128.61 (CH), 126.3 (CH), 126.1 (CH), 125.5 (CH), 105.8 (CH), 104.5 (CH), 61.7 (CH_2), 61.7 (CH_2), 49.0 (CH), 48.8 (CH), 48.7 (CH), 48.6 (CH_2), 48.5 (CH_2), 48.4 (CH_2), 41.99 (CH_2), 41.96 (CH_2), 38.3 (CH_2), 29.0 (CH_2), 28.97 (CH), 28.95 (CH), 27.98 (CH), 21.41 (CH_3), 21.38 (CH_3), 21.36 (CH_3), 19.0 (CH_3), 18.9 (CH_2), 13.98 (CH_3), 13.95 (CH_3), 13.51 (CH_3), 13.49 (CH_3). **IR** (ATR): 2961, 1655, 1529, 1492, 1444, 1256, 1220, 1095, 1027, 980, 836, 812 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 393 (100) $[M+Na]^+$, 371 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{22}H_{27}O_5$ $[M+H]^+$: 371.1853, found: 371.1858.

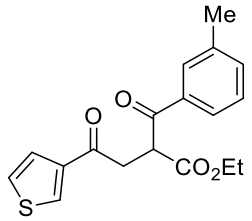
Ethyl 2-(4-methylbenzoyl)-4-oxo-4-phenylbutanoate (31)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoylchloride (30.8 mg, 0.20 mmol), benzaldehyde (106 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **31** as colorless oil (25.9 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.01 – 7.99 (m, 4H), 7.60 – 7.55 (m, 1H), 7.49 – 7.44 (m, 2H), 7.33 – 7.27 (m, 2H), 5.10 (dd, *J* = 7.2, 6.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.78 (dd, *J* = 18.2, 7.2 Hz, 1H), 3.72 (dd, *J* = 18.2, 6.4 Hz, 1H), 2.43 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 197.0 (C_q), 194.4 (C_q), 169.4 (C_q),

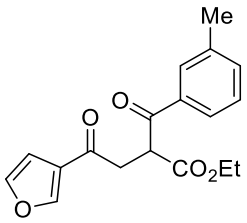
144.6 (C_q), 136.2 (C_q), 133.6 (C_q), 133.5 (CH), 129.4 (CH), 129.1 (CH), 128.6 (CH), 128.2 (CH), 61.7 (CH_2), 48.8 (CH), 38.2 (CH_2), 21.7 (CH_3), 14.0 (CH_3). **IR** (ATR): 2982, 2925, 2190, 1674, 1468, 1239, 1019, 688, 578, 417 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 347 (100) $[M+Na]^+$, 325 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{20}H_{21}O_4$ $[M+H]^+$: 325.1434, found: 325.1435.

Ethyl 2-(3-methylbenzoyl)-4-oxo-4-(thiophen-3-yl)butanoate (32)



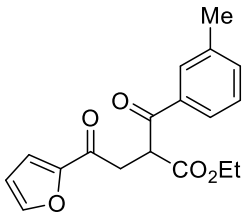
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), thiophene-3-carbaldehyde (112 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **32** as colorless oil (34.3 mg, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 2.8, 1.3 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.55 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.32 (dd, *J* = 5.1, 2.8 Hz, 1H), 5.09 (dd, *J* = 7.3, 6.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.70 (dd, *J* = 18.0, 7.3 Hz, 1H), 3.62 (dd, *J* = 18.0, 6.4 Hz, 1H), 2.43 – 2.42 (m, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 194.9 (C_q), 191.2 (C_q), 169.3 (C_q), 141.3 (C_q), 138.5 (C_q), 136.0 (C_q), 134.4 (CH), 132.6 (CH), 129.4 (CH), 128.6 (CH), 126.8 (CH), 126.5 (CH), 126.2 (CH), 61.7 (CH_2), 48.7 (CH), 39.1 (CH_2), 21.4 (CH_3), 13.9 (CH_3). **IR** (ATR): 2975, 2936, 1744, 1738, 1686, 1363, 1266, 1159, 1076, 1019 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 353 (100) $[M+Na]^+$, 331 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{19}O_4S$ $[M+H]^+$: 331.0999, found: 331.0998.

Ethyl 4-(furan-3-yl)-2-(3-methylbenzoyl)-4-oxobutanoate (33)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), furan-3-carbaldehyde (96.0 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **33** as colorless oil (37.6 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (dd, *J* = 1.4, 0.8 Hz, 1H), 7.88 – 7.87 (m, 2H), 7.47 – 7.34 (m, 3H), 6.76 (dd, *J* = 1.4, 0.8 Hz, 1H), 5.08 (dd, *J* = 7.3, 6.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.55 (dd, *J* = 17.8, 7.3 Hz, 1H), 3.48 (dd, *J* = 17.8, 6.5 Hz, 1H), 2.42 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 194.8 (C_q), 191.6 (C_q), 169.2 (C_q), 147.6 (C_q), 144.3 (C_q), 138.5 (C_q), 136.0 (CH), 134.4 (CH), 129.4 (CH), 128.6 (CH), 127.0 (CH), 126.2 (CH), 108.5 (CH), 61.8 (CH_2), 48.5 (CH), 39.4 (CH_2), 21.4 (CH_3), 13.9 (CH_3). **IR** (ATR): 3054, 1736, 1680, 1455, 1333, 1276, 1183, 1150, 1078, 1032 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 337 (100) $[M+Na]^+$, 315 (15) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{19}O_5$ $[M+H]^+$: 315.1227, found: 315.1229.

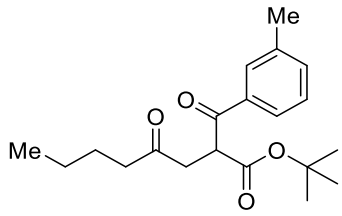
Ethyl 4-(furan-2-yl)-2-(3-methylbenzoyl)-4-oxobutanoate (34)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), furan-2-carbaldehyde (96.0 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **34** as colorless oil (35.2 mg, 56%

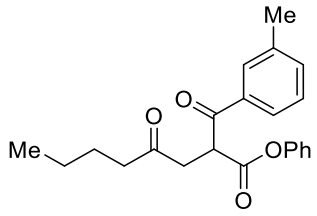
yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.12 (dd, J = 1.4, 0.8 Hz, 1H), 7.87 (td, J = 1.8, 0.8 Hz, 2H), 7.47 – 7.34 (m, 3H), 6.76 (dd, J = 1.9, 0.8 Hz, 1H), 5.08 (dd, J = 7.3, 6.5 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.62 (dd, J = 17.8, 7.3 Hz, 1H), 3.48 (dd, J = 17.8, 6.5 Hz, 1H), 2.42 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 194.8 (C_q), 185.9 (C_q), 169.2 (C_q), 152.1 (C_q), 146.7 (CH), 138.5 (C_q), 136.0 (C_q), 134.4 (CH), 129.4 (CH), 128.6 (CH), 126.2 (CH), 117.6 (CH), 112.4 (CH), 61.7 (CH_2), 48.5 (CH), 37.6 (CH_2), 21.4 (CH_3), 13.9 (CH_3). **IR** (ATR): 1736, 1673, 1512, 1417, 1364, 1277, 1029, 791, 687, 430 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 337 (100) $[M+Na]^+$, 315 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{19}O_5$ $[M+H]^+$: 315.1227, found: 315.1224.

Tert-butyl-2-(3-methylbenzoyl)-4-oxooctanoate (35)



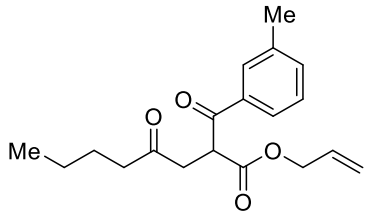
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), *tert*-butyl acrylate (51.2 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **35** as colorless oil (40.5 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.83 – 7.78 (m, 2H), 7.39 – 7.33 (m, 2H), 4.81 (dd, J = 7.6, 6.2 Hz, 1H), 3.15 (dd, J = 18.0, 7.6 Hz, 1H), 3.04 (dd, J = 18.0, 6.2 Hz, 1H), 2.54 – 2.47 (m, 2H), 2.41 (s, 3H), 1.59 – 1.54 (m, 2H), 1.33 (s, 9H), 1.32 – 1.24 (m, 2H), 0.91 – 0.88 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.2 (C_q), 195.3 (C_q), 168.4 (C_q), 138.3 (C_q), 136.3 (C_q), 134.1 (CH), 129.4 (CH), 128.4 (CH), 126.1 (CH), 82.2 (C_q), 50.0 (CH), 42.5 (CH_2), 41.3 (CH_2), 27.7 (CH_3), 25.9 (CH_2), 22.3 (CH_2), 21.4 (CH_3), 13.9 (CH_3). **IR** (ATR): 2929, 2854, 1736, 1684, 1449, 1368, 1275, 1143, 1000, 936 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 355 (100) $[M+Na]^+$, 333 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{29}O_4$ $[M+H]^+$: 333.2060, found: 333.2061.

Phenyl 2-(3-methylbenzoyl)-4-oxooctanoate (36)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), phenyl acrylate (59.2 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **36** as colorless oil (53.1 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 – 7.86 (m, 2H), 7.48 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 – 6.98 (m, 1H), 7.02 – 6.96 (m, 2H), 5.15 (t, J = 6.9 Hz, 1H), 3.31 – 3.13 (m, 2H), 2.53 (dd, J = 8.0, 6.9 Hz, 2H), 2.43 (s, 3H), 1.65 – 1.57 (m, 2H), 1.37 – 1.28 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.7 (C_q), 194.6 (C_q), 168.1 (C_q), 150.4 (C_q), 138.7 (C_q), 135.7 (C_q), 134.6 (CH), 129.3 (CH), 129.3 (CH), 128.7 (CH), 126.1 (CH), 126.0 (CH), 121.2 (CH), 48.9 (CH), 42.4 (CH_2), 41.4 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 21.3 (CH_3), 13.8 (CH_3). **IR** (ATR): 2958, 1734, 1685, 1585, 1368, 1253, 1150, 843, 691 cm-1. MS (ESI) m/z (relative intensity): 375 (100) $[M+Na]^+$, 353 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1747, found: 353.1751.

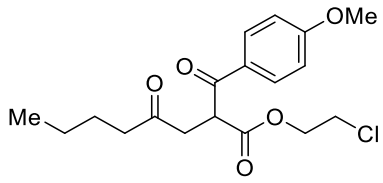
Allyl 2-(3-methylbenzoyl)-4-oxooctanoate (37)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), allyl acrylate (44.8 mg, 0.40

mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **37** as colorless oil (41.7 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 – 7.80 (m, 2H), 7.41 – 7.33 (m, 2H), 5.84 – 5.74 (m, 1H), 5.23 – 5.14 (m, 2H), 4.95 (dd, *J* = 7.3, 6.5 Hz, 1H), 4.58 – 4.56 (m, 2H), 3.22 – 3.09 (m, 2H), 2.52 – 2.47 (m, 2H), 2.41 (s, 3H), 1.59 – 1.55 (m, 2H), 1.35 – 1.28 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 194.8 (C_q), 169.1 (C_q), 138.6 (C_q), 135.9 (C_q), 134.4 (CH), 131.4 (CH), 129.4 (CH), 128.6 (CH), 126.1 (CH), 118.5 (CH_2), 66.1 (CH_2), 48.6 (CH), 42.4 (CH_2), 41.5 (CH_2), 25.8 (CH_2), 22.3 (CH_2), 21.4 (CH_3), 13.8 (CH_3). **IR** (ATR): 2985, 1737, 1685, 1466, 1367, 1275, 1153, 1096, 784, 691 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 339 (100) $[M+Na]^+$, 317 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{25}O_4$ $[M+H]^+$: 317.1747, found: 317.1746.

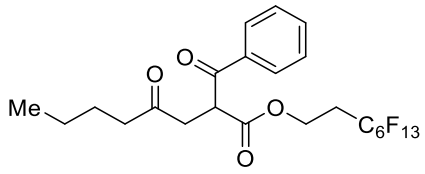
2-chloroethyl 2-(4-methoxybenzoyl)-4-oxooctanoate (38)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methoxybenzoyl chloride (34.0 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), 2-chloroethyl acrylate (53.6 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **38** as colorless oil (46.7 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.09 – 8.02 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 4.96 (t, *J* = 6.9 Hz, 1H), 4.36 (t, *J* = 5.8 Hz, 2H), 3.91 (s, 3H), 3.62 (q, *J* = 5.1 Hz, 2H), 3.19 (d, *J* = 6.9 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.35 (q, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.9 (C_q), 192.5 (C_q), 169.1 (C_q), 164.0 (C_q), 131.3 (CH), 128.6 (C_q), 113.9 (CH), 64.8 (CH_2), 55.5 (CH_3), 48.2 (CH), 42.4 (CH_2), 41.3 (CH_2), 41.1 (CH_2), 25.8 (CH_2), 22.2 (CH_3), 13.8 (CH_3). **IR** (ATR): 1860, 1752, 1680, 1530, 1262, 889, 763, 592, 446, 425 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 377 (100) $[M+Na]^+$, 355 (15) $[M+H]^+$. **HR-MS** (ESI)

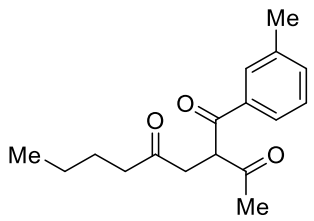
$C_{18}H_{24}{}^{35}ClO_5$ $[M+H]^+$: 355.1307, found: 355.1310.

3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl 2-benzoyl-4-oxooctanoate (39)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), benzoyl chloride (28.0 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate (167 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **39** as colorless oil (82.6 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.06 – 7.97 (m, 2H), 7.63 – 7.56 (m, 1H), 7.48 (dd, J = 8.3, 6.8 Hz, 2H), 4.96 (t, J = 6.9 Hz, 1H), 4.38 (t, J = 6.4 Hz, 2H), 3.16 (dd, J = 7.0, 1.7 Hz, 2H), 2.49 (t, J = 7.4 Hz, 2H), 2.44 – 2.25 (m, 2H), 1.62 – 1.53 (m, 2H), 1.36 – 1.28 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 207.6 (C_q), 194.3 (C_q), 168.9 (C_q), 135.7 (C_q), 133.7 (CH), 128.8 (CH), 127.6 (CH), 57.3 (CH_2), 48.4 (CH), 42.3 (CH_2), 41.3 (CH_2), 30.2 (CH_2), 25.8 (CH_2), 22.2 (CH_3), 13.6 (CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$): δ = -81.1, -113.8, -122.0, -123.0, -123.7, -126.3. **IR** (ATR): 2764, 2451, 1826, 1644, 1530, 1420, 1254, 1057, 978, 665 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 631 (100) $[M+Na]^+$, 609 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{24}H_{24}F_{13}O_4$ $[M+H]^+$: 609.1305, found: 609.1305.

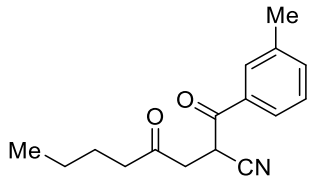
3-(3-methylbenzoyl)nonane-2,5-dione (40)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8

mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), but-3-en-2-one (28.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to obtain **40** as colorless oil (39.5 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.81 – 7.78 (m, 2H), 7.45 – 7.34 (m, 2H), 5.07 (t, J = 6.7 Hz, 1H), 3.18 – 3.12 (m, 1H), 2.99 – 2.93 (m, 1H), 2.47 (td, J = 7.3, 4.3 Hz, 2H), 2.41 (s, 3H), 2.16 (s, 3H), 1.60 – 1.50 (m, 2H), 1.34 – 1.25 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.1 (C_q), 202.6 (C_q), 196.5 (C_q), 138.9 (C_q), 136.1 (C_q), 134.7 (CH), 129.3 (CH), 128.9 (CH), 126.1 (CH), 56.8 (CH), 42.4 (CH_2), 41.3 (CH_2), 29.4 (CH_3), 25.9 (CH_2), 22.3 (CH_2), 21.4 (CH_3), 13.8 (CH_3). **IR** (ATR): 2950, 2895, 1960, 1875, 1692, 1552, 1502, 1276, 939, 756. cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 297 (100) $[M+Na]^+$, 275 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{23}O_3$ $[M+H]^+$: 275.1642, found: 275.1645.

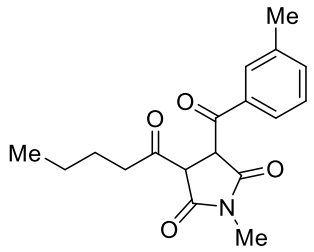
2-(3-Methylbenzoyl)-4-oxooctanenitrile (41)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), acrylonitrile (21.2 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to obtain **41** as colorless oil (22.6 mg, 44% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 – 7.81 (m, 2H), 7.49 – 7.37 (m, 2H), 4.82 (dd, J = 9.0, 4.4 Hz, 1H), 3.46 (dd, J = 18.0, 9.0 Hz, 1H), 3.01 (dd, J = 18.0, 4.4 Hz, 1H), 2.56 – 2.46 (m, 2H), 2.43 (s, 3H), 1.62 – 1.56 (m, 2H), 1.36 – 1.30 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 205.7 (C_q), 189.0 (C_q), 139.0 (C_q), 135.4 (C_q), 133.9 (CH), 129.3 (CH), 128.8 (CH), 126.1 (CH), 116.9 (C_q), 42.1 (CH), 40.6 (CH_2), 32.9 (CH_2), 25.6 (CH_2), 22.1 (CH_2), 21.3 (CH_3), 13.7 (CH_3). **IR** (ATR): 3020, 1738, 1650, 1530, 1264, 908, 727, 711, 701, 650 cm^{-1}. **MS** (ESI) *m/z*

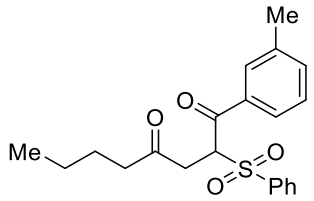
(relative intensity): 280 (100) $[M+Na]^+$, 258 (30) $[M+H]^+$. **HR-MS** (ESI) $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489, found: 258.1487.

1-Methyl-3-(3-methylbenzoyl)-4-pentanoylpyrrolidine-2,5-dione (42)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), 1-methyl-1*H*-pyrrole-2,5-dione (44.4 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to obtain **42** as colorless oil (27.7 mg, 45% yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.59 – 7.58 (m, 1H), 7.49 – 7.40 (m, 2H), 7.37 – 7.27 (m, 1H), 3.92 (d, J = 18.2 Hz, 1H), 3.05 (s, 3H), 3.11 – 2.96 (m, 2H), 2.40 (s, 3H), 2.39 – 2.29 (m, 1H), 1.55 – 1.42 (m, 2H), 1.24 – 1.08 (m, 2H), 0.77 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 200.4 (C_q), 191.3 (C_q), 173.5 (C_q), 170.6 (C_q), 139.4 (C_q), 135.4 (CH), 133.4 (C_q), 129.7 (CH), 129.1 (CH), 126.3 (CH), 73.5 (CH), 41.2 (CH), 35.3 (CH_2), 25.6 (CH_3), 25.4 (CH_2), 21.7 (CH_2), 21.4 (CH_3), 13.6 (CH_3). **IR** (ATR): 2960, 2873, 1736, 1607, 1467, 1367, 1277, 1227, 1183, 1149 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 338 (100) $[M+Na]^+$. **HR-MS** (ESI) $C_{18}H_{21}NO_4Na$ $[M+ Na]^+$: 338.1363, found: 338.1363.

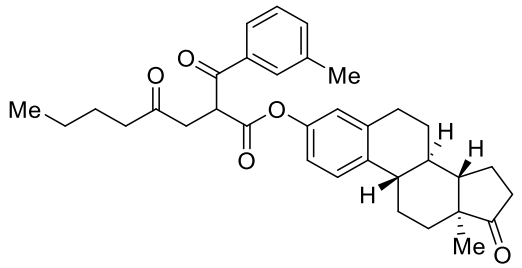
2-(Phenylsulfonyl)-1-(m-tolyl)octane-1,4-dione (43)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %),

$NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), (vinylsulfonyl)benzene (67.2 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 3/1) to obtain **43** as colorless oil (55.0 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 – 7.68 (m, 3H), 7.63 – 7.62 (m, 1H), 7.61 – 7.55 (m, 1H), 7.47 – 7.42 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 1H), 5.53 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.50 (dd, *J* = 18.0, 10.8 Hz, 1H), 3.29 (dd, *J* = 18.0, 3.0 Hz, 1H), 2.46 – 2.41 (m, 2H), 2.34 (s, 3H), 1.55 – 1.43 (m, 2H), 1.31 – 1.20 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 206.5 (C_q), 191.6 (C_q), 138.7 (C_q), 136.7 (C_q), 136.5 (C_q), 134.6 (CH), 134.3 (CH), 129.5 (CH), 129.3 (CH), 129.0 (CH), 128.4 (CH), 126.4 (CH), 65.4 (CH), 42.1 (CH_2), 40.7 (CH_2), 25.6 (CH_2), 22.1 (CH_2), 21.3 (CH_3), 13.7 (CH_3). **IR** (ATR): 2862, 1736, 1684, 1684, 1569, 1430, 1189, 1111, 1068, 690 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 395 (100) $[M+Na]^+$, 373 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{21}H_{25}O_4S$ $[M+H]^+$: 373.1468, found: 373.1464.

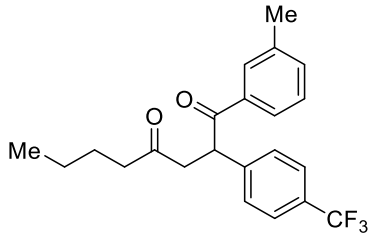
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 2-(3-methylbenzoyl)-4-oxooctanoate (44)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (86.2 mg, 1.0 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclo penta[*a*]phenanthren-3-yl acryl ate (130 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to obtain **44** as colorless oil (61.2 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.95 – 7.82 (m, 2H), 7.47 – 7.39 (m, 2H), 7.29 – 7.24 (m, 1H), 6.81 – 6.71 (m, 2H), 5.16 (t, *J* = 6.9 Hz, 1H), 3.29 (dd, *J* =

18.1, 6.9 Hz, 1H), 3.19 (dd, *J* = 18.1, 6.7 Hz, 1H), 2.93 – 2.83 (m, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 2.30 – 1.95 (m, 5H), 1.68 – 1.28 (m, 12H), 0.92 (d, *J* = 4.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 220.7 (C_q), 207.7 (C_q), 194.7 (C_q), 168.4 (C_q), 148.3 (C_q), 138.7 (C_q), 138.0 (C_q), 137.7 (C_q), 135.7 (C_q), 134.6 (CH), 129.4 (CH), 128.7 (CH), 126.3 (CH), 126.1 (CH), 121.2 (CH), 118.4 (CH), 50.4 (CH), 48.9 (C_q), 47.9 (CH), 44.1 (CH), 42.5 (CH), 41.4 (CH_2), 37.9 (CH_2), 36.2 (CH_2), 35.8 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 26.3 (CH_2), 25.8 (CH_2), 25.7 (CH_2), 22.2 (CH_2), 21.5 (CH_3), 21.4 (CH_3), 13.8 (CH_3). **IR** (ATR): 2959, 1737, 1674, 1569, 1466, 1394, 1154, 1015, 769, 470 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 551 (100) $[M+Na]^+$, 529 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{34}H_{41}O_5$ $[M+H]^+$: 529.2949, found: 529.2955.

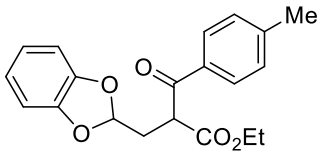
1-(*m*-tolyl)-2-(4-(trifluoromethyl)phenyl)octane-1,4-dione (45)



The reaction of sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), 3-methylbenzoyl chloride (30.8 mg, 0.20 mmol), valeraldehyde (103.4 mg, 1.2 mmol), 4-(trifluoromethyl)styrene (137.6 mg, 0.80 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) in acetone (1.0 mL) under N_2. After 24 h, purification by column chromatography on silica gel (*n*-hexane/EtOAc = 20/1) to obtain **45** as colorless oil (21.1 mg, 28% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 – 7.76 (m, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.29 (m, 2H), 5.25 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.62 (dd, *J* = 17.9, 9.8 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.59 – 2.42 (m, 2H), 2.40 (s, 3H), 1.65 – 1.54 (m, 2H), 1.38 – 1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 208.7 (C_q), 198.5 (C_q), 142.7 (d, *J* = 1.5 Hz, C_q), 138.4 (C_q), 136.0 (C_q), 134.0 (C_q), 129.5 (q, *J* = 32.6 Hz, CH), 129.2 (CH), 128.43 (CH), 128.42 (CH), 126.04 (q, *J* = 7.1 Hz, CH), 126.03 (CH), 124.0 (q, *J* = 272.1 Hz, C_q), 48.1 (CH), 47.0 (CH_2), 42.5 (CH_2), 25.7 (CH_2), 22.2 (CH_2), 21.3 (CH_3), 13.8 (CH_3). **^{19}F NMR** (377

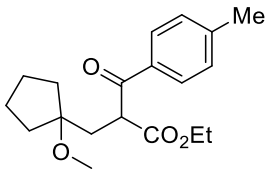
MHz, $CDCl_3$): δ = -62.6. **IR** (ATR): 2940, 2855, 1980, 1865, 1774, 1652, 1473, 1020, 945, 886 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 399 (100) $[M+Na]^+$, 377 (5) $[M+H]^+$. **HR-MS** (ESI) $C_{22}H_{24}F_3O_2$ $[M+H]^+$: 377.1723, found: 377.1728.

Ethyl 2-(benzo[d][1,3]dioxol-2-ylmethyl)-3-oxo-3-(p-tolyl)propanoate (46)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 1,3-benzodioxole (244 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **46** as colorless oil (46.9 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.92 – 7.85 (m, 2H), 7.25 – 7.22 (m, 2H), 6.82 – 6.71 (m, 3H), 6.70 – 6.61 (m, 1H), 6.23 (t, *J* = 4.3 Hz, 1H), 4.69 (t, *J* = 6.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.78 – 2.63 (m, 2H), 2.40 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 193.7 (C_q), 169.1 (C_q), 147.3 (C_q), 144.6 (C_q), 133.2 (C_q), 129.3 (CH), 128.9 (CH), 121.5 (CH), 109.2 (CH), 108.6 (CH), 61.7 (CH_2), 47.9 (CH), 33.5 (CH_2), 21.6 (CH_3), 13.9 (CH_3). **IR** (ATR): 2958, 1737, 1679, 1607, 1409, 1367, 1270, 1183, 1028, 717 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 363 (100) $[M+Na]^+$, 341 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{20}H_{21}O_5$ $[M+H]^+$: 341.1384, found: 341.1384.

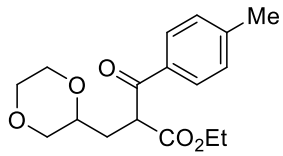
Ethyl 2-((1-methoxycyclopentyl)methyl)-3-oxo-3-(p-tolyl)propanoate (47)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), methoxycyclopentane (200 mg, 2.0 mmol), ethyl acrylate (40.0 mg,

0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **47** as colorless oil (25.4 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.94 – 7.89 (m, 2H), 7.26 – 7.24 (m, 2H), 4.55 (dd, *J* = 6.6, 5.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.00 (s, 3H), 2.40 (dd, *J* = 14.9, 6.6 Hz, 1H), 2.39 (s, 3H), 2.31 (dd, *J* = 14.9, 5.4 Hz, 1H), 1.86 – 1.76 (m, 1H), 1.69 – 1.53 (m, 5H), 1.46 – 1.39 (m, 1H), 1.34 – 1.31 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 191.4 (C_q), 172.9 (C_q), 145.9 (C_q), 135.0 (C_q), 130.7 (CH), 128.0 (CH), 86.0 (C_q), 61.4 (CH_2), 49.8 (CH), 49.3 (CH_3), 35.6 (CH_2), 35.5 (CH_2), 34.4 (CH_2), 23.4 (CH_2), 23.3 (CH_2), 21.6 (CH_3), 13.9 (CH_3). **IR** (ATR): 2959, 1736, 1712, 1608, 1412, 1367, 1256, 1183, 854, 682 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 341 (100) $[M+Na]^+$, 319 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{27}O_4$ $[M+H]^+$: 319.1904, found: 319.1907.

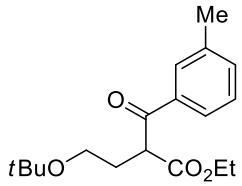
Ethyl 2-((1,4-dioxan-2-yl)methyl)-3-oxo-3-(p-tolyl)propanoate (48)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 1,4-dioxane (176 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **48** as colorless oil (37.3 mg, 61% yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.89 – 7.78 (m, 2H), 7.43 – 7.33 (m, 2H), 4.65 – 4.62 (m, 1H), 4.22 – 4.08 (m, 2H), 3.78 – 3.44 (m, 6H), 3.29 – 3.26 (m, 1H), 2.42 (s, 3H), 2.17 – 2.14 (m, 1H), 1.95 – 1.92 (m, 1H), 1.17 – 1.14 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 195.5 (C_q), 169.9 (C_q), 169.7 (C_q), 138.5 (C_q), 136.6 (C_q), 135.8 (C_q), 134.3 (CH), 129.3 (CH), 129.2 (CH), 128.5 (CH), 126.1 (CH), 126.0 (CH), 73.2 (CH), 72.7 (CH), 71.1 (CH_2), 71.0 (CH_2), 66.7 (CH_2), 66.6 (CH_2), 66.4 (CH_2), 66.4 (CH_2), 61.4 (CH_2), 49.8 (CH), 49.2 (CH), 30.7 (CH_3), 30.6 (CH_3), 21.3 (CH_2), 14.0 (CH_3), 13.9 (CH_3). **IR** (ATR): 1736, 1681, 1607, 1448, 1331, 1272, 1215, 1182, 759,

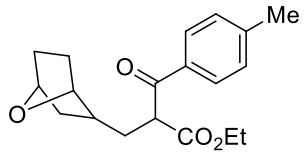
698 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 329 (100) $[M+Na]^+$, 307 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{17}H_{23}O_5$ $[M+H]^+$: 307.1540, found: 307.1543.

Ethyl 4-butoxy-2-(3-methylbenzoyl)butanoate (49)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 2-methoxy-2-methylpropane (176 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **49** as colorless oil (37.9 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 – 7.80 (m, 2H), 7.39 – 7.32 (m, 2H), 4.63 (dd, J = 7.3, 6.5 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.42 – 3.38(m, 2H), 2.41 (s, 3H), 2.28 – 2.17 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H), 1.11 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 196.1 (C_q), 170.2 (C_q), 138.4 (C_q), 136.3 (C_q), 134.2 (CH), 129.4 (CH), 128.5 (CH), 126.1 (CH), 72.8 (C_q), 61.2 (CH_2), 58.7 (CH_2), 50.7 (CH), 30.0 (CH_2), 27.4 (CH_3), 21.4 (CH_3), 14.1 (CH_3). **IR** (ATR): 1745, 1736, 1686, 1564, 1276, 1259, 1159, 765, 748, 463 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 329 (100) $[M+Na]^+$, 307 (10) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{27}O_4$ $[M+H]^+$: 307.1904, found: 307.1908.

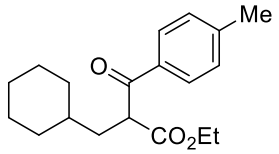
Ethyl 2-((7-oxabicyclo[2.2.1]heptan-2-yl)methyl)-3-oxo-3-(p-tolyl)propano ate (50)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 7-oxabicyclo[2.2.1]heptane (196 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel

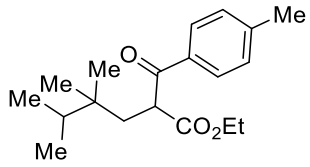
column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **50** as colorless oil (36.6 mg, 58% yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.86 (m, 2H), 7.28 – 7.25 (m, 2H), 4.55 (dd, *J* = 7.3, 3.7 Hz, 1H), 4.34 – 4.21 (m, 2H), 4.15 – 4.11 (m, 2H), 2.41 (s, 3H), 2.20 – 2.07 (m, 1H), 1.88 – 1.59 (m, 5H), 1.40 – 1.27 (m, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 194.7 (C_q), 170.1 (C_q), 144.5 (C_q), 133.8 (C_q), 129.5 (CH), 128.7 (CH), 80.2 (CH), 76.5 (CH), 61.4 (CH_2), 52.2 (CH), 41.4 (CH), 38.0 (CH_2), 34.4 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 21.7 (CH_3), 14.0 (CH_3). **IR** (ATR): 2958, 2874, 1719, 1689, 1585, 1276, 1260, 766, 748, 416 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 339 (100) $[M+Na]^+$, 317 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{25}O_4$ $[M+H]^+$: 317.1747, found: 317.1751.

Ethyl 2-(cyclohexylmethyl)-3-oxo-3-(p-tolyl)propanoate (51)



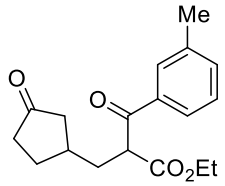
The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), cyclohexane (168 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **51** as colorless oil (33.8 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.38 (dd, *J* = 8.0, 6.3 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.90 – 1.88 (m, 1H), 1.86 – 1.82 (m, 2H), 1.71 – 1.60 (m, 4H), 1.28 – 1.11 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 1H), 0.95 – 0.87 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 195.0 (C_q), 170.4 (C_q), 144.3 (C_q), 133.7 (C_q), 129.4 (CH), 128.7 (CH), 61.2 (CH_2), 51.7 (CH), 36.3 (CH_2), 35.8 (CH), 33.3 (CH_2), 33.0 (CH_2), 26.4 (CH_2), 26.09 (CH_2), 26.07 (CH_2), 21.6 (CH_3), 14.0 (CH_3). **IR** (ATR): 1718, 1652, 1560, 1477, 1264, 896, 765, 732, 702, 668 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 325 (100) $[M+Na]^+$, 303 (30) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{27}O_3$ $[M+H]^+$: 303.1955, found: 303.1955.

Ethyl 4,4,5-trimethyl-2-(4-methylbenzoyl)hexanoate (52)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), 2,3-dimethylbutane (172 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **52** as colorless oil (42.3 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 4.36 (t, *J* = 5.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.05 (dd, *J* = 5.9, 4.0 Hz, 2H), 1.52 – 1.45 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.79 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 195.2 (C_q), 170.8 (C_q), 144.3 (C_q), 133.7 (C_q), 129.4 (CH), 128.9 (CH), 61.4 (CH_2), 50.2 (CH), 38.0 (C_q), 36.3 (CH), 35.6 (CH_2), 24.1 (CH_3), 23.9 (CH_3), 21.7 (CH_3), 17.5 (CH_3), 14.0 (CH_3). **IR** (ATR): 2958, 1736, 1713, 1673, 1511, 1466, 1260, 1028, 844, 748 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 327 (100) $[M+Na]^+$, 305 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{29}O_3$ $[M+H]^+$: 327.1931, found: 327.1932.

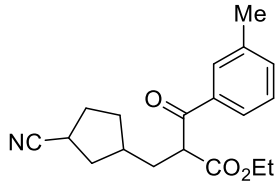
Ethyl 3-oxo-2-((3-oxocyclopentyl)methyl)-3-(m-tolyl)propanoate (53)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), cyclopentanone (168 mg, 2.0 mmol.), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **53** as colorless oil (35.6 mg, 55%

yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.85 – 7.76 (m, 2H), 7.45 – 7.33 (m, 2H), 4.40 – 4.30 (m, 1H), 4.19 – 4.11 (q, *J* = 7.1, 2H), 2.42 (s, 3H), 2.30 – 2.12 (m, 7H), 1.90 – 1.81 (m, 1H), 1.58 – 1.56 (m, 1H), 1.17 (t, *J* = 7.1, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 218.4 (C_q), 194.8 (C_q), 169.8 (C_q), 138.8 (C_q), 136.1 (C_q), 134.6 (CH), 129.1 (CH), 128.7 (CH), 125.8 (CH), 61.6 (CH_2), 52.8 (CH), 45.0 (CH_2), 38.5 (CH_2), 35.4 (CH), 34.6 (CH_2), 29.6 (CH_2), 21.4 (CH_3), 14.0 (CH_3). **IR** (ATR): 1788, 1649, 1570, 1366, 1264, 1240, 1146, 909, 728, 702 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 325 (100) $[M+Na]^+$, 303 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{22}O_4Na$ $[M+Na]^+$: 325.1410, found: 325.1412.

Ethyl 2-((3-cyanocyclopentyl)methyl)-3-oxo-3-(m-tolyl)propanoate (54)

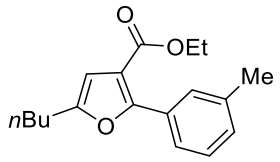


The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), cyclopentanecarbonitrile (190 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to obtain **54** as colorless oil (33.1 mg, 53% yield, r.r = 1.5/1, d.r. = 1.2/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.85 (m, 2H), 7.30 – 7.27 (m, 2H), 4.31 – 4.25 (m, 1H), 4.17 – 4.11 (m, 2H), 2.90 – 2.64 (m, 1H), 2.42 (s, 3H), 2.21 – 1.84 (m, 7H), 1.66 – 1.52 (m, 1H), 1.30 – 1.20 (m, 1H), 1.18 – 1.13 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 194.18 (C_q), 194.16 (C_q), 194.13 (C_q), 194.11 (C_q), 169.80 (C_q), 169.77 (C_q), 169.76 (C_q), 169.74 (C_q), 144.7 (CH), 133.5 (CH), 129.5 (CH), 128.70 (CH), 128.69 (CH), 123.2 (CH), 61.5 (CH_2), 61.5 (CH_2), 53.13 (CH), 53.03 (CH), 38.0 (CH_2), 37.97 (CH_2), 37.74 (CH_2), 37.69 (CH_2), 37.39 (CH_2), 37.4 (CH_2), 37.0 (CH_2), 34.2 (CH_2), 34.1 (CH_2), 34.0 (CH_2), 32.0 (CH_2), 31.9 (CH), 31.4 (CH), 30.8 (CH_2), 30.7 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 27.3 (CH_3), 27.2 (CH_3), 27.2 (CH_3), 21.7 (CH_3), 14.0 (CH_3). **IR** (ATR): 2982, 2190, 1962, 1732, 1397,

1286, 1181, 1163, 1019, 768 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 336 (100) $[M+Na]^+$, 314 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{19}H_{24}O_3N$ $[M+H]^+$: 314.1751, found: 314.1751.

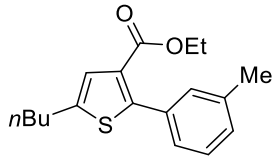
6. Synthetic Utility of the Method

Ethyl 5-butyl-2-(m-tolyl)furan-3-carboxylate (55)



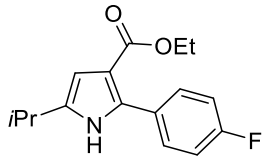
In a 10 mL round-bottom flask equipped with a magnetic stir bar, a mixture of 1,4-ketocarbonyl compound **4** (30.4 mg, 0.10 mmol) and p-toluenesulfonic acid (17.2 mg, 0.10 mmol) was added to toluene (1.0 mL) and the mixture was refluxed for 2 h. The reaction mixture was allowed to cool down to room temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **55** as colorless oil (26.3 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.91 – 7.68 (m, 2H), 7.31 – 7.25 (m, 1H), 7.21 – 7.09 (m, 1H), 6.43 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.74 – 2.55 (m, 2H), 2.41 (s, 3H), 1.73 – 1.62 (m, 2H), 1.47 – 1.37 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.9 (C_q), 155.9 (C_q), 155.3 (C_q), 137.5 (C_q), 130.1 (C_q), 129.7 (CH), 128.7 (CH), 127.9 (CH), 125.4 (CH), 114.2 (C_q), 107.9 (CH), 60.3 (CH_2), 29.9 (CH_2), 27.4 (CH_2), 22.2 (CH_2), 21.5 (CH_2), 14.2 (CH_3), 13.8 (CH_3). **IR** (ATR): 2959, 2849, 1718, 1558, 1464, 1276, 1230, 1134, 1040, 908, 733 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 309 (100) $[M+Na]^+$, 287 (40) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found: 287.1640.

Ethyl 5-butyl-2-(m-tolyl)thiophene-3-carboxylate (56)



In a 10 mL round-bottom flask equipped with a magnetic stir bar, a mixture of 1,4-ketocarbonyl compound **4** (30.4 mg, 0.10 mmol) and Lawesson's reagent (101 mg, 0.25 mmol) was added to anhydrous toluene (1.0 mL) and the mixture was refluxed for 24 h. The reaction mixture was allowed to cool down to room temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 20/1) to obtain **56** as colorless oil (24.7 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.29 – 7.25 (m, 3H), 7.17 – 7.16 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.82 – 2.73 (m, 2H), 2.38 (s, 3H), 1.71 – 1.64 (m, 2H), 1.46 – 1.39 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.6 (C_q), 148.6 (C_q), 144.2 (C_q), 137.4 (C_q), 133.7 (C_q), 130.4 (CH), 129.0 (CH), 127.7 (CH), 127.6 (C_q), 126.9 (CH), 126.5 (CH), 60.3 (CH_2), 33.5 (CH_2), 29.6 (CH_2), 22.2 (CH_2), 21.4 (CH_3), 14.1 (CH_3), 13.8 (CH_3). **IR** (ATR): 1735, 1654, 1554, 1460, 1226, 908, 733, 727, 701, 650 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 325 (100) $[M+Na]^+$, 303 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{18}H_{23}O_2S$ $[M+H]^+$: 303.1413, found: 303.1412.

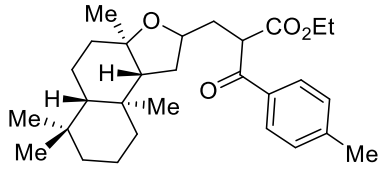
Ethyl 2-(3-fluorophenyl)-5-isopropyl-1H-pyrrole-3-carboxylate (57)



In a 10 mL round-bottom flask equipped with a magnetic stir bar, a mixture of ethyl 2-(4-fluorobenzoyl)-5-methyl-4-oxohexanoate (29.4 mg, 0.10 mmol) and ammonium acetate (77.0 mg, 1.0 mmol) was added to absolute ethanol (2.0 mL) and the mixture was refluxed for 24 h. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **57** as colorless oil (23.4 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.58 – 7.49 (m, 2H), 7.11 – 7.02 (m, 2H), 6.41 (dd, *J* = 3.0, 0.9 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.93 – 2.89 (m, 1H), 1.29 (d, *J* = 6.9 Hz,

6H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 165.1 (C_q), 162.5 (d, $J_{C\text{-}F}$ = 247.7 Hz, C_q), 138.9 (C_q), 134.8 (C_q), 130.8 (d, $J_{C\text{-}F}$ = 8.3 Hz,) (C_q), 128.5 (d, $J_{C\text{-}F}$ = 3.4 Hz, C_q), 115.0 (d, J = 21.6 Hz, CH), 111.9 (CH), 106.6 (CH), 59.6 (CH_2), 26.9 (CH), 22.4 (CH_3), 14.4 (CH_3). **IR** (ATR): 2960, 1665, 1529, 1492, 1444, 1220, 1113, 1095, 836, 780 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 298 (100) $[M+Na]^+$, 276 (40) $[M+H]^+$. **HR-MS** (ESI) $C_{16}H_{19}FNO_2$ $[M+H]^+$: 276.1394, found: 276.1398.

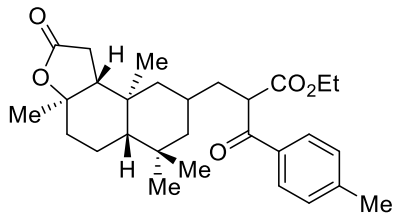
3-oxo-2-(((3a*R*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a tetramethyldodecahydronaphtho[2, 1-*b*]furan-2-yl)methyl)-3-(*p*-tolyl)propanoate (58)



The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), (10.0 mg, , 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), (-)-Ambroxide (236 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **58** as colorless oil (46.3 mg, 51% yield, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.97– 7.92 (m, 2H), 7.28 – 7.25 (m, 2H), 4.66 – 4.53 (m, 1H), 4.18 – 4.01 (m, 2H), 2.41 (m, 3H), 2.39 – 1.95 (m, 2H), 1.99 – 1.74 (m, 3H), 1.76 – 1.45 (m, 3H), 1.44 – 1.25 (m, 7H), 1.21 – 1.15 (m, 3H), 1.17 – 1.10 (m, 3H), 1.09– 1.02 (m, 2H), 0.85 – 0.82 (m, 3H), 0.81 – 0.77 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 195.44, 195.40, 170.4, 170.2, 134.2, 133.2, 129.3, 129.22, 129.19, 129.11, 129.05, 128.9, 81.3, 81.2, 73.3, 72.9, 61.23, 61.15, 59.1, 58.9, 57.2, 57.1, 57.0, 51.7, 50.6, 50.3, 42.43, 42.39, 42.3, 40.0, 39.9, 39.8, 39.7, 36.8, 36.5, 36.0, 33.5, 33.0, 33.0, 29.6, 28.6, 28.5, 21.6, 21.5, 21.1, 21.0, 20.5, 20.5, 18.4, 18.3, 18.3, 15.5, 15.0, 14.9, 14.0, 13.96. **IR** (ATR): 2956, 2730, 1818, 1678, 1530, 1227, 1110, 1061, 1040, 908, 756 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 477 (100) $[M+Na]^+$, 455 (20) $[M+H]^+$. **HR-MS** (ESI) $C_{29}H_{43}O_4$ $[M+H]^+$: 455.3156, found: 455.3151.

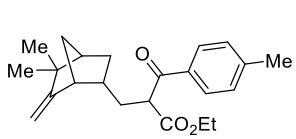
Ethyl 3-oxo-2-(((3a*R*,5a*S*,9a*S*,9b*R*)-3a,6,6,9a-tetramethyl-2-oxododecahy dronaph

tho[2,1-*b*]furan-8-yl)methyl)-3-(*p*-tolyl)propanoate (59)

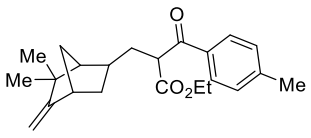


The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, , 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), Sclareolide (250 mg, 1.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **59** as colorless oil (43.9 mg, 47% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.85 (m, 2H), 7.29 – 7.27 (m, 2H), 4.39 – 4.27 (m, 1H), 4.17 – 4.11 (m, 2H), 2.42 (s, 3H), 2.40 – 2.34 (m, 1H), 2.21 – 2.16 (m, 1H), 2.09 – 2.03 (m, 1H), 2.00 – 1.77 (m, 4H), 1.69 – 1.57 (m, 2H), 1.54 – 1.37 (m, 2H), 1.37 – 1.32 (m, 1H), 1.31 (s, 3H), 1.29 – 1.19 (m, 2H), 1.19 – 1.15 (m, 3H), 1.03 – 0.96 (m, 1H), 0.93 – 0.85 (m, 6H), 0.83 – 0.71 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 194.70, 194.65, 176.64, 176.60, 170.2, 170.1, 144.50, 144.49, 129.49, 129.46, 129.4, 128.71, 128.66, 128.6, 86.23, 86.21, 61.4, 61.3, 59.04, 58.98, 59.0, 56.57, 56.56, 51.61, 51.58, 49.2, 48.8, 46.4, 46.1, 38.6, 38.6, 36.52, 36.51, 35.95, 35.9, 33.66, 33.65, 33.2, 33.1, 28.7, 28.64, 28.61, 27.13, 27.05, 21.66, 21.59, 21.55, 21.4, 21.3, 20.4, 15.8, 15.7, 14.1, 14.03, 13.99. **IR** (ATR): 3050, 2960, 1834, 1769, 1653, 1430, 1100, 975, 876, 693 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 491 (100) $[M+Na]^+$, 469 (40) $[M+H]^+$. **HR-MS** (ESI) $C_{29}H_{41}O_5$ $[M+H]^+$: 469.2949, found: 469.2952.

Ethyl 2-(((1*R*,2*R*,4*R*)-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-yl)methyl)-3-oxo-3-(*p*-tolyl)propanoate (59) and ethyl 2-(((1S,4S)-6,6-dimethyl-5-methylenebicyclo[2.2.1]heptan-2-yl)methyl)-3-oxo-3-(p-tolyl)propanoate (60´)



60 major

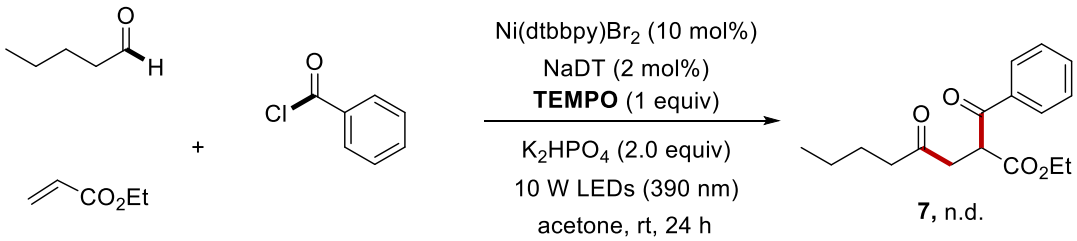


60' minor

The general procedure was followed using sodium decatungstate (10.0 mg, 2.0 mol %), $NiBr_2$•dtbbpy (10.0 mg, , 10 mol %), acetone (1.0 mL), 4-methylbenzoyl chloride (30.8 mg, 0.20 mmol), Camphene (272 mg, 2.0 mmol), ethyl acrylate (40.0 mg, 0.40 mmol), and K_2HPO_4 (69.6 mg, 0.40 mmol) and was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to obtain **60** as colorless oil (43.6 mg, 58% yield, yield, r.r = 1.2/1, d.r. = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 – 7.88 (m, 4H), 7.28 – 7.26 (m, 4H), 4.71 (s, 1H), 4.70 (s, 1H), 4.71 – 4.62 (m, 2H), 4.50 – 4.45 (m, 2H), 4.34 – 4.27 (m, 2H), 4.16 – 4.10 (m, 4H), 2.66 – 2.62 (m, 1H), 2.48 – 2.43 (m, 1H), 2.42 (s, 6H), 2.13 – 1.80 (m, 6H), 1.76 – 1.46 (m, 6H), 1.39 – 1.32 (m, 2H), 1.20 – 1.14 (m, 6H), 1.05 – 0.94 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 195.1, 195.0, 194.8, 194.7, 170.2, 170.1, 165.2, 165.1, 165.0, 144.4, 133.89, 133.87, 129.4, 128.72, 128.71, 128.67, 99.90, 99.86, 99.76, 99.67, 61.28, 52.89, 52.87, 52.69, 52.67, 52.6, 51.7, 51.5, 48.4, 47.0, 42.2, 41.3, 39.19, 39.15, 37.10, 37.06, 35.8, 35.6, 35.3, 35.2, 34.3, 34.2, 34.1, 34.0, 33.1, 33.0, 32.4, 32.3, 29.59, 29.55, 29.3, 25.58, 25.56, 25.2, 25.1, 21.7, 14.04, 14.01. **IR** (ATR): 2670, 1873, 1769, 1654, 1558, 1478, 1257, 1036, 937, 872 cm^{-1}. **MS** (ESI) *m/z* (relative intensity): 377 (100) $[M+Na]^+$, 355 (40) $[M+H]^+$. **HR-MS** (ESI) $C_{23}H_{30}O_3Na$ $[M+Na]^+$: 377.2087, found: 377.2096.

7. Mechanistic Investigations

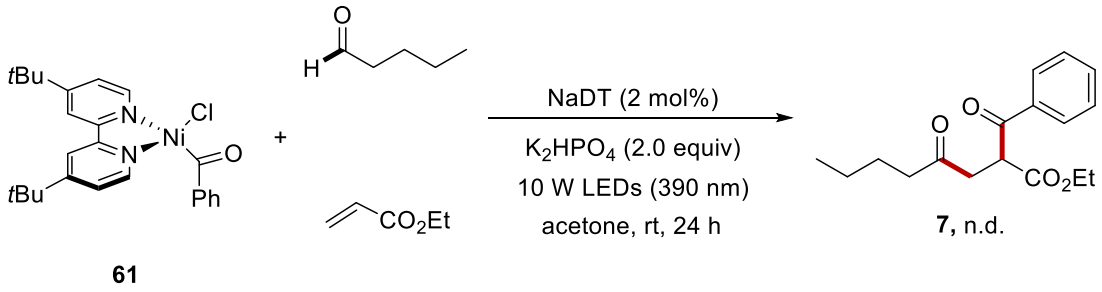
Addition of TEMPO (1.0 equiv.) strongly inhibited the three-component coupling reaction, suggesting that this transformation involved a radical intermediate.



Scheme S1. Radical inhibition experiment.

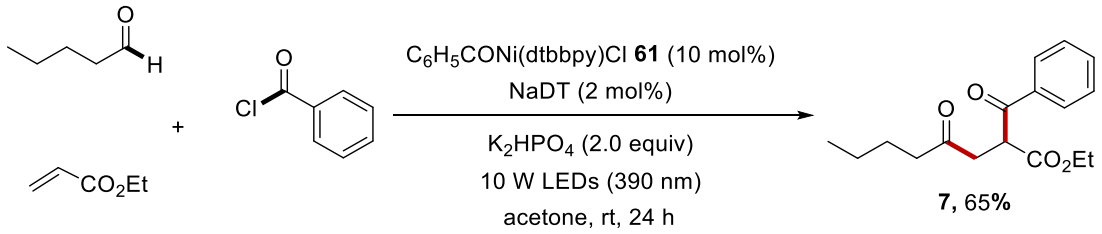
We have no found the corresponding 1,4-diketone **7** when the stoichiometric reaction

of nickel (II) complex **61** (prepared according to the previously reported procedure[3]) was treated with valeraldehyde (**1**) and ethyl acrylate (**2**), probably because of nickel (II) complex **59** instability with irradiation of a blue LED in the absence of acyl chlorides.



Scheme S2. The stoichiometric reaction of Ac-Ni (II) complex **61**.

The general procedure was followed using sodium decatungstate (10 mg, 0.004 mmol, 2.0 mol%), **61** (9.4 mg, 0.02 mmol, 10 mol%), acetone (1.0 mL), benzoyl chloride (28 mg, 0.20 mmol, 1.0 equiv.), valeraldehyde (86.2 mg, 1.0 mmol, 5.0 equiv.), ethyl acrylate (40.0 mg, 0.40 mmol, 2.0 equiv.), and K_2HPO_4 (69.6 mg, 0.40 mmol, 2.0 equiv.) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **7** as colorless oil (37.7 mg, 65% yield).



Scheme S3. The catalytic reaction of Ac-Ni (II) complex **61**.

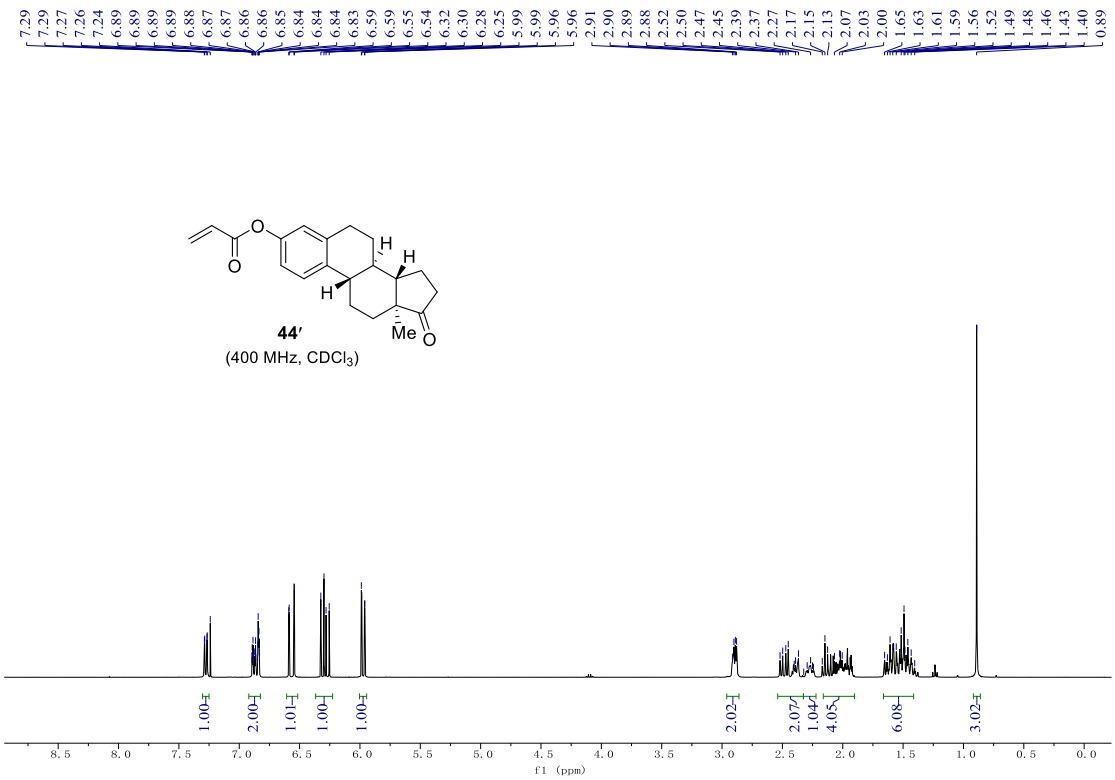
8. References

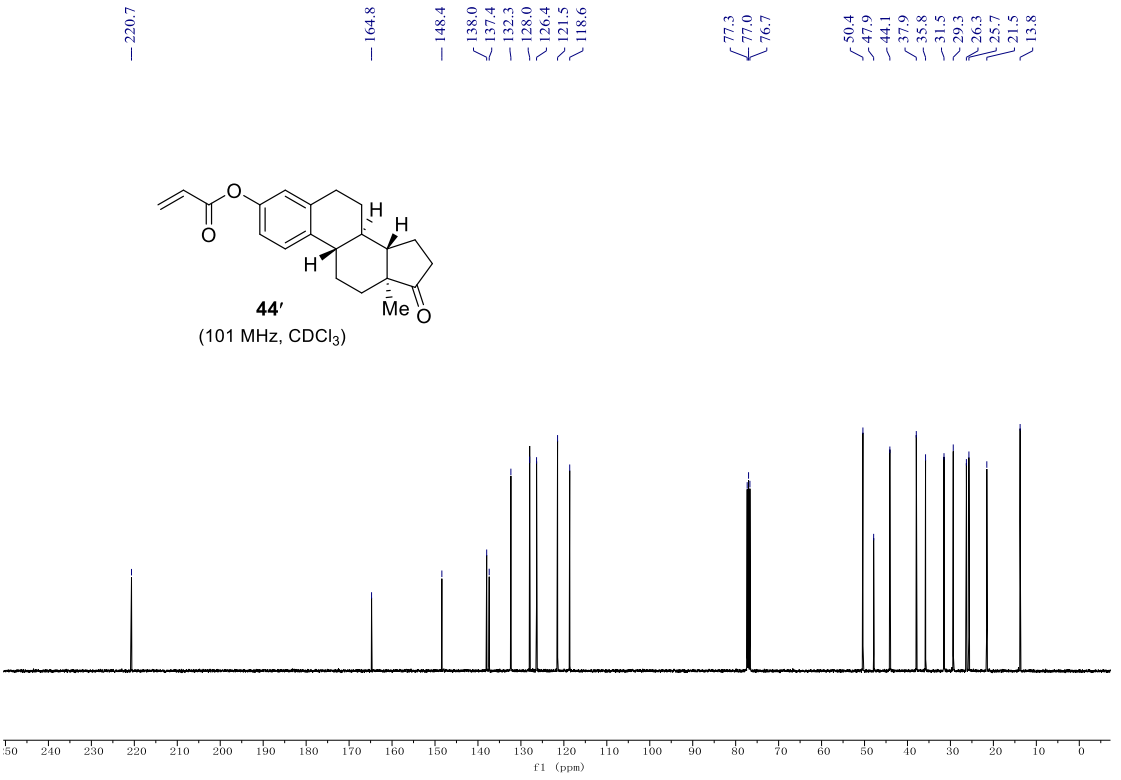
[1] P. J. Sarver, V. Bacauanu, D. M. Schultz, D. A. DiRocco, Y.-H. Lam, E. C. Sherer, D. W. C. MacMillan, *Nature* **2020**, *12*, 459-467.

[2] S. Xu, H. Chen, Z. Zhou, W. Kong, *Angew. Chem. Int. Ed.* **2021**, *60*, 7405–7411; *Angew. Chem.* **2021**, *133*, 7481-7487.

[3] Z. Sun, N. Kumagai, M. Shibasaki, *Org Lett*. **2017**, *19*, 3727-3730.

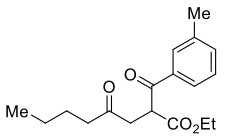
9. NMR Spectra





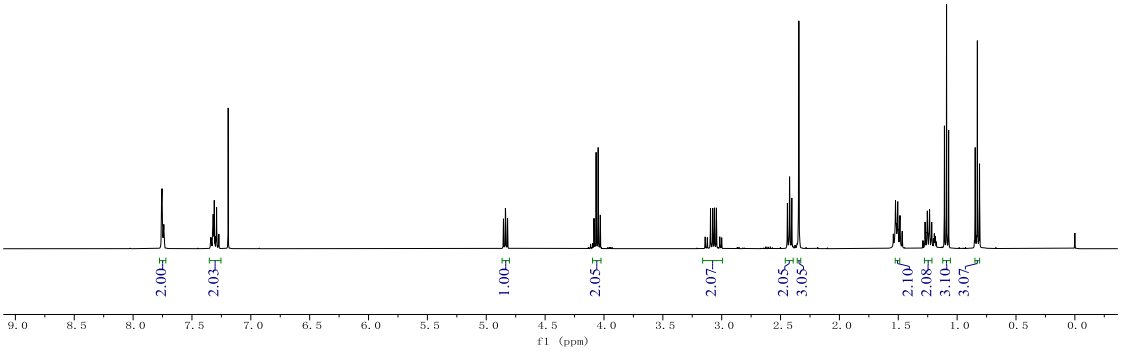
44′

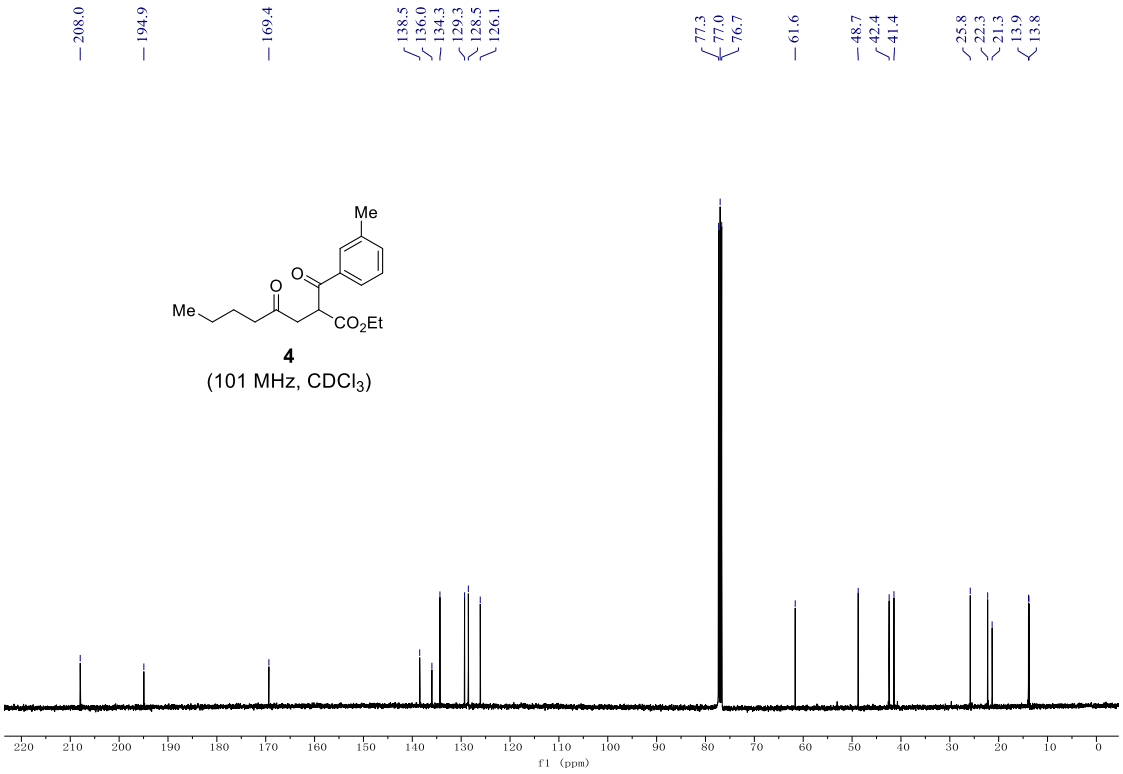
(101 MHz, $CDCl_3$)



4

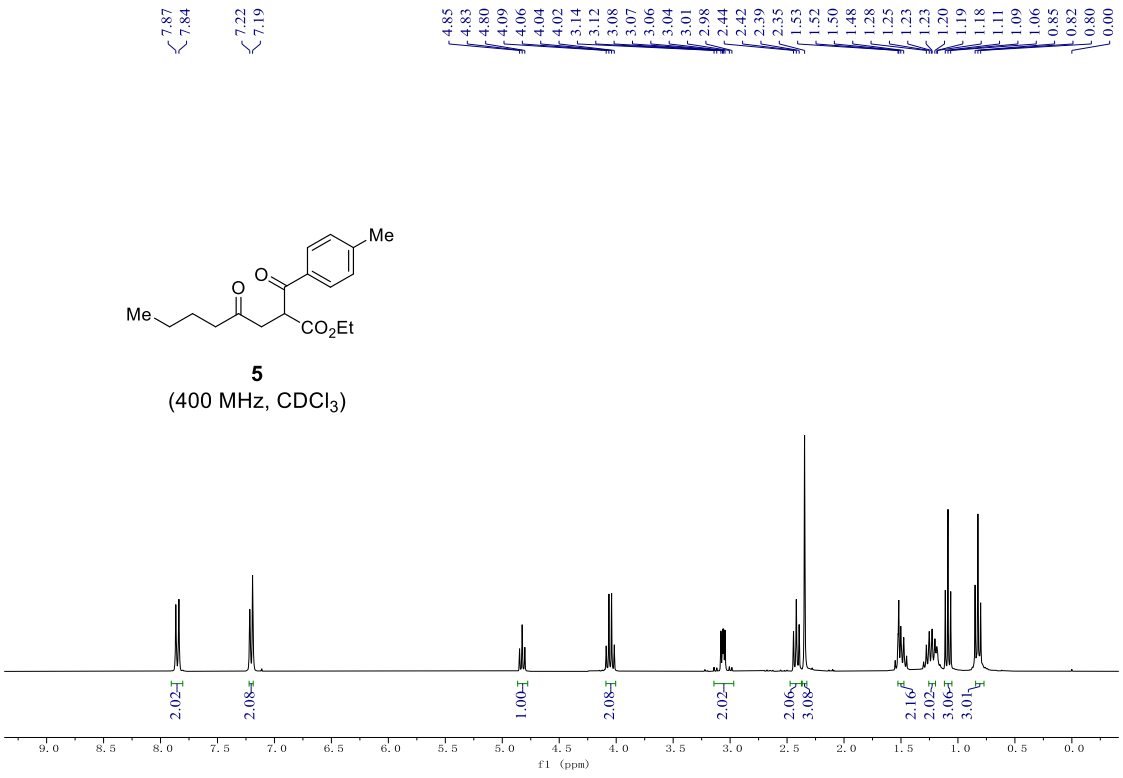
(400 MHz, $CDCl_3$)





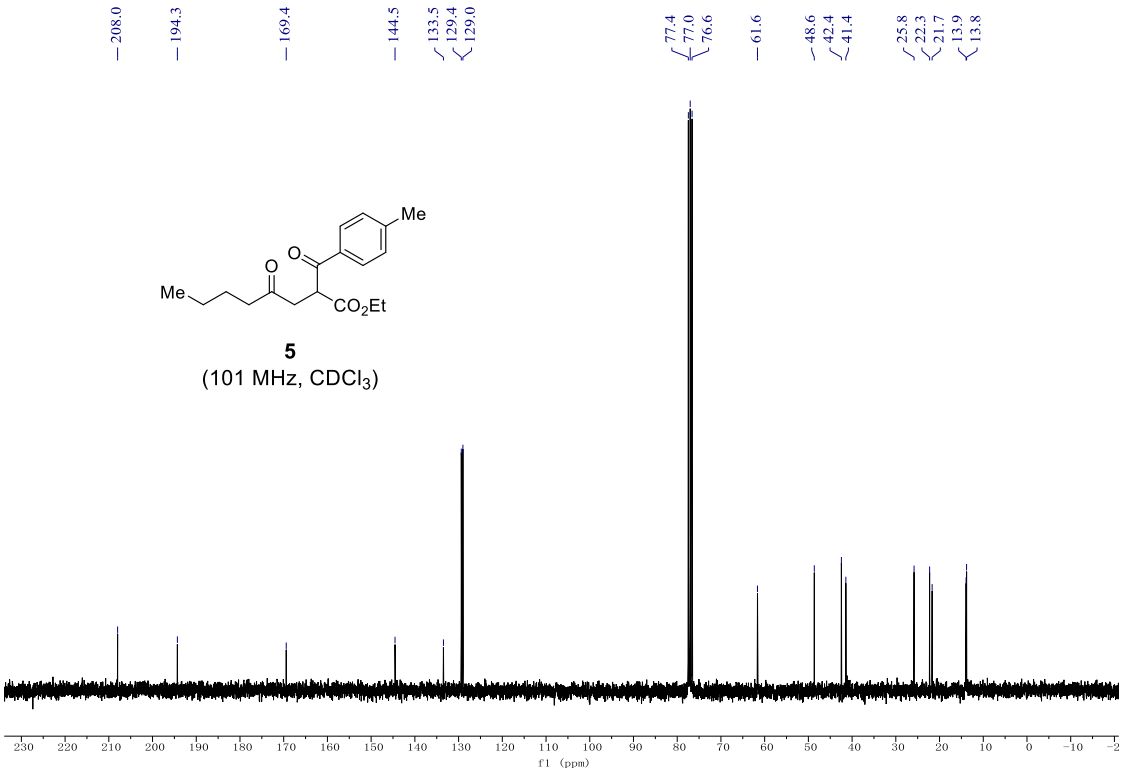
4

(101 MHz, $CDCl_3$)

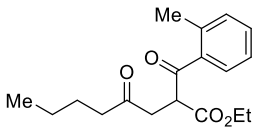


5

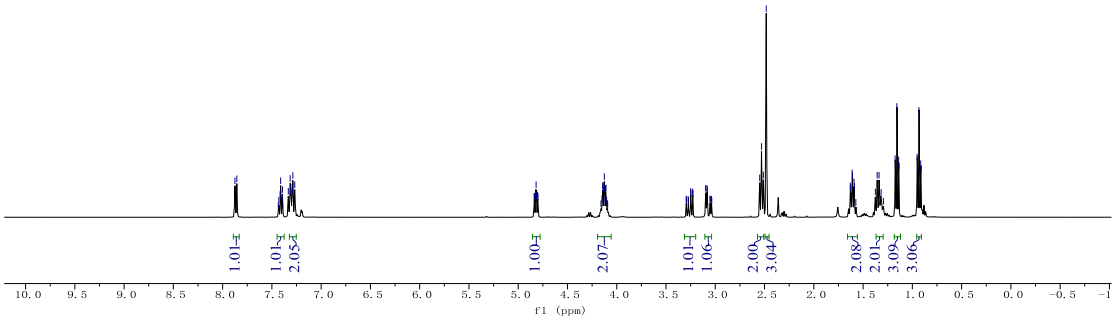
(400 MHz, $CDCl_3$)



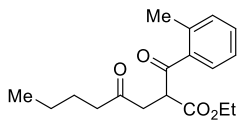
5
(101 MHz, $CDCl_3$)



6
(400 MHz, $CDCl_3$)

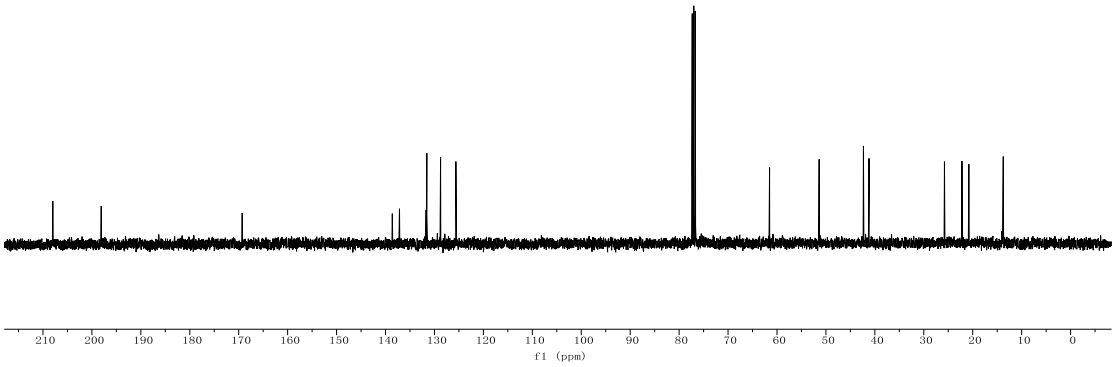


208.0
198.1
169.3
138.6
137.1
131.7
131.6
128.7
125.6
77.3
77.0
76.7
61.5
51.4
42.3
41.2
25.8
22.2
20.8
13.8
13.8



6

(101 MHz, $CDCl_3$)



8.01
8.01
8.00
7.99
7.99
7.99
7.98
7.58
7.56
7.56
7.55
7.54
7.54
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.24
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4.88
4.13
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1.13
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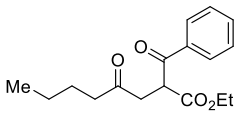
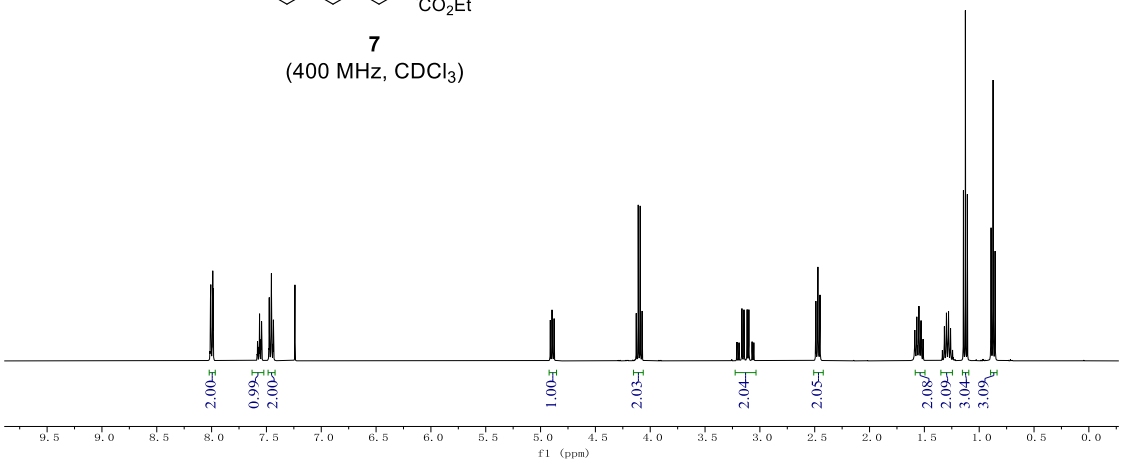
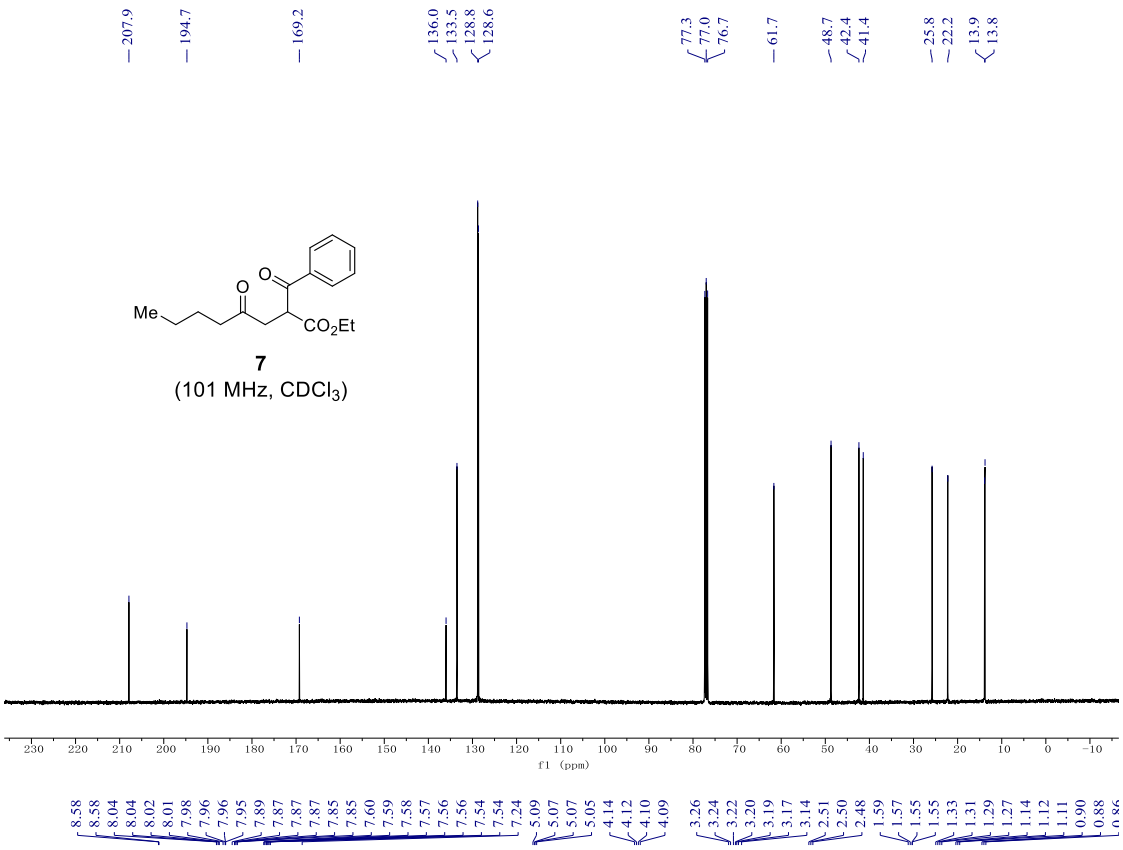
0.89
0.87
0.86



7

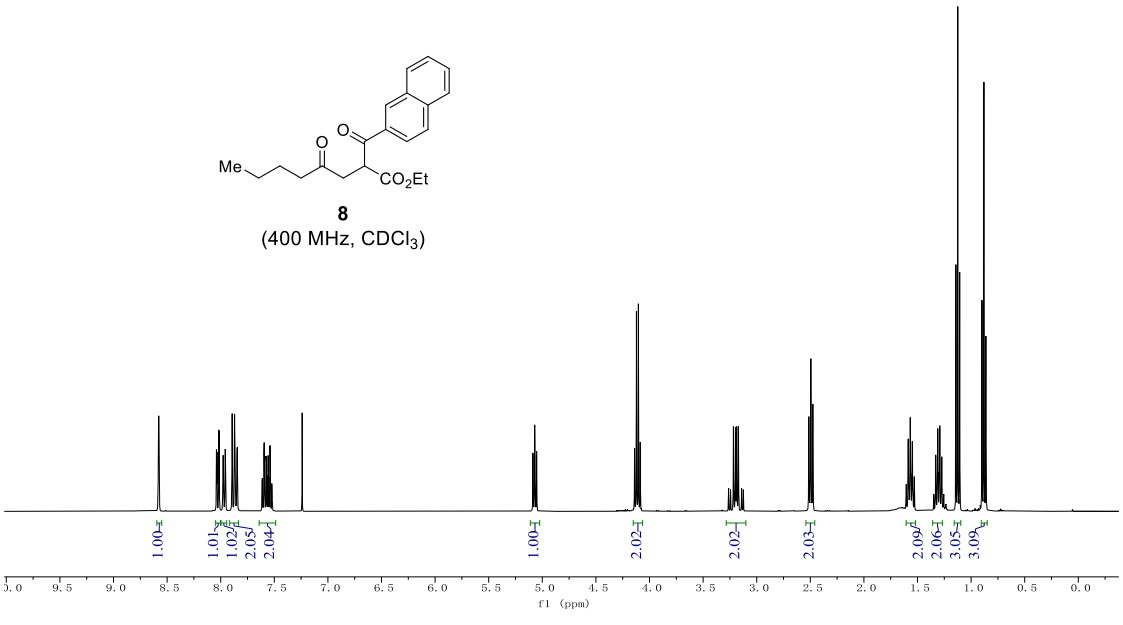
(400 MHz, $CDCl_3$)





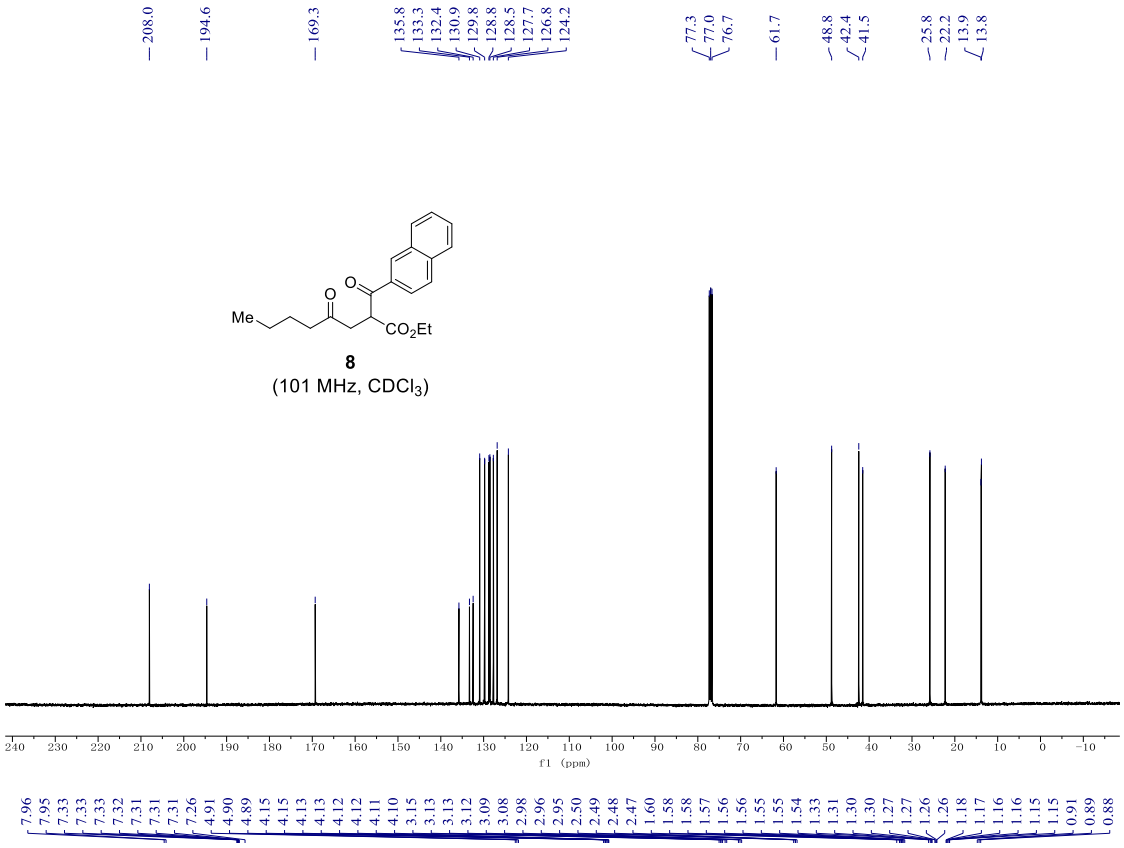
7

(101 MHz, $CDCl_3$)



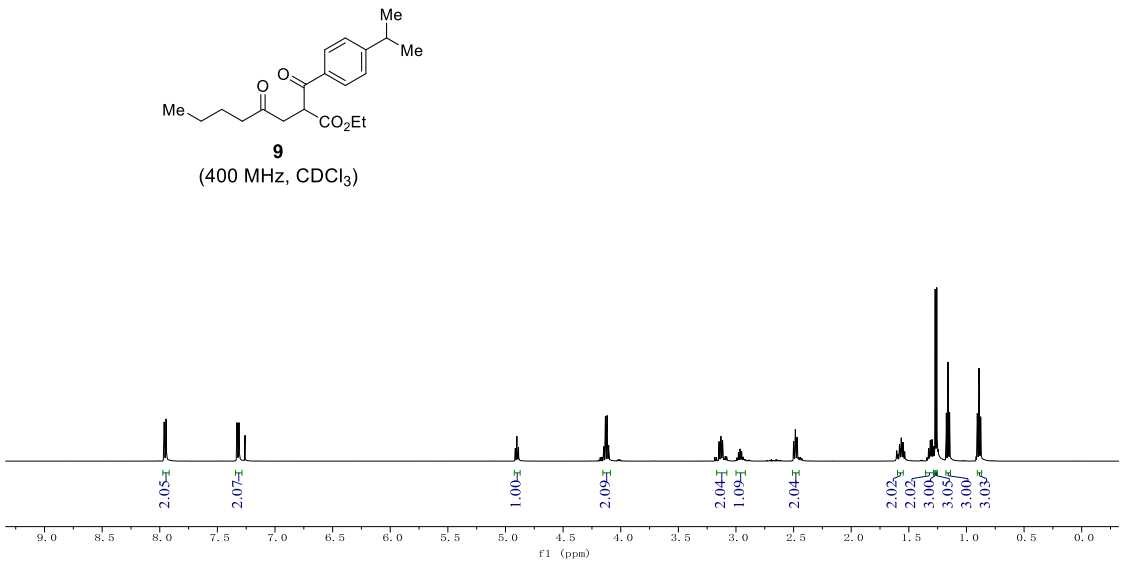
8

(400 MHz, $CDCl_3$)



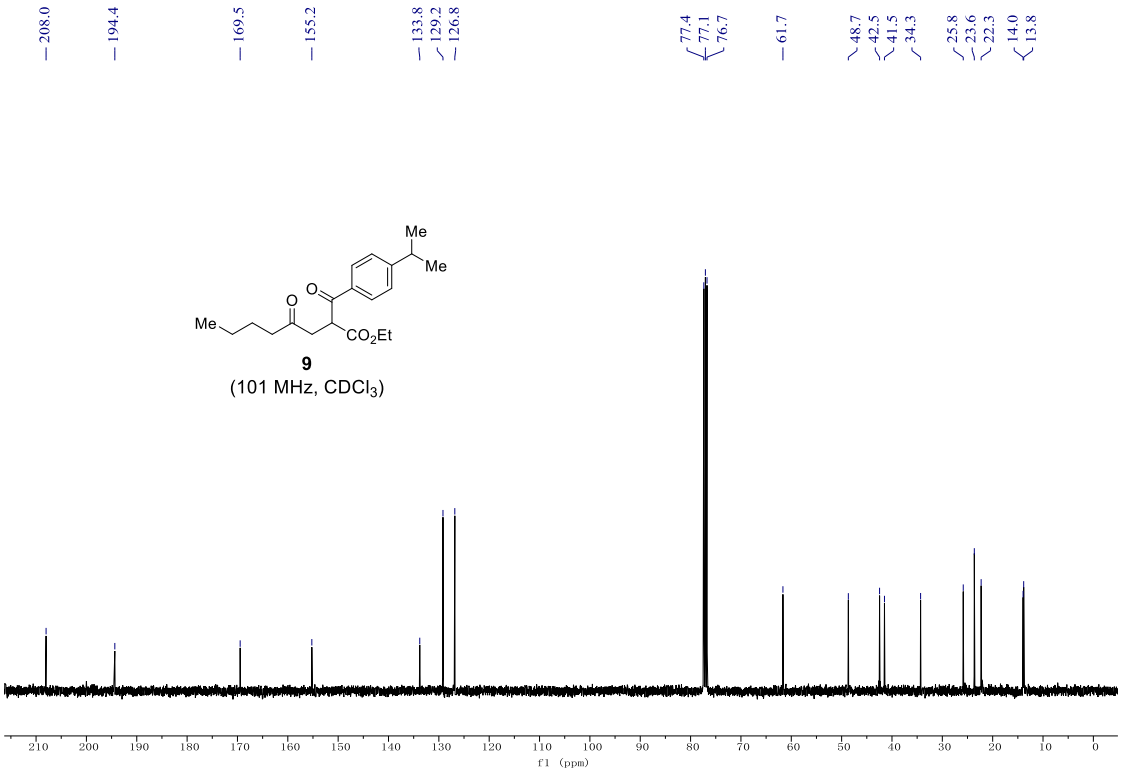
8

(101 MHz, $CDCl_3$)



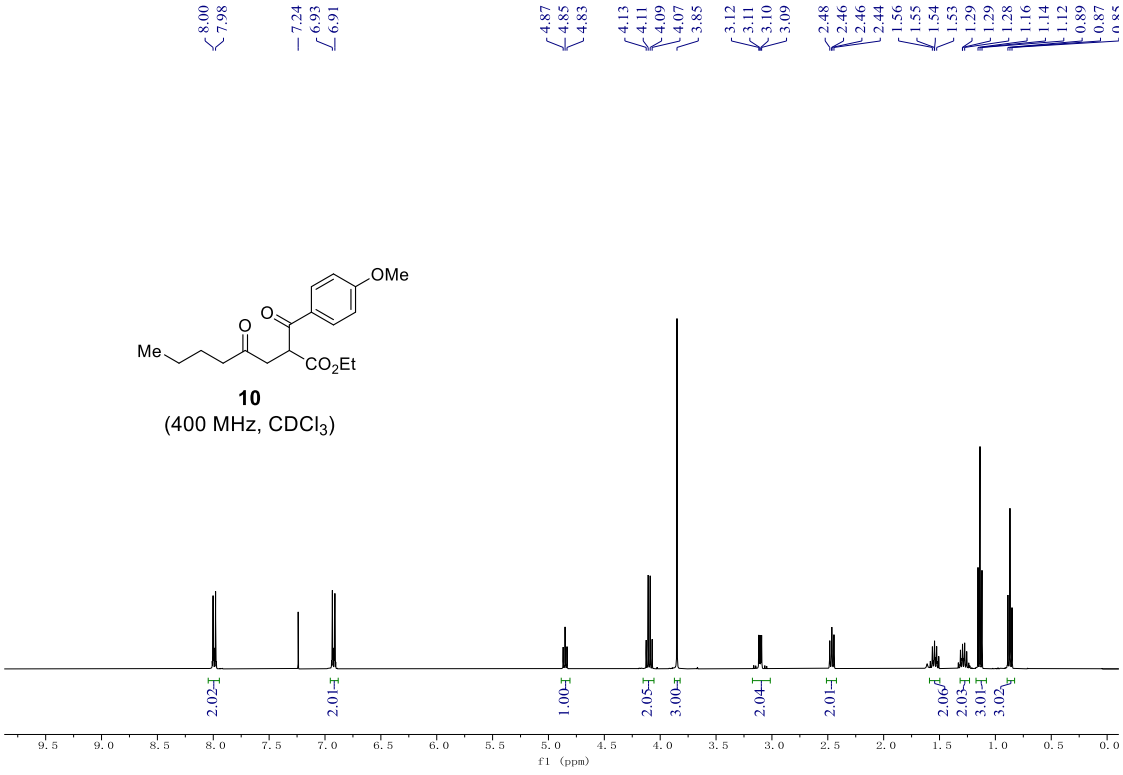
9

(400 MHz, $CDCl_3$)



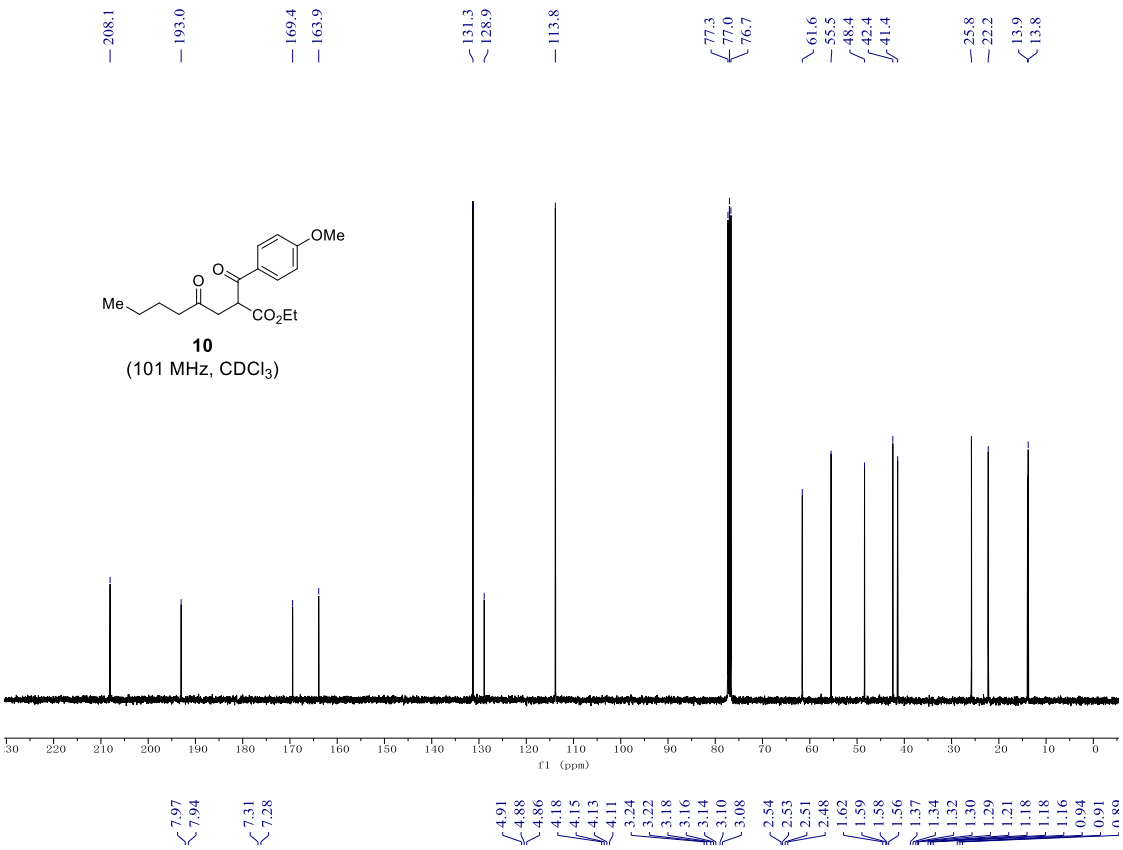
9

(101 MHz, $CDCl_3$)

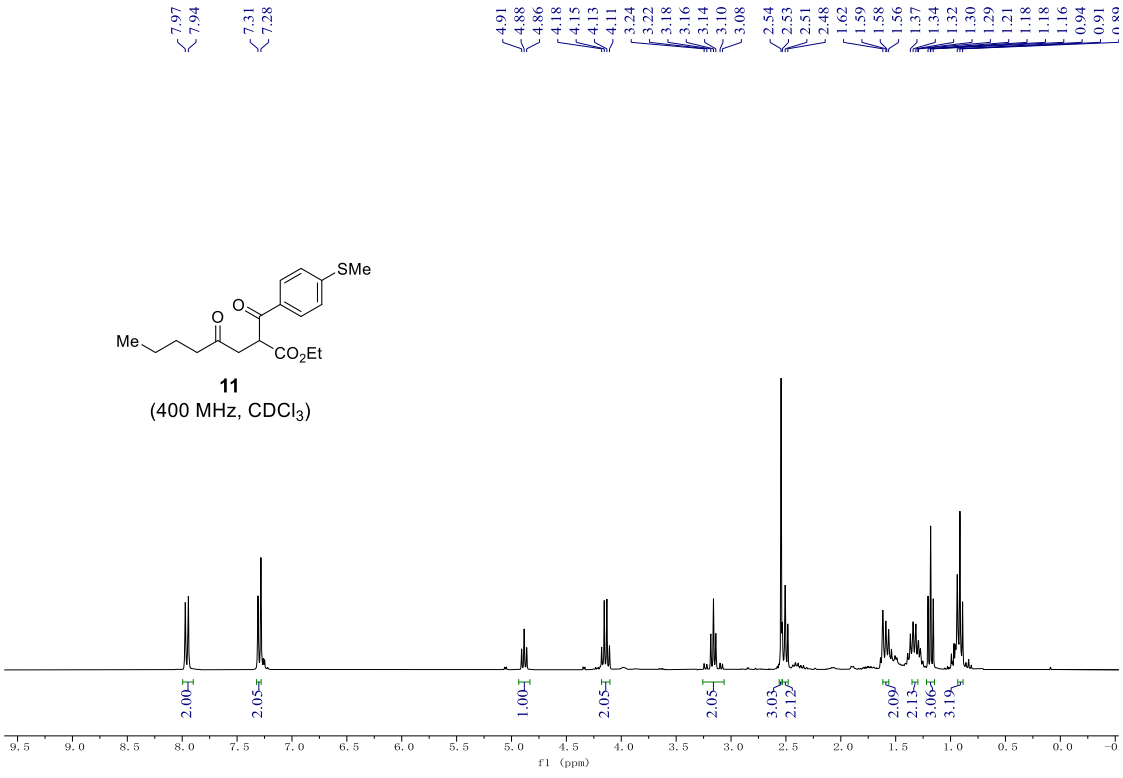


10

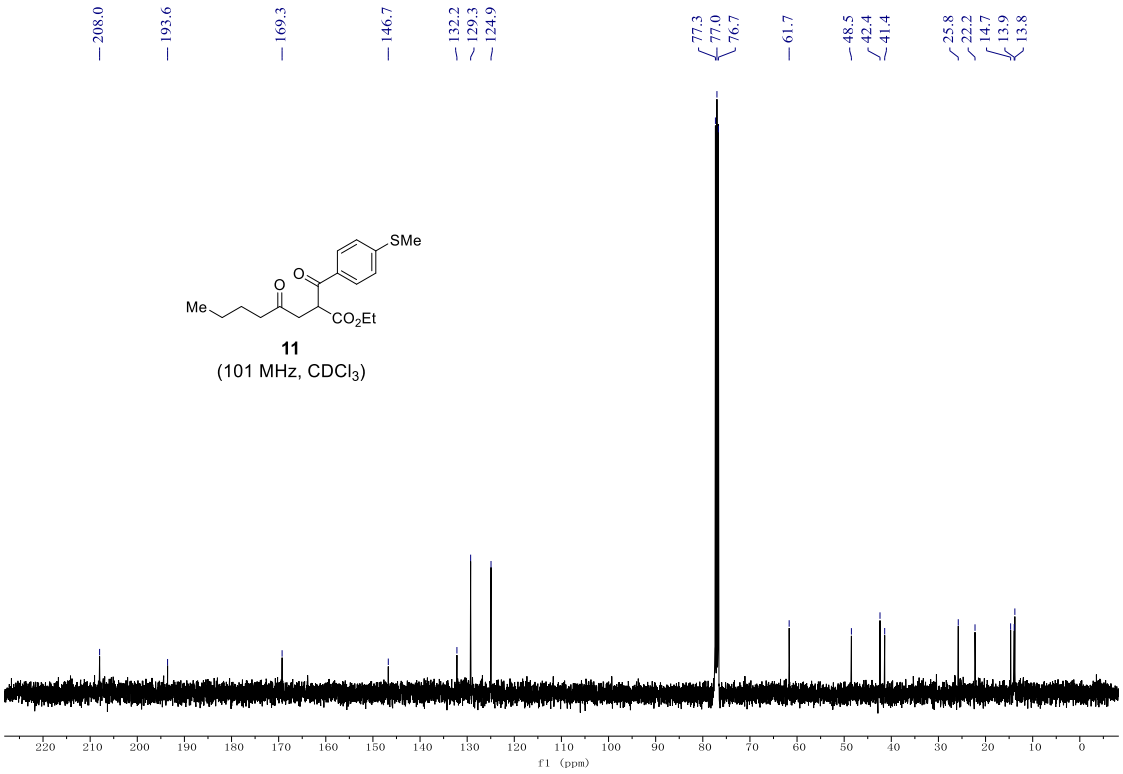
(400 MHz, $CDCl_3$)



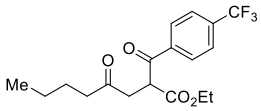
10
(101 MHz, $CDCl_3$)



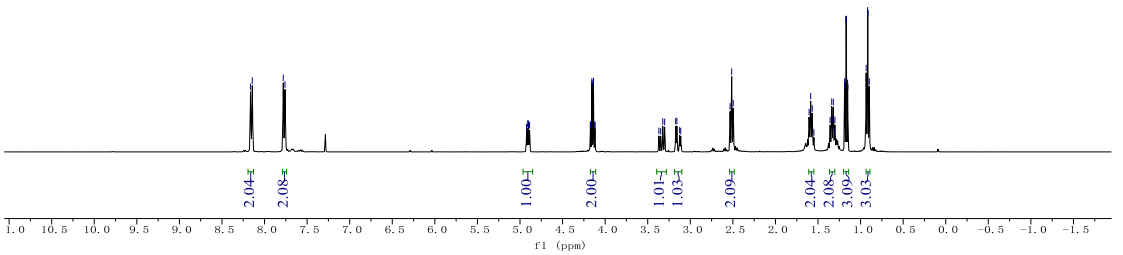
11
(400 MHz, $CDCl_3$)

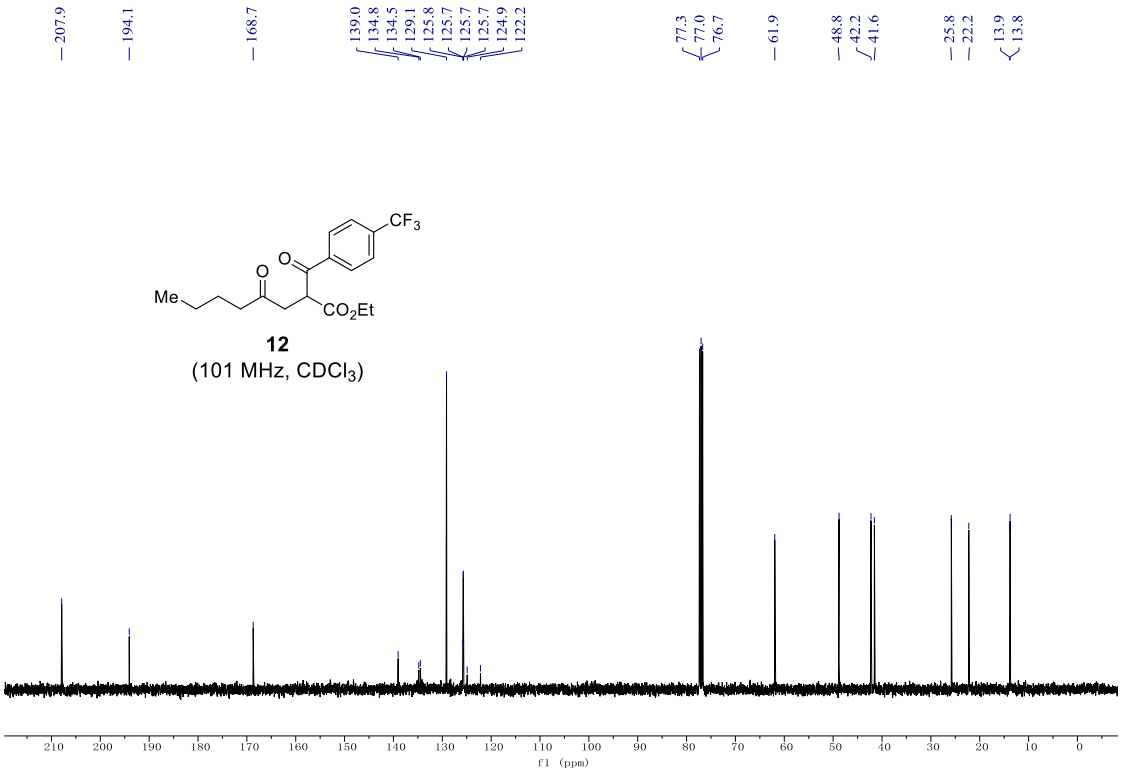


11
(101 MHz, $CDCl_3$)

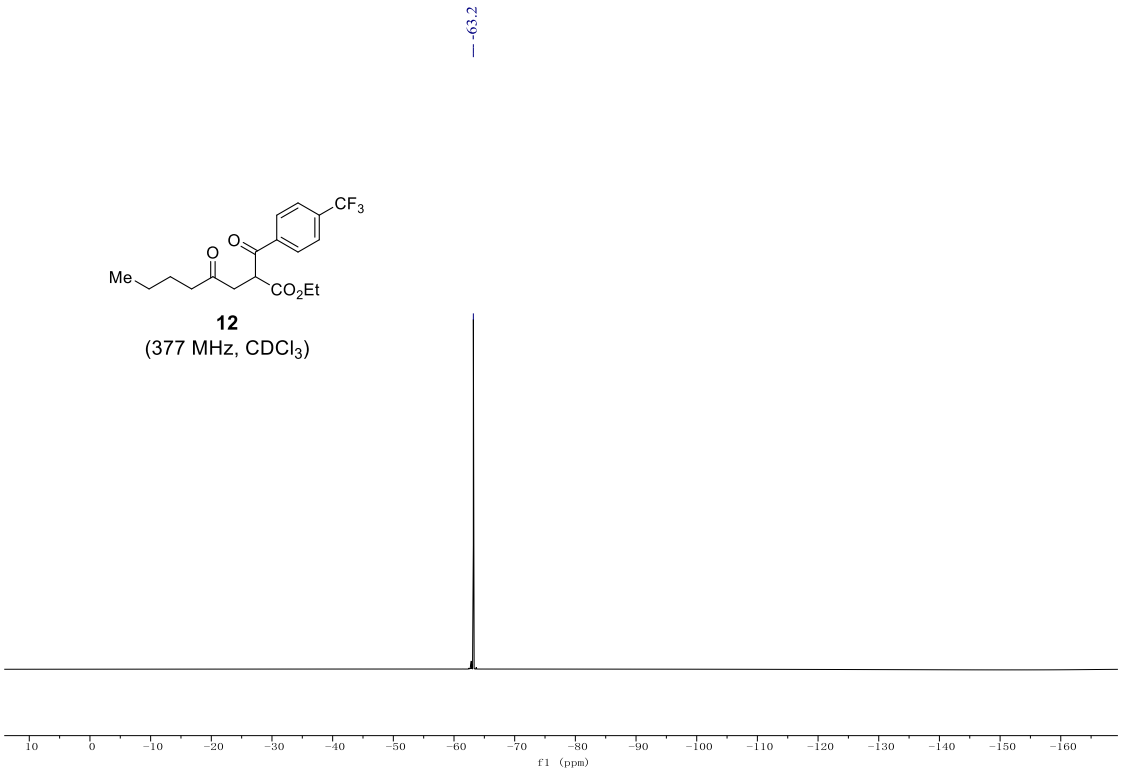


12
(400 MHz, $CDCl_3$)

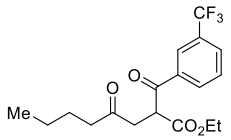




12
(101 MHz, $CDCl_3$)

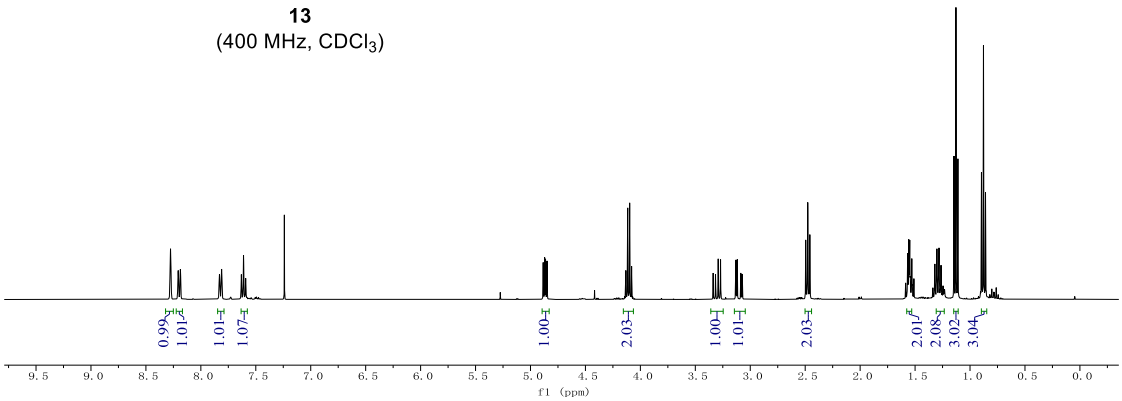


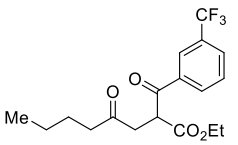
12
(377 MHz, $CDCl_3$)



13

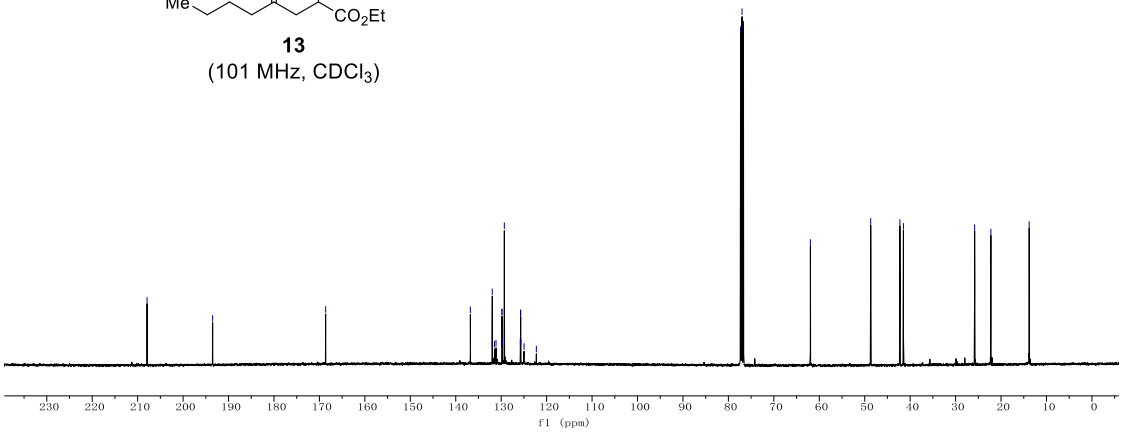
(400 MHz, $CDCl_3$)





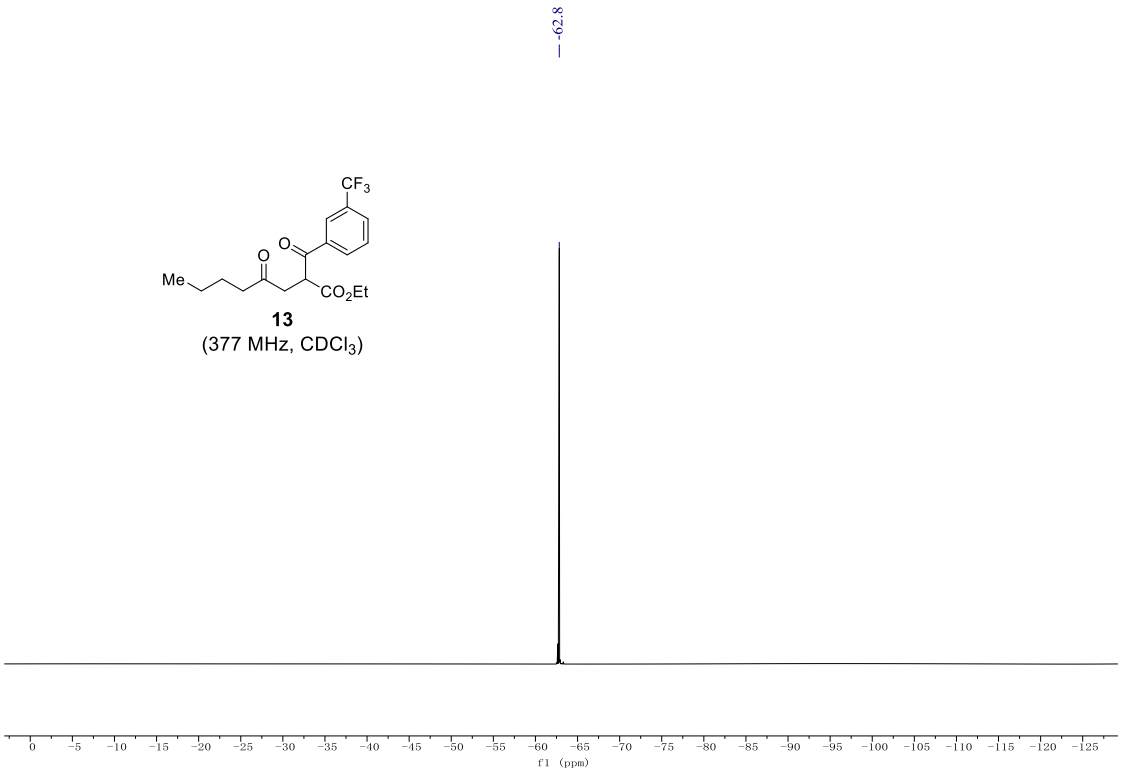
13

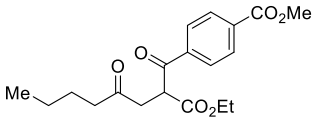
(101 MHz, $CDCl_3$)



13

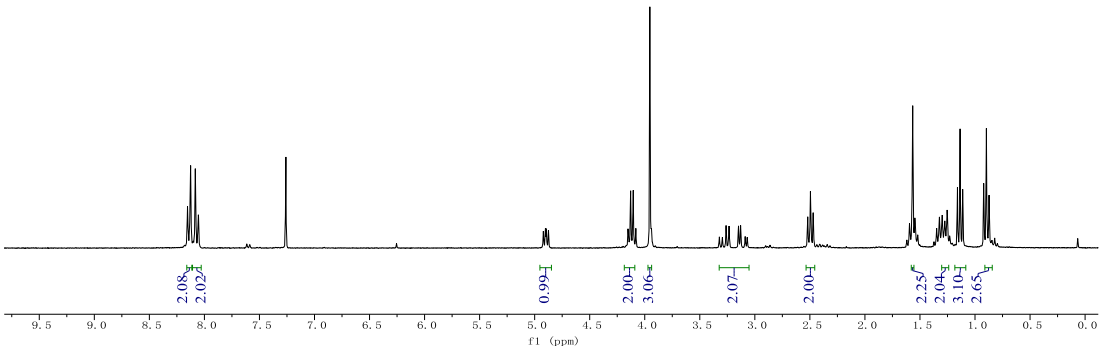
(377 MHz, $CDCl_3$)

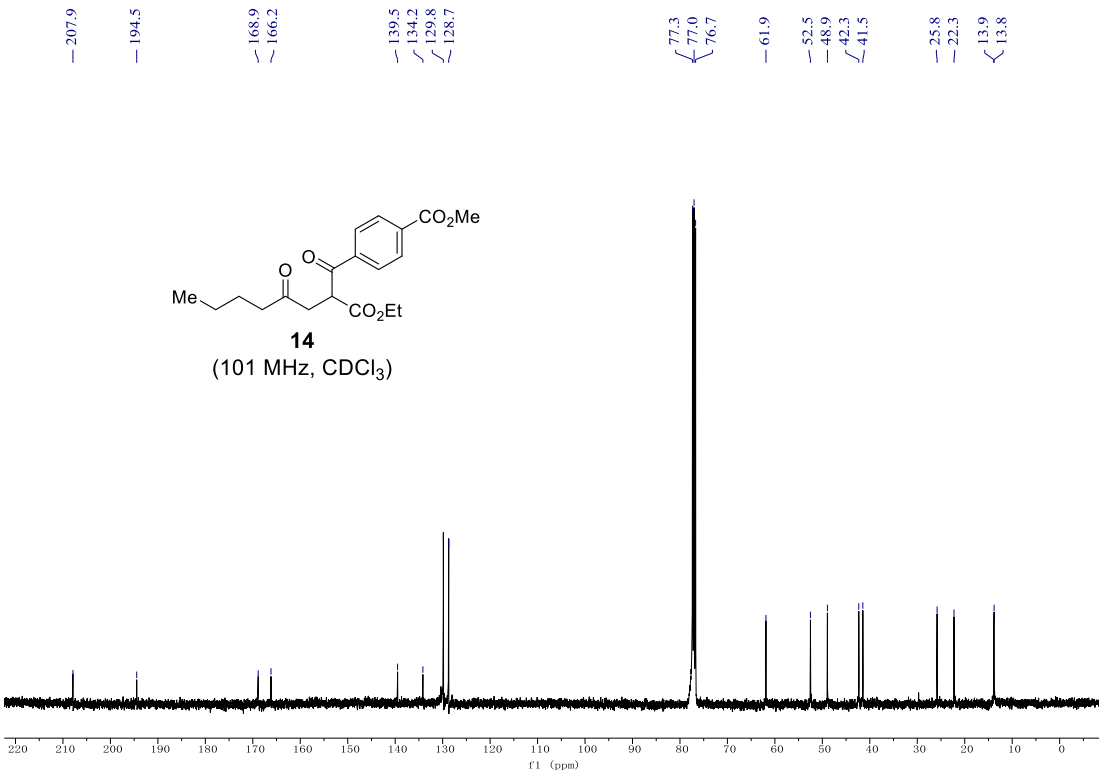




14

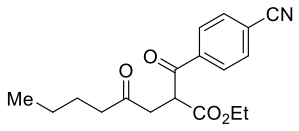
(400 MHz, $CDCl_3$)





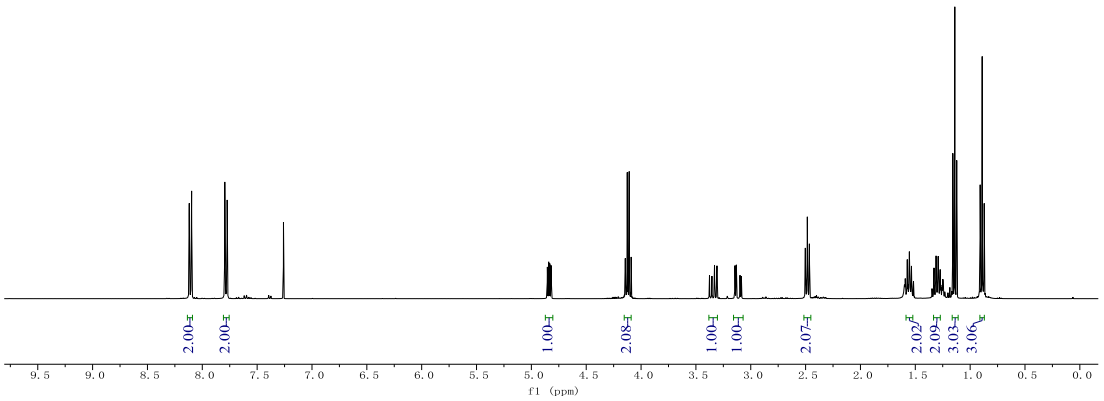
14

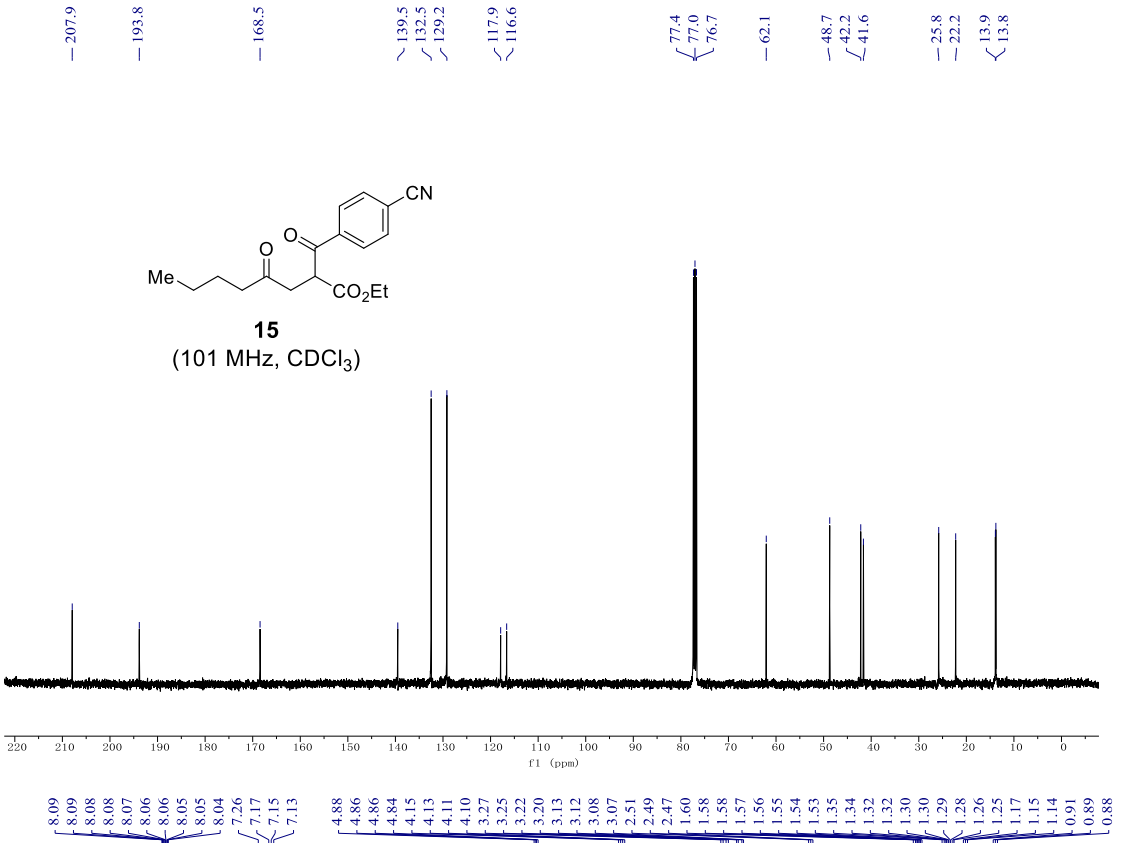
(101 MHz, $CDCl_3$)



15

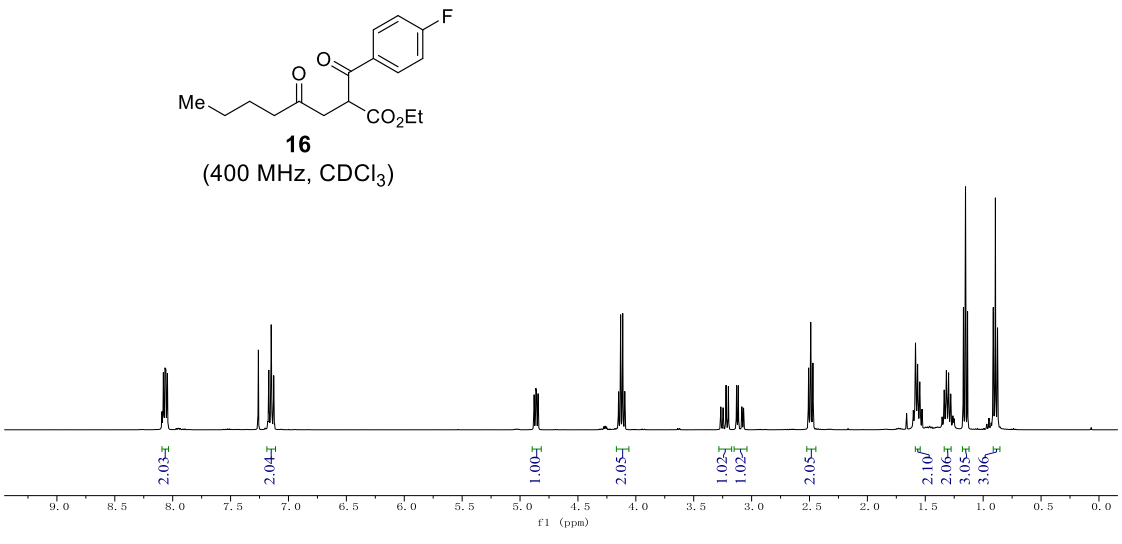
(400 MHz, $CDCl_3$)





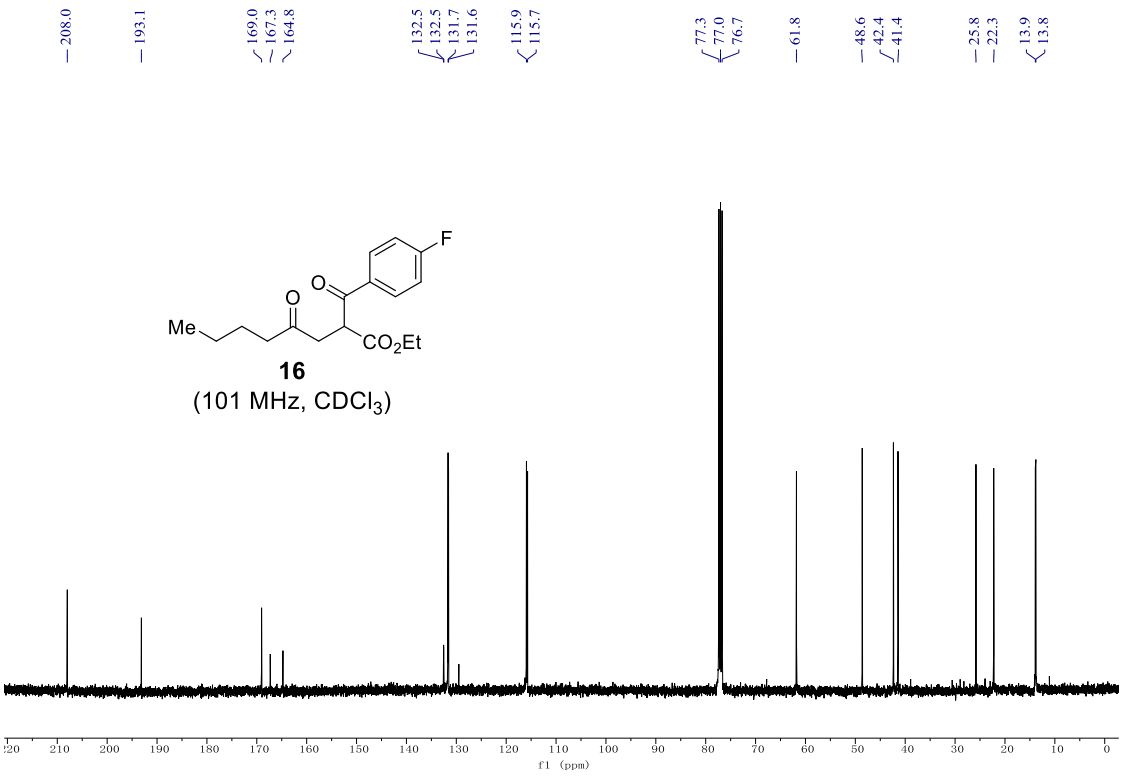
15

(101 MHz, $CDCl_3$)



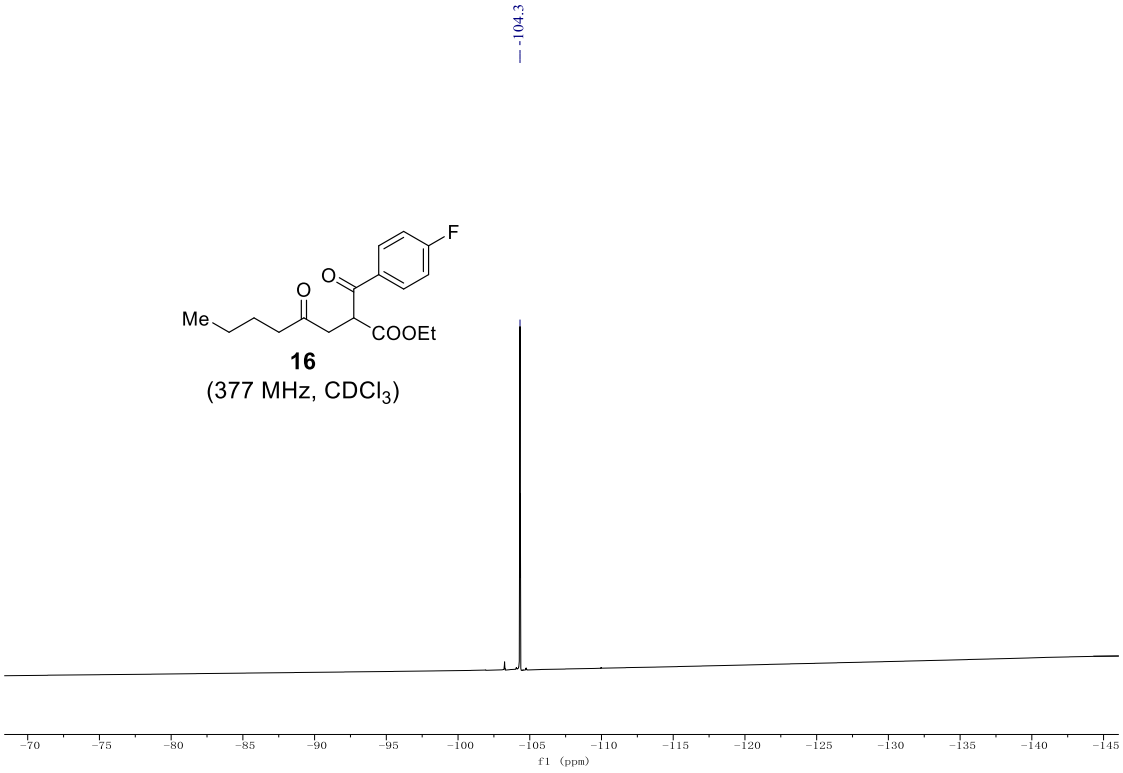
16

(400 MHz, $CDCl_3$)



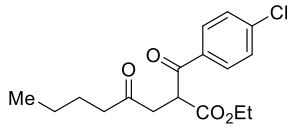
16

(101 MHz, $CDCl_3$)



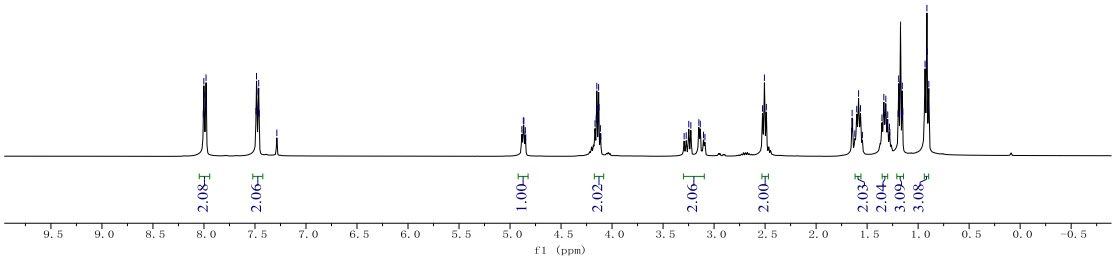
16

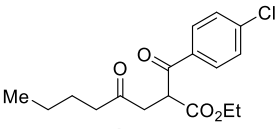
(377 MHz, $CDCl_3$)



17

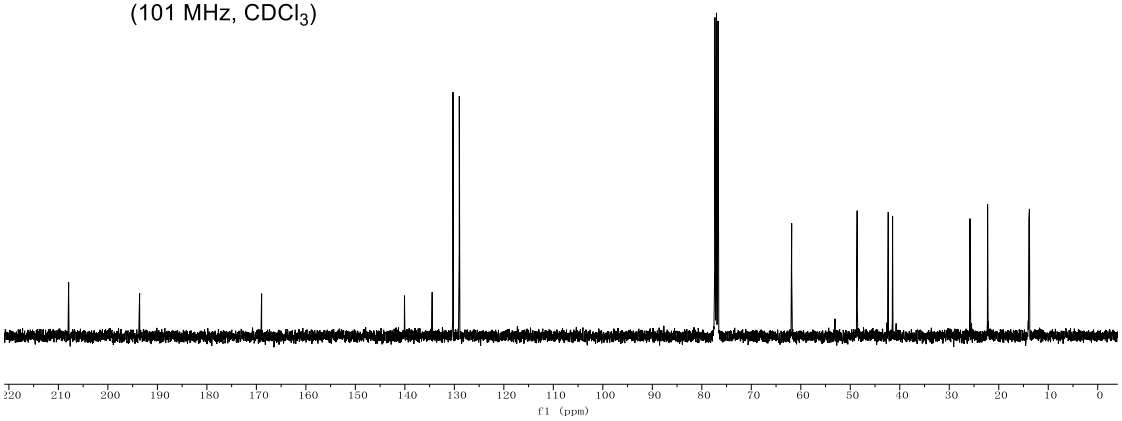
(400 MHz, $CDCl_3$)

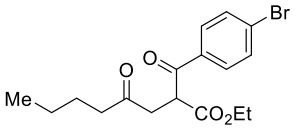




17

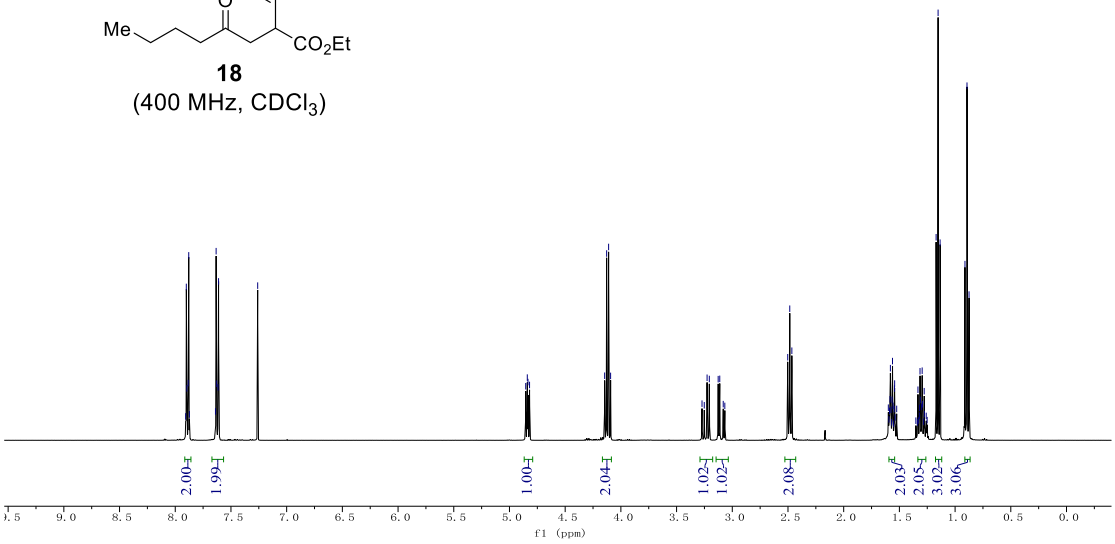
(101 MHz, $CDCl_3$)





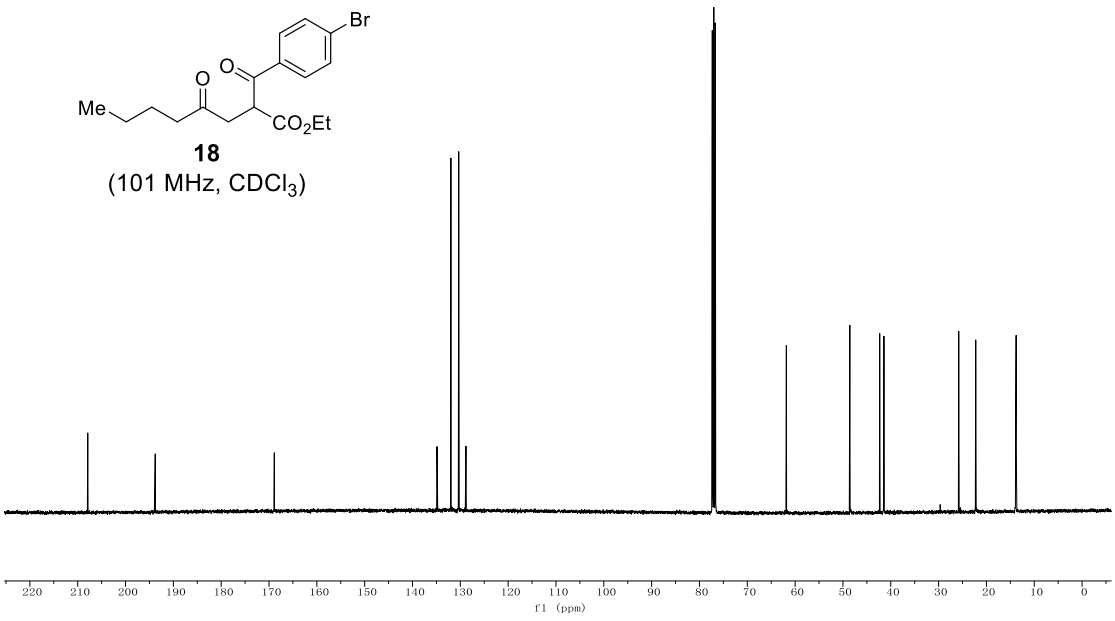
18

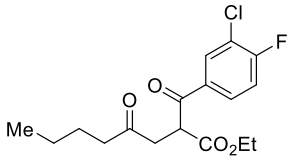
(400 MHz, $CDCl_3$)



18

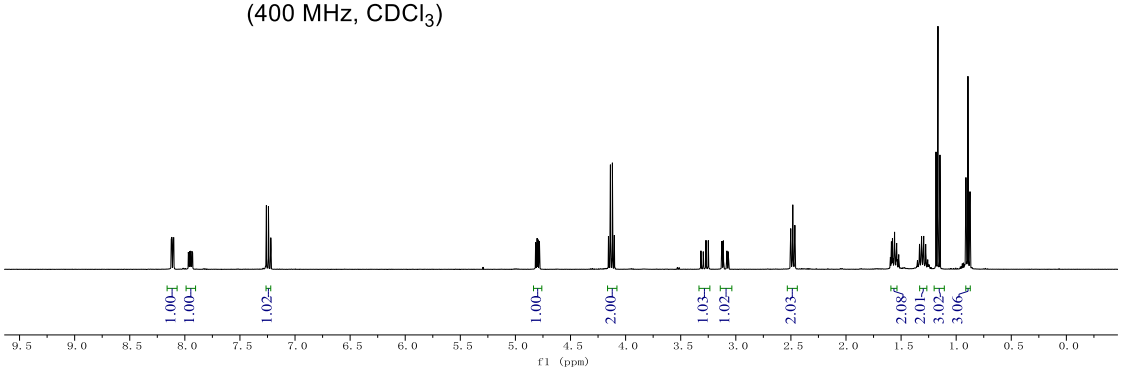
(101 MHz, $CDCl_3$)

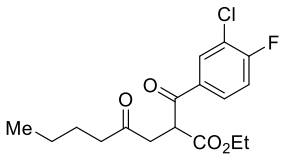




19

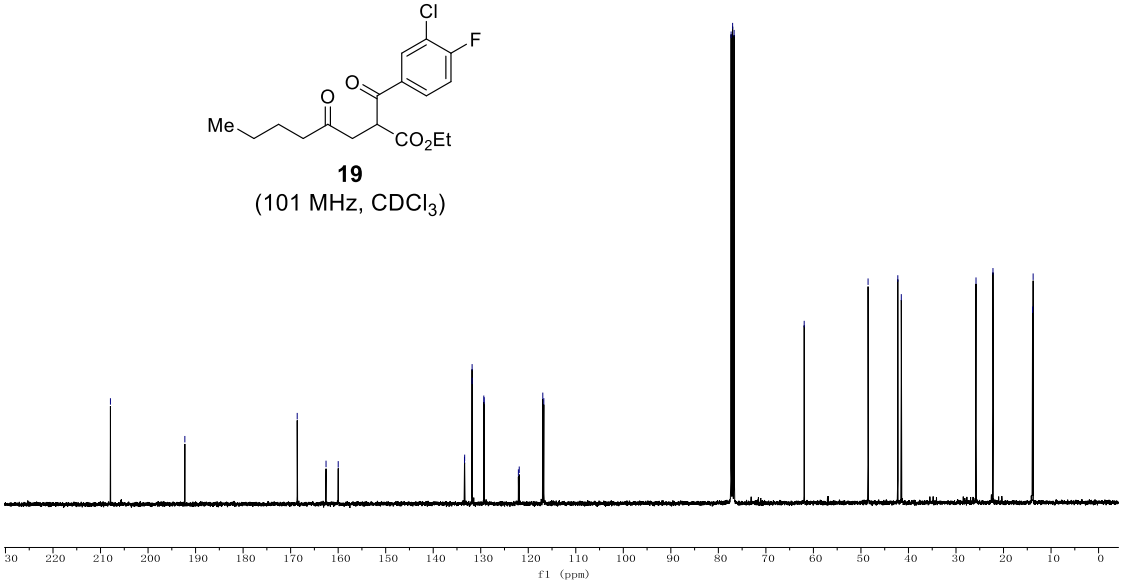
(400 MHz, $CDCl_3$)





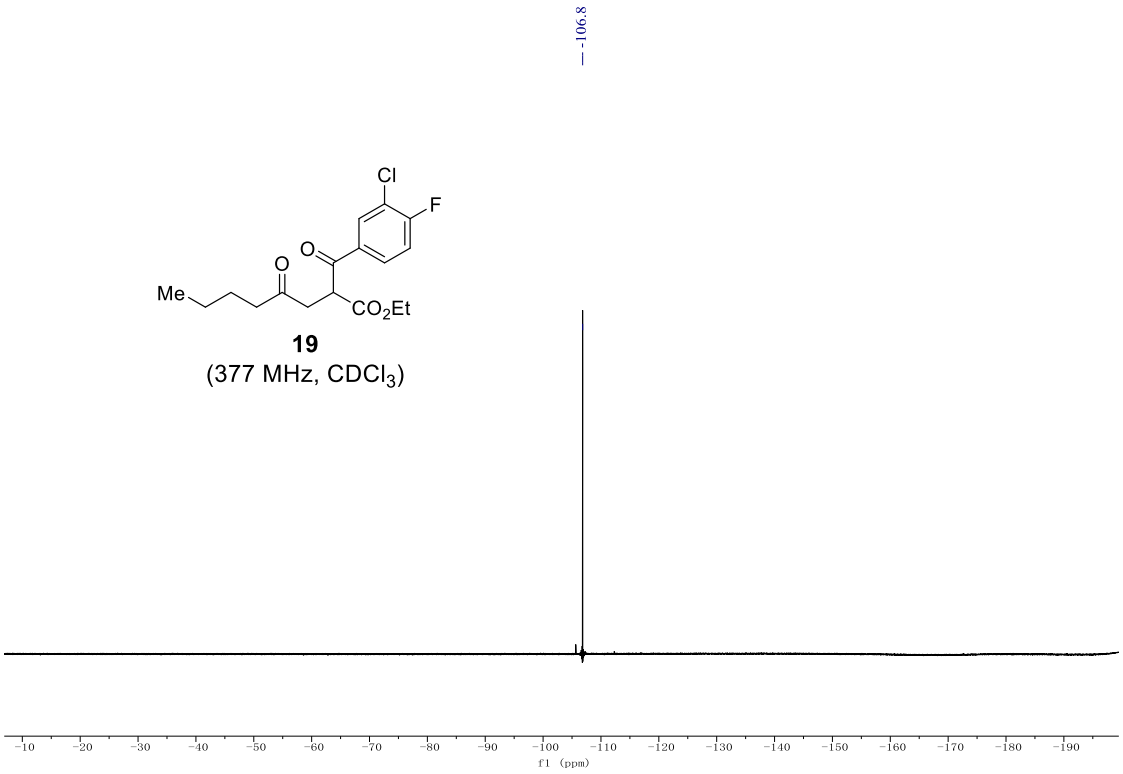
19

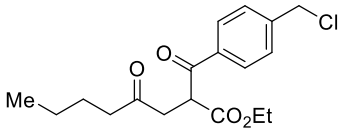
(101 MHz, $CDCl_3$)



19

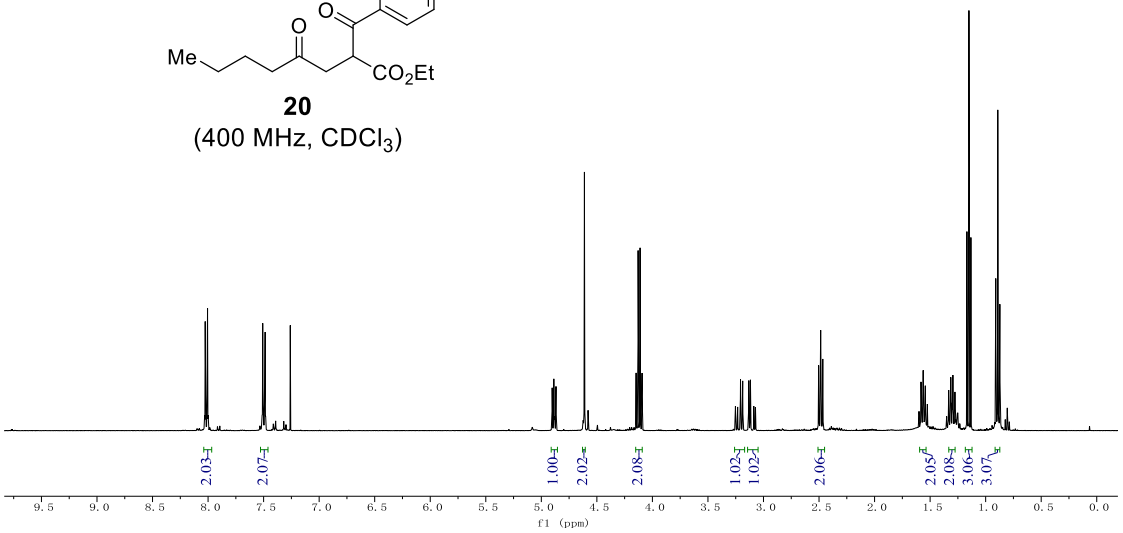
(377 MHz, $CDCl_3$)

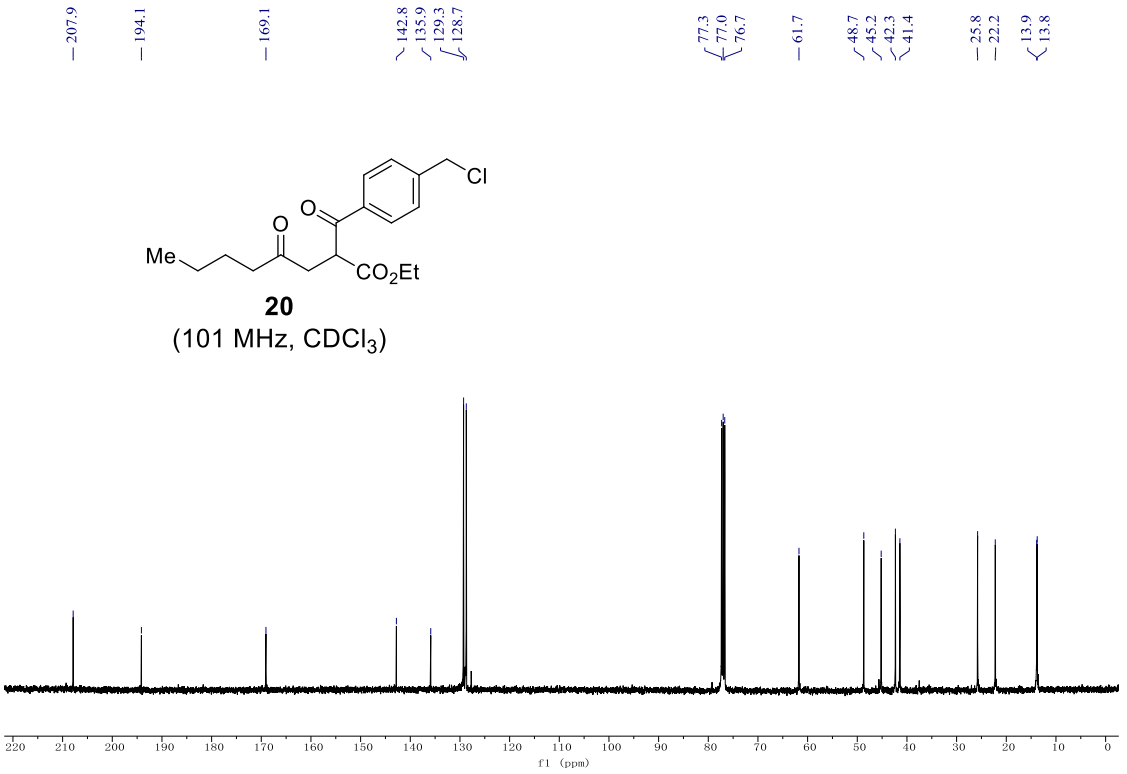




20

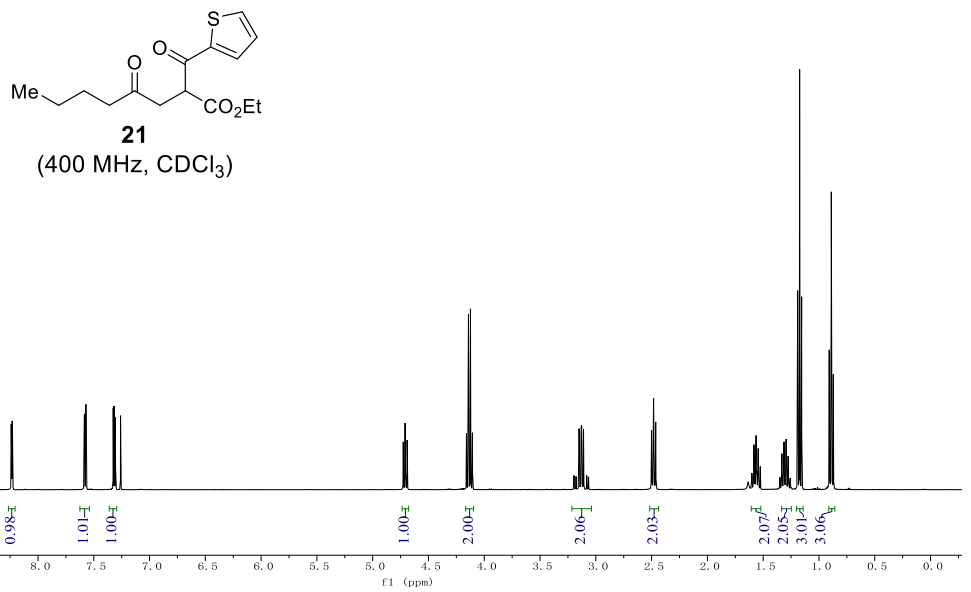
(400 MHz, $CDCl_3$)





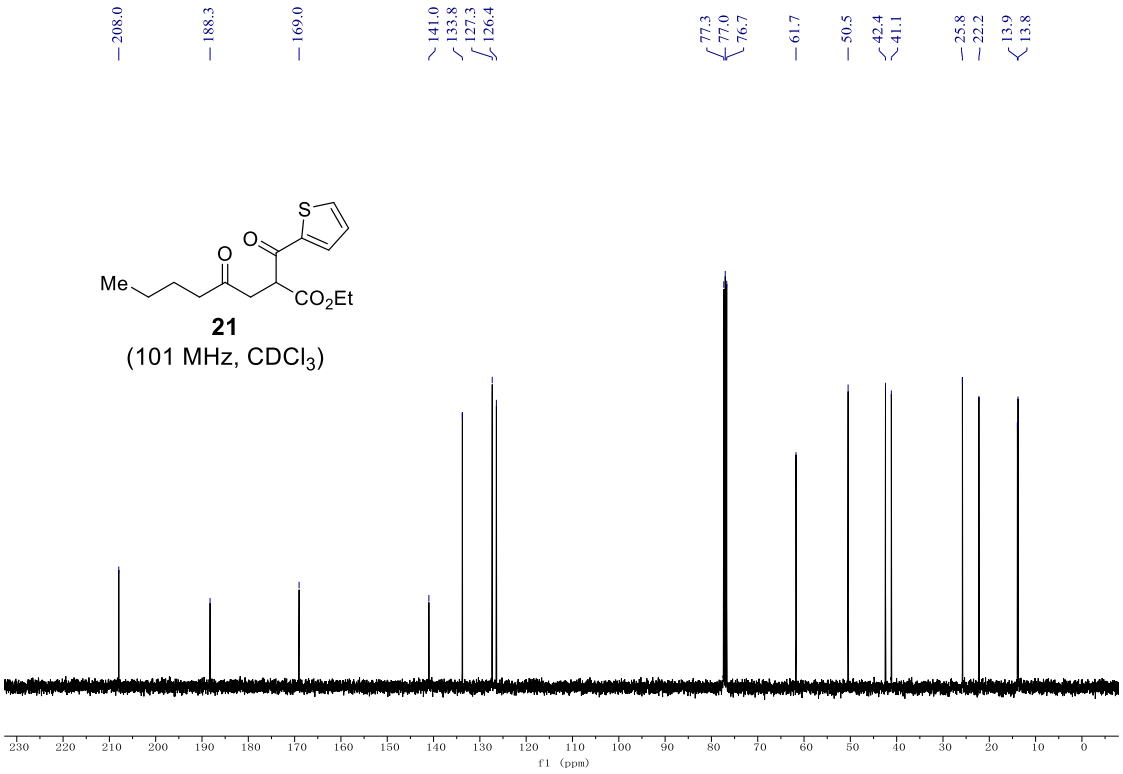
20

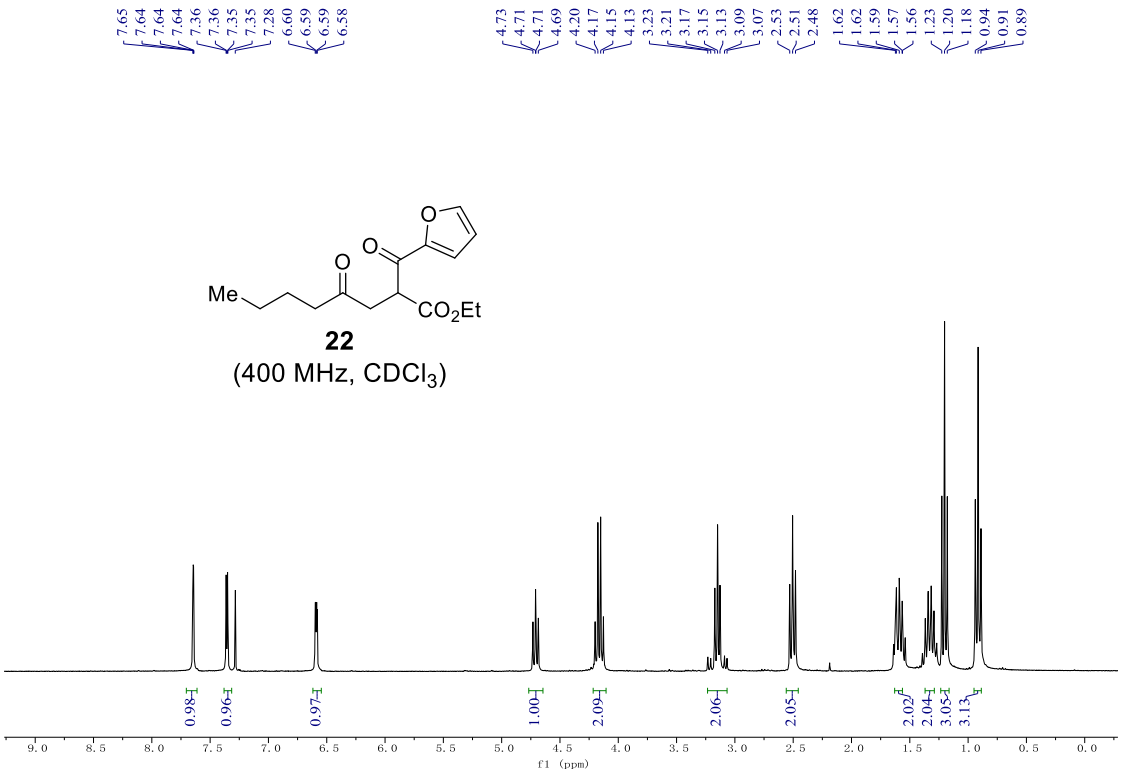
(101 MHz, $CDCl_3$)

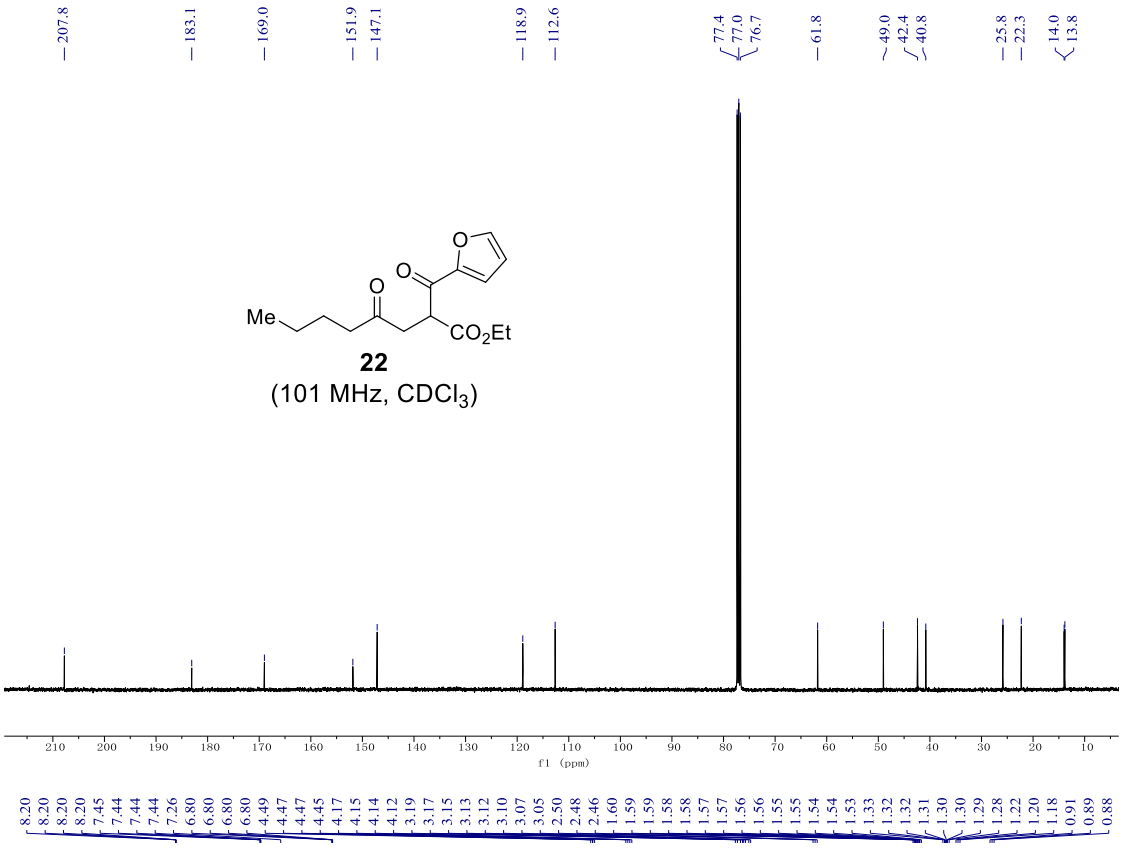


21

(400 MHz, $CDCl_3$)

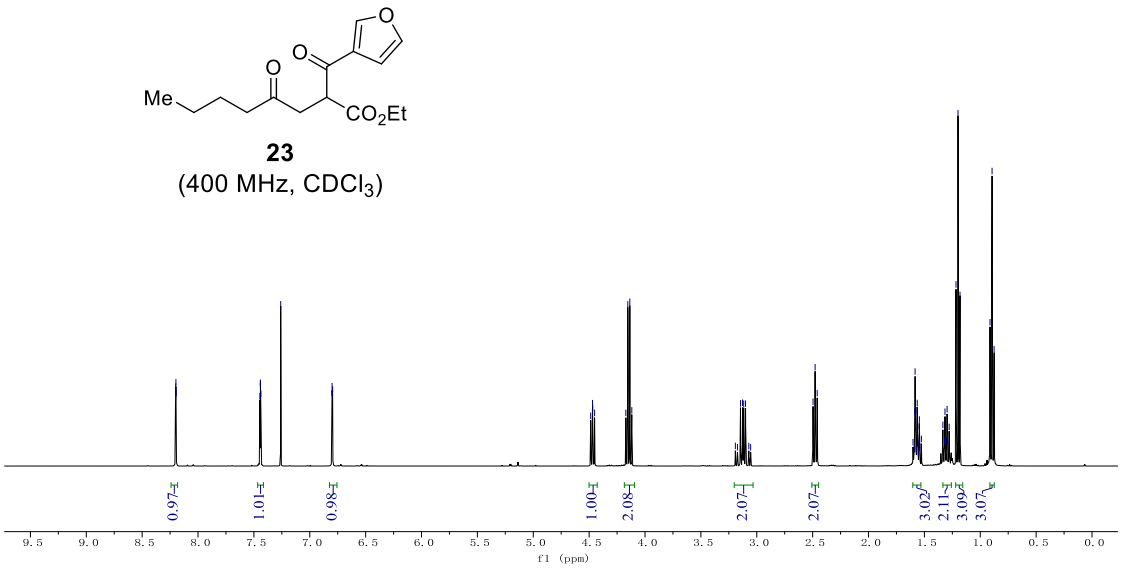

208.0
188.3
169.0
141.0
133.8
127.3
126.4
77.3
77.0
76.7
61.7
50.5
42.4
41.1
25.8
22.2
13.9
13.8
S
O
O
Me
CO2Et
21
(101 MHz, CDCl3)
f1 (ppm)


7.65
7.64
7.64
7.64
7.36
7.36
7.35
7.35
7.35
7.28
6.60
6.59
6.59
6.58
4.73
4.71
4.71
4.69
4.20
4.17
4.15
4.13
3.23
3.21
3.17
3.15
3.13
3.09
3.07
2.53
2.51
2.48
1.62
1.62
1.59
1.57
1.56
1.23
1.20
1.18
0.94
0.91
0.89
O
O
O
Me
CO2Et
22
(400 MHz, CDCl3)
0.98
0.96
0.97
1.00
2.09
2.06
2.05
2.02
2.04
3.05
3.13
f1 (ppm)



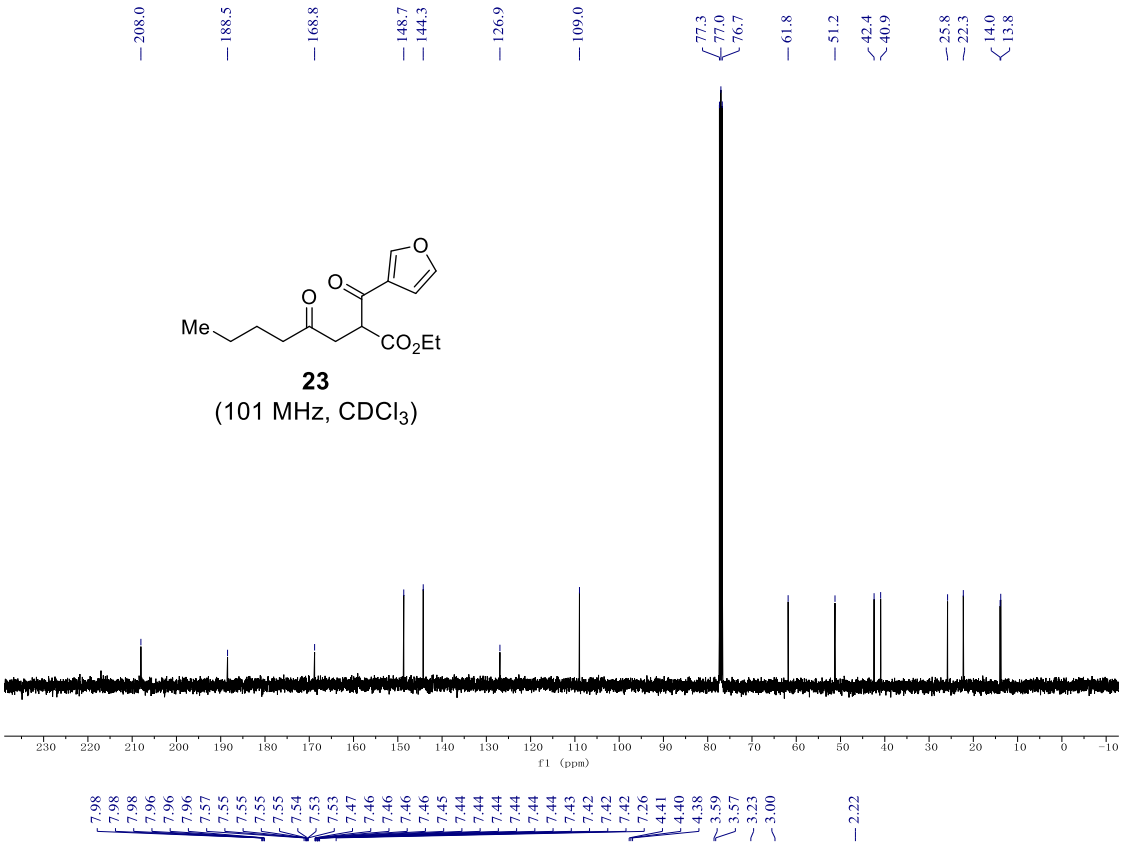
22

(101 MHz, $CDCl_3$)



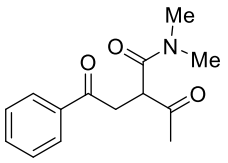
23

(400 MHz, $CDCl_3$)



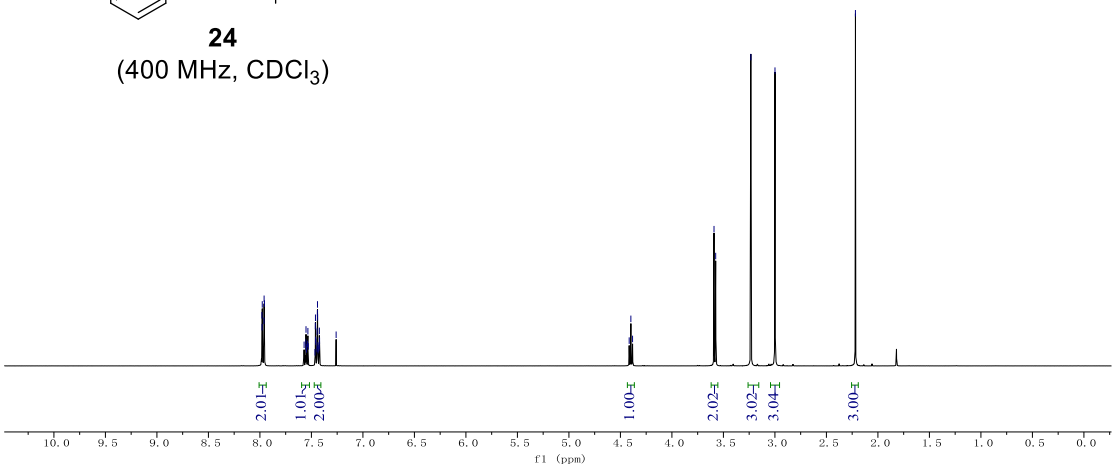
23

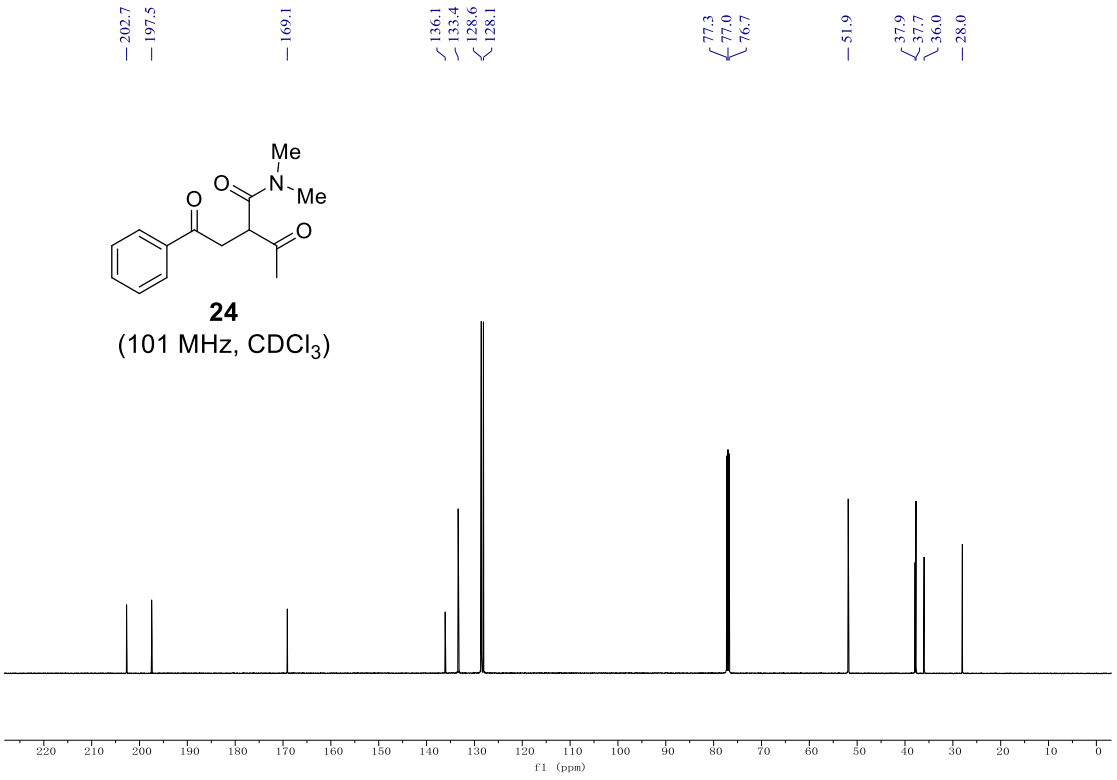
(101 MHz, $CDCl_3$)



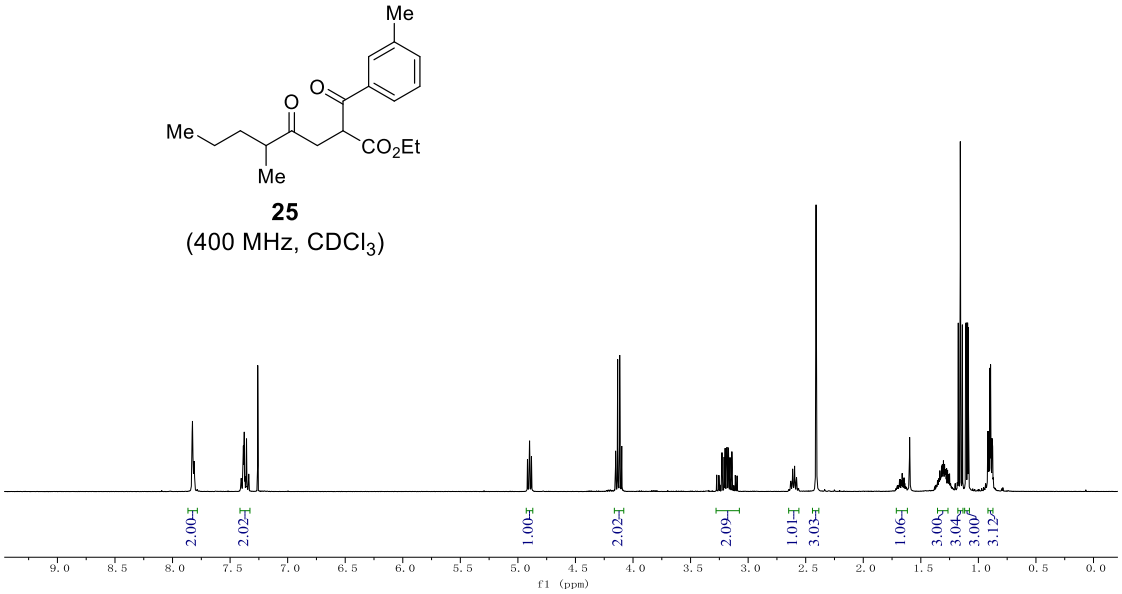
24

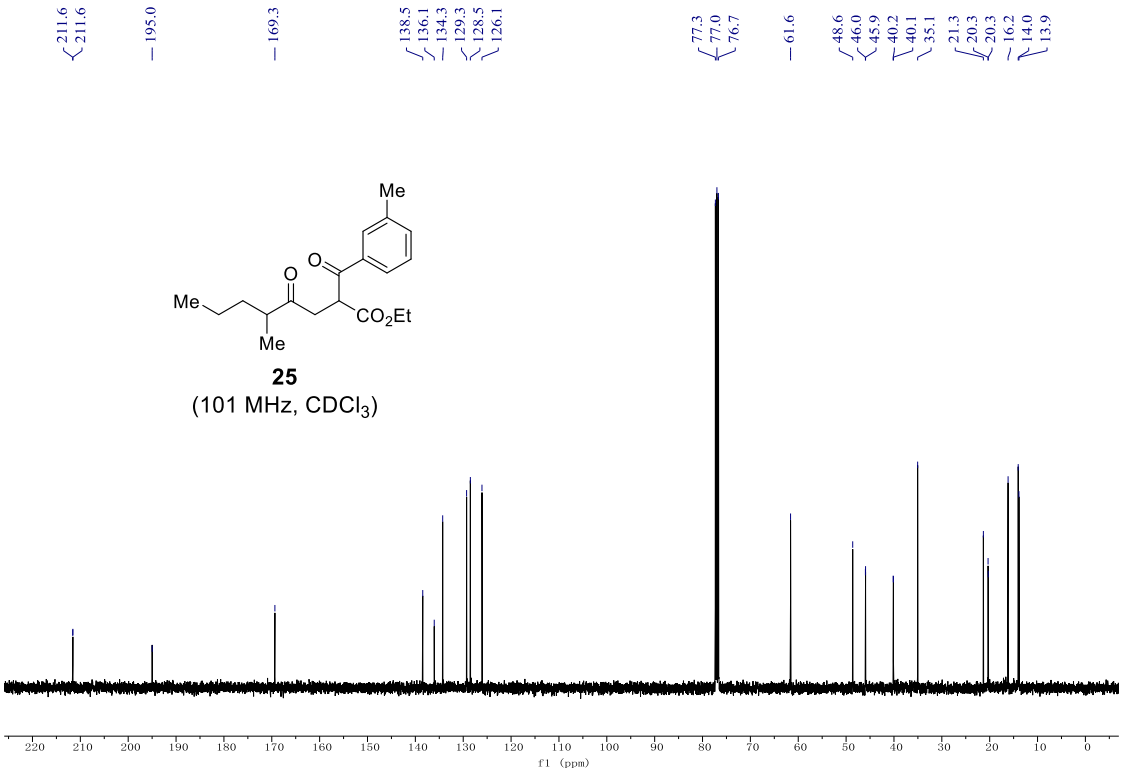
(400 MHz, $CDCl_3$)

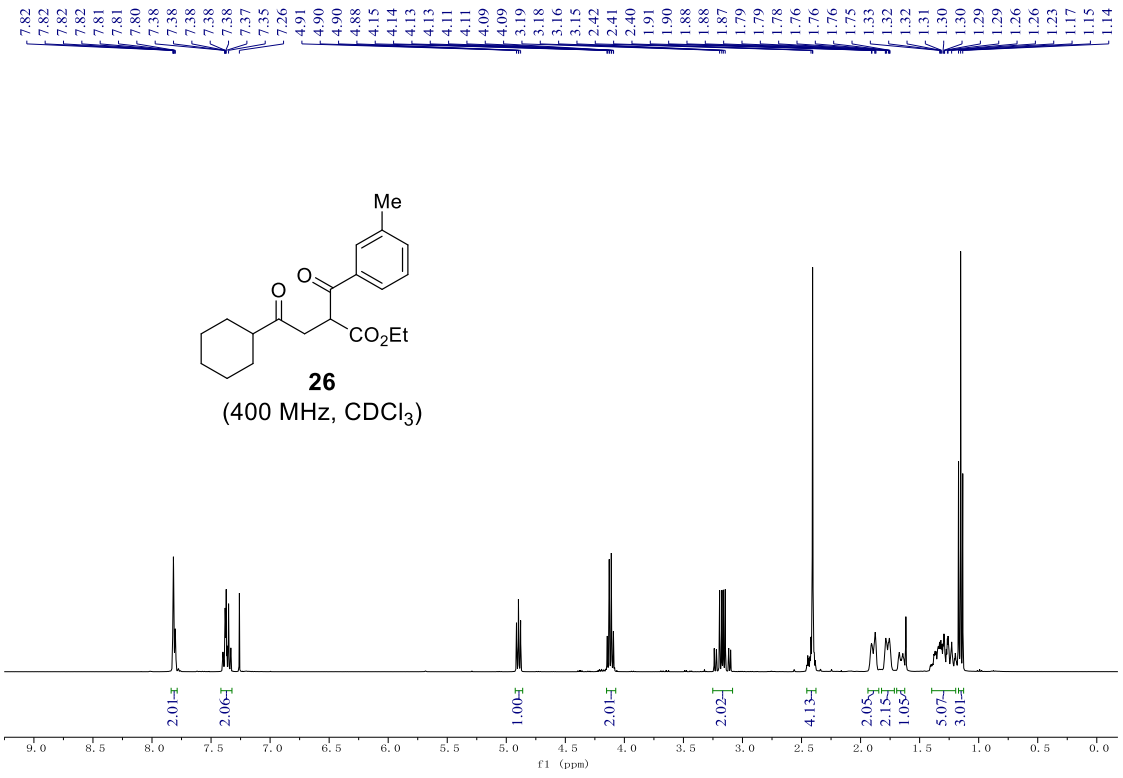


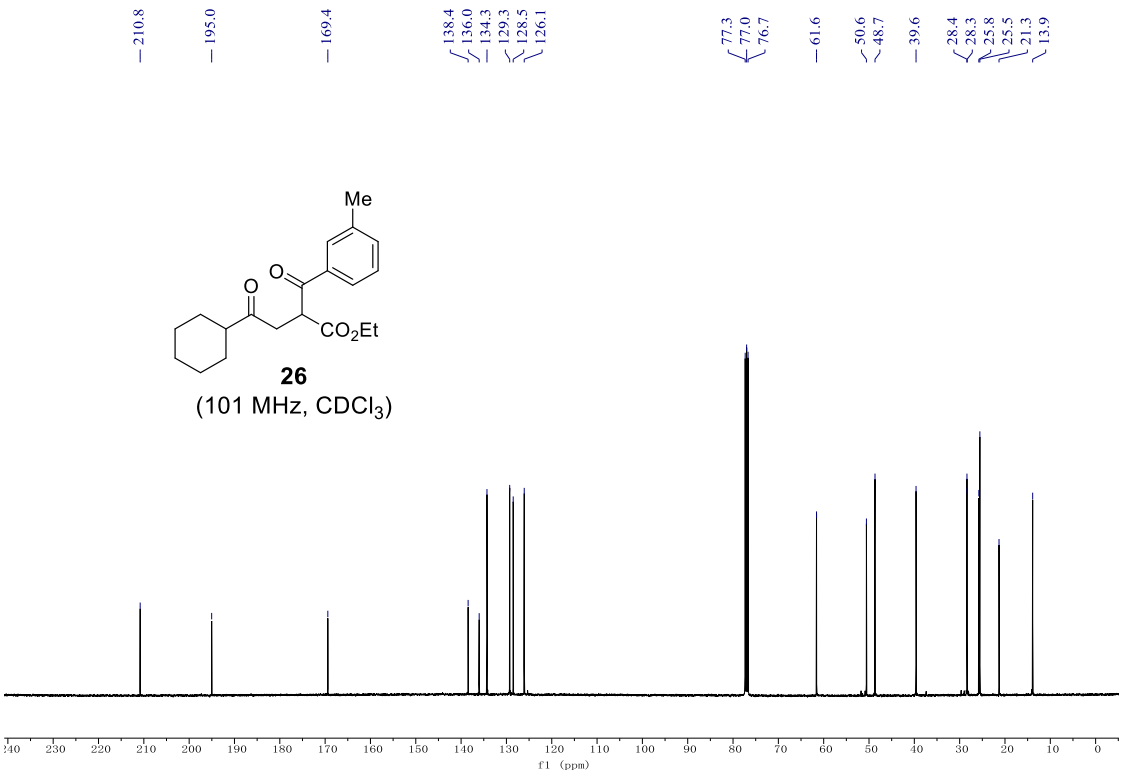

202.7
197.5
169.1
136.1
133.4
128.6
128.1
77.3
77.0
76.7
51.9
37.9
37.7
36.0
28.0
Me
O
N
Me
O
O
24
(101 MHz, CDCl3)
f1 (ppm)


7.83
7.83
7.83
7.82
7.82
7.82
7.81
7.81
7.39
7.39
7.39
7.38
7.38
7.38
7.38
7.38
7.36
4.92
4.90
4.90
4.88
4.15
4.13
4.12
4.10
3.23
3.21
3.20
3.19
3.18
3.17
3.16
3.14
2.60
2.41
2.41
1.32
1.31
1.31
1.30
1.30
1.30
1.29
1.28
1.17
1.16
1.14
1.11
1.10
1.09
1.09
0.92
0.91
0.91
0.90
0.89
0.89
0.89
0.88
0.88


Me
O
O
Me
CO2Et
Me
25
(400 MHz, CDCl3)
2.00
2.02
1.00
2.02
2.09
1.01
3.03
1.06
3.00
3.04
3.00
3.12
f1 (ppm)

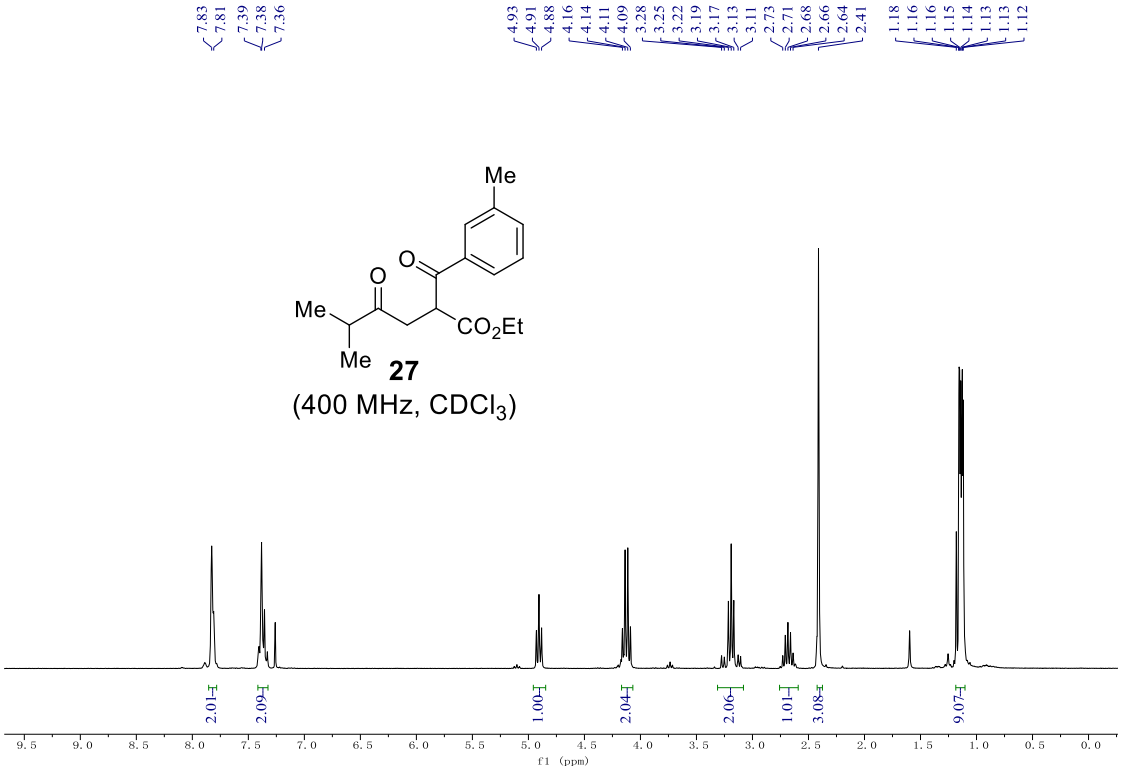

211.6
211.6
195.0
169.3
138.5
136.1
134.3
129.3
128.5
126.1
77.3
77.0
76.7
61.6
48.6
46.0
45.9
40.2
40.1
35.1
21.3
20.3
20.3
16.2
14.0
13.9
Me
O
O
Me
CO2Et
Me
25
(101 MHz, CDCl3)
f1 (ppm)


7.82
7.82
7.82
7.81
7.81
7.80
7.38
7.38
7.38
7.38
7.37
7.35
7.26
4.91
4.90
4.90
4.88
4.15
4.14
4.13
4.13
4.11
4.11
4.09
4.09
3.19
3.18
3.16
3.15
2.42
2.41
2.40
1.91
1.90
1.88
1.88
1.87
1.79
1.79
1.78
1.76
1.76
1.76
1.75
1.33
1.32
1.32
1.31
1.30
1.30
1.29
1.29
1.26
1.26
1.23
1.17
1.15
1.14
Me
O
O
CO2Et
26
(400 MHz, CDCl3)
2.01
2.06
1.00
2.01
2.02
4.13
2.05
2.15
1.05
5.07
3.01
f1 (ppm)



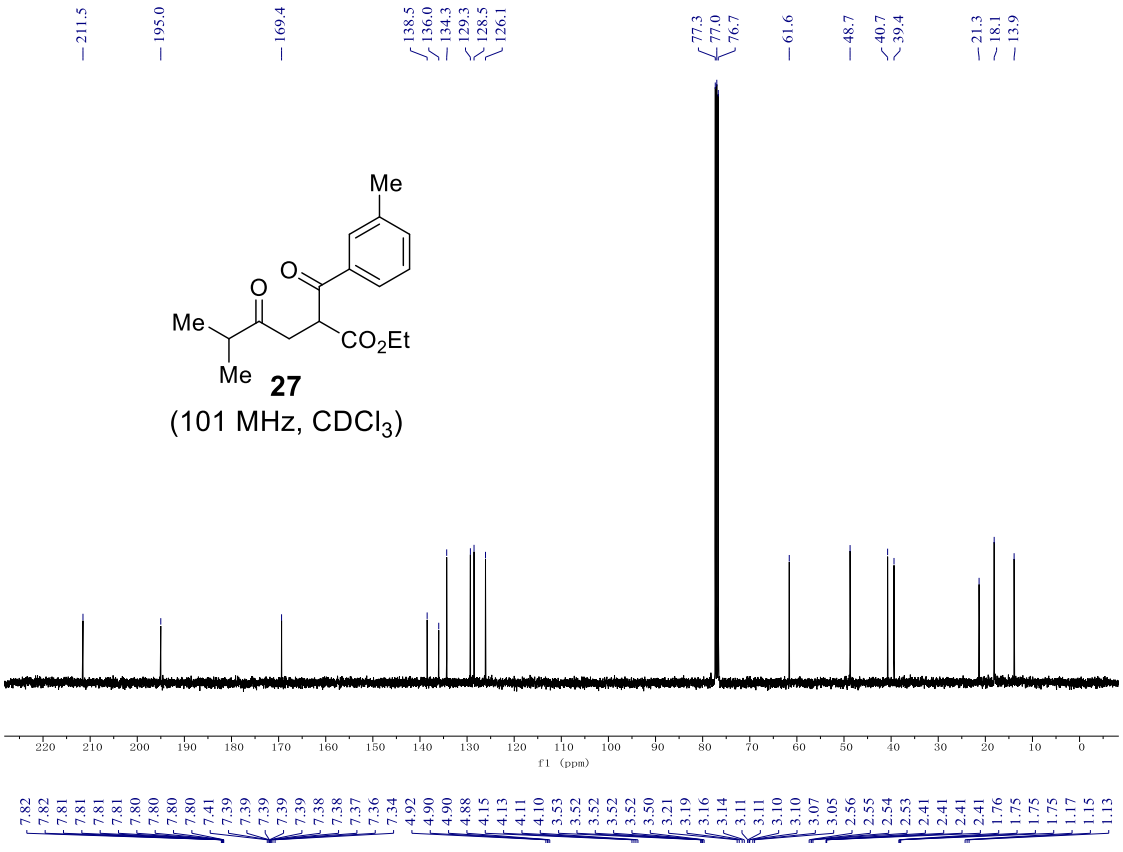
26

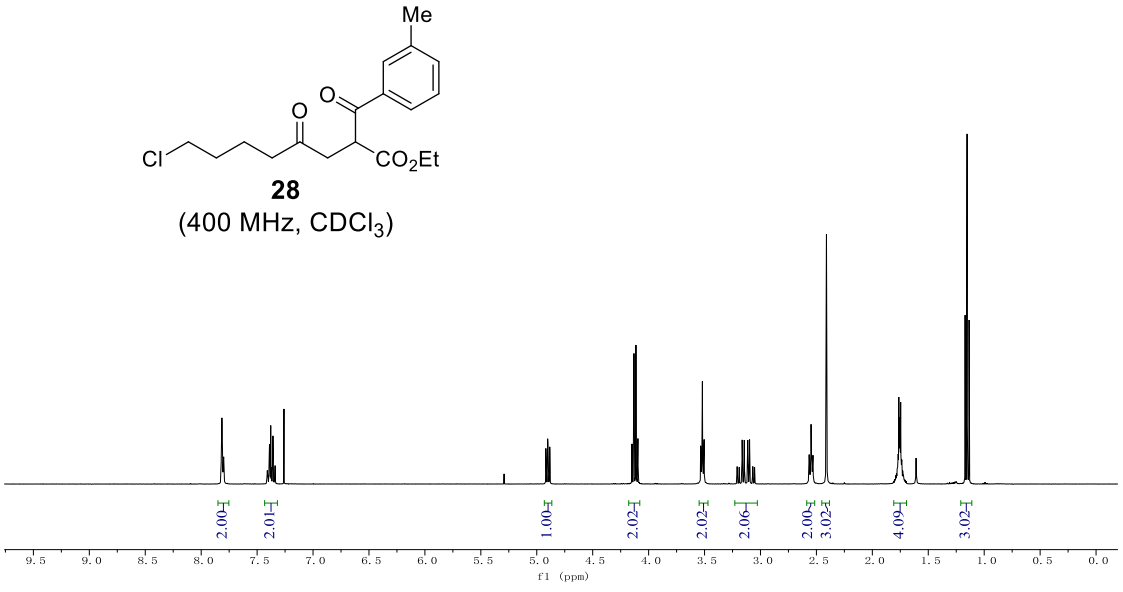
(101 MHz, $CDCl_3$)

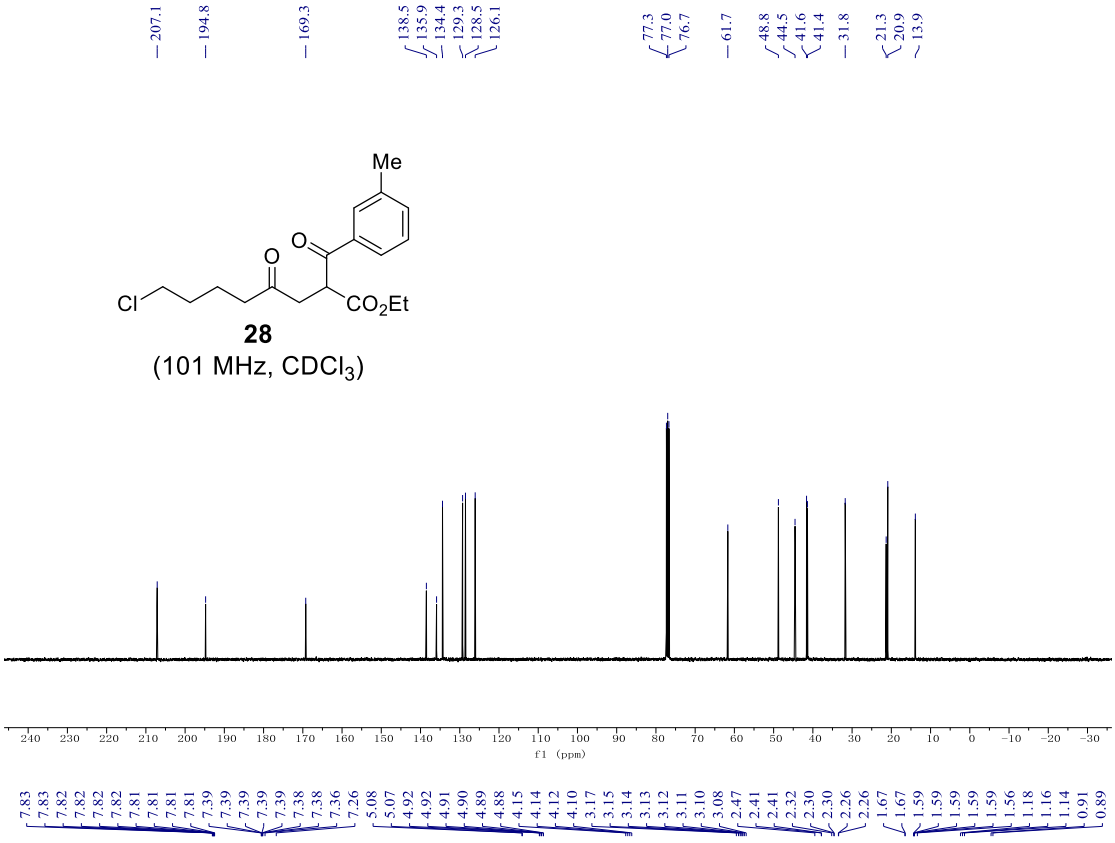


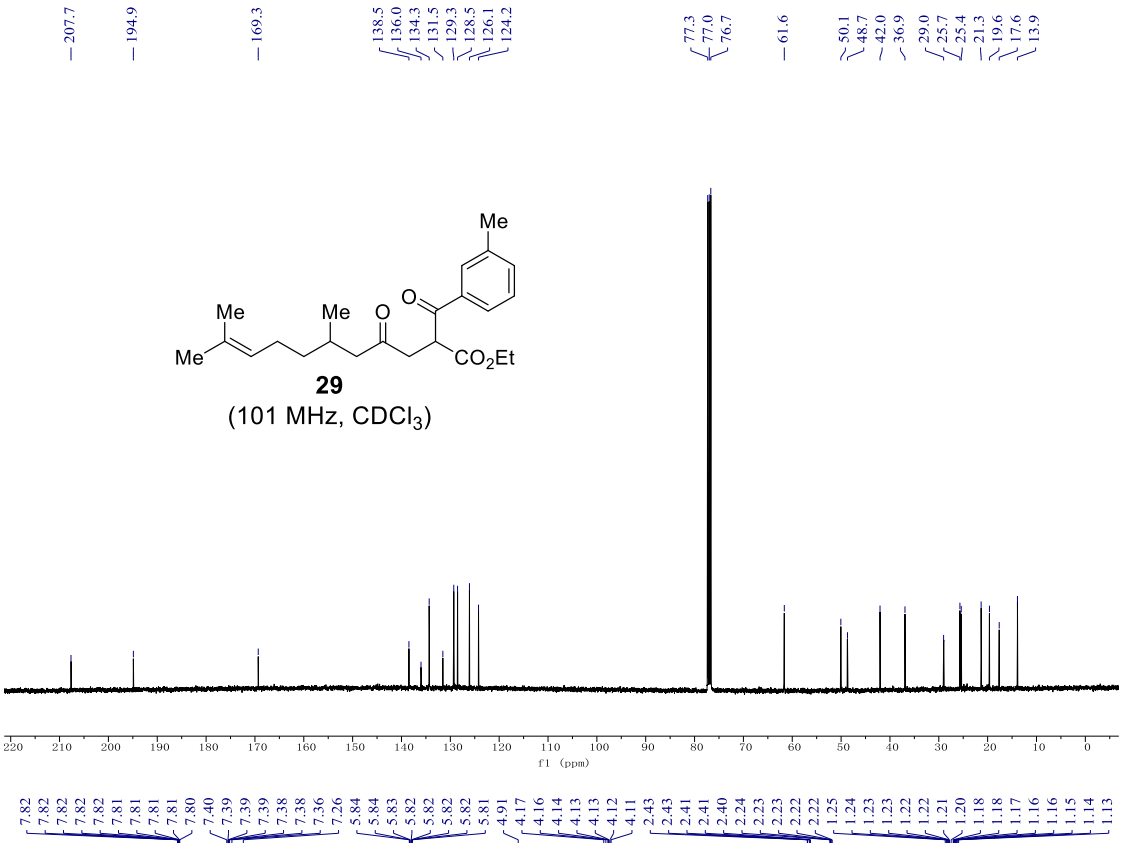
27

(400 MHz, $CDCl_3$)


211.5
195.0
169.4
138.5
136.0
134.3
129.3
128.5
126.1
77.3
77.0
76.7
61.6
48.7
40.7
39.4
21.3
18.1
13.9
Me
O
O
Me
CO2Et
Me
27
(101 MHz, CDCl3)
f1 (ppm)

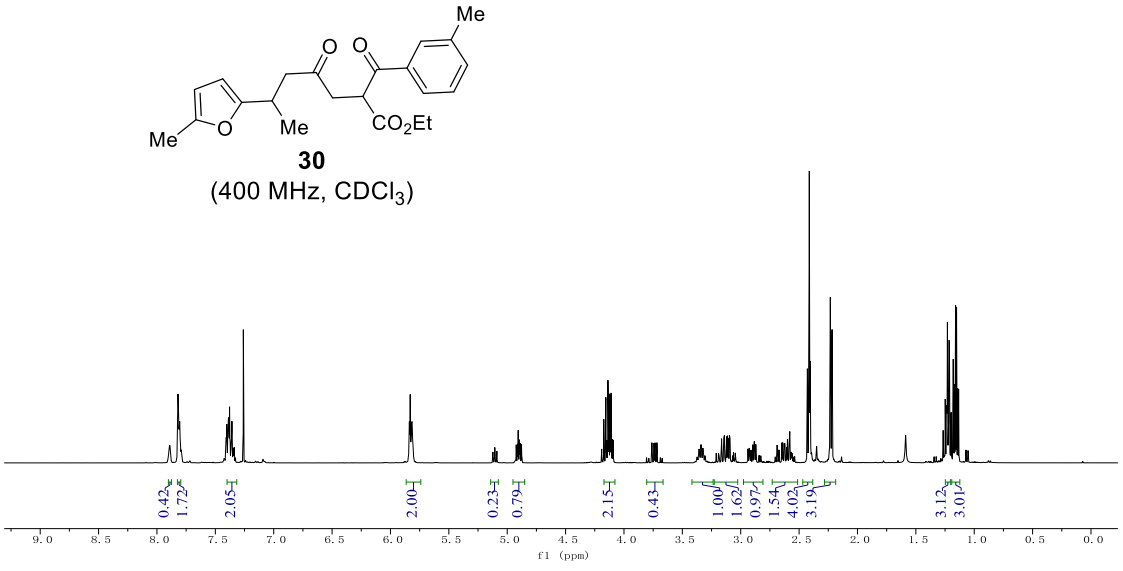

Me
O
O
Cl
CO2Et
28
(400 MHz, CDCl3)
f1 (ppm)


207.1
194.8
169.3
138.5
135.9
134.4
129.3
128.5
126.1
77.3
77.0
76.7
61.7
48.8
44.5
41.6
41.4
31.8
21.3
20.9
13.9
Me
O
O
Cl
CO2Et
28
(101 MHz, CDCl3)
f1 (ppm)
7.83
7.83
7.82
7.82
7.82
7.81
7.81
7.81
7.81
7.39
7.39
7.39
7.39
7.38
7.38
7.36
7.26
5.08
5.07
4.92
4.92
4.91
4.90
4.89
4.88
4.15
4.14
4.12
4.10
3.17
3.15
3.14
3.13
3.12
3.11
3.10
3.08
2.47
2.41
2.41
2.32
2.30
2.30
2.26
2.26
1.67
1.67
1.59
1.59
1.59
1.59
1.59
1.56
1.18
1.16
1.14
0.91
0.89
Me
Me
Me
O
O
CO2Et
29
(400 MHz, CDCl3)
2.08
2.01
1.07
1.00
2.09
2.09
1.09
3.02
1.02
4.05
3.06
1.10
3.00
3.01
f1 (ppm)



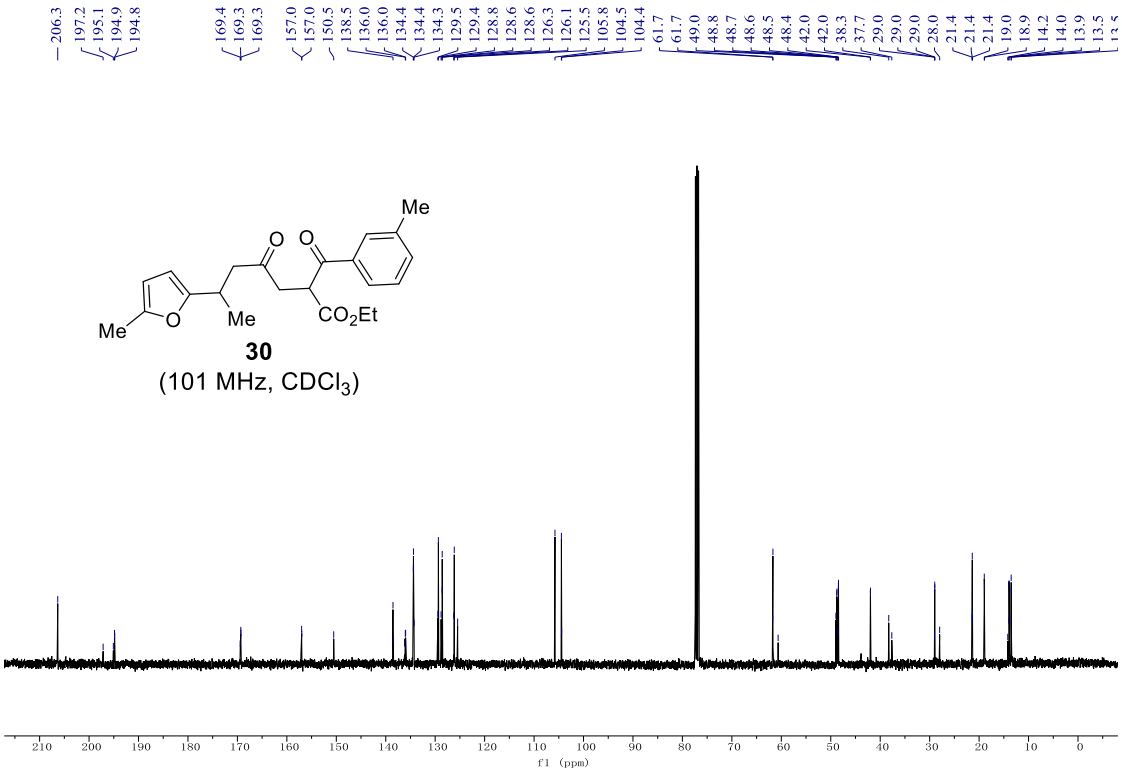
29

(101 MHz, $CDCl_3$)



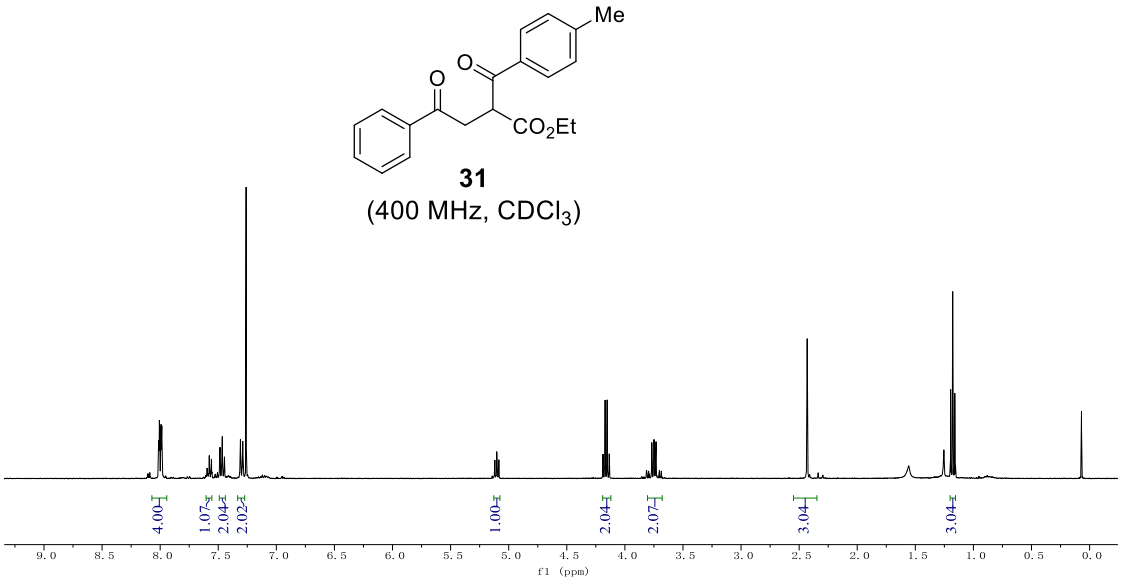
30

(400 MHz, $CDCl_3$)



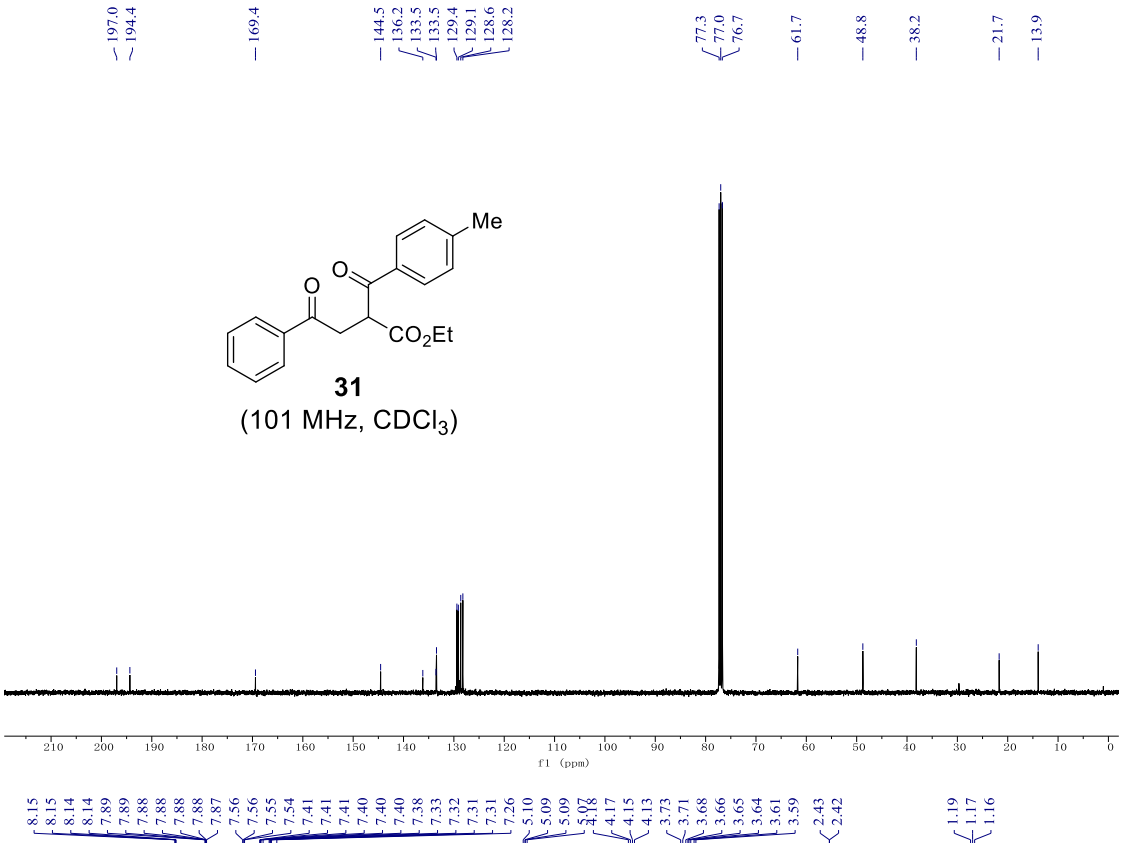
30

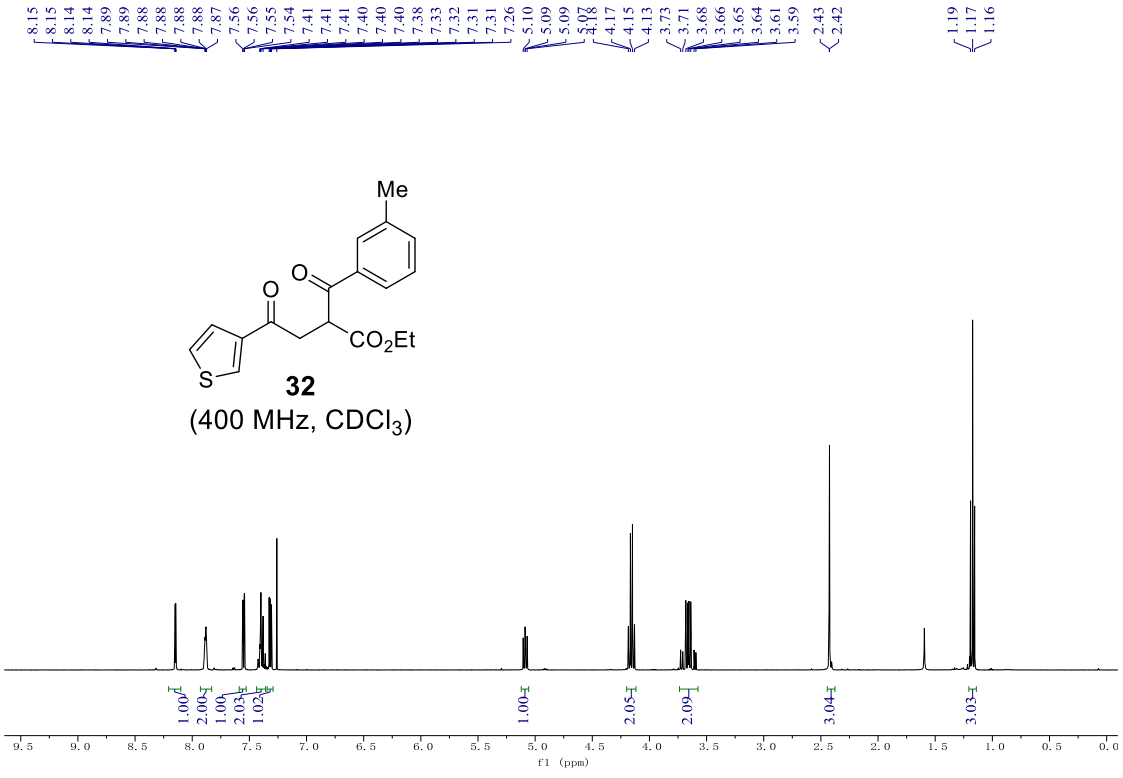
(101 MHz, $CDCl_3$)

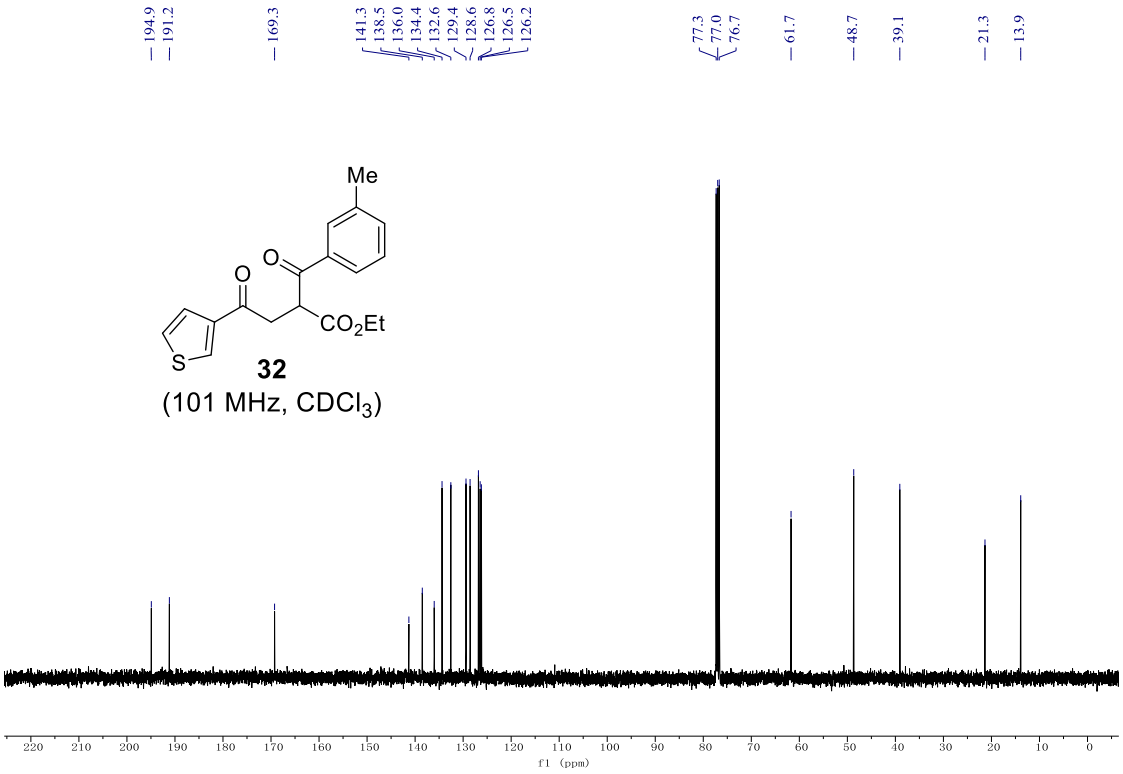


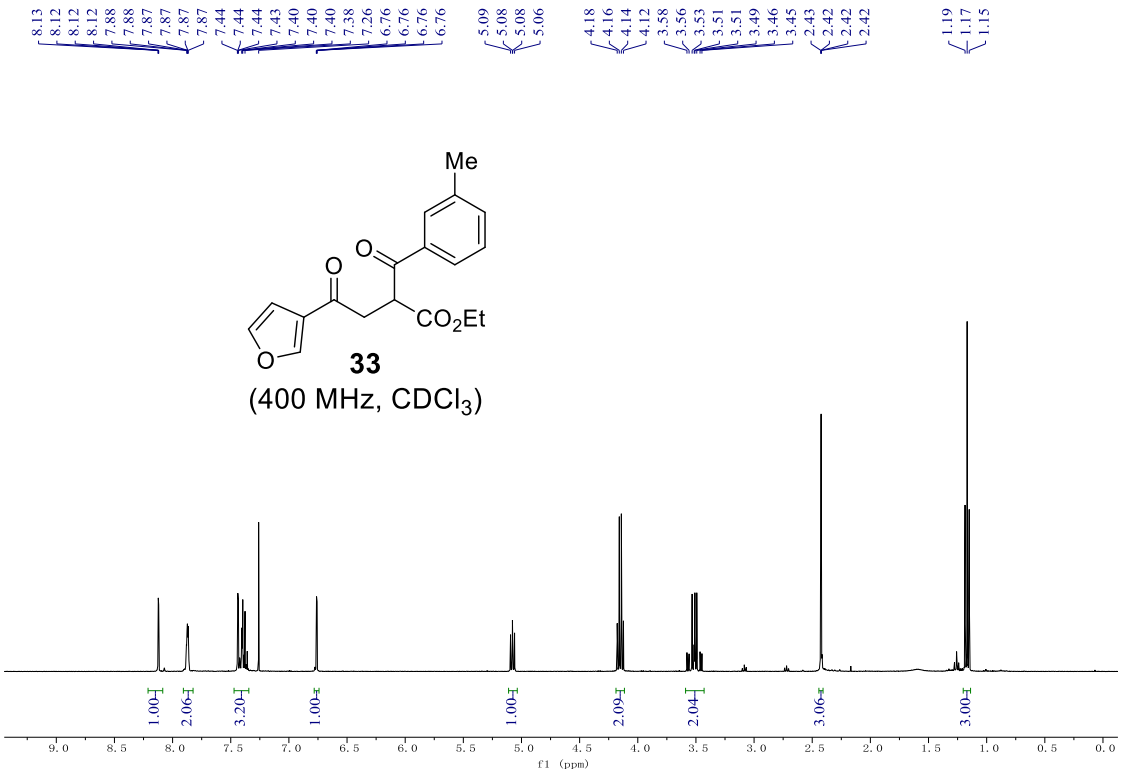
31

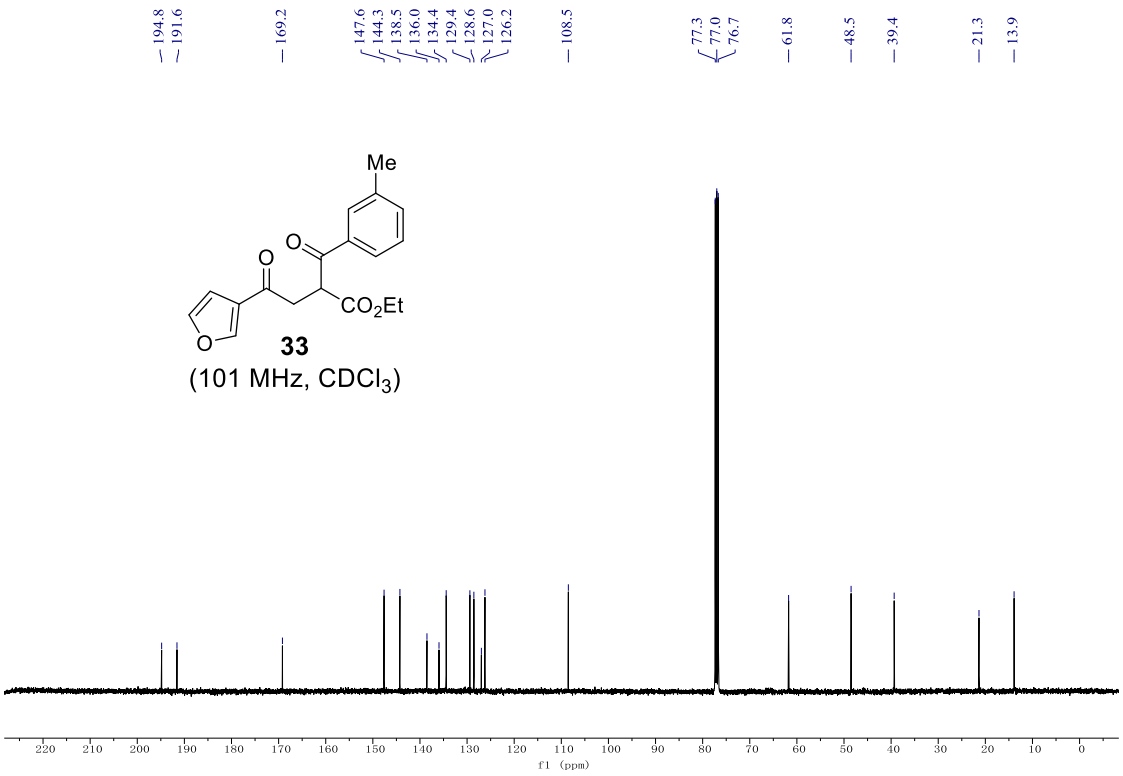
(400 MHz, $CDCl_3$)

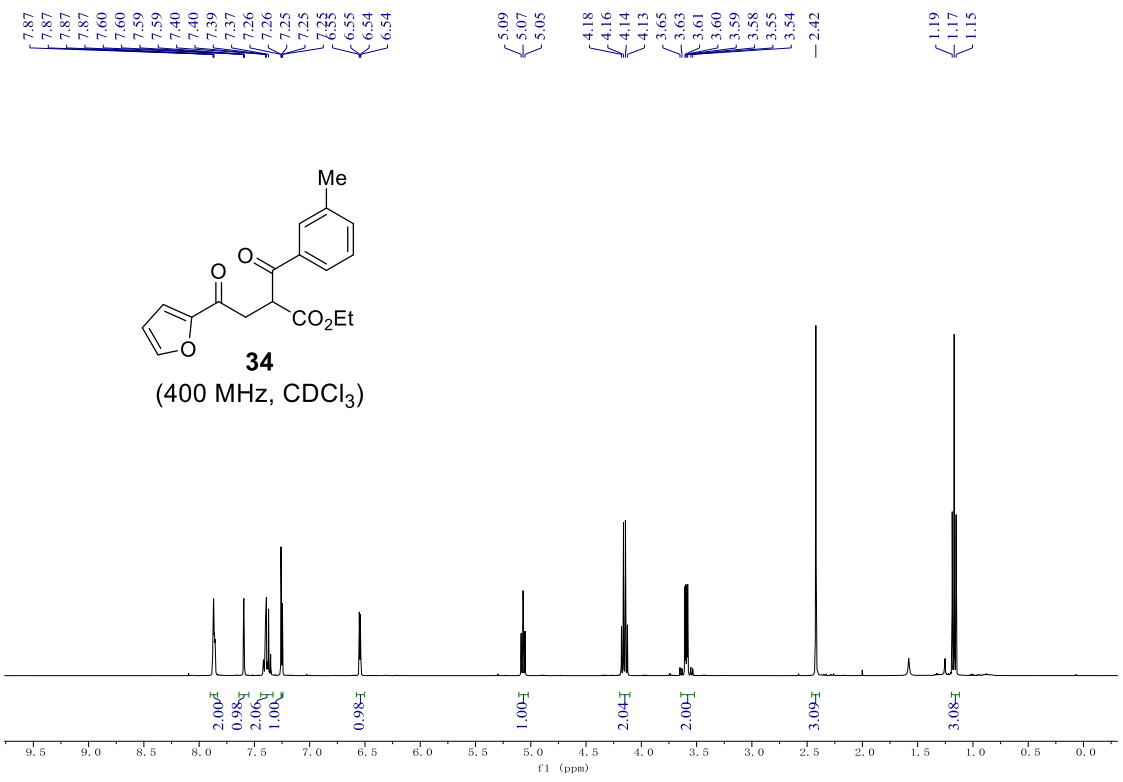

197.0
194.4
169.4
144.5
136.2
133.5
133.5
129.4
129.1
128.6
128.2
77.3
77.0
76.7
61.7
48.8
38.2
21.7
13.9
Me
O
O
CO2Et
31
(101 MHz, CDCl3)
f1 (ppm)

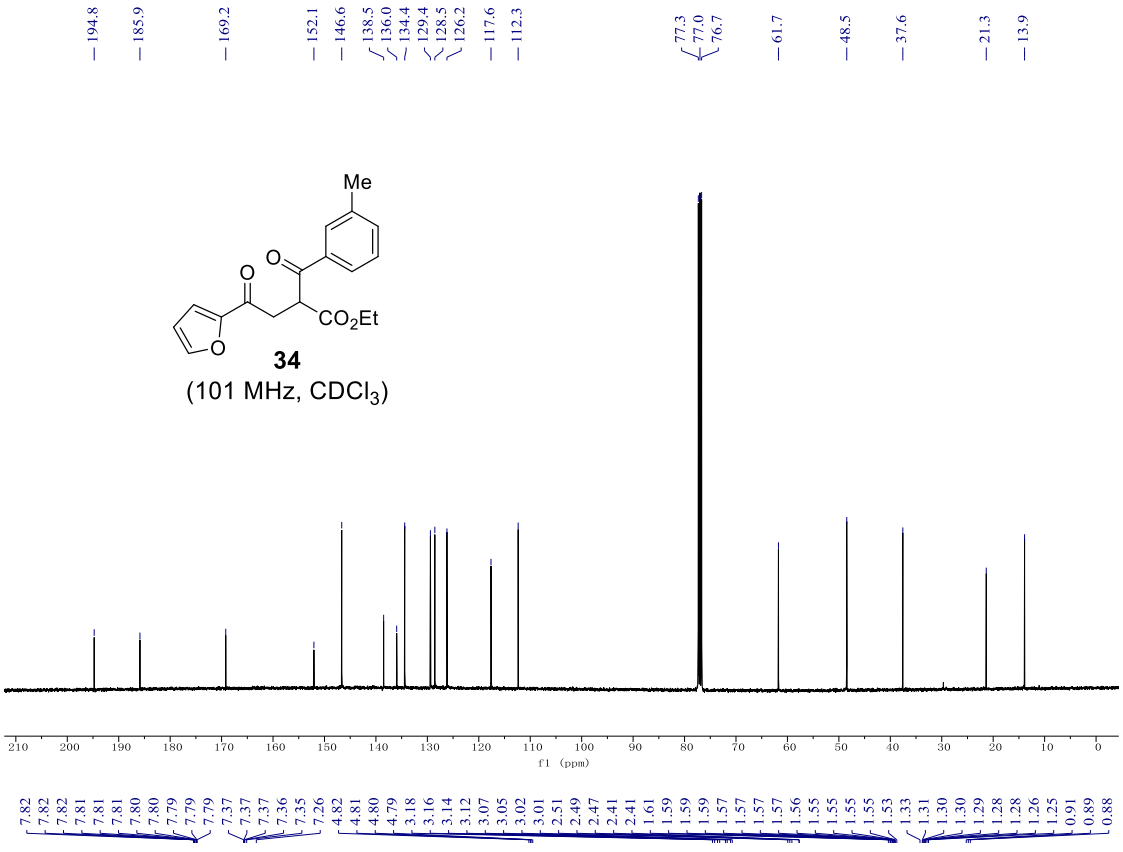

Me
O
O
CO2Et
S
32
(400 MHz, CDCl3)
f1 (ppm)

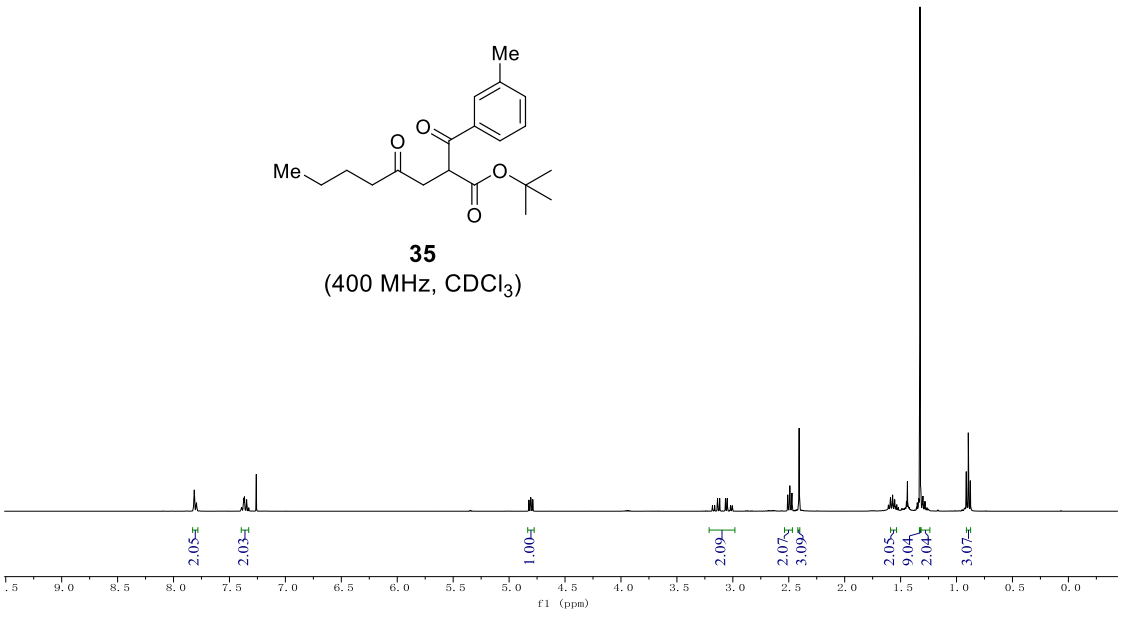

194.9
191.2
169.3
141.3
138.5
136.0
134.4
132.6
129.4
128.6
126.8
126.5
126.2
77.3
77.0
76.7
61.7
48.7
39.1
21.3
13.9
Me
O
O
CO2Et
S
32
(101 MHz, CDCl3)
f1 (ppm)

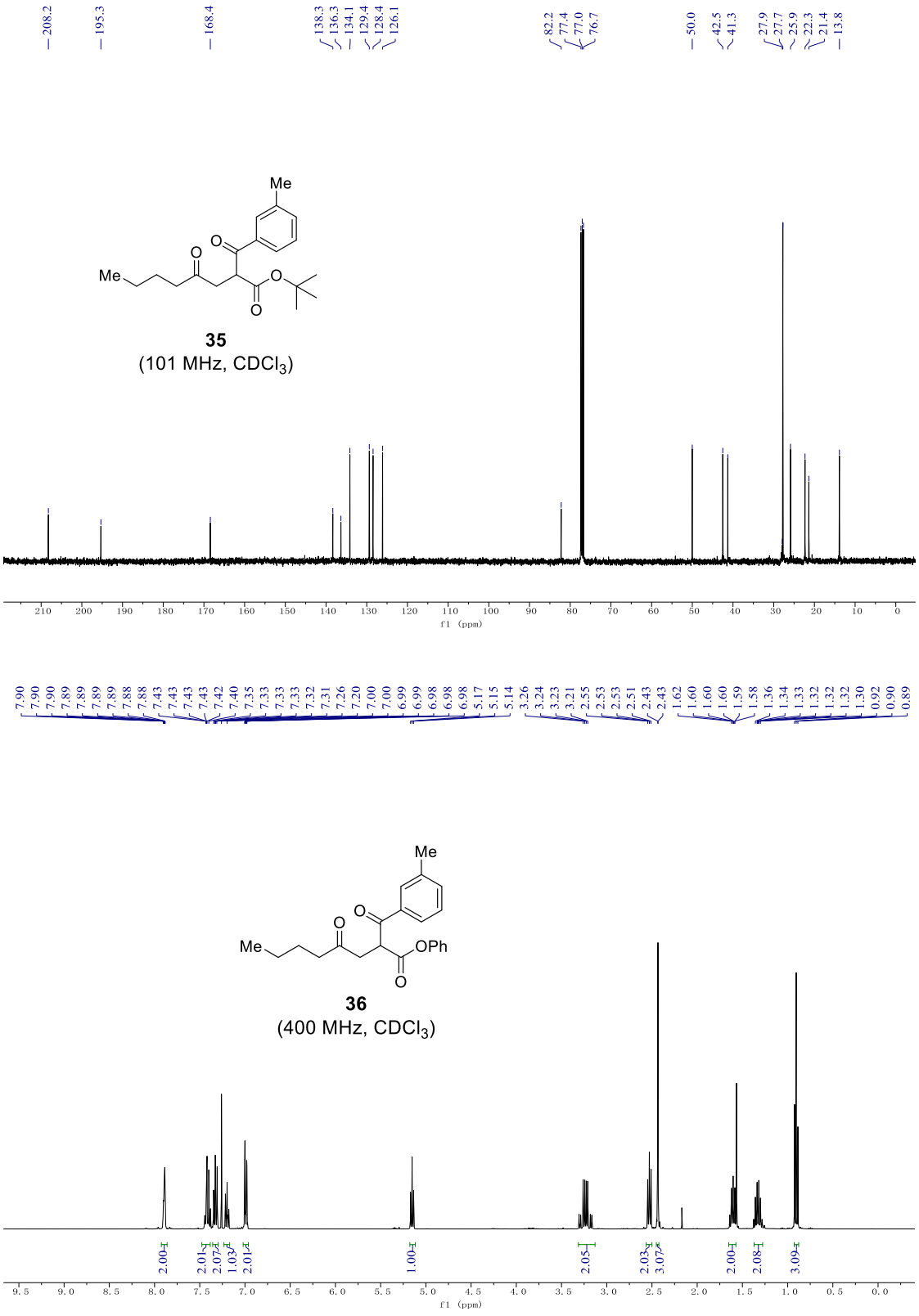

8.13
8.12
8.12
8.12
7.88
7.88
7.87
7.87
7.87
7.87
7.44
7.44
7.44
7.43
7.40
7.40
7.40
7.38
7.26
6.76
6.76
6.76
6.76
5.09
5.08
5.08
5.06
4.18
4.16
4.14
4.12
3.58
3.56
3.53
3.51
3.51
3.49
3.46
3.45
2.43
2.42
2.42
2.42
1.19
1.17
1.15
Me
O
O
CO2Et
O
33
(400 MHz, CDCl3)
1.00
2.06
3.20
1.00
1.00
2.09
2.04
3.06
3.00
f1 (ppm)

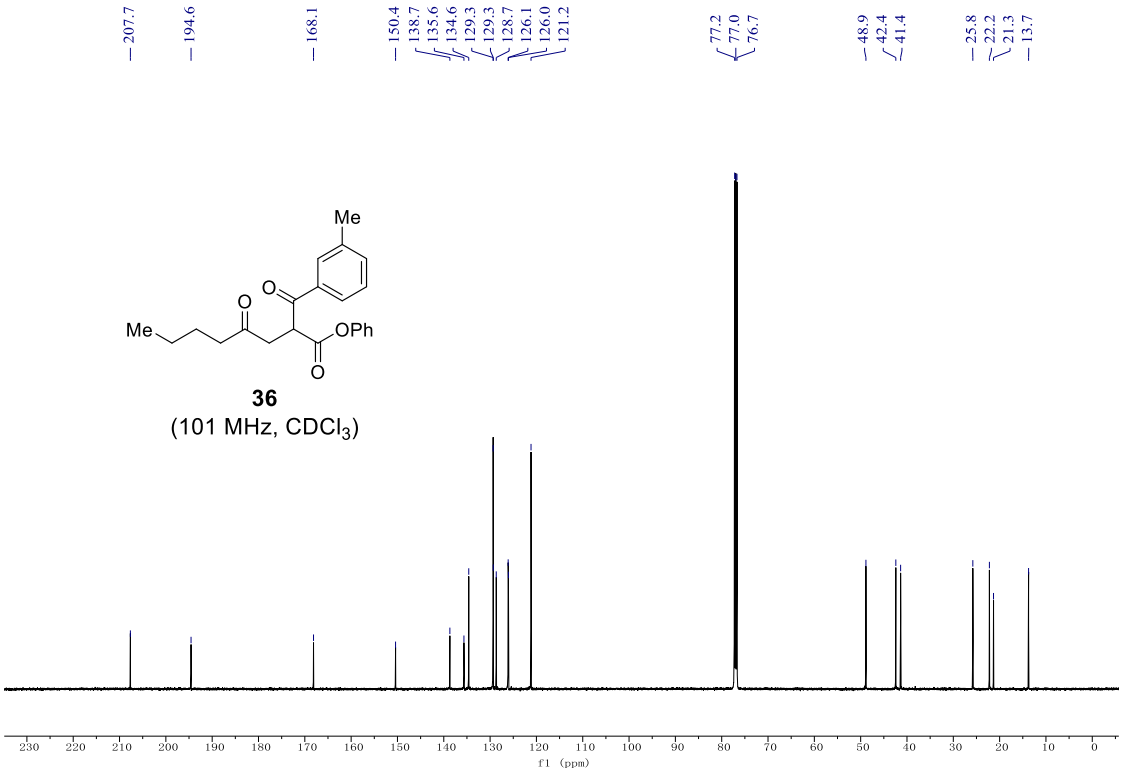

194.8
191.6
169.2
147.6
144.3
138.5
136.0
134.4
129.4
128.6
127.0
126.2
108.5
77.3
77.0
76.7
61.8
48.5
39.4
21.3
13.9
Me
O
O
CO2Et
O
33
(101 MHz, CDCl3)
f1 (ppm)

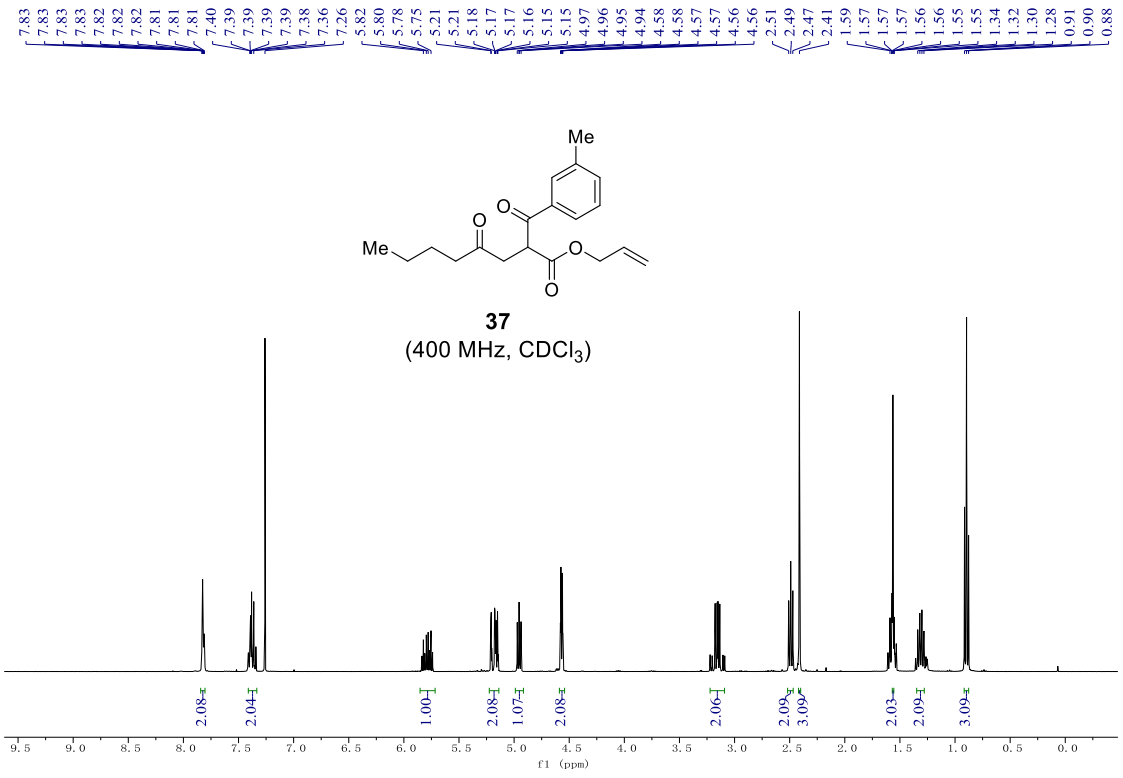

7.87
7.87
7.87
7.87
7.60
7.60
7.59
7.59
7.40
7.40
7.39
7.37
7.26
7.26
7.25
7.25
7.25
6.55
6.55
6.54
6.54
6.54
5.09
5.07
5.05
4.18
4.16
4.14
4.13
3.65
3.63
3.61
3.60
3.59
3.58
3.55
3.54
2.42
1.19
1.17
1.15
Me
O
O
CO2Et
O
34
(400 MHz, CDCl3)
2.00
0.98
2.06
1.00
0.98
1.00
2.04
2.00
3.09
3.08
f1 (ppm)

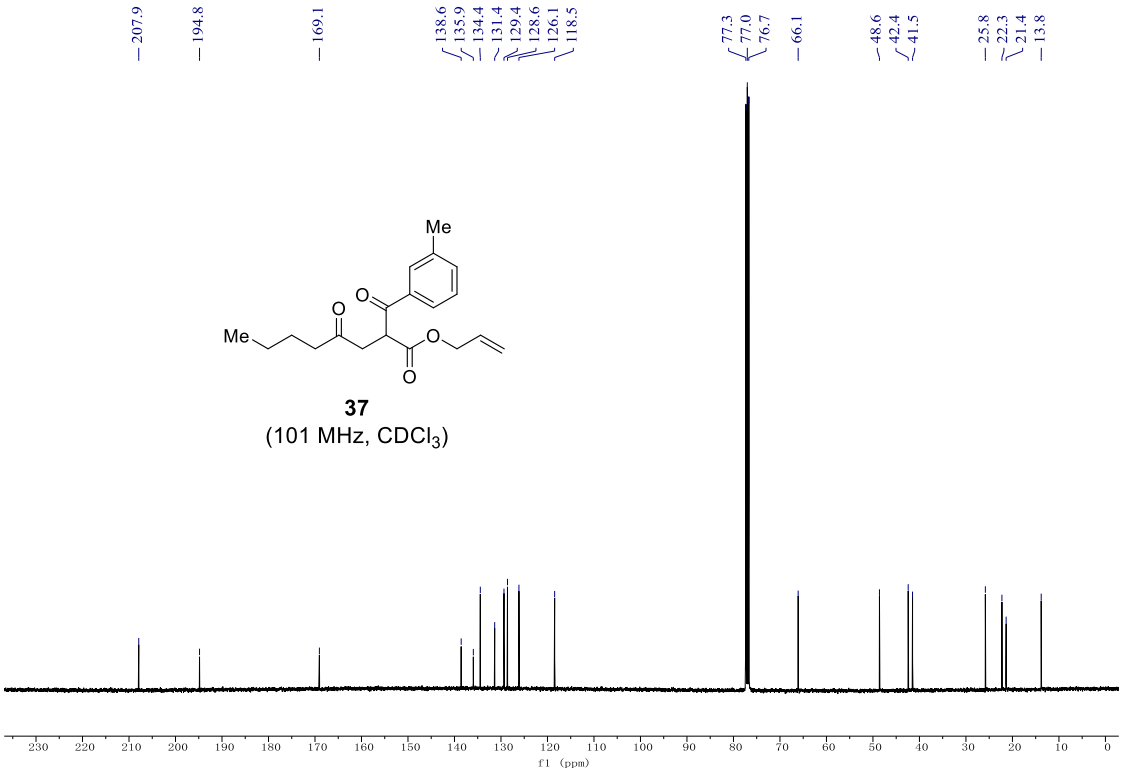

194.8
185.9
169.2
152.1
146.6
138.5
136.0
134.4
129.4
128.5
126.2
117.6
112.3
77.3
77.0
76.7
61.7
48.5
37.6
21.3
13.9
Me
O
O
CO2Et
O
34
(101 MHz, CDCl3)
f1 (ppm)


Me
O
O
Me
O
O
35
(400 MHz, CDCl3)
2.05
2.03
1.00
2.09
2.07
3.09
2.05
9.04
2.04
3.07
f1 (ppm)


208.2
195.3
168.4
138.3
136.3
134.1
129.4
128.4
126.1
82.2
77.4
77.0
76.7
50.0
42.5
41.3
27.9
27.7
25.9
22.3
21.4
13.8
Me
O
O
Me
O
O
35
(101 MHz, CDCl3)
f1 (ppm)
7.90
7.90
7.90
7.89
7.89
7.89
7.89
7.88
7.88
7.43
7.43
7.43
7.43
7.42
7.40
7.35
7.33
7.33
7.33
7.32
7.31
7.26
7.20
7.00
7.00
7.00
6.99
6.99
6.98
6.98
6.98
5.17
5.15
5.14
3.26
3.24
3.23
3.21
2.55
2.53
2.53
2.51
2.43
2.43
1.62
1.60
1.60
1.60
1.59
1.58
1.36
1.34
1.33
1.32
1.32
1.32
1.30
0.92
0.90
0.89
Me
O
O
Me
OPh
O
36
(400 MHz, CDCl3)
2.00
2.01
2.07
1.03
2.01
1.00
2.05
2.03
3.07
2.00
2.08
3.09
f1 (ppm)

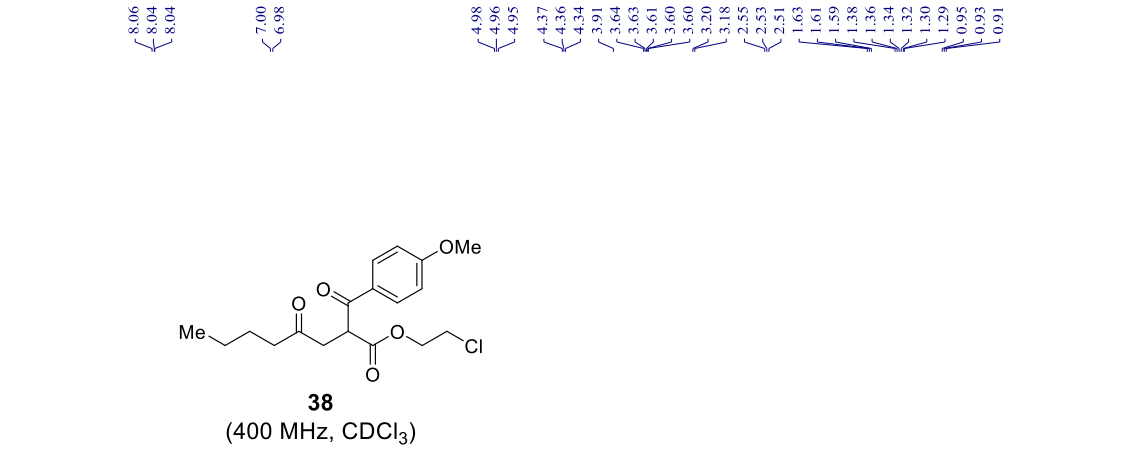

207.7
194.6
168.1
150.4
138.7
135.6
134.6
129.3
129.3
128.7
126.1
126.0
121.2
77.2
77.0
76.7
48.9
42.4
41.4
25.8
22.2
21.3
13.7
Me
O
O
Me
OPh
O
36
(101 MHz, CDCl3)
f1 (ppm)


7.83
7.83
7.83
7.82
7.82
7.82
7.81
7.81
7.81
7.40
7.39
7.39
7.39
7.39
7.38
7.36
7.26
5.82
5.80
5.78
5.75
5.21
5.21
5.18
5.17
5.17
5.16
5.15
5.15
4.97
4.96
4.95
4.94
4.58
4.58
4.57
4.57
4.56
4.56
2.51
2.49
2.47
2.41
1.59
1.57
1.57
1.57
1.56
1.56
1.55
1.55
1.34
1.32
1.30
1.28
0.91
0.90
0.88
Me
O
O
Me
O
O
37
(400 MHz, CDCl3)
2.08
2.04
1.00
2.08
1.07
2.08
2.06
2.09
3.09
2.03
2.09
3.09
f1 (ppm)



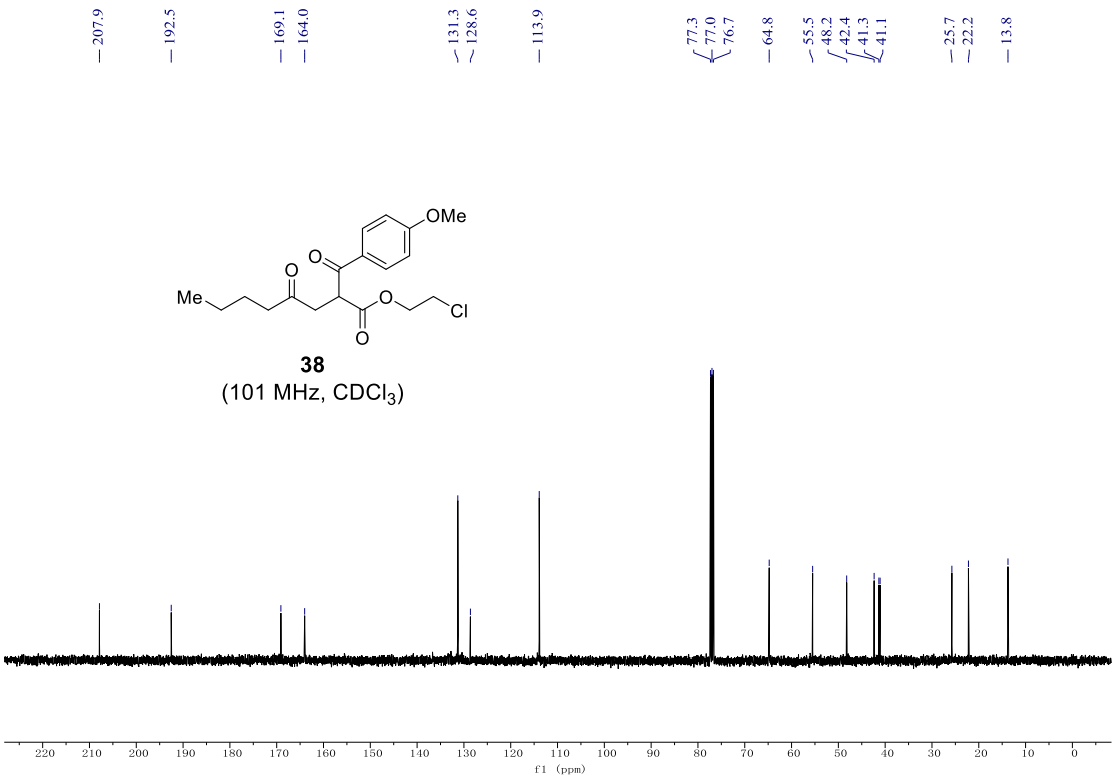
37

(101 MHz, $CDCl_3$)



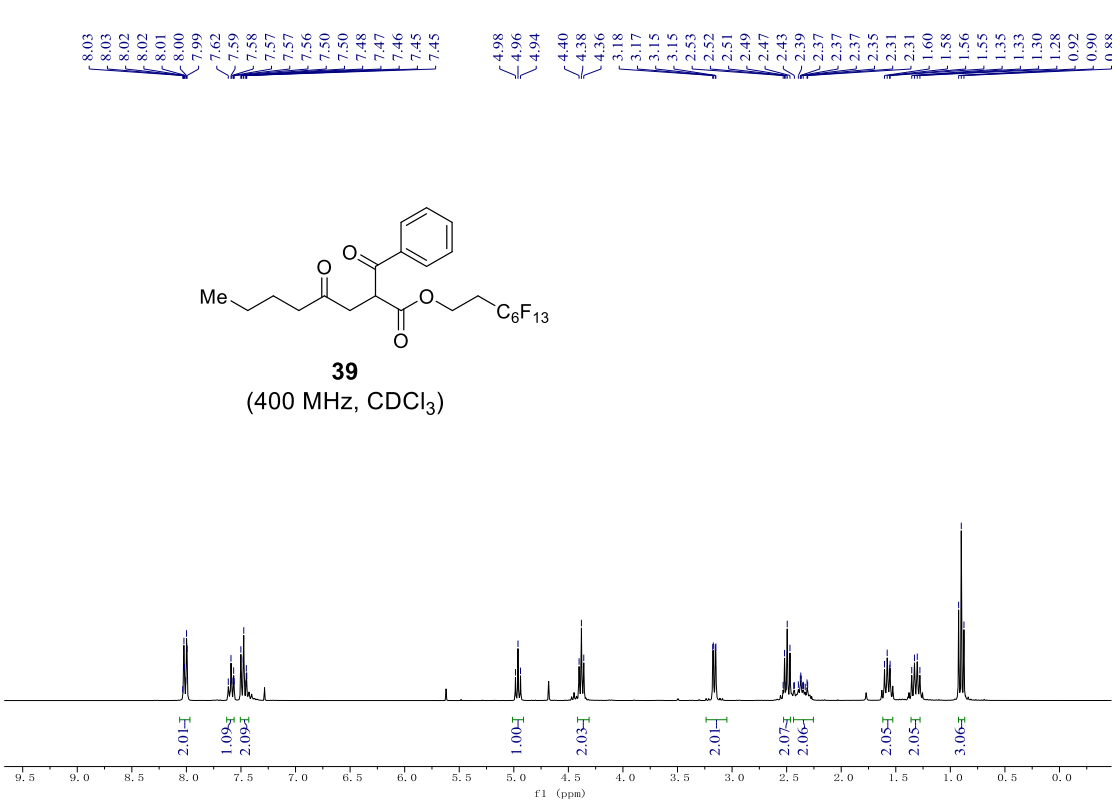
38

(400 MHz, $CDCl_3$)



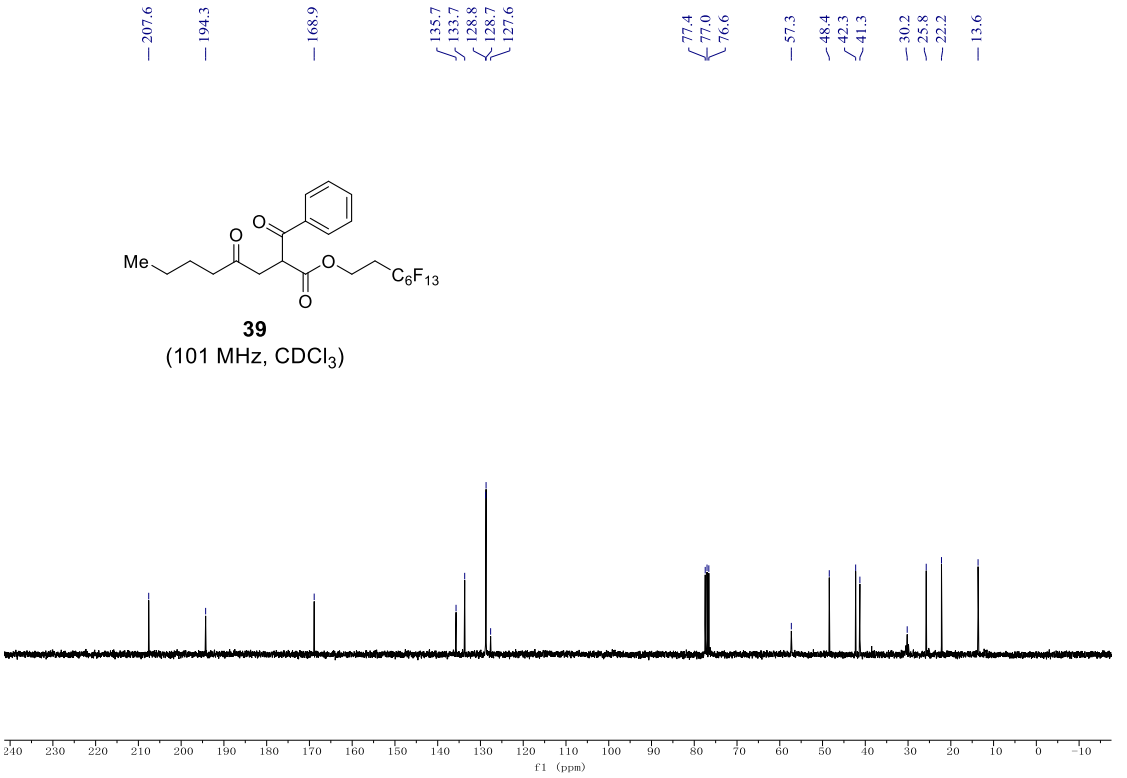
38

(101 MHz, $CDCl_3$)



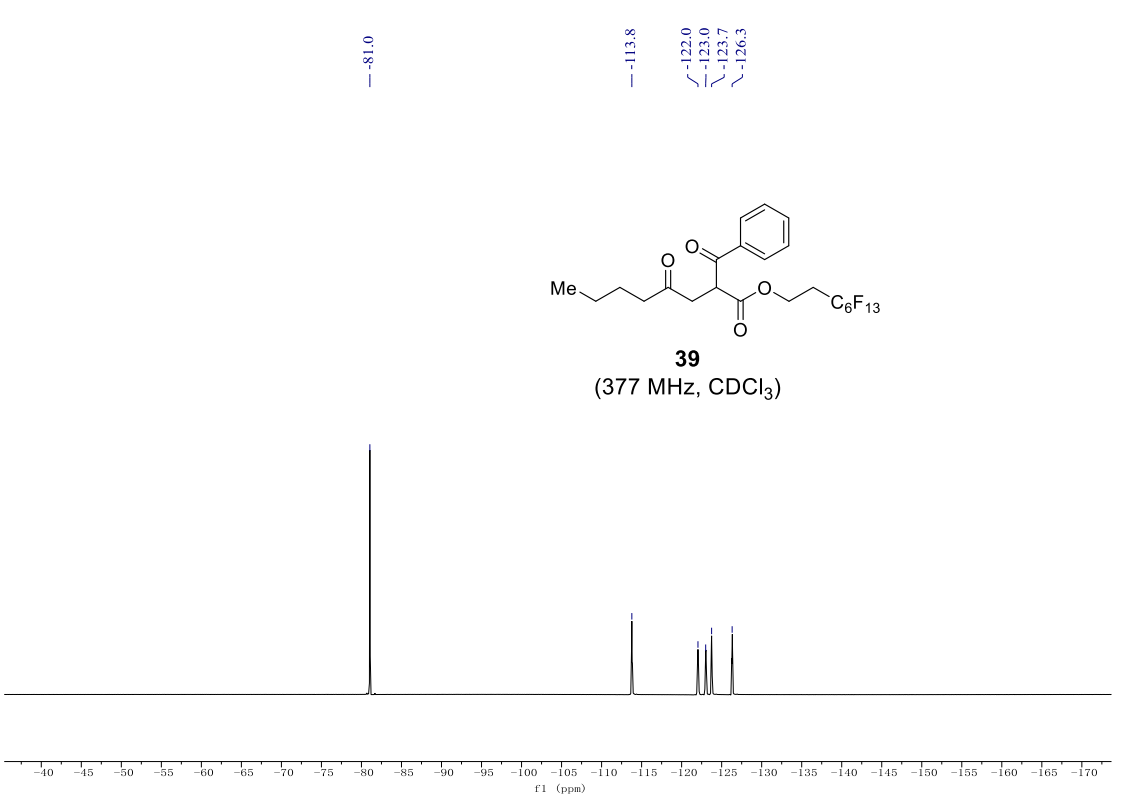
39

(400 MHz, $CDCl_3$)



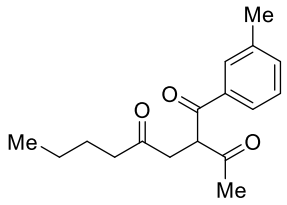
39

(101 MHz, $CDCl_3$)



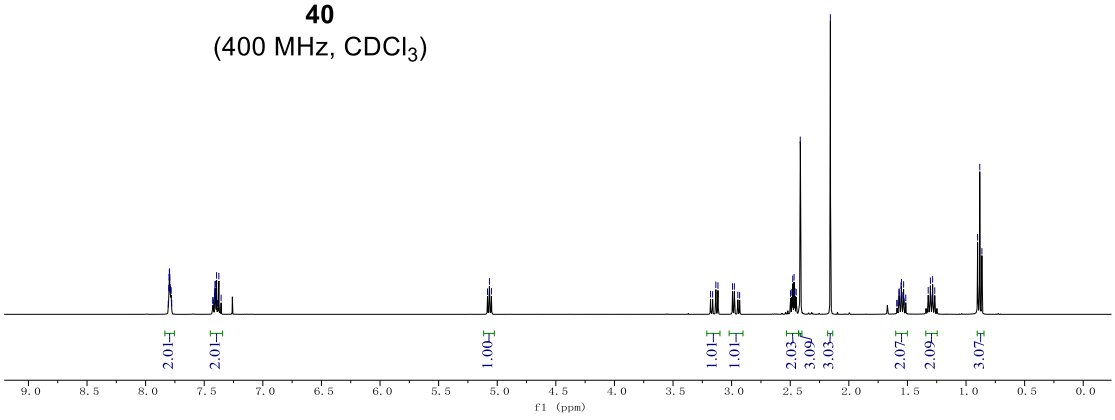
39

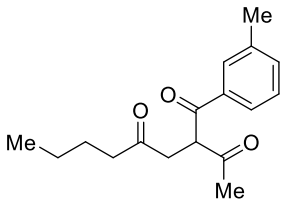
(377 MHz, $CDCl_3$)



40

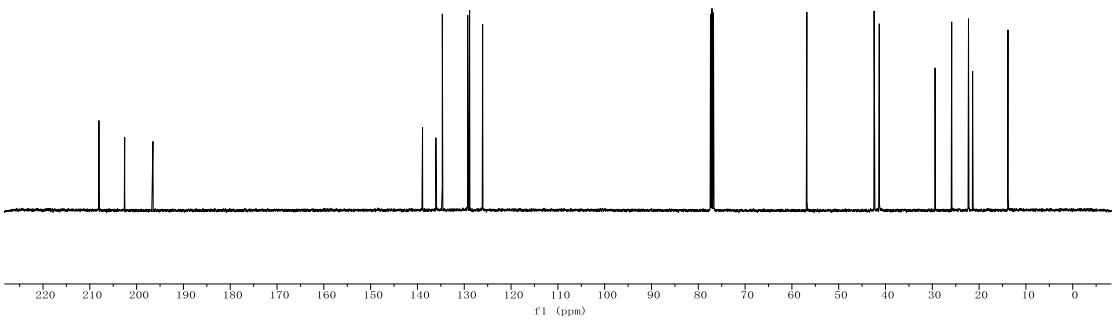
(400 MHz, $CDCl_3$)

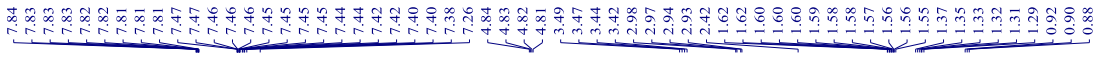


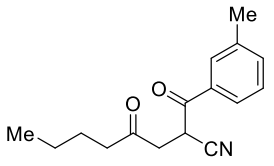


40

(101 MHz, $CDCl_3$)

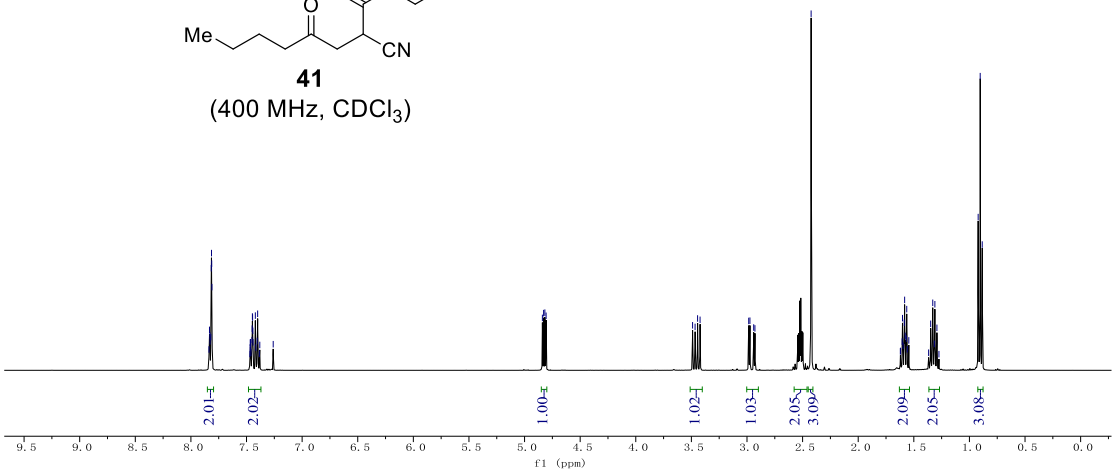


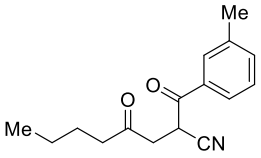




41

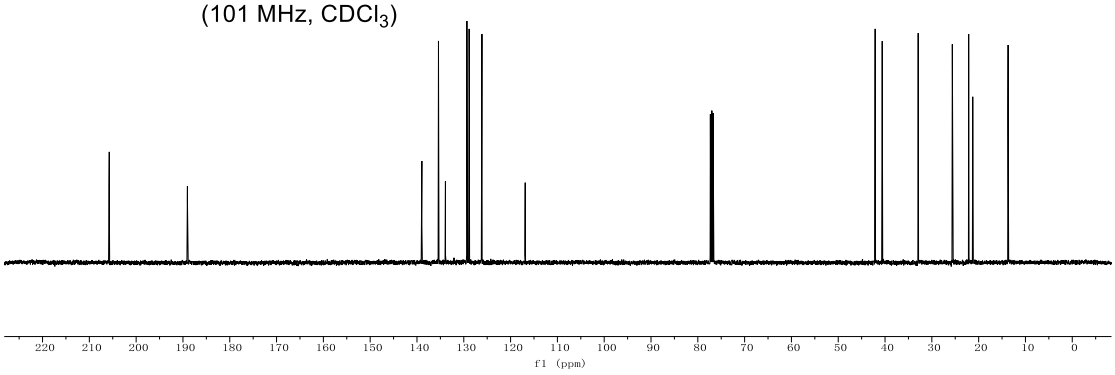
(400 MHz, $CDCl_3$)

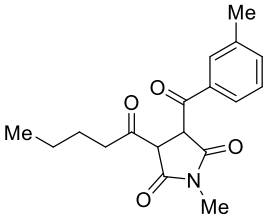




41

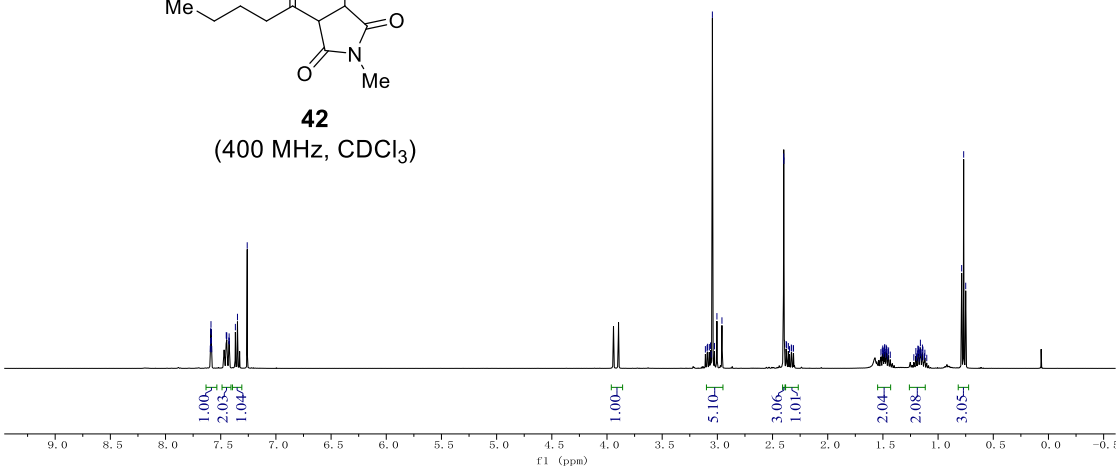
(101 MHz, $CDCl_3$)

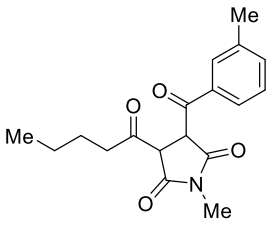




42

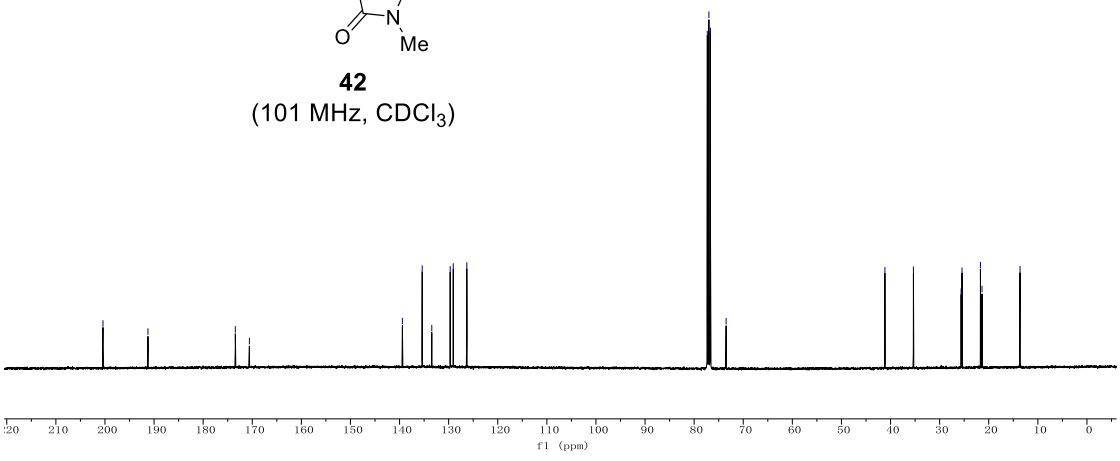
(400 MHz, $CDCl_3$)

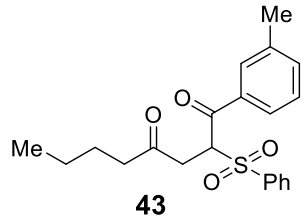




42

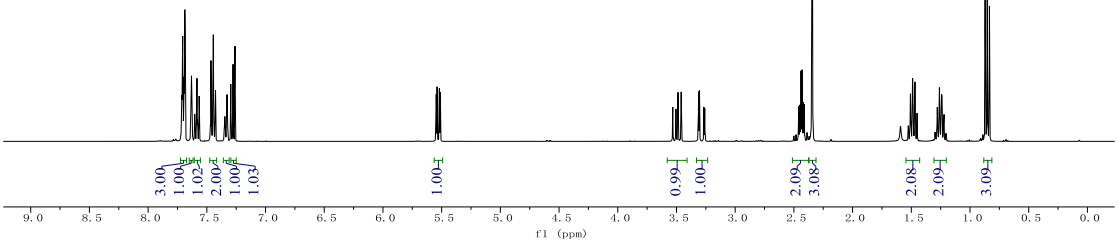
(101 MHz, $CDCl_3$)





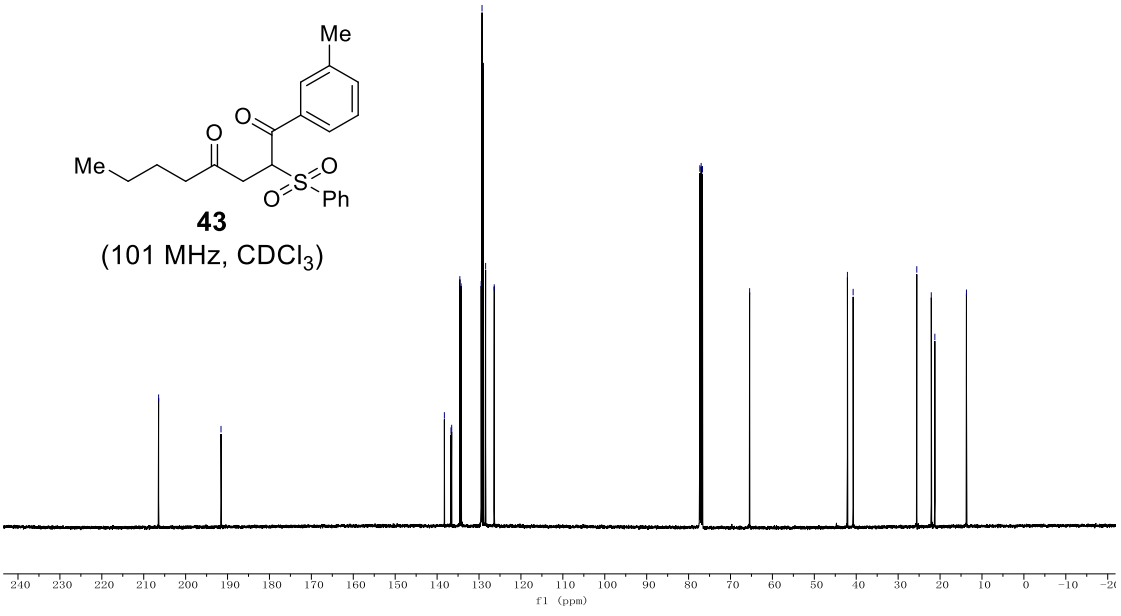
43

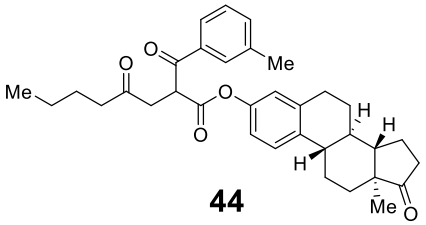
(400 MHz, $CDCl_3$)



43

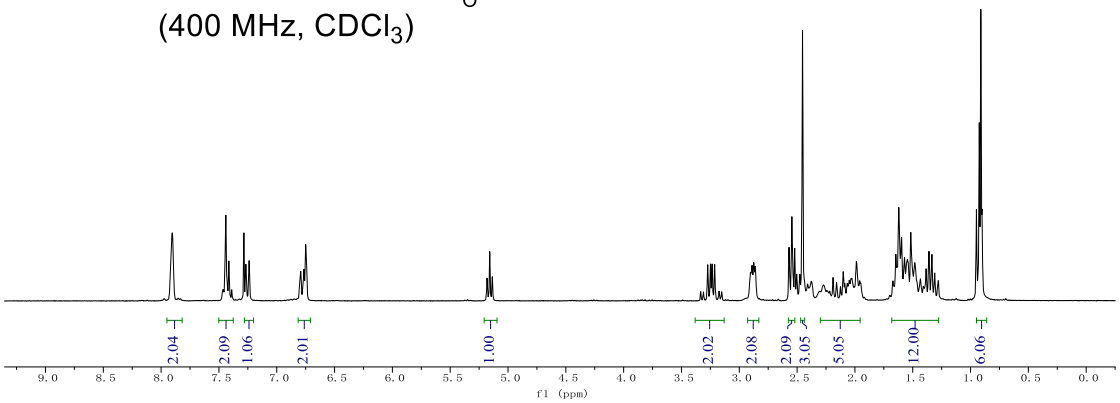
(101 MHz, $CDCl_3$)





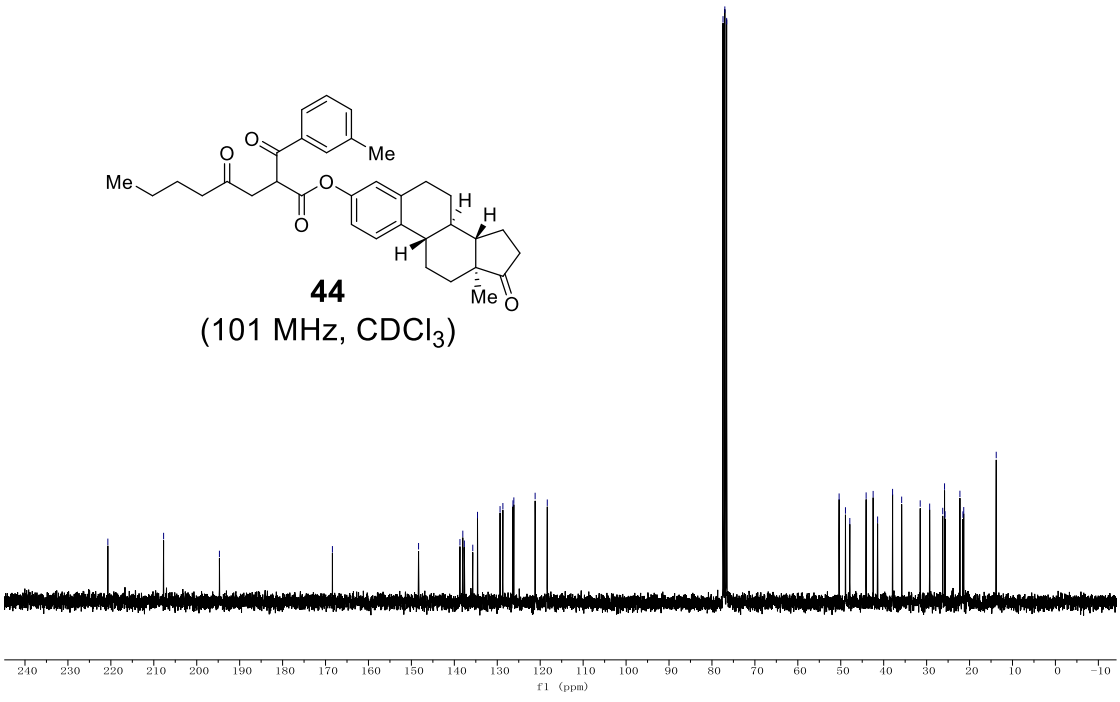
44

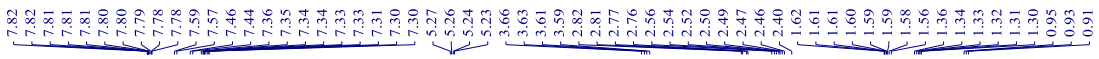
(400 MHz, $CDCl_3$)

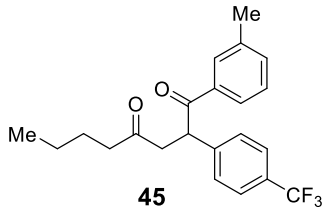


44

(101 MHz, $CDCl_3$)

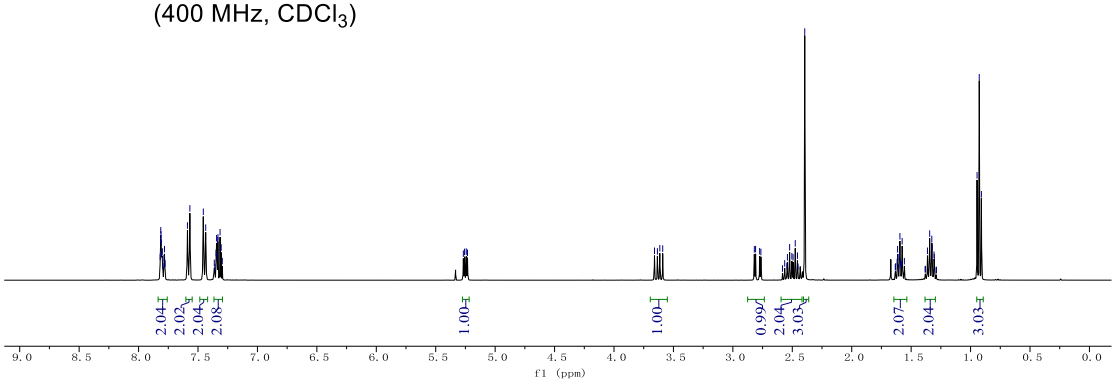


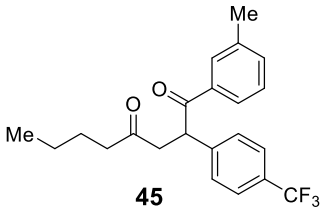




45

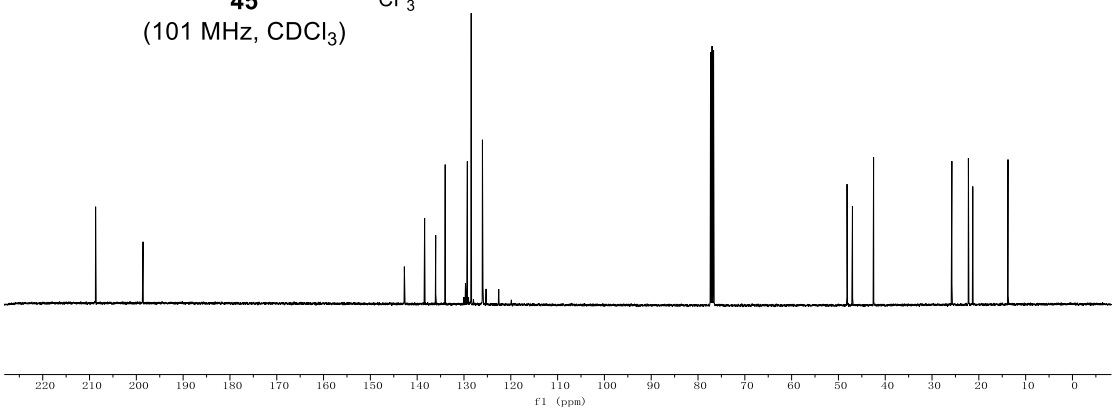
(400 MHz, $CDCl_3$)





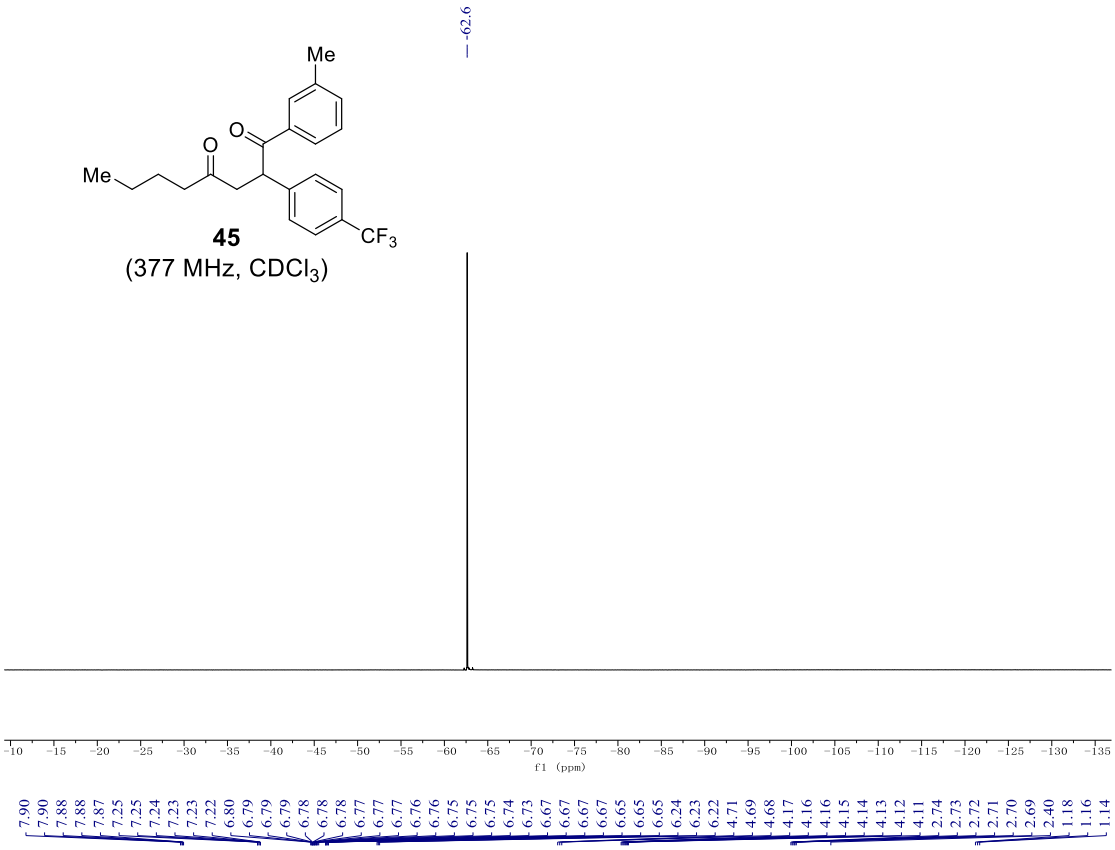
45

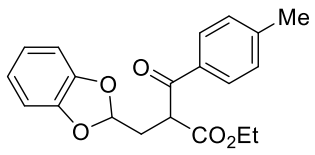
(101 MHz, $CDCl_3$)



45

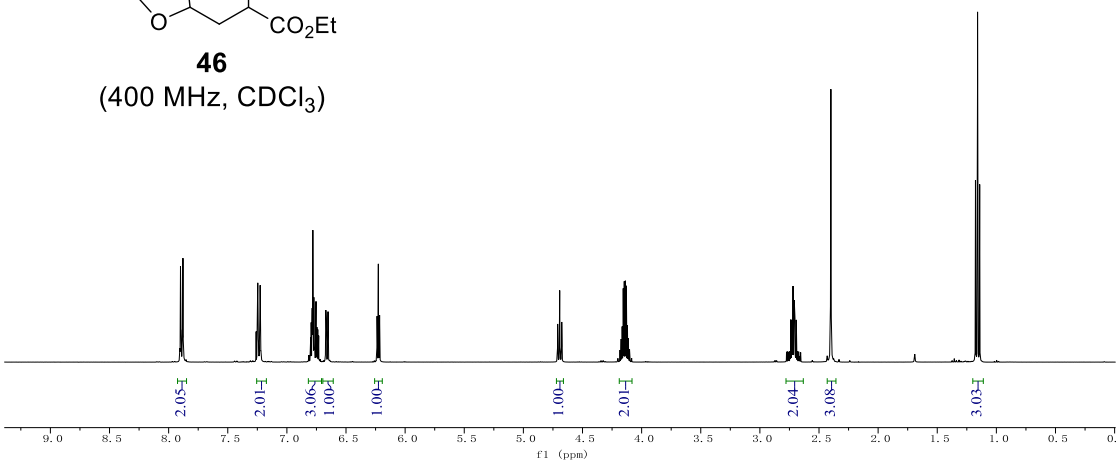
(377 MHz, $CDCl_3$)

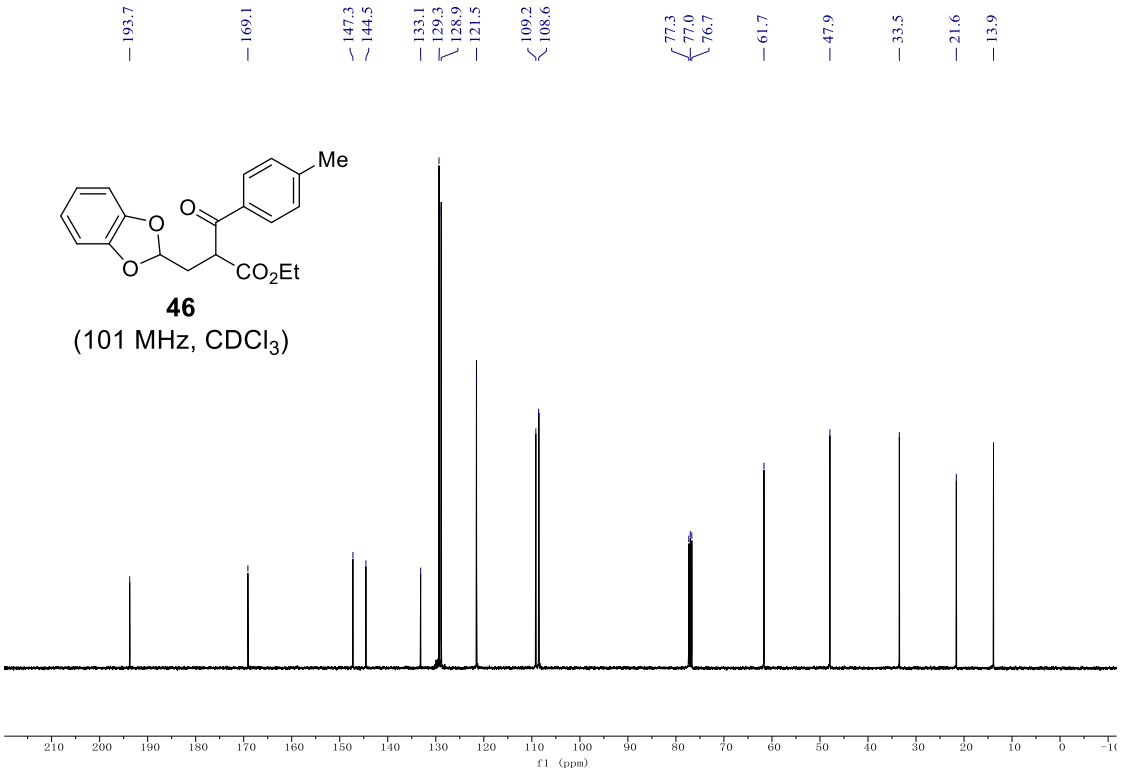




46

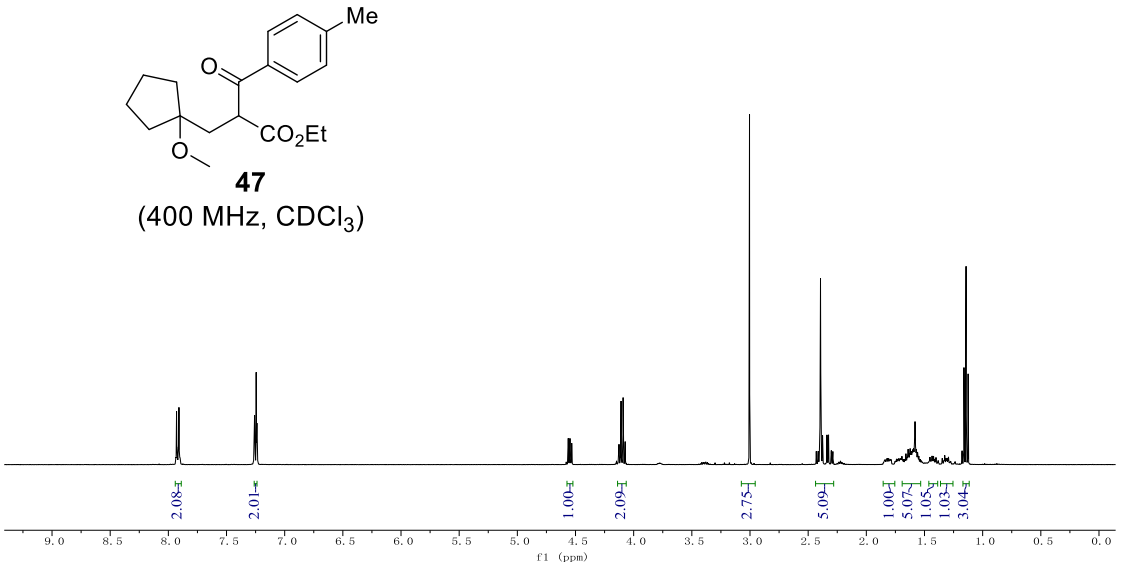
(400 MHz, $CDCl_3$)





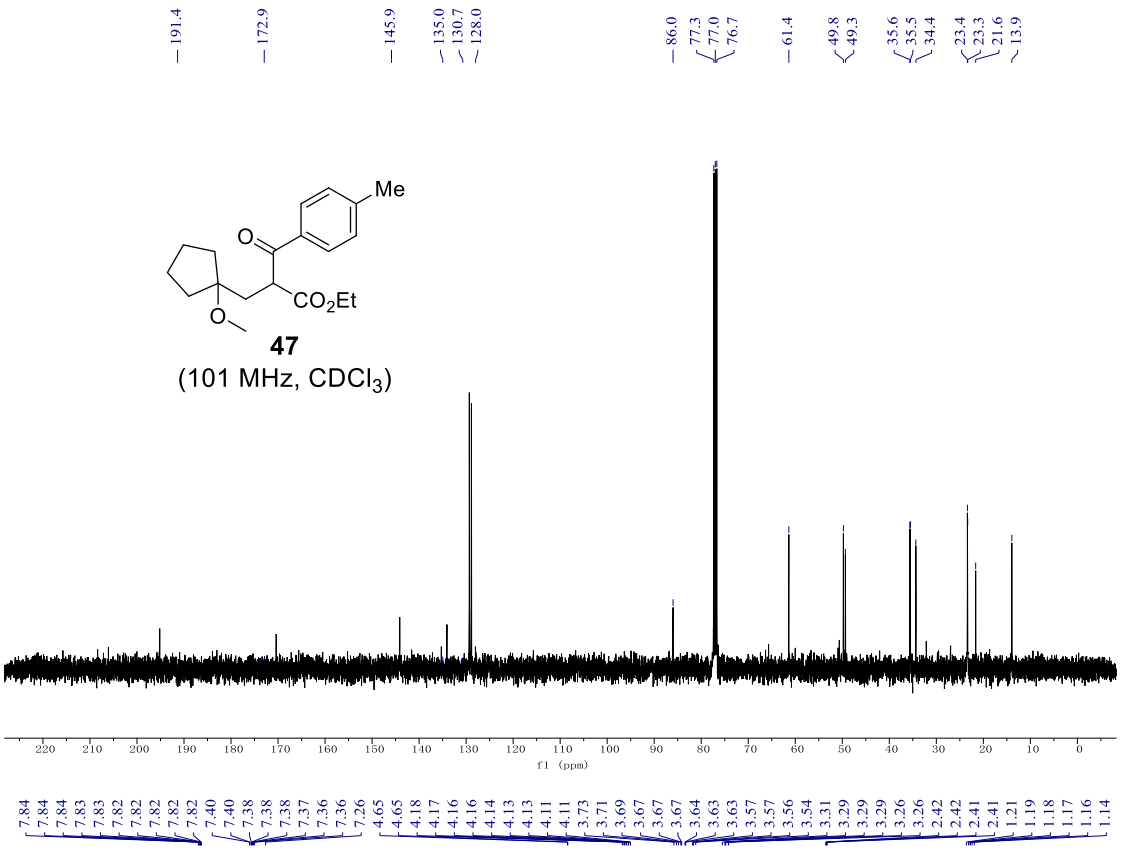
46

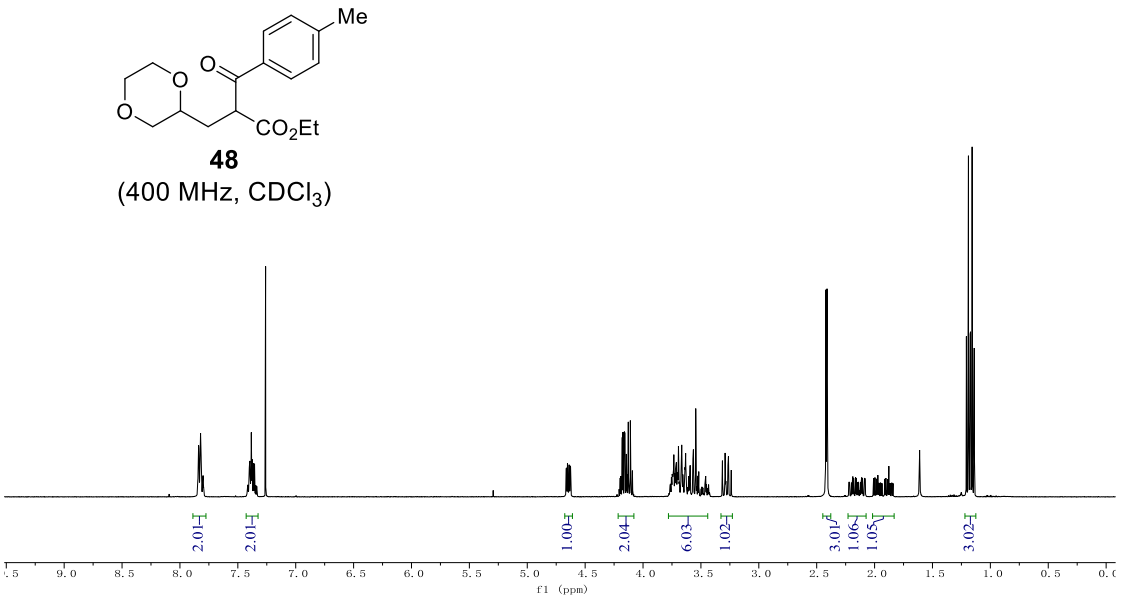
(101 MHz, $CDCl_3$)

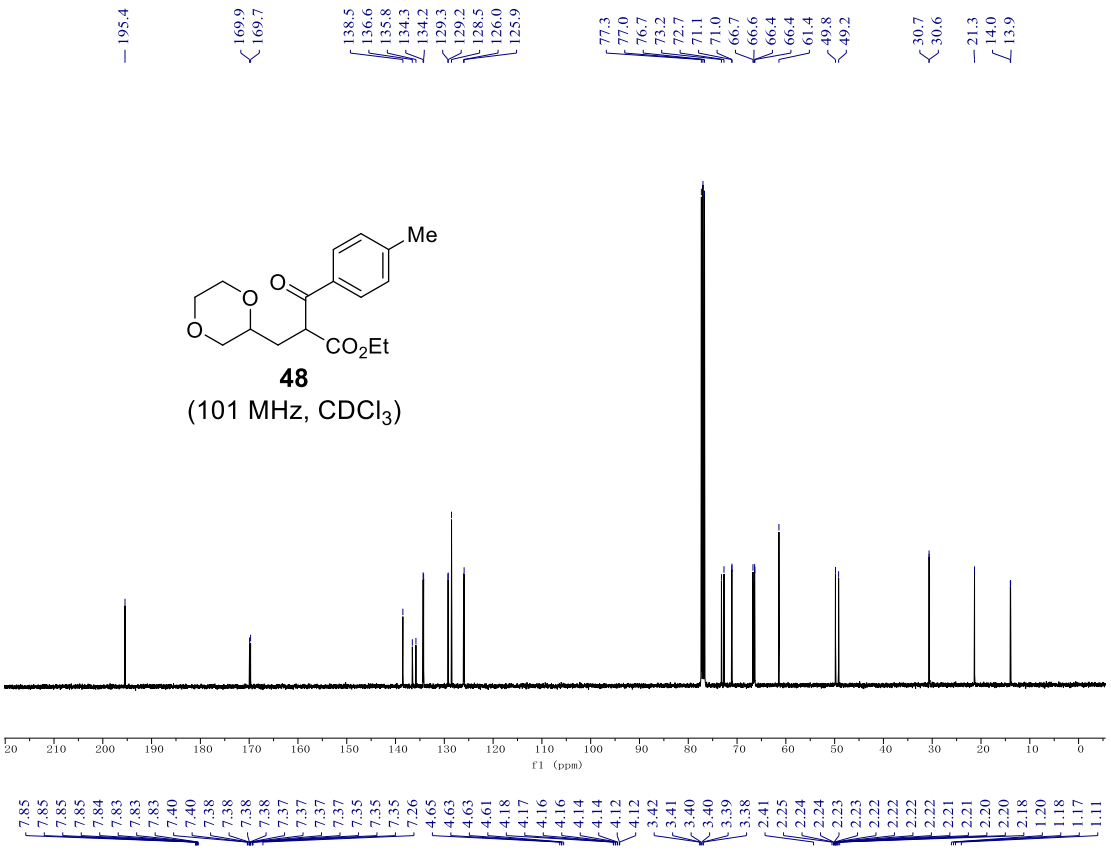


47

(400 MHz, $CDCl_3$)

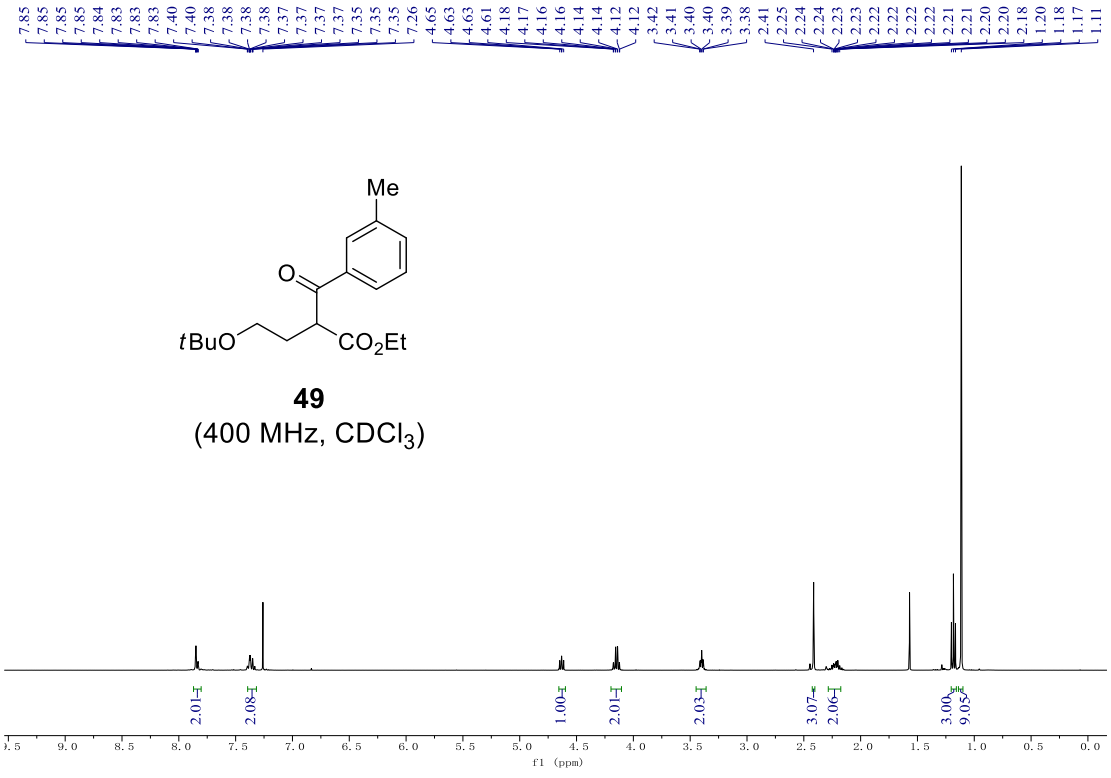

191.4
172.9
145.9
135.0
130.7
128.0
86.0
77.3
77.0
76.7
61.4
49.8
49.3
35.6
35.5
34.4
23.4
23.3
21.6
13.9
Me
O
CO2Et
O
47
(101 MHz, CDCl3)
f1 (ppm)


Me
O
O
O
CO2Et
48
(400 MHz, CDCl3)
2.01
2.01
1.00
2.04
6.03
1.02
3.01
1.06
1.05
3.02
f1 (ppm)



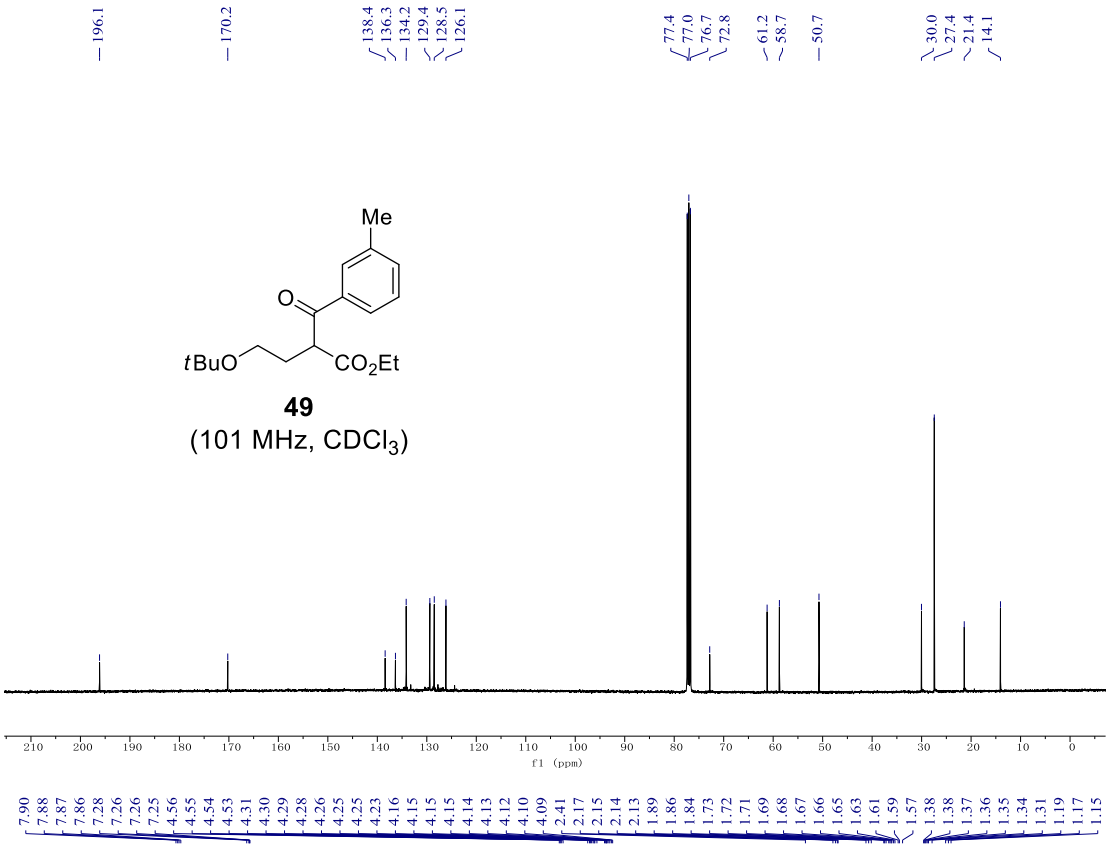
48

(101 MHz, $CDCl_3$)



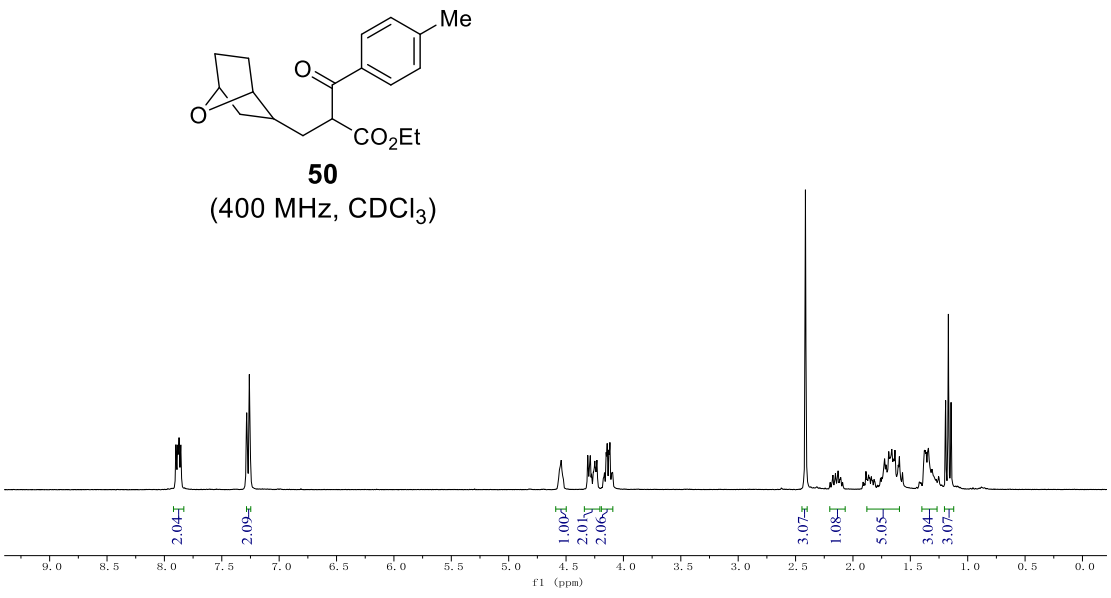
49

(400 MHz, $CDCl_3$)



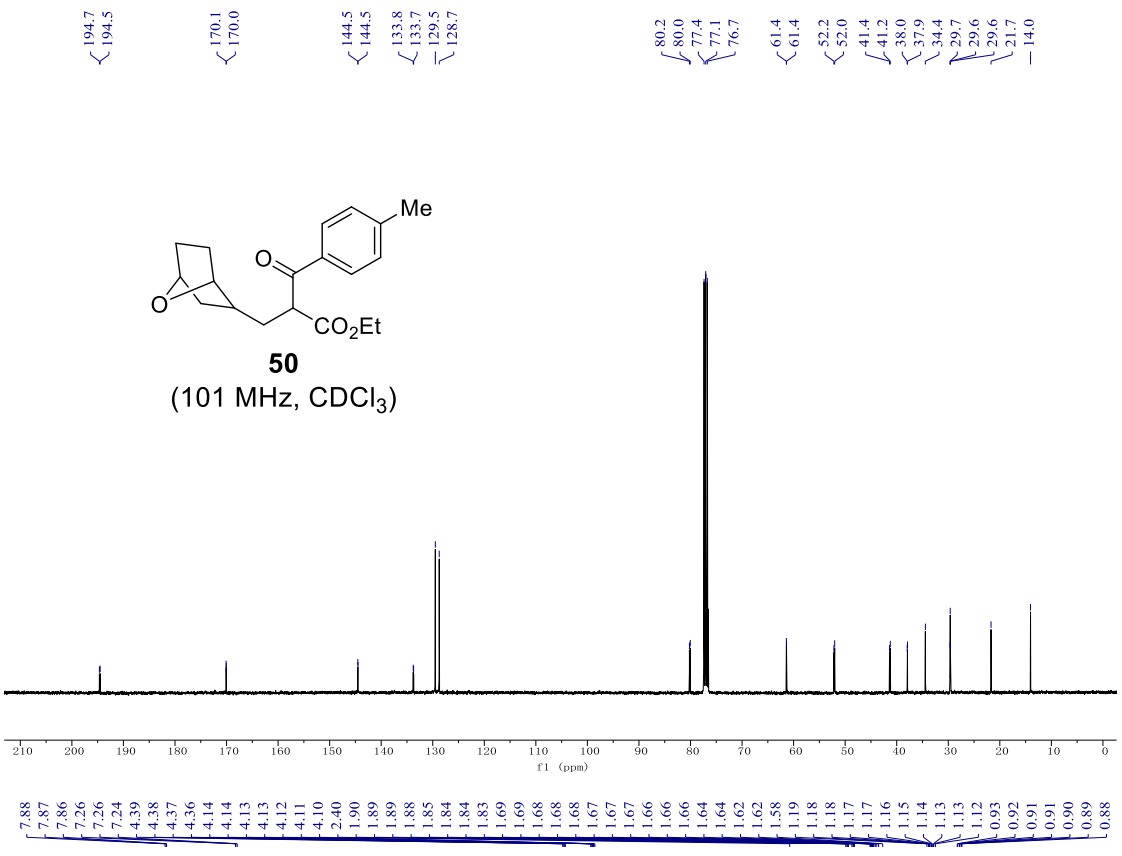
49

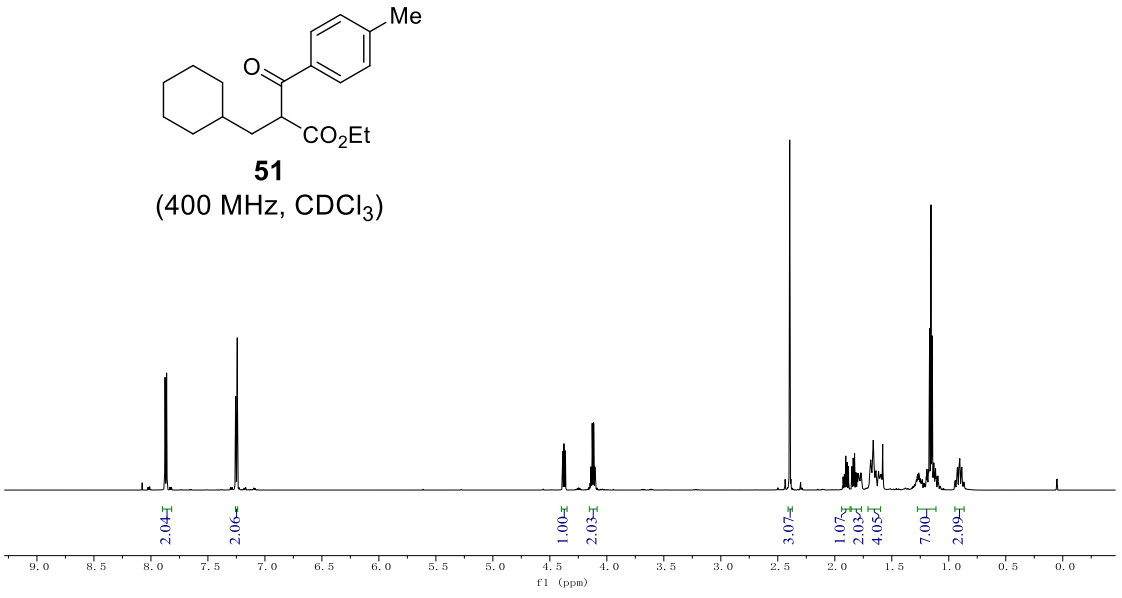
(101 MHz, $CDCl_3$)

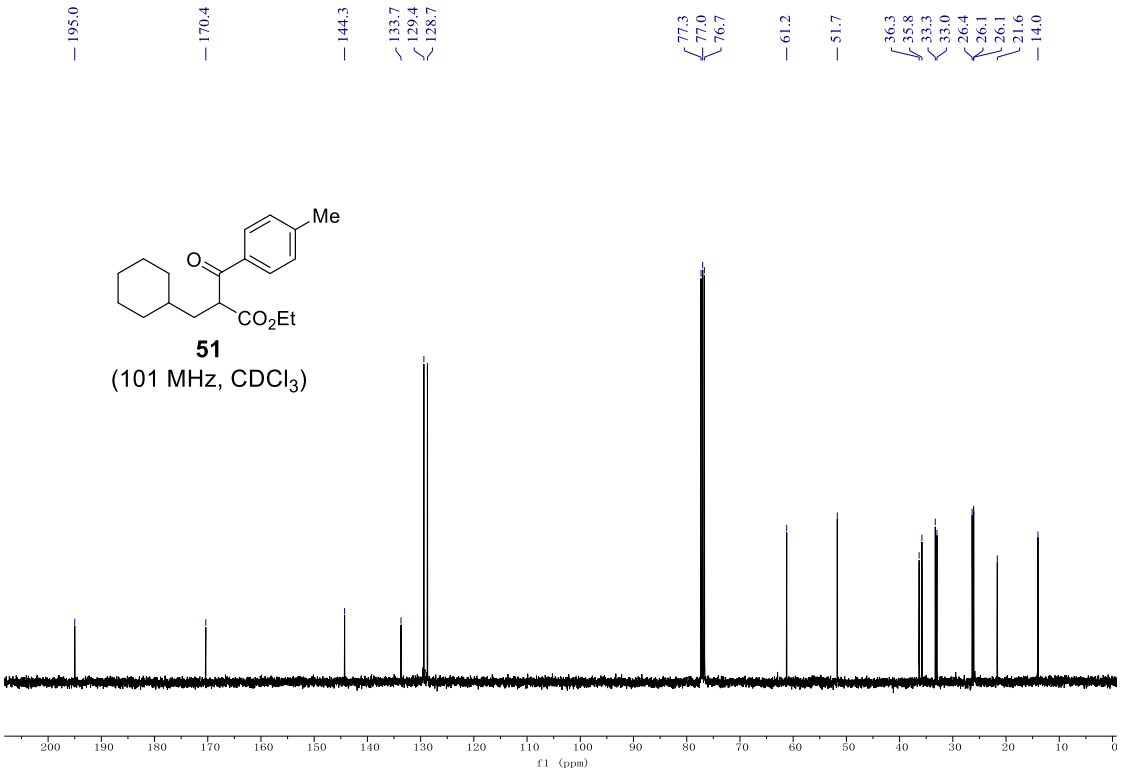


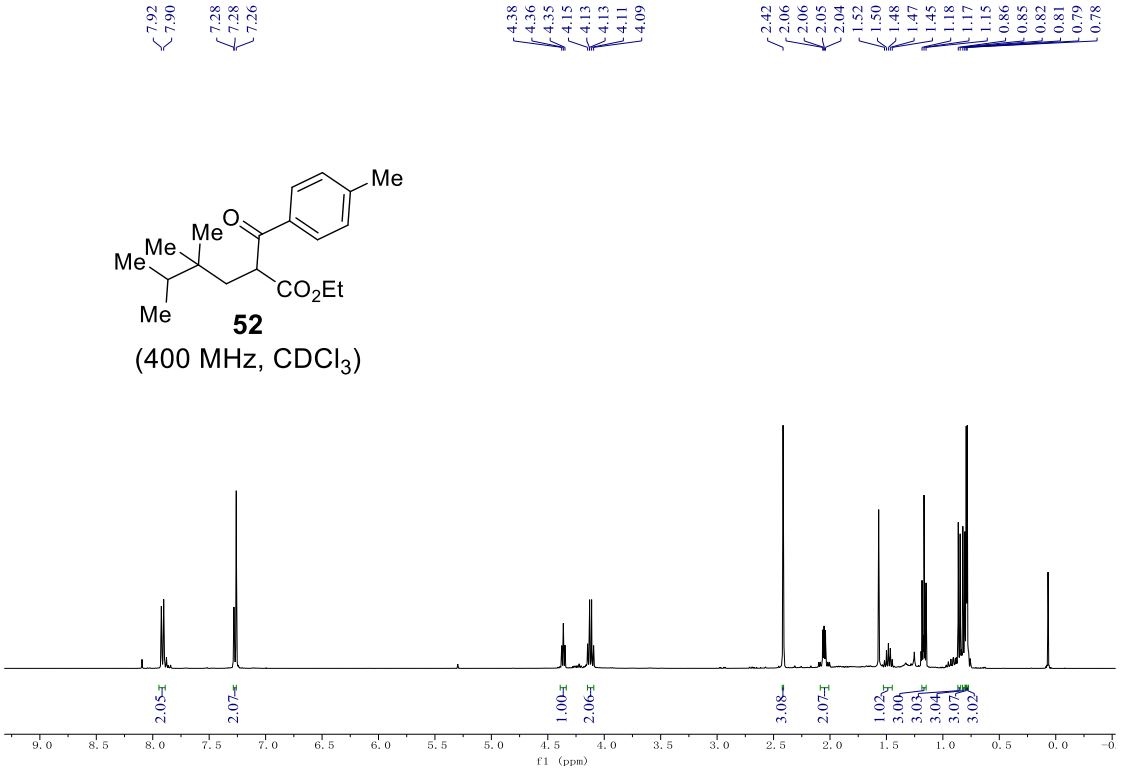
50

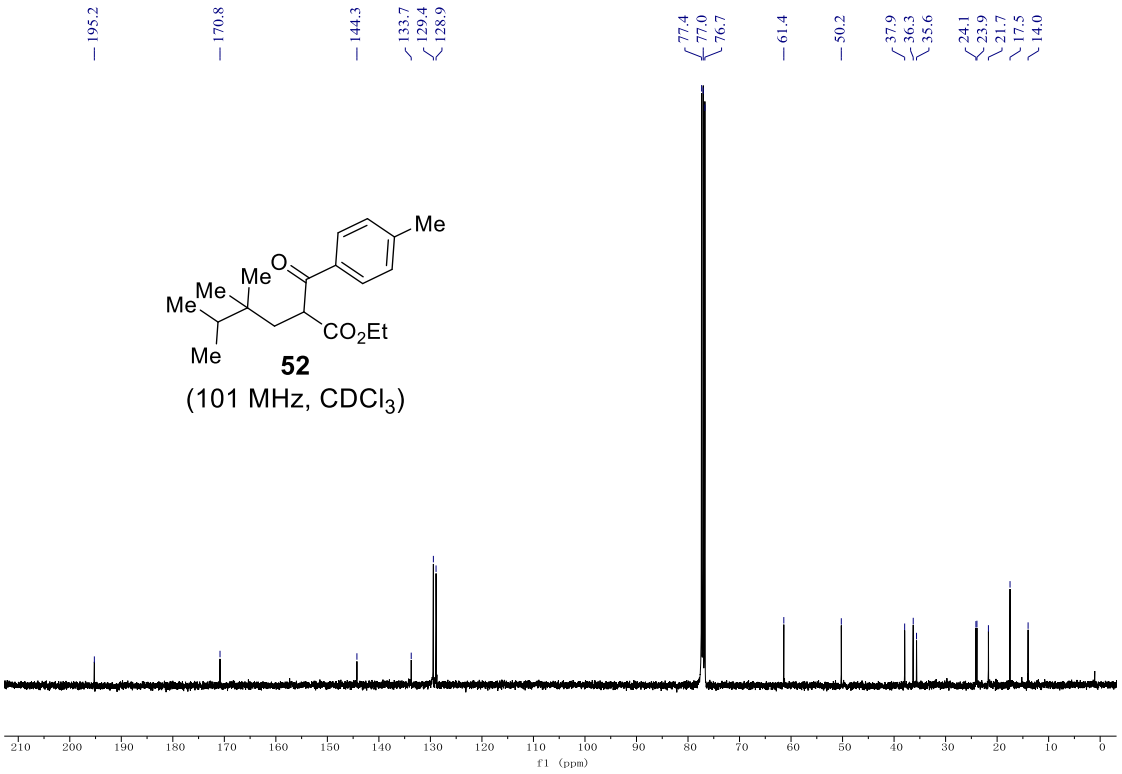
(400 MHz, $CDCl_3$)


194.7
194.5
170.1
170.0
144.5
144.5
133.8
133.7
129.5
128.7
80.2
80.0
77.4
77.1
76.7
61.4
61.4
52.2
52.0
41.4
41.2
38.0
37.9
34.4
29.7
29.6
29.6
21.7
14.0
Me
O
O
CO2Et
50
(101 MHz, CDCl3)
f1 (ppm)
7.88
7.87
7.86
7.26
7.26
7.24
4.39
4.38
4.37
4.36
4.14
4.14
4.13
4.13
4.12
4.11
4.10
2.40
1.90
1.89
1.89
1.88
1.85
1.84
1.84
1.83
1.69
1.69
1.68
1.68
1.68
1.67
1.67
1.67
1.66
1.66
1.66
1.64
1.64
1.62
1.62
1.58
1.19
1.18
1.18
1.17
1.17
1.16
1.15
1.14
1.13
1.13
1.12
0.93
0.92
0.91
0.91
0.90
0.89
0.88


Me
O
CO2Et
51
(400 MHz, CDCl3)
2.04
2.06
1.00
2.03
3.07
1.07
2.03
4.05
7.00
2.09
f1 (ppm)

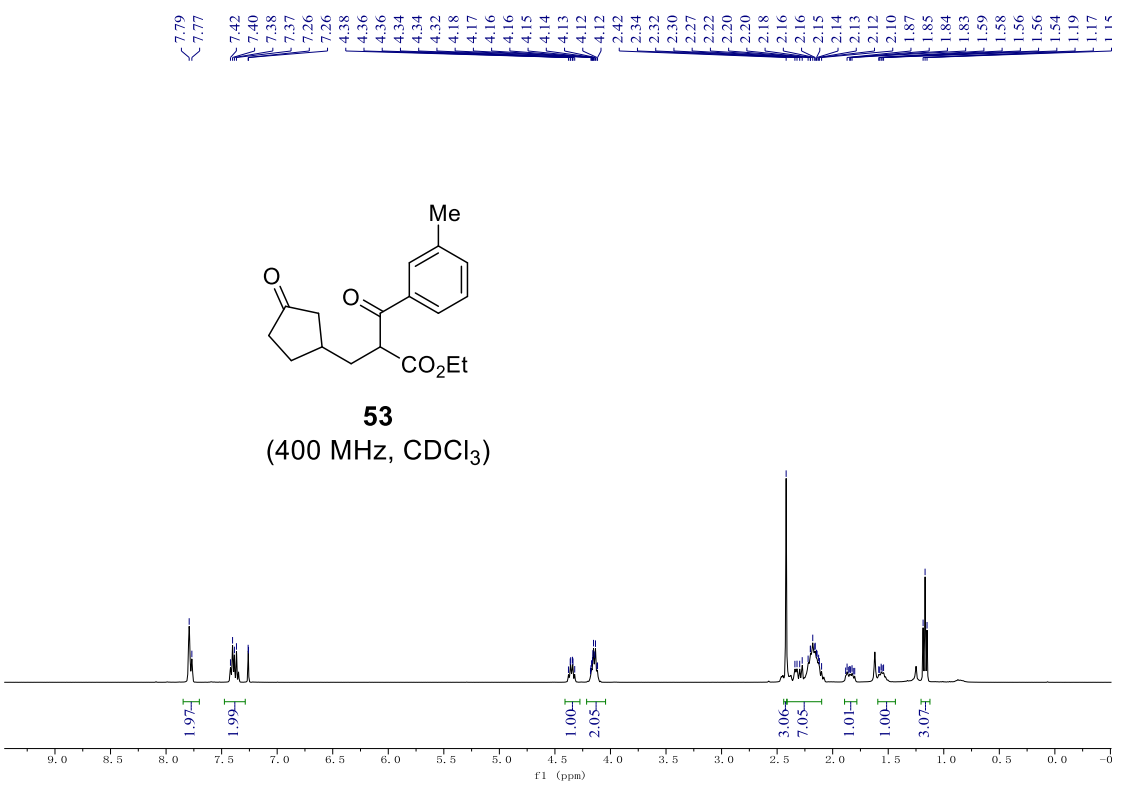

195.0
170.4
144.3
133.7
129.4
128.7
77.3
77.0
76.7
61.2
51.7
36.3
35.8
33.3
33.0
26.4
26.1
26.1
21.6
14.0
Me
O
CO2Et
51
(101 MHz, CDCl3)
f1 (ppm)


7.92
7.90
7.28
7.28
7.26
4.38
4.36
4.35
4.15
4.13
4.13
4.11
4.09
2.42
2.06
2.06
2.05
2.04
1.52
1.50
1.48
1.47
1.45
1.18
1.17
1.15
0.86
0.85
0.82
0.81
0.79
0.78
Me
O
Me
Me
Me
Me
CO2Et
52
(400 MHz, CDCl3)
2.05
2.07
1.00
2.06
3.08
2.07
1.02
3.00
3.03
3.04
3.07
3.02
f1 (ppm)



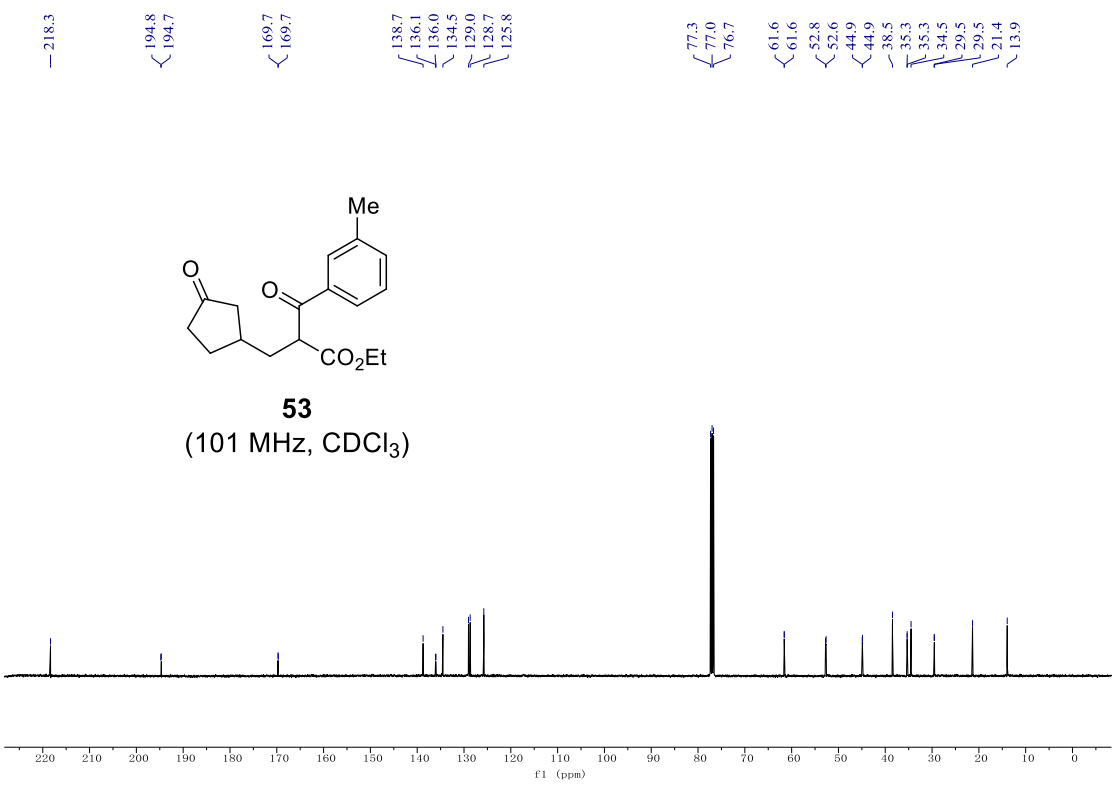
52

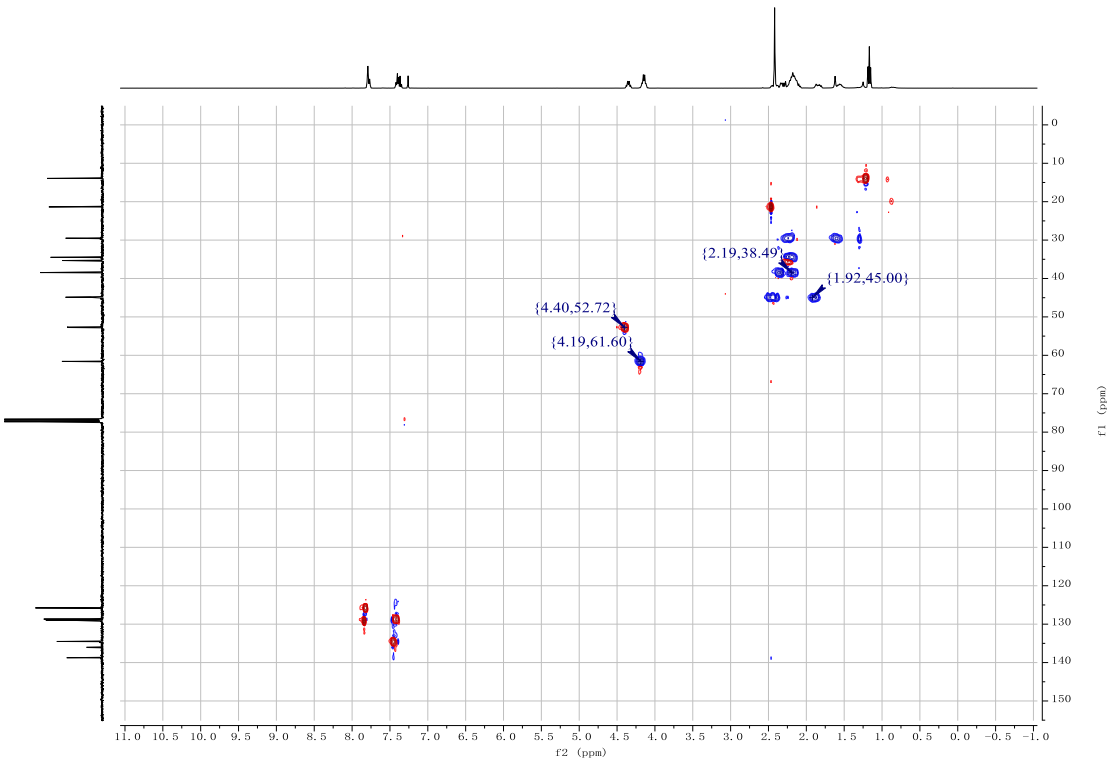
(101 MHz, $CDCl_3$)

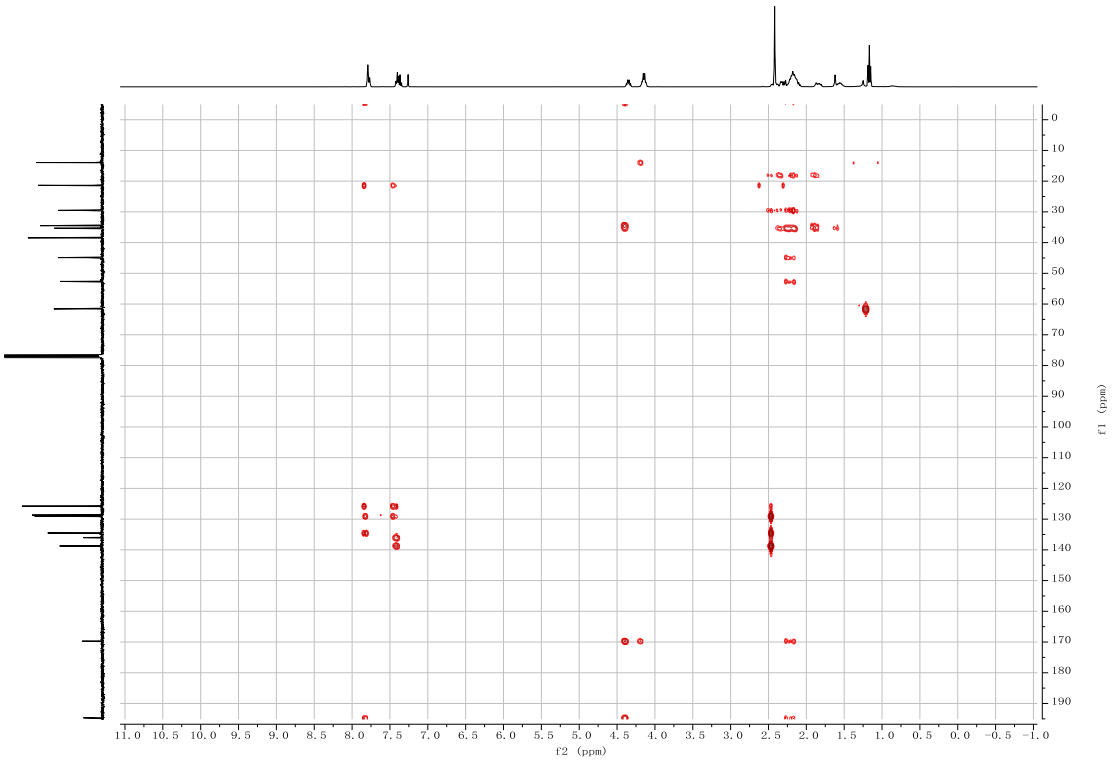


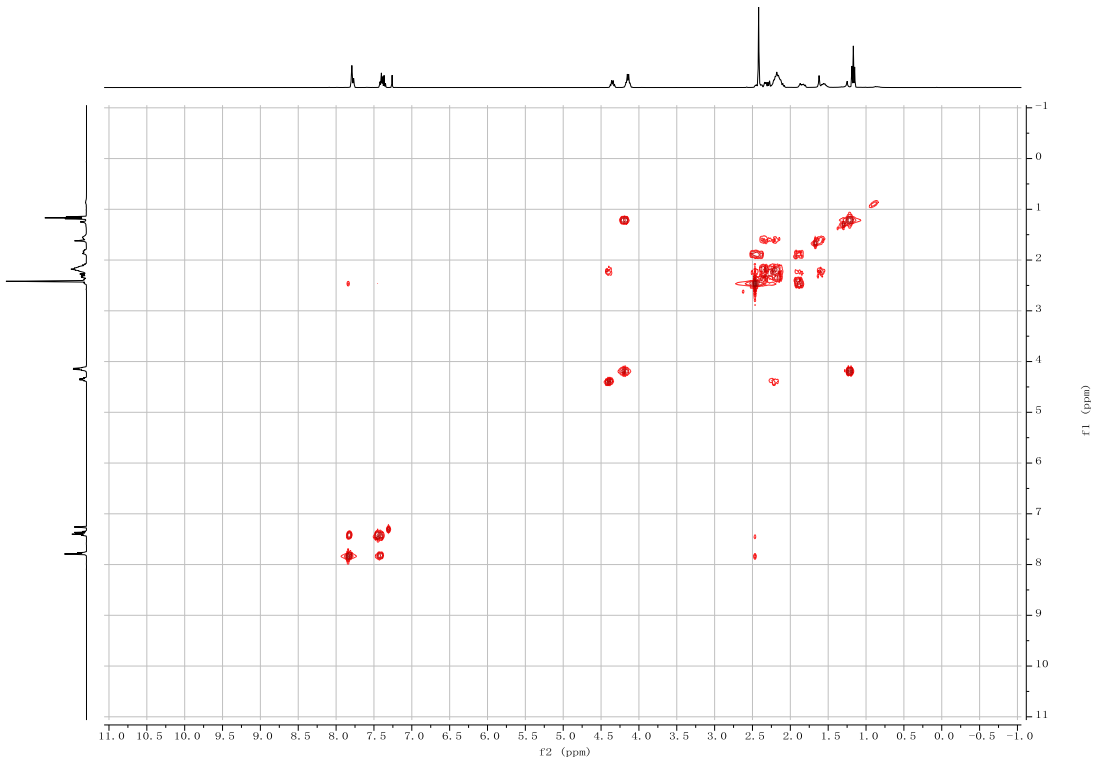
53

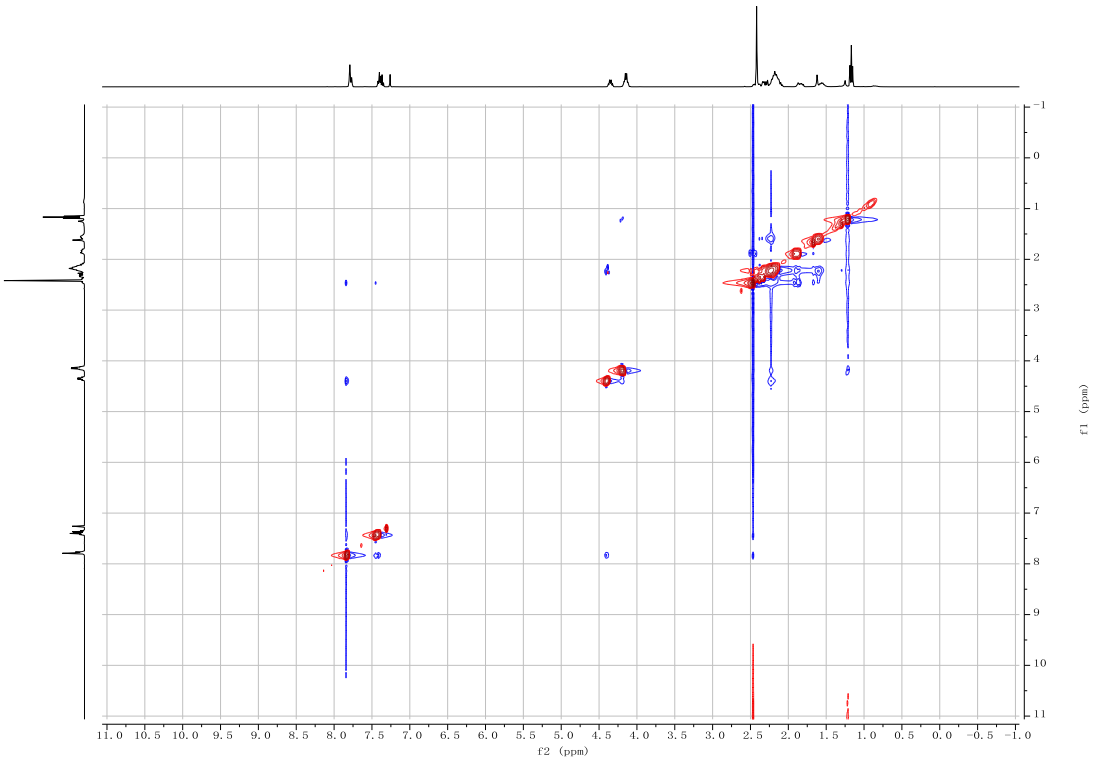
(400 MHz, $CDCl_3$)

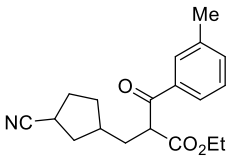

218.3
194.8
194.7
169.7
169.7
138.7
136.1
136.0
134.5
129.0
128.7
125.8
77.3
77.0
76.7
61.6
61.6
52.8
52.6
44.9
44.9
38.5
35.3
35.3
34.5
29.5
29.5
21.4
13.9
Me
O
O
CO2Et
53
(101 MHz, CDCl3)
f1 (ppm)


{2.19,38.49}
{1.92,45.00}
{4.40,52.72}
{4.19,61.60}
f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

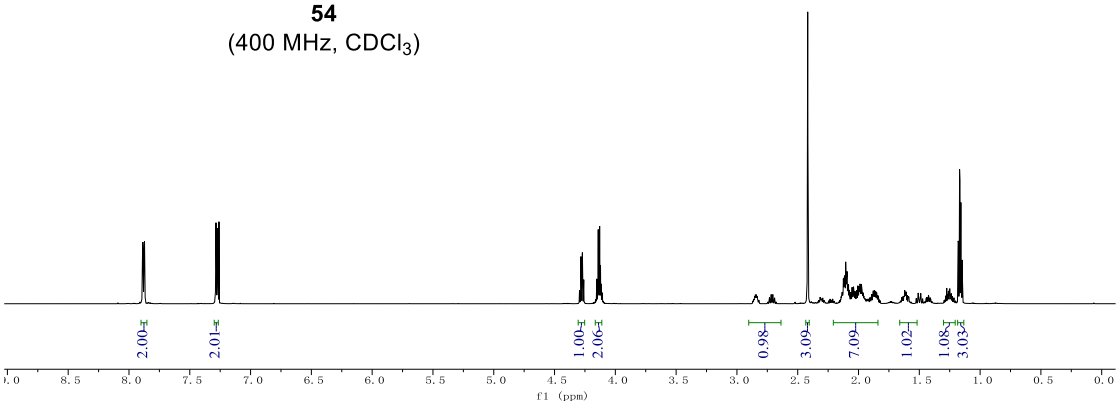

f2 (ppm)
f1 (ppm)

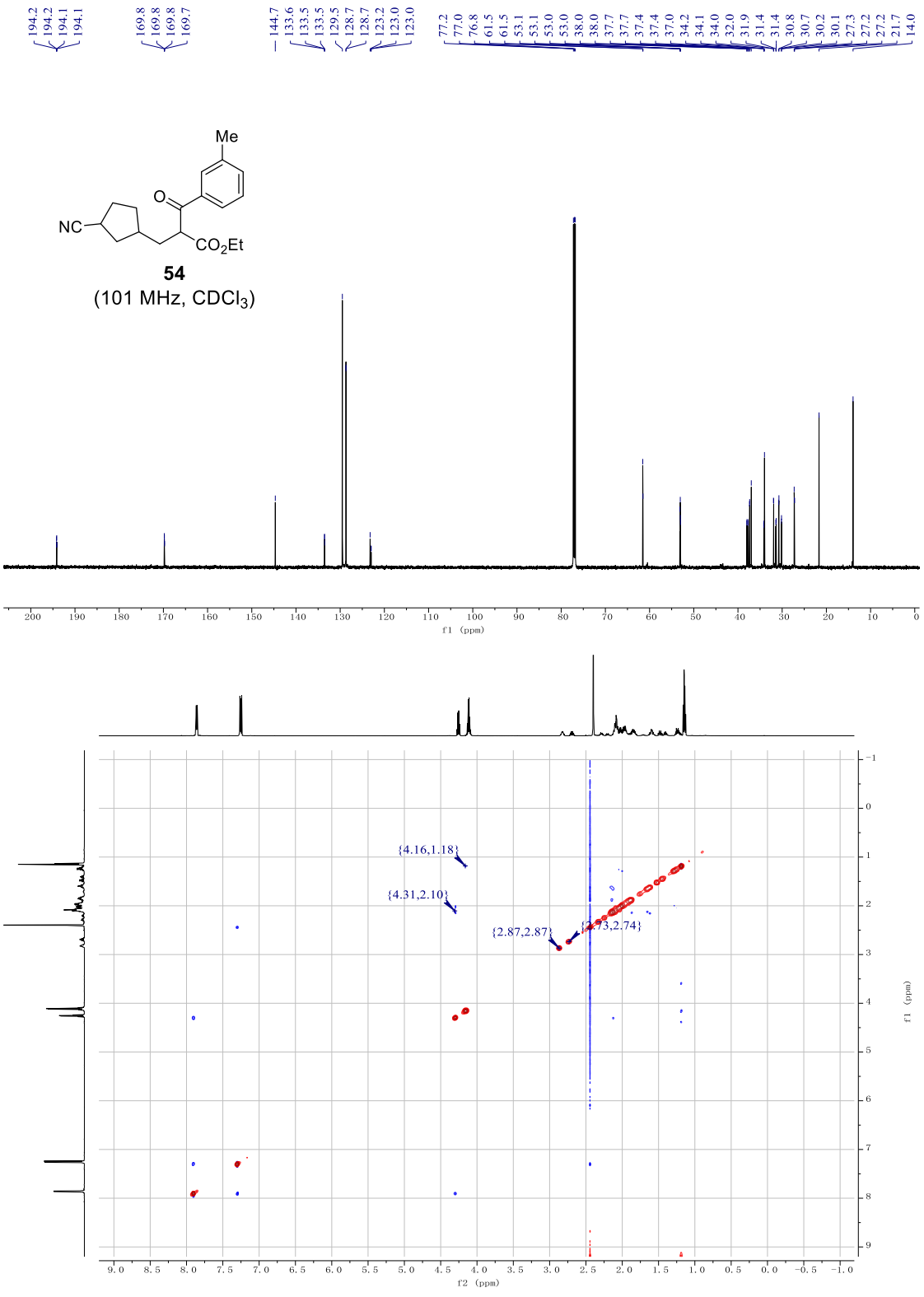


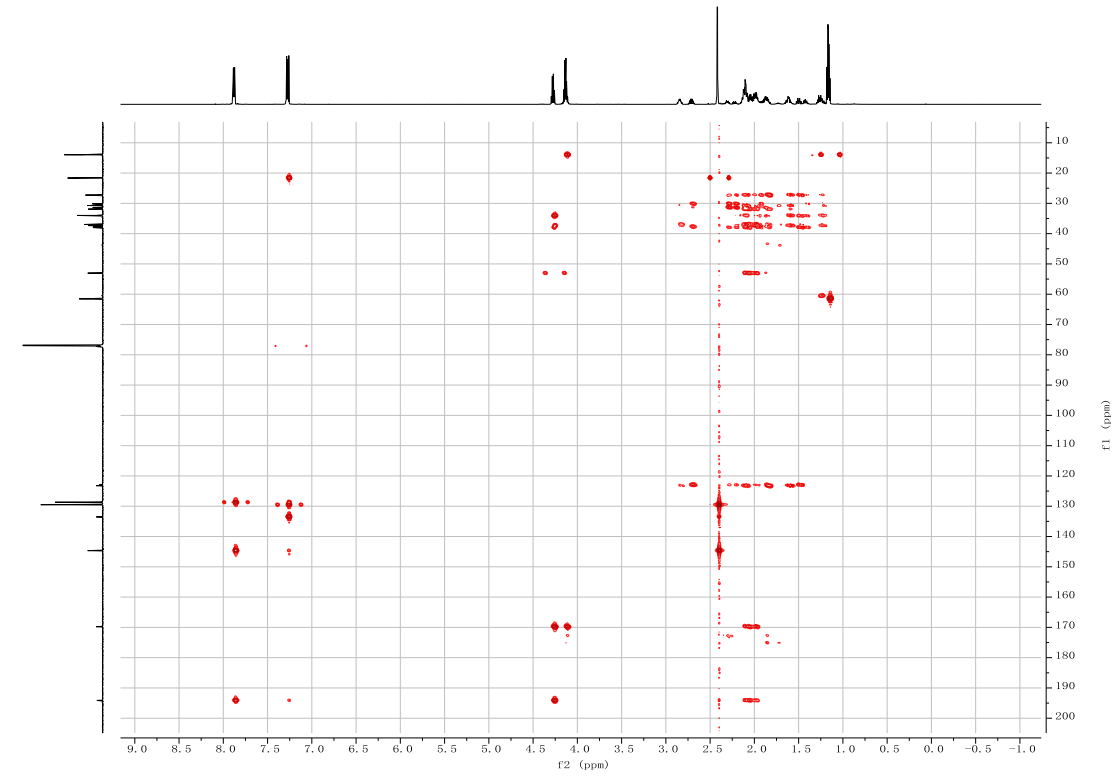


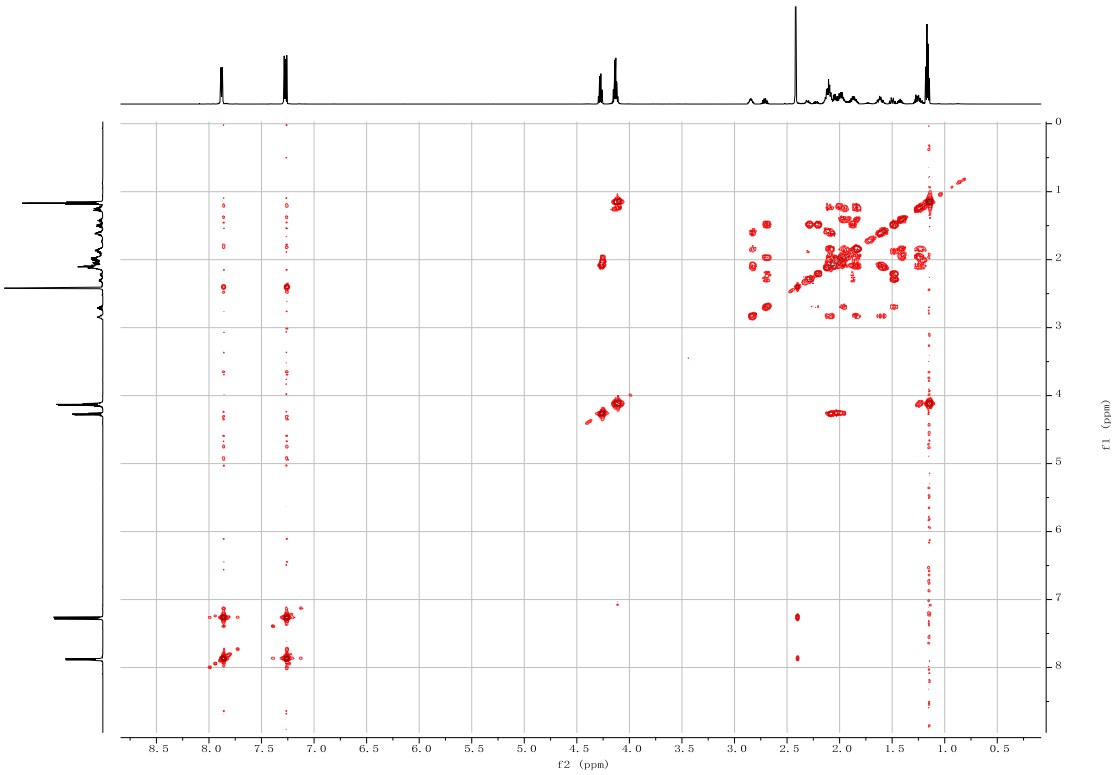
54

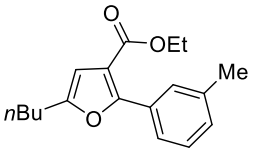
(400 MHz, $CDCl_3$)




194.2
194.2
194.1
194.1
169.8
169.8
169.8
169.7
144.7
133.6
133.5
133.5
129.5
128.7
128.7
123.2
123.0
123.0
77.2
77.0
76.8
61.5
61.5
53.1
53.1
53.0
53.0
38.0
38.0
37.7
37.7
37.4
37.4
37.0
34.2
34.1
34.0
32.0
31.9
31.4
31.4
30.8
30.7
30.2
30.1
27.3
27.2
27.2
21.7
14.0
Me
O
NC
CO2Et
54
(101 MHz, CDCl3)
f1 (ppm)
{4.16,1.18}
{4.31,2.10}
{2.87,2.87}
{2.73,2.74}
f2 (ppm)
f1 (ppm)

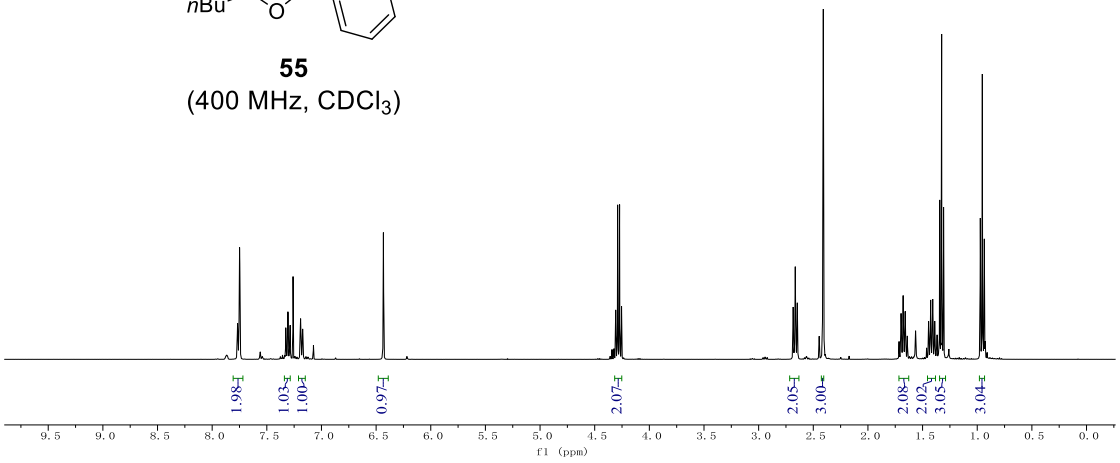

f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)



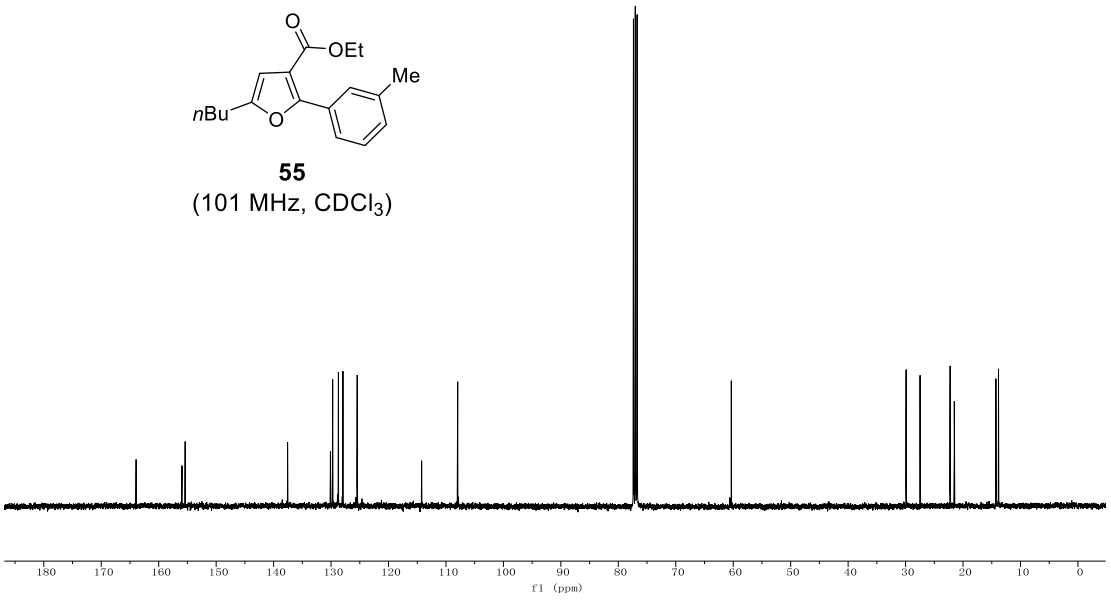
55

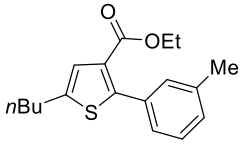
(400 MHz, $CDCl_3$)



55

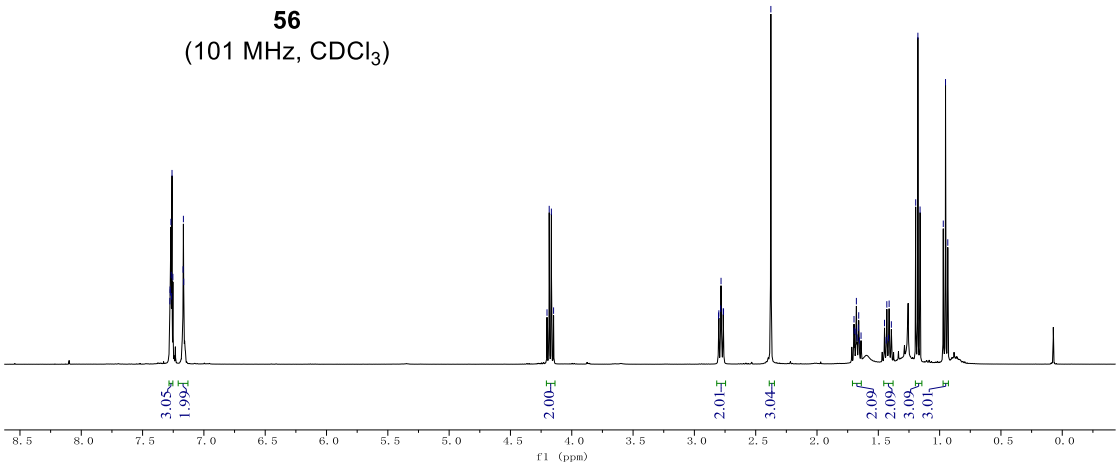
(101 MHz, $CDCl_3$)

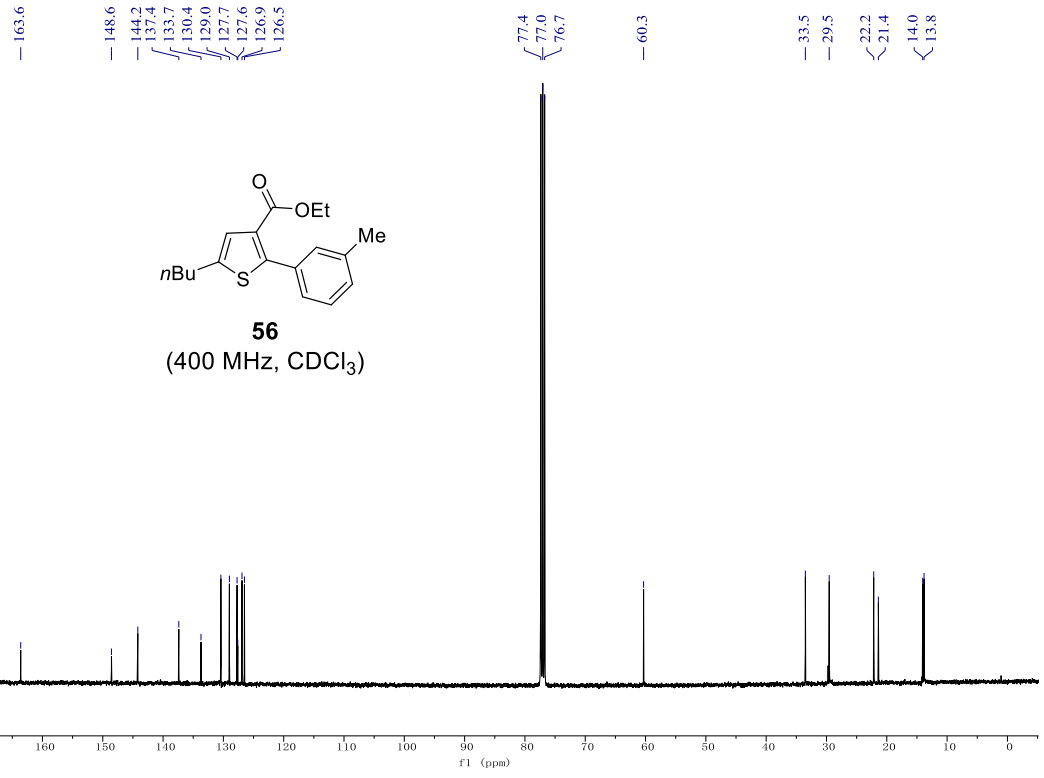




56

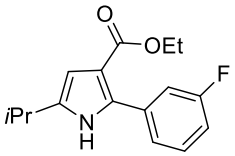
(101 MHz, $CDCl_3$)





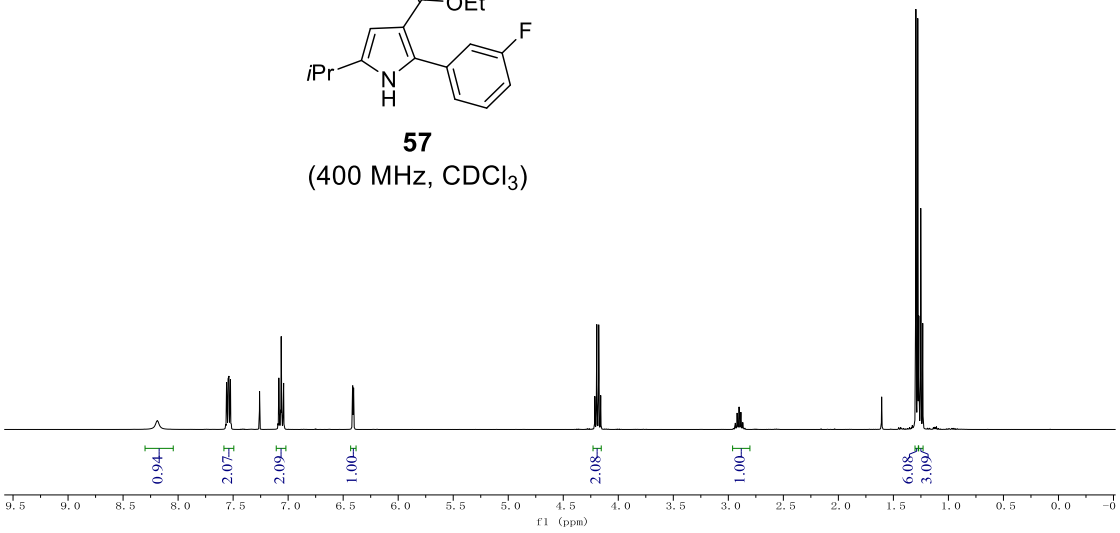
56

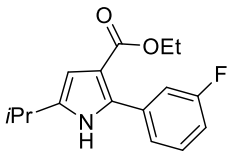
(400 MHz, $CDCl_3$)



57

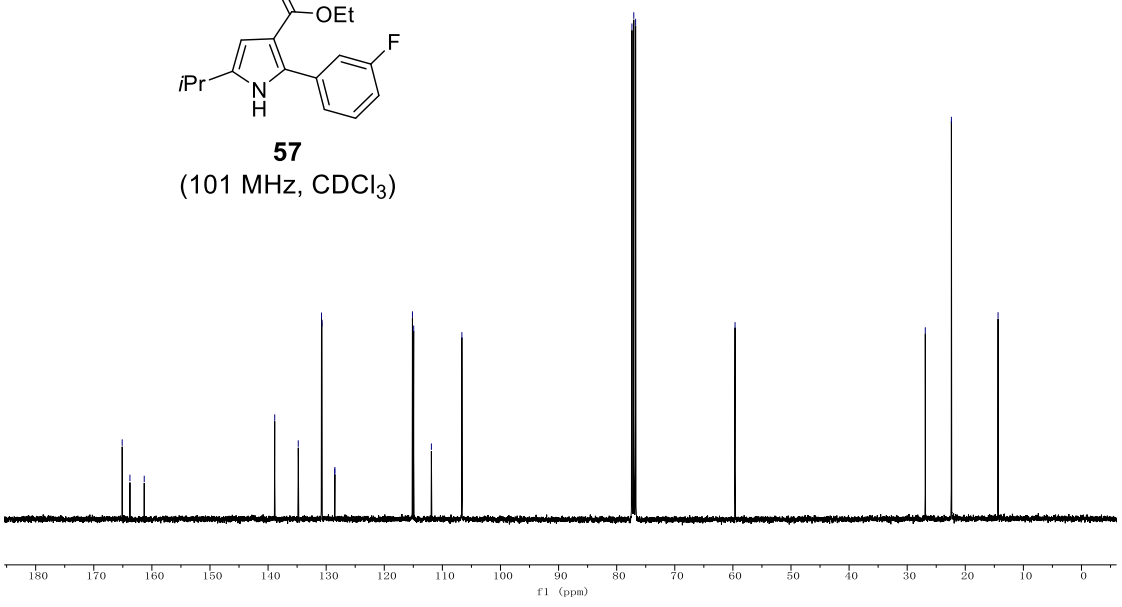
(400 MHz, $CDCl_3$)

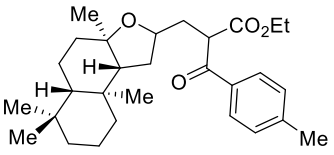




57

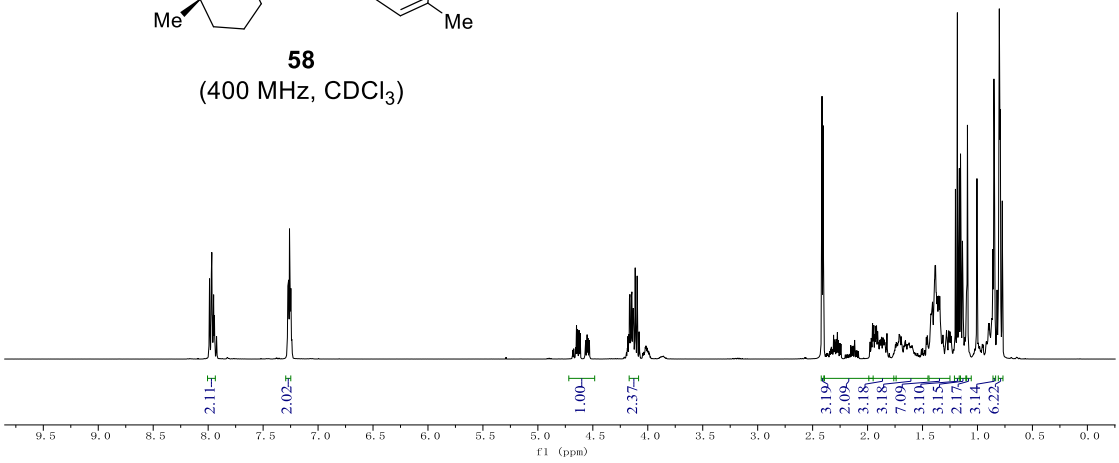
(101 MHz, $CDCl_3$)





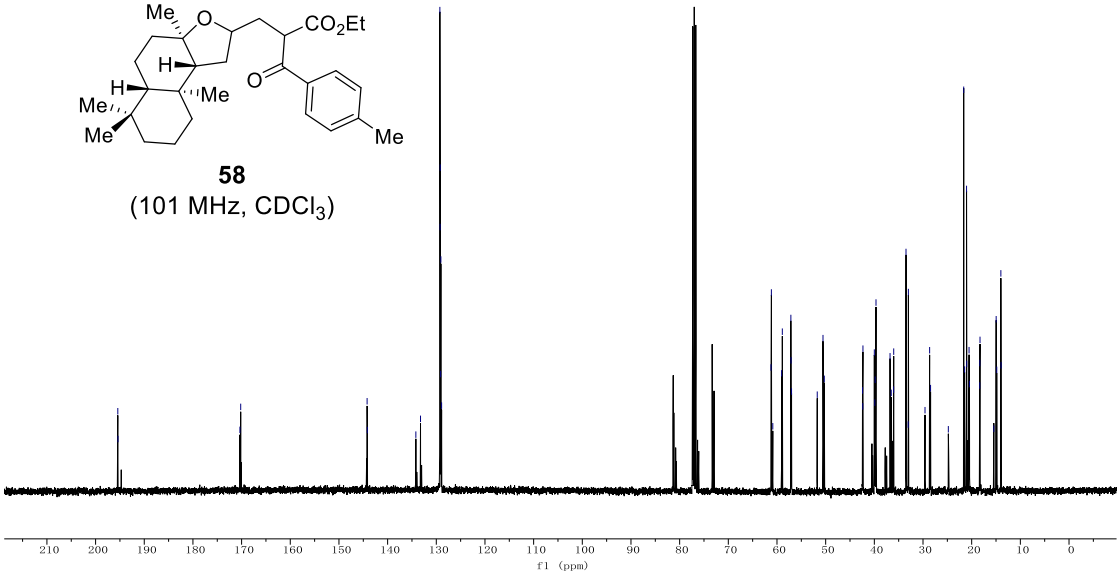
58

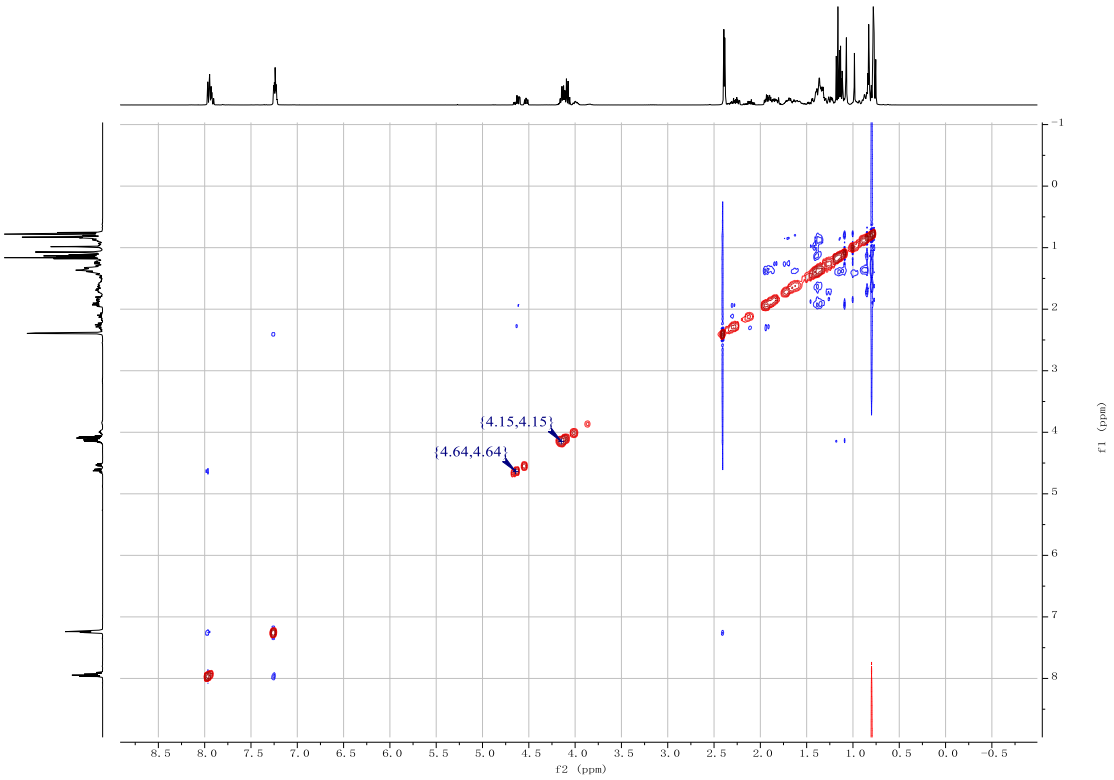
(400 MHz, $CDCl_3$)

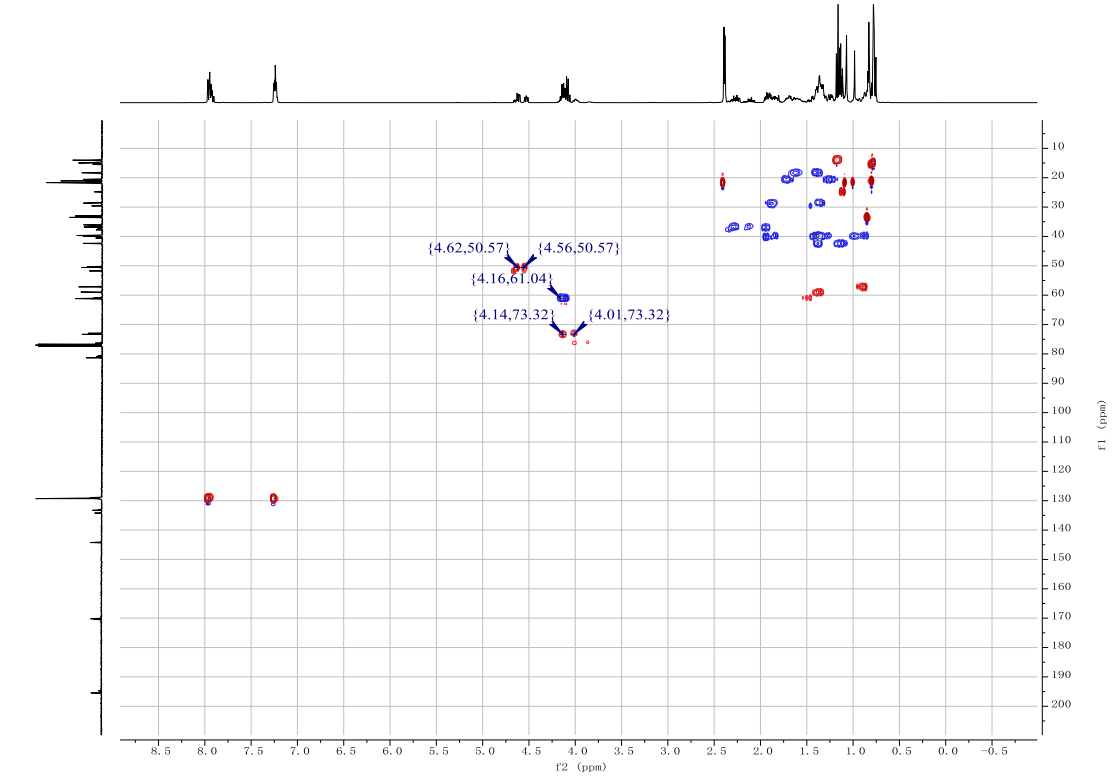


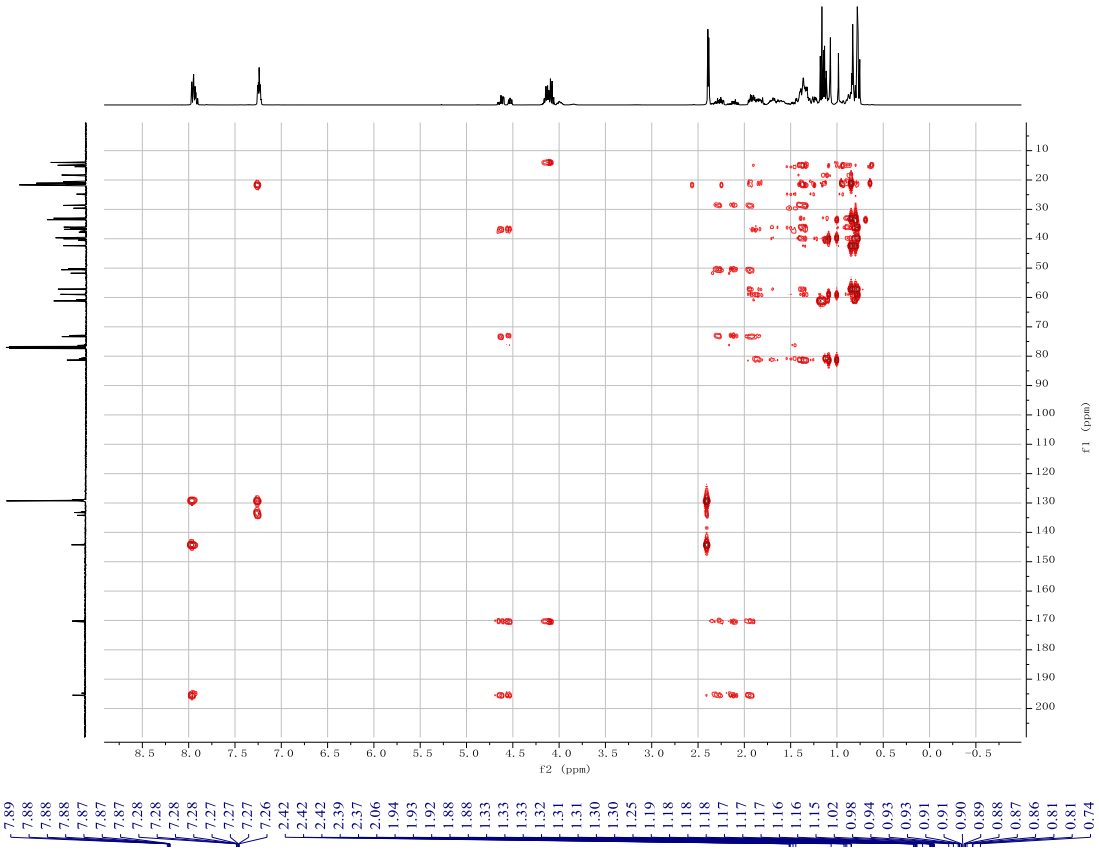
58

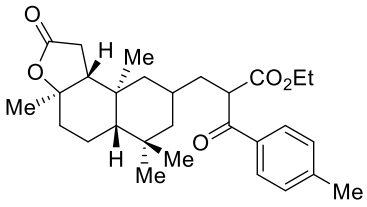
(101 MHz, $CDCl_3$)




{4.15,4.15}
{4.64,4.64}
f2 (ppm)
f1 (ppm)

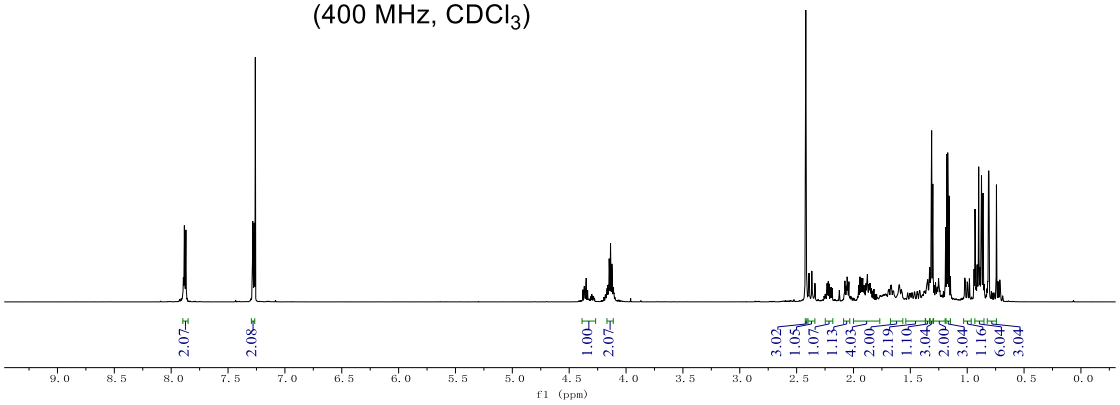

{4.62,50.57}
{4.56,50.57}
{4.16,61.04}
{4.14,73.32}
{4.01,73.32}
f2 (ppm)
f1 (ppm)

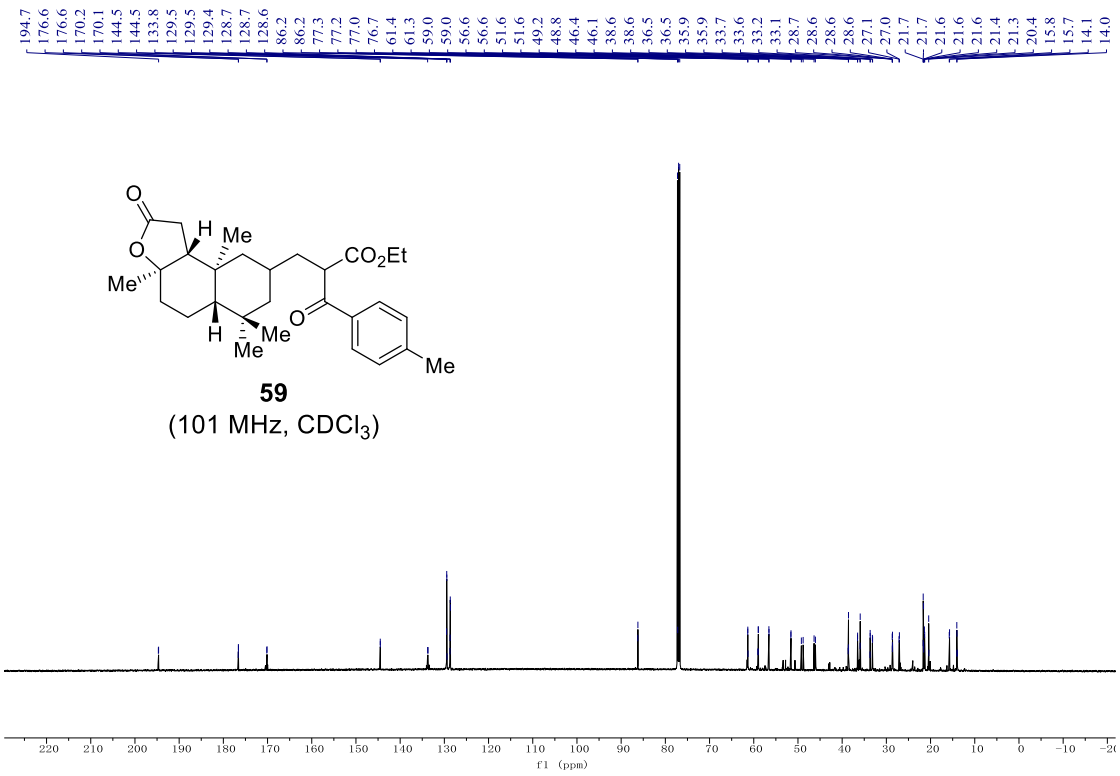


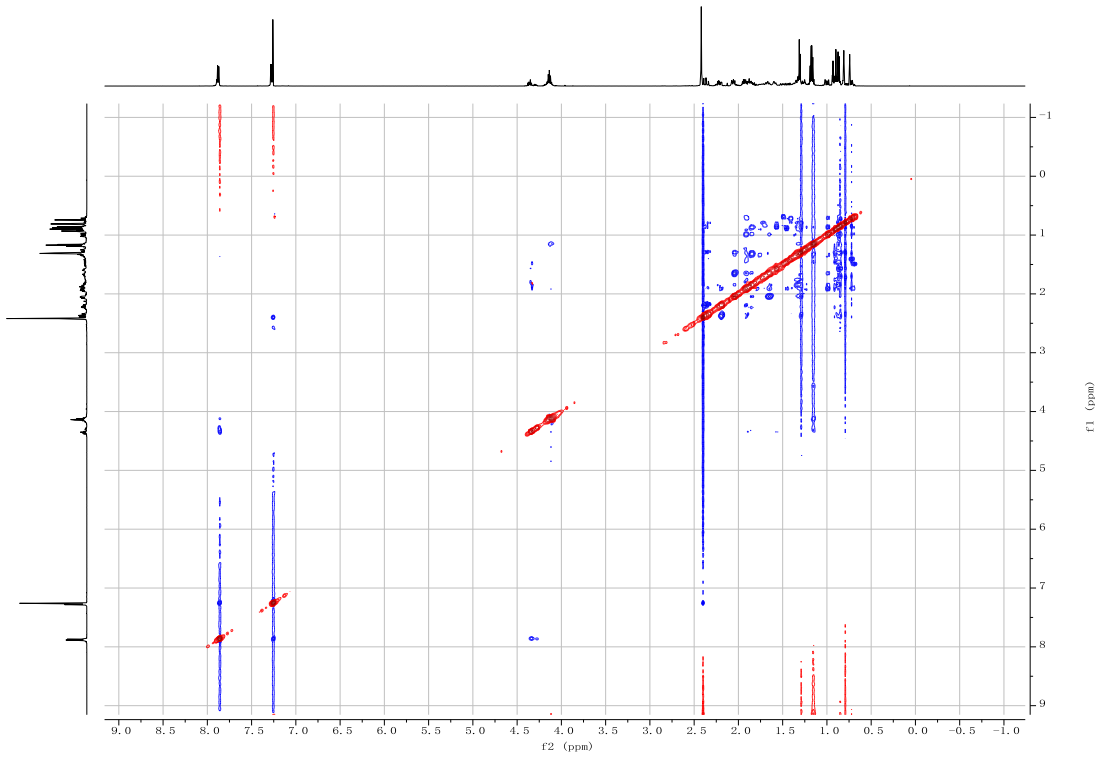


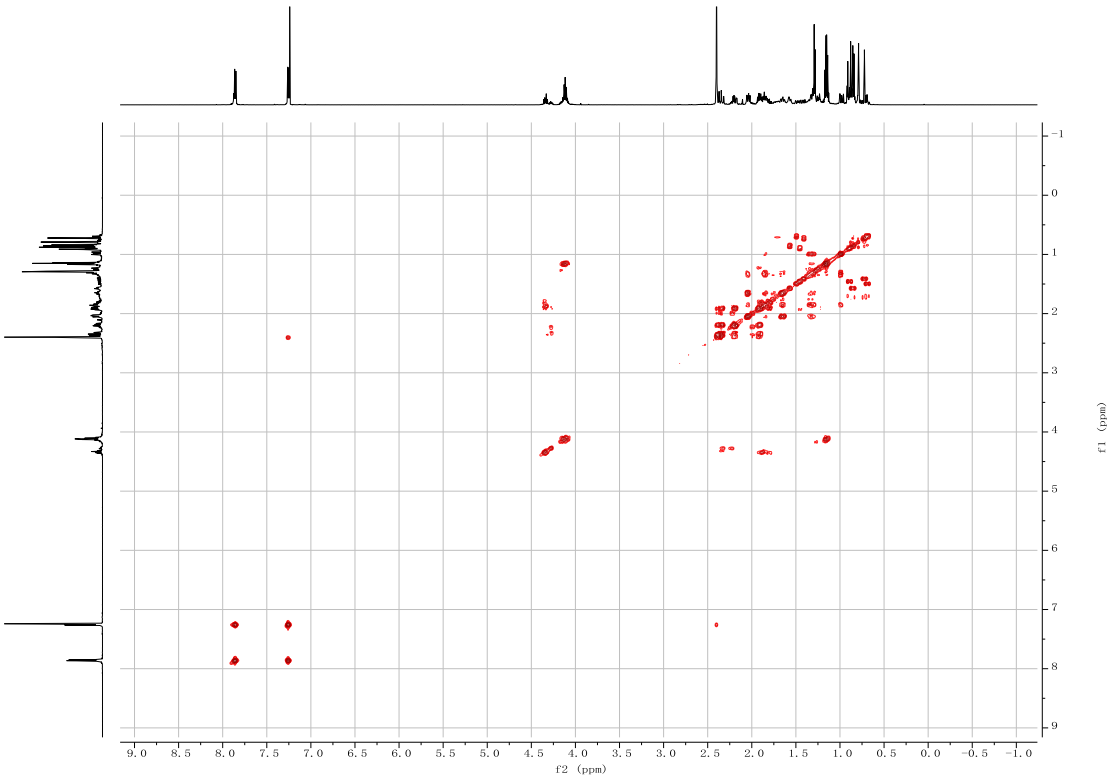
59

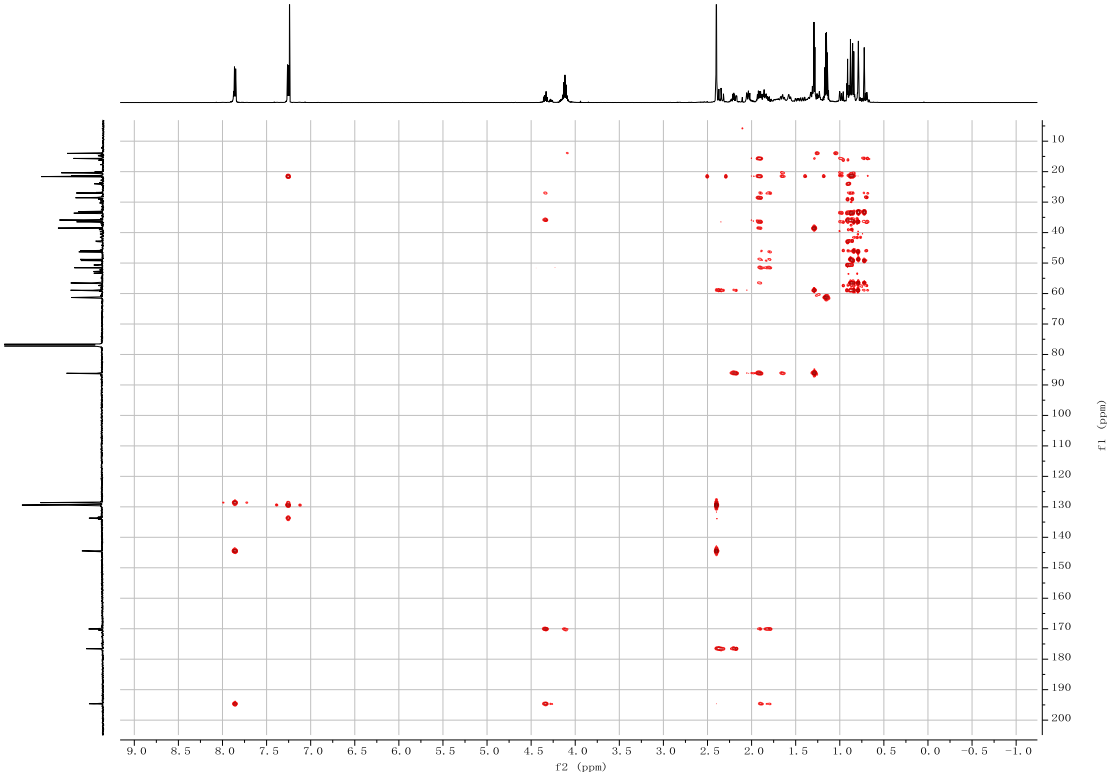
(400 MHz, $CDCl_3$)

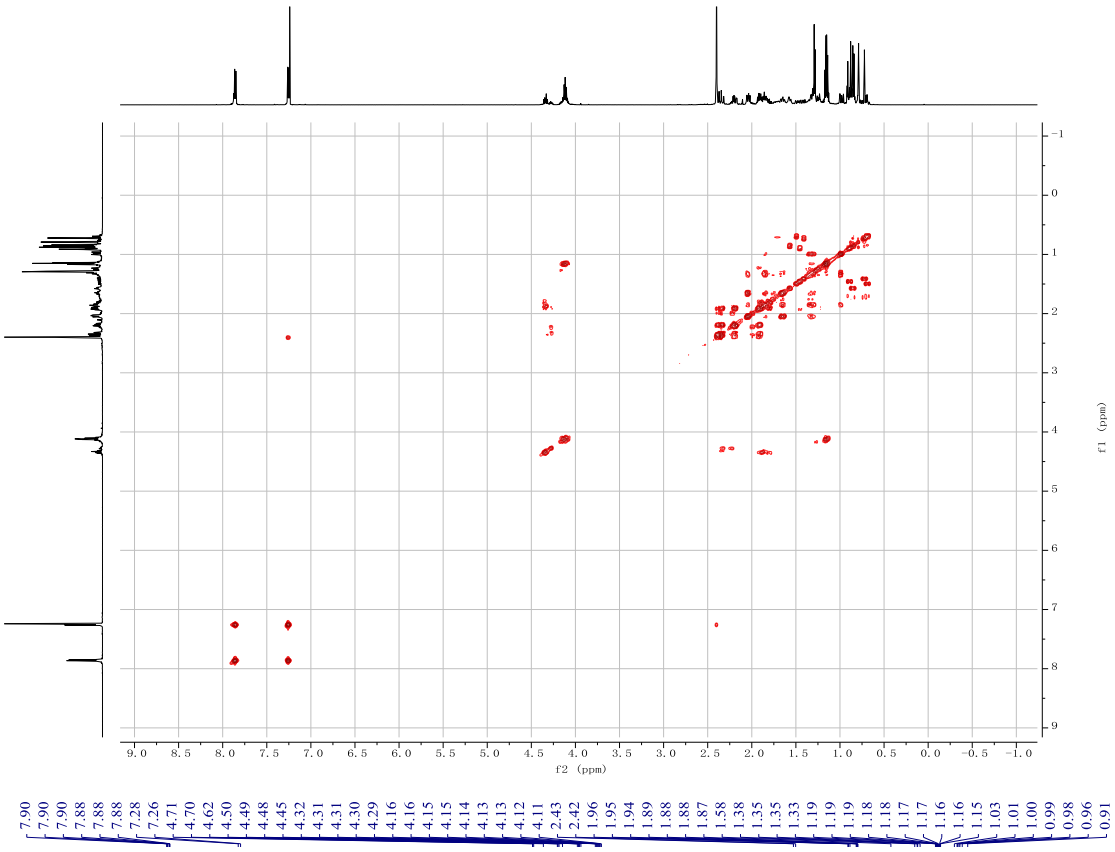


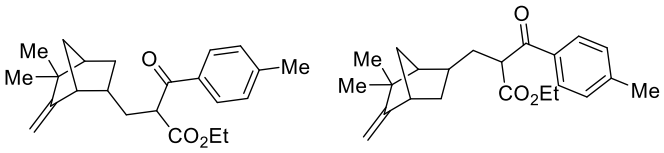

194.7
176.6
176.6
170.2
170.1
144.5
144.5
133.8
129.5
129.5
129.4
128.7
128.7
128.6
86.2
77.3
77.2
77.0
76.7
61.4
61.3
59.0
59.0
56.6
56.6
51.6
51.6
49.2
48.8
46.4
46.1
38.6
38.6
36.5
36.5
35.9
35.9
33.7
33.6
33.2
33.1
28.7
28.6
28.6
28.6
27.1
27.0
21.7
21.7
21.6
21.6
21.6
21.4
21.3
20.4
15.8
15.7
14.1
14.0
O
H
Me
O
Me
CO2Et
O
H
Me
Me
Me
59
(101 MHz, CDCl3)
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)



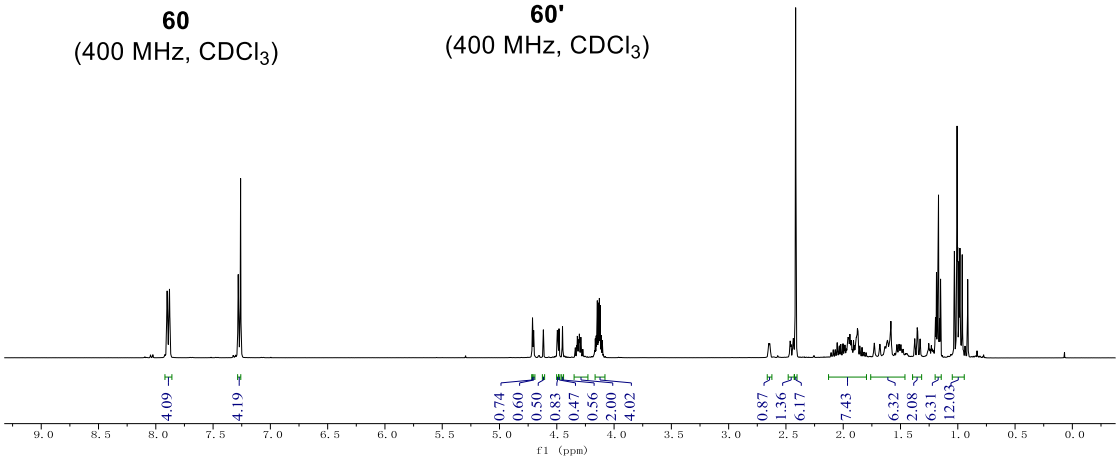


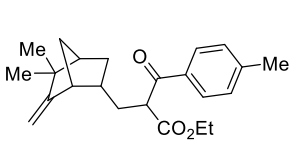
60

(400 MHz, $CDCl_3$)

60'

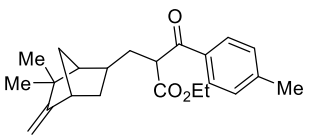
(400 MHz, $CDCl_3$)





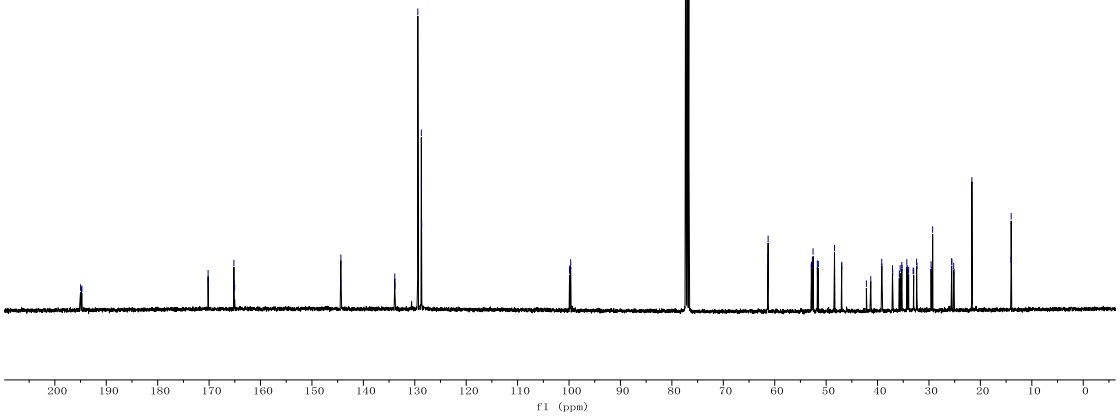
60

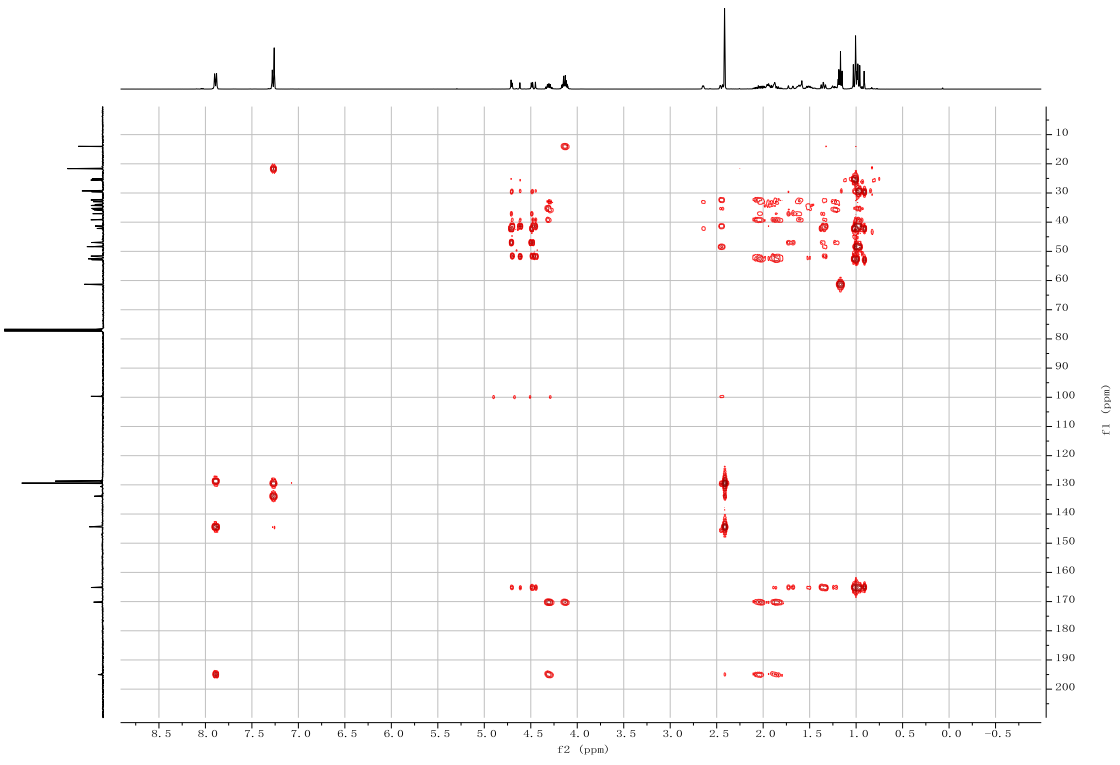
(101 MHz, $CDCl_3$)

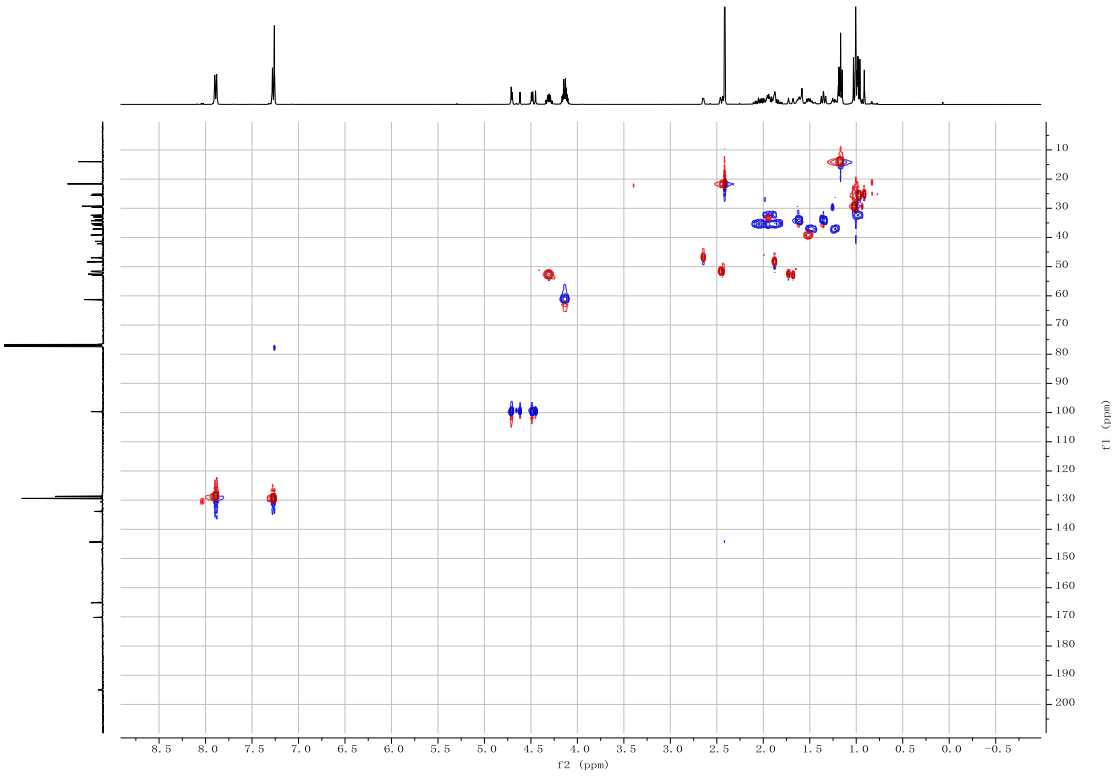


60'

(101 MHz, $CDCl_3$)






f2 (ppm)
f1 (ppm)