Electronic Supplementary Information for

Highly nucleophilic vitamin B_{12}-assisted nickel-catalysed reductive coupling of aryl halides with non-activated alkyl tosylates

Kimihiro Komeyama,* Ryo Ohata, Shinnosuke Kiguchi and Itaru Osaka
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University
1-4-1 Kagamiyama, Higashi-Hiroshima City, Hiroshima 739-8527, Japan
E-mail: kkome@hiroshima-u.ac.jp

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1. General Information.

All reactions were performed under argon. A flash column chromatography was performed with silica gel 60 (Kanto Chemical Co., Inc., 40–50 nm). TLC monitoring was carried out on silica gel aluminum sheets (Merck, type 60 F_{254}). Gas chromatography (GC) monitoring was performed on a Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were measured on Varian-400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 101 MHz) spectrometer or Varian-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 126 MHz) spectrometers, calibrated from residual deuterated chloroform at 7.26 ppm or tetramethylsilane at 0.00 ppm for ^{1}H NMR spectra and at 77.0 ppm for ^{13}C NMR spectra. Mass spectrum (MS) was recorded on Shimadzu GCMS-QP2010SE (EI, 70 eV). Melting points were determined using melting point system Mettler Toledo MP90 and were unrecorded. High-resolution mass spectrum (HRMS) was performed by LTQ Orbitrap XL from Thermo Fisher Scientific in the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University.

2. Materials.

N,*N*-Dimethylformamide (DMF) and chlorotrimethylsilane (TMSCl) were dried over activated molecular sieves 4Å, distilled and stored with activated MS 4Å under argon. $NiBr_2$, vitamin B_{12} (cyanocobalamin from Nacalai tesque Inc., [CAS: 68-19-9]), methylcobalamin hydrate (from Tokyo Chemical Industry Co., Ltd., [CAS: 288315-09-3]), manganese powder (99.9%, from Kanto Chemical Co., Inc.) and all ligands were purchased and used as received. $NiBr_2$(2,2'-bpy)[1] and $CoCl(dmgH)_2(py)$[2] were prepared by reported method. All alkyl tosylates were prepared from the corresponding alcohols by the reported methods.[3] Unless otherwise noted, commercially available reagents were used as received without further purification.

3. General procedure for the cross coupling (example: entry 1, Table 1).

In an Schlenk tube, Mn powder (28 mg, 0.5 mmol) was placed and heated at 400 ºC for 5–10 minutes under vacuum. After cooling, the Schlenk tube was charged with $NiBr_2$ (5.5 mg, 0.025 mmol), 2,2'-bipyridine (3.9 mg, 0.025 mmol), KI (42 mg, 0.25 mmol) and vitamin B_{12} (33.9 mg, 0.025 mmol). After that, DMF (1.0 mL) and TMSCl (10 µL) were successively added. The mixture was stirred for 10 minutes at ambient temperature. 4-Iodo anisole **2a** (59 mg, 0.25 mmol) and cyclohexyl tosylate (95 mg, 0.38 mmol) were added at one, and the resulting mixture was stirred at 30 ºC. After 30 hours, the reaction mixture was quenched with water, diluted with ethyl acetate and added dimethyl terephthalate as an internal standard. GC yields of cross-coupling

product **3a** and homo-coupling product **4** were determined from the solution (Figure S1). The aqueous phase was extracted with ethyl acetate, the combined organic phases was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by a silica gel flash chromatography to get the cross coupling product **2a** (30 mg, 64% yield). The characterization of **3a** was carried out based on the reported date.[4]

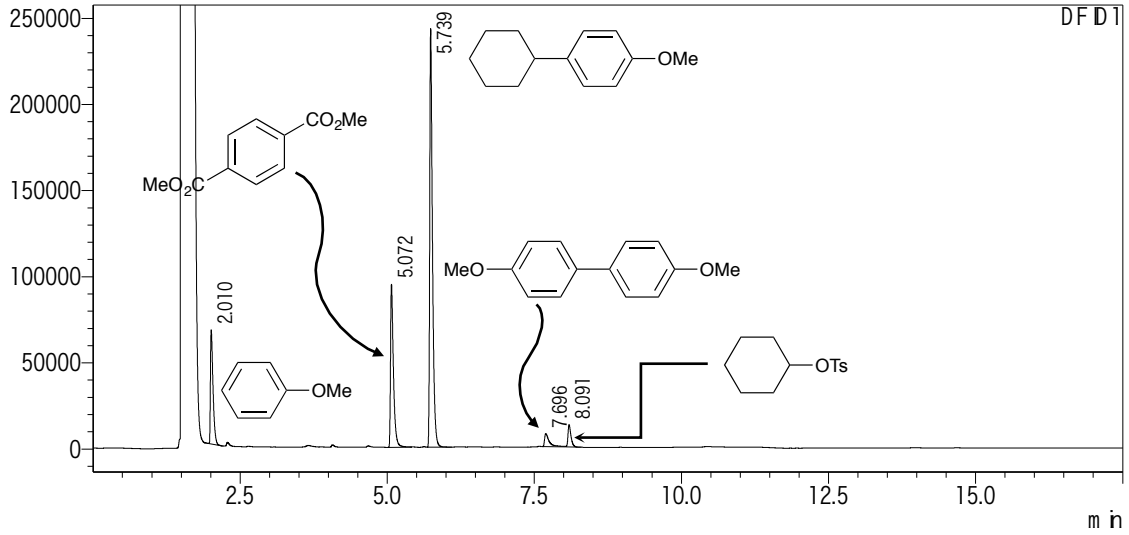


Figure S1. GC chart of the crude product in the Ni/VB_{12}-catalysed cross-coupling of cyclohexyl tosylate (**1a**) and 4-anisyl iodide (**2a**) at 30 ºC for 30 h (entry 1, Table 1).

4. Control experiment for the reaction of cyclohexyl tosylate with KI.

In an Schlenk tube, cyclohexyl tosylate (64 mg, 0.25 mmol), DMF (1 mL) and KI (42 mg, 0.25 mmol) were added. The mixture was stirred for 30 h at 30 ºC. After complete the reaction, the mixture was quenched with water and deluded with ethyl acetate. A gas chromatography measurement of the organic layer clearly showed no formation of cyclohexyl iodide, which must be appeared at about 2.7 minutes under the conditions.

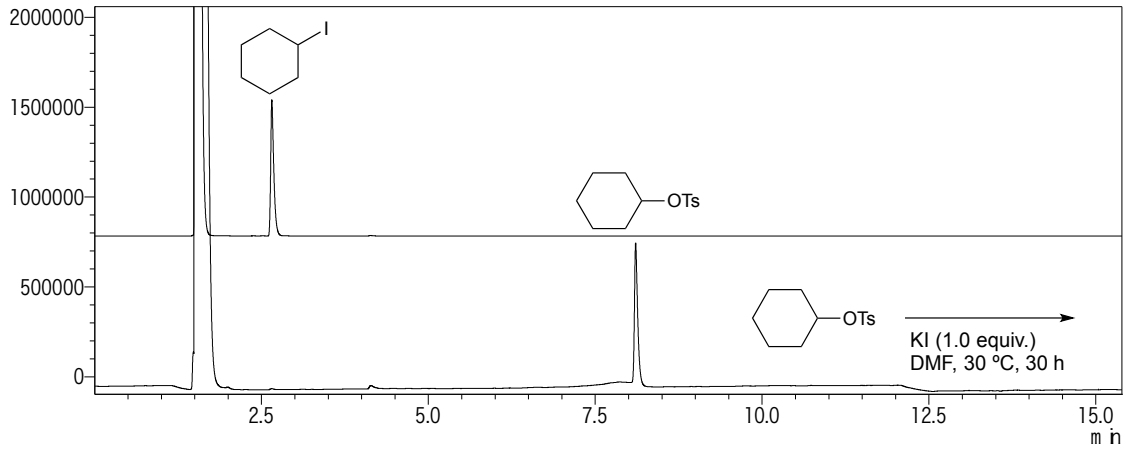


Figure S1. GC chart of iodocyclohexane (up); the crude product of cyclohexyl tosylate (**1a**) and KI at 30 ºC for 30 h (bottom).

5. Reaction of *c*-HexOTs (1a) with 4-MeOC$_6$H$_4$I (2a) without Ni cat. (entry 2 in Table 1).

In an Schlenk tube, Mn powder (28 mg, 0.5 mmol) was placed and heated at 400 ºC for 5 – 10 min under vacuum. After cooling, the Schlenk tube was charged with vitamin B_{12} (33.9 mg, 0.025 mmol) and KI (42 mg, 0.25 mmol). After that, DMF (1.0 mL) and TMSCl (10μL) were successively added, followed by stirring for 10 min at ambient temperature.4-anisyl iodide (**2a**, 58.5 mg, 0.25 mmol) and cyclohexyl tosylate (**1a**, 95.3 mg, 0.38 mmol) were added at one, and the resulting mixture was stirred at 30 ºC for 30 hours. The reaction mixture was quenched with water, diluted with ethyl acetate.

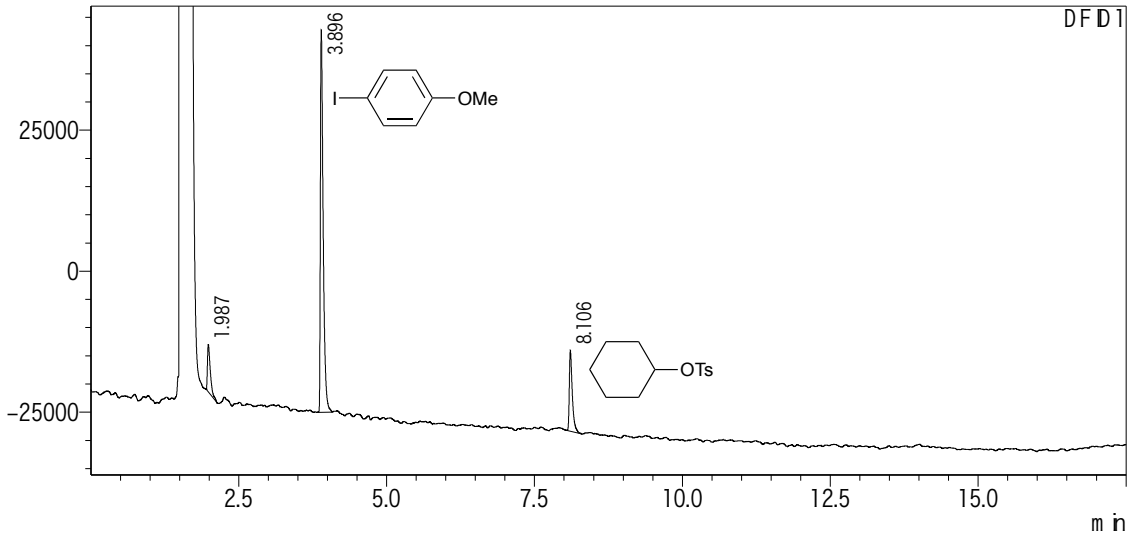


Figure S2. GC chart of the crude product (entry 2 Table 1).

6. Reaction of *c*-HexOTs (1a) with 4-$MeOC_6H_4I$ (2a) without VB_{12} cat. (entry 3 in Table 3).

In an Schlenk tube, Mn powder (28 mg, 0.5 mmol) was placed and heated at 400 ºC for 5 – 10 min under vacuum. After cooling, the Schlenk tube was charged with vitamin B_{12} (33.9 mg, 0.025 mmol) and KI (42 mg, 0.25 mmol). After that, DMF (1.0 mL) and TMSCl (10μL) were successively added, followed by stirring for 10 min at ambient temperature.4-iodo anisole (58.5 mg, 0.25 mmol) and cyclohexyl tosylate (95.3 mg, 0.38 mmol) were added at one, and the resulting mixture was stirred at 30 ºC for 30 hours. The reaction mixture was quenched with water, diluted with ethyl acetate. The aqueous phase was extracted with ethyl acetate. A gas chromatography measurement of the organic layer was carried out, and the following chart was obtained.

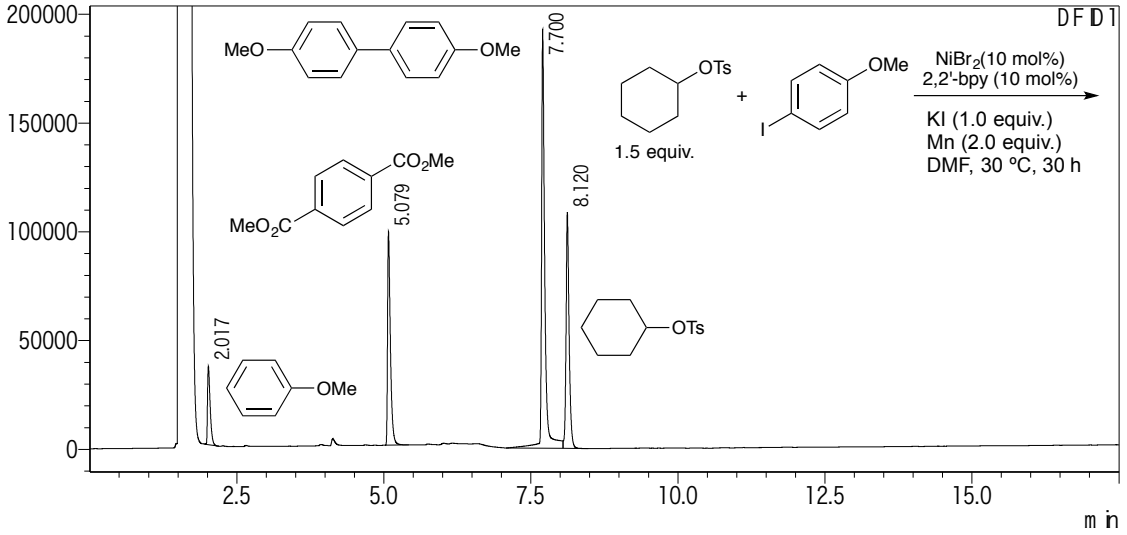


Figure S3. GC chart of the crude product (entry 3 Table 1).

7. Alkylation of methylcobalamin with 2-bromonaphthalene with Ni cat. (Eq. 1).

In an Schlenk tube, Mn powder (28 mg, 0.5 mmol) and molecular sieves 4Å (125 mg, beads from Merck; Lot. No.: 1.05708.0250) was placed and heated at 400 ºC for 5 – 10 min under vacuum. After cooling, the Schlenk tube was charged with $NiBr_2$(2,2'-bpy) (9.4 mg, 0.025 mmol, 10 mol%), DMF (2.5 mL) and TMSCl (10μL) were successively added, followed by stirring for 10 min at ambient temperature. 2-bromonaphthalene (52 mg, 0.25 mmol) and methylcobalamin hydrate (336 mg, ca. 0.25 mmol) were added at one, and the resulting mixture was stirred at 30 ºC for 30 hours. The reaction mixture was quenched with water and then dilute d with ethyl acetate. The aqueous phase was extracted with ethyl acetate. The combined organic phases was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the crude

product was obtained. The yields of products were determined by NMR using anisole as an internal standard. In the absence of molecular sieves, 2-methylnaphthalene and naphthalene was obtained in 10% and 50% yields, respectively. It is known that super-reduced VB_{12s} can react with water to give hydrido-cobalamin, which might cause the hydrodebromination.[5]

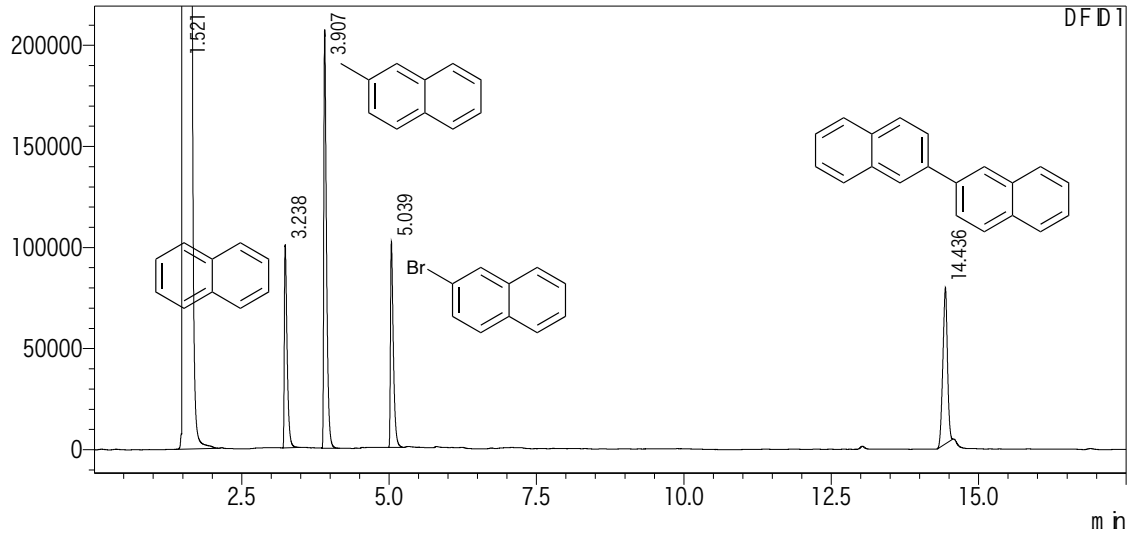


Figure S4. GC chart of the crude product (Eq. 1).

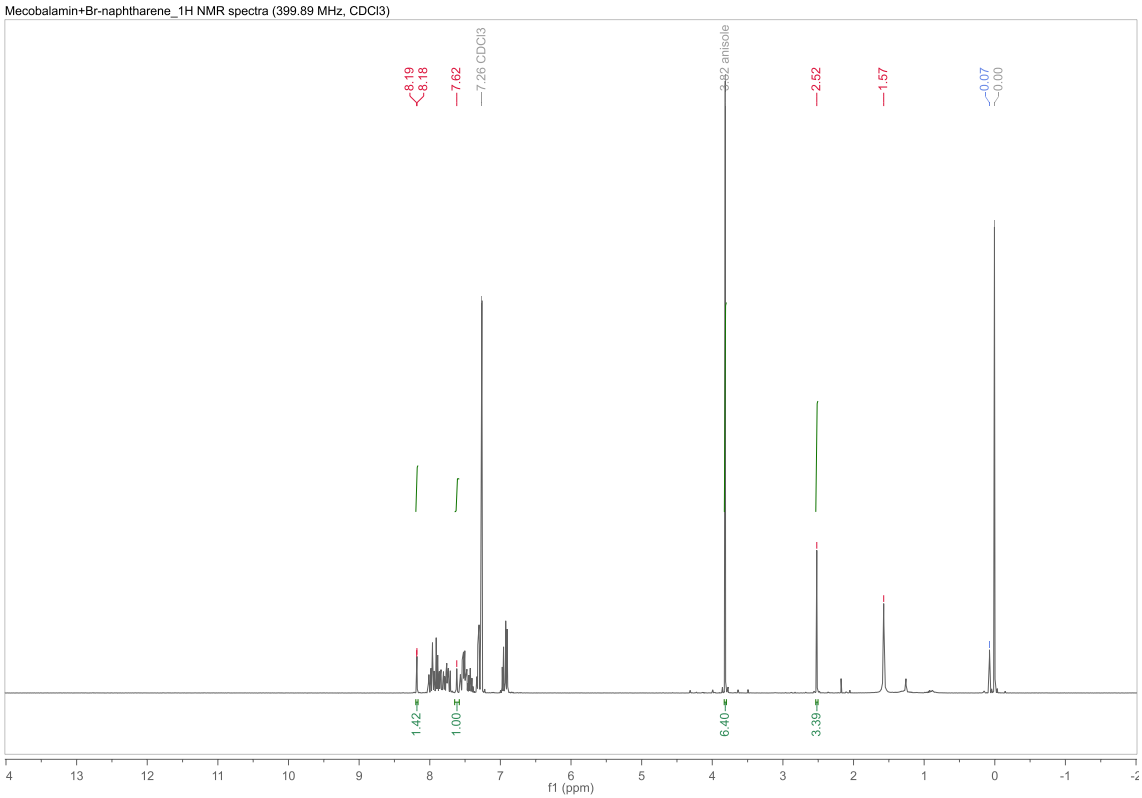
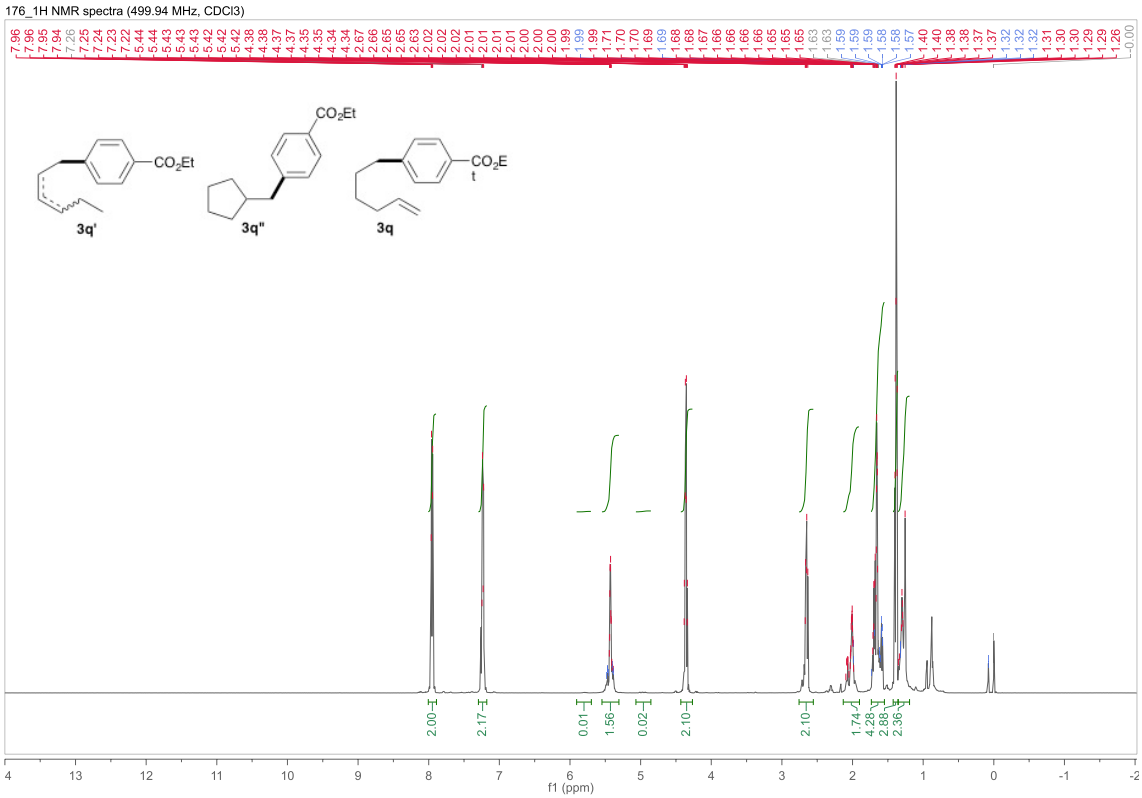


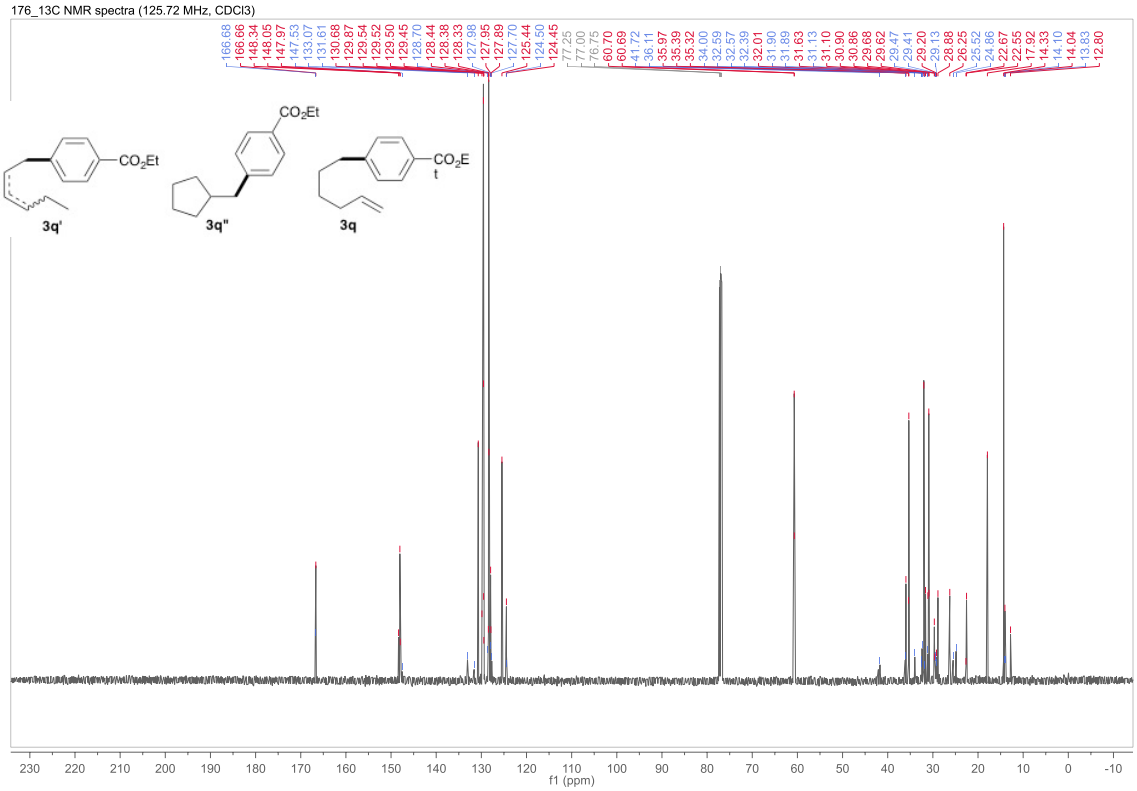
Figure S3. NMR chart of the crude product (Eq. 1) with anisole (3.82 ppm, 3H) as an

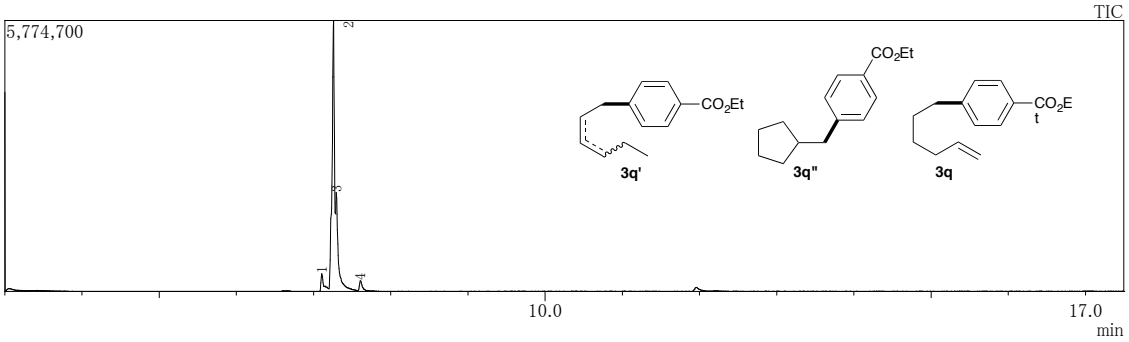
internal standard. 8.18 – 8.19 ppm (2-Brnaphthalene, 1H), 7.62 and 2.52 ppm (2-Menaphthalene, 1H and 3H).

8. Radical-clock experiment (Eq. 2) using 5-hexenyl tosylate (1q) and 4-(EtO_2C)C_6H_4I.

In an Schlenk tube, Mn powder (28 mg, 0.5 mmol) was placed and heated at 400 ºC for 5–10 minutes under vacuum. After cooling, the Schlenk tube was charged with $NiBr_2$(2,2'-bpy) (9.4 mg, 0.025 mmol, 10 mol%), KI (42 mg, 0.25 mmol) and vitamin B_{12} (33.9 mg, 0.025 mmol). After that, DMF (1.0 mL) and TMSCl (10 µL) were successively added. The mixture was stirred for 10 minutes at ambient temperature. 4-Iodo ethyl benzoate (69 mg, 0.25 mmol) and 5-hexenyl tosylate (**1q**, 95 mg, 0.38 mmol) were added at one, and the resulting mixture was stirred at 30 ºC. After 30 hours, the reaction mixture was quenched with water, diluted with ethyl acetate. The aqueous phase was extracted with ethyl acetate, the combined organic phases was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by a silica gel flash chromatography to afford the mixture of cross-coupling products **3q'** and cyclized product **3q** in 68% total yield. The ratio (**3q'**:**3q"**:**3q** = 80:20:trace) was estimated by ^{1}H NMR measurement of the mixture.




176_13C NMR spectra (125.72 MHz, CDCl3)
166.68
166.66
148.34
148.05
147.97
147.53
133.07
131.61
130.88
129.87
129.54
129.52
129.45
128.70
128.44
128.38
128.33
127.98
127.95
127.89
127.70
125.44
124.50
124.45
77.25
77.00
76.75
60.70
60.69
41.72
36.11
35.97
35.39
35.32
34.00
32.59
32.57
32.39
32.01
31.90
31.89
31.63
31.13
31.10
30.90
30.86
29.68
29.62
29.47
29.41
29.20
29.13
28.88
26.25
25.52
24.86
22.67
22.55
17.92
14.33
14.10
14.04
13.83
12.80
CO2Et
3q'
CO2Et
3q"
CO2E
t
3q
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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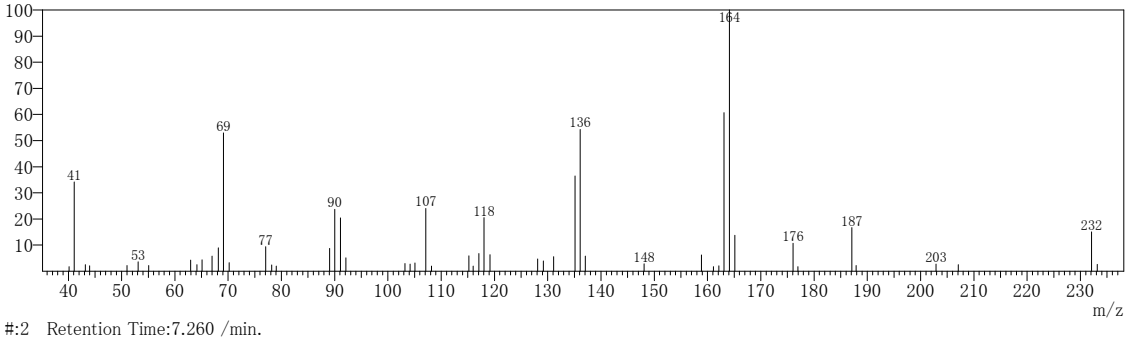

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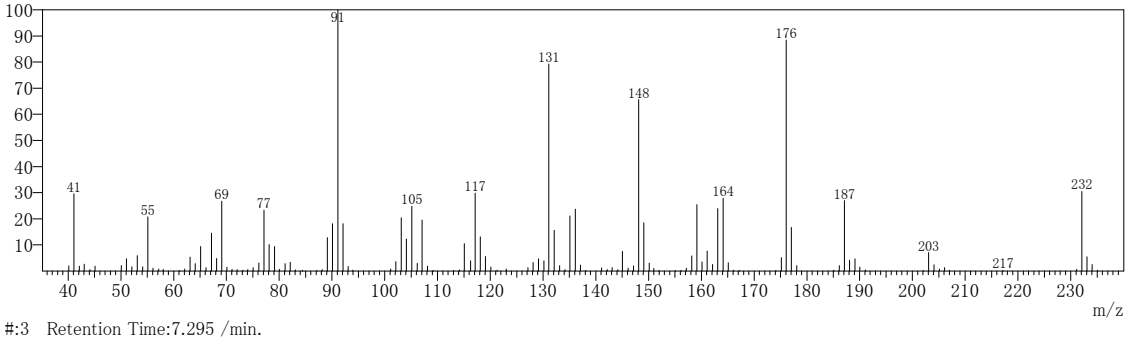

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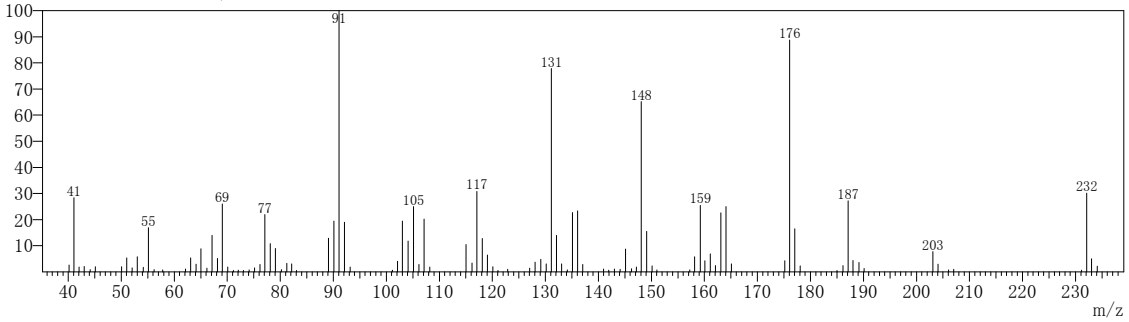

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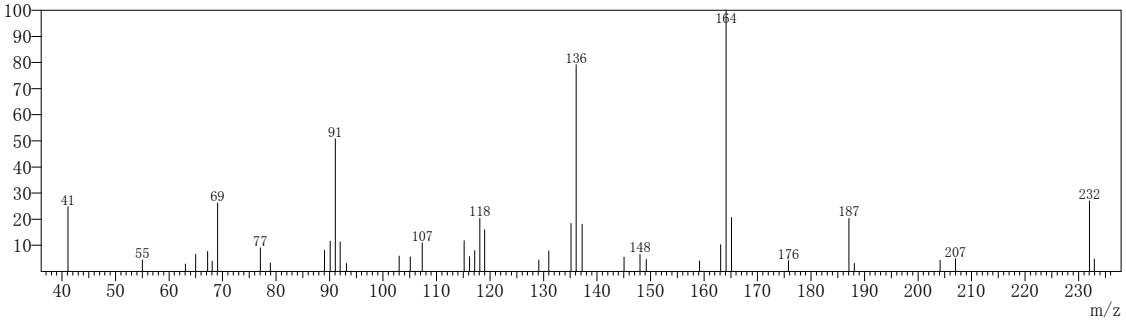
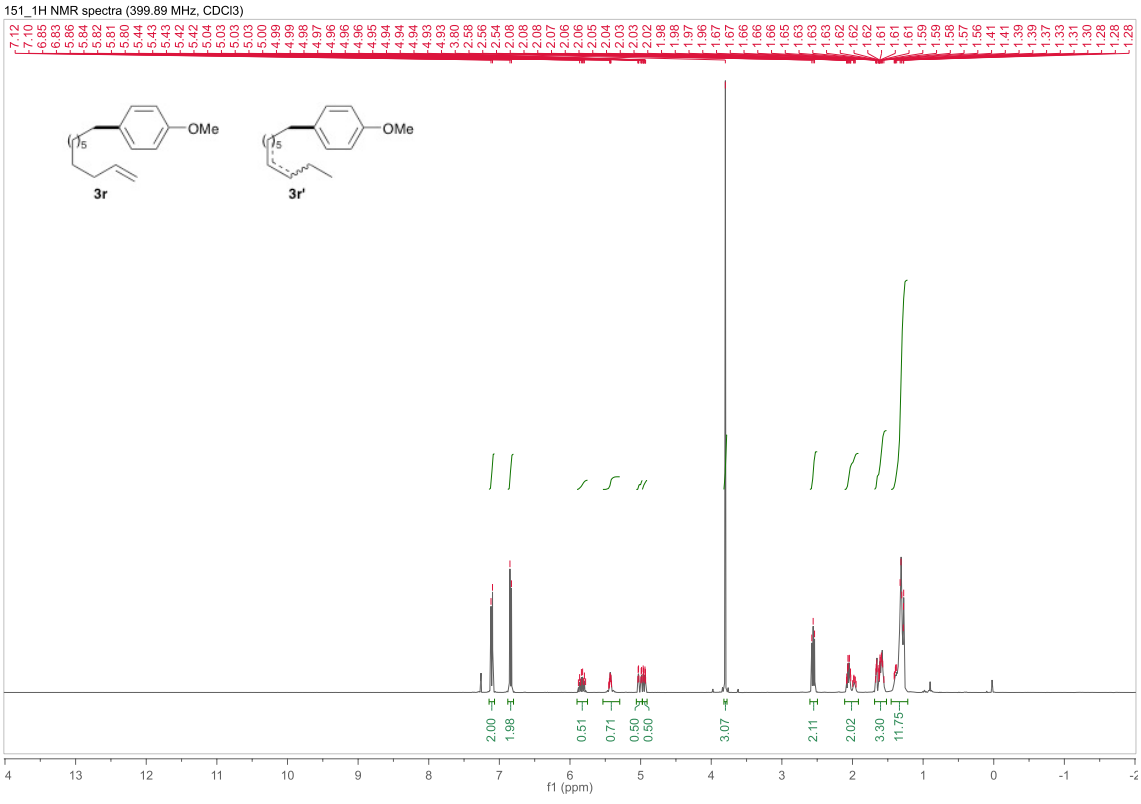
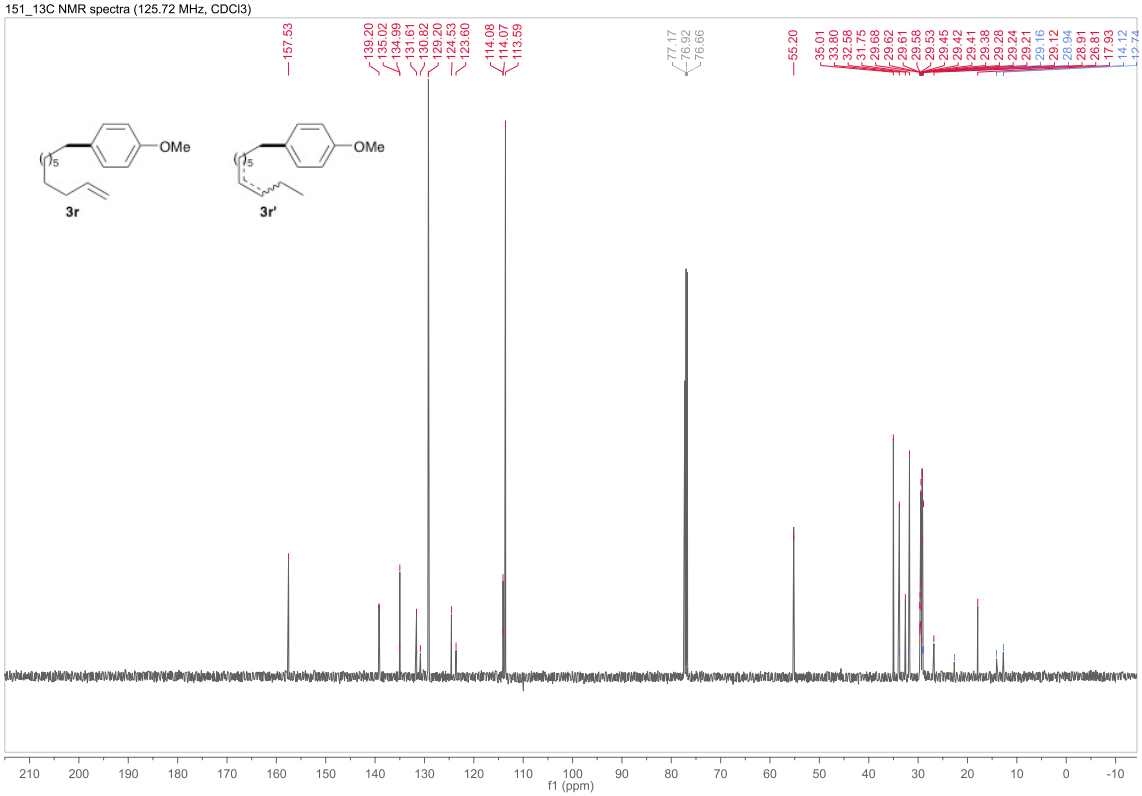


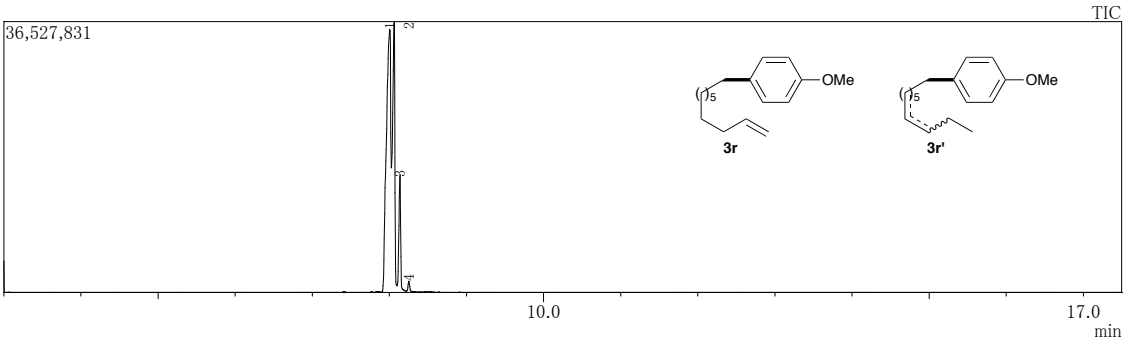
9. Reaction of 9-decenyl tosylate (1r) with 4-iodoanisole (2a) (Eq. 3).

In an Schlenk tube, Mn powder (28 mg, 0.5 mmol) was placed and heated at 400 ºC for 5–10 minutes under vacuum. After cooling, the Schlenk tube was charged with $NiBr_2$(2,2'-bpy) (9.4 mg, 0.025 mmol, 10 mol%), KI (42 mg, 0.25 mmol) and vitamin B_{12} (33.9 mg, 0.025 mmol). After that, DMF (1.0 mL) and TMSCl (10 µL) were successively added. The mixture was stirred for 10 minutes at ambient temperature. 4-iodoanisole (**2a**, 59 mg, 0.25 mmol) and 9-decenyl tosylate (**1r**, 116 mg, 0.38 mmol) were added at one, and the resulting mixture was stirred at 30 ºC. After 30 hours, the reaction mixture was quenched with water, diluted with ethyl acetate. The aqueous phase was extracted with ethyl acetate, the combined organic phases was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by a silica gel flash chromatography to afford the mixture of cross-coupling products **3r** and **3r'** in 64% total yield. The ratio (**3r**:**3r'**= 58:42) was estimated by ^{1}H NMR measurement of the mixture.



151_13C NMR spectra (125.72 MHz, CDCl3)





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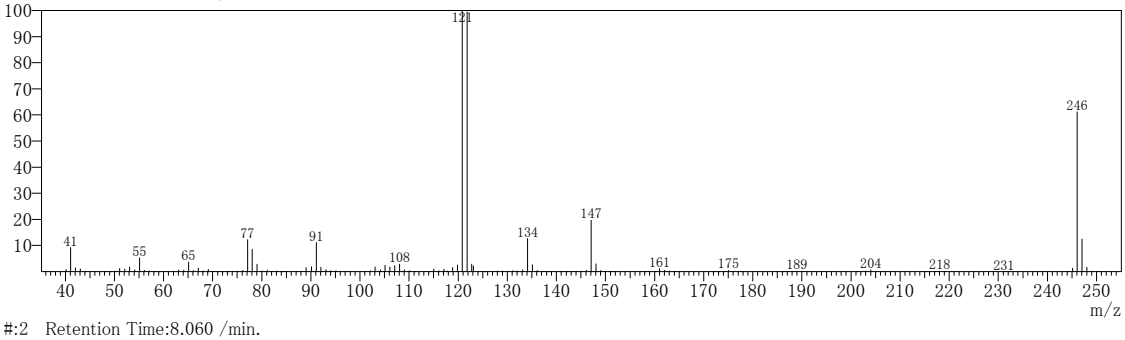

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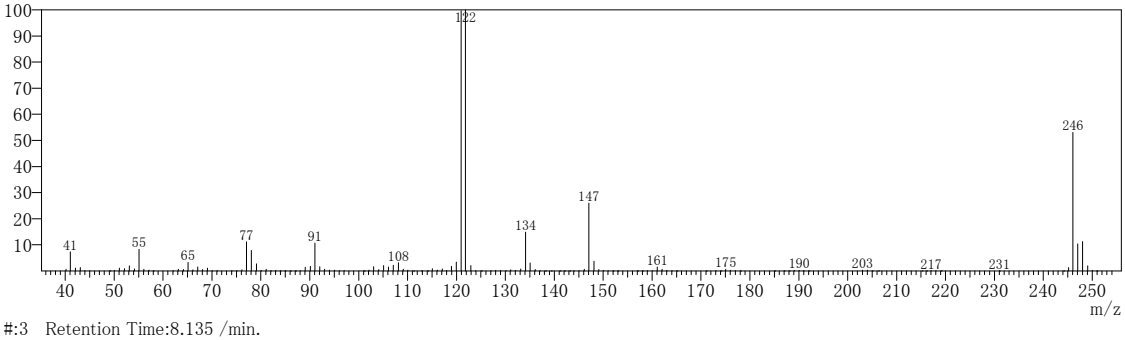

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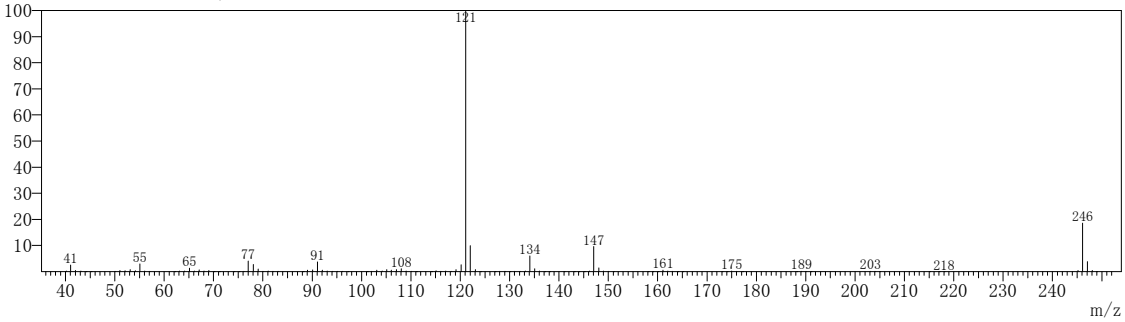

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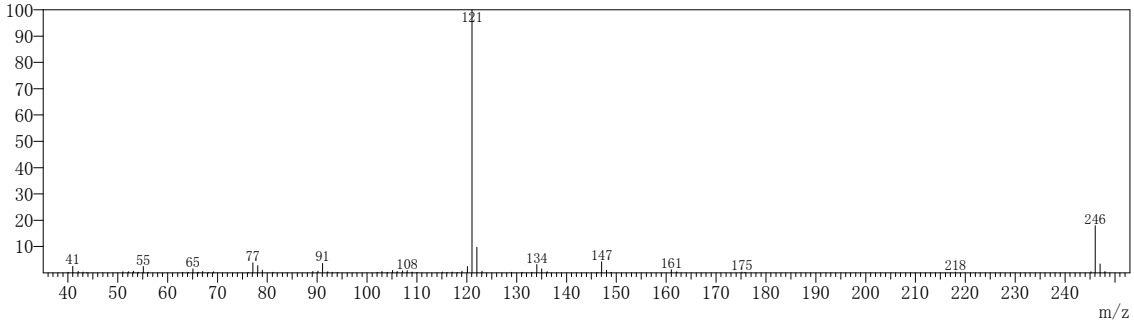
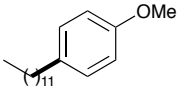
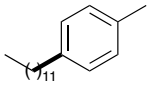


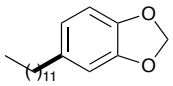
10. Spectral date for products (Table 2)



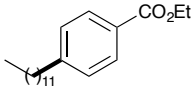
1-Dodecyl-4-methoxybenzene (3b).[6] Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 2.60 – 2.52 (m, 2H), 1.59 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.20 (m, 18H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.46, 134.96, 129.13, 113.52, 55.13, 34.97, 31.86, 31.71, 29.62, 29.61, 29.58, 29.55, 29.47, 29.30, 29.22, 22.63, 14.0; EI-MS *m/z* (relative intensity): 276 (M^+, 17),121 (100).



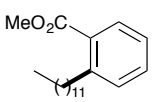
1-Dodecyl-4-methylbenzene(3c).[4] Isolated as colorless oil; ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.07 (s, 4H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 1.70 – 1.55 (m, 2H), 1.43 – 1.15 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.93, 134.95, 128.94, 128.31, 35.49, 31.89, 31.61, 29.63, 29.57, 29.49, 29.31, 22.64, 20.92, 14.05; EI-MS *m/z* (relative intensity): 260 (M^+, 25), 105 (100).



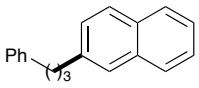
5-Dodecylbenzo[*d*][1,3]dioxole (3d). Isolated as white solid (melting point: 30–31 ºC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 2.58 – 2.46 (m, 2H), 1.57 (p, *J* = 7.2 Hz, 2H), 1.28 (d, *J* = 14.4 Hz, 18H), 0.89 (t, *J*= 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.38, 145.31, 136.80, 120.96, 108.81, 107.96, 100.62, 35.67, 31.90, 31.76, 29.66, 29.65, 29.62, 29.58, 29.50, 29.34, 29.18, 22.67, 14.10; EI-MS *m/z* (relative intensity): 290 (M^+, 50), 135 (50); HRMS calcd for $C_{19}H_{30}O_2$ [M^+]: 290.4470, found: 290.4465.



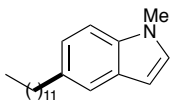
Ethyl 4-dodecylbenzoate (3e).[7] Isolated as colorless oil; ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.36 (q, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.61 (q, *J* = 6.8, 6.2 Hz, 2H), 1.48 – 1.07 (m, 21H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.30, 147.94, 129.10, 127.90, 127.50, 60.18, 35.44, 31.35, 30.59, 29.07, 28.99, 28.89, 28.78, 28.67, 22.11, 13.77, 13.52; EI-MS *m/z* (relative intensity): 318 (M^+, 100), 290 (13), 273 (36), 177 (31), 164 (42), 149 (18), 136 (30), 119 (23), 105 (21), 91 (89).



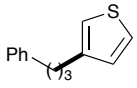
Methyl 2-dodecylbenzoate (3f).[8] Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.16 (m, 2H), 3.86 (s, 3H), 2.94 – 2.87 (m, 2H), 1.61 – 1.50 (m, 2H), 1.34 – 1.24 (m, 18H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.23, 144.69, 131.73, 130.86, 130.48, 129.45, 125.59, 51.85, 34.44, 31.90, 31.82, 29.74, 29.67, 29.65, 29.62, 29.61, 29.51, 29.34, 22.67, 14.11; EI-MS *m/z* (relative intensity): 304 (M^+, 35), 273 (100), 163 (22), 150 (72), 145 (23), 131 (98), 118 (69), 91 (41).



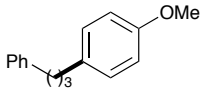
2-(2-Phenylpropyl)naphthalene (3g). Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 – 6.53 (m, 3H), 6.41 (s, 1H), 6.28 – 6.17 (m, 2H), 6.15 – 6.05 (m, 3H), 6.00 (d, *J* = 7.3 Hz, 3H), 1.61 (t, *J* = 7.7 Hz, 2H), 1.48 (t, *J* = 7.8 Hz, 2H), 0.85 (p, *J* = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.22, 139.74, 133.58, 131.94, 128.44, 128.30, 127.80, 127.57, 127.37, 127.33, 126.39, 125.83, 125.74, 125.05, 35.54, 35.42, 32.82; EI-MS *m/z* (relative intensity): 246 (M^+, 30), 142 (100); HRMS calcd for $C_{19}H_{18}$ [M^+]: 246.1409, found: 246.1401.



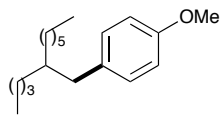
5-dodecyl-*N*-methylindole (3h). Isolated as red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.5 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.44 (dd, *J* = 3.0, 0.8 Hz, 1H), 3.78 (s, 3H), 2.77 – 2.70 (m, 2H), 1.74 – 1.64 (m, 2H), 1.44 – 1.27 (m, 18H), 0.92 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.16, 133.70, 128.66, 128.51, 122.47, 119.83, 108.73, 100.30, 35.98, 32.71, 32.33, 31.86, 29.63, 29.58, 29.55, 29.33, 29.30, 22.63, 14.07; EI-MS *m/z* (relative intensity): 299 (M^+, 39), 144 (100); HRMS calcd for $C_{21}H_{33}N$ [M^+]: 299.2613, found: 299.2614.



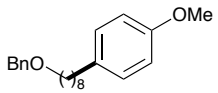
3-(3-Phenylpropyl)thiophene (3i). Isolated as thin-yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 3H), 7.19 – 7.12 (m, 3H), 6.93 – 6.88 (m, 2H), 2.63 (q, *J* = 7.7 Hz, 4H), 1.98 – 1.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.49, 142.10, 128.36, 128.22, 128.11, 125.67, 125.14, 119.95, 35.33, 31.98, 29.67; EI-MS *m/z* (relative intensity): 173 (98), 155 (43), 118 (32), 104 (30), 91 (100); HRMS calcd for $C_{13}H_{14}S$ [M^+]: 202.0816, found: 202.0810.



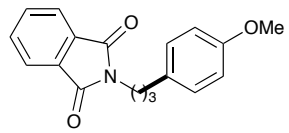
1-(4-Anisyl)-3-phenylpropane (3j).[1] Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 2.67 (t, *J* = 7.7 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.96 (p, *J* = 7.6, 7.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.65, 142.32, 134.31, 129.26, 128.40, 128.25, 125.66, 113.66, 55.20, 35.34, 34.47, 33.18; EI-MS *m/z* (relative intensity): 226 (M^+, 38), 134 (15), 121 (100).



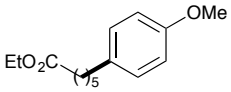
1-(2-Butyloctyl)-4-methoxybenzene (3k). Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.46 (d, *J* = 7.0 Hz, 2H), 1.64 – 1.46 (m, 1H), 1.39 – 1.10 (m, 16H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.49, 133.87, 130.05, 113.36, 55.23, 39.74, 39.54, 33.06, 32.74, 31.91, 29.70, 28.80, 26.53, 23.06, 22.69, 14.15, 14.12; EI-MS *m/z* (relative intensity): 276 (M^+, 10); 121 (100); HRMS calcd for $C_{19}H_{32}O$ [M^+]: 276.2453, found: 276.2451



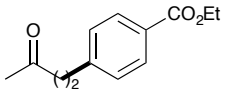
1-(8-Benzyloxyoctyl)-4-methoxybenzene (3l). Isolate as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 5H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.50 (d, *J* = 1.5 Hz, 2H), 3.78 (s, 3H), 3.50 – 3.42 (m, 2H), 2.56 – 2.50 (m, 2H), 1.66 – 1.52 (m, 6H), 1.40 – 1.22 (m, 6H); ^{13}C NMR (126 MHz, cdcl$_3$) δ 157.53, 138.67, 134.96, 129.20, 128.30, 127.58, 127.42, 113.59, 72.83, 70.47, 55.21, 35.00, 31.72, 29.74, 29.66, 29.43, 29.18, 26.16; EI-MS *m/z* (relative intensity): 326 (M^+, 32), 235 (51), 217 (15), 161 (34), 147 (21), 122 (96), 121 (100), 91 (95); HRMS calcd for $C_{22}H_{30}O_2$ [M^+]: 326.2246, found: 326.2251.



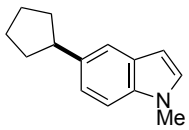
2-(3-(4-methoxyphenylpropyl)isoindoline-1,3-dione (3m). Isolate as white solid (melting point: 92–93 ºC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 3.72 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.99 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.13, 161.51, 137.55, 136.78, 135.83, 132.90, 126.85, 117.47, 58.92, 41.49, 35.97, 33.75; EI-MS *m/z* (relative intensity): 295 (M^+, 55), 161 (28), 147 (30), 121 (100); HRMS calcd for $C_{18}H_{17}NO_3$ [M^+]: 295.1208, found: 295.1195



Ethyl 6-(4-methoxyphenyl)hexanoate (3n). Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.55 (t, *J* = 7.7 Hz, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.64 – 1.55 (m, 2H), 1.41 – 1.28 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.61, 157.46, 134.41, 129.04, 113.48, 60.00, 55.04, 34.60, 34.11, 31.16, 28.50, 24.66, 14.07; EI-MS *m/z* (relative intensity): 250 (M^+, 15), 121 (100); HRMS calcd for $C_{15}H_{22}O_3$ [M^+]: 250.1569, found: 250.1562.



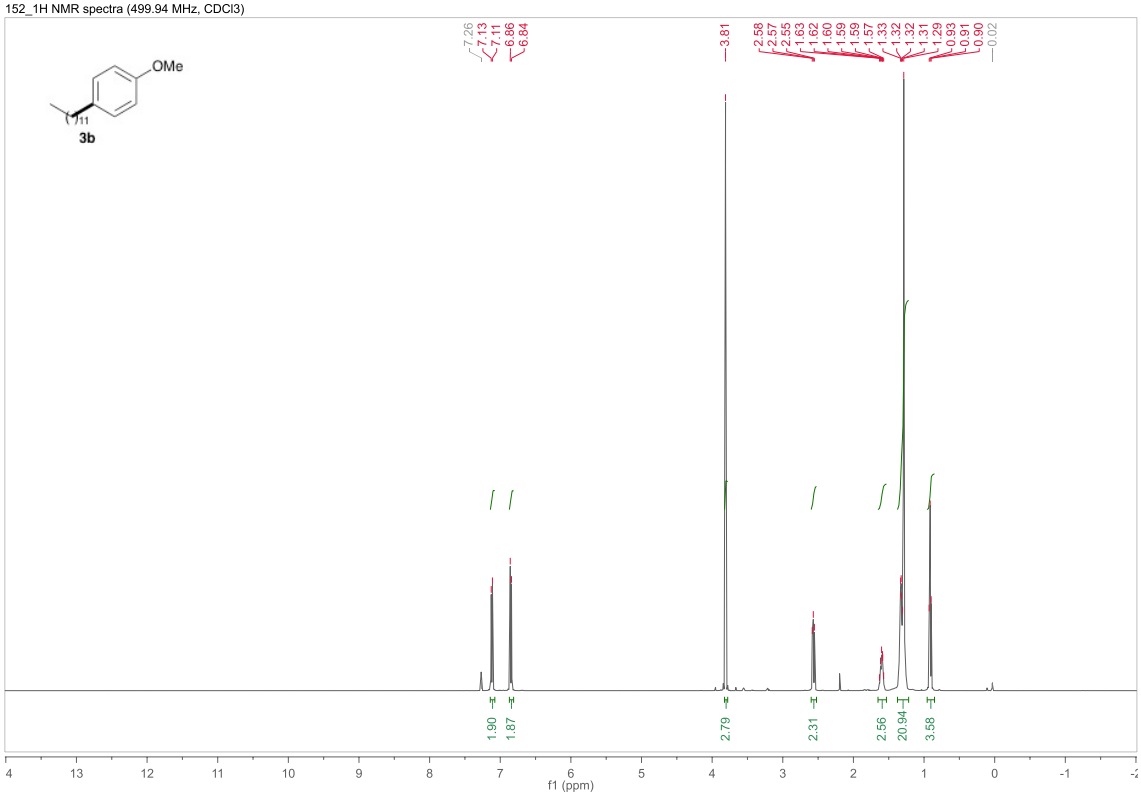
Ethyl 4-(3-oxobutyl)benzoate (3o). Isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $cdcl_3$) δ 207.27, 166.46, 146.33, 129.73, 128.41, 128.26, 60.78, 44.55, 30.04, 29.56, 14.29; EI-MS *m/z* (relative intensity): 220 (M^+, 92), 191 (10), 177 (51), 175 (93), 163 (26), 149 (61), 131 (31), 105 (74); 43 (100); HRMS calcd for $C_{13}H_{16}O_3$ [M^+]: 220.1099, found: 220.1093



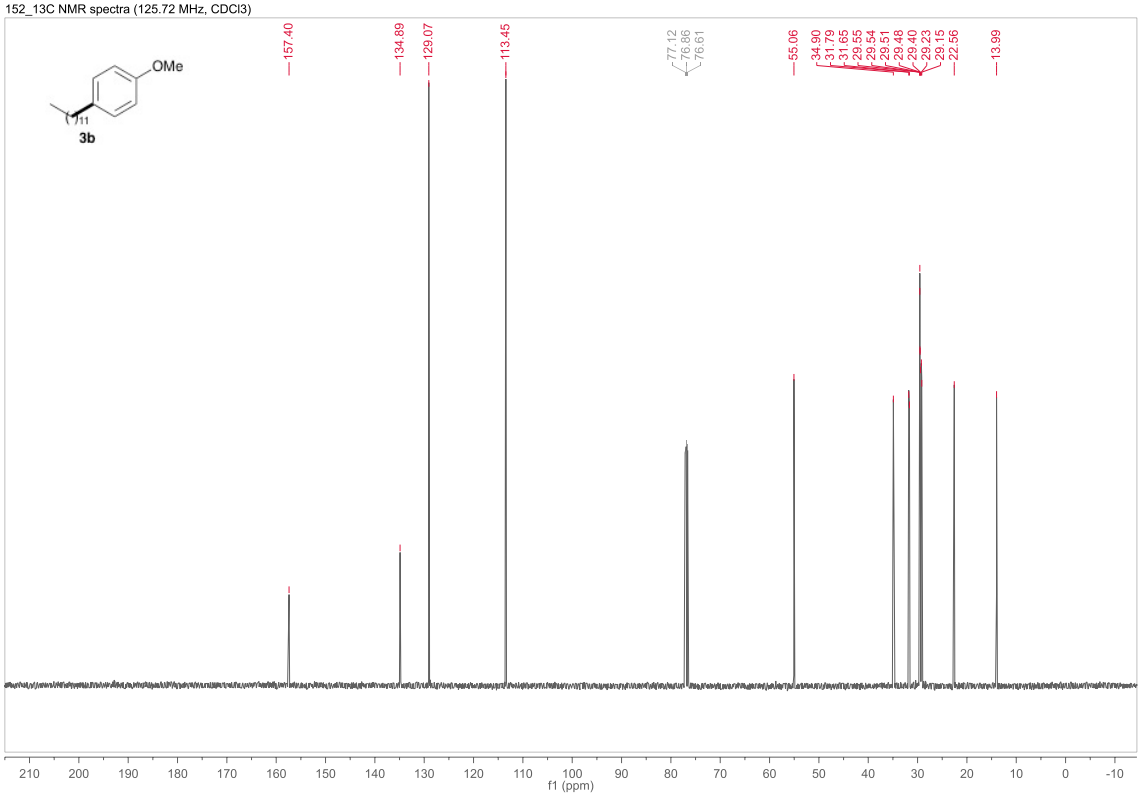
5-Cyclopentyl-*N*-methylindole (3p). Isolated as yellow oil; ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.04 – 6.91 (m, 1H), 6.48 – 6.33 (m, 1H), 3.74 (s, 3H), 3.09 (p, *J* = 8.7, 8.3 Hz, 1H), 2.09 (d, *J* = 10.1 Hz, 2H), 1.99 – 1.53 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.31, 135.42, 128.86, 128.59, 121.38, 118.51, 108.90, 100.54, 46.05, 35.10, 32.74, 25.5; EI-MS *m/z* (relative intensity): 199 (M^+, 100), 184 (8), 170 (76), 157 (19), 144 (35), 131 (13), 115 (9); HRMS calcd for $C_{14}H_{17}N$ [M^+]: 199.1361, found: 199.1358.

11. NMR spectra of products.

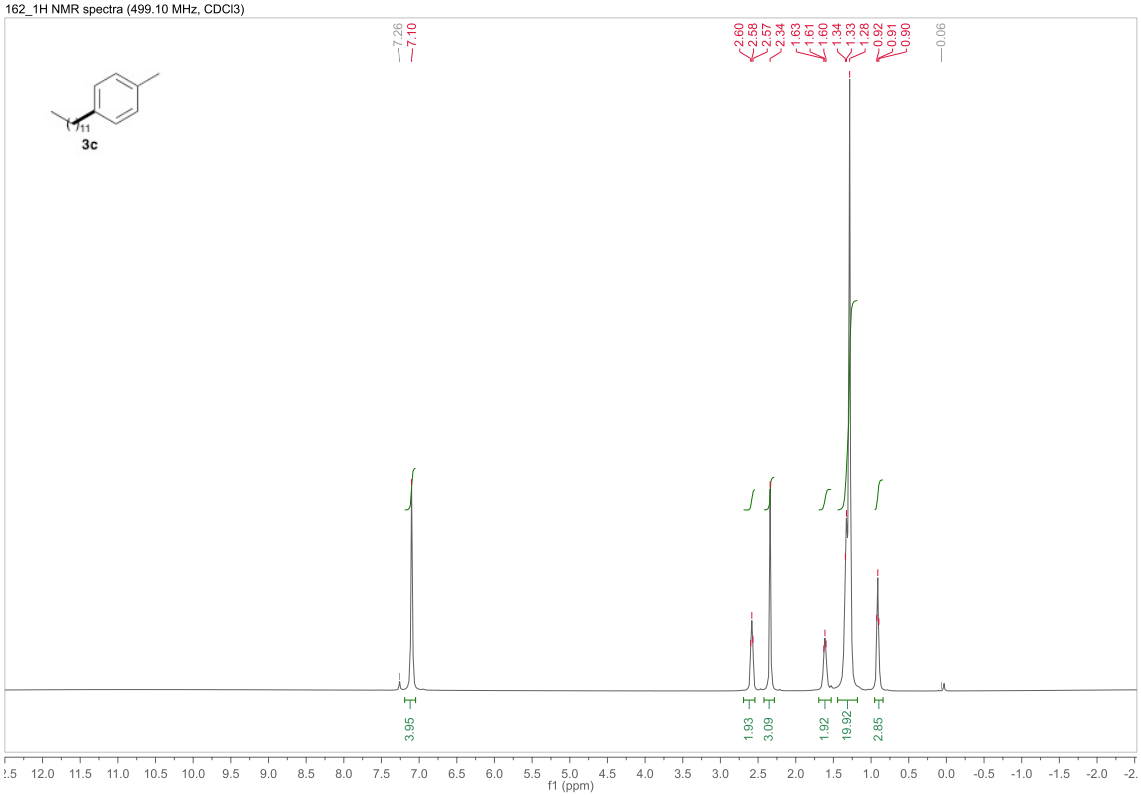
152_1H NMR spectra (499.94 MHz, CDCl3)



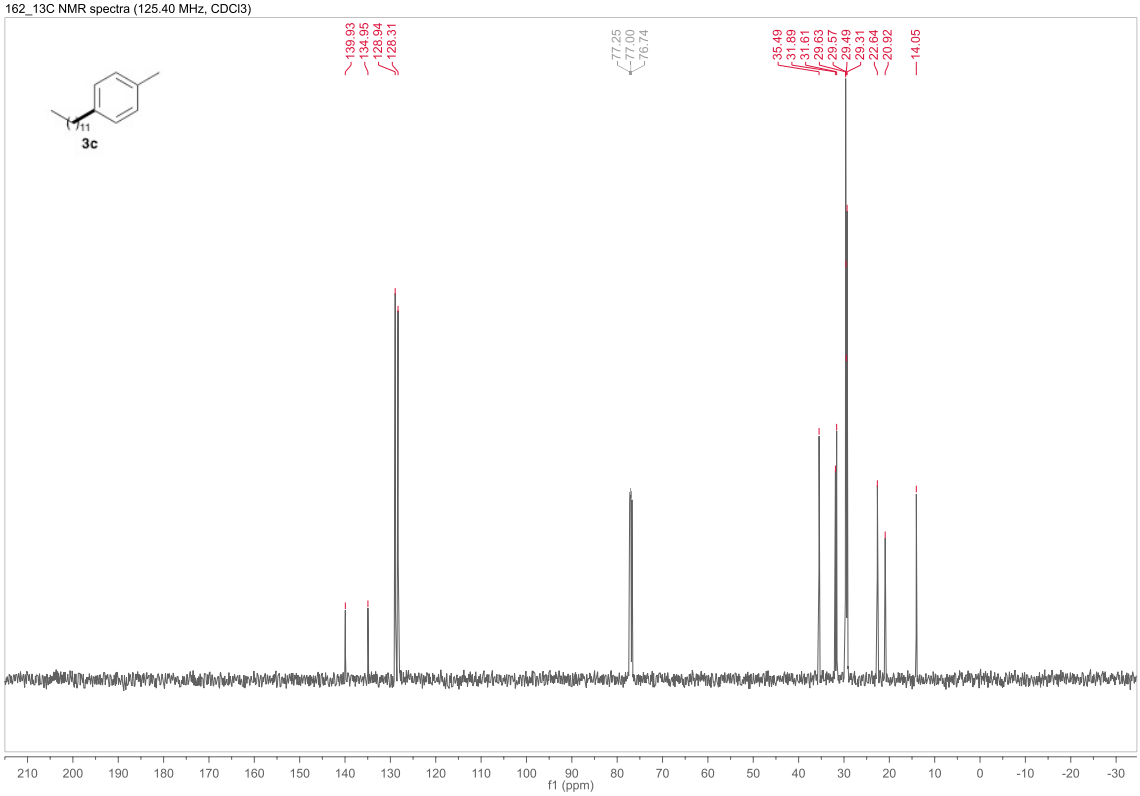
152_13C NMR spectra (125.72 MHz, CDCl3)



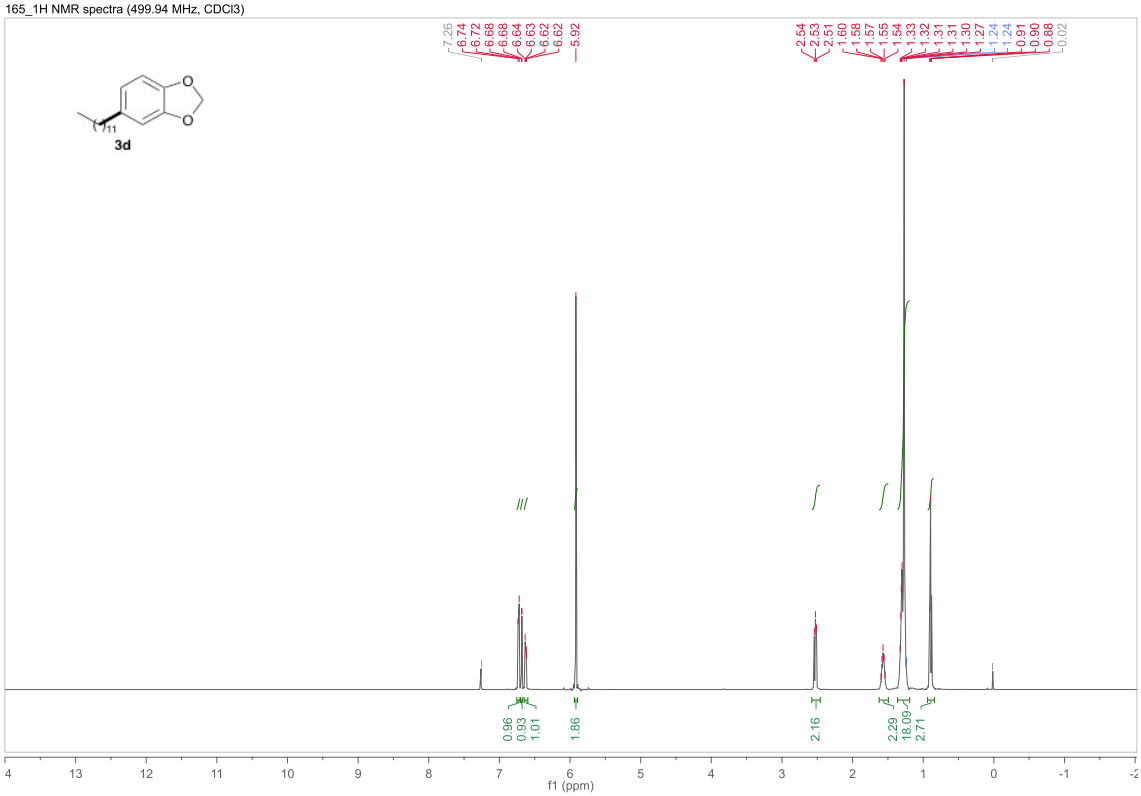
162_1H NMR spectra (499.10 MHz, CDCl3)



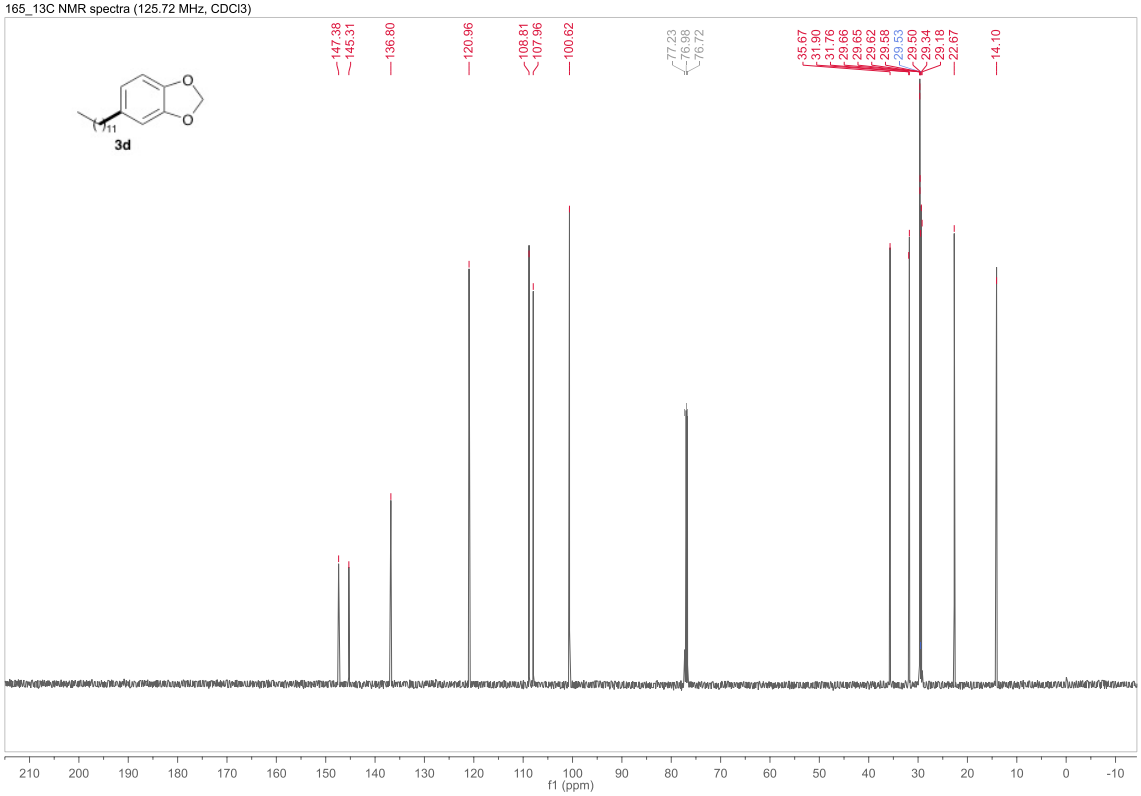
162_13C NMR spectra (125.40 MHz, CDCl3)



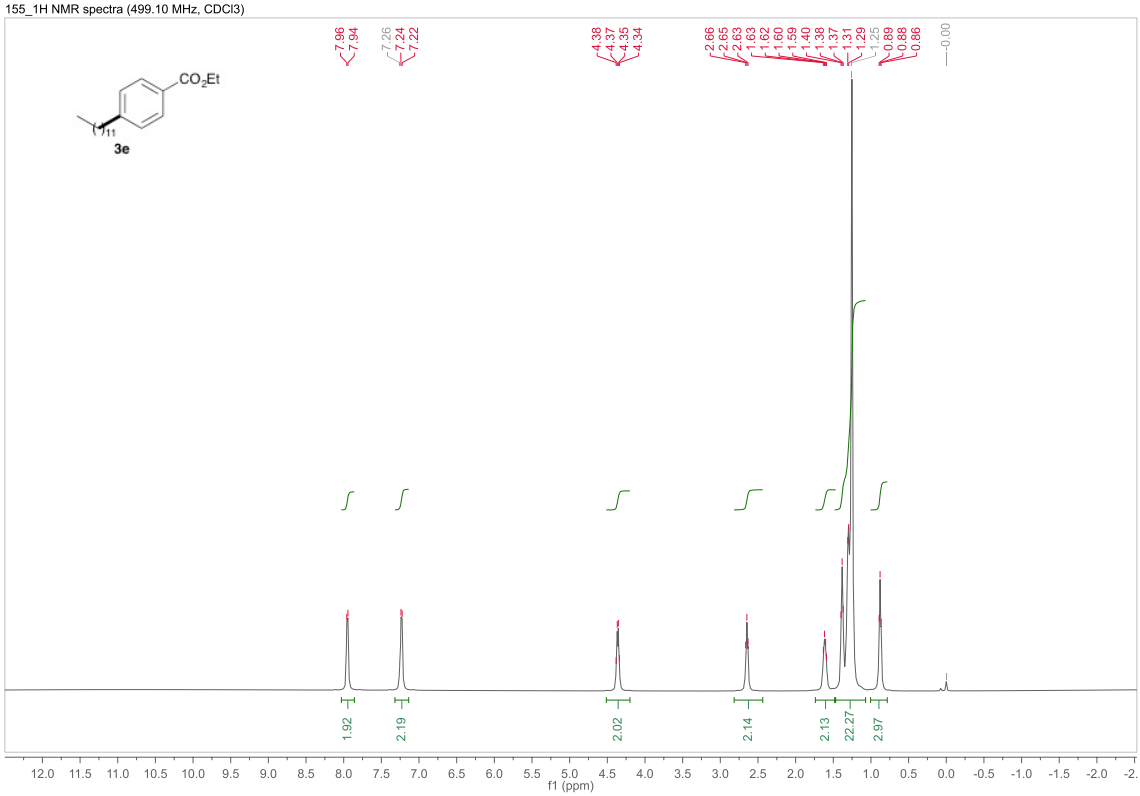
165_1H NMR spectra (499.94 MHz, CDCl3)



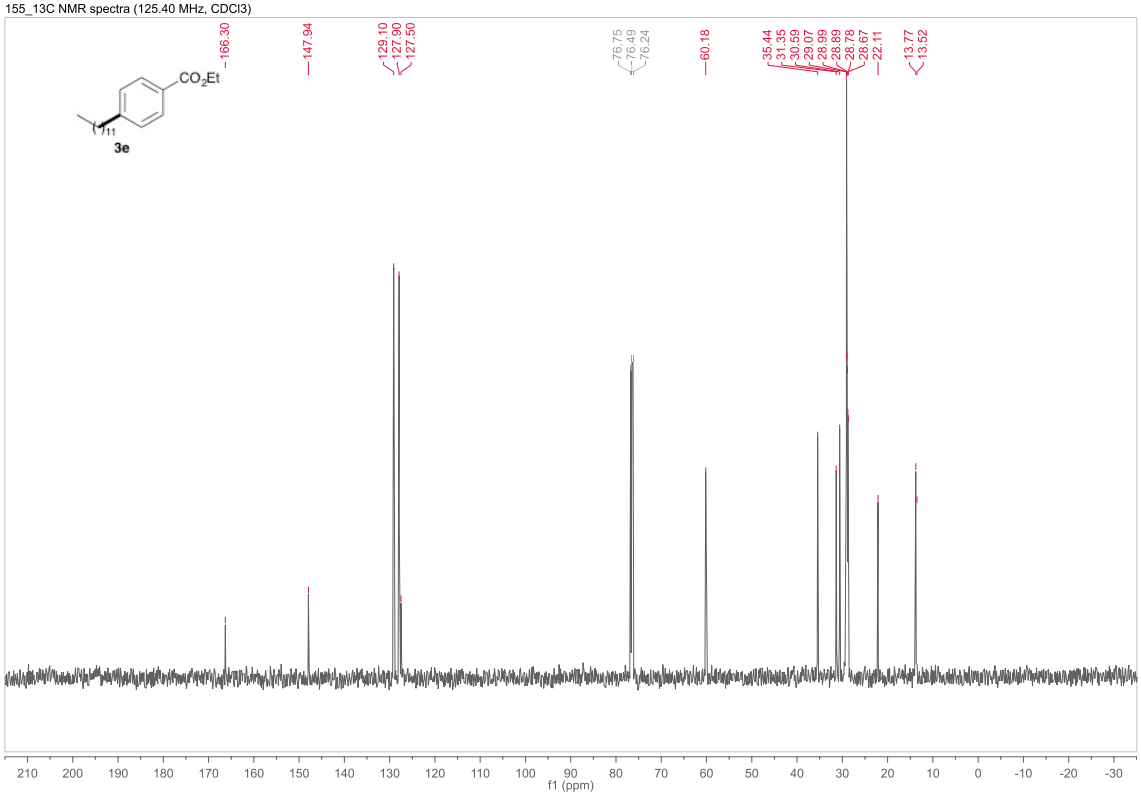
165_13C NMR spectra (125.72 MHz, CDCl3)



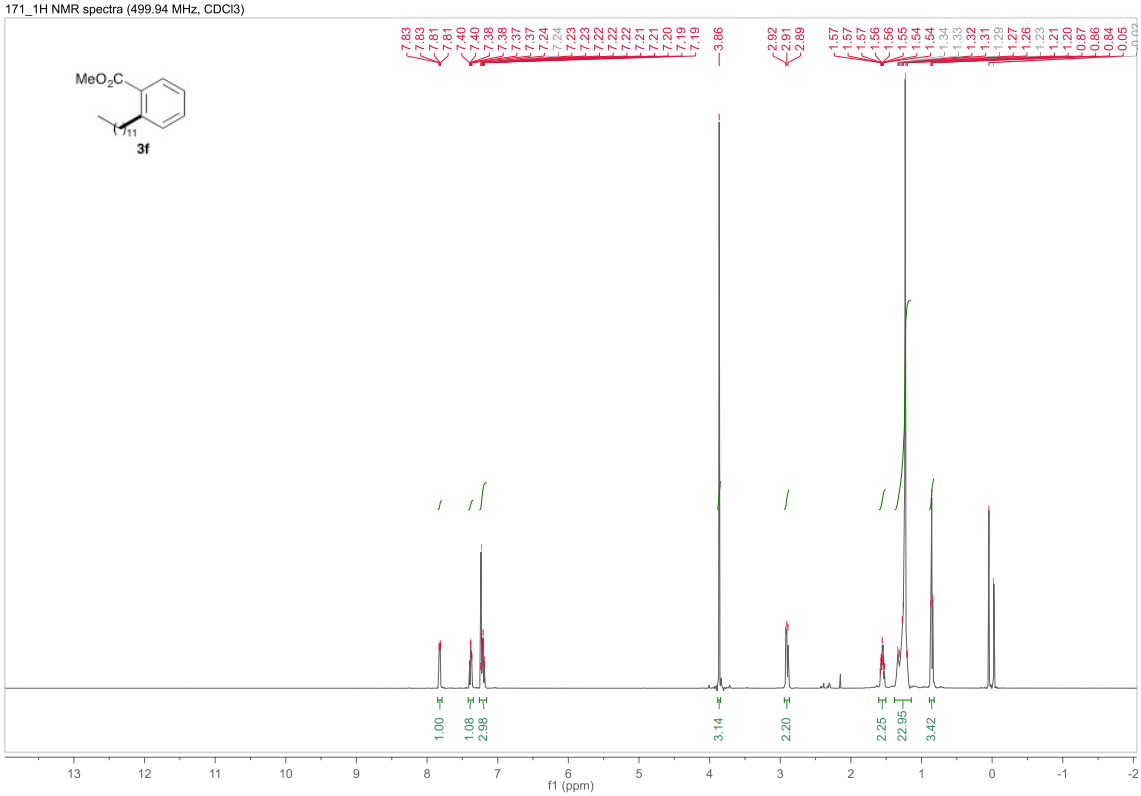
155_1H NMR spectra (499.10 MHz, CDCl3)



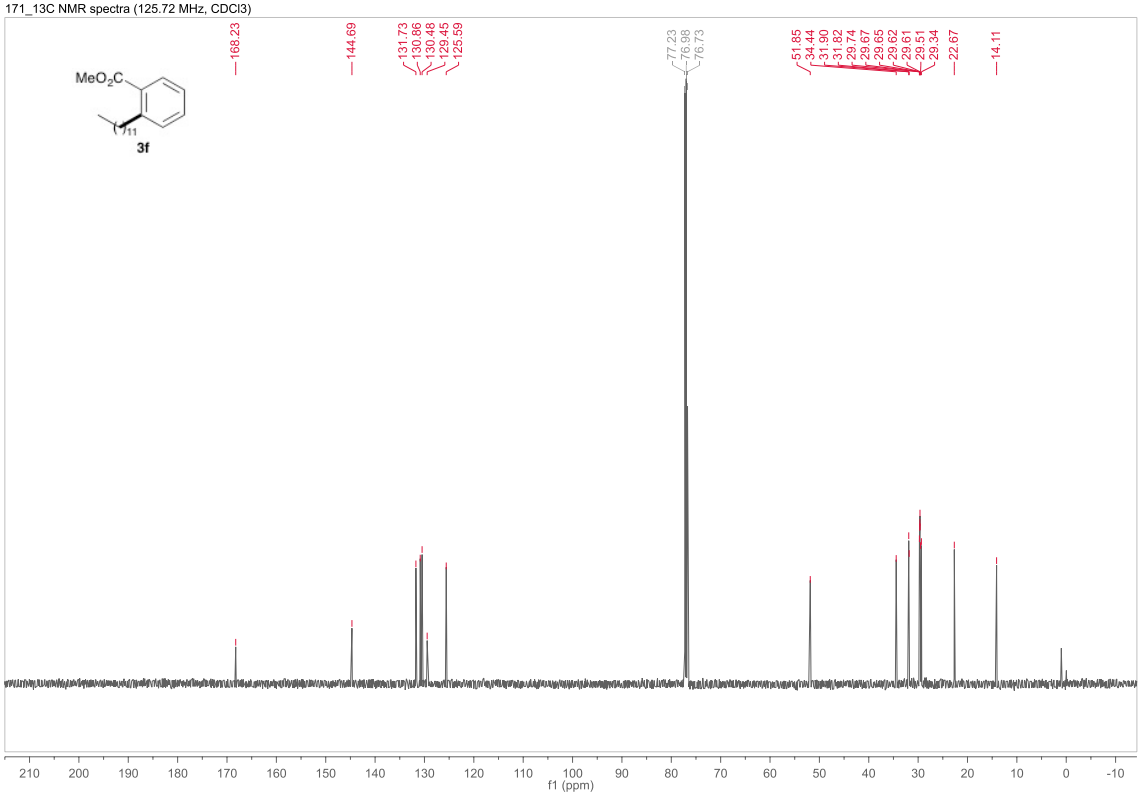
155_13C NMR spectra (125.40 MHz, CDCl3)



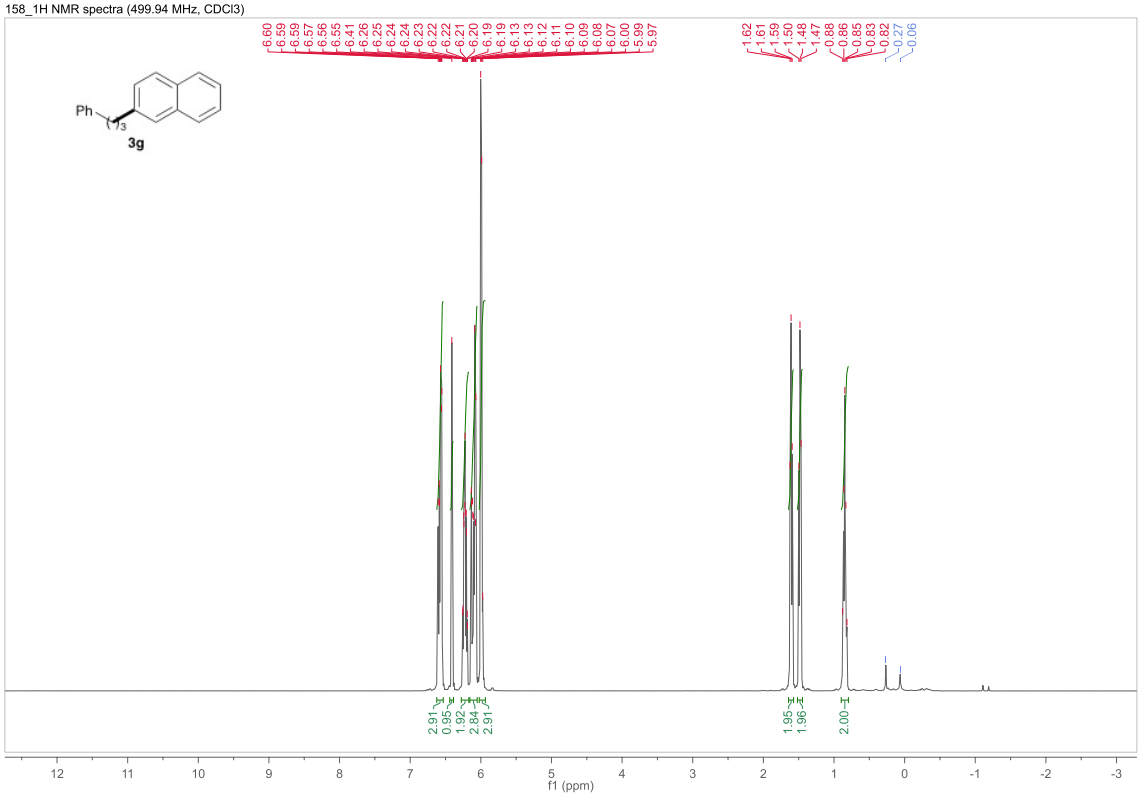
171_1H NMR spectra (499.94 MHz, CDCl3)



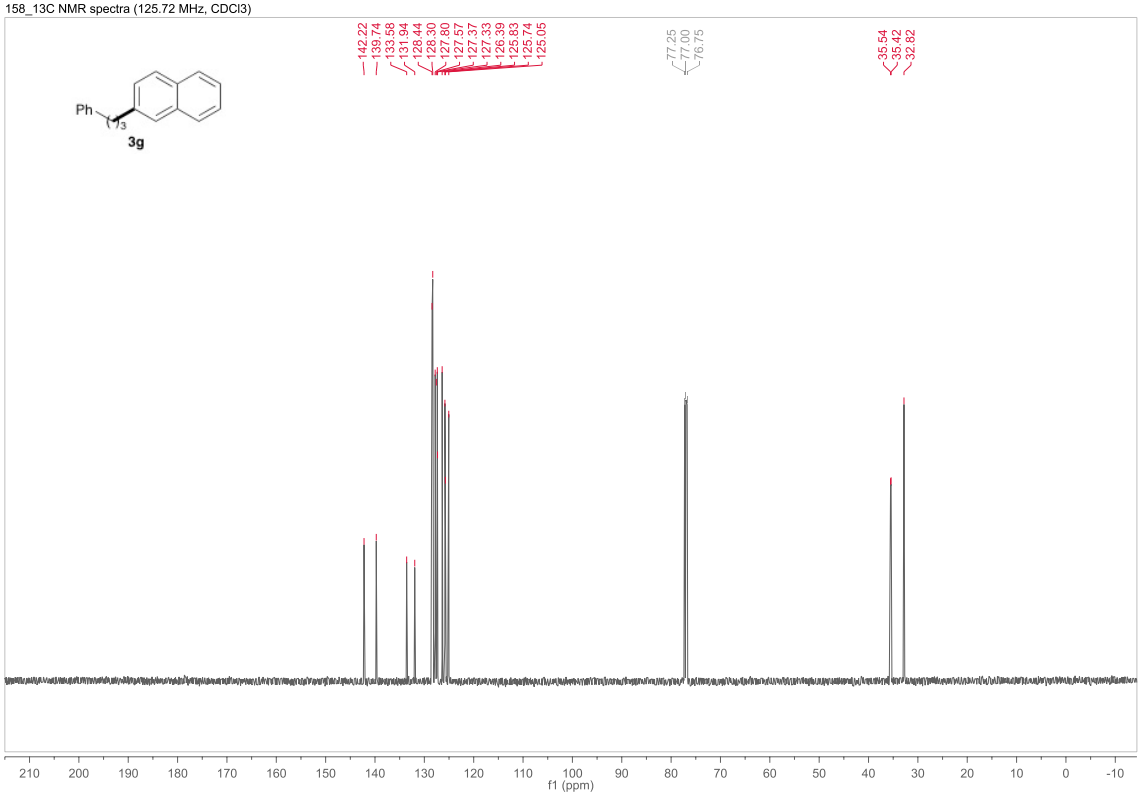
171_13C NMR spectra (125.72 MHz, CDCl3)



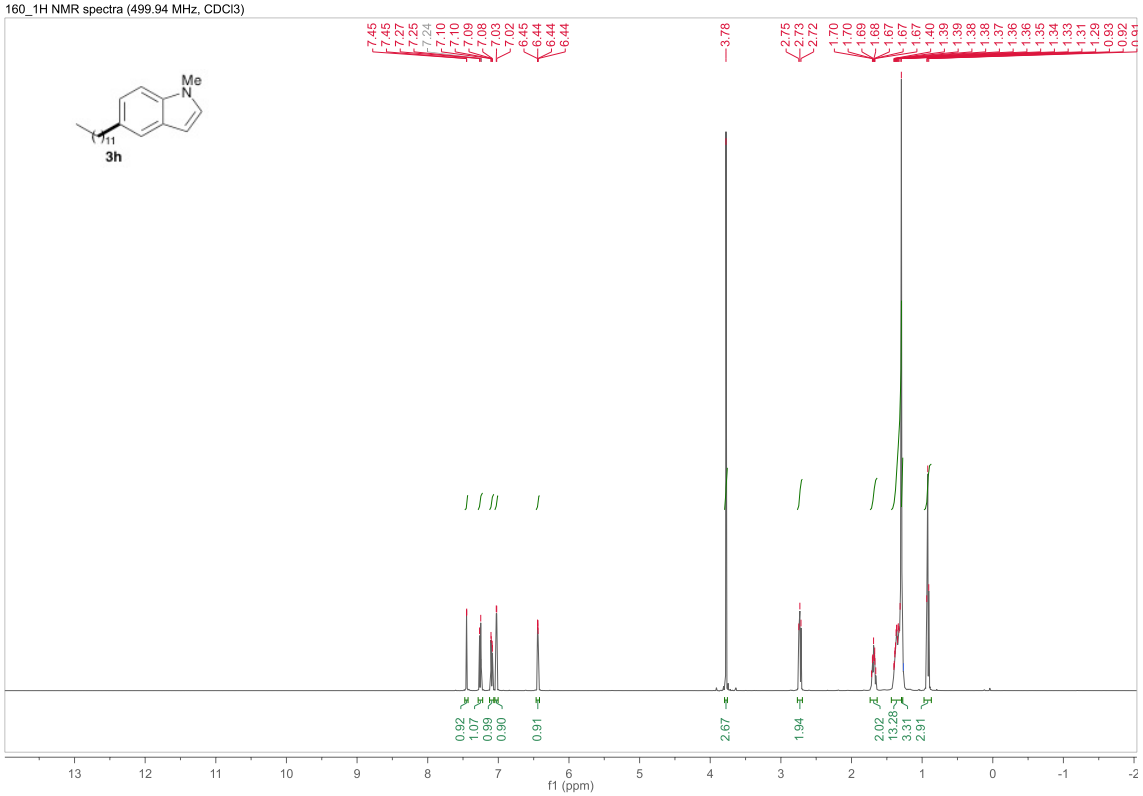
158_1H NMR spectra (499.94 MHz, CDCl3)



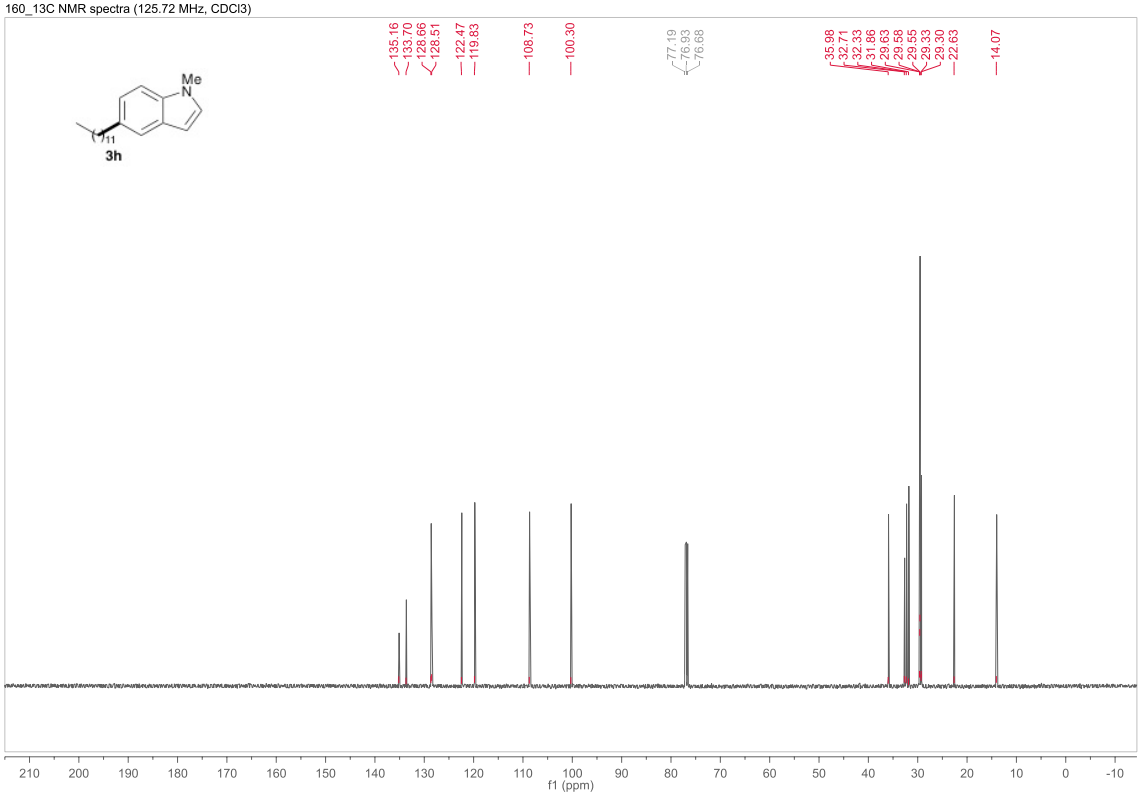
158_13C NMR spectra (125.72 MHz, CDCl3)



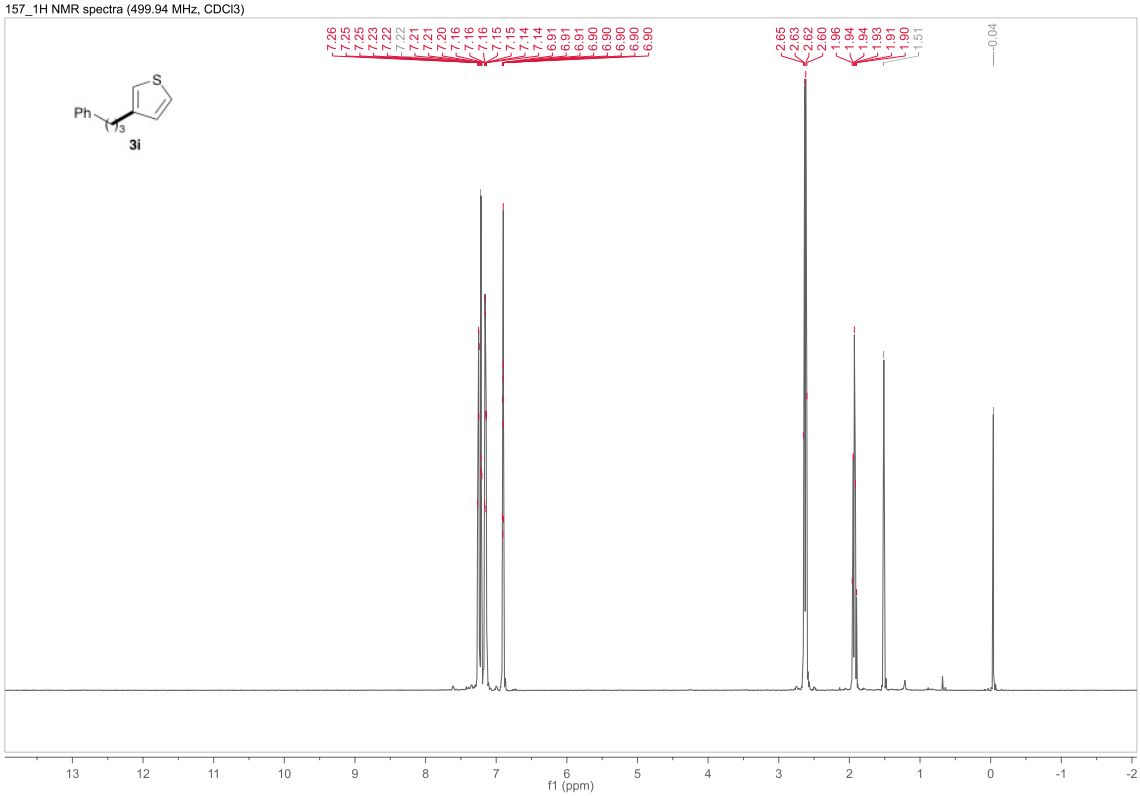
160_1H NMR spectra (499.94 MHz, CDCl3)



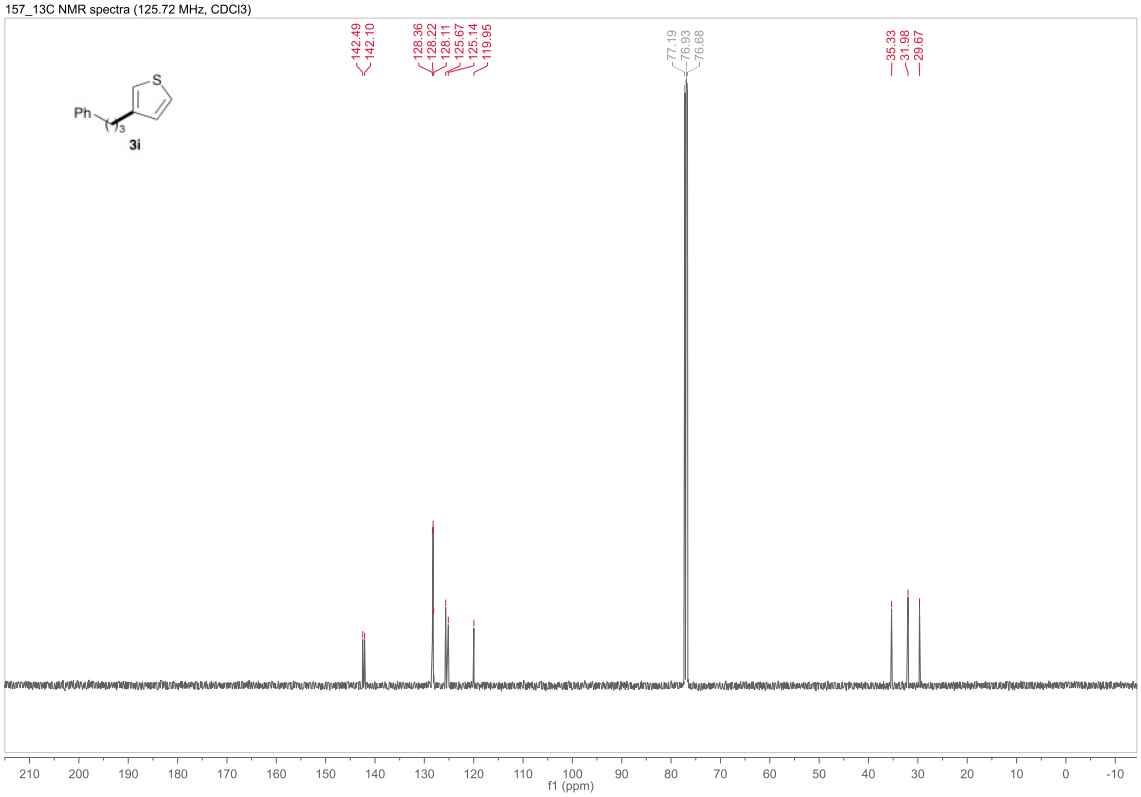
160_13C NMR spectra (125.72 MHz, CDCl3)



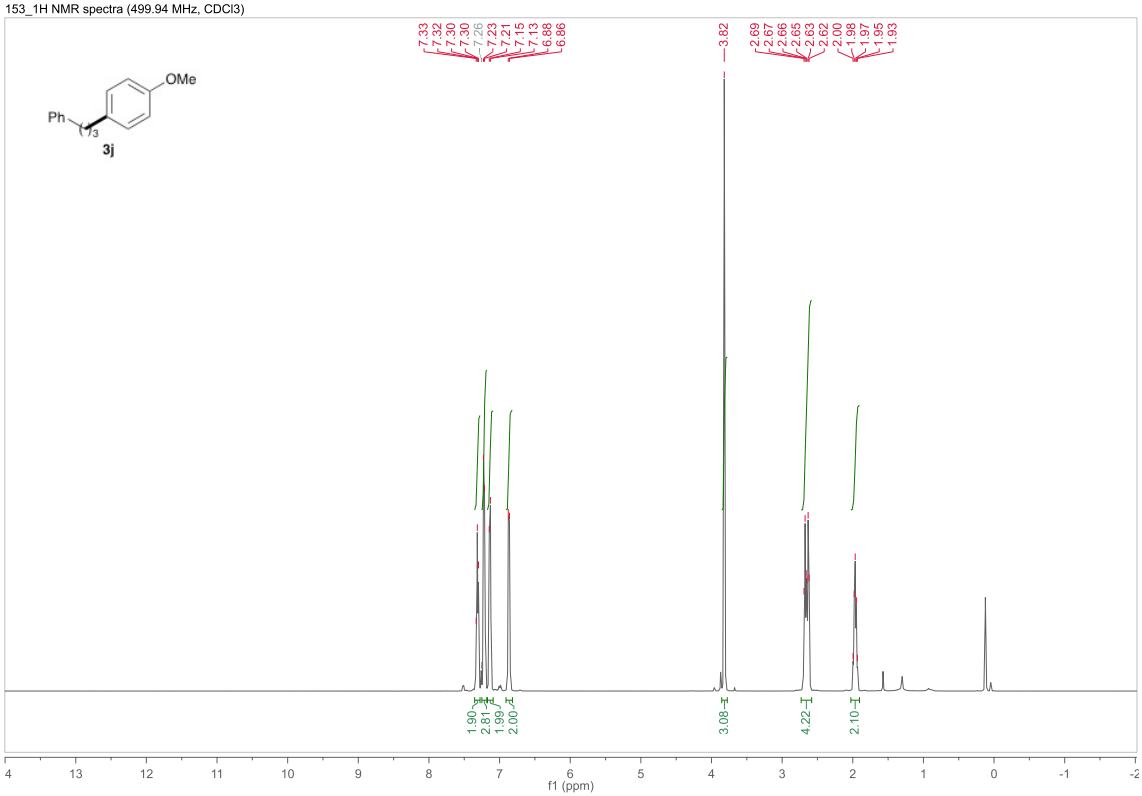
157_1H NMR spectra (499.94 MHz, CDCl3)



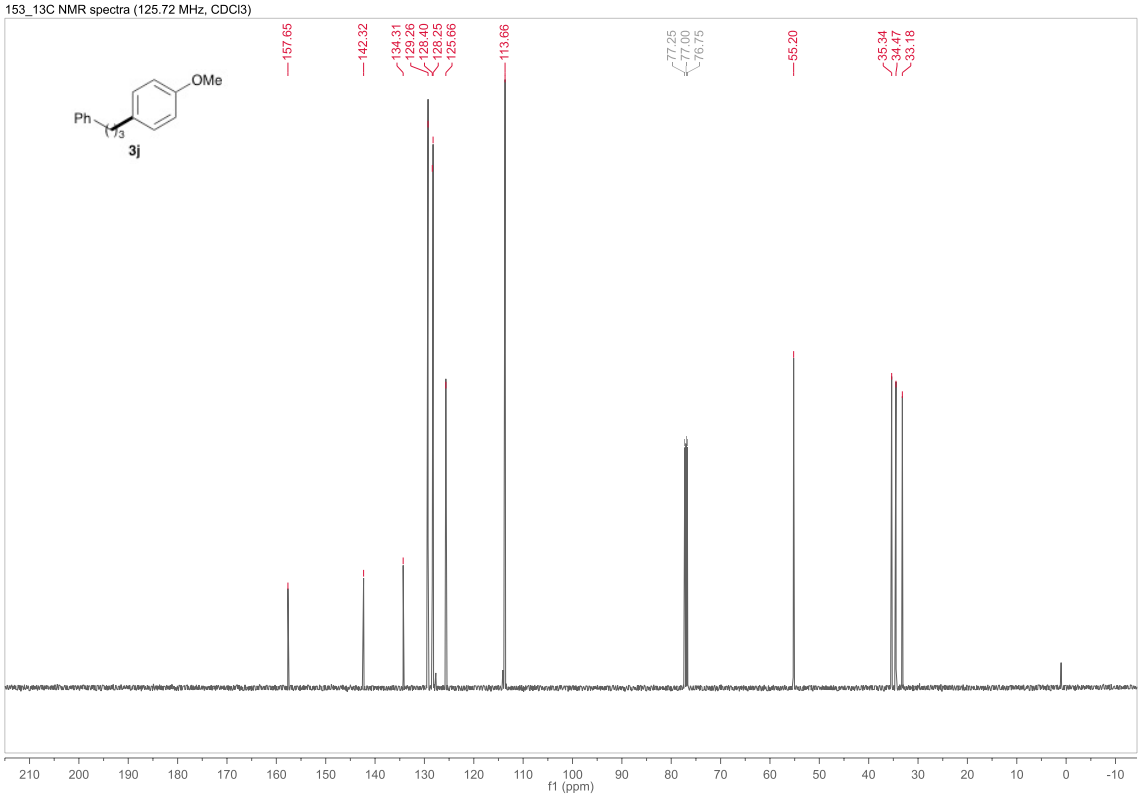
157_13C NMR spectra (125.72 MHz, CDCl3)



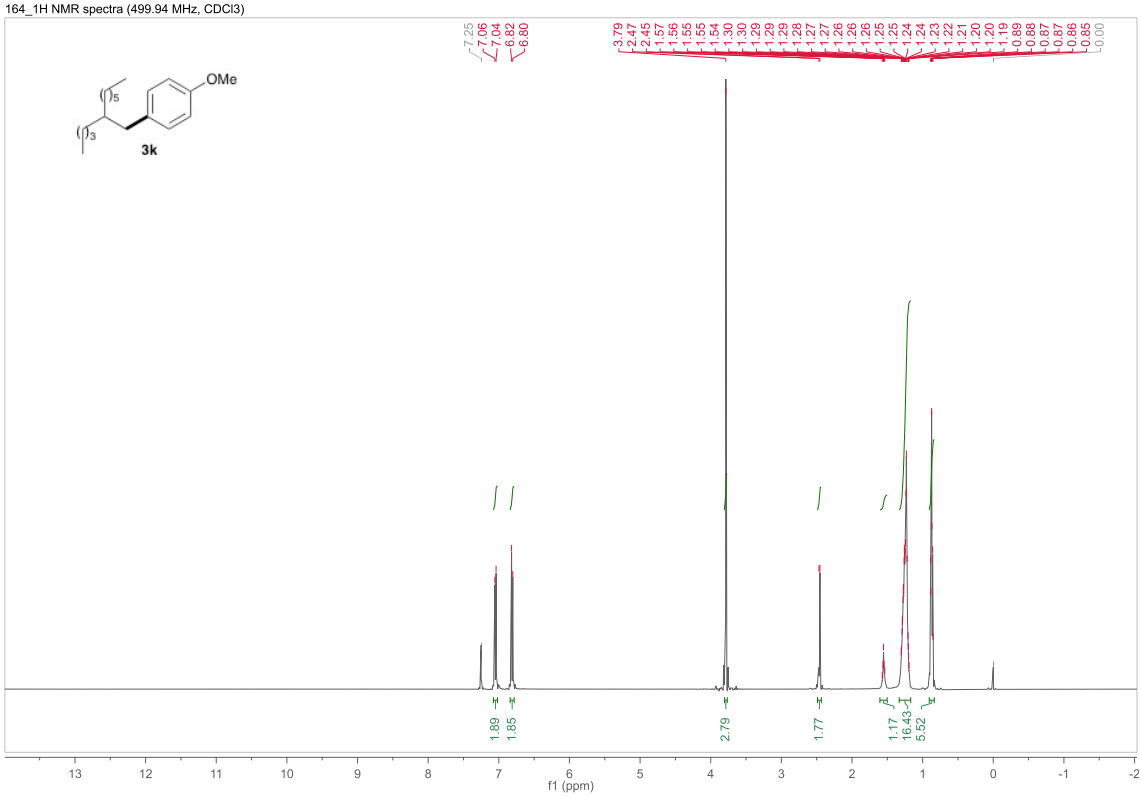
153_1H NMR spectra (499.94 MHz, CDCl3)



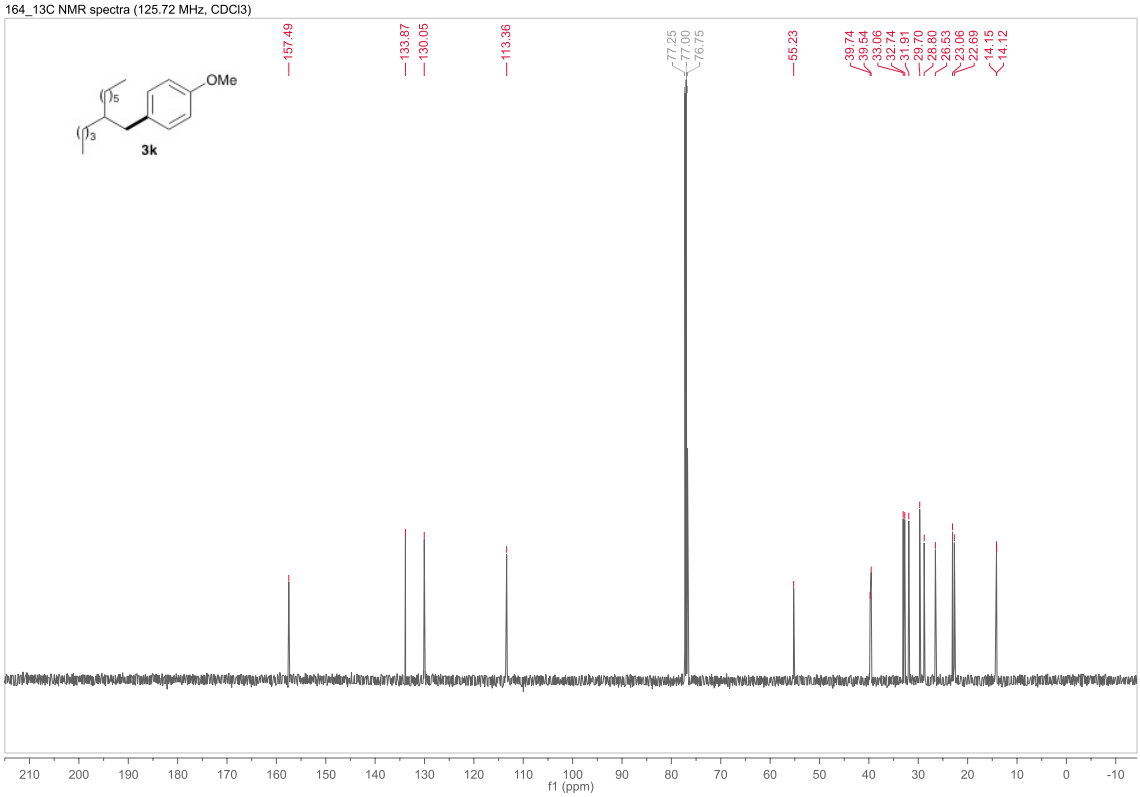
153_13C NMR spectra (125.72 MHz, CDCl3)



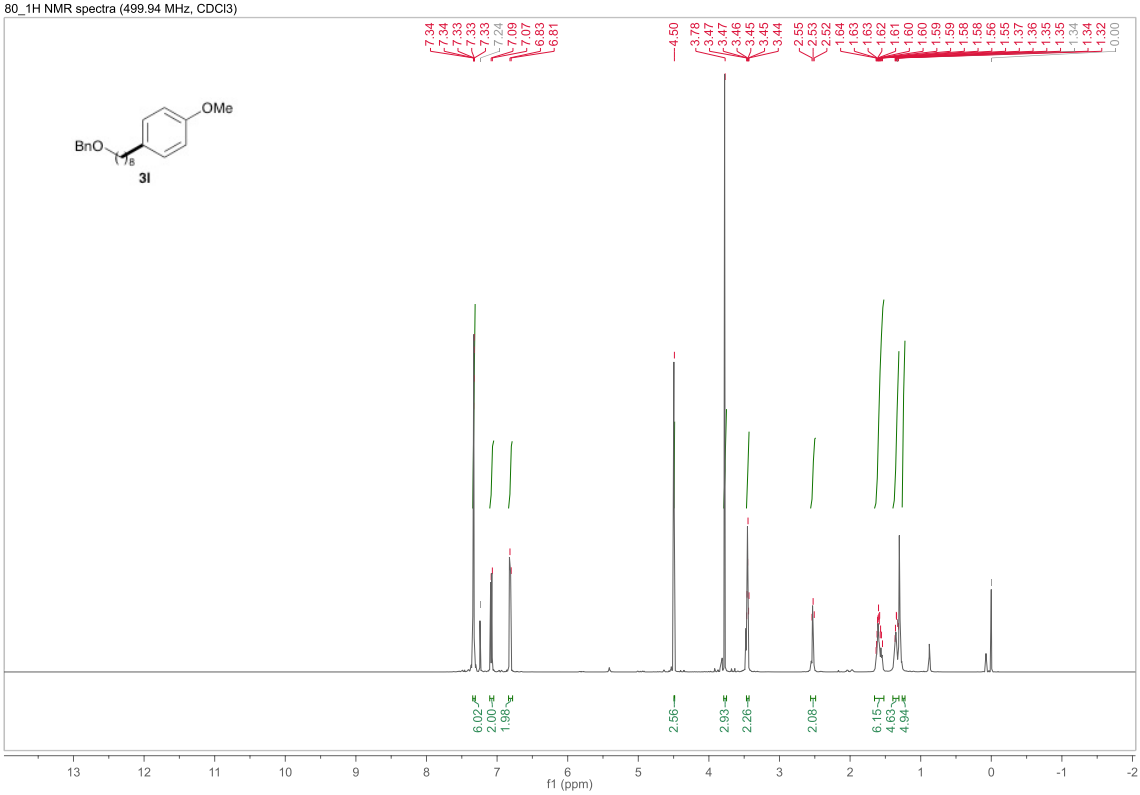
164_1H NMR spectra (499.94 MHz, CDCl3)



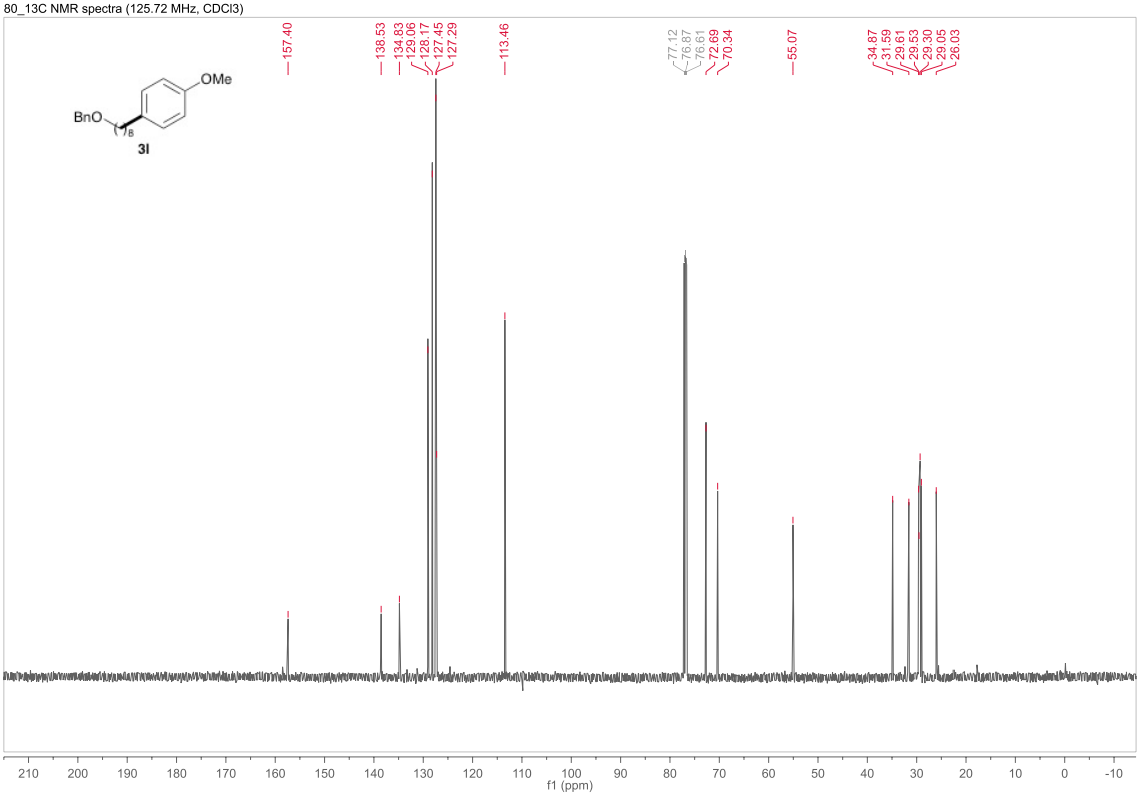
164_13C NMR spectra (125.72 MHz, CDCl3)



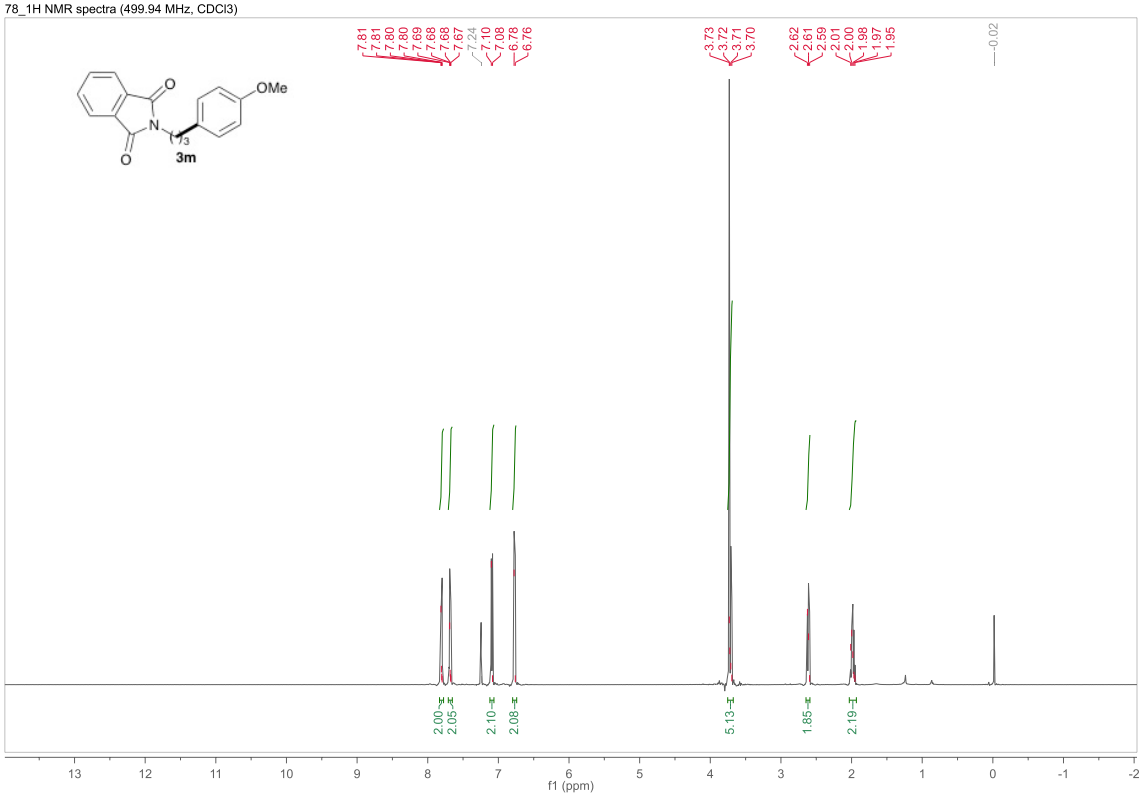
80_1H NMR spectra (499.94 MHz, CDCl3)



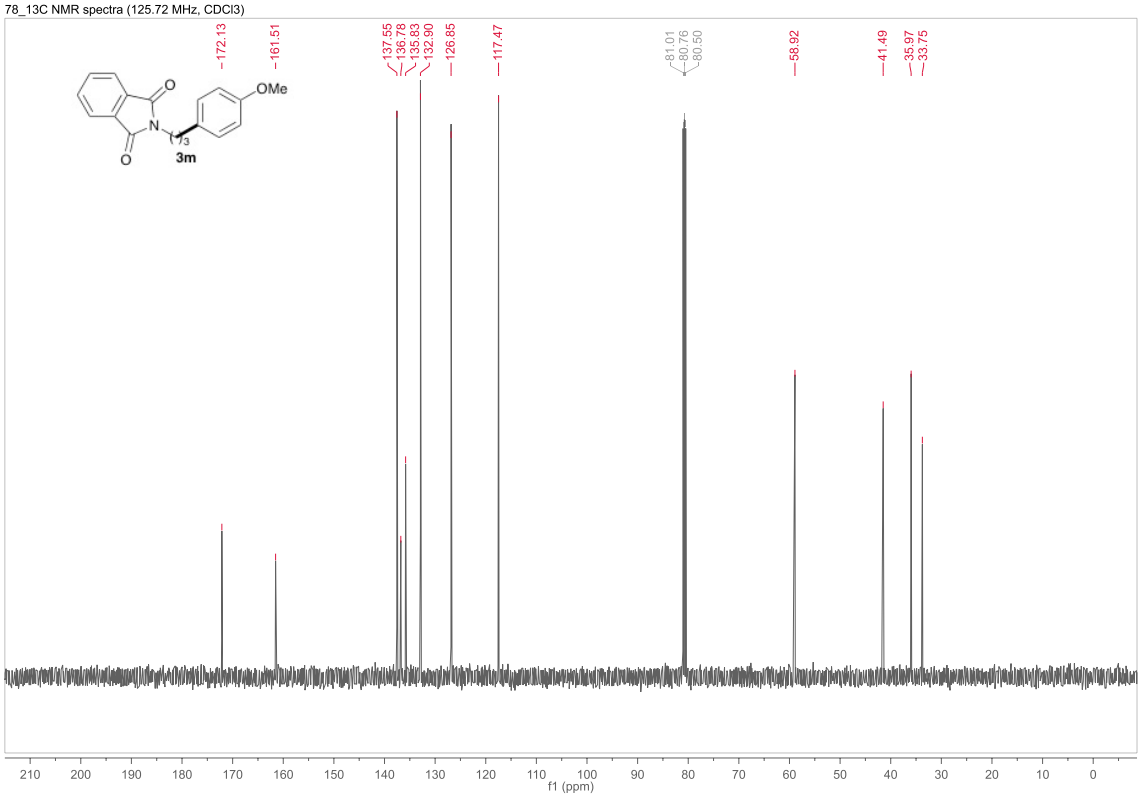
80_13C NMR spectra (125.72 MHz, CDCl3)



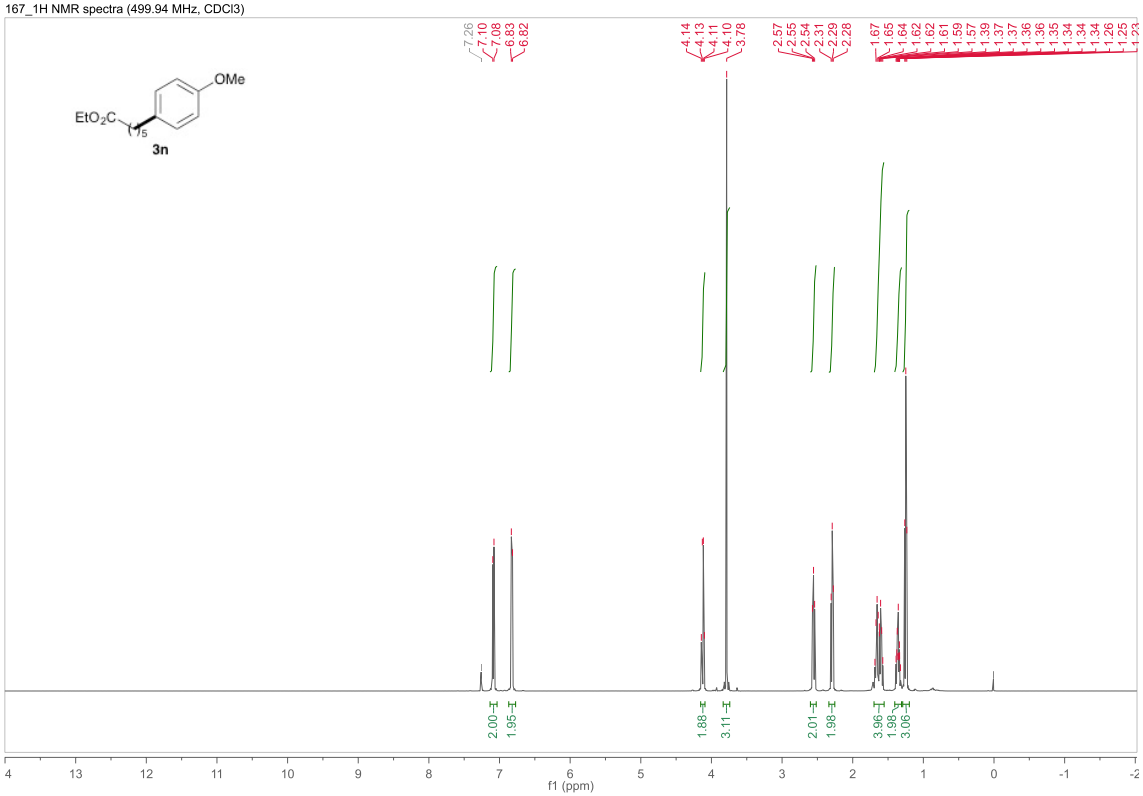
78_1H NMR spectra (499.94 MHz, CDCl3)



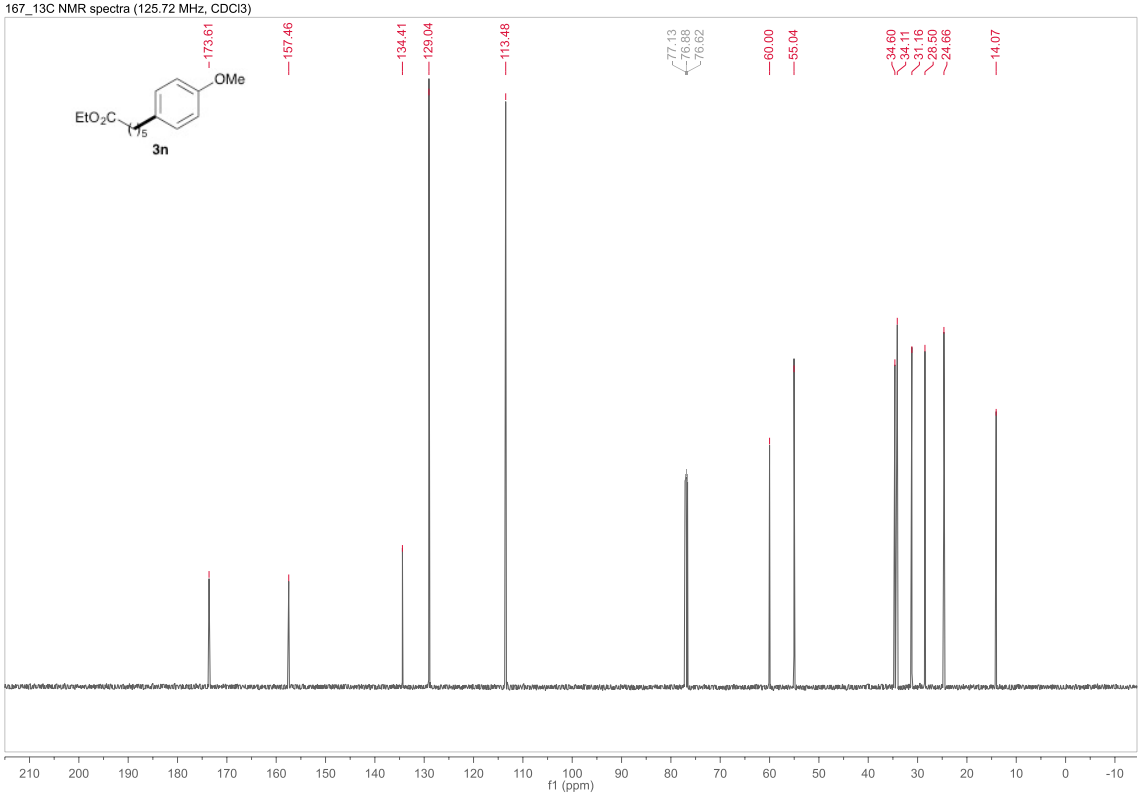
78_13C NMR spectra (125.72 MHz, CDCl3)



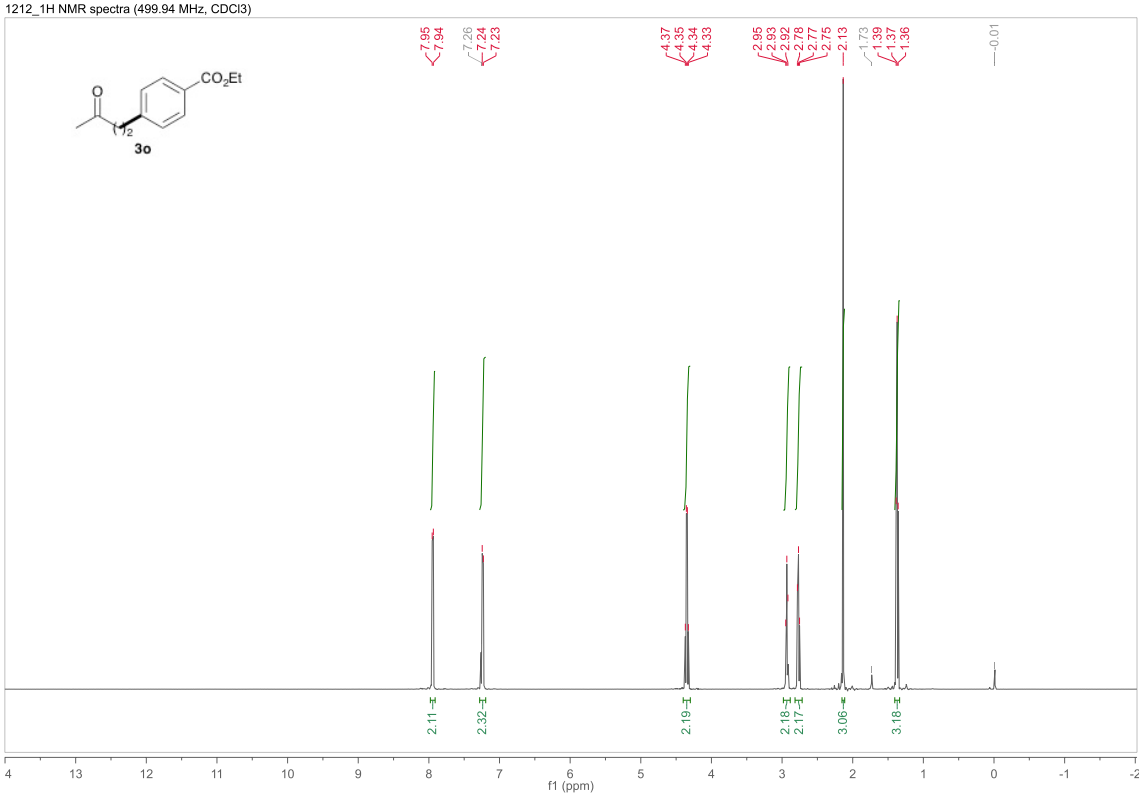
167_1H NMR spectra (499.94 MHz, CDCl3)



167_13C NMR spectra (125.72 MHz, CDCl3)

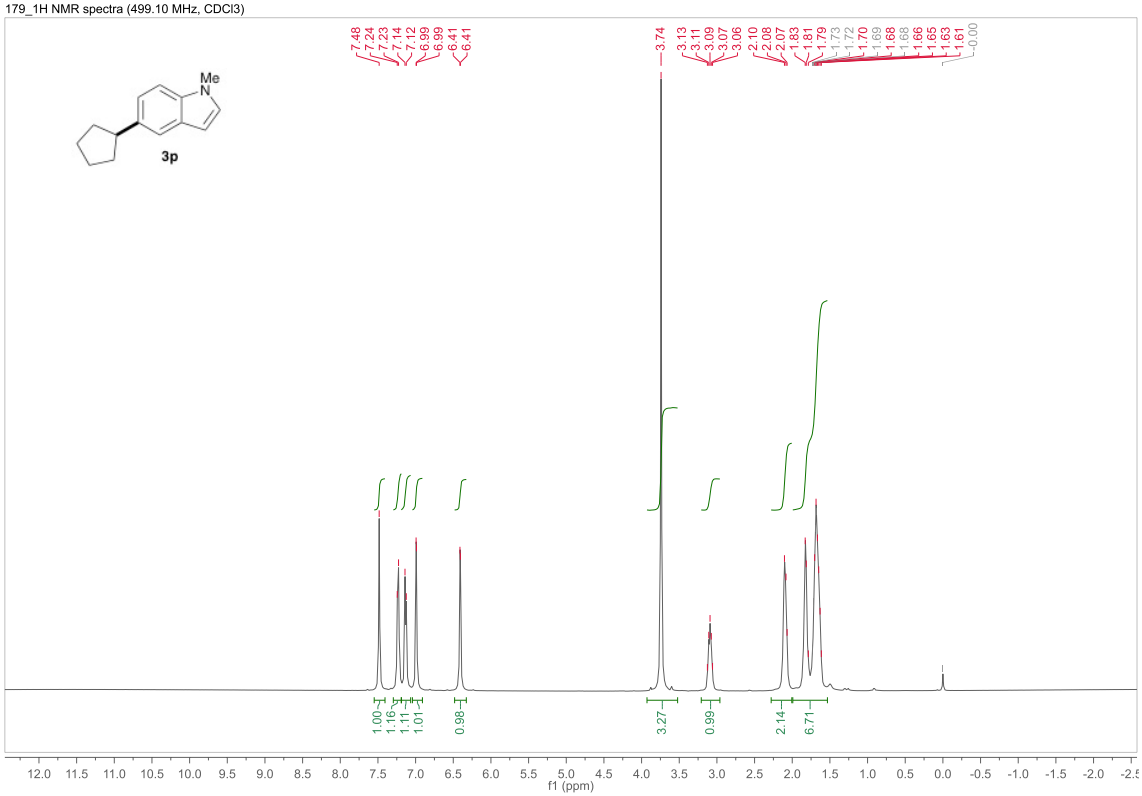


1212_1H NMR spectra (499.94 MHz, CDCl3)

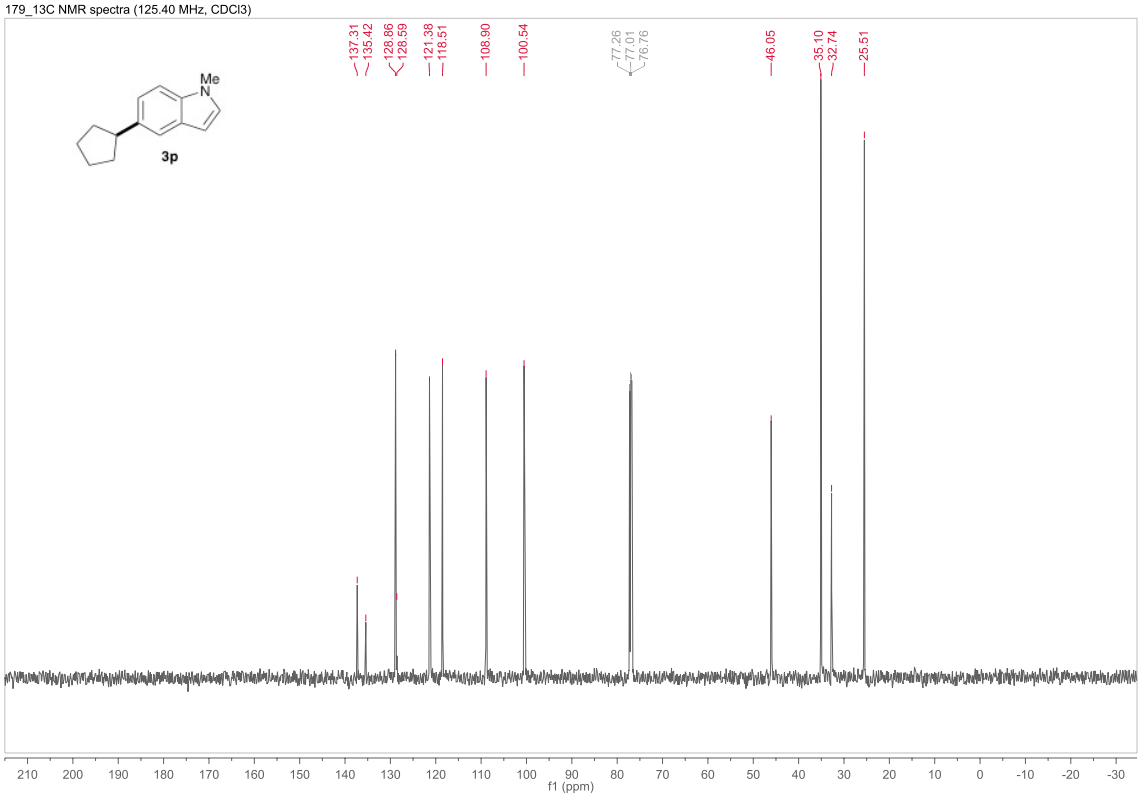


1212_13C NMR spectra (125.72 MHz, CDCl3)

179_1H NMR spectra (499.10 MHz, CDCl3)



179_13C NMR spectra (125.40 MHz, CDCl3)



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