

Supporting Information for

Radical C-C Bond Cleavage/Addition Cascade of Benzyl Cycloketone

Oxime Ethers Enabled by Photogenerated Cyclic Iminyl Radicals

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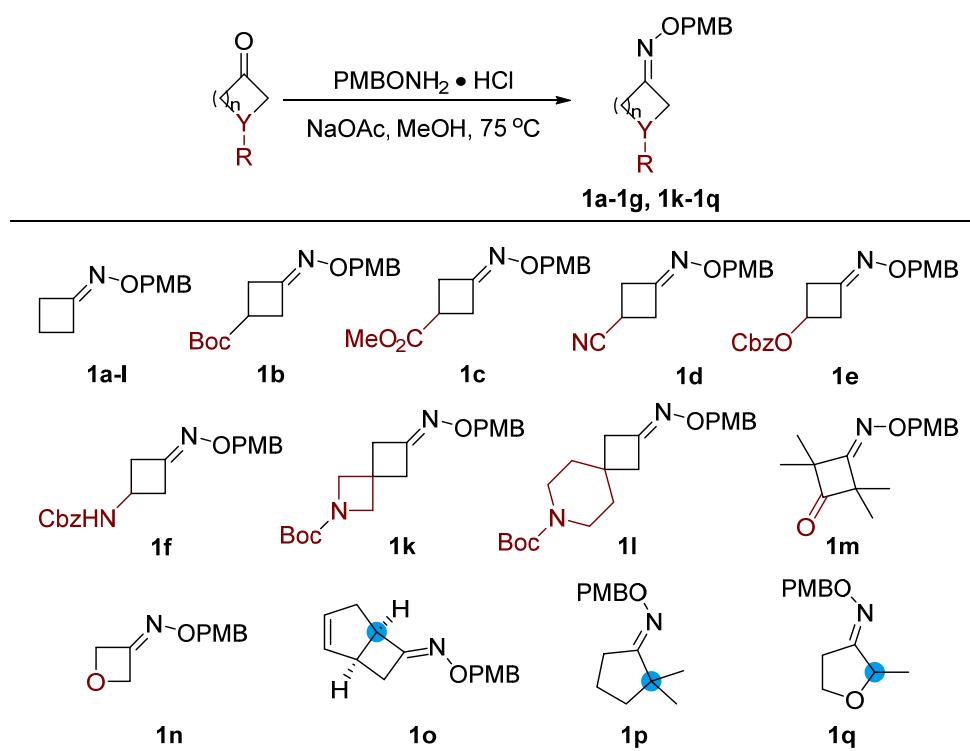
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1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^1H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 or 150 MHz with complete proton decoupling spectrophotometers. The high resolution mass spectra (HRMS) were measured on Bruker micrOTOF II by ESI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Benzyl Cycloketone Oxime Ethers

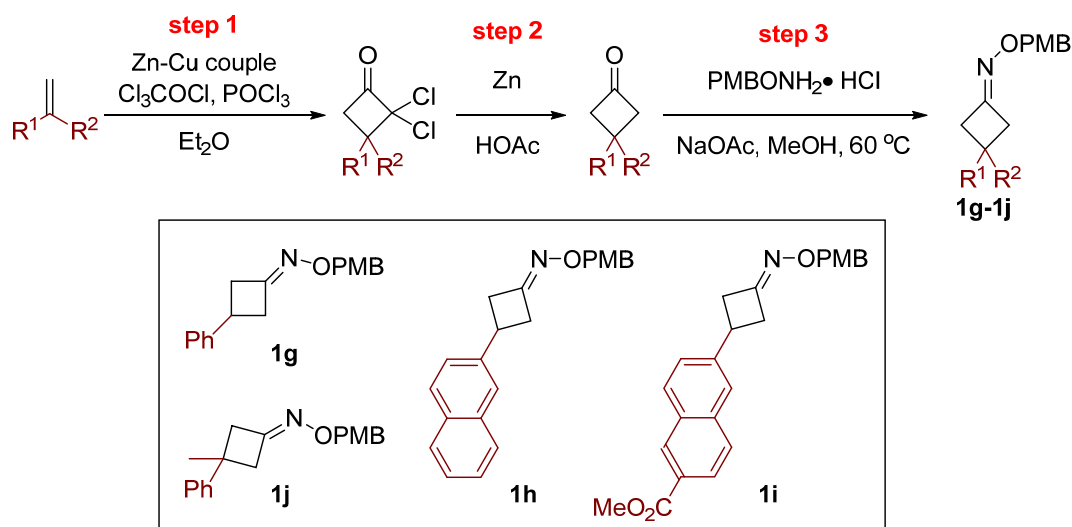
2.1 Preparation of Benzyl Cycloketone Oxime Ethers 1a-1g, 1k-1q



The hydroxylamine hydrochloride was prepared according to the literature.¹

To hydroxylamine hydrochloride (1.2 equiv) and sodium acetate (1.2 equiv) was added the solution of ketone in MeOH (0.3 M). The reaction mixture was warmed up to 75°C and stirred overnight. The resulting mixture was cooled down to room temperature, diluted with brine and EtOAc and extracted with EtOAc . The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel provided the oxime esters.

2.2 Preparation of Benzyl Cyclobutanone Oxime Ethers 1g-1j



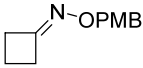
To a 250 mL three-necked flask under argon were added alkene derivative² (1.0 equiv), zinc-copper couple (3.0 equiv), and anhydrous ether (0.5 M). To this was added a solution of trichloroacetyl chloride (2.0 equiv) and phosphorus oxychloride (1.1 equiv) in ether (0.5 M) over 1 h through an addition funnel. The suspension was stirred overnight at reflux. The resulting mixture was filtered through a pad of Celite and was washed with ether (80 mL). The organic solution was successively washed with water (30 mL), a saturated aqueous solution of NaHCO₃ (30 mL) and brine (30 mL), and dried over Na₂SO₄. Then the solution was filtered, concentrated and used in the next step without further purification.

A mixture of 2,2-dichlorocyclobutanones (1.0 equiv) and zinc dust (4.0 equiv) in acetic acid (10 mL) was stirred at room temperature for 2 h and then heated at 80 °C for 5 h. The resulting mixture was allowed to cool to room temperature, then, the solution was diluted with water (30 mL) and extracted with ether (3*20 mL). The organic phase was washed successively with a saturated solution of aqueous NaHCO₃ (3*30 mL), water (30 mL) and brine (30 mL), then dried over Na₂SO₄ and concentrated in vacuum. The crude material was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate to afford various cyclobutanones.

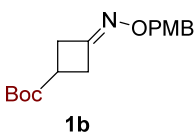
The following steps are same as the mentioned above.

2.3 Spectral Data of Substrates

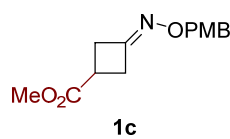
cyclobutanone O-(4-methoxybenzyl) oxime 1a-I

 **1a-I** was prepared from the corresponding cyclobutanone (5.0 mmol) as colorless oil (690 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.28 Hz, 2H), 6.88 (d, *J* = 7.90 Hz, 2H), 4.96 (s, 2H), 3.80 (s, 3H), 2.91 (t, *J* = 8.72 Hz, 3H), 2.01 – 1.93 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 159.2, 130.2, 129.8, 113.8, 77.4, 77.1, 76.8, 75.3, 55.3, 31.7, 31.3, 14.6. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₁₂H₁₅NNaO₂: 228.0995, found: 228.0995.

tert-butyl 3-(((4-methoxybenzyl)oxy)imino)cyclobutane-1-carboxylate 1b

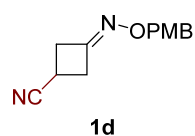
 **1b** was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.20 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.63 Hz, 2H), 6.88 (d, *J* = 8.66 Hz, 2H), 4.97 (s, 2H), 3.79 (s, 3H), 3.12 – 3.01 (m, 5H), 1.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 173.2, 159.4, 154.3, 130.0, 129.9, 113.8, 81.0, 77.5, 77.1, 76.8, 75.5, 55.3, 35.5, 35.1, 32.3, 28.0. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₁₇H₁₃NNaO₄: 328.1519, found: 328.1520.

methyl 3-(((4-methoxybenzyl)oxy)imino)cyclobutane-1-carboxylate **1c**



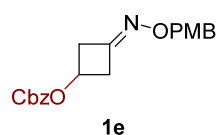
1c was prepared from the corresponding cyclobutanone (5.0 mmol) as colorless oil (1.02 g, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.41 Hz, 2H), 6.87 (m, *J* = 8.51 Hz, 2H), 4.96 (s, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 3.24–3.08 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 159.4, 153.7, 129.9, 113.8, 77.5, 77.2, 76.9, 75.6, 55.2, 52.2, 35.6, 35.2, 31.2. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₁₄H₁₇NNaO₄: 286.1050, found: 286.1054.

3-(((4-methoxybenzyl)oxy)imino)cyclobutane-1-carbonitrile **1d**



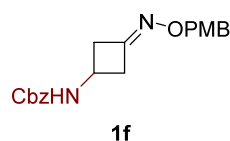
1d was prepared from the corresponding cyclobutanone (5.0 mmol) as colorless oil (986 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.41 Hz, 2H), 6.88 (d, *J* = 8.45 Hz, 2H), 4.97 (s, 2H), 3.79 (s, 3H), 3.37–3.09 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 150.7, 130.1, 129.5, 121.2, 113.9, 77.5, 77.2, 76.9, 76.0, 55.3, 37.3, 37.0, 16.1. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₁₃H₁₄N₂NaO₂: 253.0947, found: 253.0948.

benzyl 3-(((4-methoxybenzyl)oxy)imino)cyclobutyl carbonate **1e**



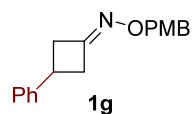
1e was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.16 g, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.37–7.25 (m, 7H), 6.88 (d, *J* = 8.63 Hz, 2H), 4.97 (s, 2H), 4.45 (s, 2H), 4.23–4.14 (m, 1H), 3.80 (s, 3H), 3.23–3.08 (m, 2H), 2.95–2.82 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 152.7, 137.5, 130.1, 129.9, 128.5, 128.0, 113.8, 77.4, 77.1, 76.8, 75.5, 71.0, 67.3, 55.3, 40.1, 39.6. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₂₀H₂₁NNaO₅: 378.1312, found: 378.1310.

benzyl 3-(((4-methoxybenzyl)oxy)imino)cyclobutyl carbamate **1f**



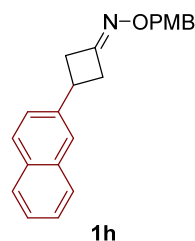
1f was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.13 g, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.25 (m, 5H), 7.27 (d, *J* = 5.02 Hz, 2H), 6.88 (d, *J* = 8.62 Hz, 2H), 5.12–5.02 (m, 3H), 4.97 (s, 2H), 4.27 (s, 1H), 3.80 (s, 3H), 3.38–3.26 (m, 2H), 2.81 (t, *J* = 22.83 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 155.6, 152.6, 136.2, 129.9, 128.6, 128.6, 128.3, 128.3, 128.2, 113.8, 77.4, 77.1, 76.8, 75.6, 66.9, 40.8, 40.5, 39.7. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₂₀H₂₂N₂NaO₄: 377.1472, found: 377.1472.

3-phenylcyclobutan-1-one O-(4-methoxybenzyl) oxime **1g**



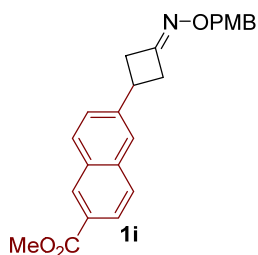
1g was prepared from the corresponding cyclobutanone (5.0 mmol) as yellow oil (900 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.20 (m, 7H), 6.88 (d, *J* = 8.46 Hz, 2H), 5.01 (s, 2H), 3.77 (s, 3H), 3.58–3.50 (m, 1H), 3.41–3.29 (m, 2H), 3.00 (dd, *J* = 13.00, 3.17 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 155.8, 144.2, 130.2, 130.0, 128.7, 126.6, 126.5, 113.9, 77.5, 77.2, 76.9, 75.6, 55.3, 39.7, 39.0, 32.9. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₁₈H₁₉NNaO₂: 304.1308, found: 304.1311.

3-(naphthalen-2-yl)cyclobutan-1-one O-(4-methoxybenzyl) oxime **1h**



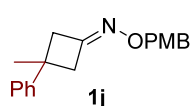
1h was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.16 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (t, *J* = 8.69 Hz, 3H), 7.65 (s, 1H), 7.48–7.42 (m, 2H), 7.35 (t, *J* = 9.17 Hz, 3H), 6.90 (d, *J* = 8.14 Hz, 2H), 5.03 (s, 2H), 3.80 (s, 3H), 3.77–3.69 (m, 1H), 3.50–3.38 (m, 2H), 3.11 (dt, *J* = 14.63, 7.32 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 155.7, 141.3, 133.2, 132.1, 130.0, 129.9, 128.4, 127.6, 126.2, 125.6, 124.8, 124.6, 113.7, 77.3, 77.0, 76.7, 75.4, 55.2, 39.5, 38.8, 33.0. HRMS (EI): *m/z* [M + Na]⁺ calcd for C₂₂H₂₁NNaO₂: 354.1465, found: 354.1466.

methyl 6-((3-(((4-methoxybenzyl)oxy)imino)cyclobutyl)-2-naphthoate **1i**



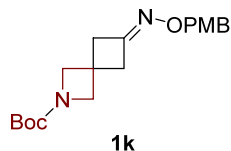
1i was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.25 g, 64%). ¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 8.06 (d, *J* = 8.41 Hz, 1H), 7.87 (dd, *J* = 38.42, 8.56 Hz, 2H), 7.69 (s, 1H), 7.39 (dd, *J* = 40.34, 8.38 Hz, 3H), 6.90 (d, *J* = 8.25 Hz, 2H), 5.03 (s, 2H), 3.98 (s, 3H), 3.82 (s, 3H), 3.79 – 3.73 (m, 1H), 3.52 – 3.41 (m, 2H), 3.16 – 3.08 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 167.2, 159.4, 155.2, 144.1, 135.5, 131.3, 130.8, 130.1, 129.9, 129.9, 127.9, 125.8, 125.7, 124.6, 113.8, 77.4, 76.7, 75.6, 55.3, 52.2, 39.4, 38.8, 33.2. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₂₄H₂₃NNaO₄: 412.1519, found: 412.1517.

3-methyl-3-phenylcyclobutan-1-one O-(4-methoxybenzyl) oxime **1j**



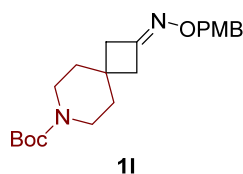
1j was prepared from the corresponding cyclobutanone (5.0 mmol) as yellow oil (1.00 g, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 4H), 7.22 – 7.18 (m, 3H), 6.88 (d, *J* = 8.40 Hz, 2H), 5.01 (s, 2H), 3.78 (s, 3H), 3.23 (t, *J* = 15.77 Hz, 2H), 2.99 (dd, *J* = 34.02, 17.55 Hz, 2H), 1.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 154.9, 148.9, 130.2, 129.8, 128.5, 126.0, 125.3, 113.8, 77.4, 77.1, 76.8, 75.4, 55.3, 44.9, 44.3, 38.0, 31.0. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₁₉H₂₁NNaO₂: 318.1465, found: 318.1468.

tert-butyl 6-(((4-methoxybenzyl)oxy)imino)-2-azaspiro[3.3]heptane-2-carboxylate **1k**



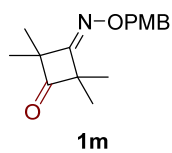
1k was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.21 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.45 Hz, 2H), 6.88 (d, *J* = 8.45 Hz, 2H), 4.96 (s, 2H), 3.97 (s, 4H), 3.79 (s, 3H), 3.07 (s, 4H), 1.43 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 159.4, 156.0, 152.8, 129.9, 129.9, 113.8, 79.7, 77.5, 77.1, 76.8, 75.6, 55.2, 42.9, 42.3, 31.8, 28.4, 22.0. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₁₉H₂₆N₂NaO₄: 369.1785, found: 369.1786.

tert-butyl 2-(((4-methoxybenzyl)oxy)imino)-7-azaspiro[3.5]nonane-7-carboxylate **1l**



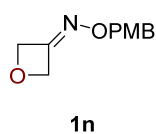
1l was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.27 g, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.60 Hz, 2H), 6.88 (d, *J* = 8.63 Hz, 2H), 4.98 (s, 2H), 3.80 (s, 3H), 3.34 (m, 4H), 2.63 (d, *J* = 3.46 Hz, 4H), 1.58 (t, *J* = 5.50 Hz, 4H), 1.45 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 154.8, 154.7, 130.0, 129.8, 113.8, 79.5, 77.4, 77.0, 76.7, 75.5, 55.3, 41.8, 41.2, 36.4, 33.2, 28.4. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₂₁H₃₀N₂NaO₄: 397.2098, found: 397.2103.

3-(((4-methoxybenzyl)oxy)imino)-2,2,4,4-tetramethylcyclobutan-1-one **1m**



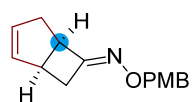
1m was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (908 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.33 Hz, 2H), 6.89 (d, *J* = 8.56 Hz, 2H), 5.02 (s, 2H), 3.82 (s, 3H), 1.37 (d, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 216.8, 164.9, 159.3, 129.8, 129.6, 113.7, 77.4, 77.0, 76.7, 75.8, 64.5, 61.9, 55.3, 21.6, 19.8. HRMS (EI): *m/z* [*M* + H]⁺ calcd for C₁₆H₂₂NO₃: 276.1594, found: 276.1592.

oxetan-3-one O-(4-methoxybenzyl) oxime **1n**



1n was prepared from the corresponding cyclobutanone (5.0 mmol) as white solid (1.04 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.36 Hz, 2H), 6.88 (d, *J* = 8.42 Hz, 2H), 4.97 (s, 2H), 4.04 (d, *J* = 20.74 Hz, 4H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 151.6, 130.0, 129.5, 113.9, 77.5, 77.2, 76.8, 75.9, 55.3, 36.2, 36.0. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₁₁H₁₃NNaO₃: 230.0788, found: 230.0788.

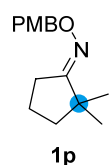
(1*S*,5*R*,*E*)-bicyclo[3.2.0]hept-2-en-6-one O-(4-methoxybenzyl) oxime **1o**



1o

1o (mixture, *E/Z* = 2:1) was prepared from the corresponding cyclobutanone (5.0 mmol) as white soild (827 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 4H), 6.89 – 6.85 (m, 3H), 5.76 (d, *J* = 3.26 Hz, 3H), 4.96 (s, 3H), 3.79 (s, 1H), 3.79 (s, 3H), 3.75 – 3.70 (m, 2H), 3.35 – 3.28 (m, 2H), 3.11 – 2.99 (m, 2H), 2.65 – 2.47 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 162.8, 159.3, 132.7, 132.0, 131.9, 131.9, 130.3, 130.1, 129.8, 129.7, 113.7, 113.7, 77.4, 77.0, 76.7, 75.4, 75.4, 55.3, 46.5, 46.3, 41.1, 40.0, 38.8, 38.4, 37.8, 35.5. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₁₅H₁₇NNaO₂: 266.1151, found: 266.1151.

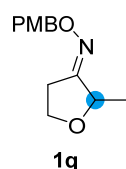
(*E*)-2,2-dimethylcyclopentan-1-one O-(4-methoxybenzyl) oxime **1p**



1p

1p was prepared from the corresponding cyclobutanone (5.0 mmol) as colorless oil (794 mg, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.68 Hz, 2H), 6.87 (d, *J* = 8.68 Hz, 2H), 4.99 (s, 2H), 3.80 (s, 3H), 2.47 (t, *J* = 7.49 Hz, 2H), 1.72 – 1.67 (m, 2H), 1.59 – 1.56 (m, 2H), 1.14 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.3, 159.1, 130.5, 129.8, 113.6, 77.4, 77.0, 76.7, 75.2, 55.3, 42.0, 41.1, 27.6, 26.6, 20.9. HRMS (EI): *m/z* [*M* + Na]⁺ calcd for C₁₅H₂₁NNaO₂: 270.1465, found: 270.1462.

(*E*)-2-methyldihydrofuran-3(2*H*)-one O-(4-methoxybenzyl) oxime **1q**



1q

1q was prepared from the corresponding cyclobutanone (5.0 mmol) as colorless oil (1.00 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.08 Hz, 2H), 6.88 (d, *J* = 8.22 Hz, 2H), 5.02 (s, 2H), 4.28 – 4.33 (q, *J* = 6.09 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.83 – 3.77 (m, 4H), 2.75 – 2.60 (m, 2H), 1.37 (d, *J* = 6.32 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 159.3, 129.8, 113.7, 77.3, 77.0, 76.7, 75.7, 74.3, 65.9, 55.2, 28.5, 18.3. HRMS (EI): *m/z* [*M* + H]⁺ calcd for C₁₃H₁₈NO₃: 236.1281, found: 236.1280.

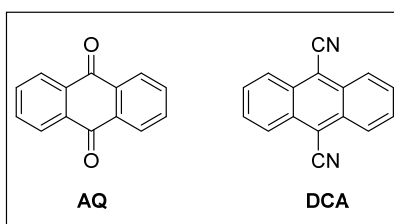
3. Detailed Optimization of Reaction Conditions and Control Experiments

3.1 Optimization of Reaction Conditions

Table S1. Screen of Photocatalysts under Blue LEDs

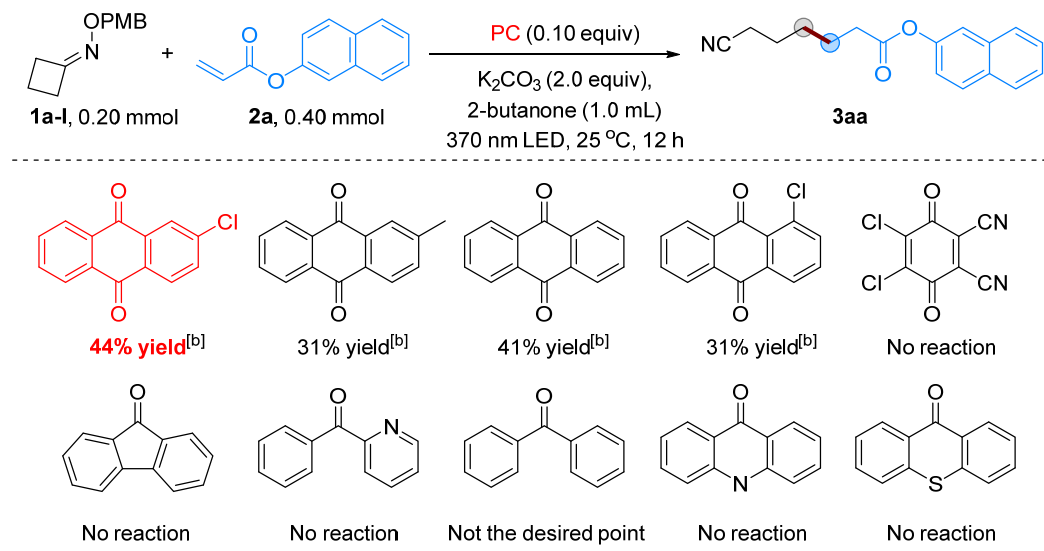


entry ^[a]	photocatalyst	yield ^[b] [%]
1	Ir[dF(CF ₃)ppy]dtbbpyPF ₆	No reaction
2	4CzIPN	No reaction
3	Fukuzumi dye	No reaction
4	Eosin Y	No reaction
5	AQ	No reaction
6	DCA	No reaction



[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), PC (2 mol%) and K₂CO₃ (55.28 mg, 2.0 equiv) in 2-butanone (1.0 mL) at rt under 7 W blue LEDs [b] Determined by isolated yield.

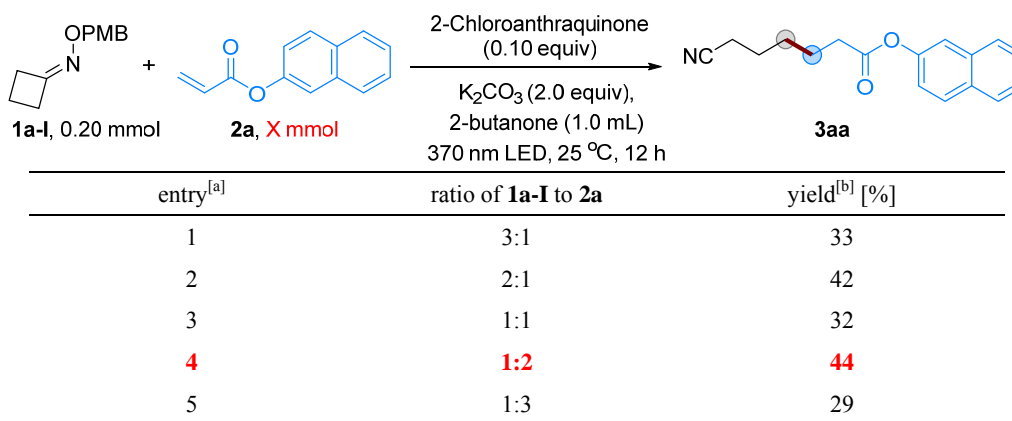
Table S2. Screen of Organic Photocatalysts under 370 nm LED



[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), PC (0.1 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in 2-butanone (1.0 mL) at rt under 370 nm LED. [b] Determined by isolated yield.

As shown in Table S2, among all the photocatalysts tested, 2-Chloroanthraquinone gave the best results in terms of yield (44% yield), and was thus selected for further optimization studies.

Table S3. Screen of Ratio of 1a-I and 2a



[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (x mmol), 2-chloroanthraquinone (24.27 mg, 0.10 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in 2-butanone (1.0 mL) at rt under 370 nm LED. [b] Determined by isolated yield.

As shown in Table S3, among all the photocatalysts tested, a 1:2 ratio gave the best results in terms of yield (44% yield), and was thus selected for further optimization studies.

Table S4. Screen of Bases

entry ^[a]	base	yield ^[b] [%]
1	K₂CO₃	44
2	NaOAc	19
3	Cs ₂ CO ₃	No reaction
4	Li ₂ CO ₃	13
5	Na ₂ CO ₃	32
6	K ₃ PO ₄	14
7	K ₂ HPO ₄	22

[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.10 equiv) and base (2.0 equiv) in 2-butanone (1.0 mL) at rt under 370 nm LED. [b] Determined by isolated yield.

As shown in Table S4, among the bases tested, K₂CO₃ gave the best results (44% yield), and was thus selected for further studies.

Table S5. Screen of Solvents

entry ^[a]	solvent	yield ^[b] [%]
1	CH ₃ CN	27
2	CH ₂ Cl ₂	20
3	DCE	13
4	toluene	21
5	DMSO	No reaction
6	DMF	19
7	CH ₃ OH	No reaction
8	THF	21
9	4-methyl-2-pentanone	15
10	cyclohexanone	43
11	2-butanone	44

[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.10 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in solvent (1.0 mL) at rt under 370 nm LED. [b] Determined by isolated yield.

As shown in Table S5, among all the solvents tested, 2-butanone gave the best results in terms of yield (44% yield), and was thus selected for further optimization studies.

Table S6. Screen of Concentration

entry ^[a]	concentration (x mL)	yield ^[b] [%]
1	1	44
2	2	43
3	4	47
4	6	35

[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.10 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in solvent (x mL) at rt under 370 nm LED. [b] Determined by isolated yield.

As shown in Table S6, among the concentration tested, 2-butanone (4 mL) gave the best result in terms of yield (47% yield) and the optimized reaction condition was confirmed.

Table S7. Screen of Equivalent of PC

entry ^[a]	equivalent	yield ^[b] [%]
1	0.1	43
2	0.2	47 (59% after 24 h)
3	0.5	67(recovery of PC: 88%)
4	1.0	54

[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), 2-chloroanthraquinone (X equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in 2-butanone (4.0 mL) at rt under 370 nm LED. [b] Determined by isolated yield.

As shown in Table S7, among the concentration tested, 2-chloroanthraquinone (24.27 mg, 0.50 equiv) gave the best result in terms of yield (67% yield) and the optimized reaction condition was confirmed.

Table S8. Screen of Protecting Group

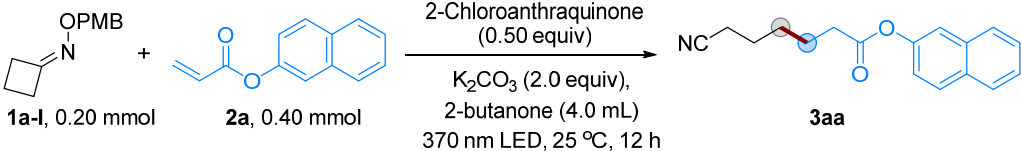
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[a] Unless otherwise noted, reactions were carried out with **1a** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in 2-butanone (4.0 mL) at rt under 370 nm LED. [b] Isolated yield. [c] ¹H NMR yield with 1,3,5-trimethoxybenzene as an internal standard.

As shown in Table S8, among the concentration tested, *p*-MeOC₄H₄ group gave the best result in terms of yield (67% yield) and the optimized reaction condition was confirmed.

3.2 Control Experiments for Synthesis of 3aa

Table S9. Control Experiments

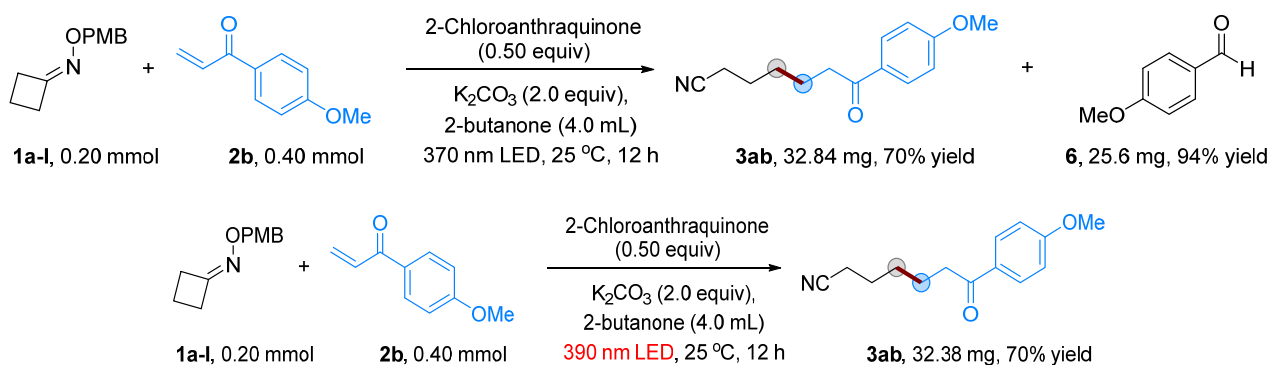
				
entry ^a	<i>hν</i>	photocatalyst	base	yield ^b (%)
1	-	+	+	No reaction
2	+	-	+	No reaction
3	+	+	-	22
4	+	+	+	67

[a] Unless otherwise noted, reactions were carried out with **1a-I** (41.06 mg, 0.20 mmol), **2a** (79.28 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) in 2-butanone (4.0 mL) at rt under 370 nm LED. [b] Determined by isolated yield.

The results of Table S9 reveal that reaction is indeed a photocatalytic process.

4. General Procedure and Spectral Data of Products

4.1 General Procedure for Synthesis of 3

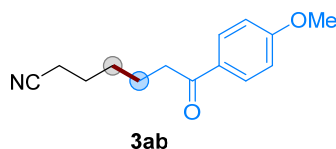


In a dried sealed tube, **1a-I** (41.06 mg, 0.20 mmol), **2b** (64.88 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in 2-butanone (4.0 mL) under a Ar atmosphere. Then, the resulting mixture was degassed via "freeze-pump-thaw" procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED (or 390 nm LED) at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel

(petroleum ether/ethylacetate 5:1) directly to give the aldehyde in 94% yield and the desired product **3ab** in 71% yield (or 70% yield) as a colorless oil.

4.2 Spectral Data of Products

7-(4-methoxyphenyl)-7-oxoheptanenitrile **3ab**

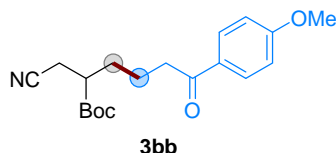


3ab

46.2 mg, colorless oil, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.93 (d, J = 8.86 Hz, 2H), 6.93 (d, J = 8.87 Hz, 2H), 3.87 (s, 3H), 2.95 (t, J = 7.22 Hz, 2H), 2.37 (t, J = 7.09 Hz, 2H), 1.78 – 1.68 (m, 4H), 1.57 – 1.51 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.4, 163.5, 130.3, 129.9, 119.7, 113.8, 55.5, 37.7, 28.4, 25.3, 23.4,

17.1. IR (in KBr): 3450, 3129, 2940, 1673, 1601, 1257, 1172 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{NNaO}_2$: 254.1151, found: 254.1150.

tert-butyl 2-(cyanomethyl)-6-(4-methoxyphenyl)-6-oxohexanoate **3bb**

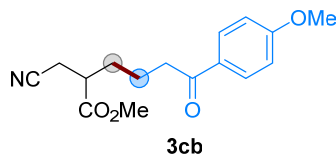


3bb

47.7 mg, colorless oil, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.98 (d, J = 8.80 Hz, 2H), 6.98 (d, J = 8.79 Hz, 2H), 3.92 (s, 3H), 3.01 (t, J = 5.35 Hz, 2H), 2.74 – 2.58 (m, 3H), 1.88 – 1.76 (m, 4H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.8, 171.7, 163.5, 130.3, 129.8, 117.9, 113.8, 113.7, 82.2, 77.4, 55.5, 42.3, 37.5, 31.1,

28.0, 21.2, 19.5. IR (in KBr): 3437, 3129, 2975, 1726, 1602, 1162 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{25}\text{NNaO}_4$: 354.1676, found: 354.1673.

methyl 2-(cyanomethyl)-6-(4-methoxyphenyl)-6-oxohexanoate **3cb**

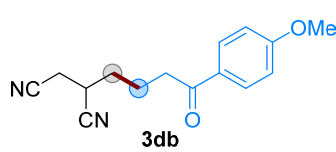


3cb

43.1 mg, colorless oil, 74% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.93 (d, J = 8.91 Hz, 2H), 6.94 (d, J = 8.89 Hz, 2H), 3.87 (s, 3H), 3.75 (s, 3H), 2.99 – 2.59 (m, 5H), 1.85 – 1.76 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.7, 172.9, 163.5, 130.2, 129.7, 117.7, 113.7, 55.4, 52.4, 41.4, 37.4, 30.8, 21.0, 19.2. IR (in KBr): 3451, 3129,

2953, 1736, 1673, 1173 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{19}\text{NNaO}_4$: 312.1206, found: 312.1210.

2-(4-(4-methoxyphenyl)-4-oxobutyl)succinonitrile **3db**

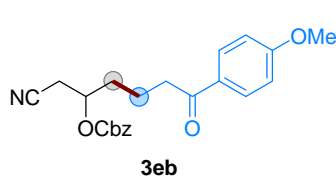


3db

37.6 mg, colorless oil, 73% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.93 (d, J = 8.91 Hz, 2H), 6.95 (d, J = 8.91 Hz, 2H), 3.88 (s, 3H), 3.03 (dt, J = 14.20, 6.54 Hz, 3H), 2.78 (d, J = 6.50 Hz, 2H), 2.05 – 1.85 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.2, 163.6, 130.2, 129.5, 118.8, 115.6, 113.8, 55.5, 36.7, 30.9, 28.4, 21.0, 20.9. IR (in

KBr): 3418, 3133, 1751, 1395, 1285, 1145 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{NaO}_2$: 279.1104, found: 279.1104.

benzyl (1-cyano-6-(4-methoxyphenyl)-6-oxohexan-2-yl) carbonate **3eb**

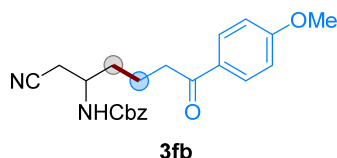


3eb

51.4 mg, colorless oil, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.91 (d, J = 8.92 Hz, 2H), 7.36 – 7.34 (m, 5H), 6.93 (d, J = 8.90 Hz, 2H), 4.67 – 4.55 (m, 2H), 3.87 (s, 3H), 3.75 – 3.72 (m, 1H), 2.93 (t, J = 6.26 Hz, 2H), 2.59 (t, J = 5.22 Hz, 2H), 1.87 – 1.72 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.2, 163.5, 137.5, 134.1, 130.3, 128.6, 128.0, 127.9, 117.6, 113.8, 74.3, 71.9, 55.5, 37.6, 33.8, 22.9, 19.8. IR (in KBr):

3447, 3131, 1670, 1398, 1171, 1090 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{23}\text{NNaO}_5$: 404.1468, found: 404.1468.

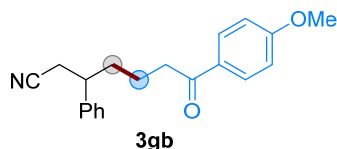
benzyl (1-cyano-6-(4-methoxyphenyl)-6-oxohexan-2-yl)carbamate **3fb**



54.7 mg, colorless oil, 72% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.92 (d, 2H), 7.37 – 7.32 (m, 5H), 6.93 (d, J = 8.78 Hz, 2H), 5.19 (d, J = 7.52 Hz, 1H), 5.11 (s, 2H), 3.87 (s, 3H), 2.99 – 2.59 (m, 4H), 1.88 – 1.72 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.0, 163.6, 155.8, 136.1, 130.3, 129.8, 128.6, 128.3, 128.1, 117.2, 113.8, 67.1, 55.5, 47.9, 37.1, 32.8, 23.8, 20.2. IR (in KBr): 3414, 1713, 1603, 1523, 1256, 1173 cm^{-1} .

HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{NaO}_4$: 403.1628, found: 403.1629.

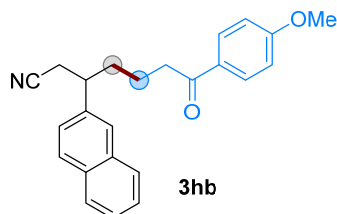
7-(4-methoxyphenyl)-7-oxo-3-phenylheptanenitrile **3gb**



41.9 mg, colorless oil, 68% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.88 (d, J = 8.75 Hz, 2H), 7.37 – 7.23 (m, 5H), 6.91 (d, J = 8.74 Hz, 2H), 3.86 (s, 3H), 3.04 – 2.87 (m, 3H), 2.62 (d, 2H), 1.92 – 1.62 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.2, 163.4, 141.3, 130.2, 129.8, 128.9, 127.5, 127.2, 118.5, 113.7, 55.4, 42.2, 37.6, 34.4, 25.2, 22.0. IR (in KBr): 3430, 3131, 2934, 1673, 1402, 1172 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_2$:

308.1645, found: 308.1642.

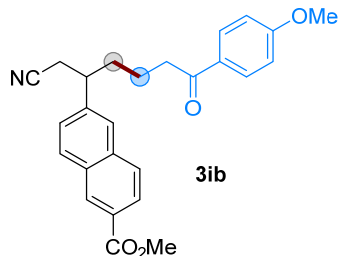
7-(4-methoxyphenyl)-3-(naphthalen-2-yl)-7-oxoheptanenitrile **3hb**



47.9 mg, colorless oil, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85 – 7.81 (m, 5H), 7.69 (s, 1H), 7.52 – 7.46 (m, 2H), 7.42 – 7.34 (m, 1H), 6.86 (d, J = 7.99 Hz, 2H), 3.83 (s, 3H), 3.19 – 3.11 (m, 1H), 2.95 – 2.82 (m, 2H), 2.70 (d, J = 6.85 Hz, 2H), 2.04 – 1.92 (m, 2H), 1.73 – 1.59 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.2, 163.3, 138.6, 133.4, 132.7, 130.2, 129.7, 128.8, 127.7, 127.6, 126.4, 126.3, 125.9, 124.7, 118.5, 113.6, 55.4, 42.3, 37.6, 34.3, 25.1, 22.0. IR (in KBr): 3437, 3130, 2359, 1670, 1397,

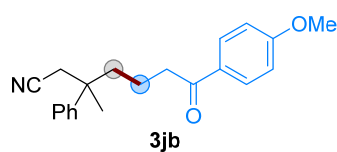
1171 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{NNaO}_2$: 380.1621, found: 380.1619.

methyl 6-(1-cyano-6-(4-methoxyphenyl)-6-oxohexan-2-yl)-2-naphthoate **3ib**



68.1 mg, colorless oil, 85% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.58 (s, 1H), 8.07 (dd, J = 8.55, 1.60 Hz, 1H), 7.95 (d, J = 8.50 Hz, 1H), 7.86 (dd, J = 8.62, 3.95 Hz, 3H), 7.74 (s, 1H), 7.43 (d, J = 8.60 Hz, 1H), 6.88 (d, J = 8.49 Hz, 2H), 3.98 (s, 3H), 3.84 (s, 3H), 3.23 – 3.16 (m, 1H), 2.99 – 2.85 (m, 2H), 2.73 (d, J = 6.86 Hz, 2H), 2.04 – 1.94 (m, 2H), 1.76 – 1.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.1, 167.2, 163.5, 141.4, 135.6, 131.9, 130.8, 130.4, 130.2, 129.8, 128.1, 127.5, 126.4, 125.8, 125.7, 118.3, 113.7, 55.5, 52.3, 42.6, 37.6, 34.3, 25.1, 22.1. IR (in KBr): 3430, 3130, 2947, 1717, 1401, 1174 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{NNaO}_4$: 438.1676, found: 438.1674.

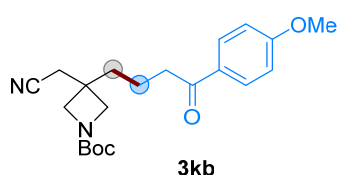
7-(4-methoxyphenyl)-3-methyl-7-oxo-3-phenylheptanenitrile **3jb**



43.1 mg, colorless oil, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.87 (d, J = 8.88 Hz, 2H), 7.38 – 7.32 (m, 5H), 6.91 (d, J = 8.89 Hz, 2H), 3.86 (s, 3H), 2.86 (t, J = 7.13 Hz, 2H), 2.67 (s, 2H), 2.00 – 1.78 (m, 2H), 1.62 – 1.56 (m, 4H), 1.50 – 1.41 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.2, 163.5, 143.9, 130.3, 130.0, 128.8, 126.9, 125.8, 118.2, 113.8, 55.5, 41.2, 40.2, 38.2, 31.7, 25.0, 19.1. IR (in KBr): 3129, 1673, 1601, 1400, 1256,

1171 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{NNaO}_2$: 344.1621, found: 344.1619.

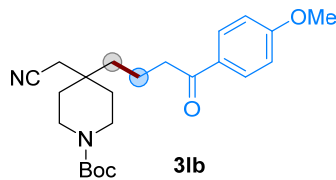
tert-butyl 3-(cyanomethyl)-3-(4-(4-methoxyphenyl)-4-oxobutyl)azetidine-1 carboxylate **3kb**



49.7 mg, colorless oil, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (d, J = 8.97 Hz, 2H), 6.95 (d, J = 8.95 Hz, 2H), 3.88 (s, 3H), 3.80 – 3.70 (m, 4H), 3.00 (t, J =

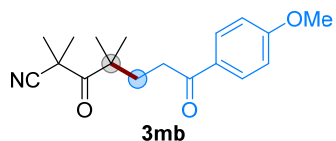
6.74 Hz, 2H), 2.69 (s, 2H), 1.83 – 1.69 (m, 4H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.7, 163.6, 156.2, 130.3, 129.8, 117.1, 113.8, 80.0, 55.5, 37.6, 36.0, 35.6, 28.3, 28.2, 25.7, 18.6. IR (in KBr): 3130, 2968, 1696, 1602, 1400, 1169 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{NaO}_4$: 395.1941, found: 395.1938.

tert-butyl 4-(cyanomethyl)-4-(4-(4-methoxyphenyl)-4-oxobutyl)piperidine-1-carboxylate 3lb



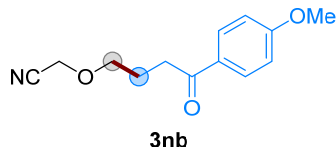
52.1 mg, colorless oil, 65% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (d, J = 8.80 Hz, 2H), 6.94 (d, J = 8.78 Hz, 2H), 3.88 (s, 3H), 3.46 – 3.49 (m, 3H), 2.98 (t, J = 6.72 Hz, 2H), 2.41 (s, 2H), 1.74 – 1.45 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.0, 163.5, 154.7, 130.2, 129.9, 117.5, 113.8, 79.7, 55.5, 38.0, 35.8, 34.3, 34.1, 28.4, 26.1, 17.5. IR (in KBr): 3420, 3130, 2361, 1681, 1400, 1169 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{32}\text{N}_2\text{NaO}_4$: 423.2254, found: 423.2249.

7-(4-methoxyphenyl)-2,2,4,4-tetramethyl-3,7-dioxoheptanenitrile 3mb



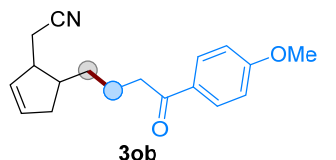
38.2 mg, colorless oil, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.95 (d, J = 8.92 Hz, 2H), 6.94 (d, J = 8.88 Hz, 2H), 3.87 (s, 3H), 2.89 (t, 2H), 2.16 (t, 2H), 1.57 (s, 6H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 208.1, 197.8, 163.4, 130.3, 129.7, 123.2, 113.7, 55.5, 49.3, 40.1, 34.1, 33.7, 26.7, 24.4. IR (in KBr): 3450, 3131, 2975, 1675, 1398, 1672 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{23}\text{NNaO}_3$: 324.1570, found: 324.1564.

2-(4-(4-methoxyphenyl)-4-oxobutoxy)acetonitrile 3nb



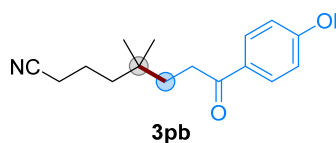
37.3 mg, colorless oil, 81% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.95 (d, 2H), 6.94 (d, J = 8.66 Hz, 2H), 4.25 (s, 2H), 3.87 (s, 3H), 3.72 – 3.63 (m, 2H), 3.04 (t, J = 7.10 Hz, 2H), 2.10 – 2.04 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 197.8, 163.4, 130.2, 129.8, 116.0, 113.7, 71.0, 56.2, 55.4, 34.2, 23.7. IR (in KBr): 3454, 3130, 2941, 1674, 1602, 1255 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{NNaO}_3$: 256.0944, found: 256.0945.

2-(4-(4-methoxyphenyl)-4-oxobutyl)cyclopent-3-ene-1-carbonitrile 3ob



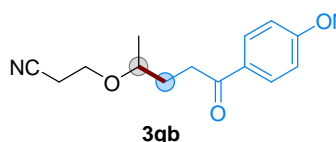
39.2 mg, colorless oil, 73% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (d, J = 8.93 Hz, 2H), 6.94 (d, J = 8.93 Hz, 2H), 5.86 – 5.83 (m, 1H), 5.65 – 5.63 (m, 1H), 3.87 (s, 3H), 2.97 (t, J = 7.44 Hz, 2H), 2.71 – 2.65 (m, 2H), 2.51 – 2.36 (m, 2H), 2.11 – 1.94 (m, 3H), 1.81 – 1.73 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.4, 163.4, 132.5, 130.7, 130.3, 129.8, 118.8, 113.7, 55.5, 48.2, 43.1, 38.7, 36.3, 29.6, 22.8. IR (in KBr): 3417, 3133, 2926, 1671, 1257, 1173 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{NNaO}_2$: 292.1308, found: 292.1307.

8-(4-methoxyphenyl)-5,5-dimethyl-8-oxooctanenitrile 3pb



34.7 mg, colorless oil, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (d, J = 8.78 Hz, 2H), 6.94 (d, 2H), 3.88 (s, 3H), 2.87 (t, 2H), 2.34 (t, J = 6.95 Hz, 2H), 1.69 – 1.60 (m, 4H), 1.42 – 1.38 (m, 2H), 0.95 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 199.2, 163.4, 130.3, 130.0, 119.8, 113.8, 55.5, 41.0, 35.9, 33.2, 32.6, 26.8, 20.4, 18.0. IR (in KBr): 3417, 3136, 2959, 1672, 1397, 1172 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{NNaO}_2$: 296.1621, found: 296.1620.

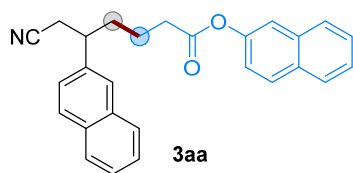
3-((5-(4-methoxyphenyl)-5-oxopentan-2-yl)oxy)propanenitrile 3qb



29.8 mg, colorless oil, 57% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.97 (d, J = 8.94 Hz, 2H), 6.93 (d, J = 8.93 Hz, 2H), 3.86 (s, 3H), 3.81 – 3.71 (m, 1H), 3.61 – 3.53 (m, 2H), 3.13 – 3.00 (m, 2H), 2.56 (t, J = 6.60 Hz, 2H), 1.98 – 1.86 (m, 2H),

1.21 (d, $J = 6.13$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 198.8, 163.4, 130.4, 130.0, 118.2, 113.7, 75.5, 63.0, 55.5, 33.8, 31.0, 19.6, 19.3. IR (in KBr): 3129, 2967, 1672, 1600, 1258, 1101 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{19}\text{NNaO}_3$: 284.1257, found: 284.1257.

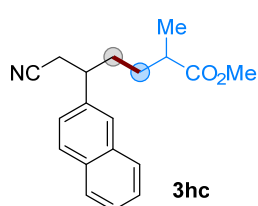
naphthalen-2-yl 6-cyano-5-(naphthalen-2-yl)hexanoate 3aa



52.7 mg, colorless oil, 67% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.83 – 7.76 (m, 3H), 7.54 – 7.40 (m, 3H), 7.20 (d, $J = 10.77$ Hz, 1H), 2.53 (t, $J = 7.38$ Hz, 2H), 2.22 (t, $J = 6.97$ Hz, 2H), 1.73 – 1.41 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.6, 148.0, 133.4, 131.1, 129.1, 127.5, 127.3, 126.3, 125.4, 120.9, 119.4, 118.2, 33.6, 27.7, 24.7, 23.7, 16.6. IR (in KBr): 2939, 2245, 1720, 1755, 1131, 750 cm^{-1} .

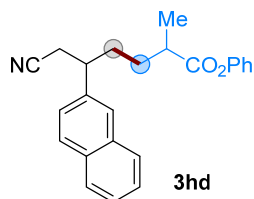
HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{NNaO}_2$: 416.1621, found: 416.1624.

methyl 6-cyano-2-methyl-5-(naphthalen-2-yl)hexanoate 3hc



59.0 mg, colorless oil, 64% yield (1:1 dr). Data of both isomers: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.84 (m, 8H), 7.66 (s, 3H), 7.52 – 7.46 (m, 5H), 7.33 (d, $J = 8.51$ Hz, 2H), 3.65 (s, 8H), 3.15 – 3.05 (m, 2H), 2.70 – 2.67 (m, 5H), 2.48 – 2.39 (m, 2H), 1.88 (dt, $J = 12.32, 5.67$ Hz, 5H), 1.54 – 1.26 (m, 4H), 1.11 – 1.09 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 176.7, 176.6, 138.6, 138.5, 133.5, 132.8, 128.9, 127.8, 127.7, 126.4, 126.4, 126.0, 124.6, 118.4, 51.7, 42.5, 42.3, 39.3, 39.1, 32.5, 32.2, 31.4, 31.3, 25.3, 25.2, 17.3, 17.1. IR (in KBr): 3417, 3133, 1731, 1635, 1396, 1163 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_2$: 318.1465, found: 318.1463.

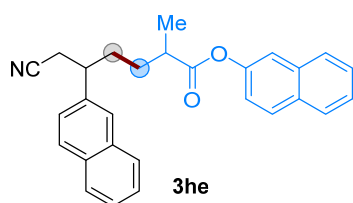
phenyl 6-cyano-2-methyl-5-(naphthalen-2-yl)hexanoate 3hd



52.1 mg, colorless oil, 73% yield (1:4 dr). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.87 – 7.69 (m, 4H, major + minor), 7.50 – 7.48 (m, 2H, major + minor), 7.38 – 7.20 (m, 4H, major + minor), 7.02 (dd, $J = 8.23, 2.09$ Hz, 2H, major + minor), 3.20 – 3.14 (m, 1H, major), 3.13 – 3.10 (m, 1H, minor), 2.76 – 2.69 (m, 2H, major), 2.67 – 2.54 (m, 1H, minor), 2.08 – 1.96 (m, 2H, major + minor), 1.82 – 1.39 (m, 3H, major + minor), 1.26 (dd, $J = 7.07, 2.29$ Hz, 3H, major + minor).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm, major + minor) 174.7, 174.6, 150.5, 138.4, 138.3, 133.4, 132.8, 129.4, 128.9, 127.7, 127.7, 126.4, 126.4, 126.0, 125.8, 124.6, 121.4, 118.4, 42.5, 42.3, 39.4, 39.4, 32.4, 32.2, 31.2, 31.2, 25.3, 25.2, 17.3, 17.0. IR (in KBr): 3130, 2936, 1752, 1393, 1193, 749 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{NNaO}_2$: 380.1621, found: 380.1620.

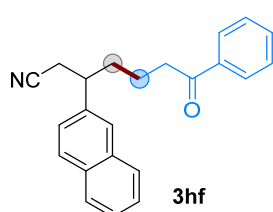
naphthalen-2-yl 6-cyano-2-methyl-5-(naphthalen-2-yl)hexanoate 3he



58.9 mg, colorless oil, 72% yield (1:6 dr). Data of both isomers: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.86 – 7.69 (m, 9H, major + minor), 7.49 – 7.33 (m, 7H, major + minor), 7.15 (d, 1H), 3.20 – 3.10 (m, 1H, major + minor), 2.79 – 2.76 (m, 1H, minor), 2.73 – 2.68 (m, 3H, major), 2.11 – 1.94 (m, 3H, major + minor), 1.85 – 1.39 (m, 3H, major + minor), 1.29 (d, $J = 6.89$ Hz, 4H, major + minor). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm, major + minor) 174.8, 167.2, 148.3, 141.3, 141.2, 135.6, 133.8, 132.0, 131.5, 130.9, 130.5, 129.5, 128.1, 127.8, 127.7, 126.7, 126.4, 125.9, 125.8, 125.6, 121.1, 118.5, 118.3, 60.5, 52.3, 42.6, 42.5, 39.5, 32.4, 32.3, 31.3, 25.2, 25.1, 21.1, 17.4, 17.1, 14.3. IR (in KBr): 3418, 3133, 1751, 1395, 1285, 1145 cm^{-1} .

HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{28}\text{H}_{25}\text{NNaO}_2$: 430.1778, found: 430.1779.

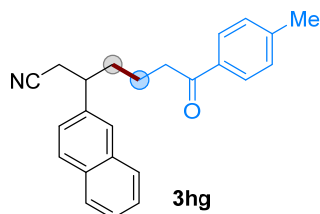
3-(naphthalen-2-yl)-7-oxo-7-phenylheptanenitrile 3hf



46.1 mg, colorless oil, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.89 – 7.81 (m, 5H), 7.70 (s, 1H), 7.55 – 7.35 (m, 7H), 3.21 – 3.13 (m, 1H), 3.04 – 2.89 (m, 2H), 2.71 (d, $J = 6.92$

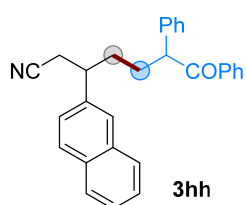
Hz, 2H), 2.05 – 1.92 (m, 2H), 1.76 – 1.63 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 199.5, 138.6, 136.6, 133.4, 133.0, 132.7, 128.8, 128.5, 127.9, 127.7, 127.6, 126.4, 126.3, 125.9, 124.7, 118.5, 42.3, 38.0, 34.3, 25.1, 21.8. IR (in KBr): 3454, 3130, 2931, 1681, 1398, 748 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{21}\text{NNaO}$: 350.1515, found: 350.1519.

3-(naphthalen-2-yl)-7-oxo-7-(p-tolyl)heptanenitrile 3hg



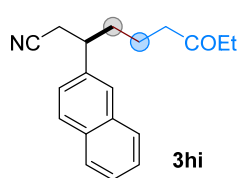
42.8 mg, colorless oil, 63% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85 – 7.76 (m, 5H), 7.69 (s, 1H), 7.50 – 7.44 (m, 2H), 7.35 (d, $J = 8.43$ Hz, 1H), 7.20 (d, $J = 7.91$ Hz, 2H), 3.19 – 3.12 (m, 1H), 3.00 – 2.87 (m, 2H), 2.70 (d, $J = 6.90$ Hz, 2H), 2.38 (s, 3H), 2.00 – 1.93 (m, 2H), 1.76 – 1.64 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 199.3, 143.9, 138.7, 134.3, 133.5, 132.8, 129.3, 128.9, 128.1, 127.8, 127.7, 126.4, 126.4, 126.0, 124.8, 118.6, 42.4, 38.0, 34.4, 25.2, 22.0, 21.7. IR (in KBr): 3421, 3130, 2931, 1678, 1399, 815 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{23}\text{NNaO}$: 364.1672, found: 364.1666.

3-(naphthalen-2-yl)-7-oxo-6,7-diphenylheptanenitrile 3hh



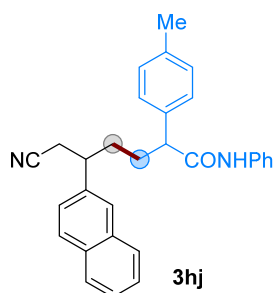
63.9 mg, colorless oil, 79% yield (1:1.3 dr). ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.88 – 7.85 (m, 5H, major + minor), 7.83 – 7.78 (m, 4H, major + minor), 7.76 – 7.74 (m, 2H, major + minor), 7.65 – 7.57 (d, 2H, major + minor), 7.49 – 7.41 (m, 7H, major + minor), 7.34 – 7.15 (m, 19H, major + minor), 4.50 – 4.48 (m, 1H, minor), 4.47 – 4.45 (m, 1H, major), 3.14 – 3.03 (m, 2H, major + minor), 2.61 – 2.58 (m, 4H, major + minor), 2.18 – 1.69 (m, 9H, major + minor). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm, major + minor) 199.4, 199.3, 139.2, 138.9, 138.6, 138.6, 136.5, 136.5, 133.5, 133.5, 133.0, 133.0, 132.8, 132.8, 129.1, 129.0, 128.9, 128.9, 128.7, 128.7, 128.6, 128.2, 128.1, 127.9, 127.8, 127.7, 127.7, 127.3, 126.5, 126.4, 126.0, 124.8, 124.8, 118.5, 53.6, 53.3, 42.6, 42.5, 32.8, 32.6, 31.8, 31.6, 25.4, 25.2. IR (in KBr): 3058, 2929, 1678, 1396, 749, 698 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{29}\text{H}_{25}\text{NNaO}$: 426.1828, found: 426.1827.

3-(naphthalen-2-yl)-7-oxononanenitrile 3hi



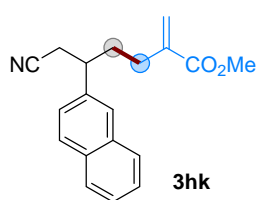
33.2 mg, colorless oil, 59% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85 – 7.80 (m, 3H), 7.67 (s, 1H), 7.51 – 7.45 (m, 2H), 7.33 (dd, $J = 8.48, 1.74$ Hz, 1H), 3.15 – 3.08 (m, 1H), 2.69 (d, 2H), 2.42 – 2.33 (m, 4H), 1.91 – 1.83 (m, 2H), 1.58 – 1.44 (m, 2H), 1.01 (t, $J = 7.33$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 211.0, 138.7, 133.5, 132.8, 128.9, 127.8, 127.7, 126.4, 126.3, 126.0, 124.7, 118.5, 42.4, 41.8, 35.9, 34.3, 25.1, 21.5, 7.8. IR (in KBr): 3130, 1709, 1397, 1112, 820, 753 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}$: 320.1515, found: 320.1516.

6-cyano-5-(naphthalen-2-yl)-N-phenyl-2-(p-tolyl)hexanamide 3hj



37.4 mg, colorless oil, 61% yield (1:1.3 dr). Data of both isomers: ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.83 – 7.75 (m, 3H), 7.61 (d, $J = 20.16$ Hz, 1H), 7.48 – 7.33 (m, 5H), 7.23 – 7.02 (m, 7H), 3.40 (t, $J = 7.10$ Hz, 1H), 3.12 – 3.05 (m, 1H), 2.62 (t, 2H), 2.32 (s, 3H), 2.24 – 1.72 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.3, 171.3, 138.6, 138.5, 137.7, 137.7, 137.6, 137.5, 136.0, 135.7, 133.5, 132.8, 129.9, 129.9, 128.9, 128.9, 128.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 126.4, 126.4, 126.4, 126.0, 126.0, 124.8, 124.8, 124.3, 119.7, 119.7, 118.5, 118.5, 53.6, 53.6, 42.5, 42.5, 32.9, 32.8, 30.9, 30.7, 25.4, 25.0, 21.1. IR (in KBr): 3100, 1678, 1531, 1398, 1290, 748 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{NaO}$: 455.2094, found: 455.2092.

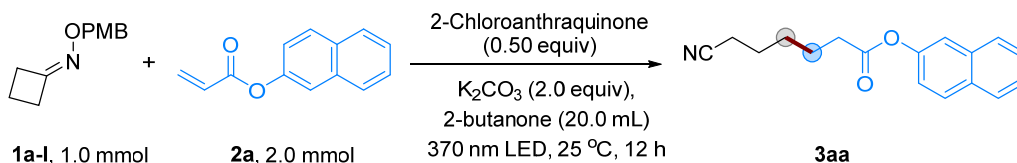
methyl 6-cyano-2-methylene-5-(naphthalen-2-yl)hexanoate 3hk



37.6 mg, colorless oil, 64% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.87 – 7.82 (m, 3H), 7.69 (s, 1H), 7.51 – 7.46 (m, 2H), 7.35 (d, J = 8.41 Hz, 1H), 6.15 (s, 1H), 5.49 (s, 1H), 3.72 (s, 3H), 3.18 – 3.11 (m, 1H), 2.70 (d, J = 6.89 Hz, 2H), 2.11 – 2.05 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 167.3, 139.5, 138.4, 133.5, 132.9, 129.0, 127.8, 127.7, 126.5, 126.4, 126.1, 125.7, 124.8, 118.4, 51.9, 41.9, 33.4, 29.9, 25.3. IR (in KBr): 3130, 1717, 1633, 1397, 1197, 820 cm^{-1} . HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{NNaO}_2$: 316.1308, found: 316.1309.

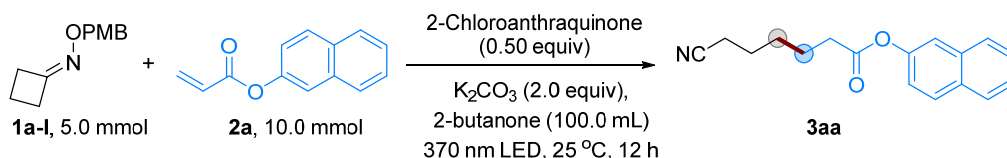
5. Preparative Utility of the Methodology

5.1 1.0 mmol Reaction



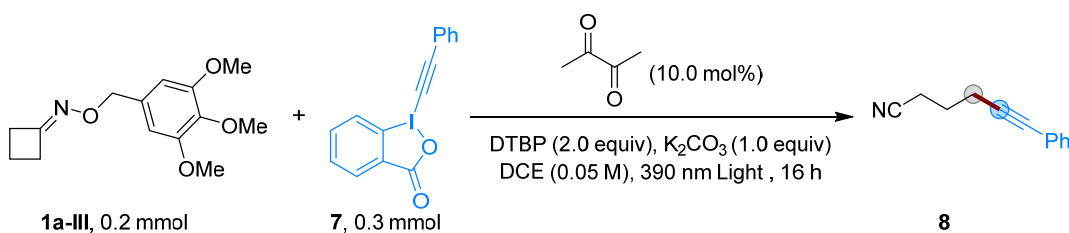
In a dried sealed tube, **1a-I** (205.30mg, 1.0 mmol), **2a** (396.14 mg, 2.0 mmol), 2-chloroanthraquinone (0.50 equiv) and K_2CO_3 (2.0 equiv) were dissolved in 2-butanone (20.0 mL) under a Ar atmosphere. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3aa** in 69% yield (184.46 mg) as a colorless oil.

5.2 Gram-scale reaction



In a dried sealed tube, **1a-I** (1.03 g, 5.0 mmol), **2b** (1.98 g, 10.0 mmol), 2-Chloroanthraquinone (0.50 equiv) and K_2CO_3 (2.0 equiv) were dissolved in 2-butanone (100.0 mL) under a Ar atmosphere. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3aa** in 64% yield (0.85 g) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.86 – 7.82 (m, 4H), 7.51 – 7.44 (m, 3H), 2.35 (dt, J = 41.98, 7.22 Hz, 4H), 1.73 – 1.62 (m, 4H), 1.51 – 1.44 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 174.1, 149.4, 134.7, 132.4, 129.4, 127.7, 127.6, 126.4, 126.1, 119.8, 118.9, 117.7, 34.4, 28.1, 25.8, 25.4, 18.4. HRMS (EI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{NNaO}_2$: 290.1151, found: 290.1151.

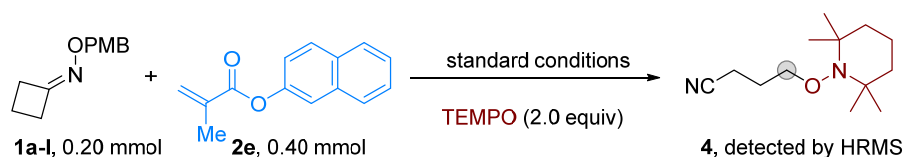
5.3 Alkynylation of cyanoalkyl radicals



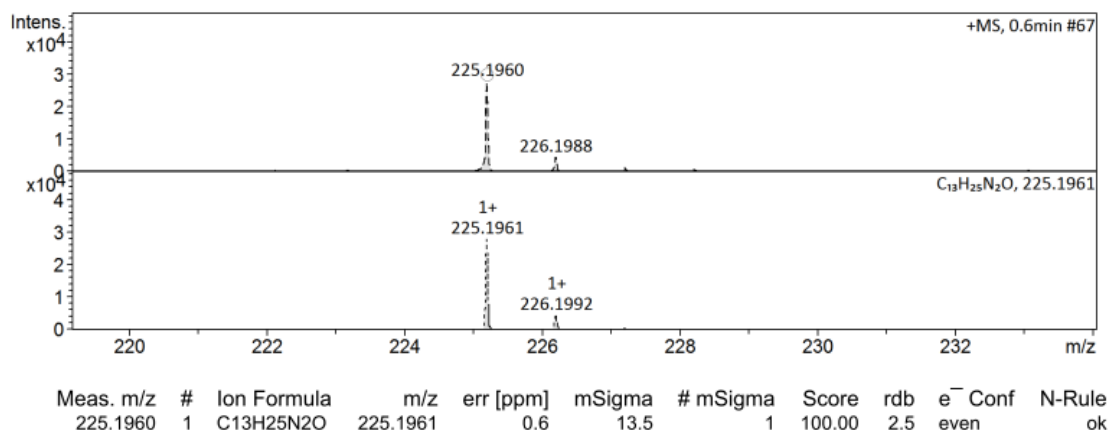
In a dried sealed tube, **1a-III** (53.06 mg, 0.2 mmol), **7** (104.44 mg, 0.3 mmol), DTBP (2.0 equiv), 2,3-Butanedione (10.0 mol%) and K₂CO₃ (1.0 equiv) were dissolved in DCE (4.0 mL). Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 390 nm LED at room temperature about 16 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 10:1) directly to give the desired product **8** in 68% yield (23.01 mg) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.41 – 7.39 (m, 2H), 7.31 – 7.29 (m, 3H), 2.63 – 2.56 (m, 4H), 2.01 – 1.94 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 132.1, 128.9, 128.6, 123.7, 119.8, 87.5, 83.0, 25.2, 19.1, 16.8. HRMS (EI): m/z [M + Na]⁺ calcd for C₁₂H₁₁NNa: 192.0784, found: 192.0784.

6. The Mechanism Studies and Spectral Data of Products

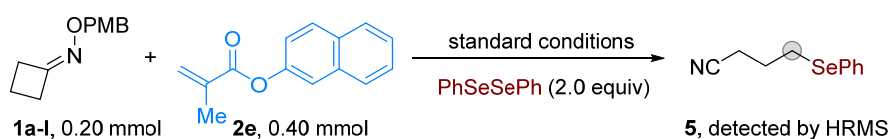
6.1 TEMPO Trapping Experiment



In a dried sealed tube, **1a-I** (41.06 mg, 0.20 mmol), **2e** (84.90 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in 2-butanone (4.0 mL) under a Ar atmosphere. Then TEMPO (2.0 equiv) was added into system. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3ae** with trace yield. The corresponding trapping product **4** was detected by HRMS. HRMS (EI): m/z [M + H]⁺ calcd for C₁₃H₂₅N₂O: 225.1961, found: 225.1960.

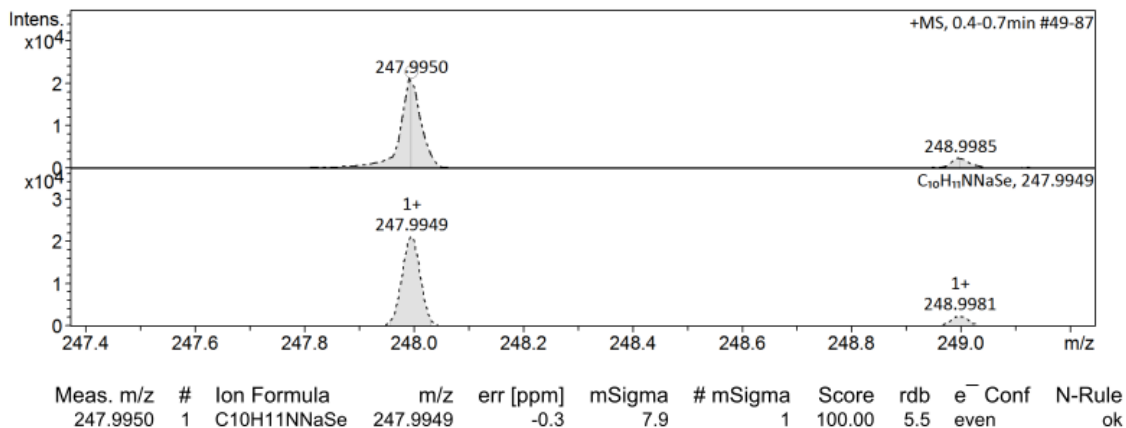


6.2 PhSeSePh Trapping Experiment



In a dried sealed tube, **1a-I** (41.06 mg, 0.20 mmol), **2e** (84.90 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in 2-butanone (4.0 mL) under a Ar atmosphere. Then TEMPO (2.0 equiv) was added into system. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times).

After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3ae** with trace yield. The corresponding trapping product **5** was detected by HRMS. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{10}H_{11}NNaSe$: 247.9949, found: 247.9950.

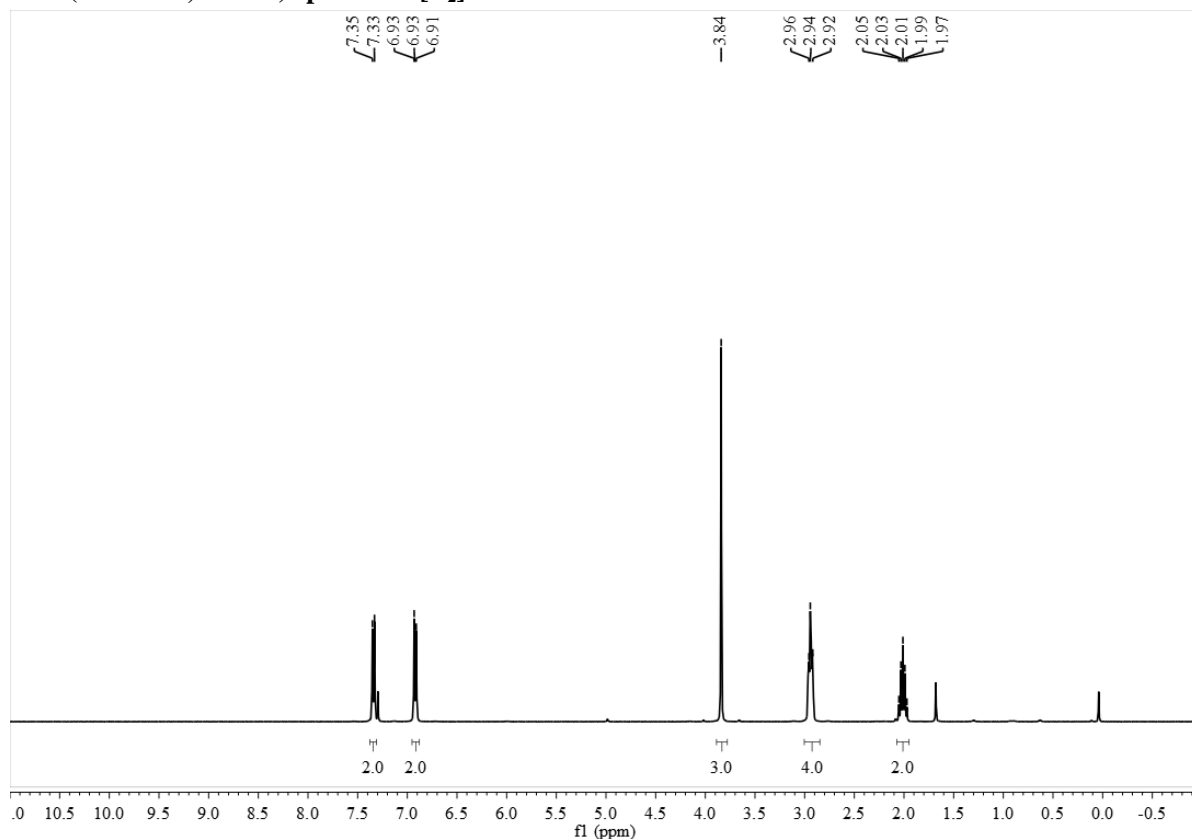


6.3 Isotope Labeling Experiment

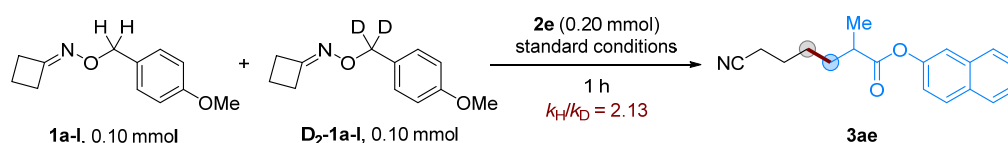
The **[D₂]-1a-I** was synthesized from benzenemethan-*d*₂-ol according to the literature.^[3]

Deuterium incorporation was detected to be over 99% by ¹H NMR in CDCl₃.

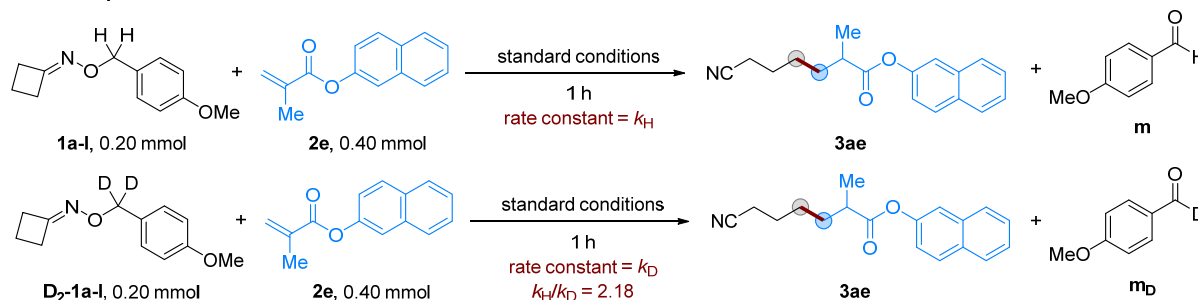
¹H NMR (400 MHz, CDCl₃) spectra of **[D₂]-1a-I**



Competitive Experiment



Parallel Experiment



Intermolecular Competitive Kinetic Isotope Effect (KIE) Experiment

In a dried sealed tube, **1a-I** (20.53 mg, 0.10 mmol), [**D**₂]-**1a-I** (20.73 mg, 0.10 mmol), **2e** (84.90 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in 2-butanone (4.0 mL) under a Ar atmosphere. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 1 h. After that, the solvent was concentrated in vacuo and residual starting material was characterized by ¹H NMR spectra. Peak areas according to ¹H-NMR were compared to give the ratio (0.72:0.28) of [**D**₂]-**1a-I** to **1a-I** in residual material. $k_{\text{H}}/k_{\text{D}}$ was calculated using the following expression^[4]: $k_{\text{H}}/k_{\text{D}} = (M/2 - 0.48m)/(M/2 - 0.52m)$

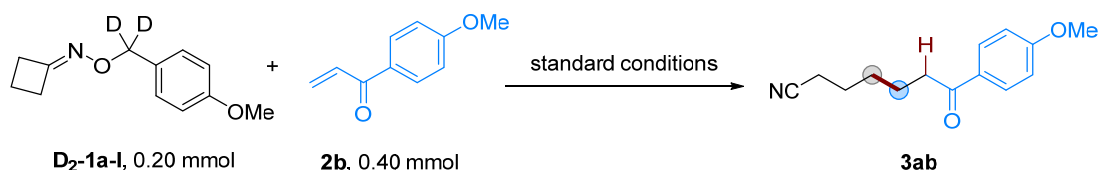
M, m represent the amount of deuterated oxime ether [**D**₂]-**1a-I** and oxime ether **1a-I** in reaction starting material and residual material, respectively. Here, M = 41.26, m = 18.61, which corresponds to $k_{\text{H}}/k_{\text{D}} = 2.13$.

Intermolecular Parallel Kinetic Isotope Effect (KIE) experiment:

In two dried sealed tubes, **1a-I** (41.05 mg, 0.20 mmol) or [**D**₂]-**1a-I** (41.45 mg, 0.20 mmol), **2e** (84.90 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in 2-butanone (4.0 mL) under a Ar atmosphere. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 1 h. After that, the solvent were concentrated in vacuo and the residue were purified by chromatography column on silica gel to give the corresponding products **3ae** (24.40 mg for **1a-I** and 11.19 mg for [**D**₂]-**1a-I**). $k_{\text{H}}/k_{\text{D}}$ was calculated using the following expression: $k_{\text{H}}/k_{\text{D}} = m/m_{\text{D}}$

m, m_D represent the amount of corresponding aldehyde with **1a-I** or [**D**₂]-**1a-I** as starting material, respectively. Here, m = 24.40 mg, m_D = 11.19 mg, which corresponds to $k_{\text{H}}/k_{\text{D}} = 2.18$.

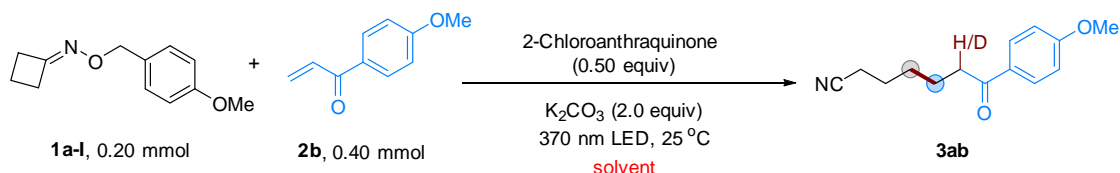
6.4 Deuterium Labeling Experiments



In a dried sealed tube, [**D**₂]-**1a-I** (41.45 mg, 0.20 mmol), **2b** (64.88 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in 2-butanone (4.0 mL) under a Ar atmosphere. Then, the

resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3ab** with 72% yield as a colorless oil.

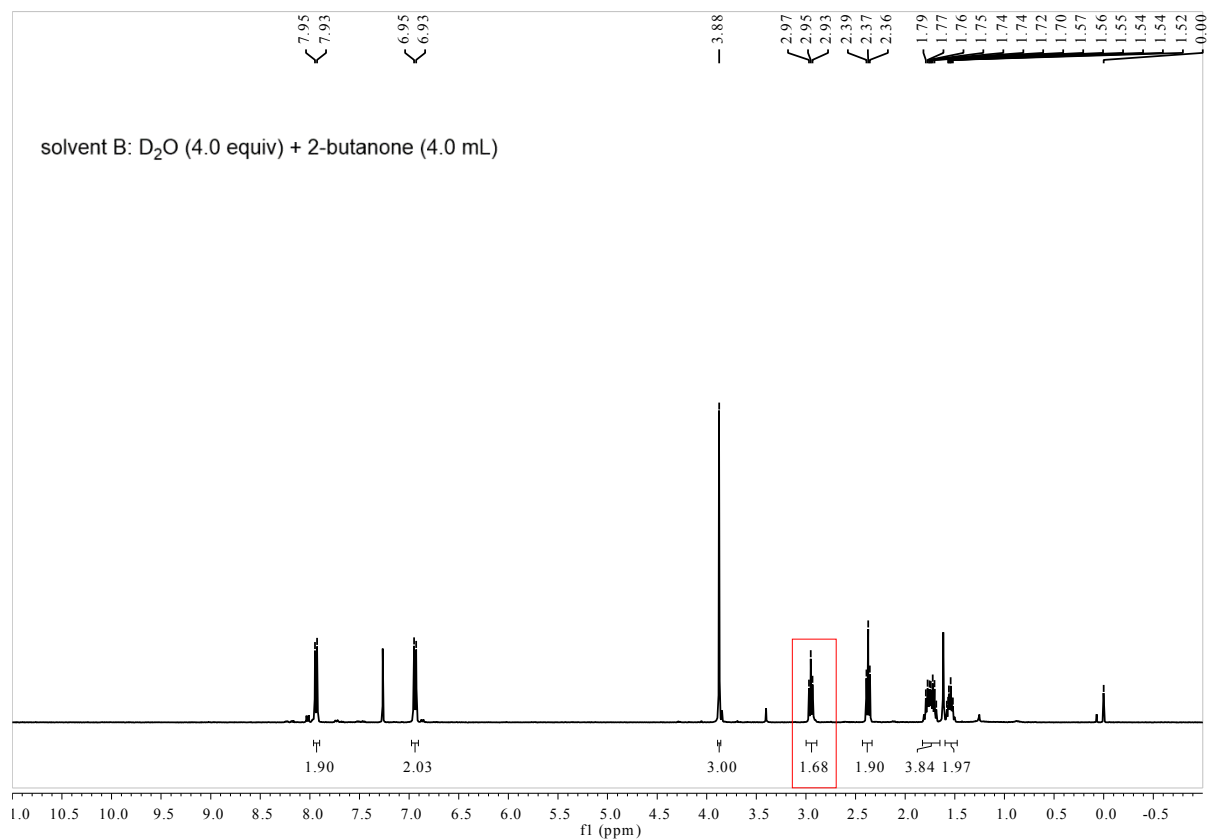
No deuterated product **3ab** was detected by ^1H -NMR, which suggests the hydrogen of product **3ab** does not come from the benzylic hydrogen of the oxime ethers [**D**₂]-**1a-I**.

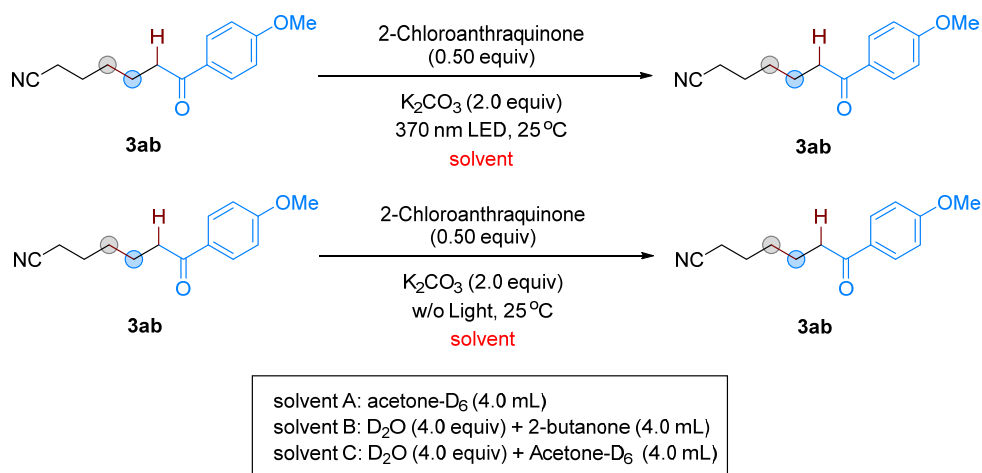
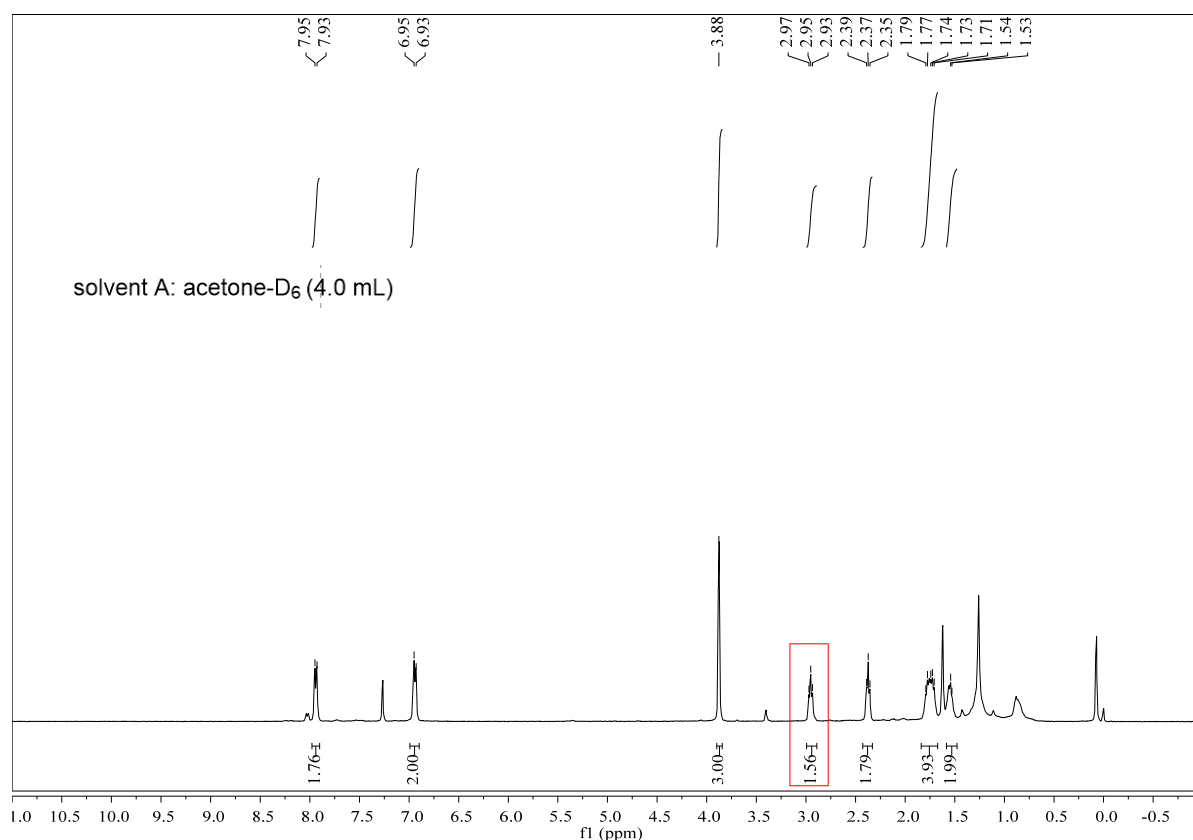


solvent A: acetone-D₆ (4.0 mL)
solvent B: D₂O (4.0 equiv) + 2-butanone (4.0 mL)
solvent C: D₂O (4.0 equiv) + acetone-D₆ (4.0 mL)

In a dried sealed tube, **1a-I** (41.06 mg, 0.20 mmol), **2b** (64.88 mg, 0.40 mmol), 2-chloroanthraquinone (24.27 mg, 0.50 equiv) and K₂CO₃ (55.28 mg, 2.0 equiv) were dissolved in solvent A or B or C under a Ar atmosphere. Then, the resulting mixture was degassed via ‘freeze-pump-thaw’ procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 370 nm LED at room temperature about 12 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3ab** as a colorless oil.

Deuterated product **3ab** was detected by ^1H -NMR, which suggests the hydrogen of product **3ab** may come from the solvent (40% D when using solvent A) and the trace amount of the system (30% D when using solvent B, 90% D when using solvent C).





In four dried sealed tubes, **3ab** (23.13 mg, 0.10 mmol), 2-chloroanthraquinone (0.50 equiv) and K_2CO_3 (2.0 equiv) were dissolved in solvents protected by Ar under above four conditions. After that, the solution was stirred about 12 h. Then, the solvent was concentrated in vacuo and the residual was characterized by 1H NMR spectra.

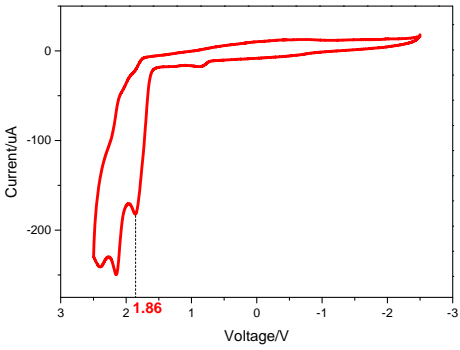
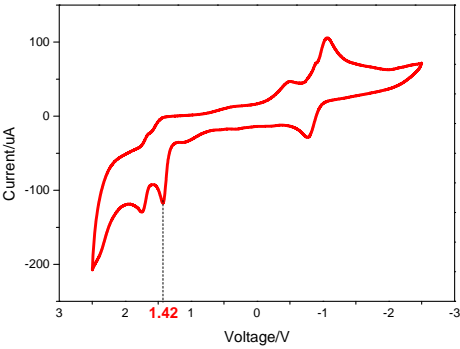
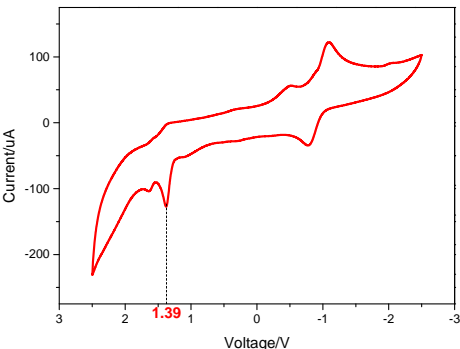
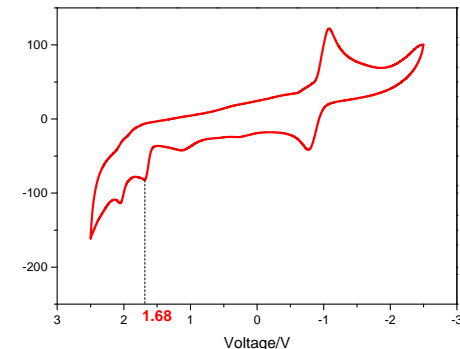
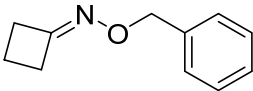
No deuterated product **3ab** was detected by 1H -NMR, which suggests the hydrogen transfer process does not take place between products.

6.5 Electrochemical Studies

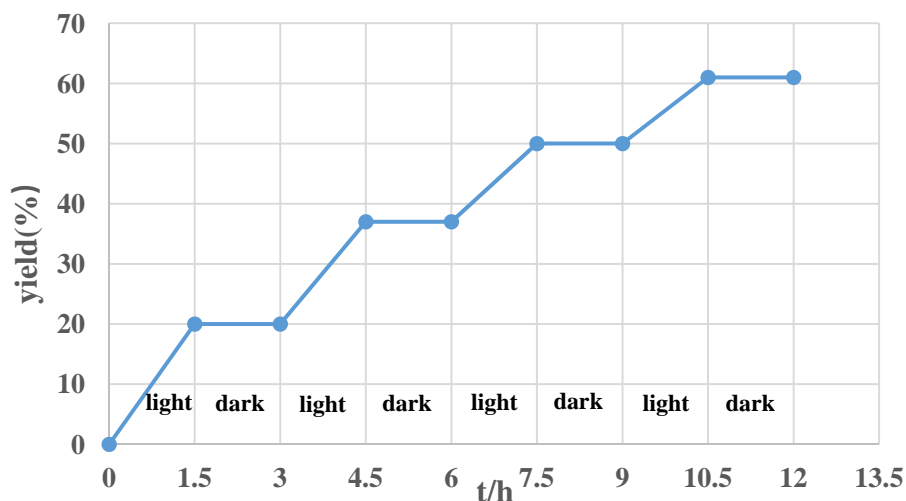
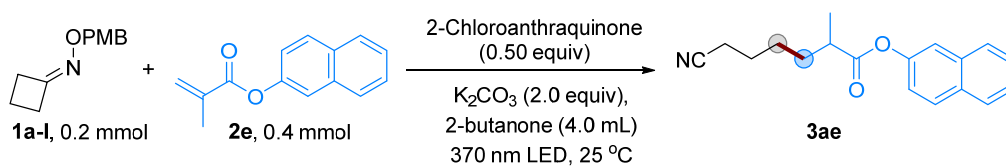
The oxidation potential of 1-Cl-AQ was +1.9 V vs. FC/FC⁺ (+2.3 V vs. SCE) according to the literature.^[1]

The cyclic voltammetry experiment was performed, and the oxidation potential of substrates with different protecting groups was determined as follows. The electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Cyclic voltammetry was performed in a three-electrode cell (volume 30 mL; MeCN as solvent, *n*-Bu₄PF₆ (0.1 M) as the supporting electrolyte, 0.1 M concentration of the tested compound) with glassy carbon

(diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and saturated calomel electrode as the reference electrode. The scan speed was $100 \text{ mV} \cdot \text{s}^{-1}$.

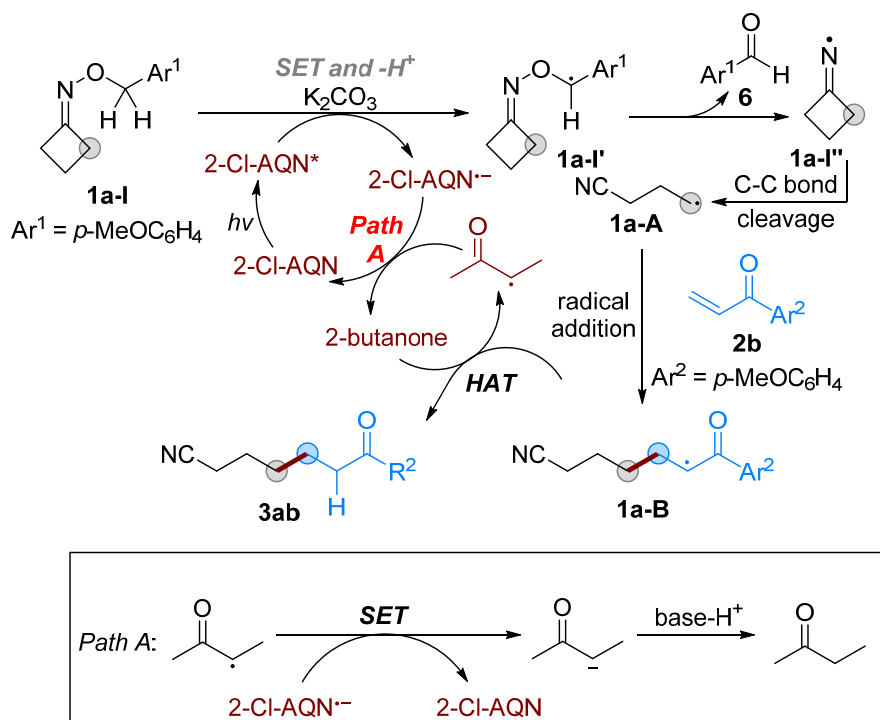
	<p>1a-I E = +1.86 versus SCE</p>
	<p>1a-II E = +1.42 versus SCE</p>
	<p>1a-III E = +1.39 versus SCE</p>
	<div data-bbox="995 1688 1248 1778" data-label="Chemical-Block">  </div> <p>1a-IV E = +1.68 versus SCE</p>

6.6 Light On-Off Experiments



The yield of **3ae** was determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The results reveal that a radical chain process is not the major reaction pathway, while it can not be completely ruled out at the current stage.

6.7 Plausible Mechanism of PCET Pathway

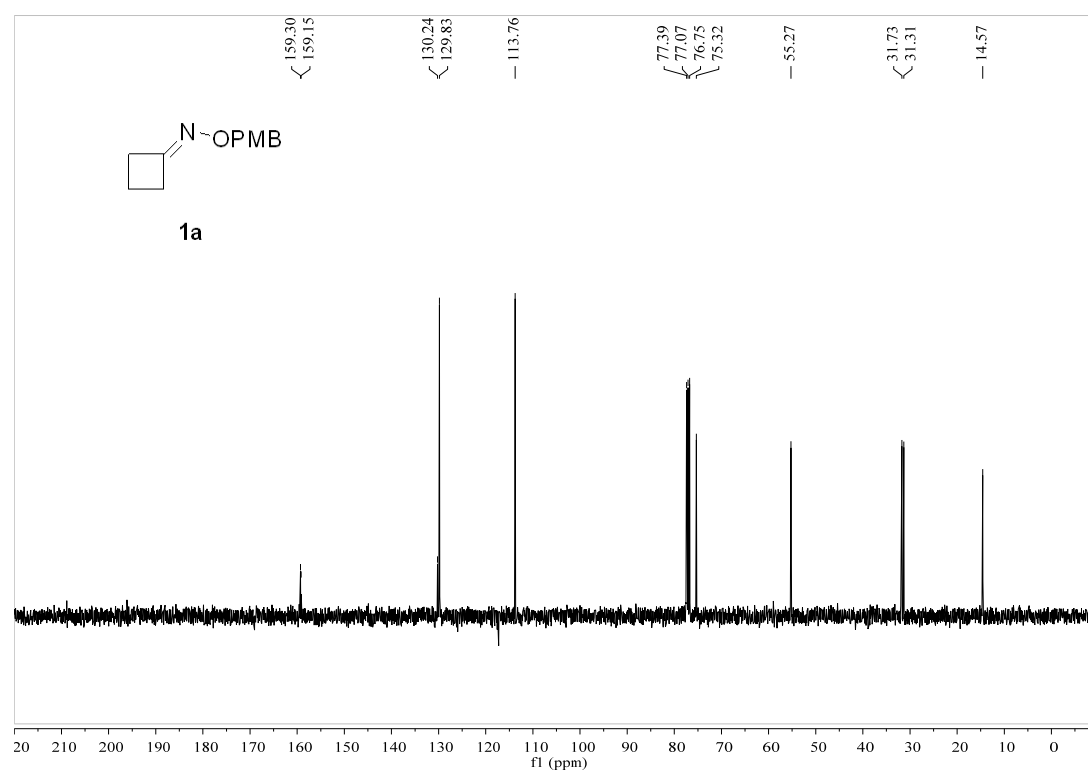
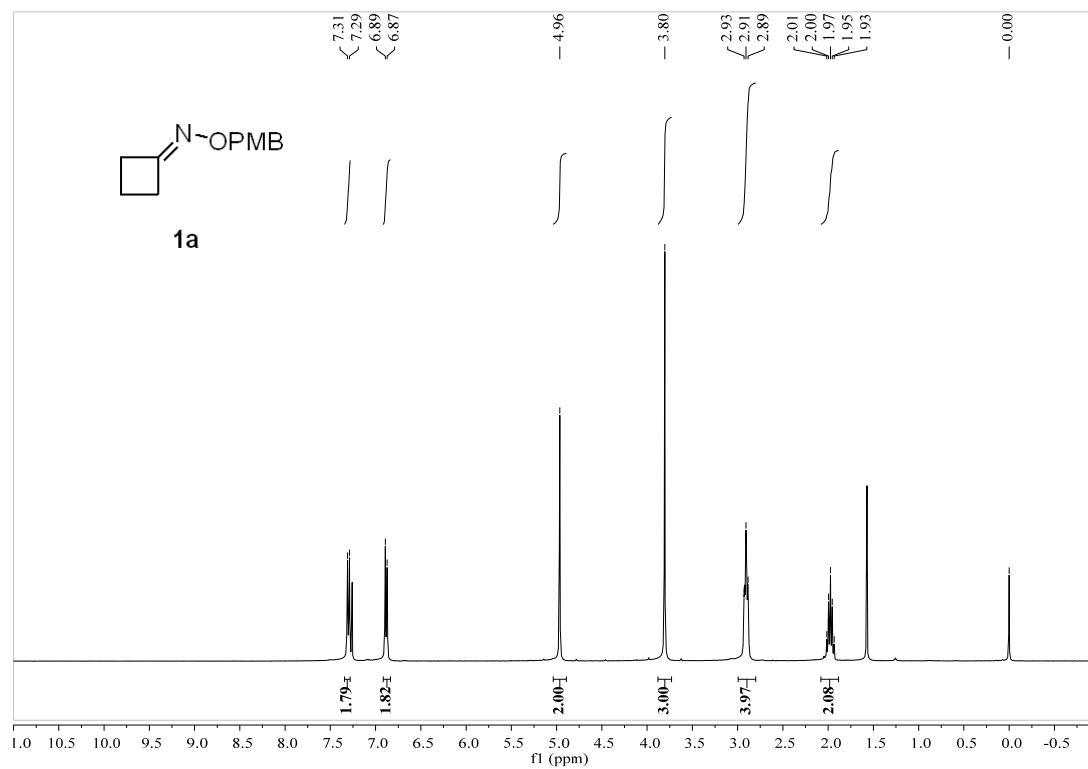


Reference:

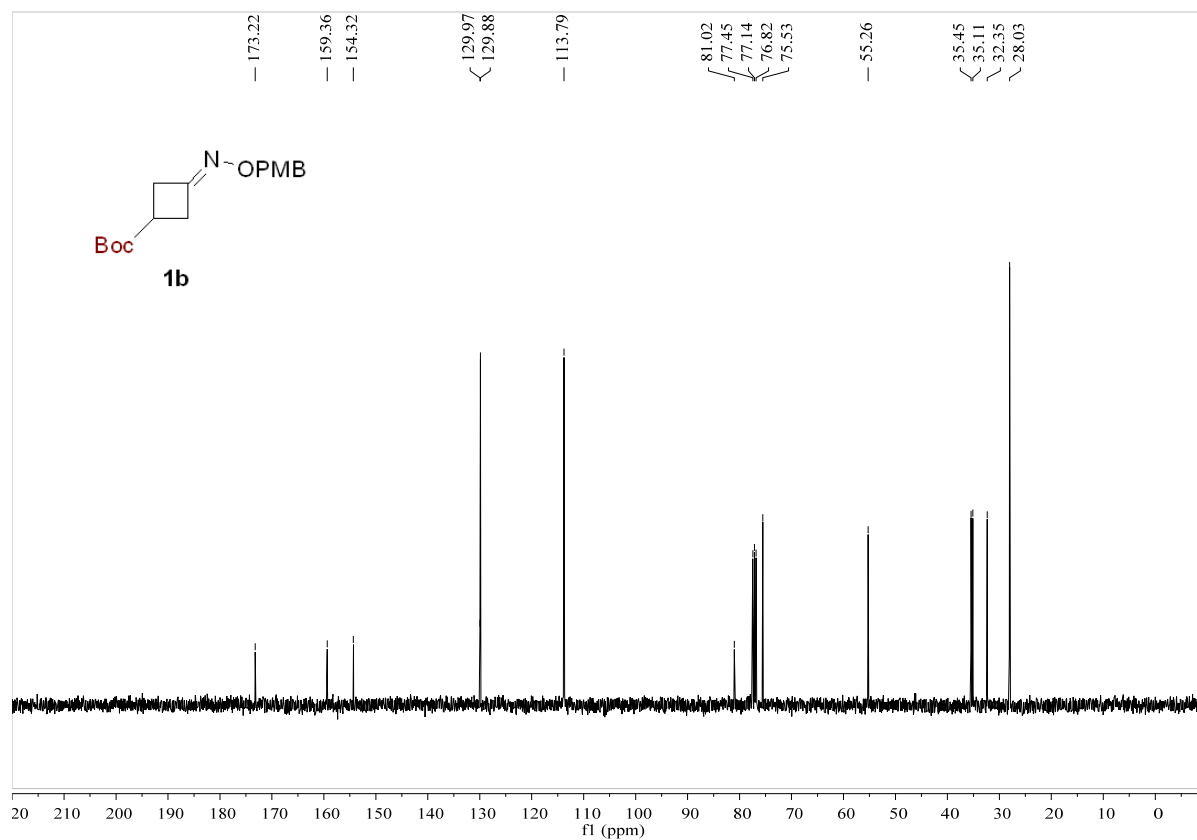
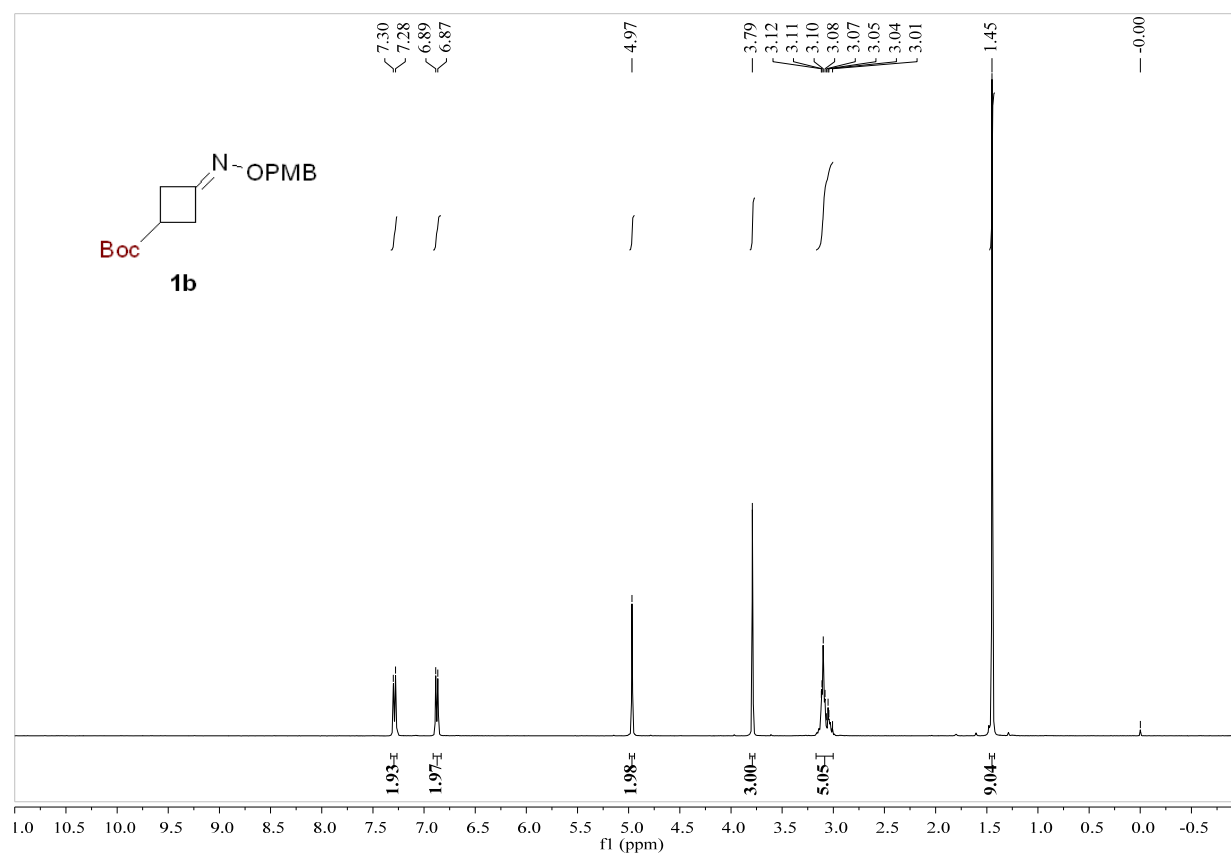
- [1] Usami, K., Yamaguchi, E., Tada, N., Itoh, A., *Org. Lett.* **2018**, *20*, 5714.
- [2] Wang, P.-Z., Yu, X.-Y., Li, C.-Y., He, B.-Q., Chen, J.-R., Xiao, W.-J., *Chem. Commun.* **2018**, *54*, 9925.
- [3] Yin, G.-Y., Wu, Y.-C., Liu, G.-S., *J. Am. Chem. Soc.* **2010**, *34*, 11978.
- [4] Gu, Y.-R., Duan, X.-H., Lin, Y., Guo, L.-N., *Org. Lett.* **2017**, *19*, 5908.

7. The Spectra of Substrates and Products

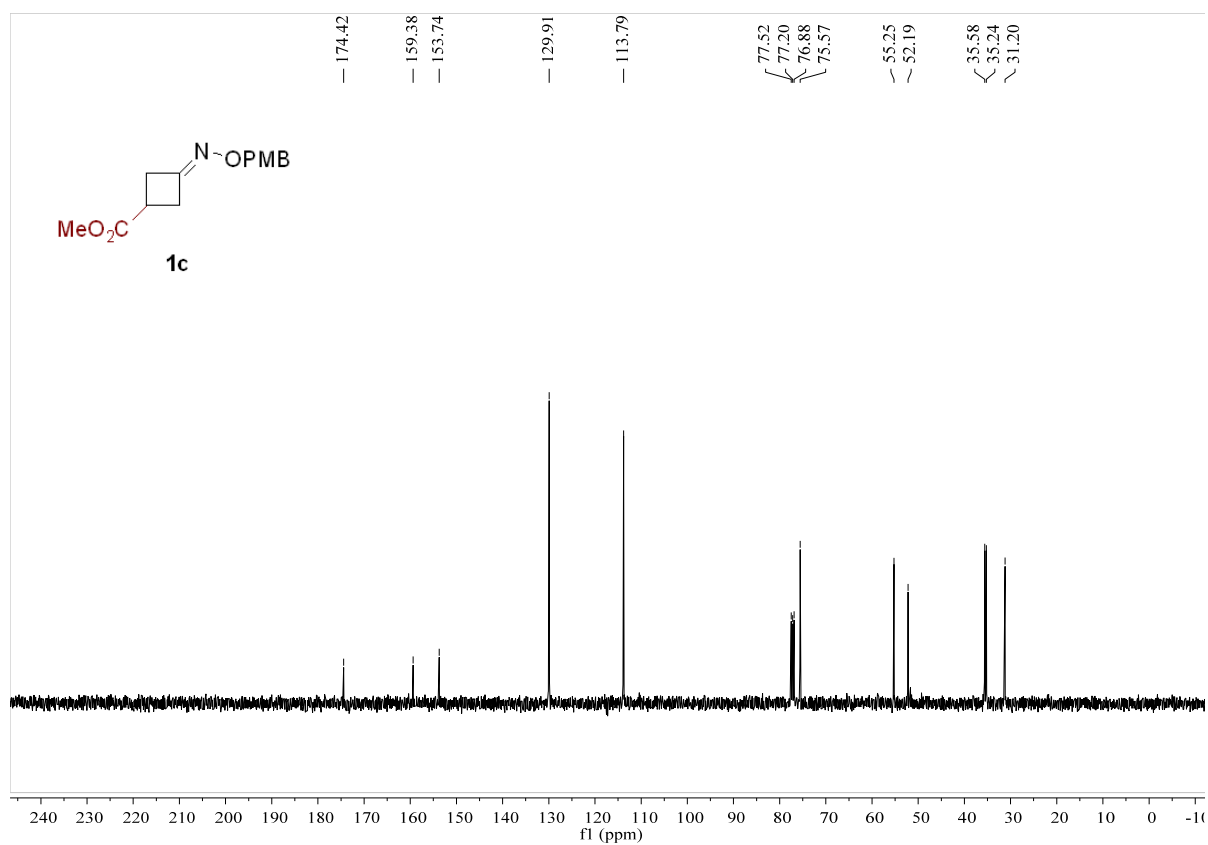
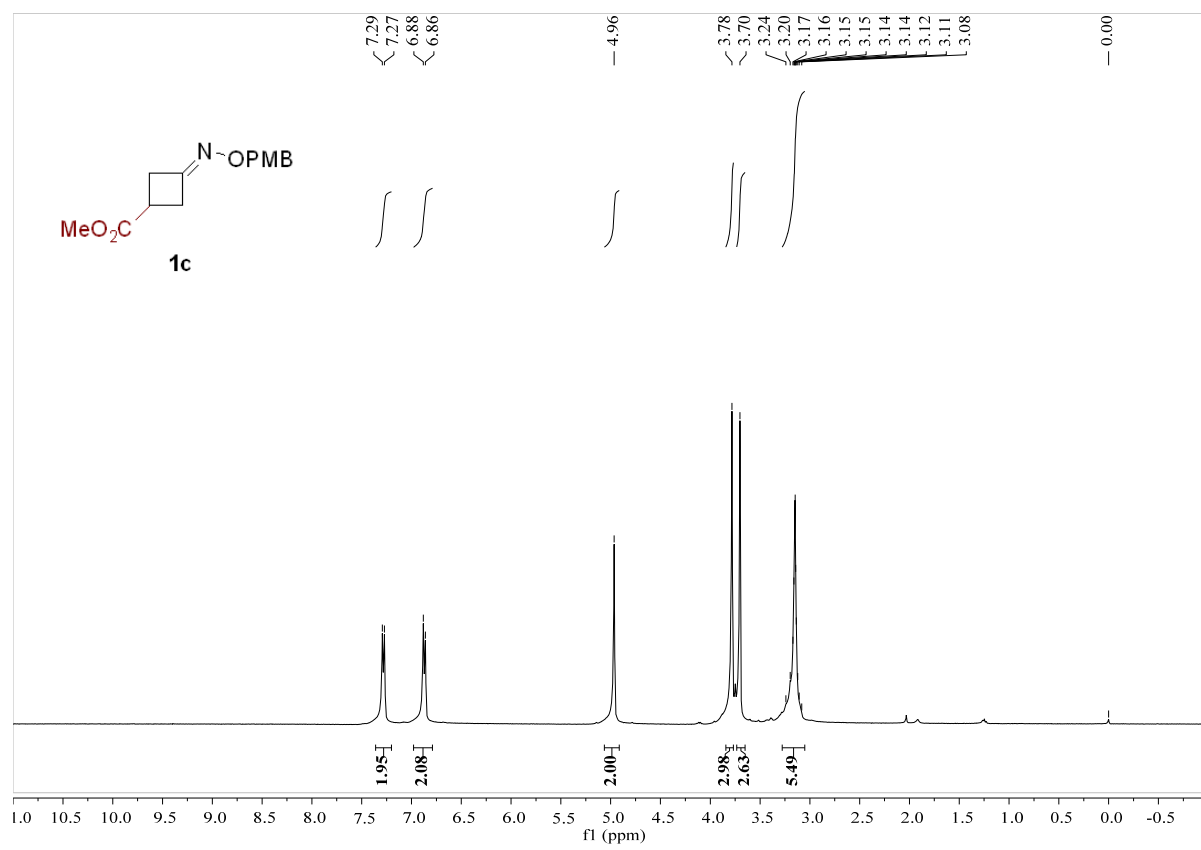
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1a**



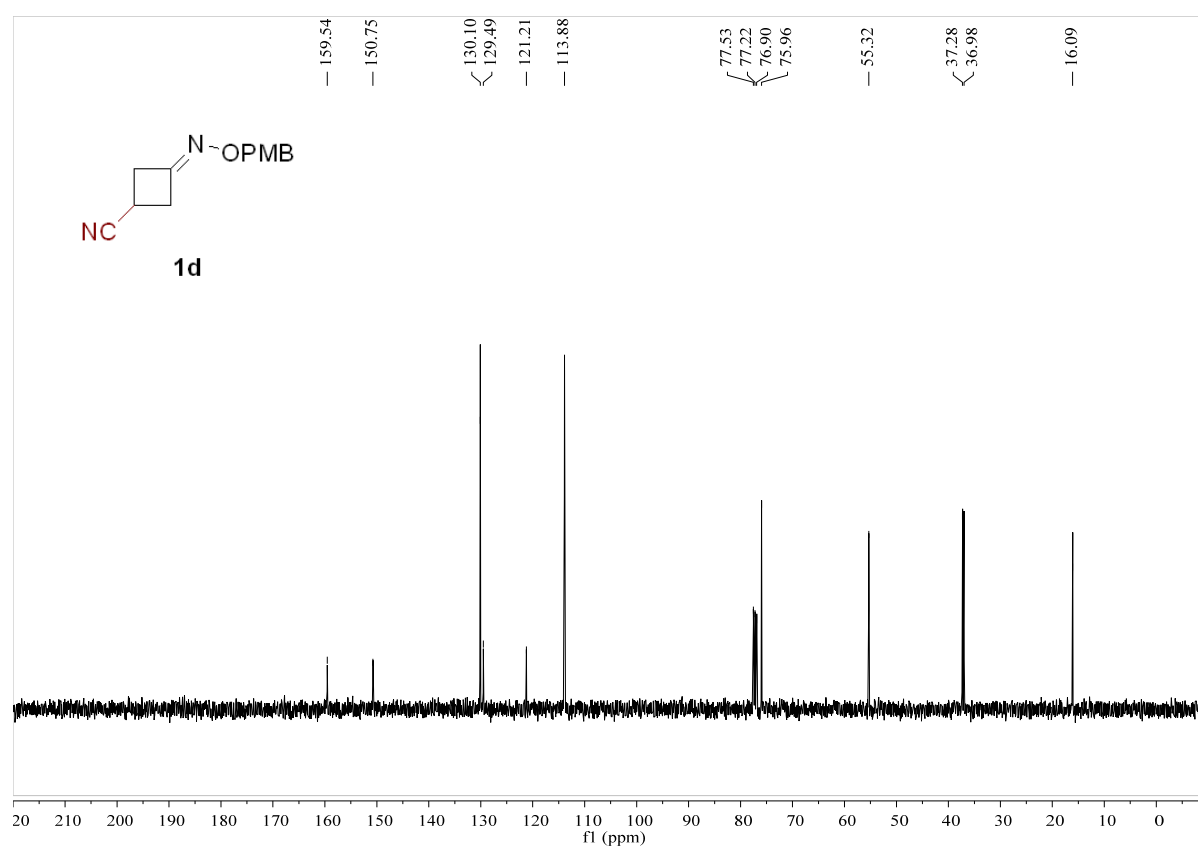
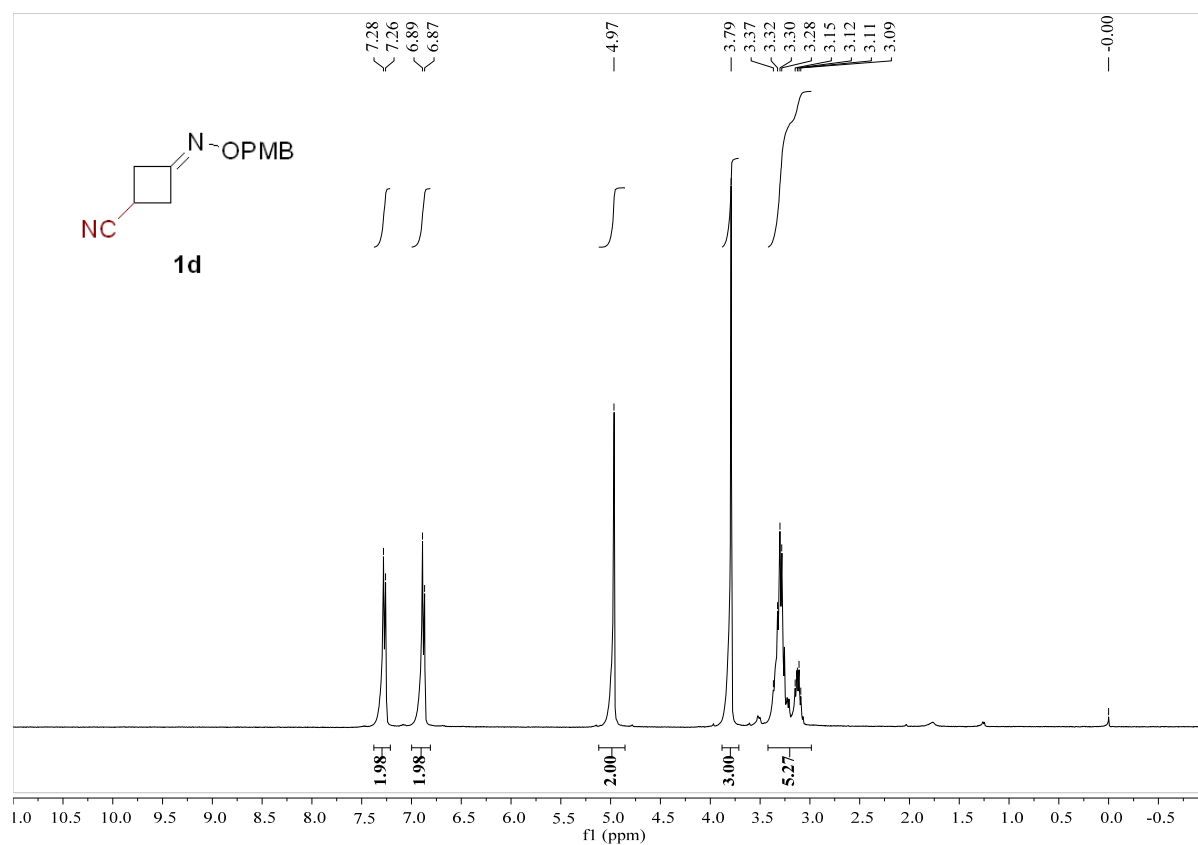
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate 1b



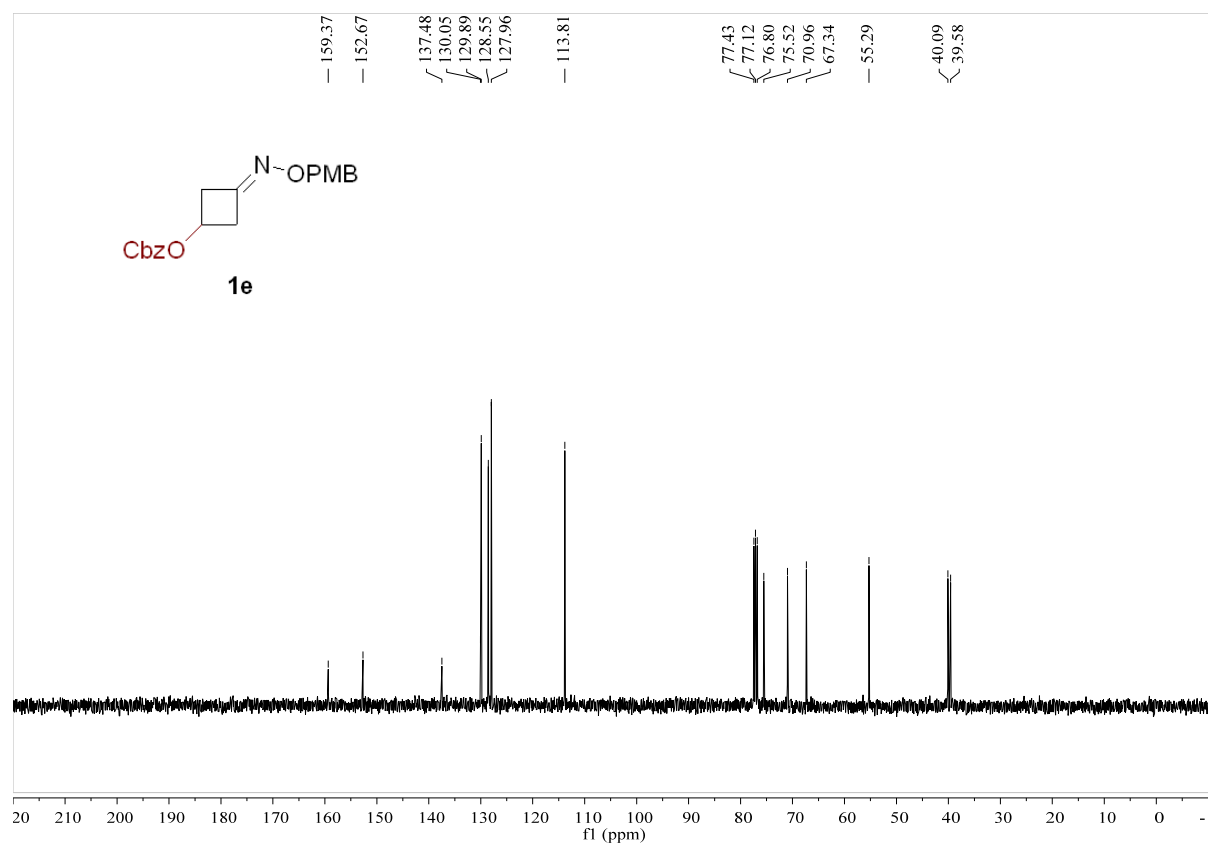
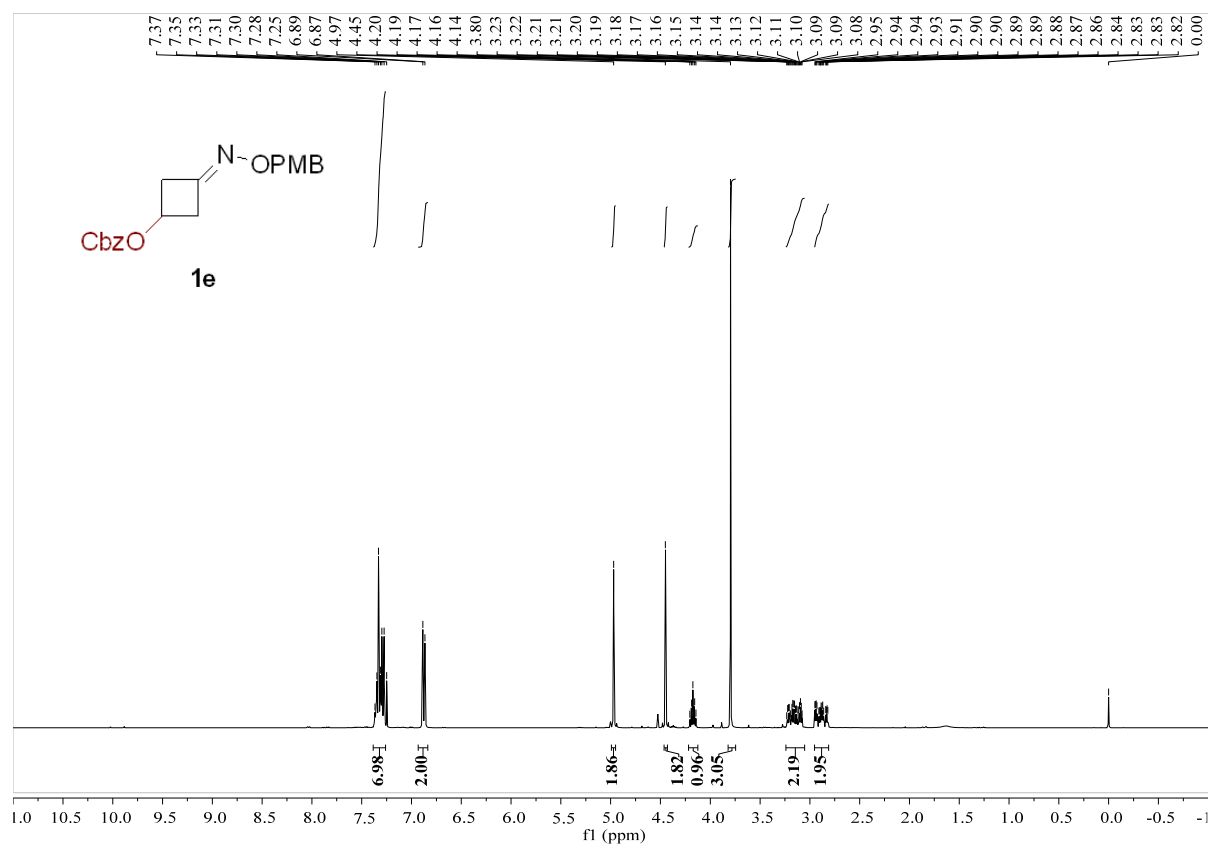
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1c**



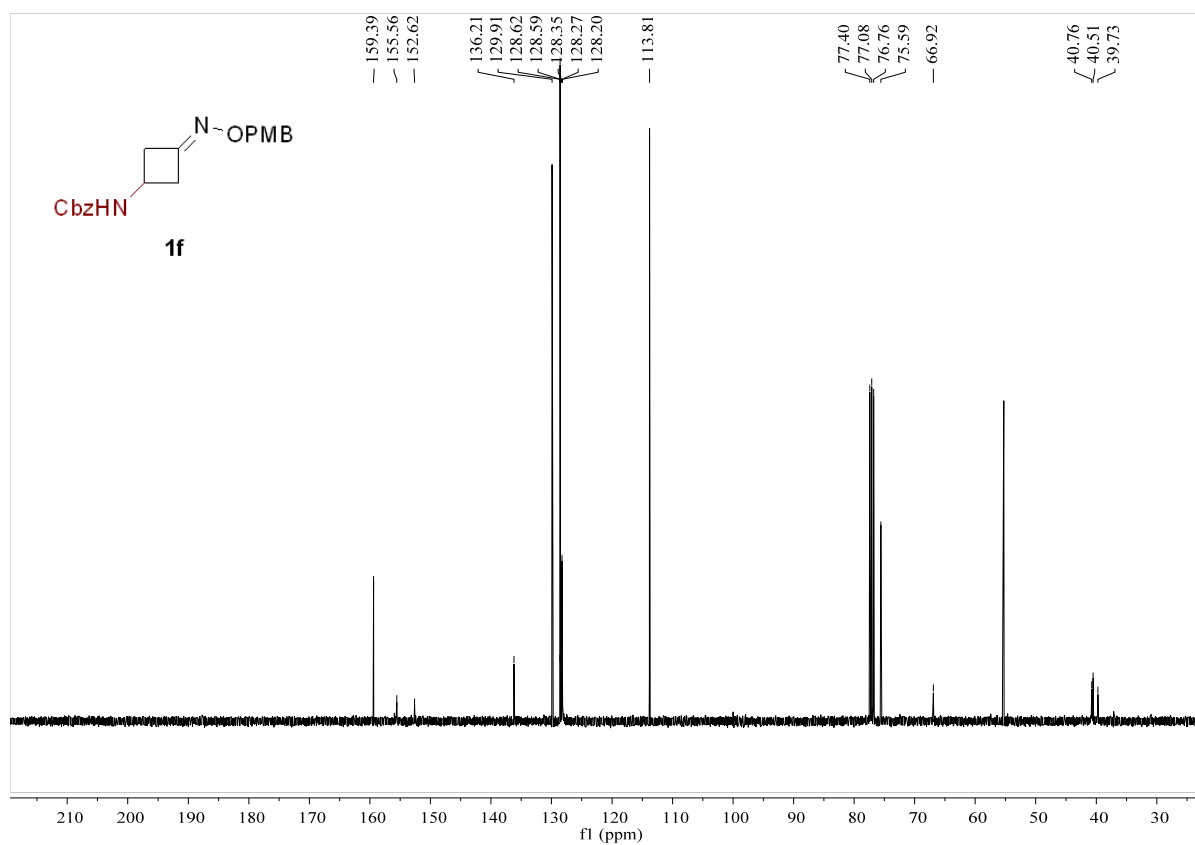
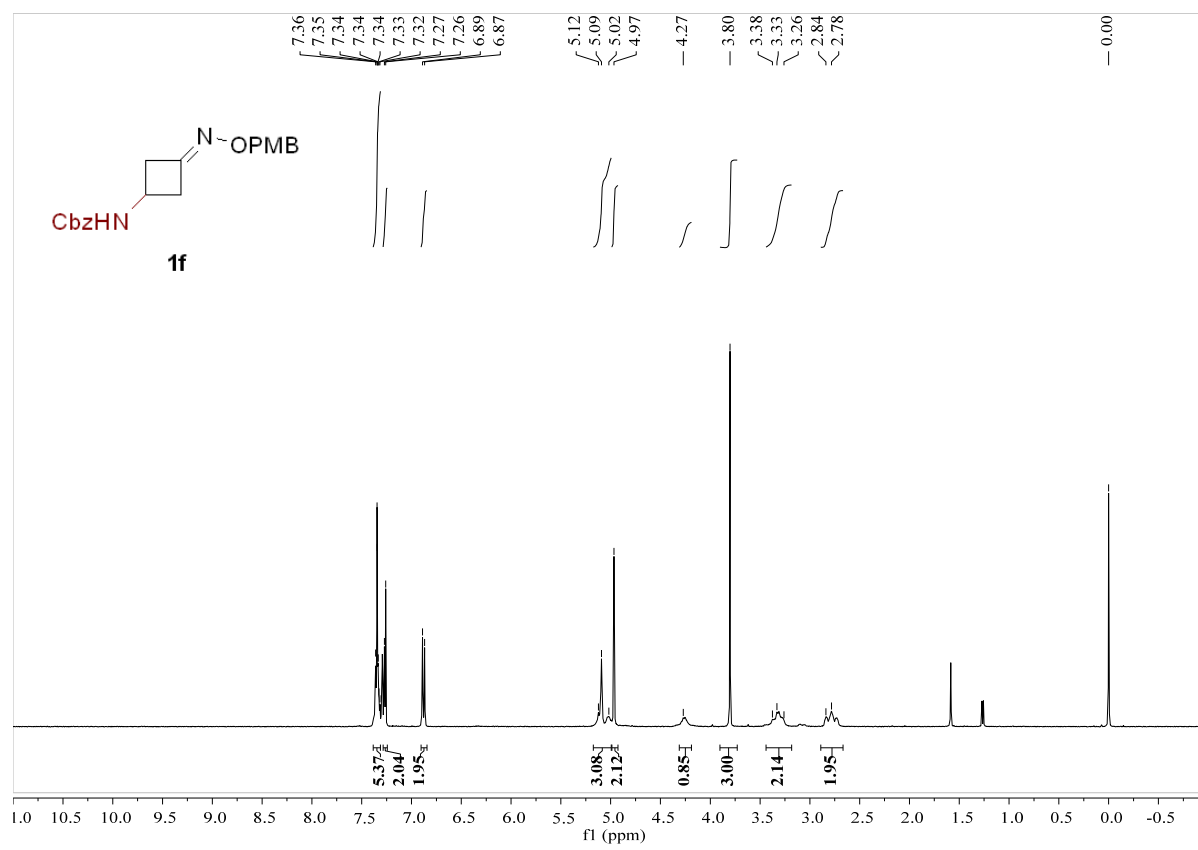
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1d**



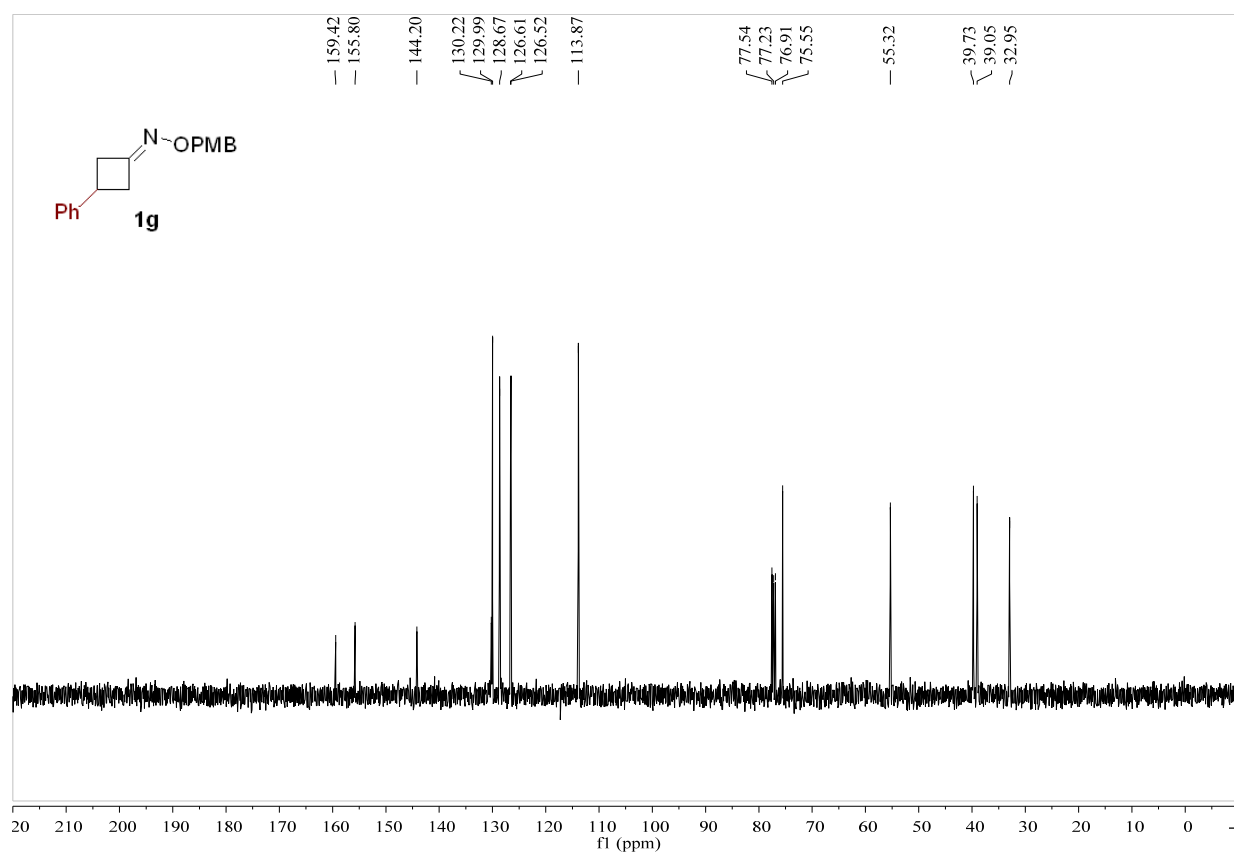
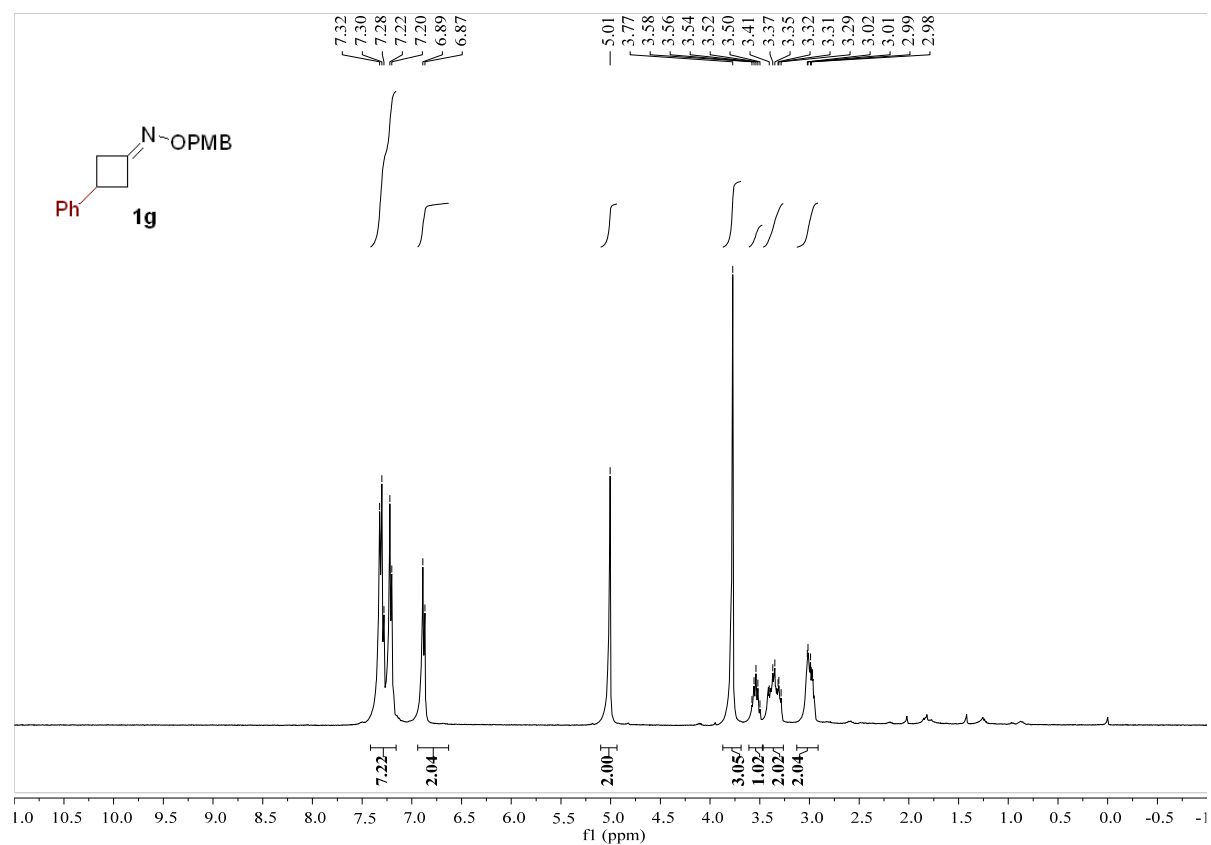
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate **1e**



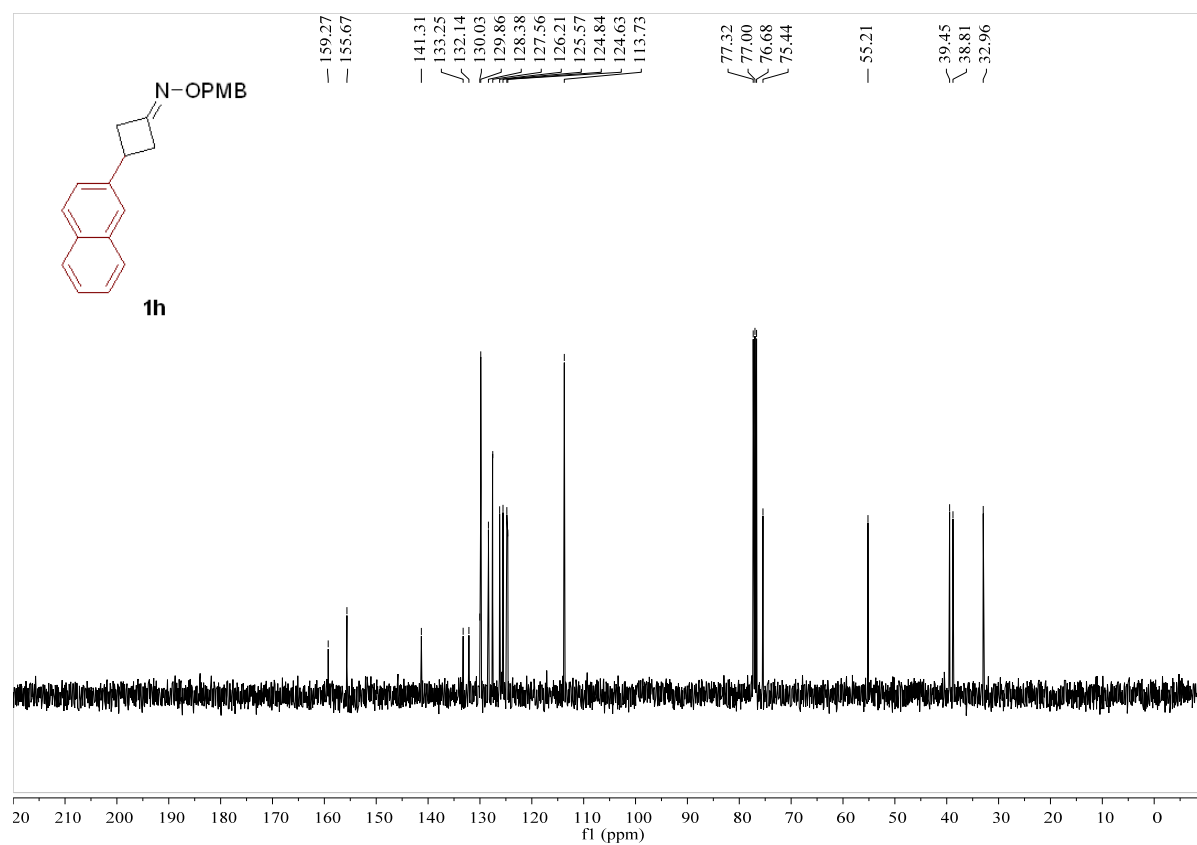
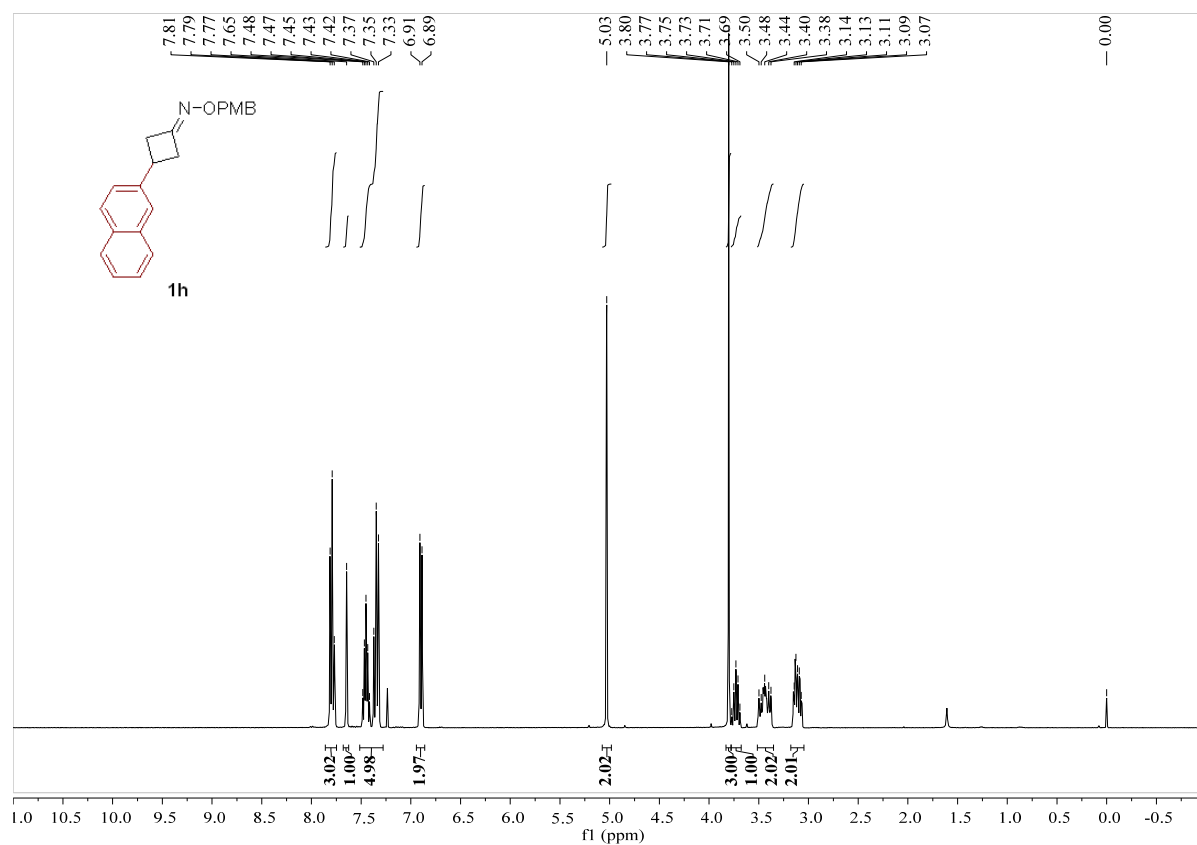
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate **1f**



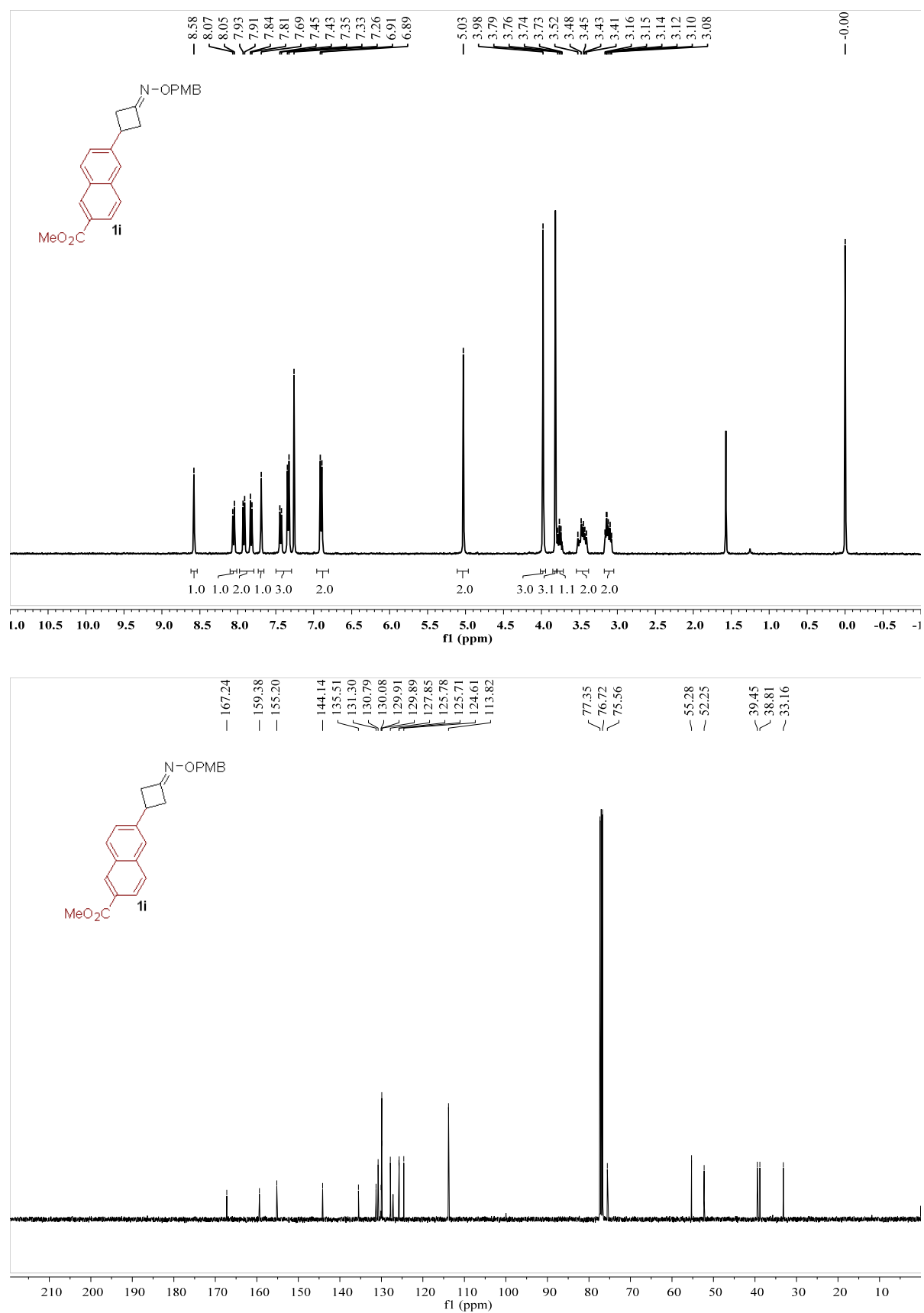
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate **1g**



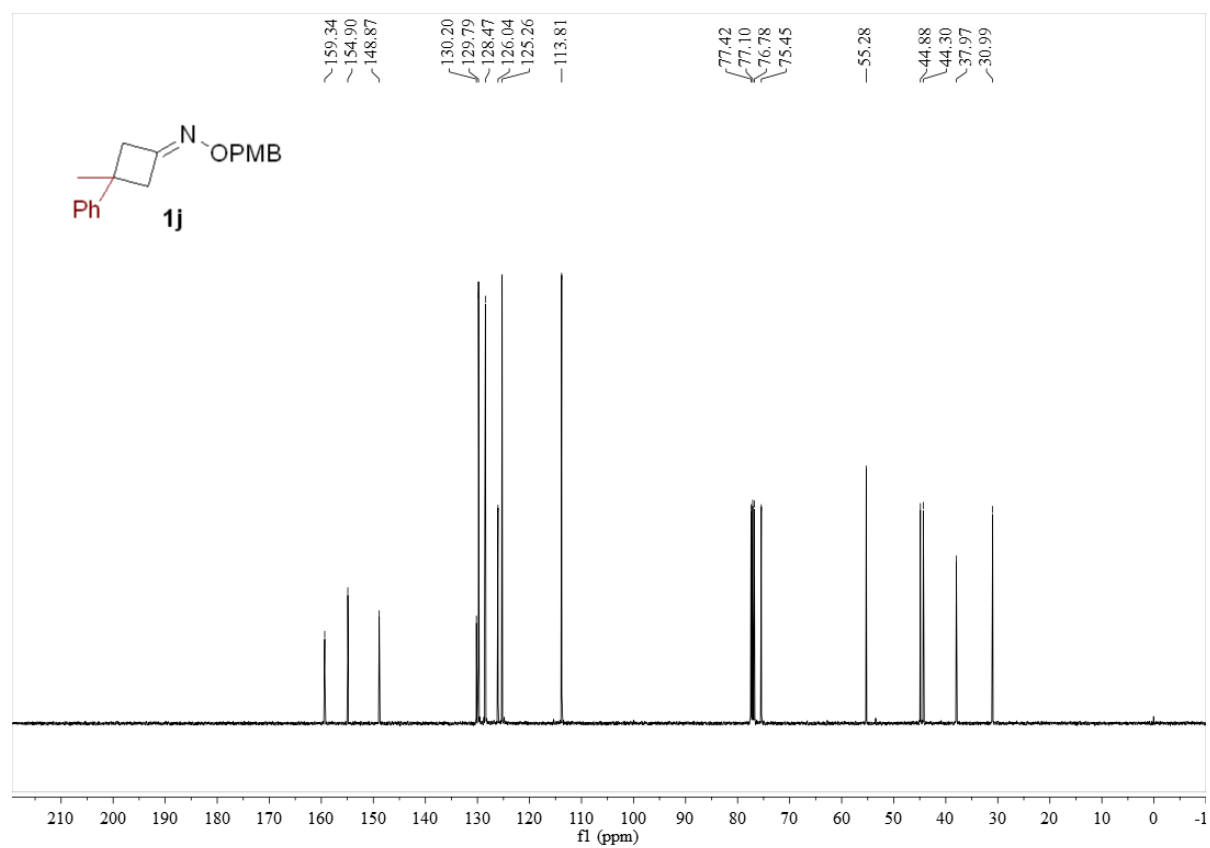
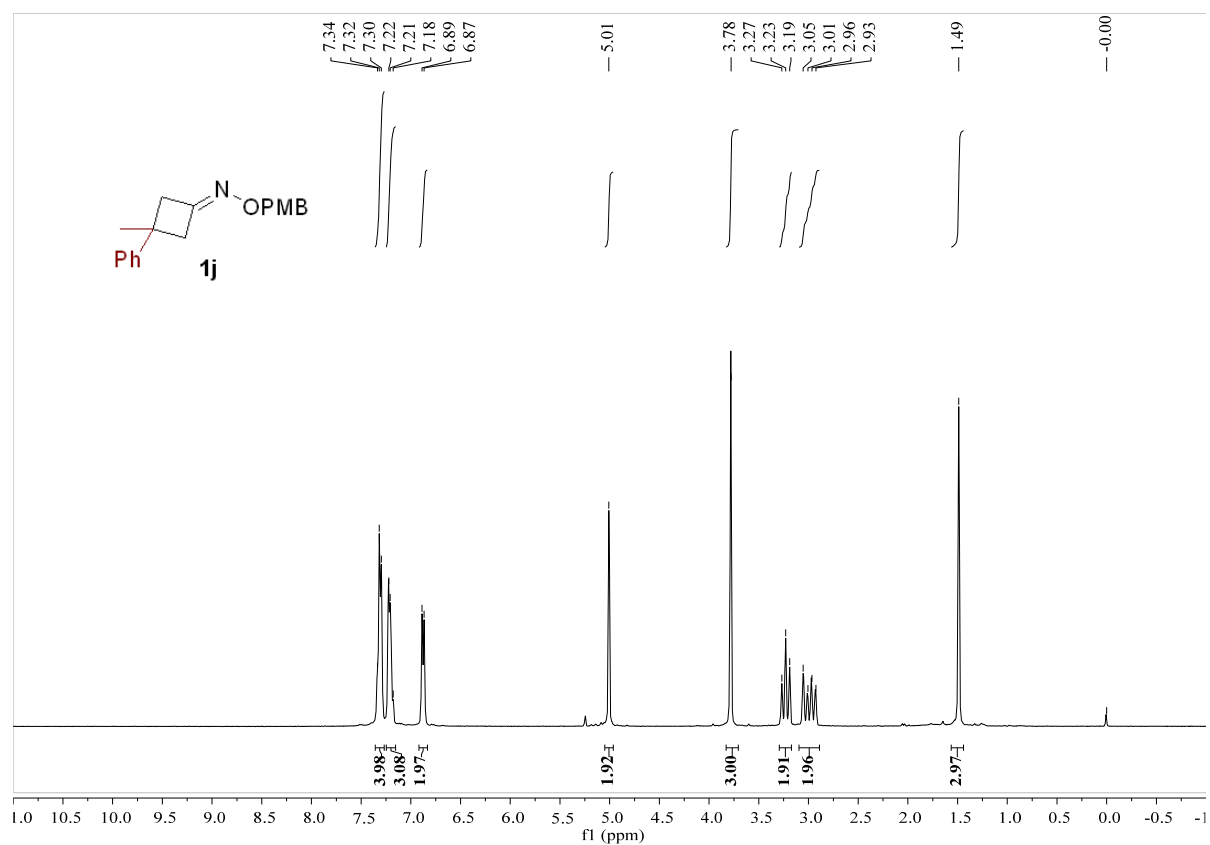
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate 1h



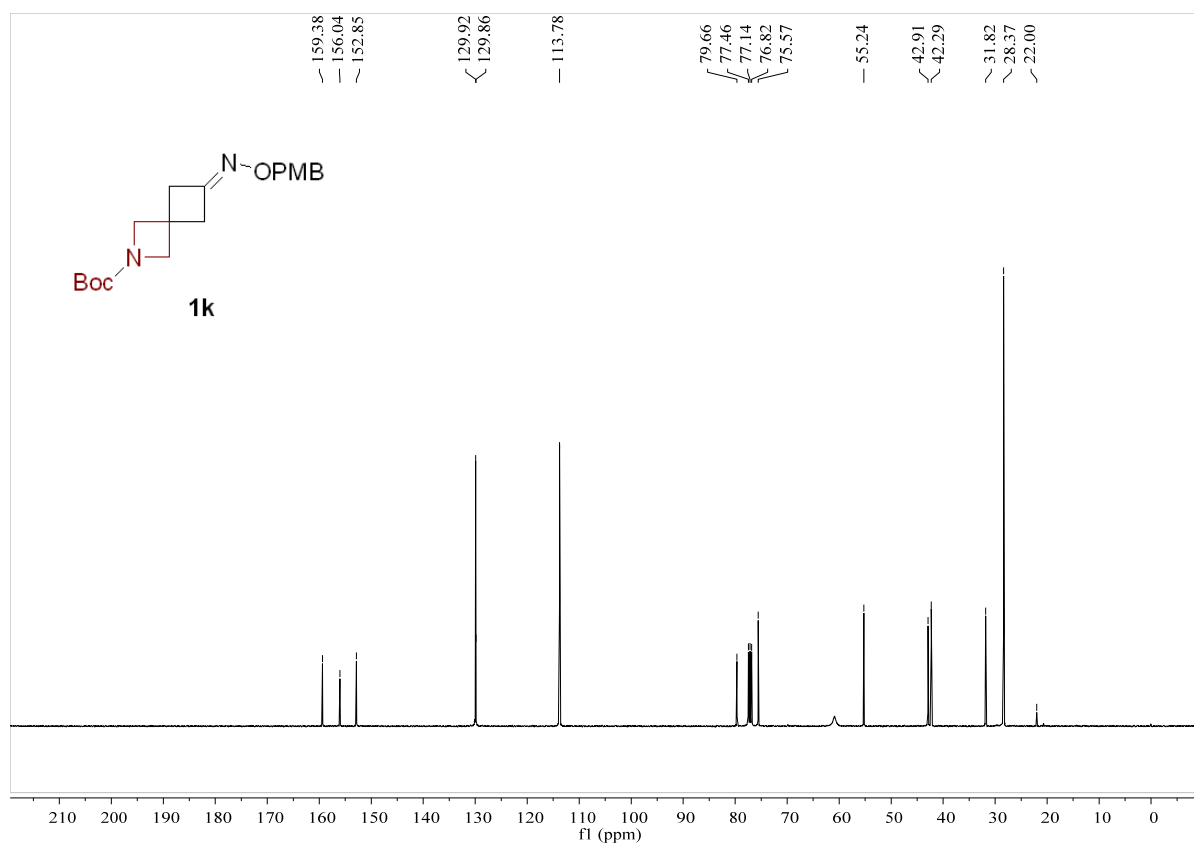
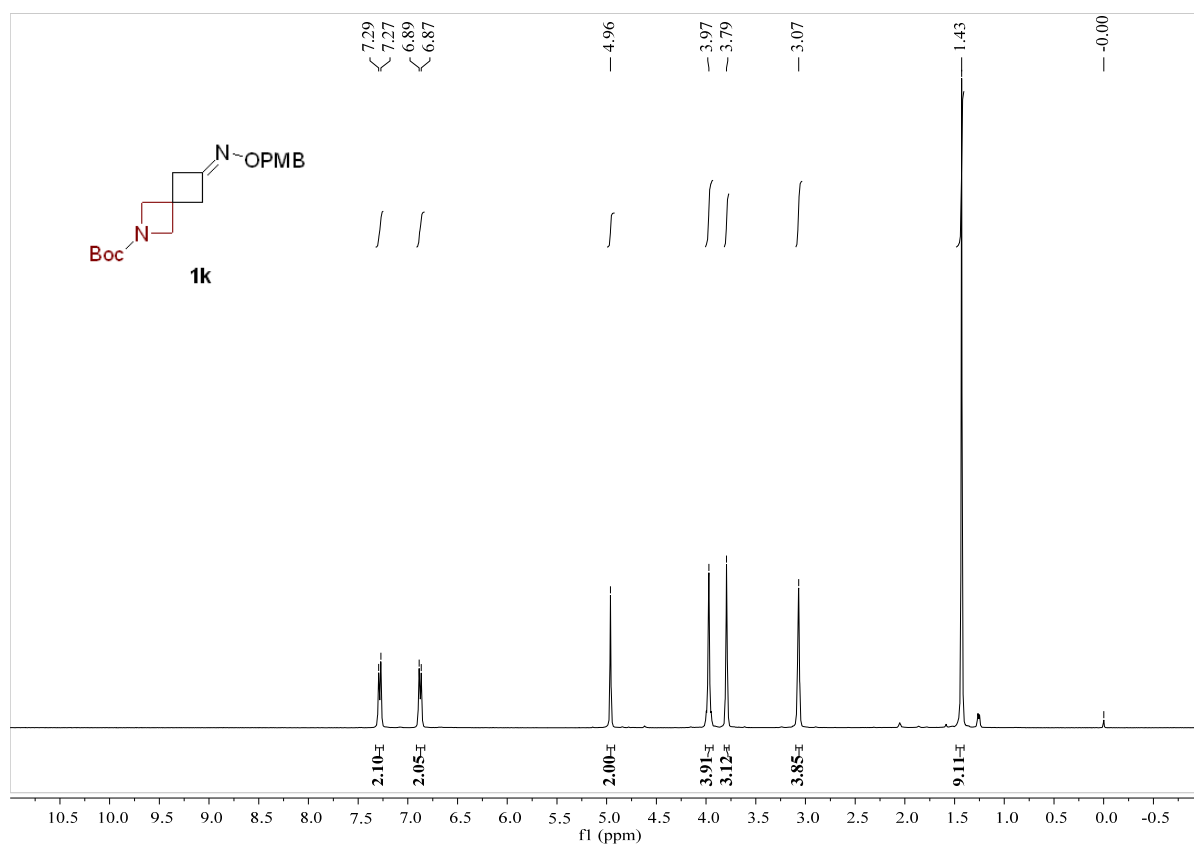
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1i**



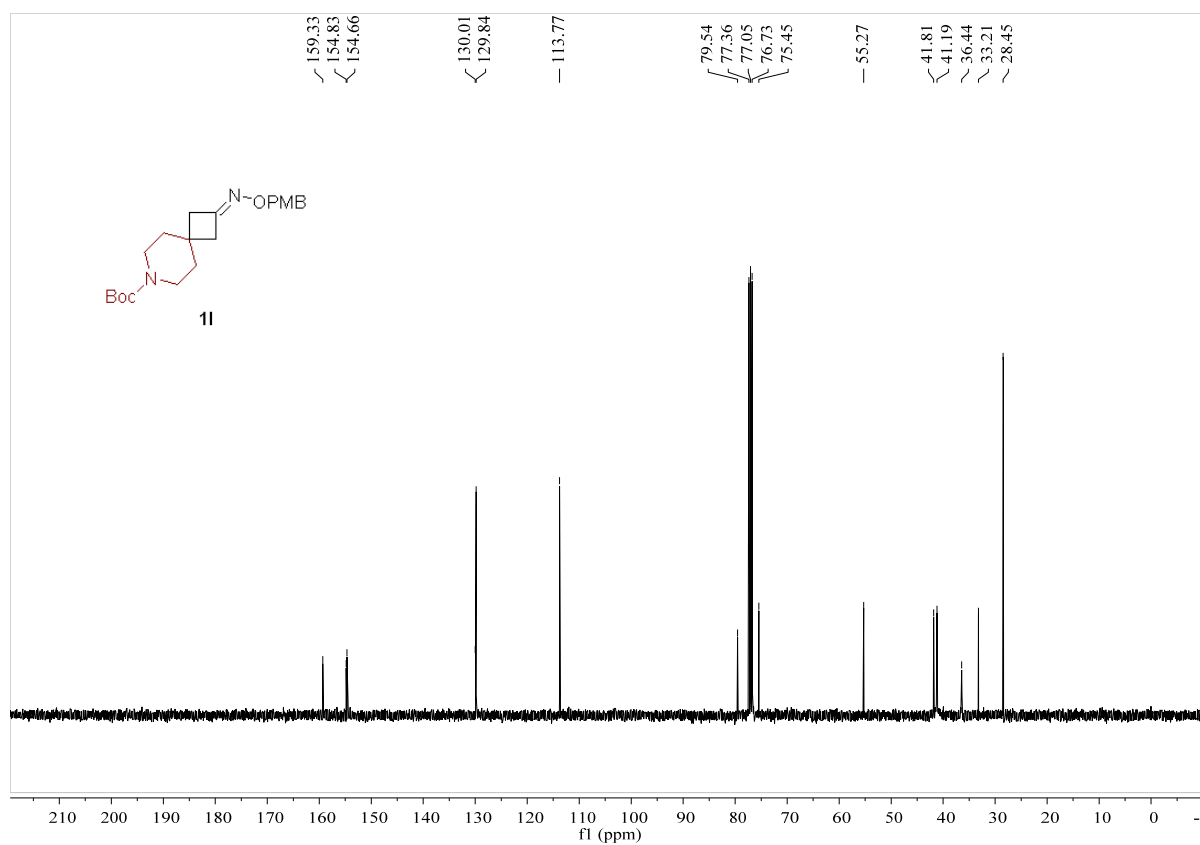
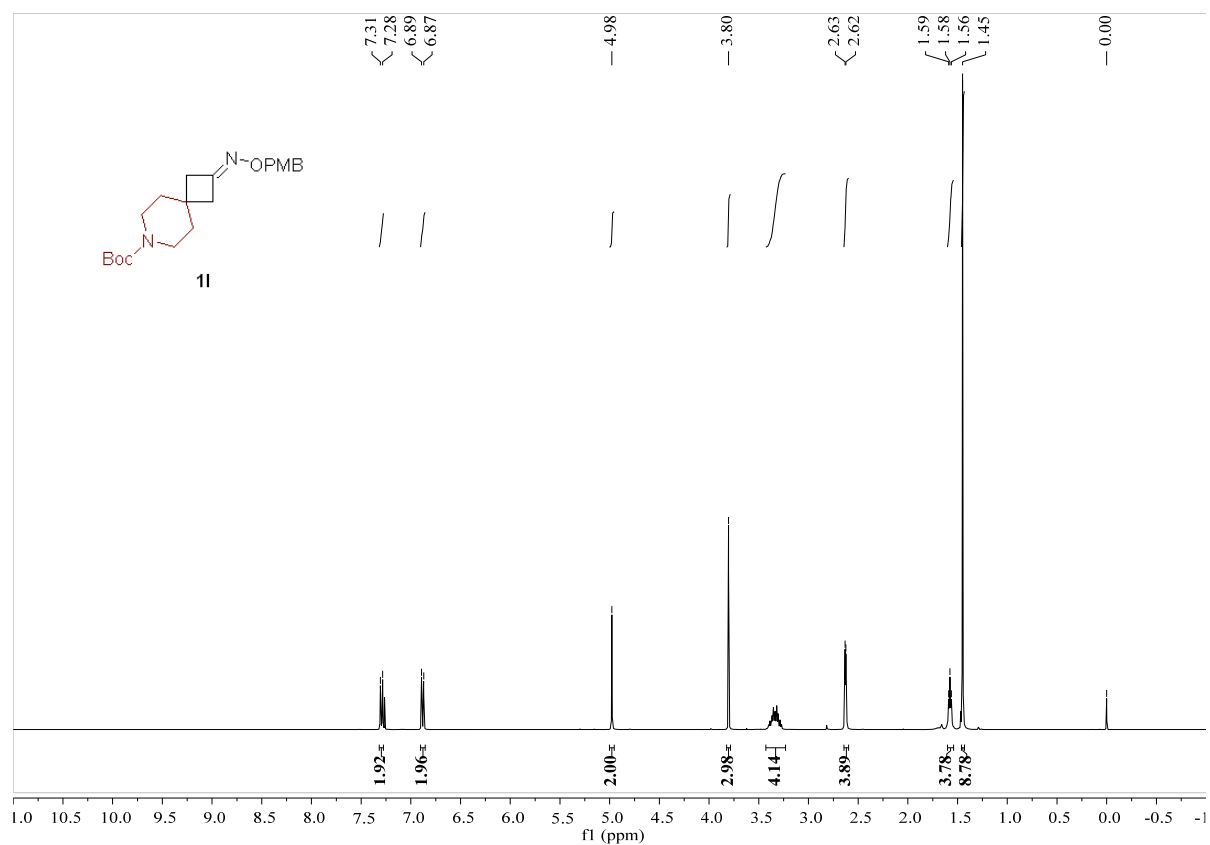
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1j**



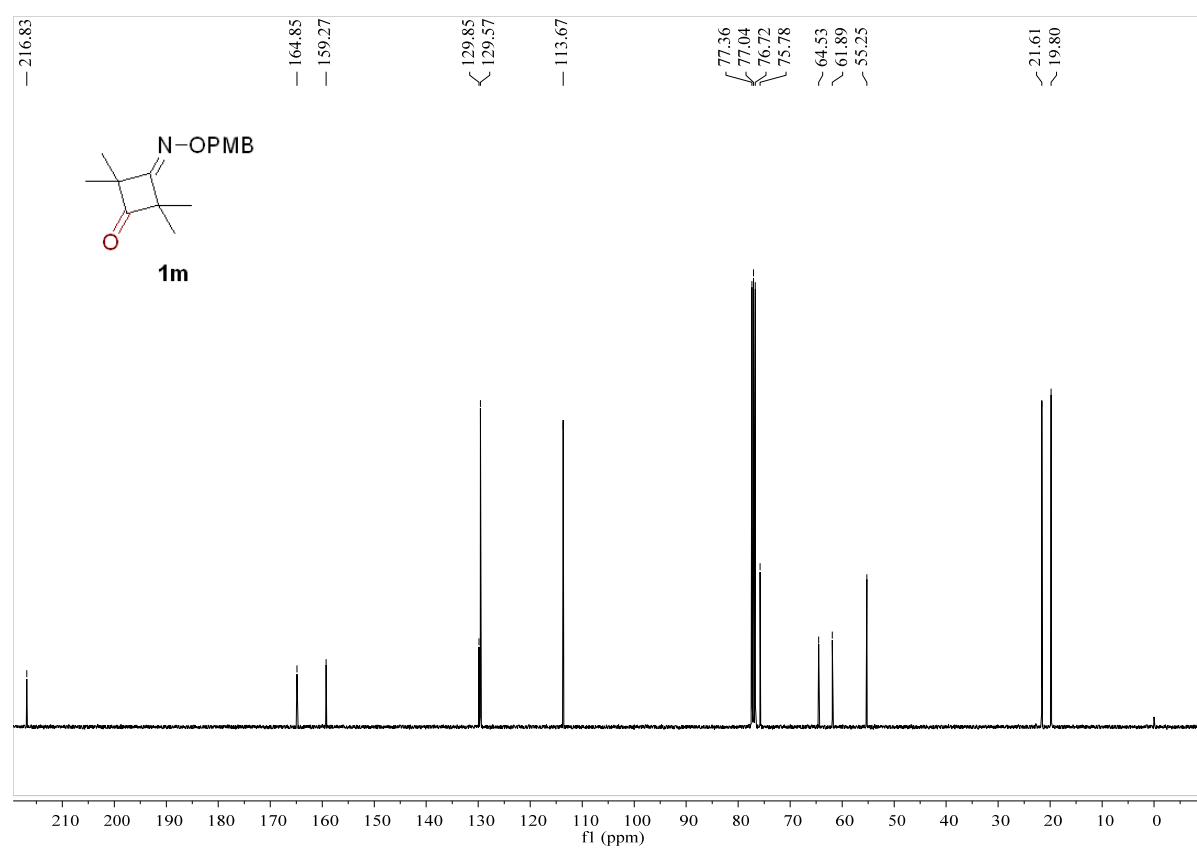
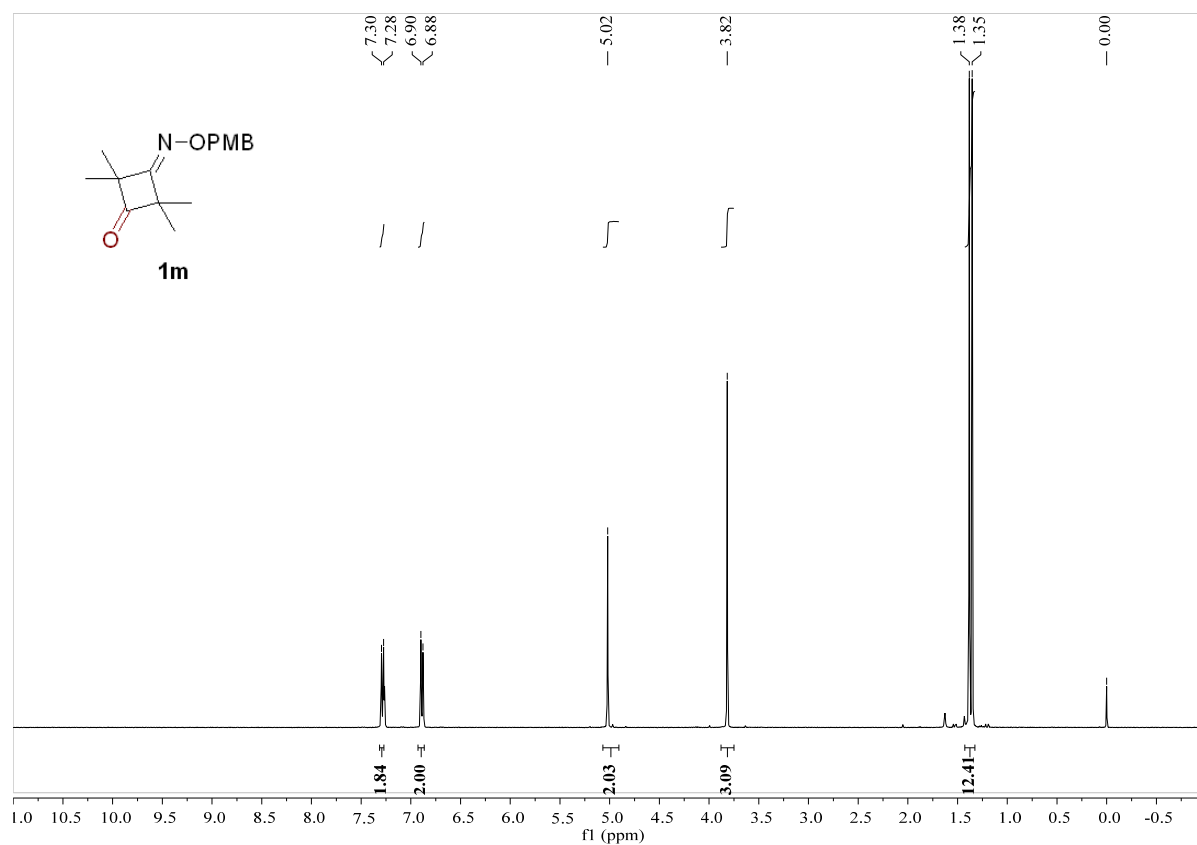
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate **1k**



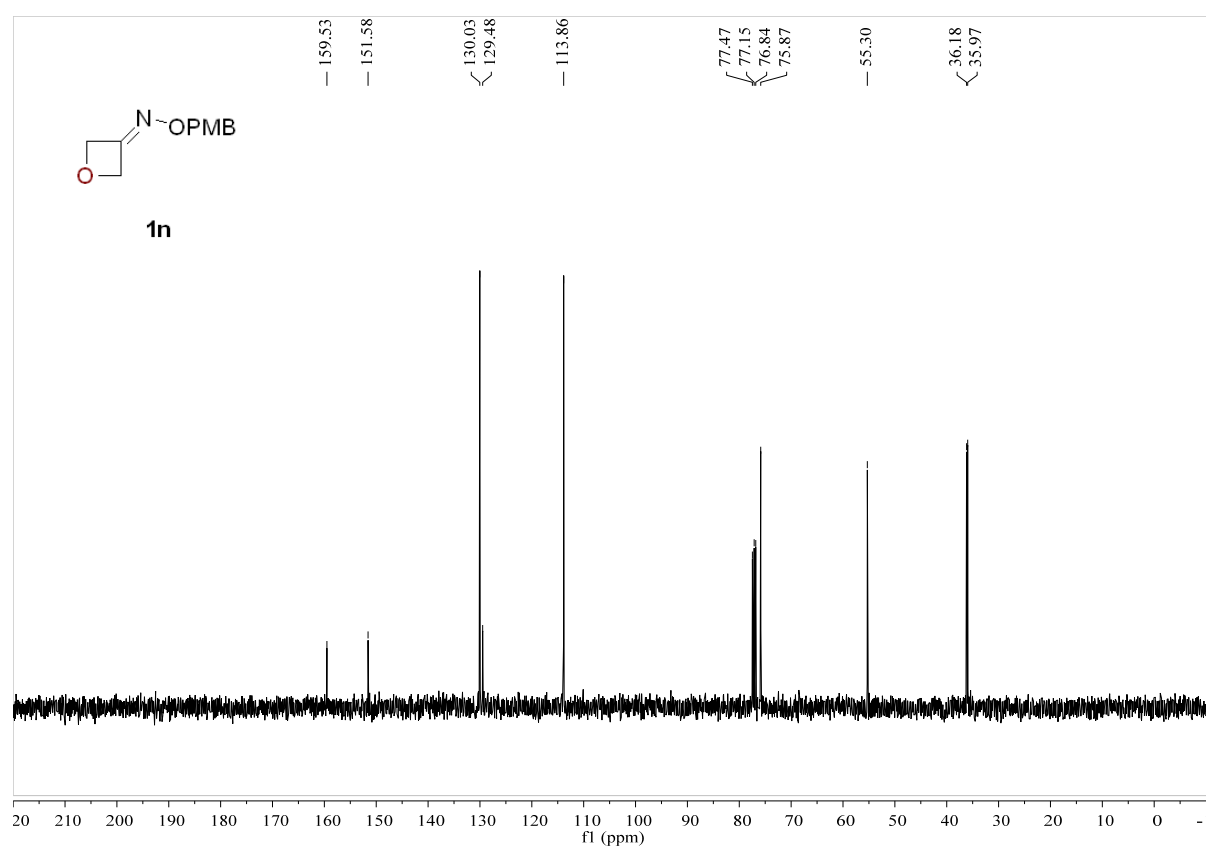
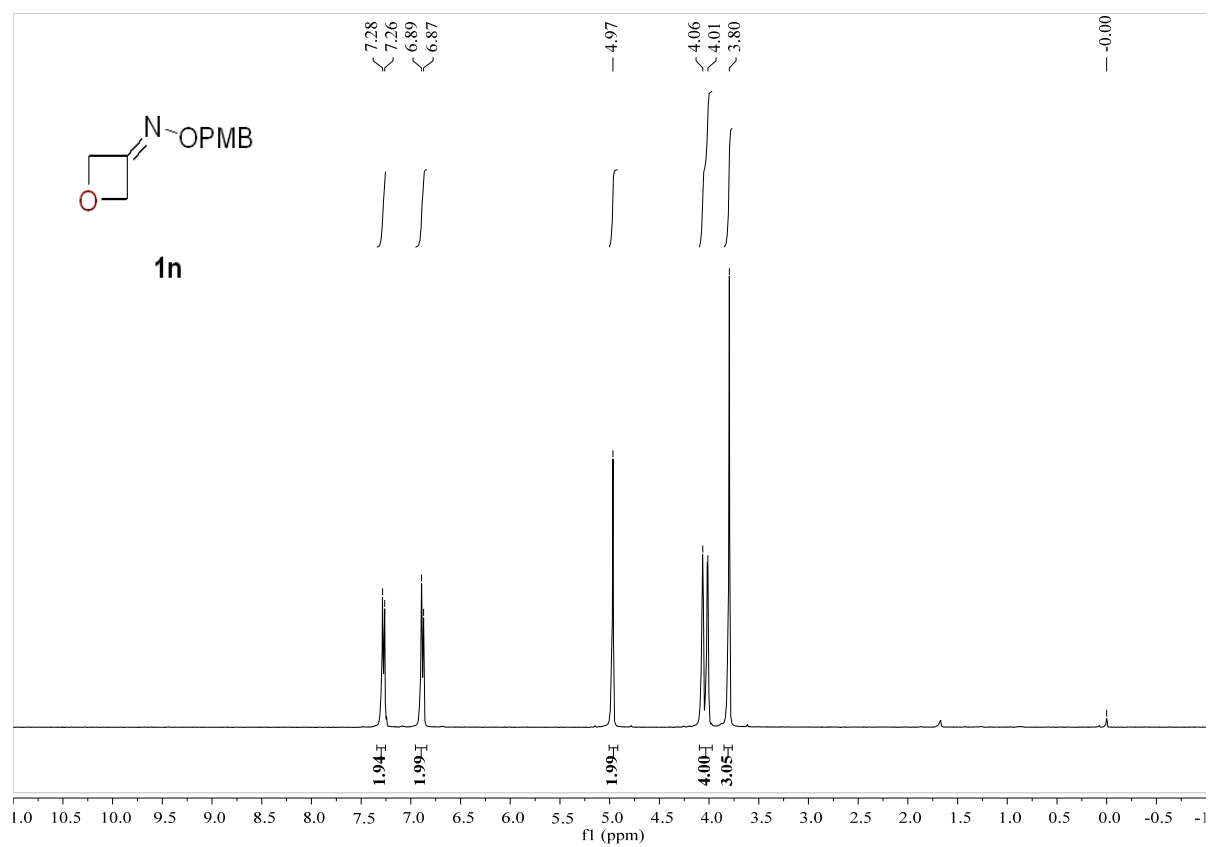
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate 11



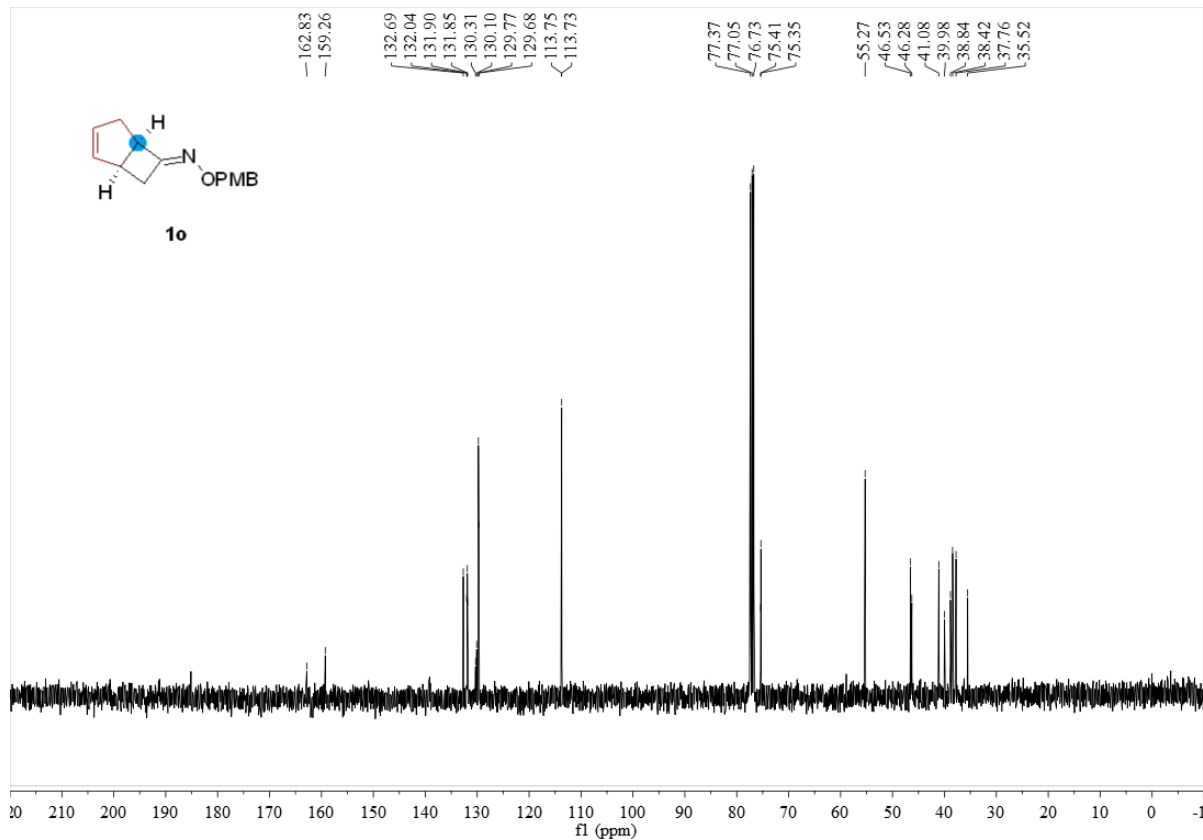
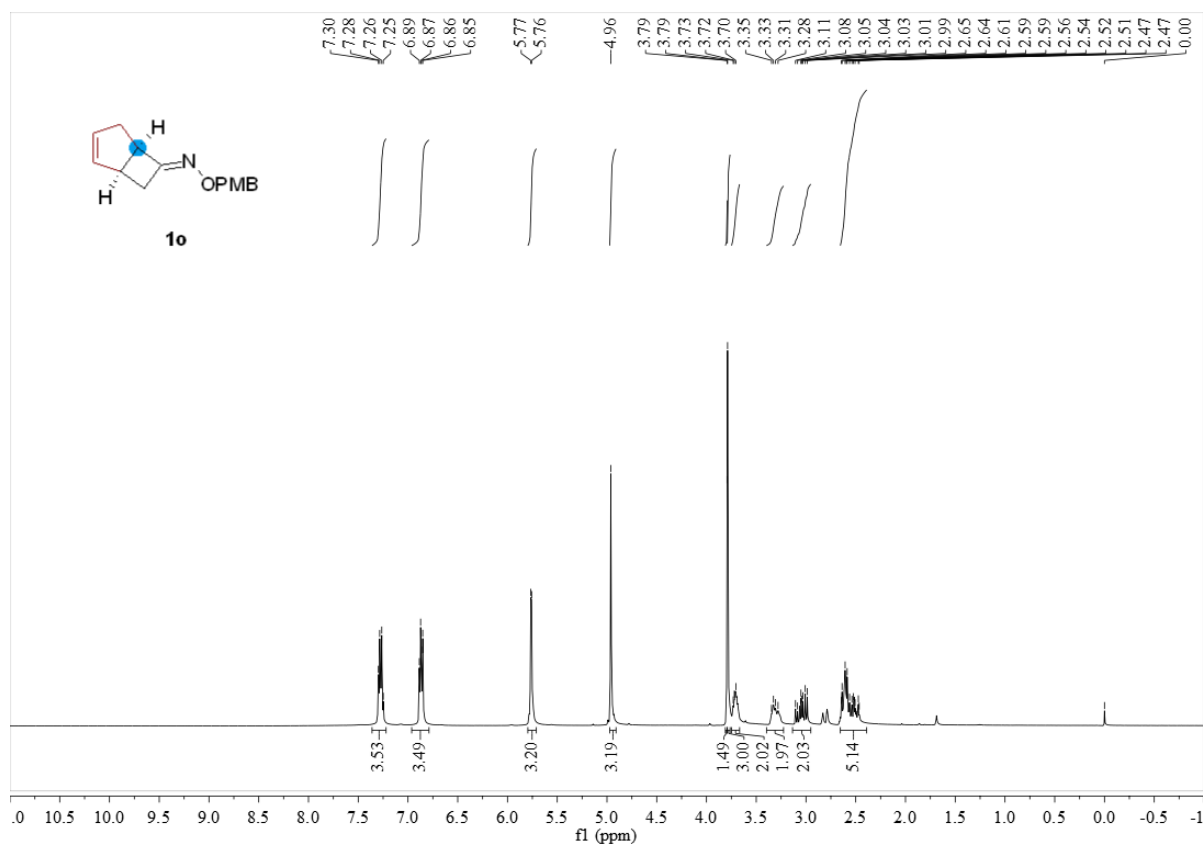
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1m**



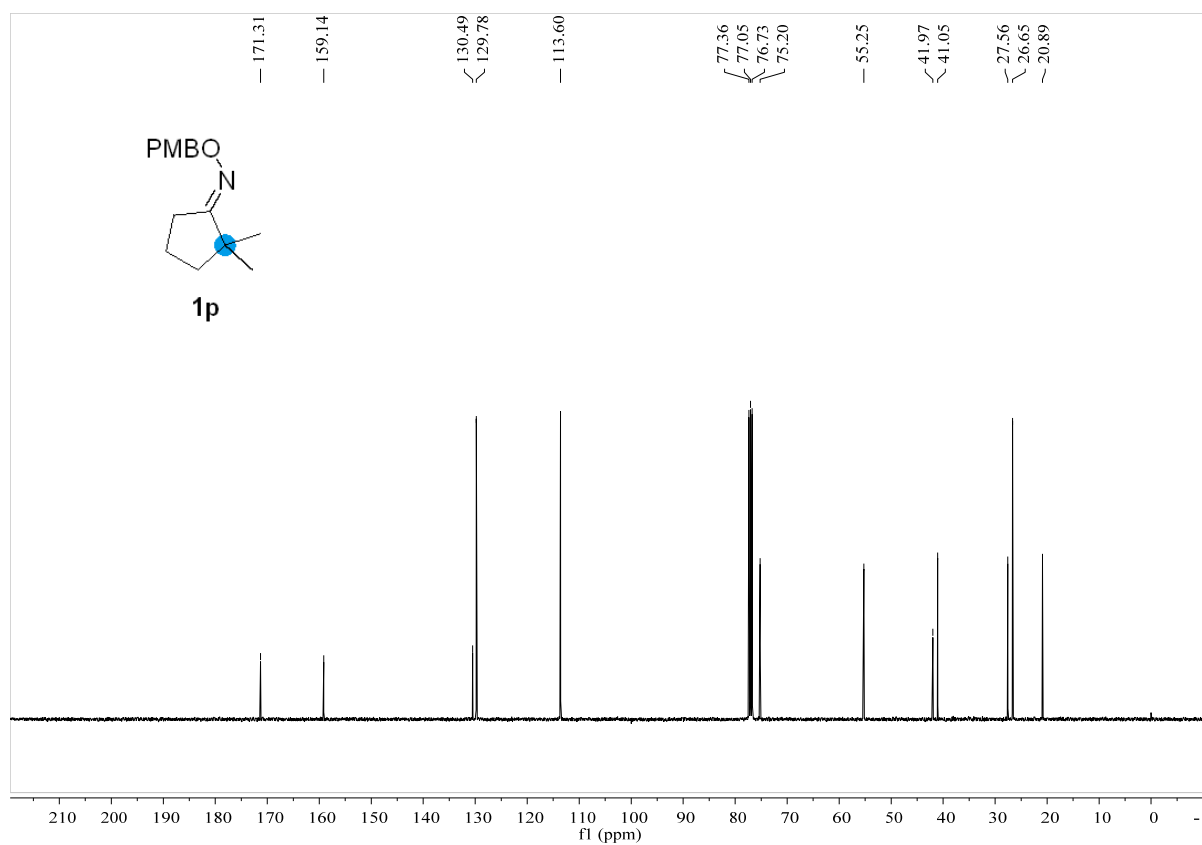
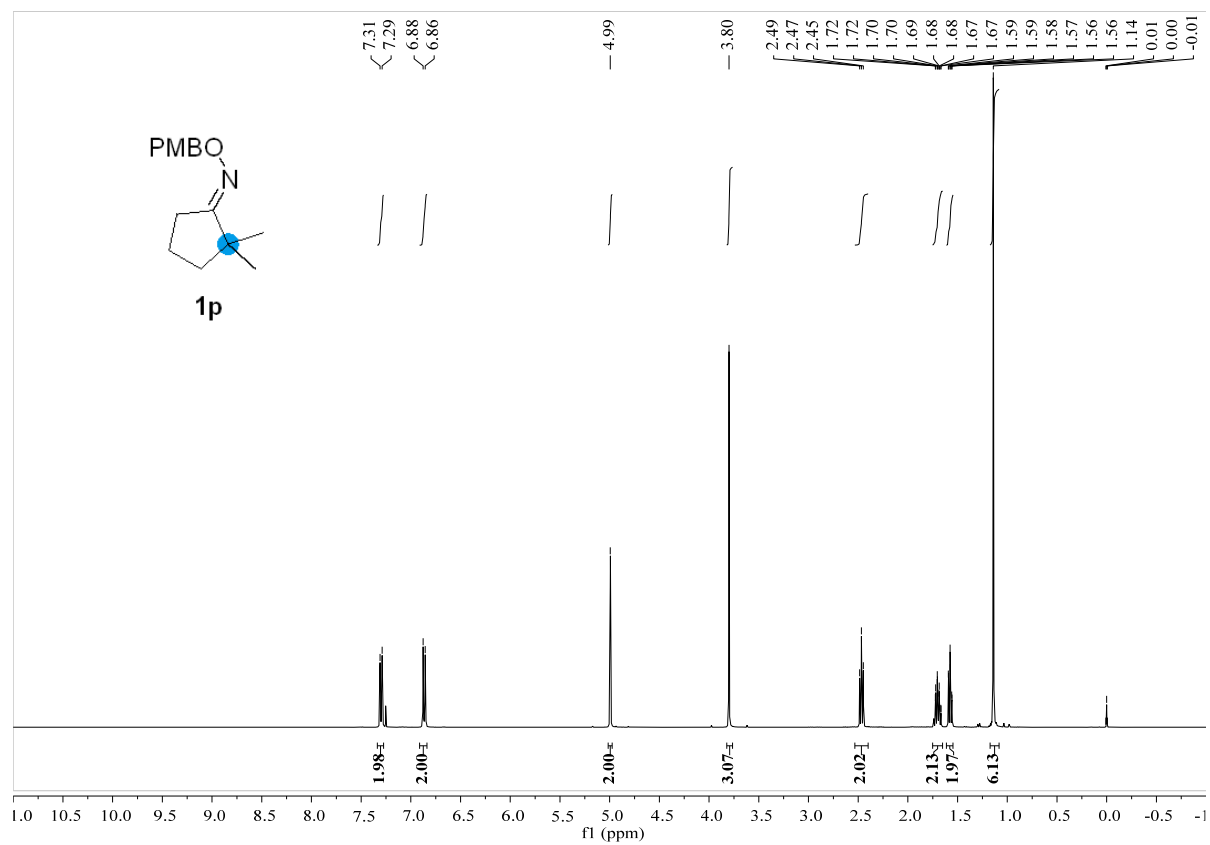
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate **1n**



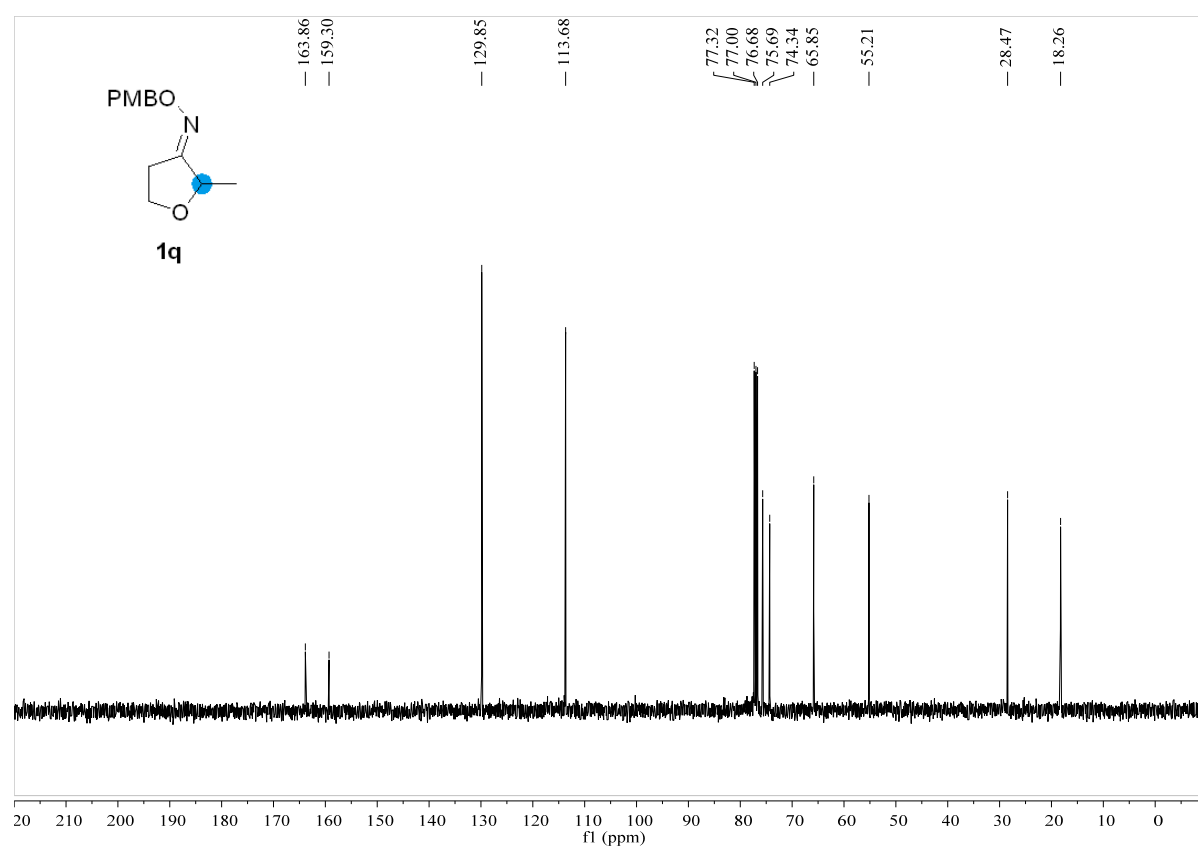
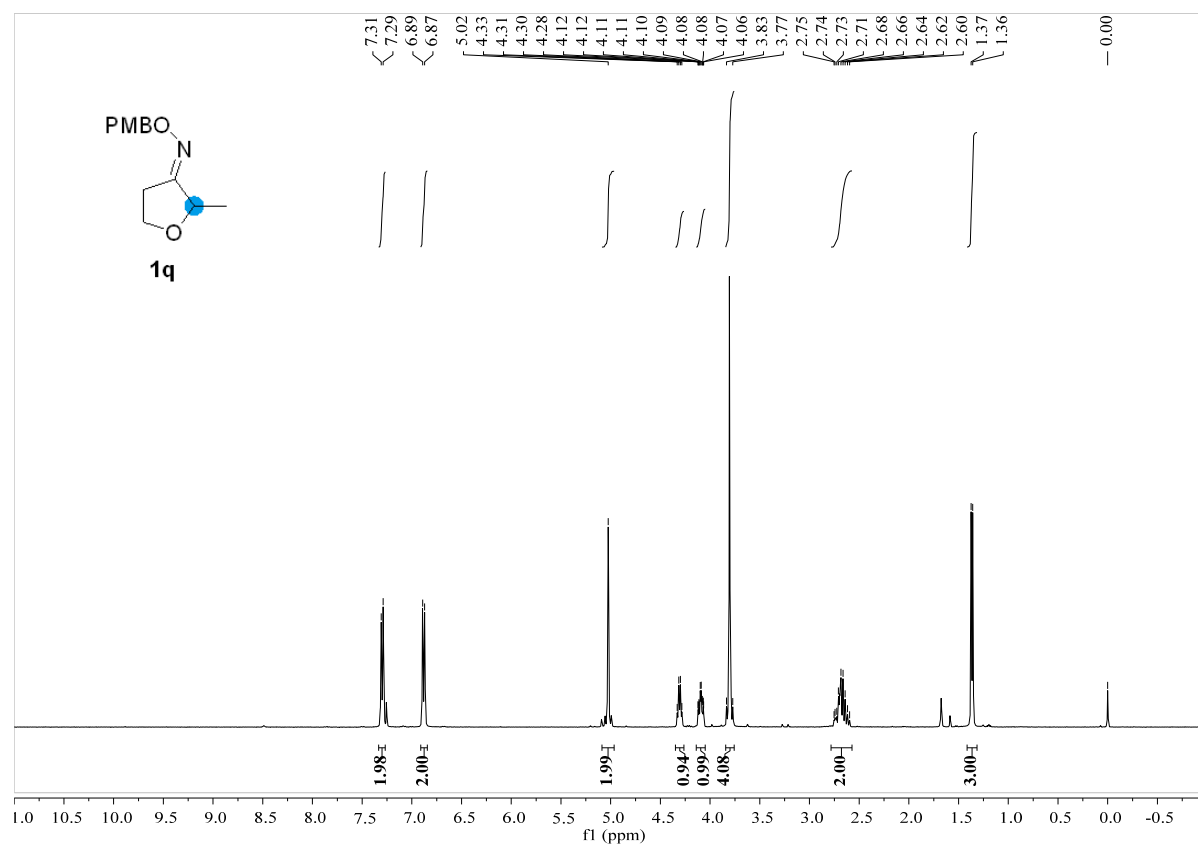
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of substrate **1o**



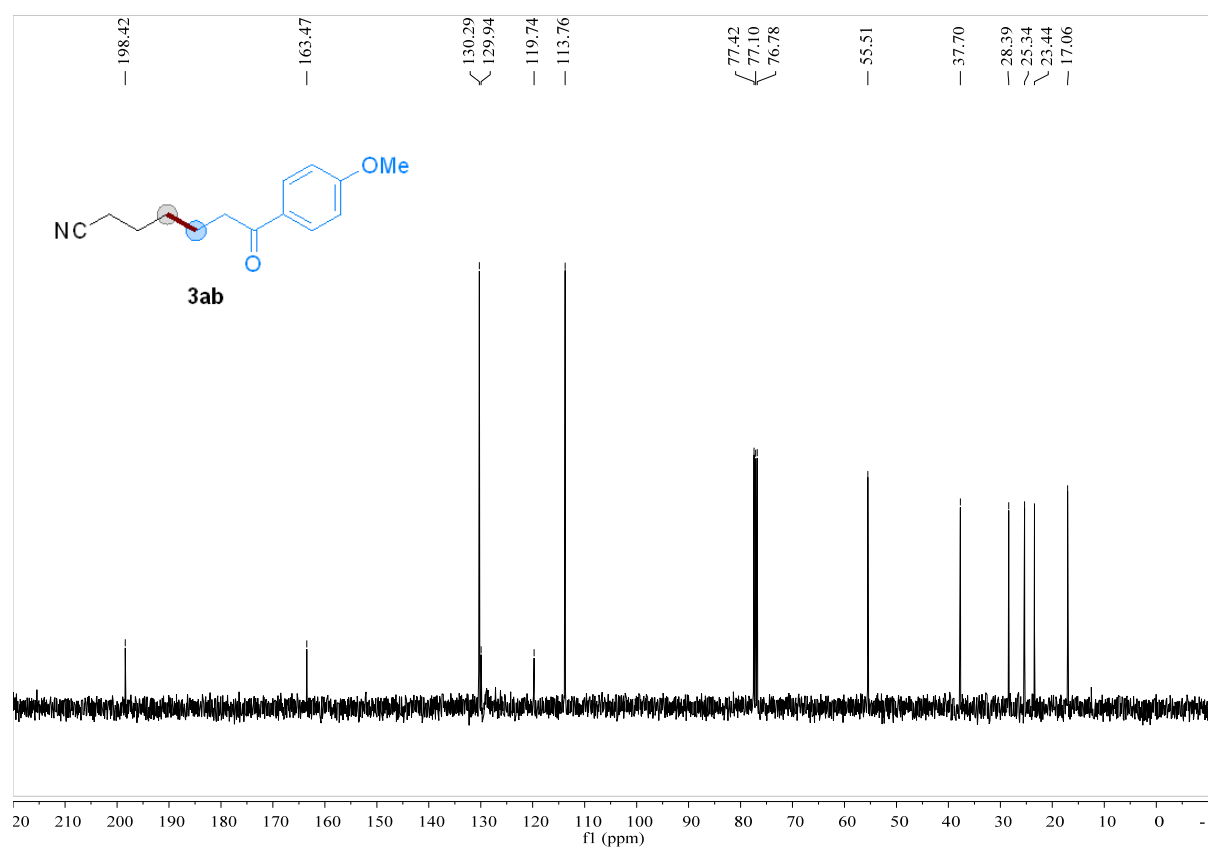
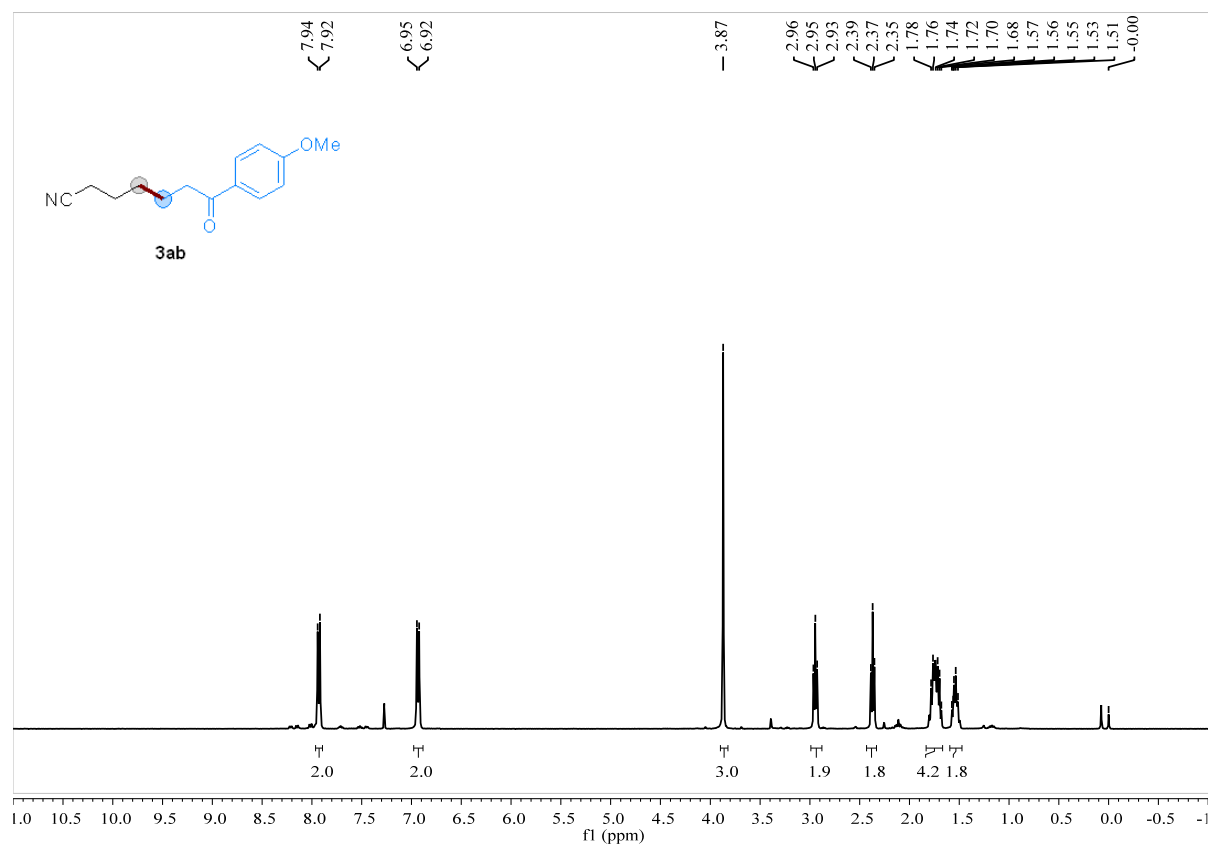
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1p**



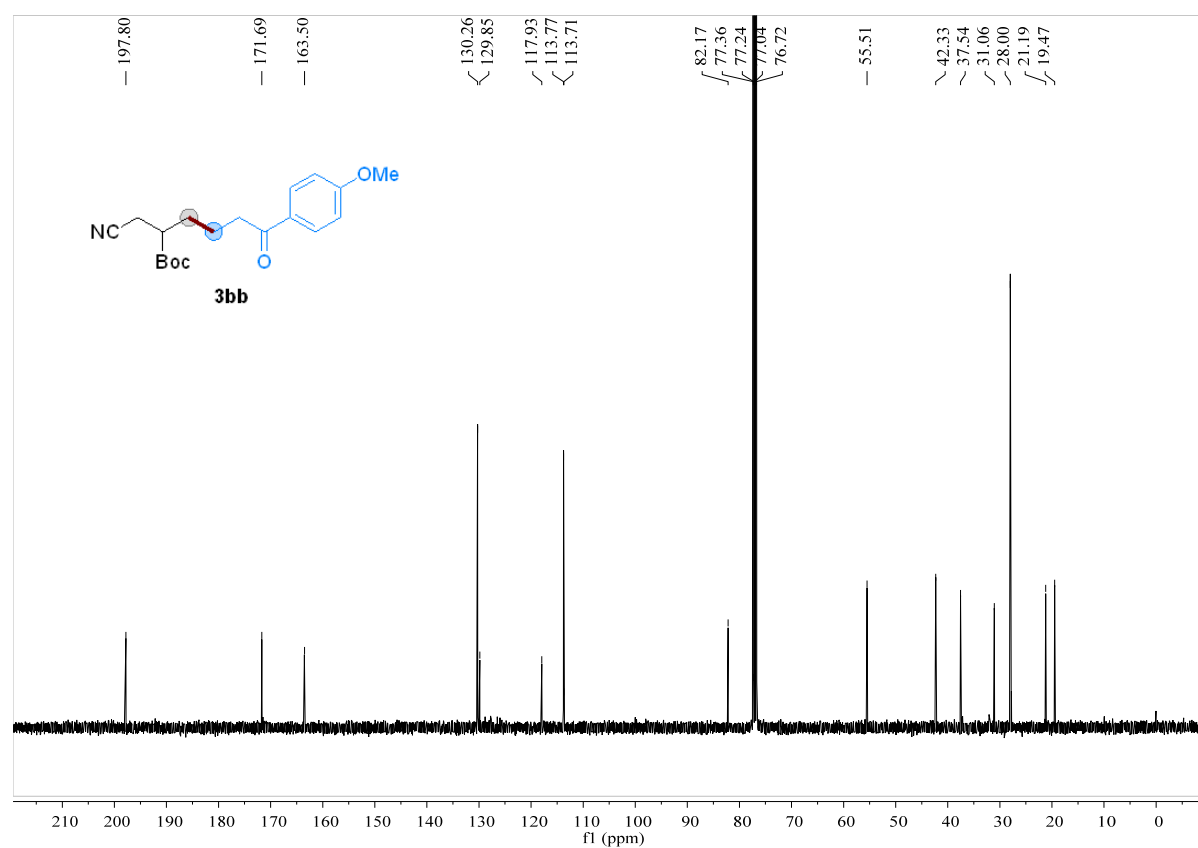
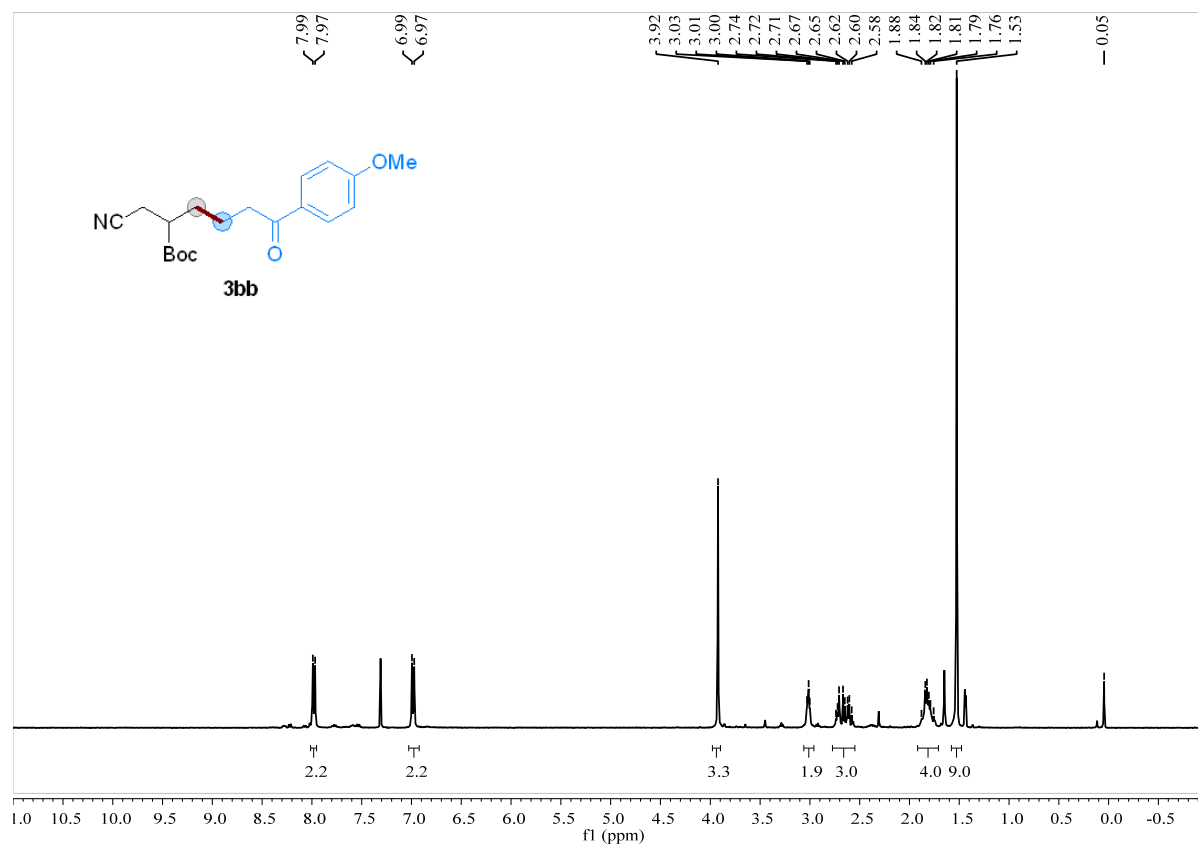
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of substrate **1q**



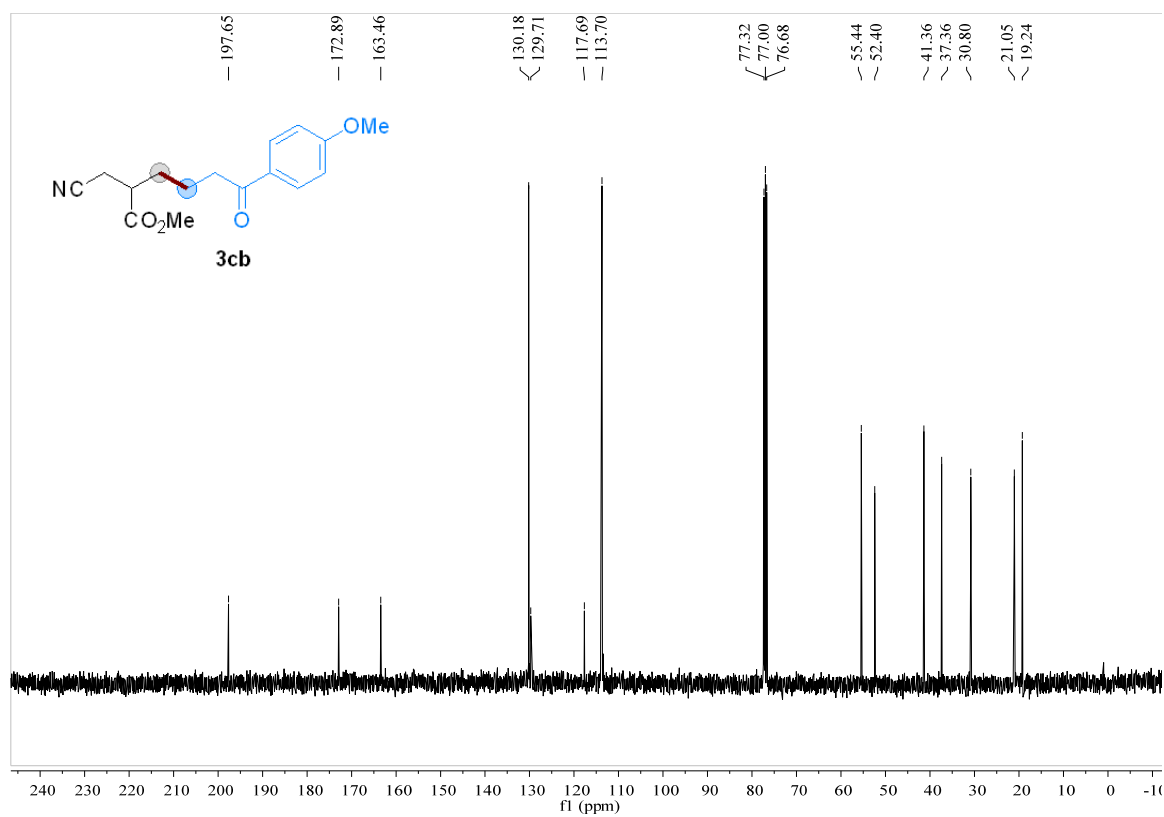
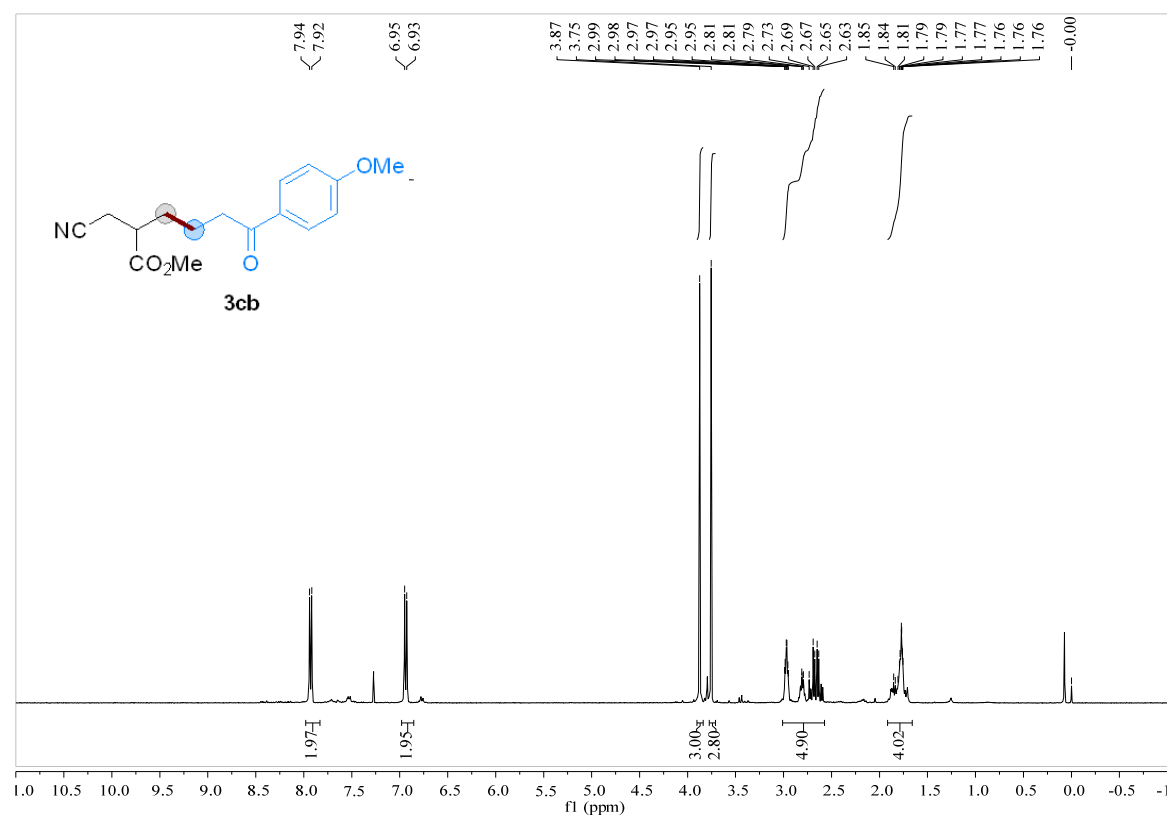
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3ab**



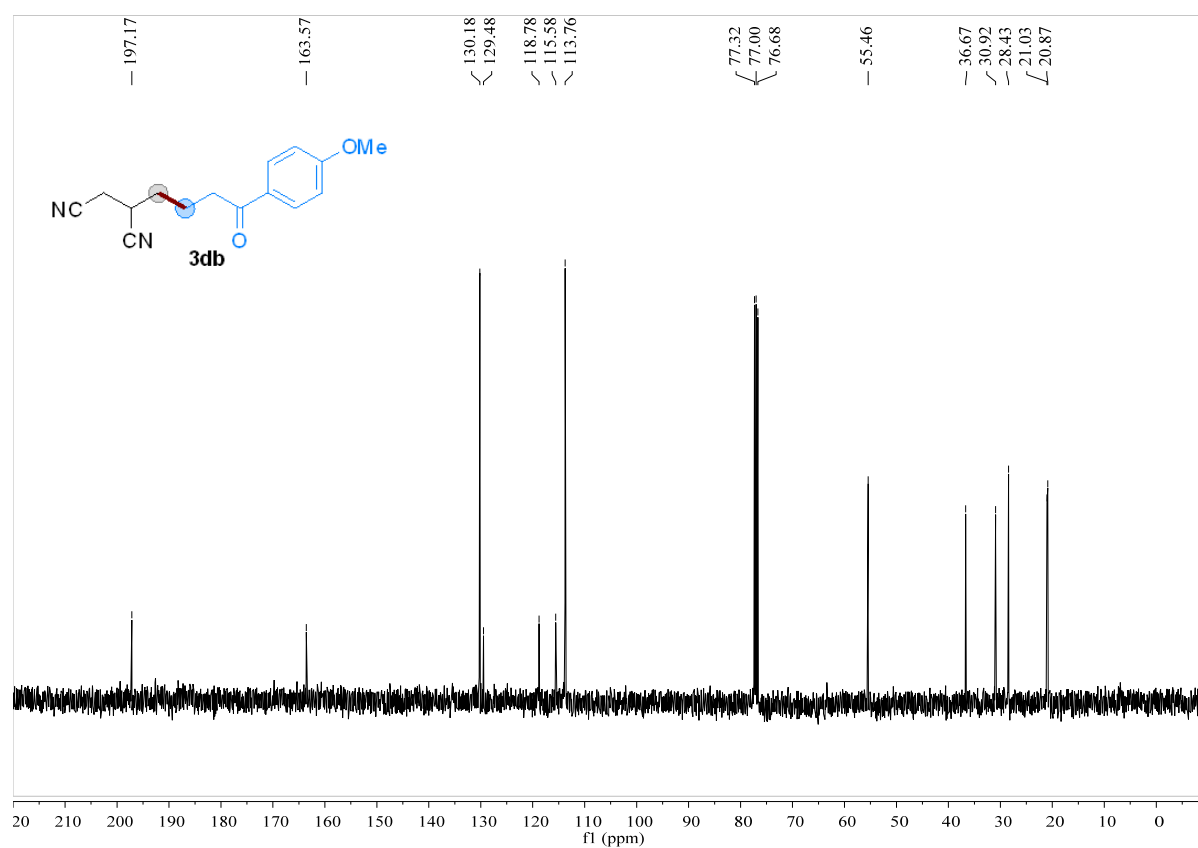
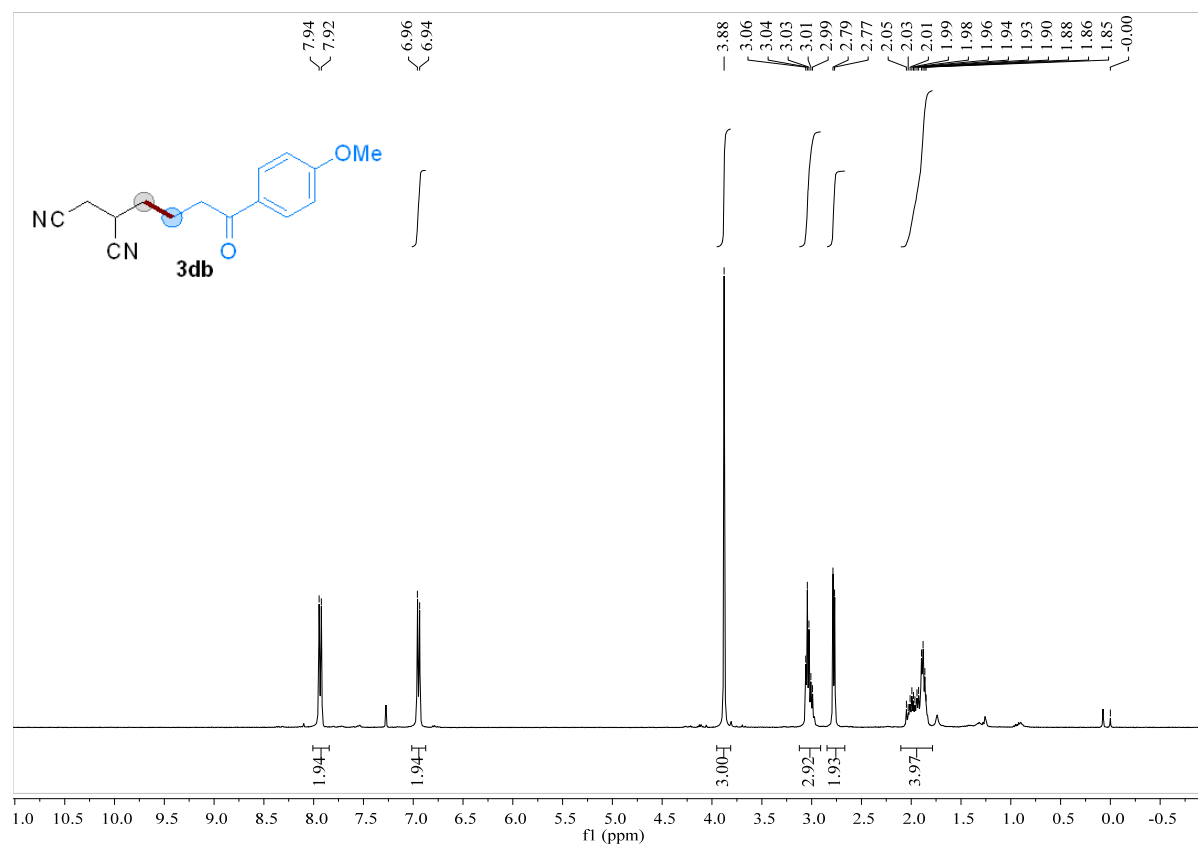
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3bb**



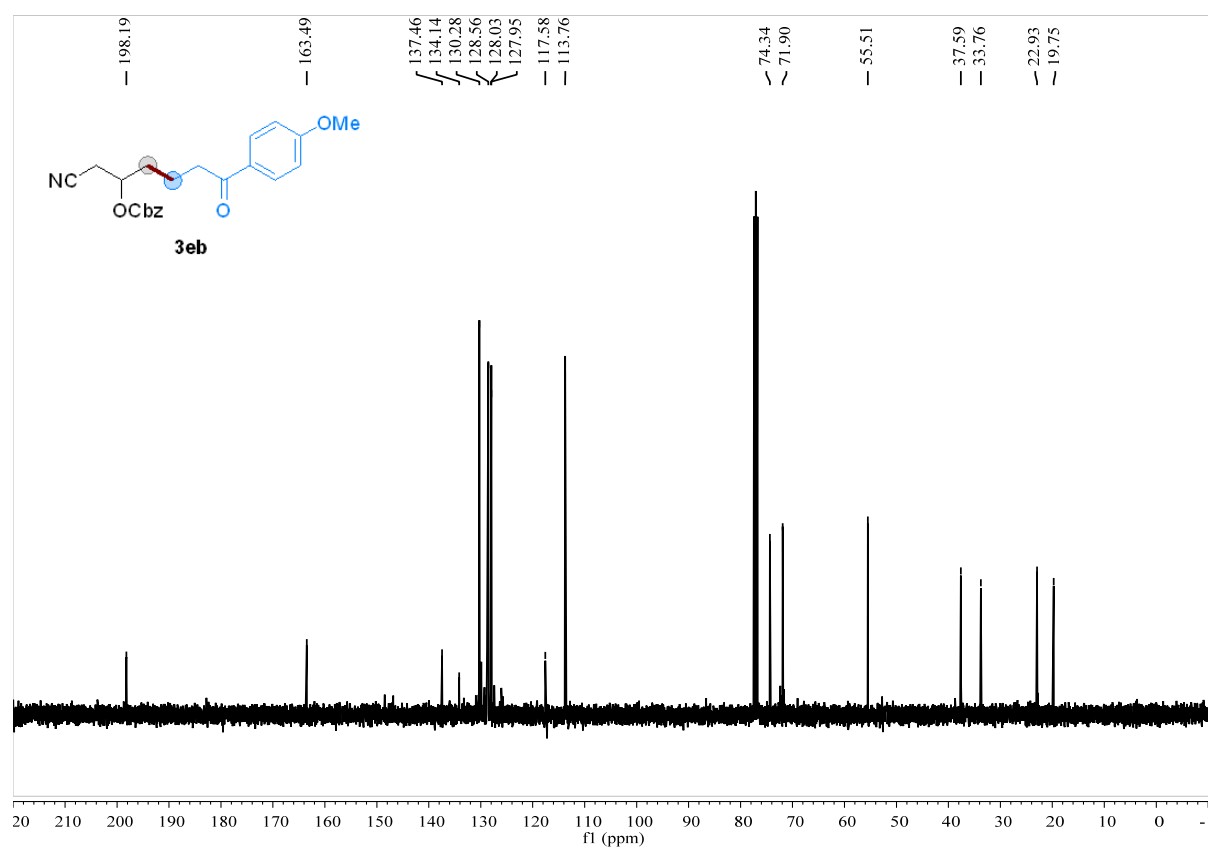
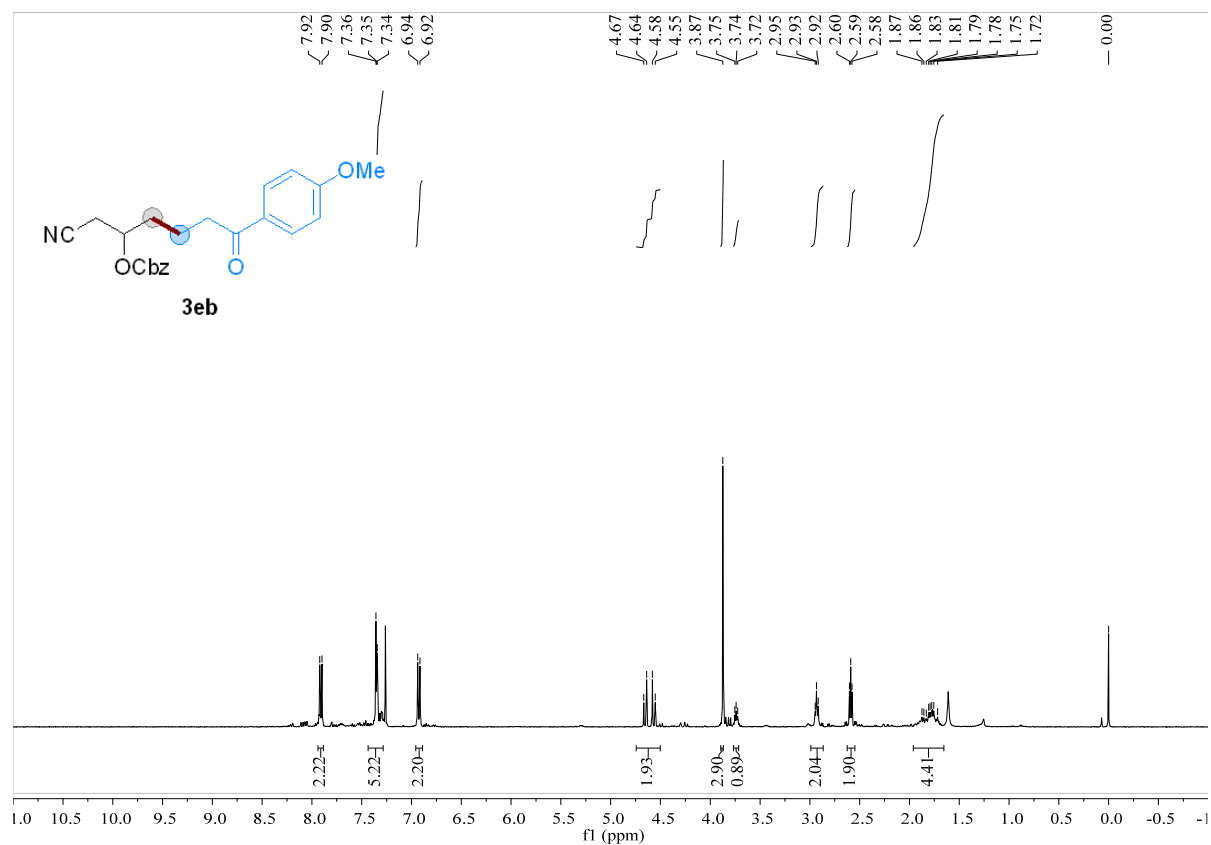
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3cb**



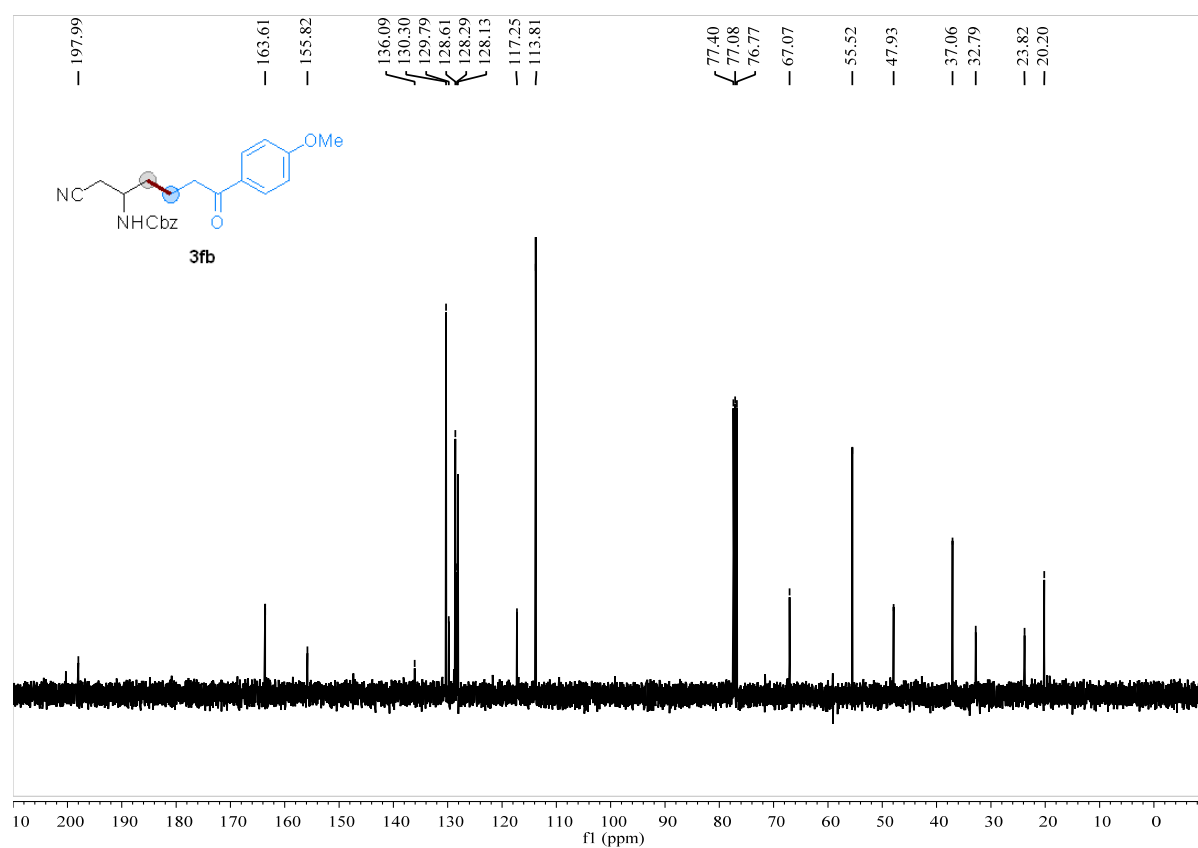
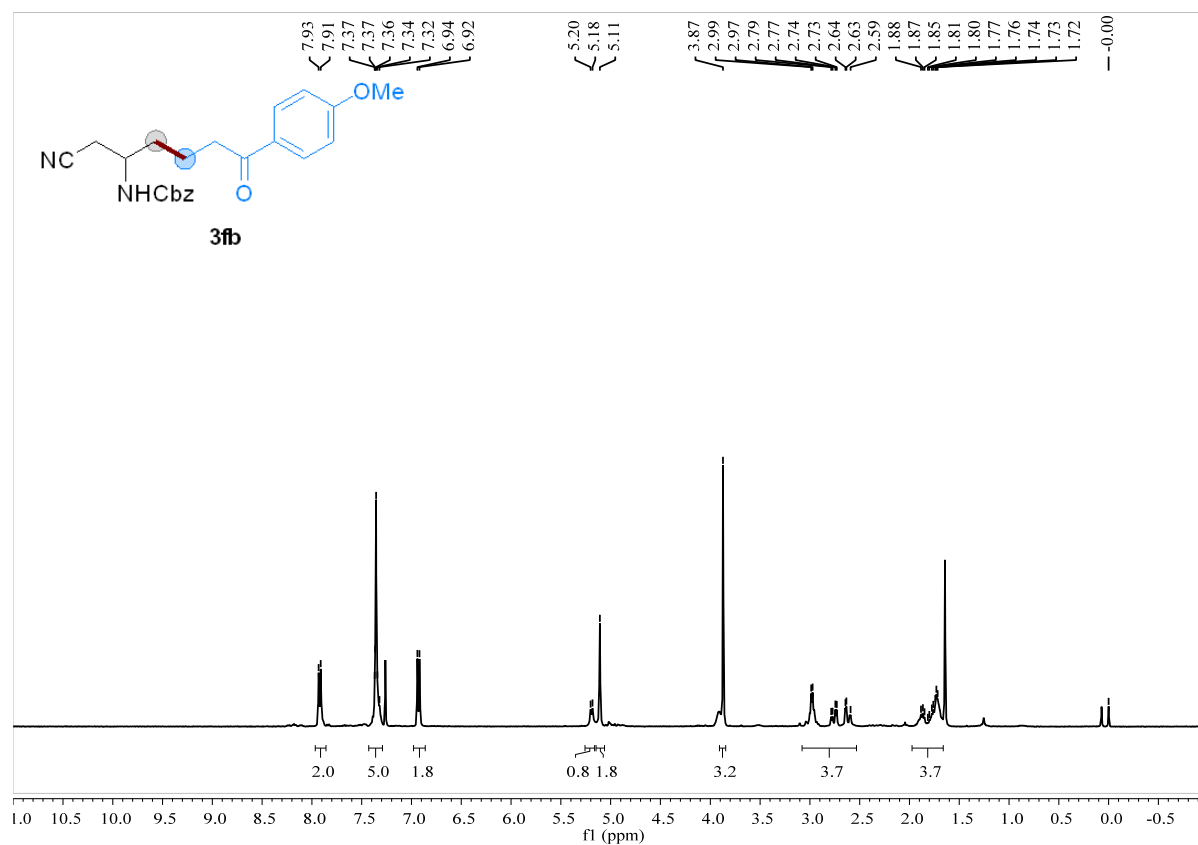
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3db**



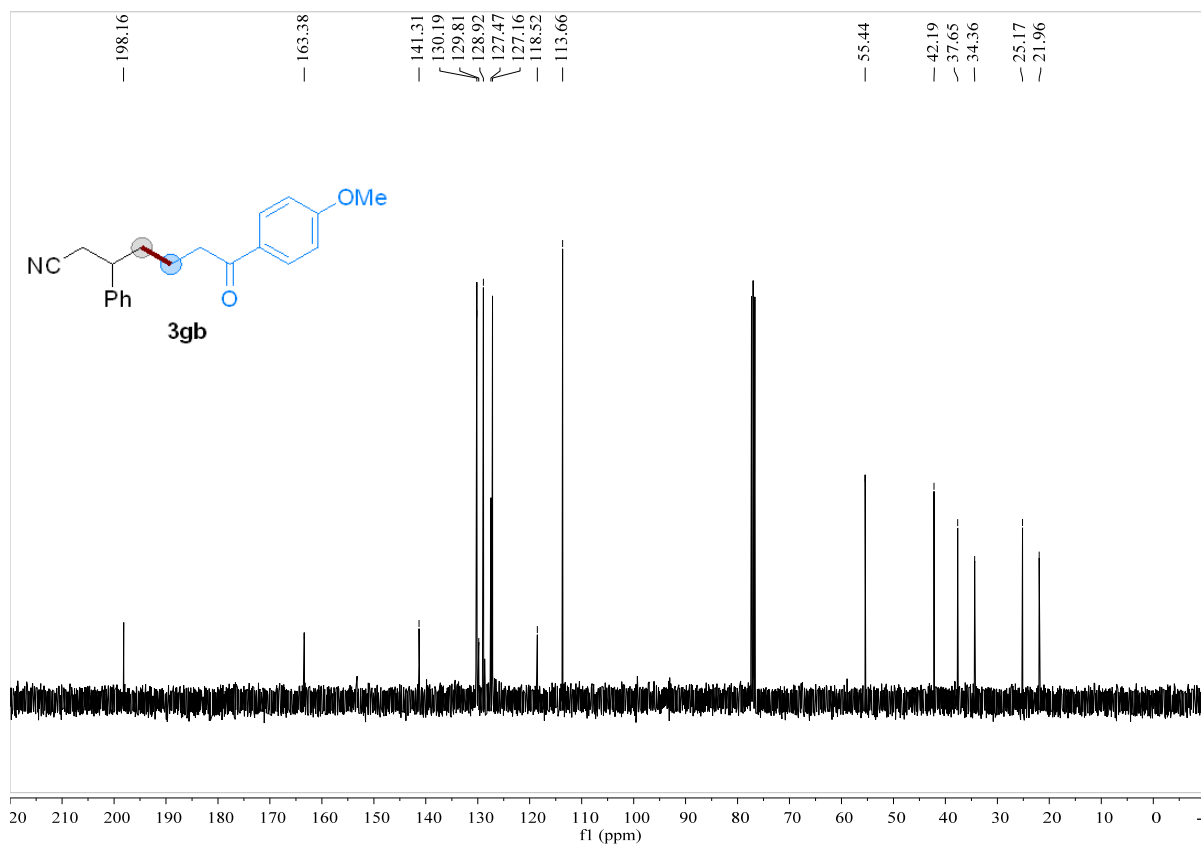
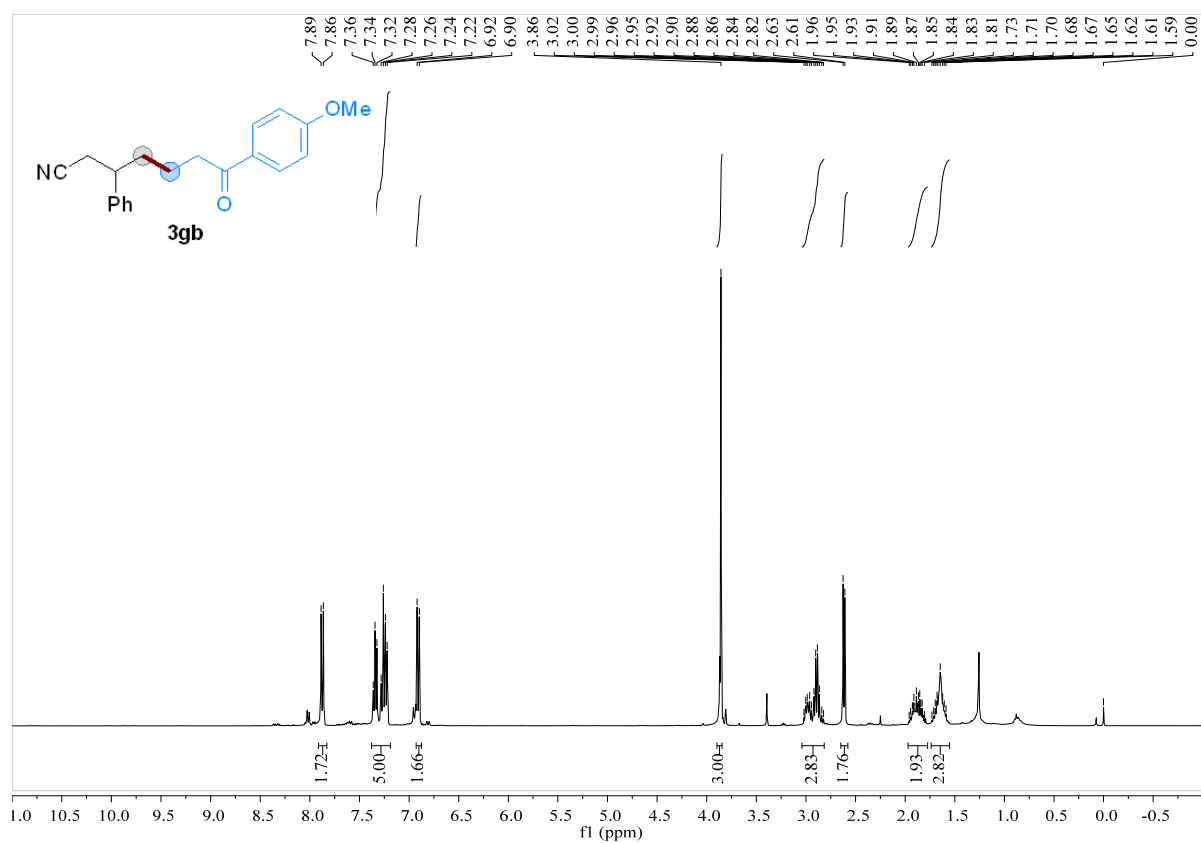
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3eb



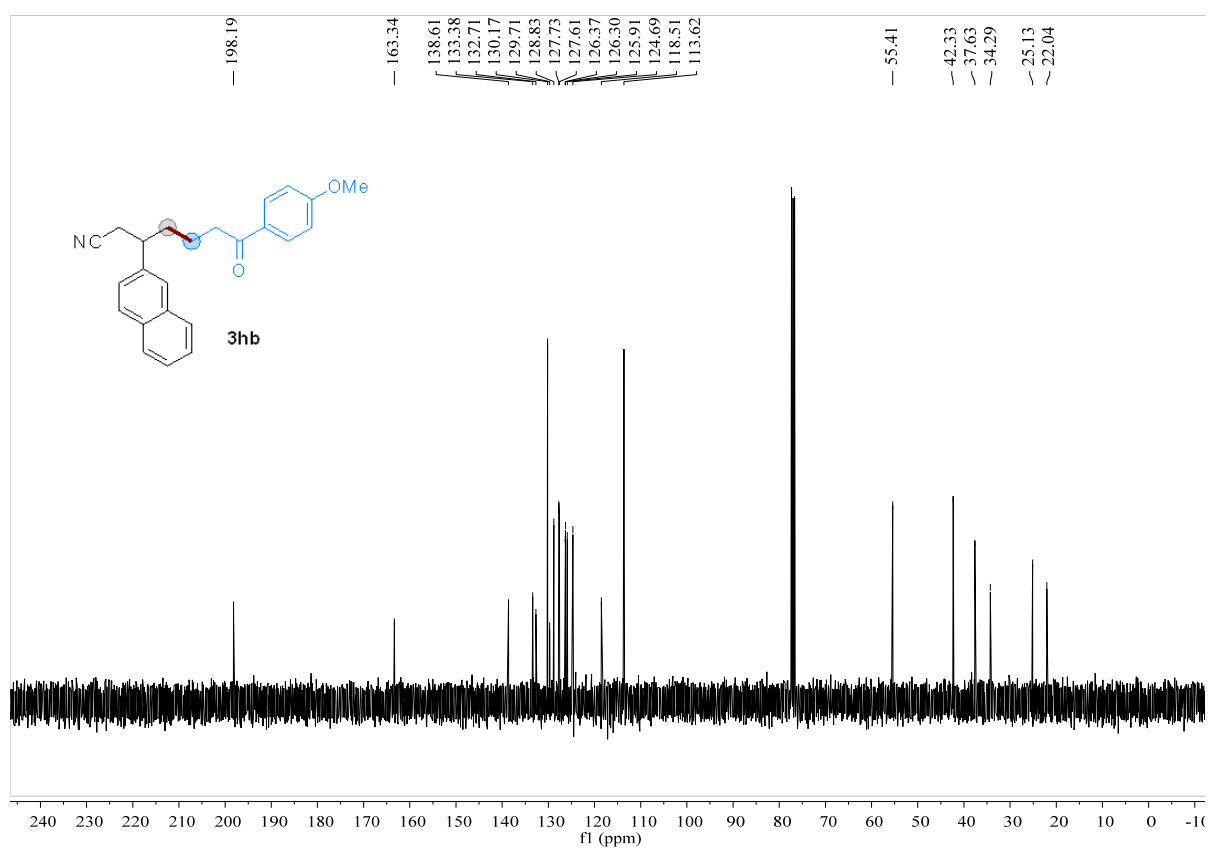
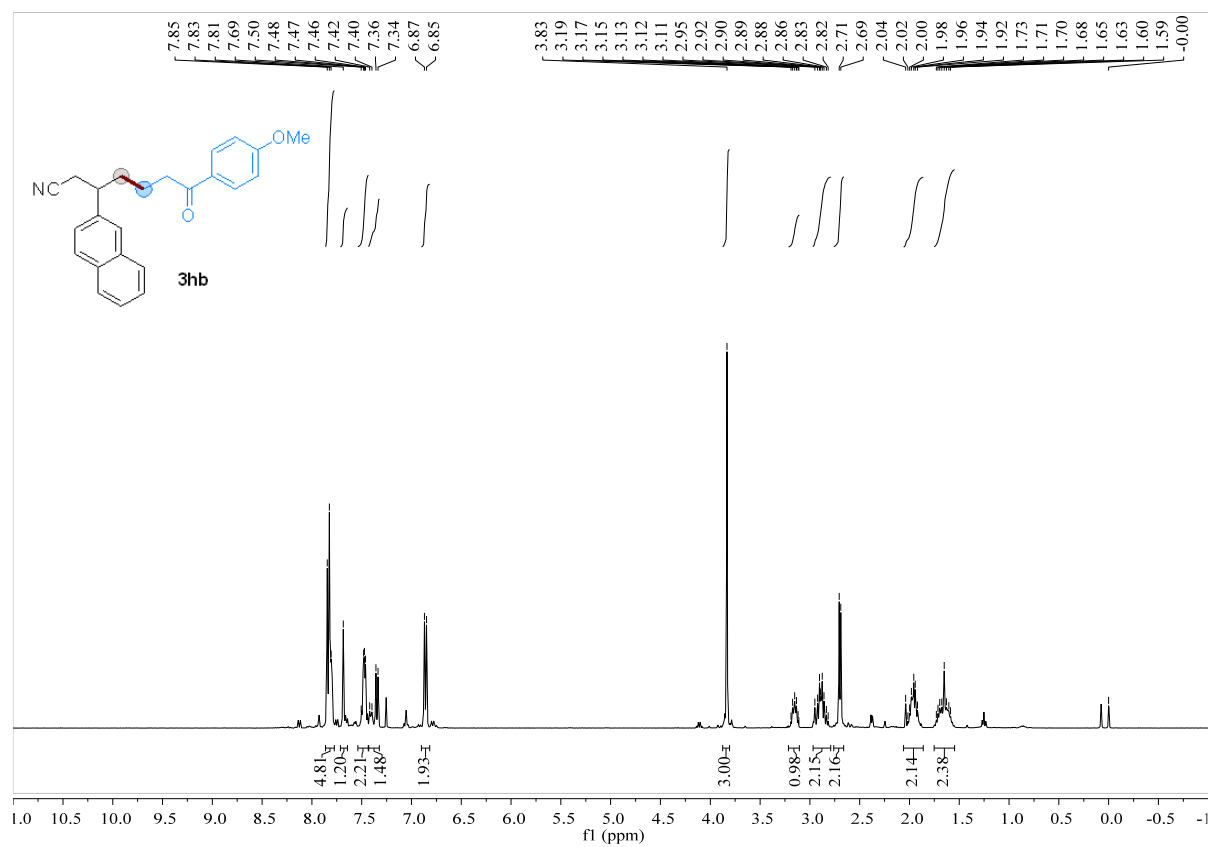
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3fb**



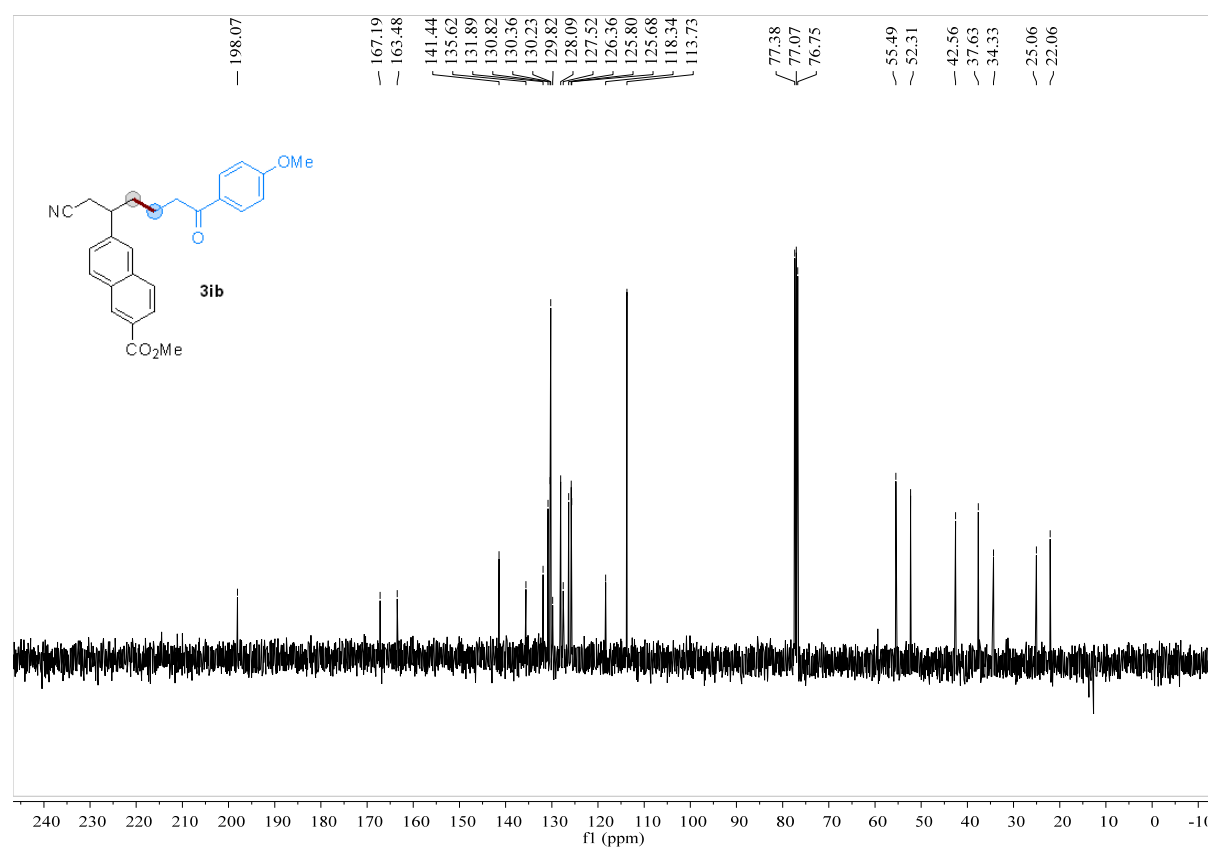
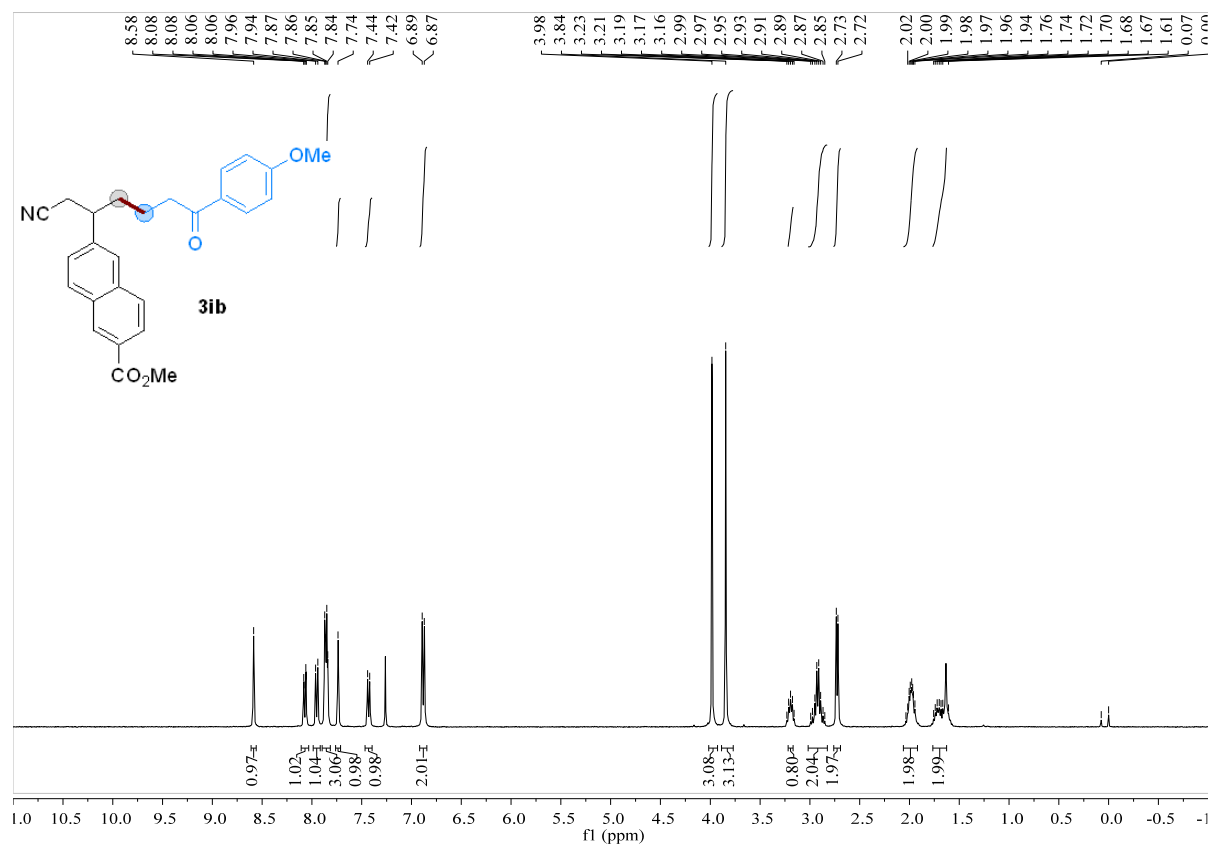
¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product **3gb**



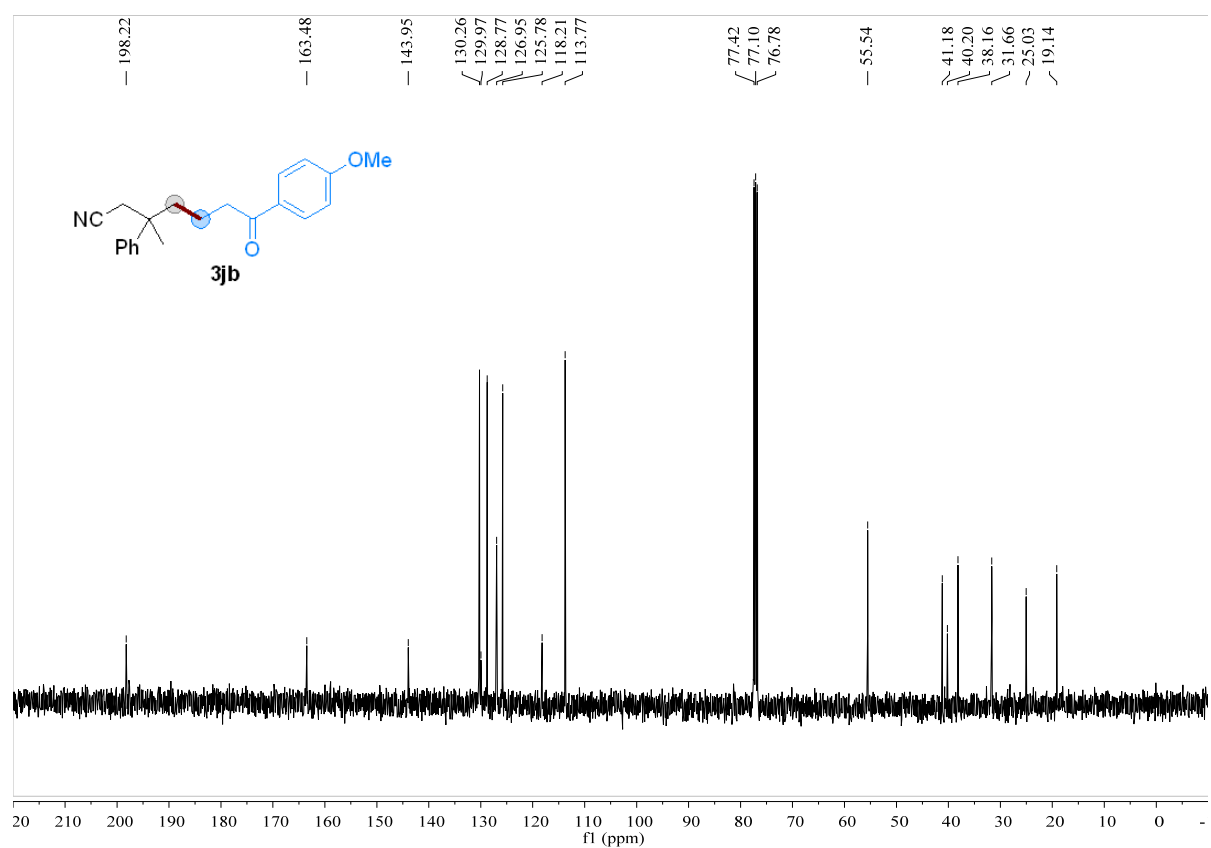
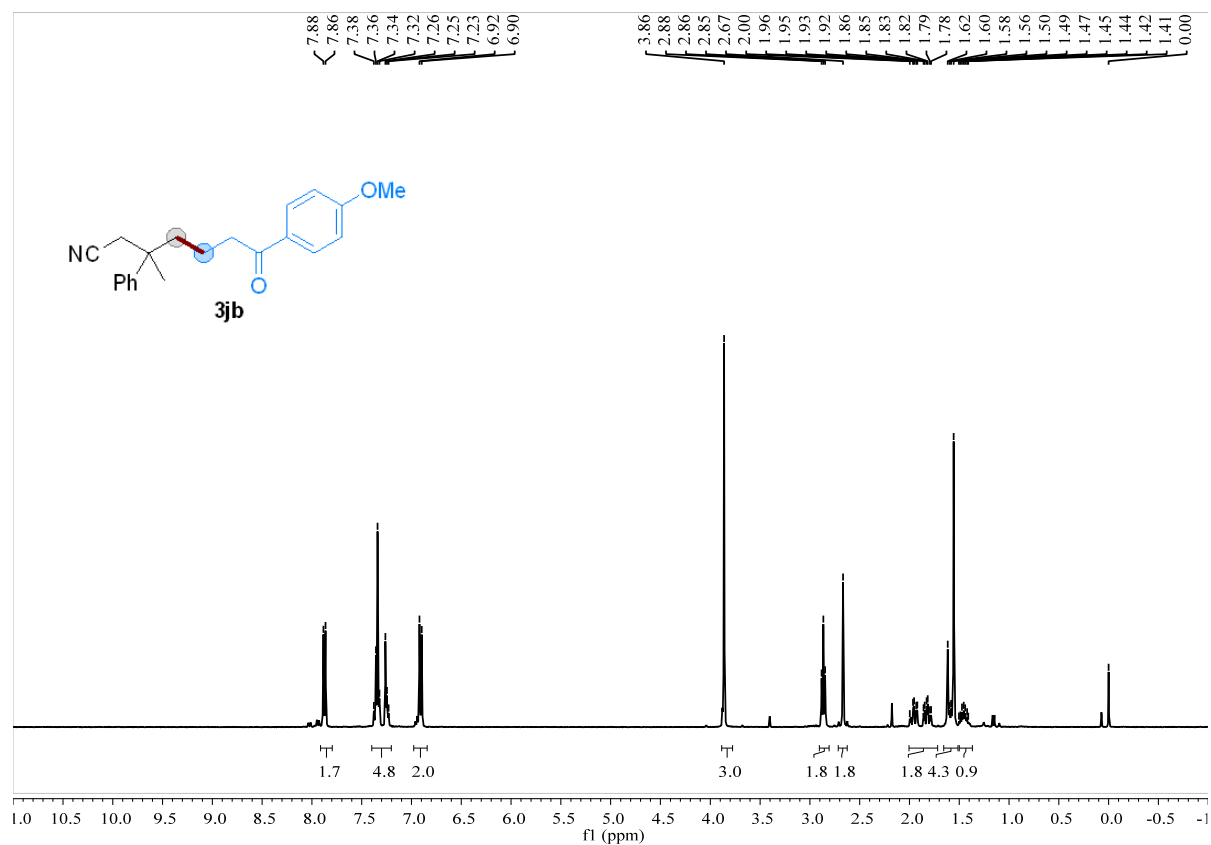
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3hb



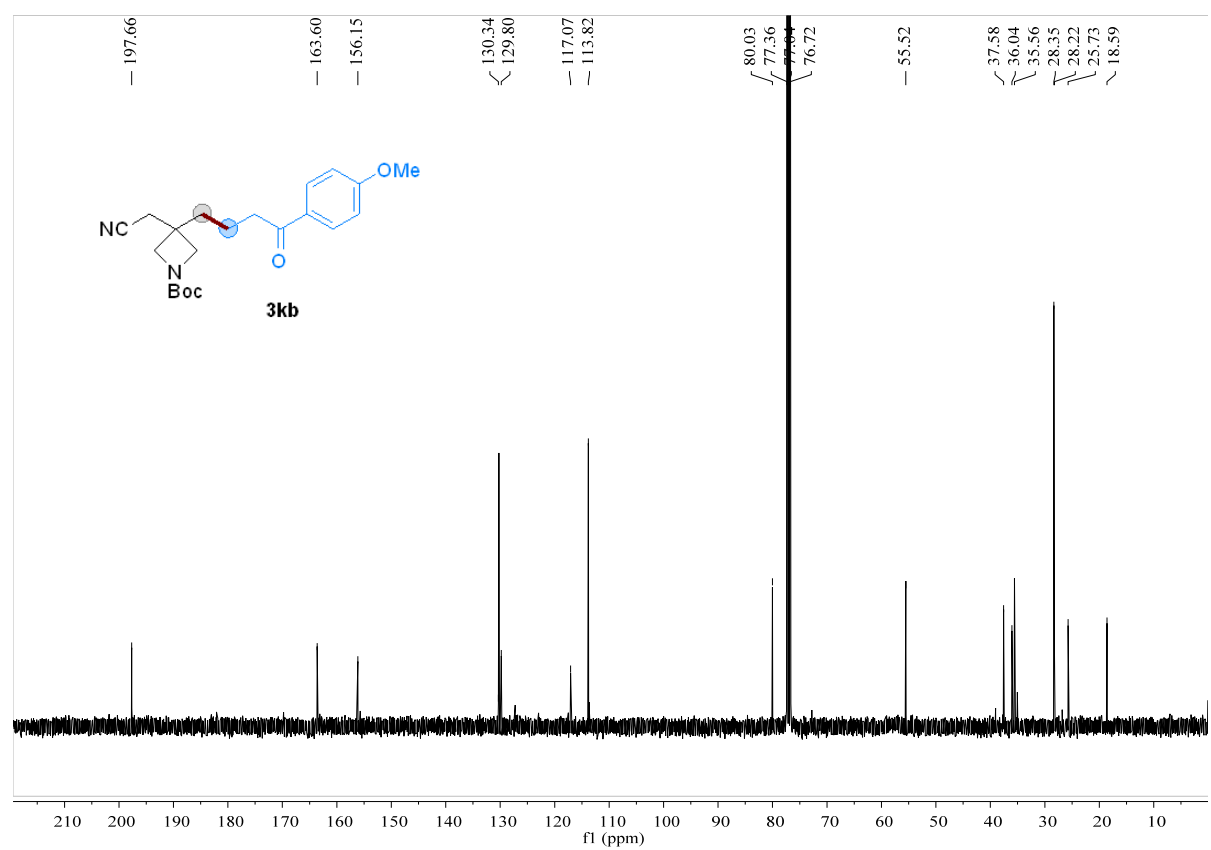
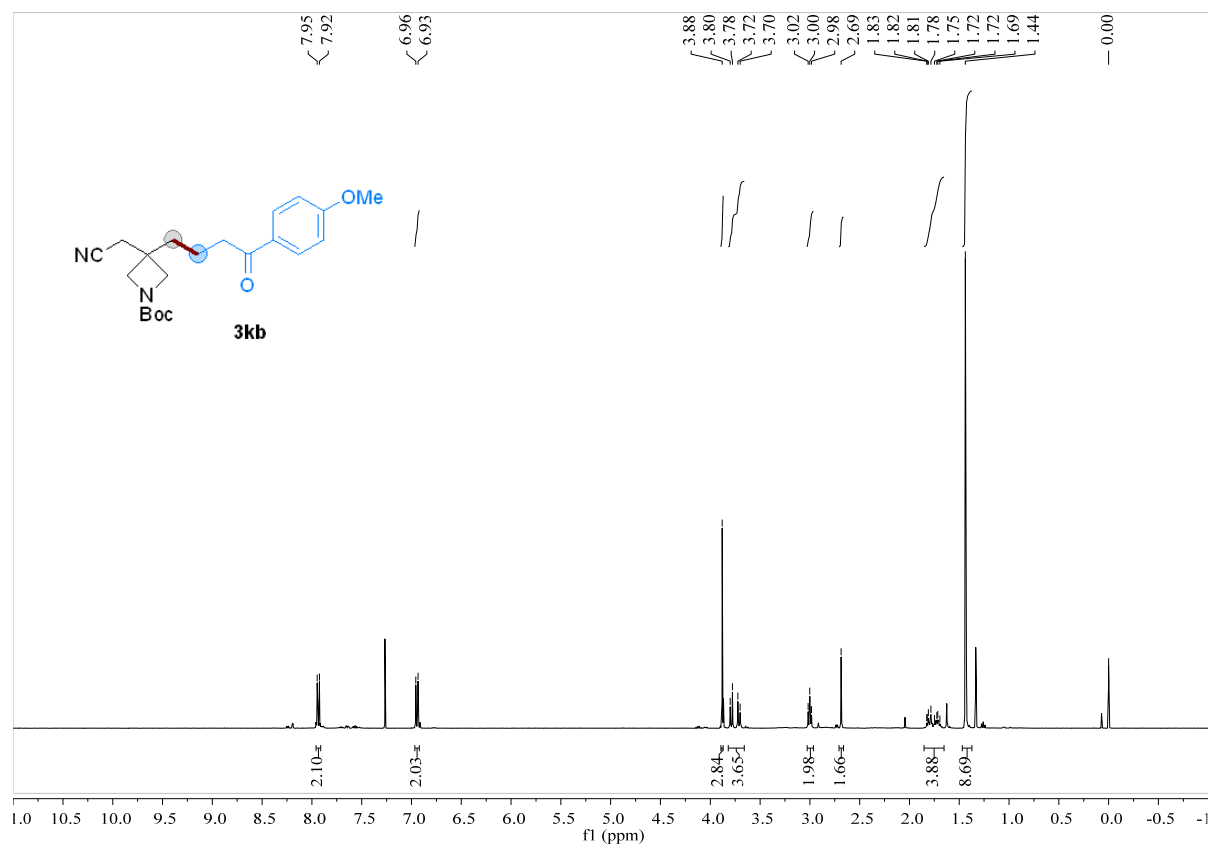
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3b**



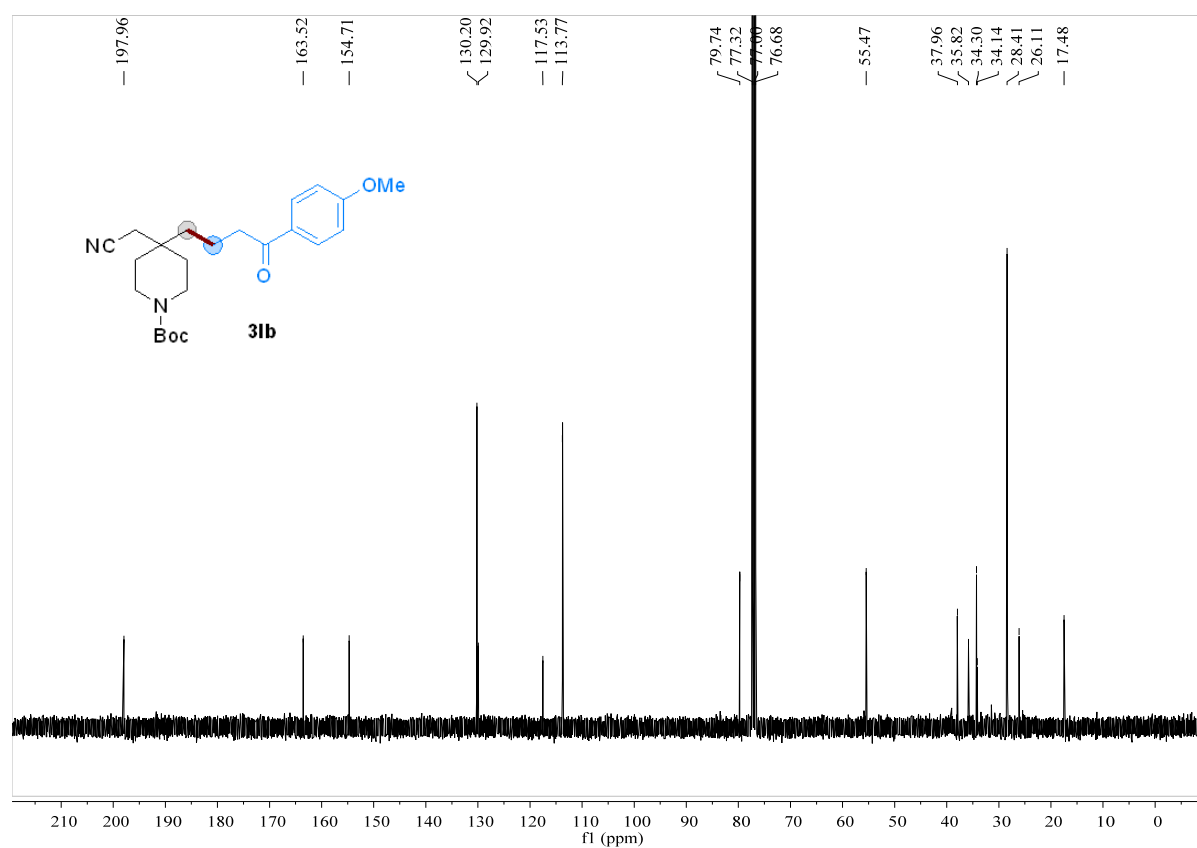
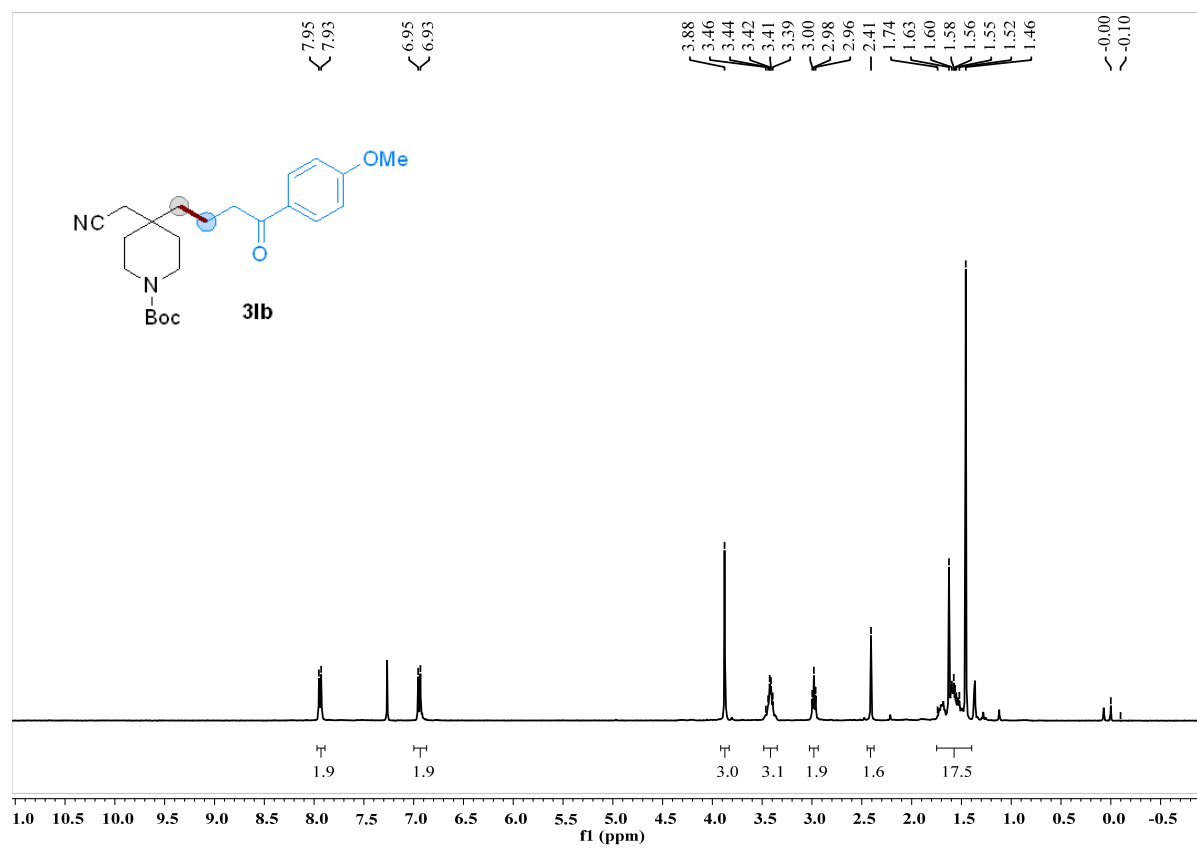
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3jb



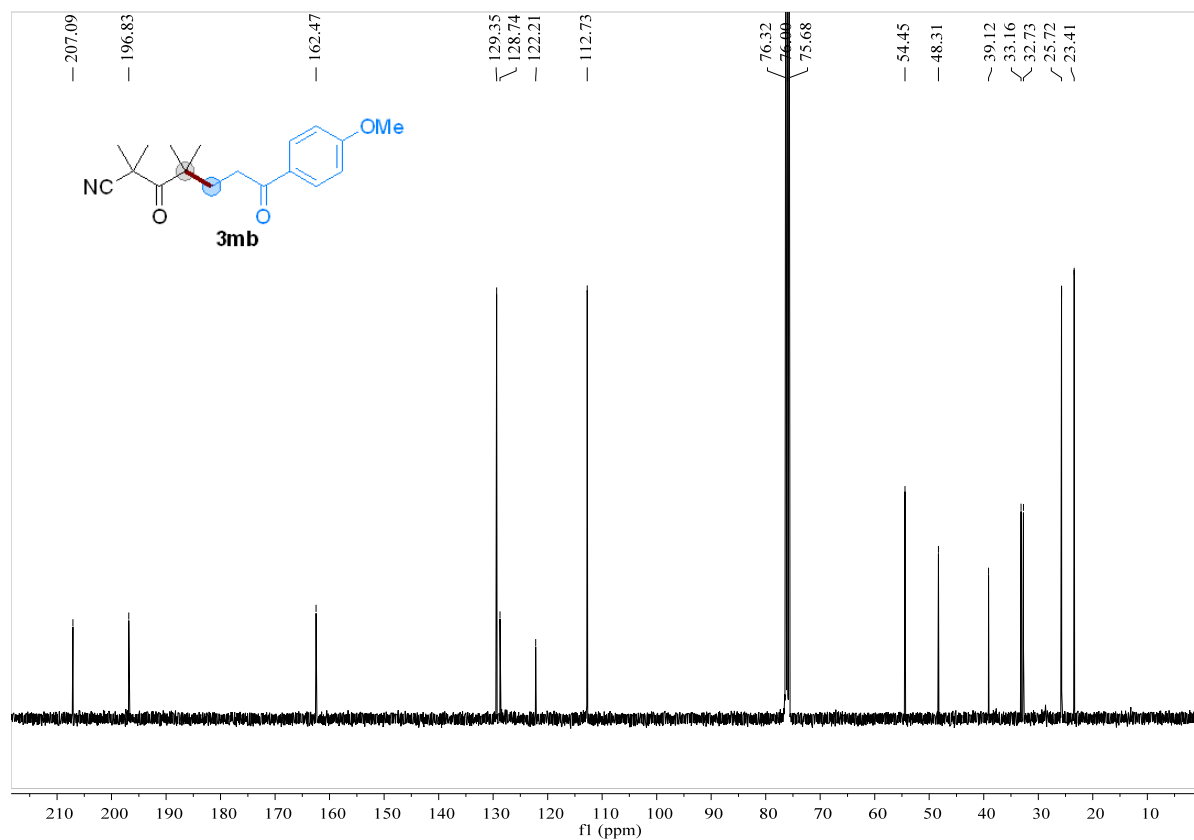
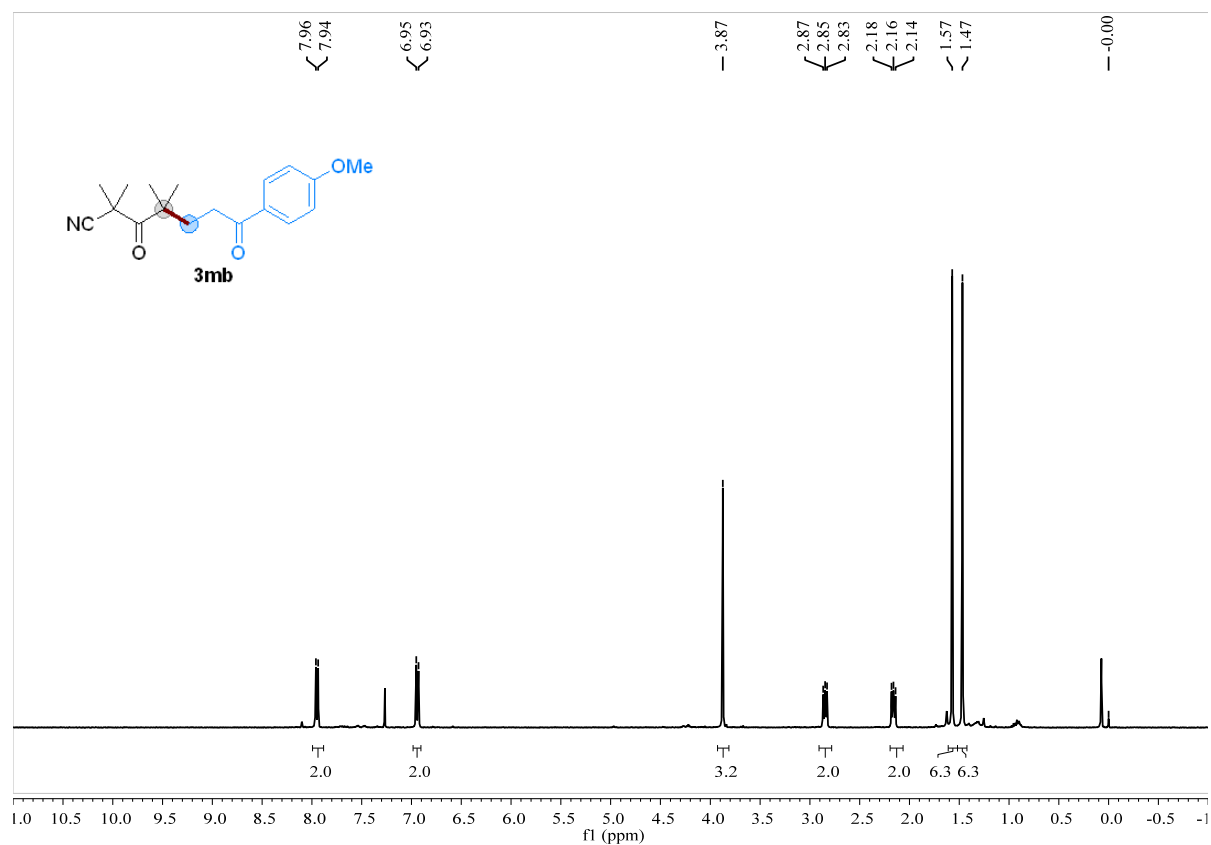
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3kb



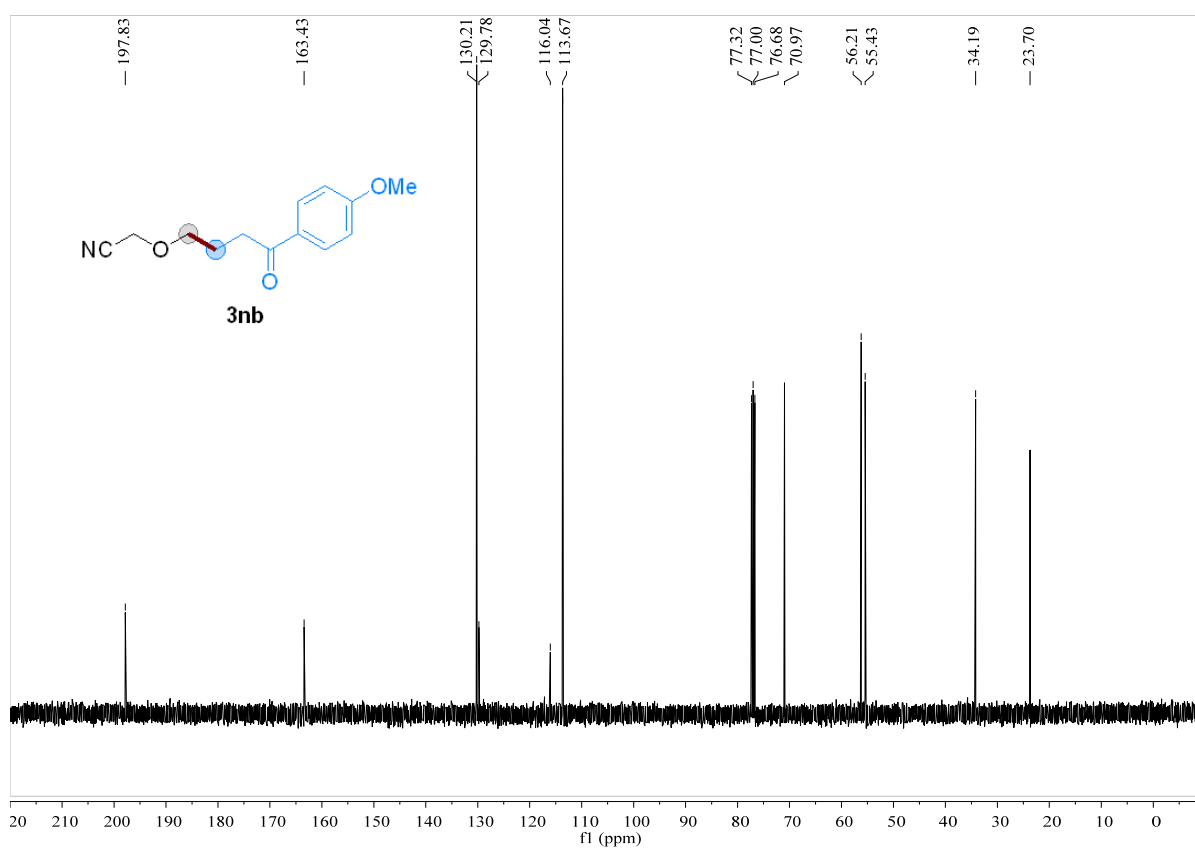
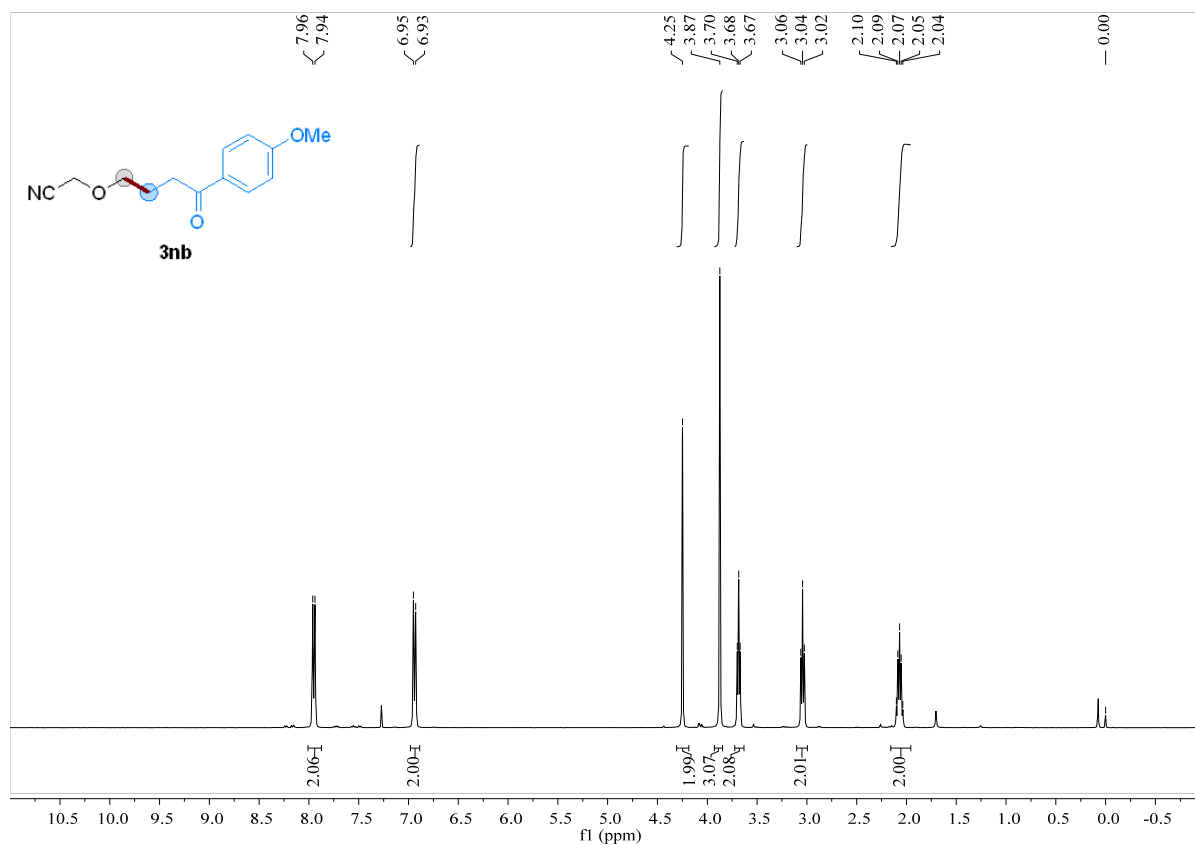
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3b**



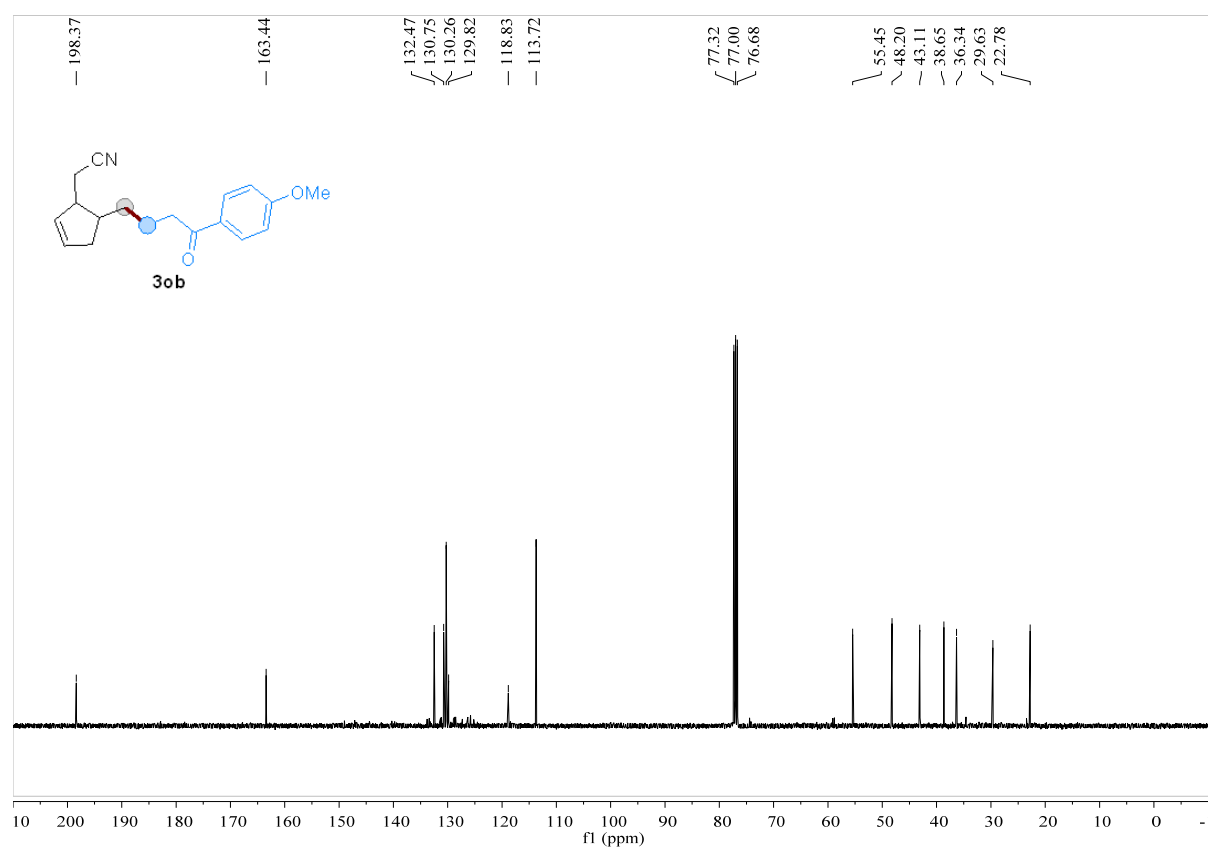
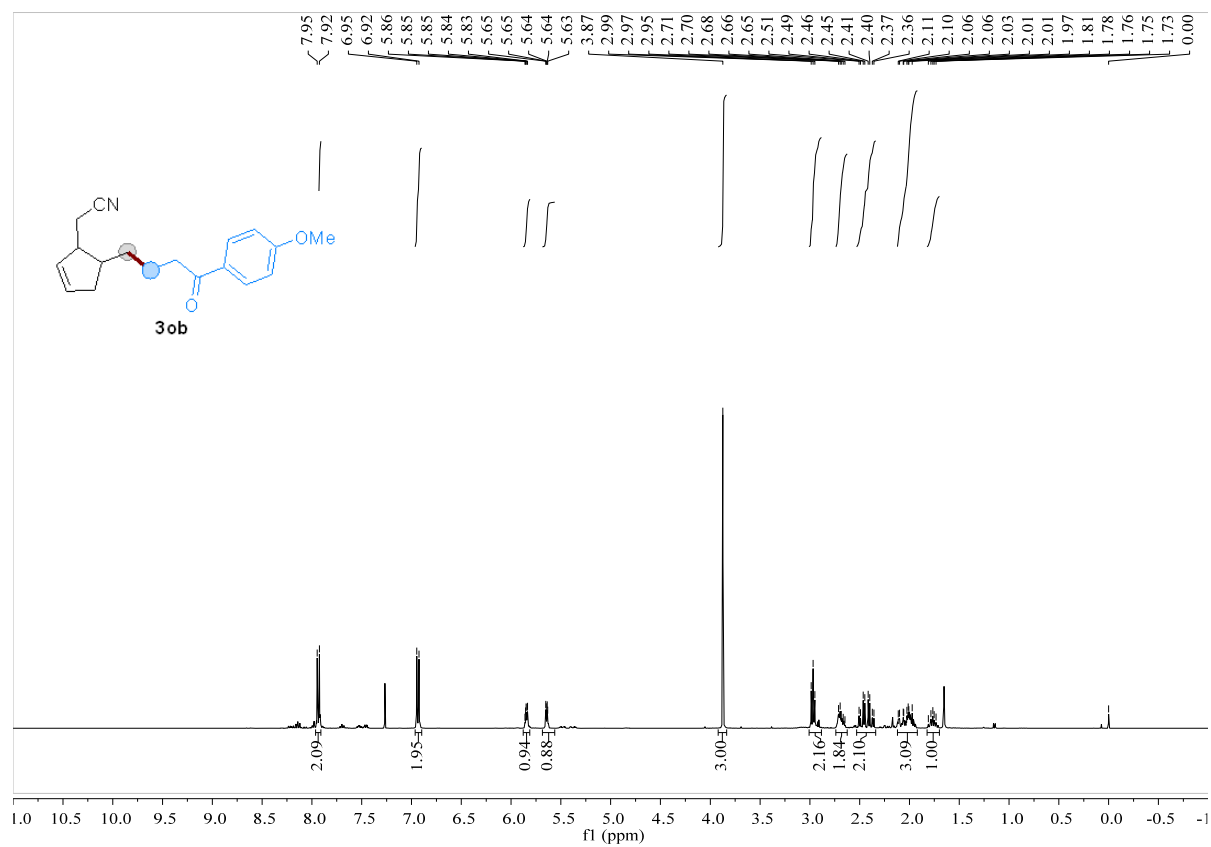
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3mb**



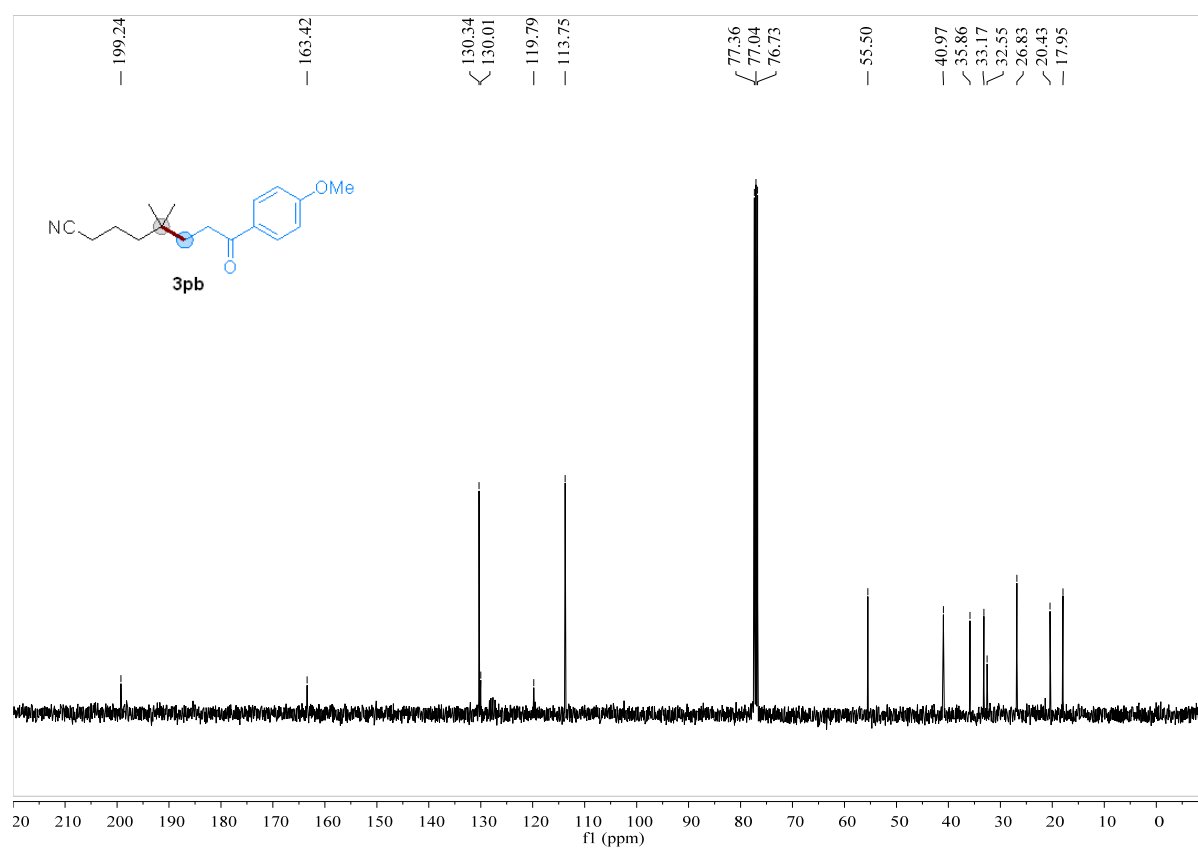
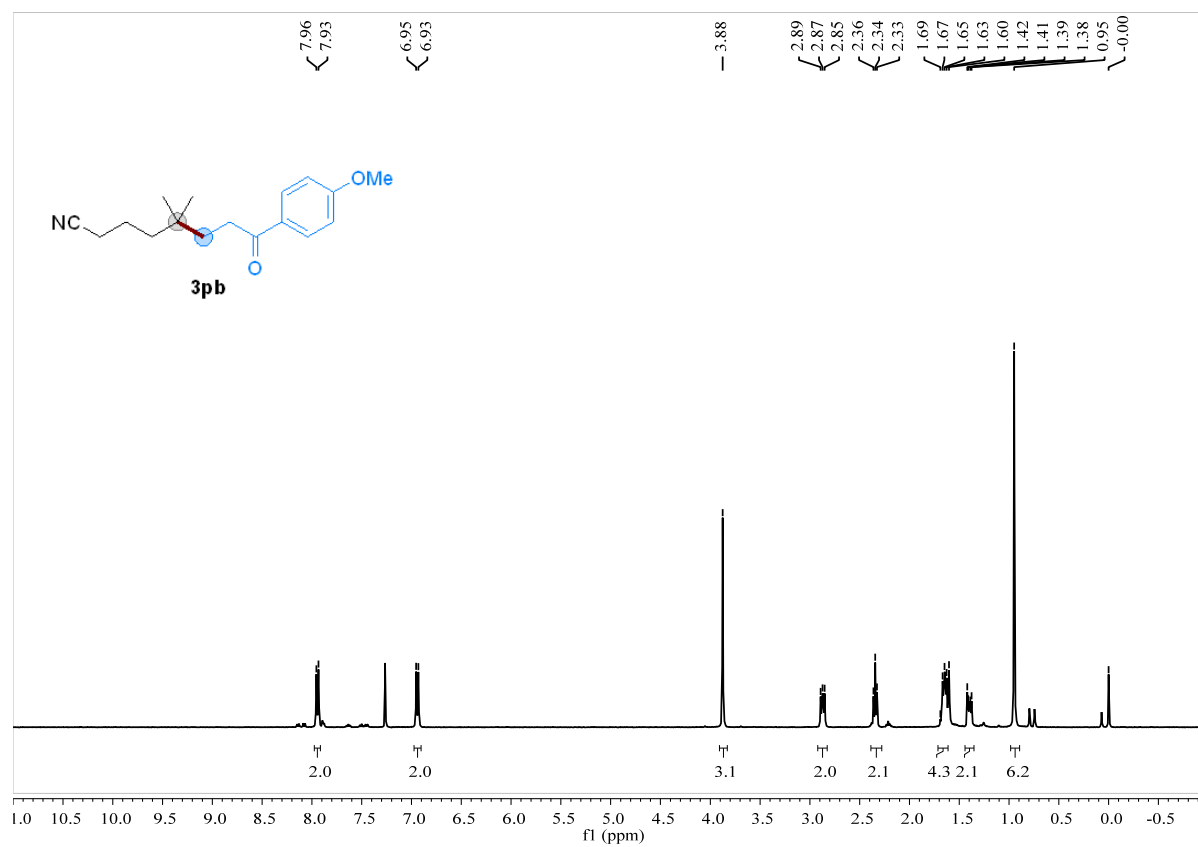
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3nb



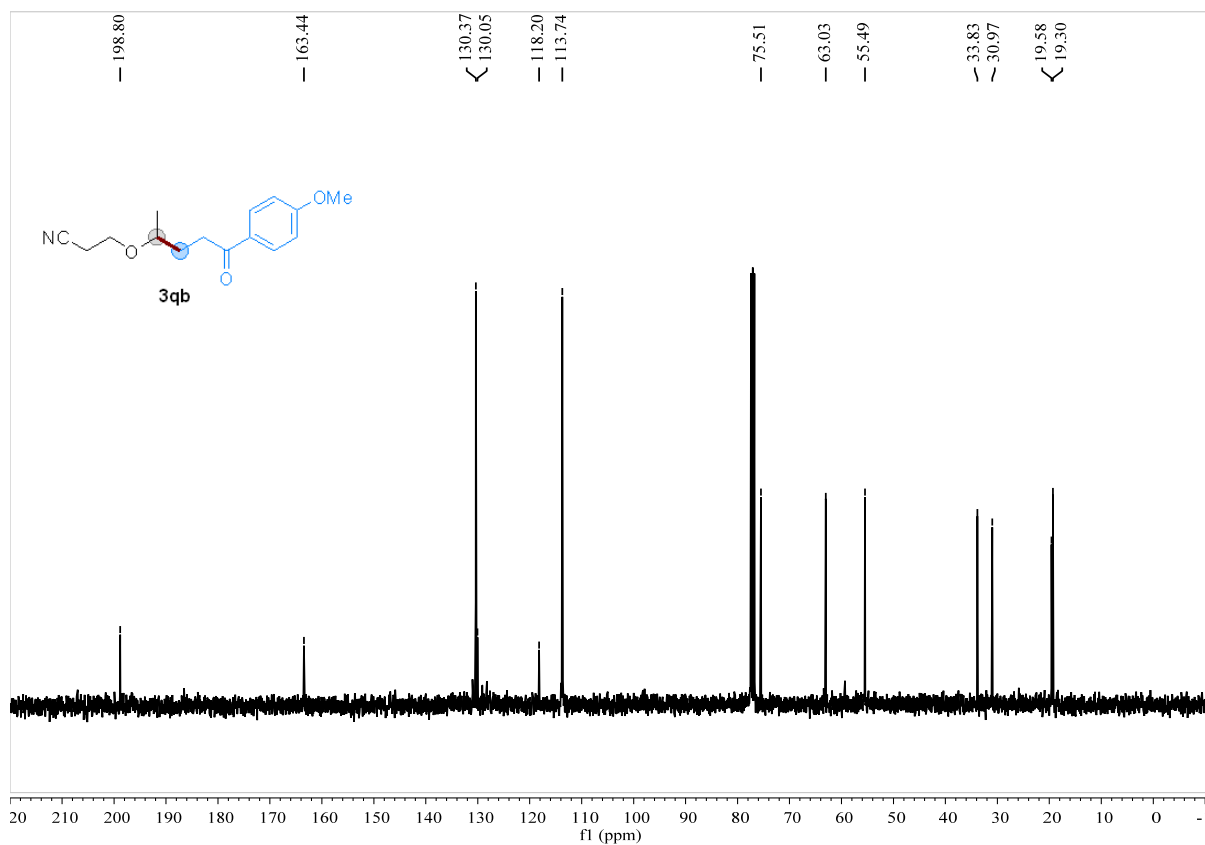
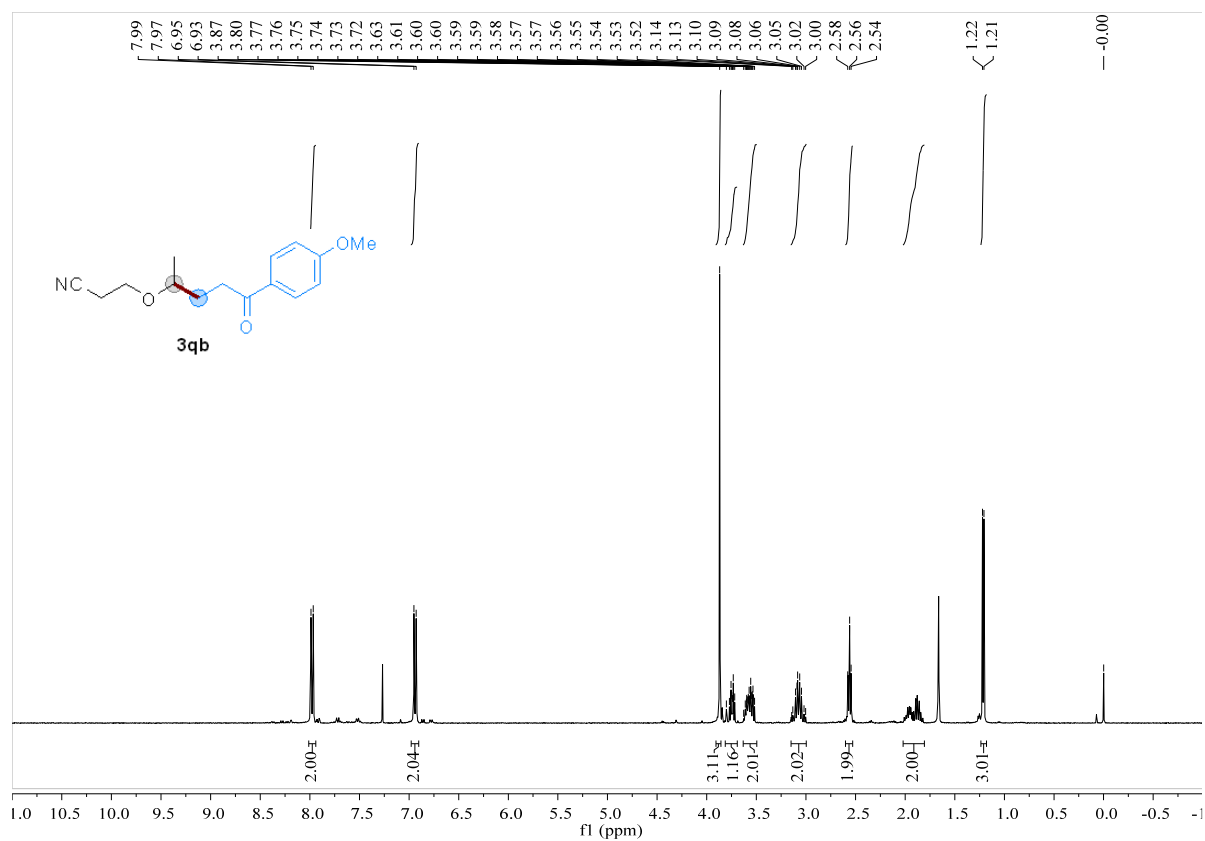
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3ob



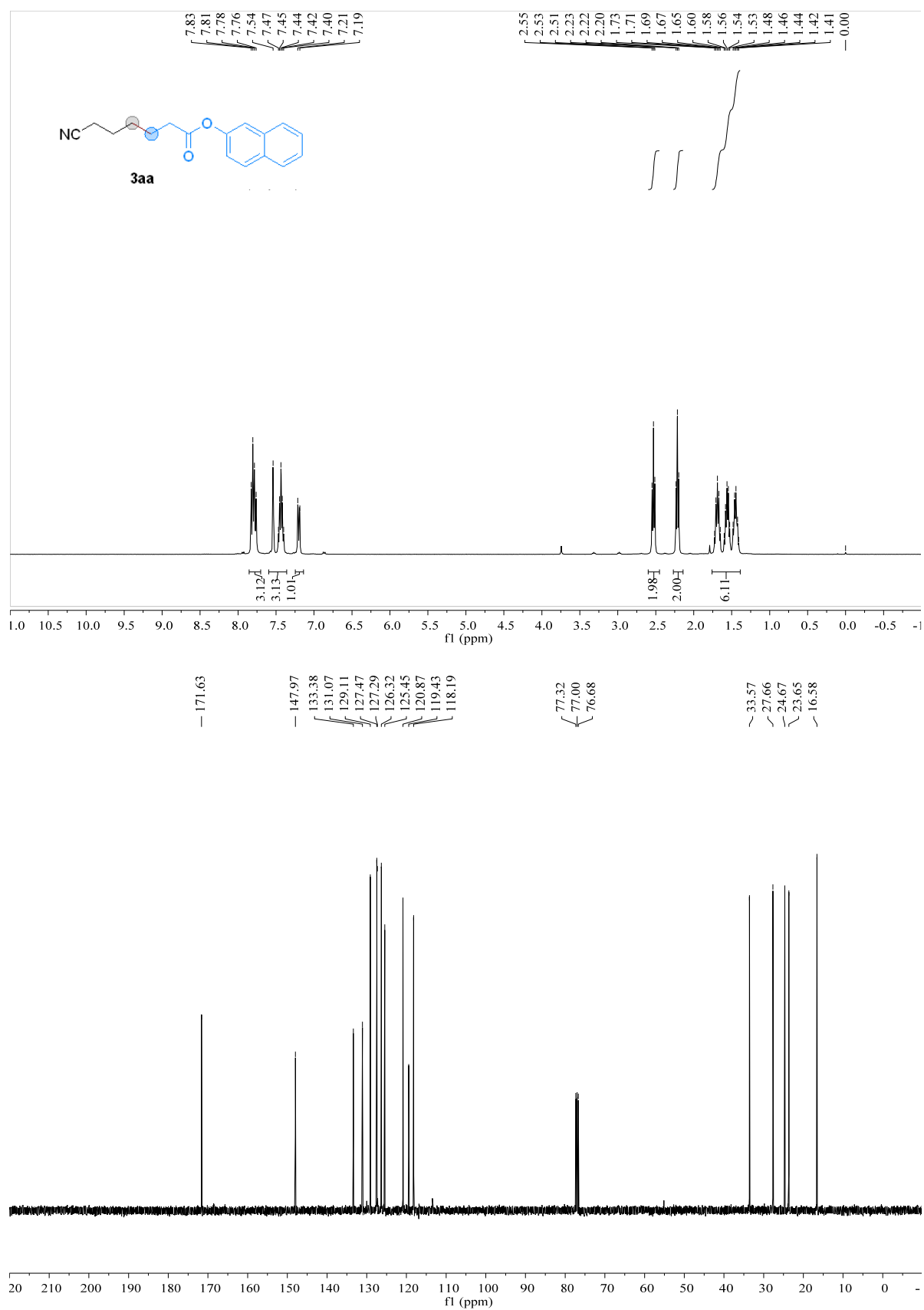
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3pb**



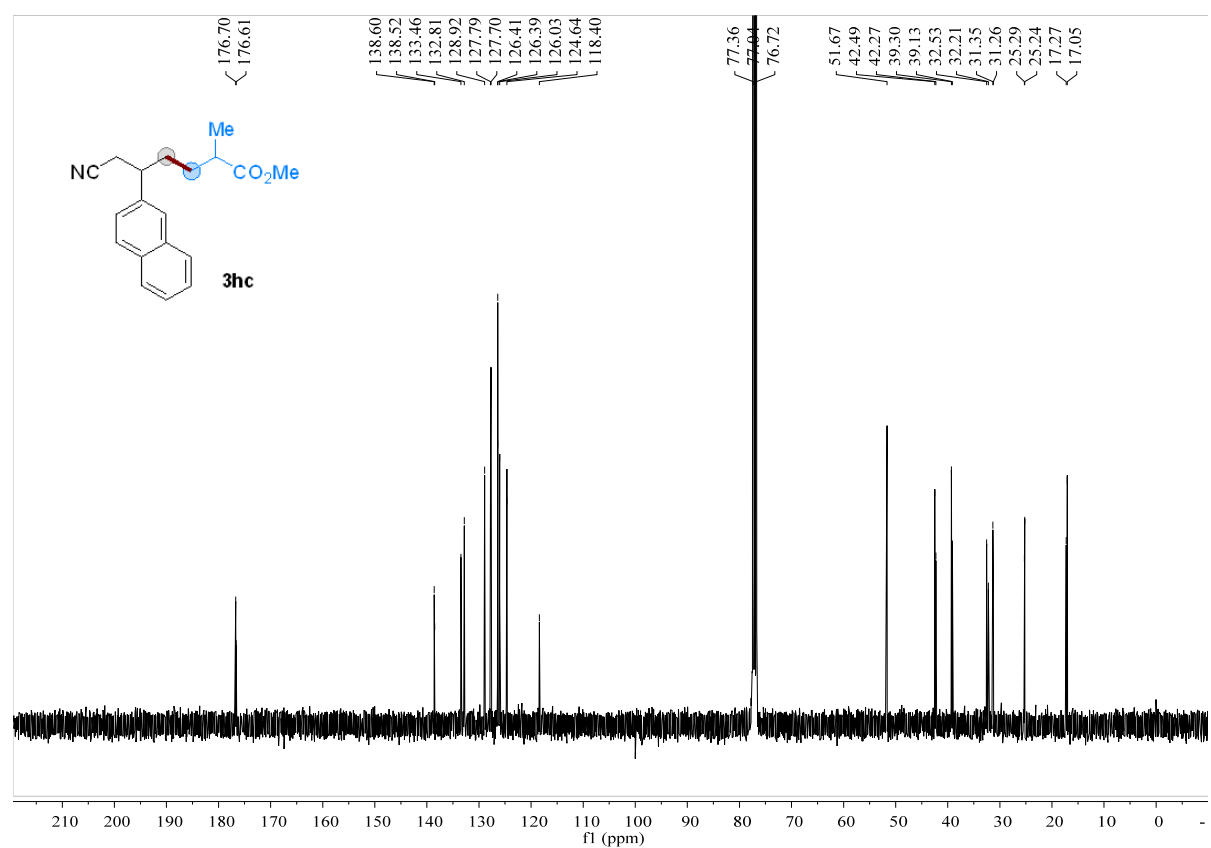
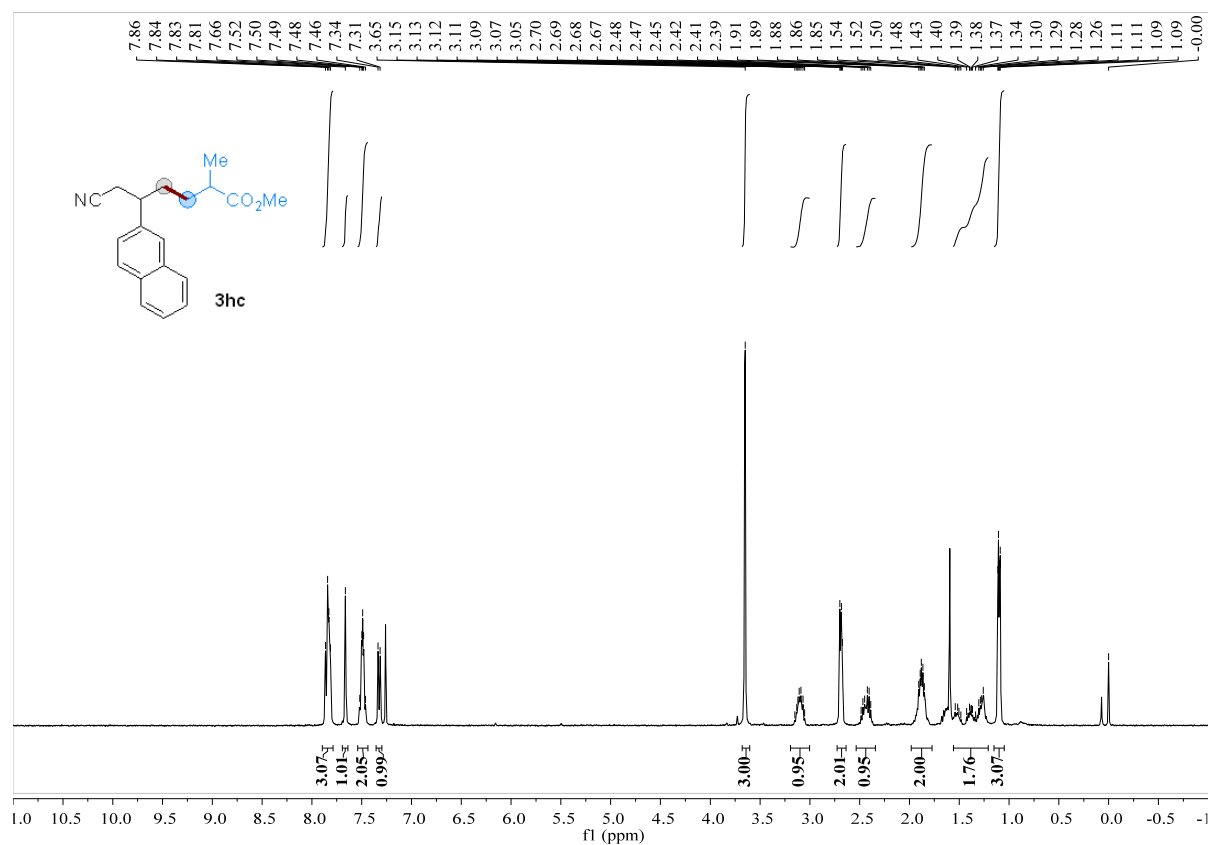
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3qb



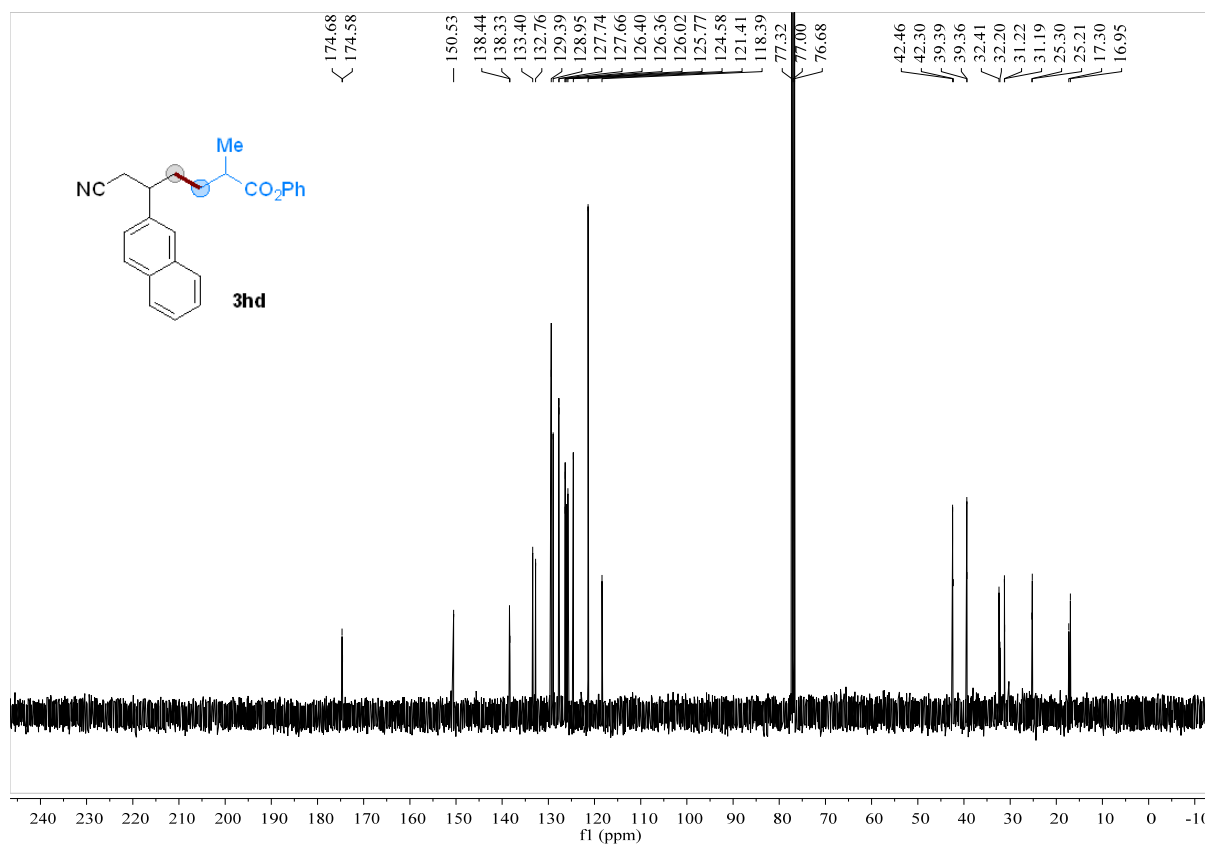
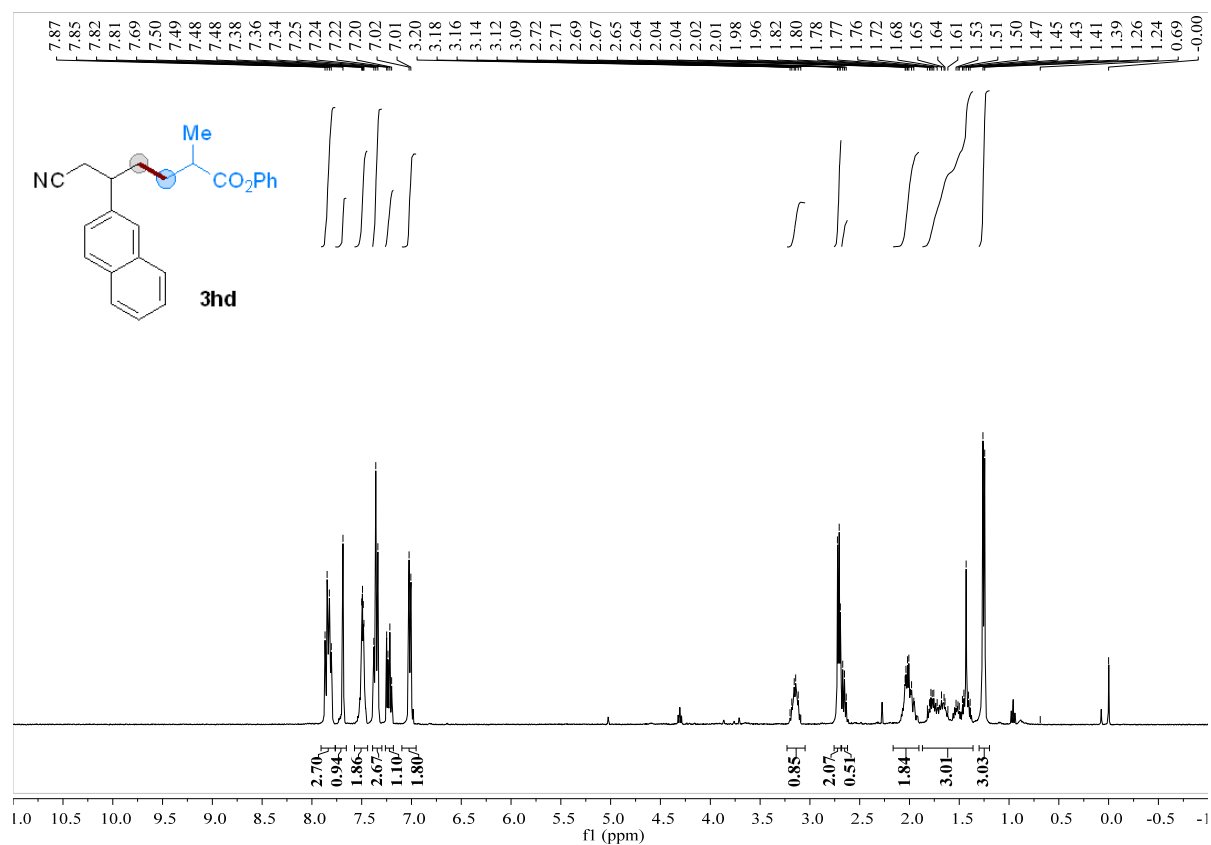
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3aa



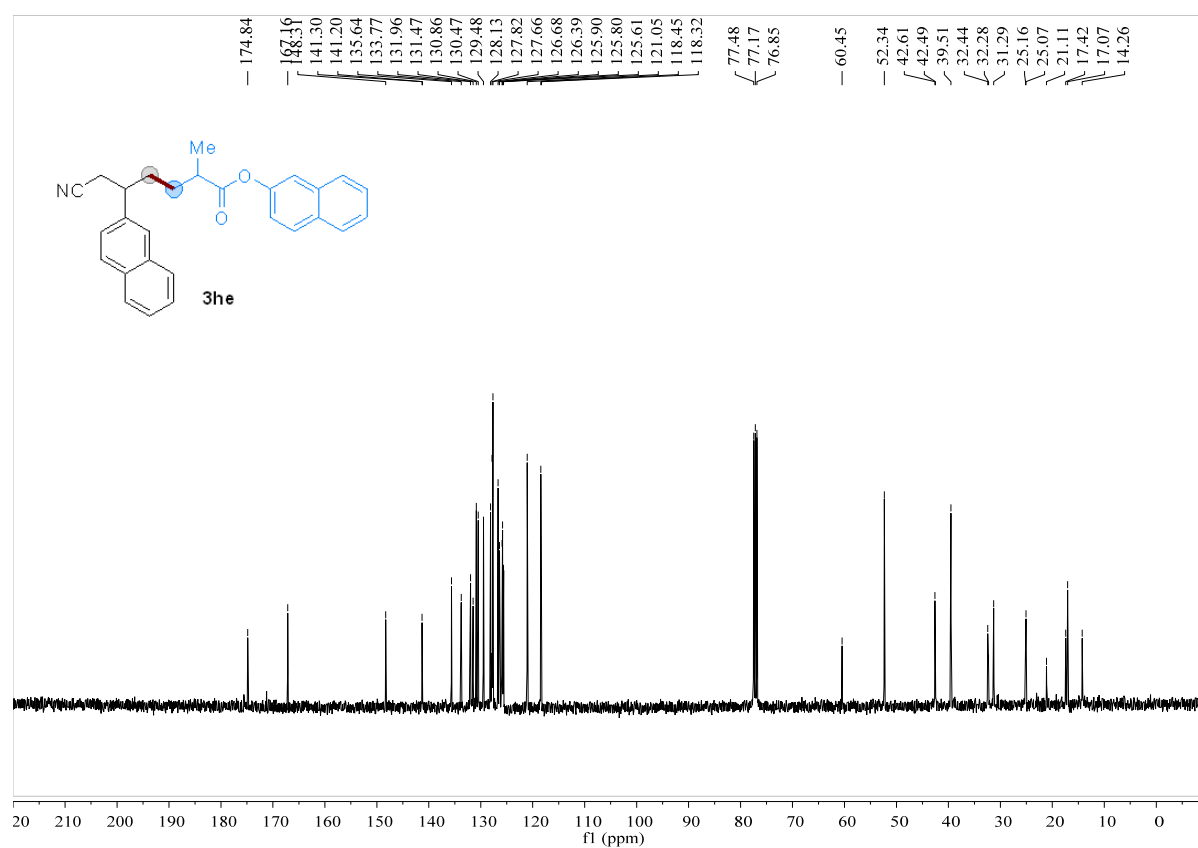
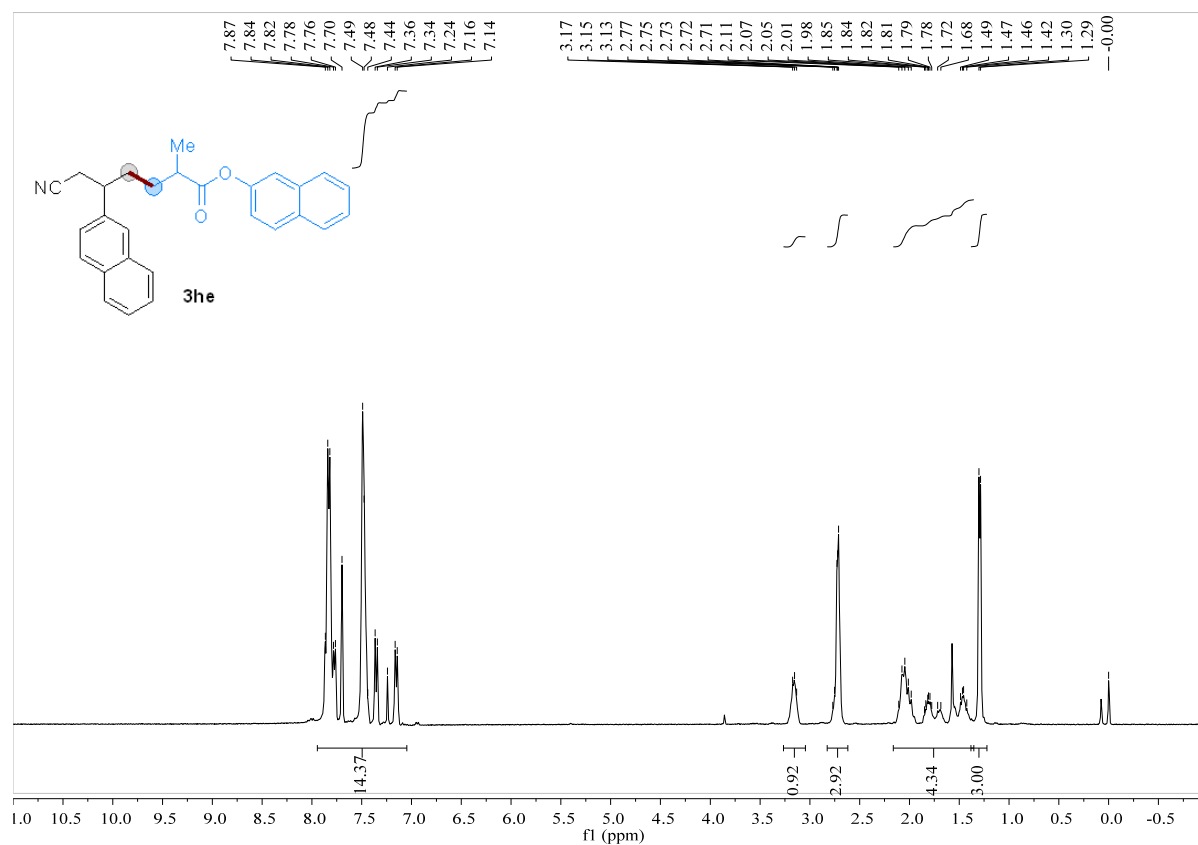
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3hc**



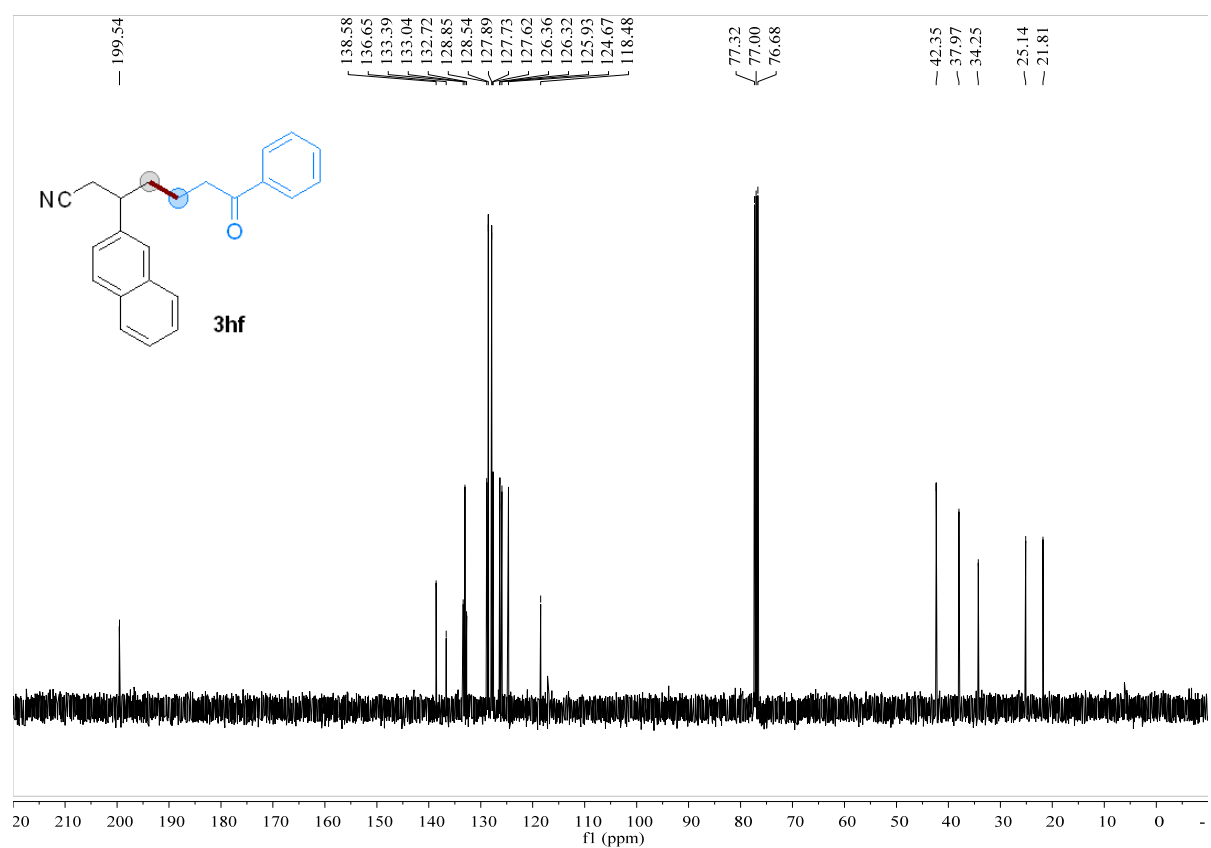
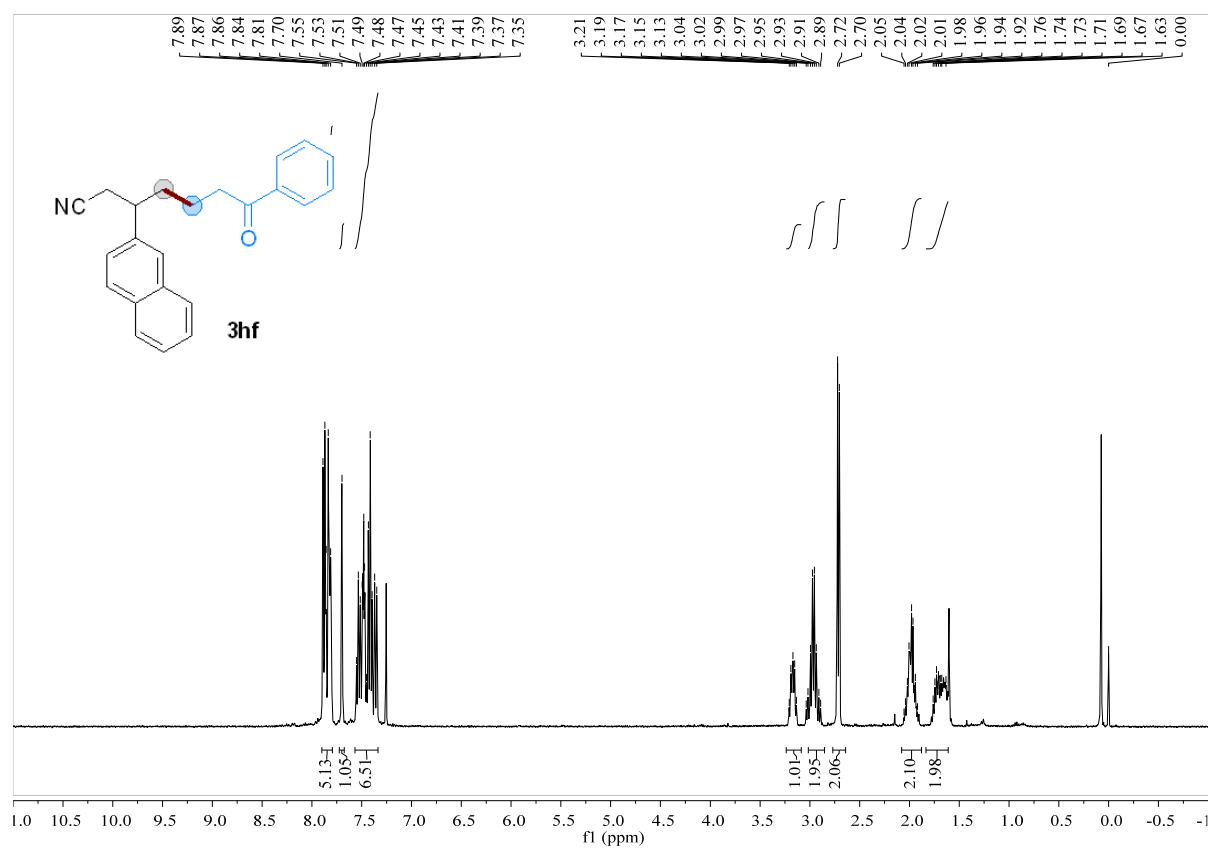
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3hd**



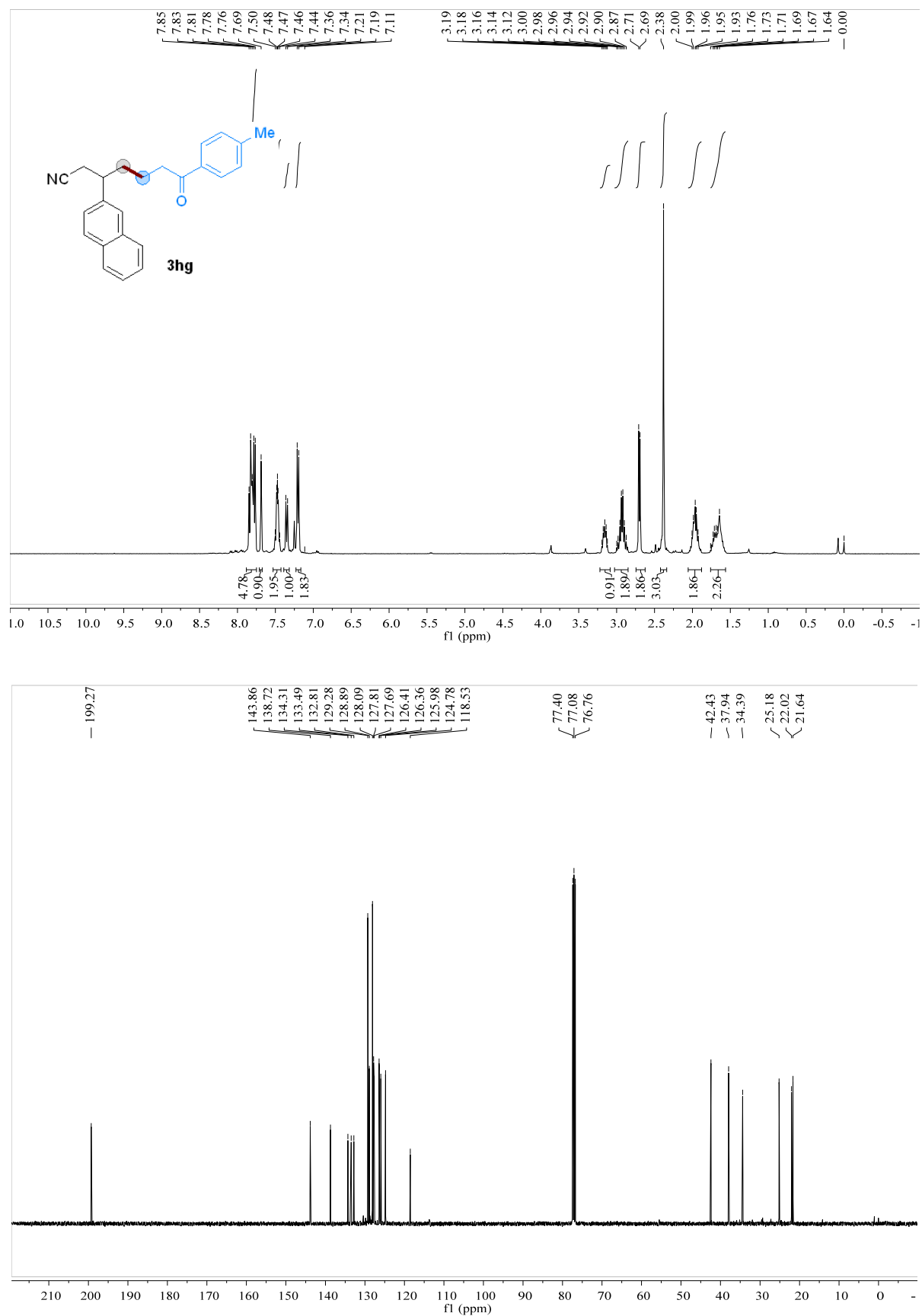
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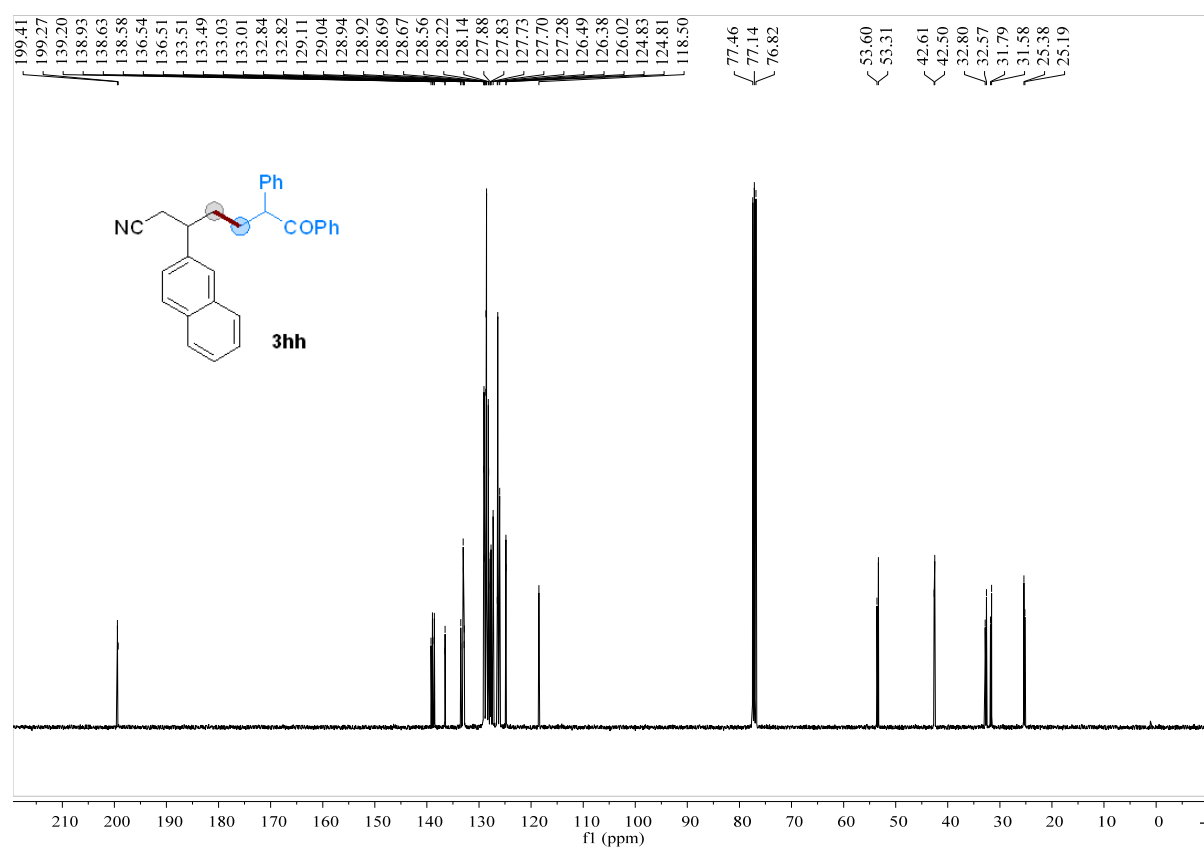
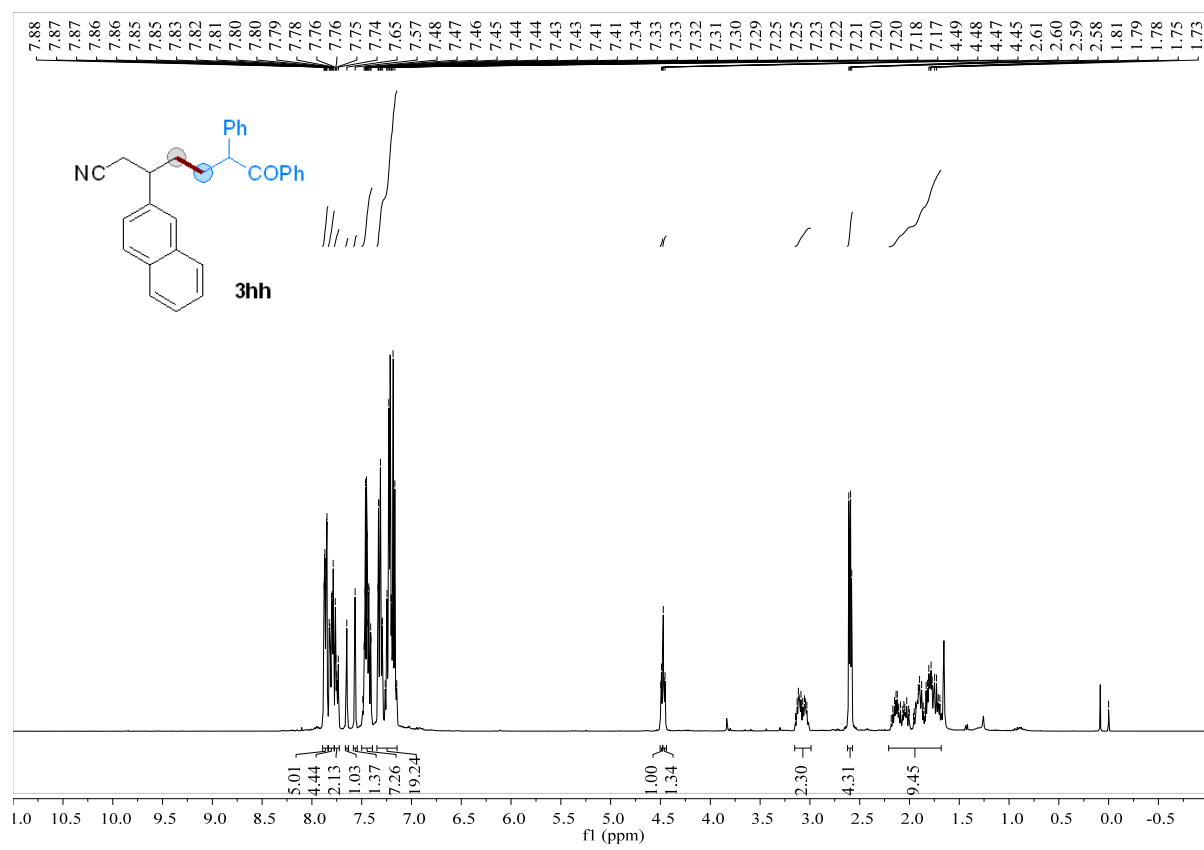
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3hf**



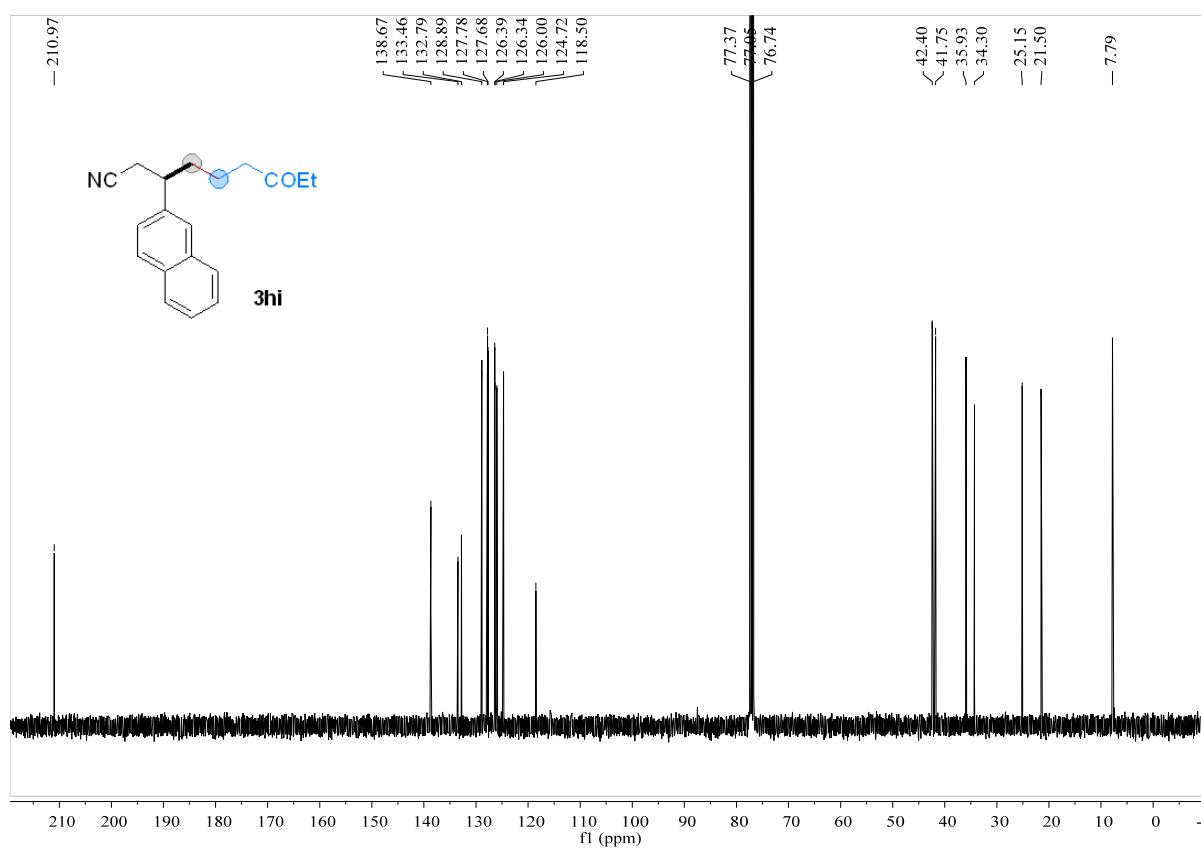
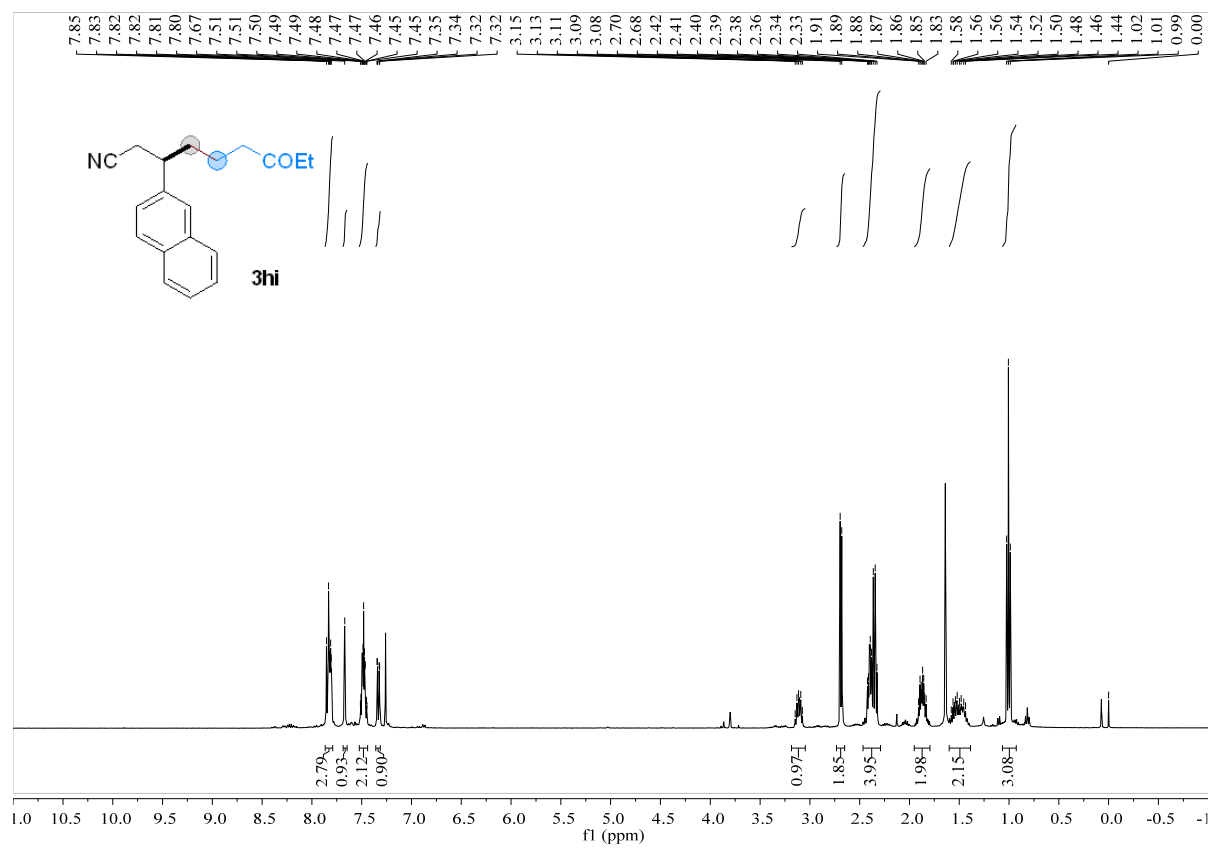
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3hg



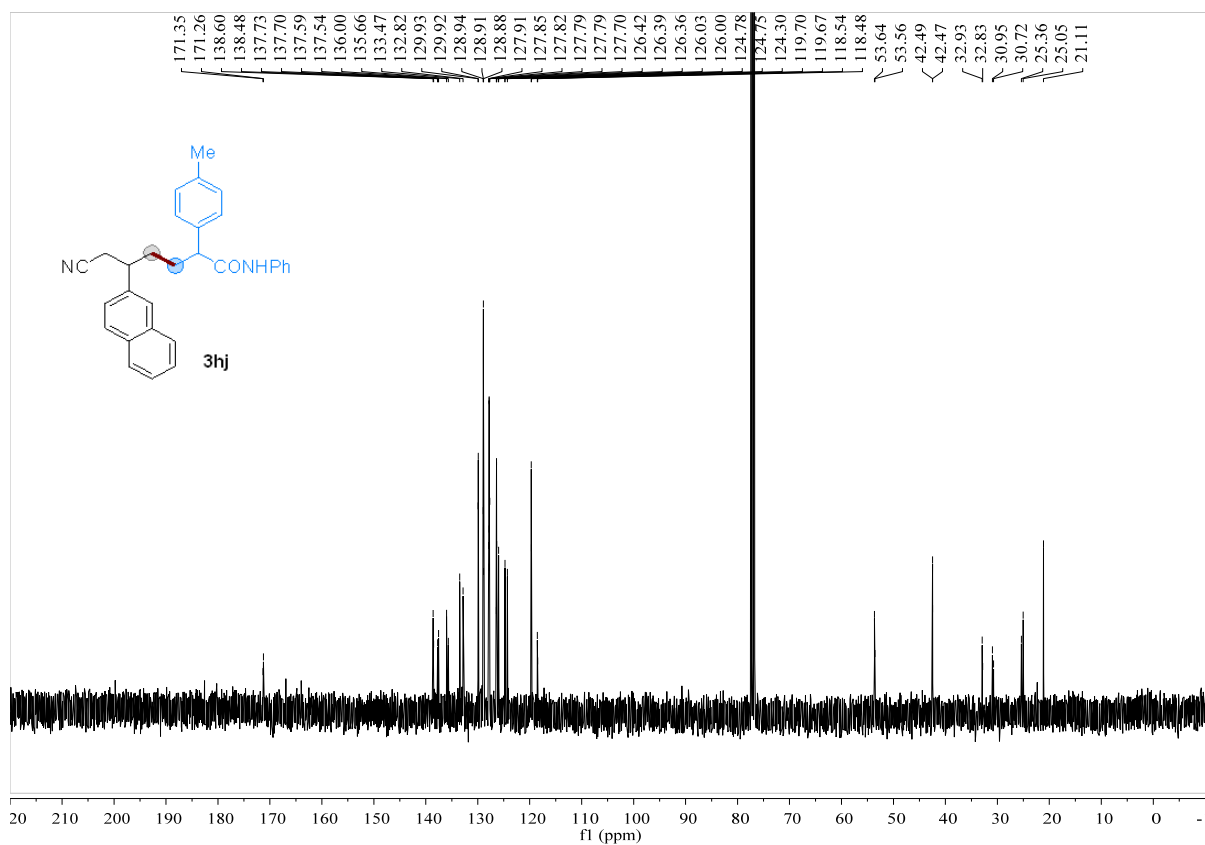
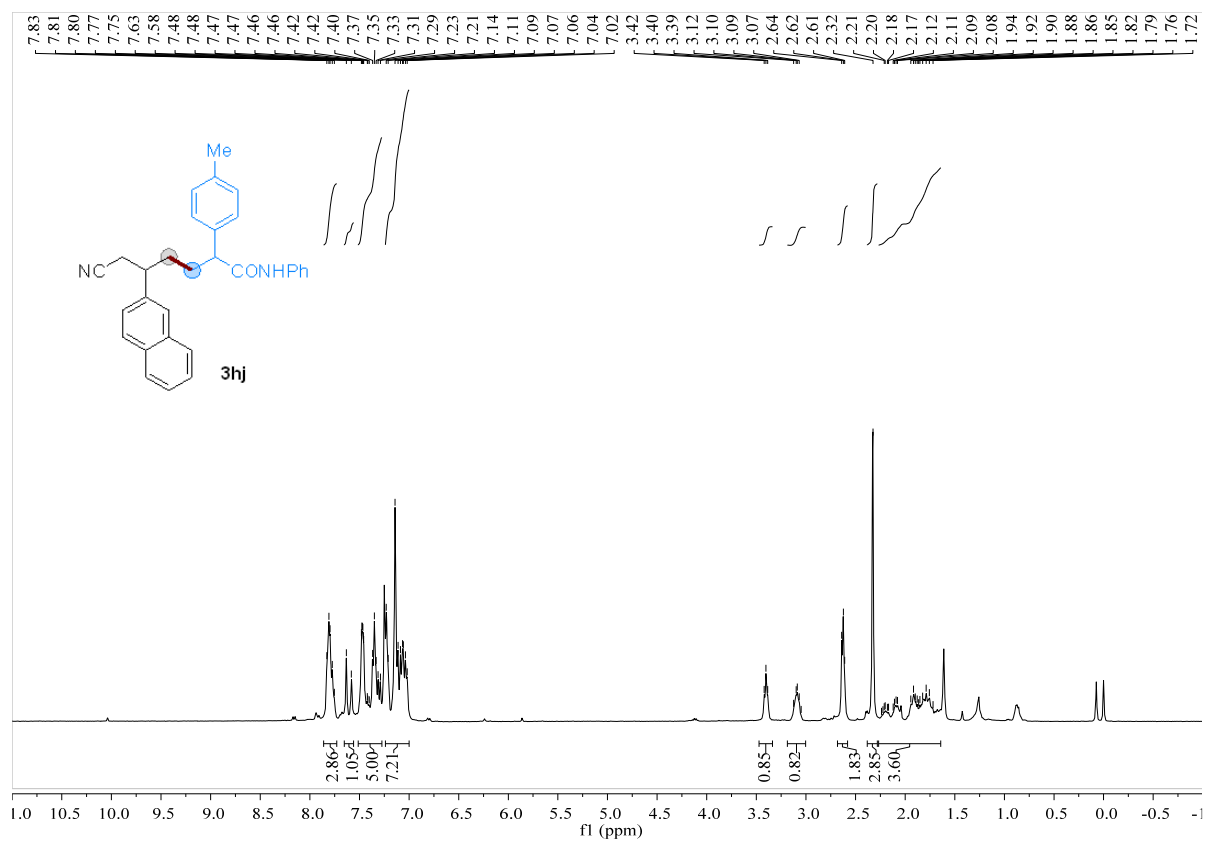
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3hh



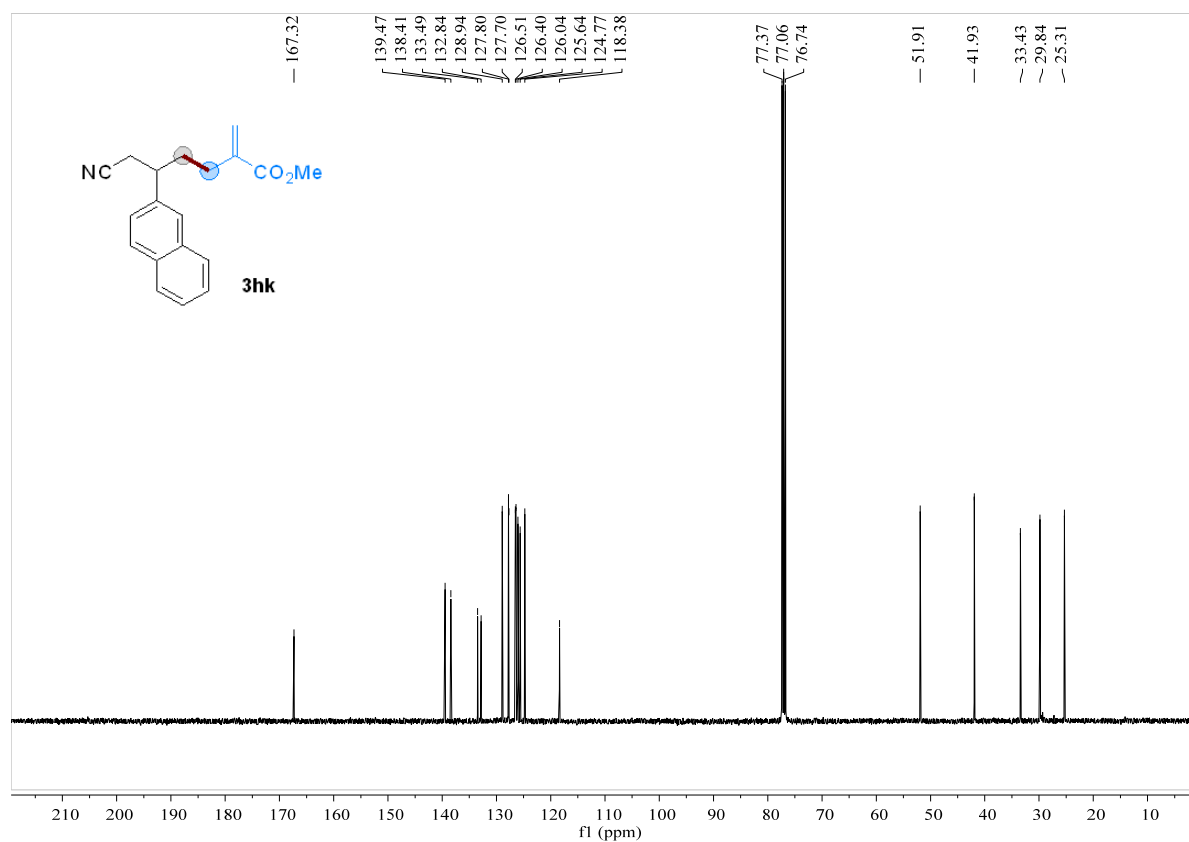
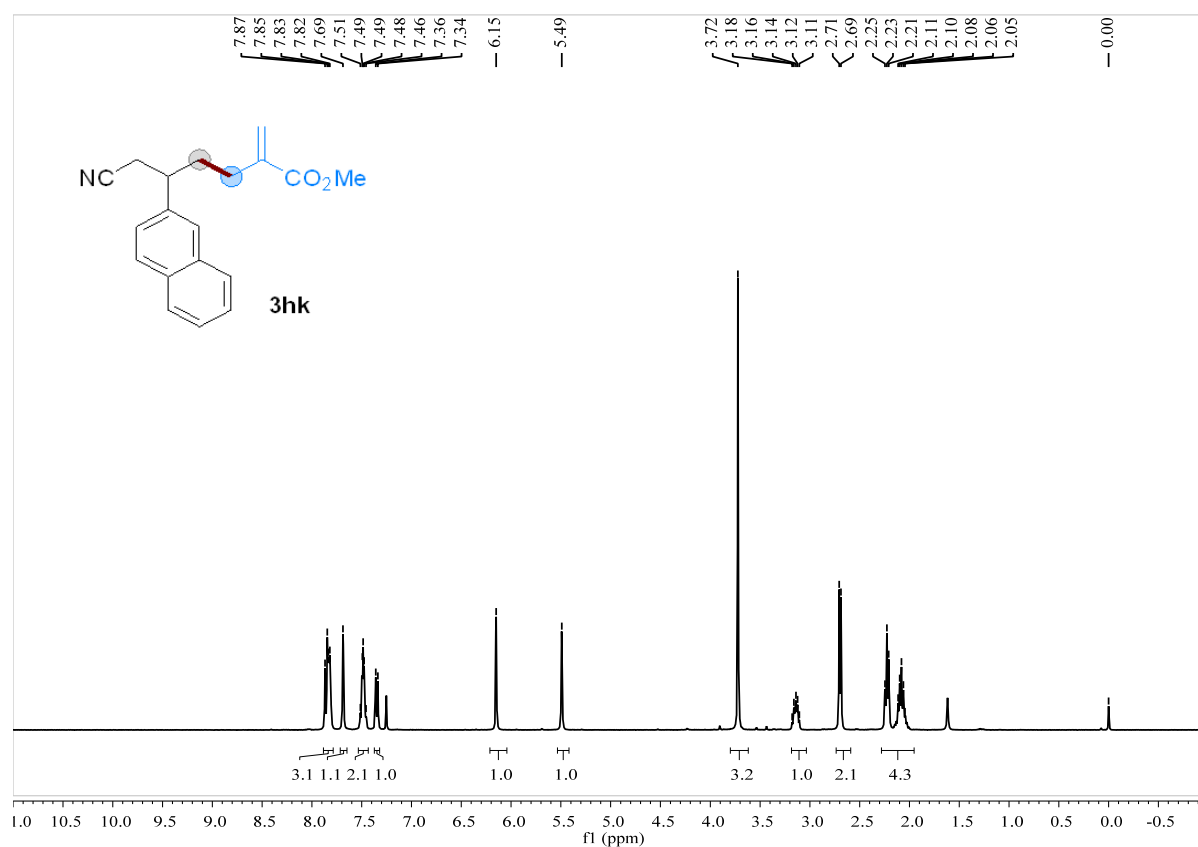
^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product **3hi**



^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3hj

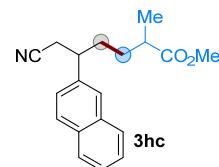
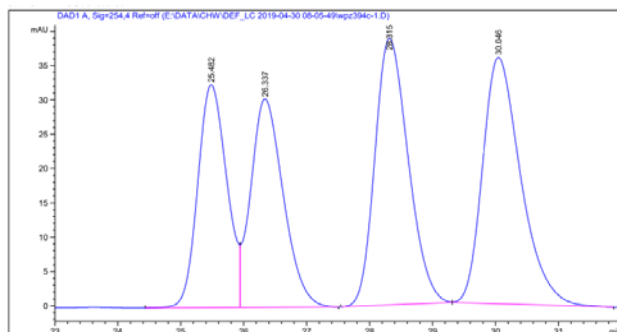


^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectra of product 3hk

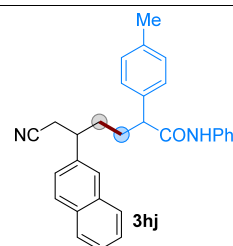
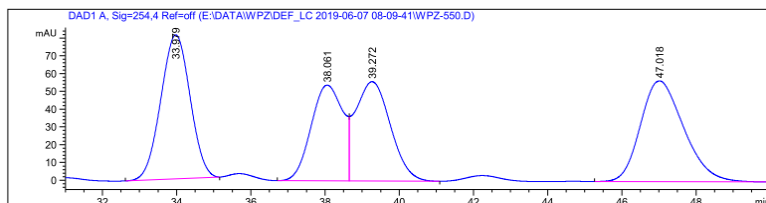


¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectra of product 5

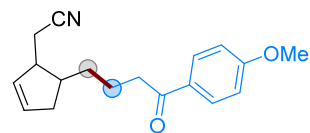
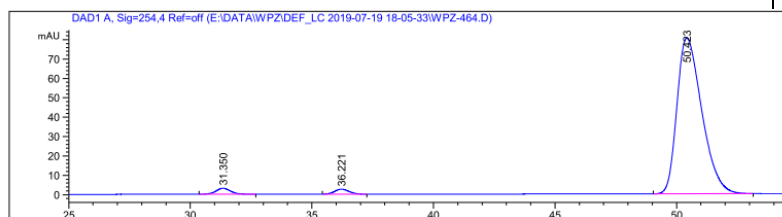
8. HPLC Data of Products



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.482	BV	0.4969	1036.95886	32.44476	20.4911
2	26.337	VB	0.5473	1091.71936	30.37651	21.5732
3	28.315	BB	0.5666	1426.06287	38.81983	28.1801
4	30.046	BB	0.6378	1505.78638	35.86969	29.7555



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.979	BB	0.8530	4439.90967	81.06363	27.9087
2	38.061	BV	0.9008	3206.64014	53.84426	20.1565
3	39.272	VB	0.9788	3663.04761	55.87712	23.0254
4	47.018	BB	1.2182	4599.10986	56.70815	28.9094



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	31.350	BB	0.5665	129.54054	3.10638	2.1764
2	36.221	BB	0.5007	107.23567	2.59210	1.8016
3	50.423	BB	1.0702	5715.34668	80.50776	96.0220