

*Supporting Information for*

**Photoinduced copper-catalyzed asymmetric radical  
three-component cross-coupling of 1,3-enynes with oxime esters  
and carboxylic acids**

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## 1. General Information

**NMR spectra:**  $^1\text{H}$  NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ( $\text{CDCl}_3$ : 7.26 ppm).  $^{13}\text{C}$  NMR spectra were recorded on 400 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ( $^{13}\text{C}\text{CDCl}_3$ : 77.0 ppm, t). Data are reported as follows: chemical shift  $\delta$ /ppm, integration ( $^1\text{H}$  only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof;  $^{13}\text{C}$  signals are singlets unless otherwise stated), coupling constants  $J$  in Hz, assignment.  $^{19}\text{F}$  NMR spectra were recorded on the same Spectrometer. All air- and moisture-sensitive reactions were performed under an atmosphere of Ar in fire dried glassware.

**High Resolution Mass Spectrometry (HRMS):** All were recorded on Bruker micrOTOF II ESI-TOF using a positive electrospray ionization ( $\text{ESI}^+$ ). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

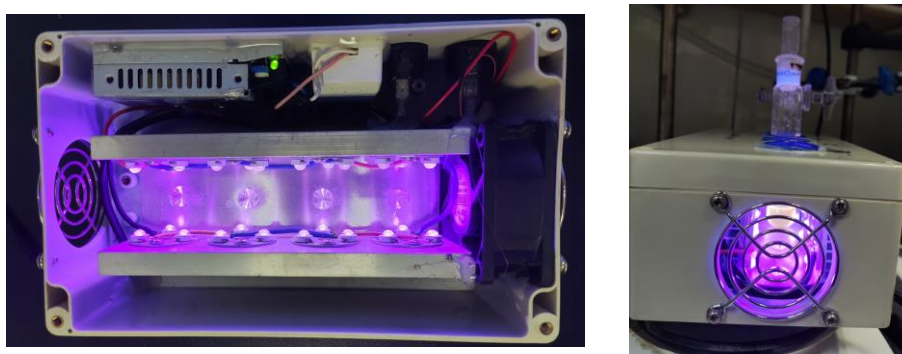
**Chromatography:** Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualisation was by ultraviolet fluorescence ( $\lambda = 254$  nm) and/or staining with Phosphomolybdic acid or potassium permanganate ( $\text{KMnO}_4$ ). Flash column chromatography was performed using 200-300 mesh silica gel. Optical rotations were measured with a polarimeter.  $[\alpha]_D$  values are reported at a given temperature ( $^\circ\text{C}$ ) in degrees  $\text{cm}^2 \cdot \text{g}^{-1}$  with concentration in g/100 mL.

**Chiral HPLC analysis:** Enantiomeric ratio (ee) values were determined by chiral HPLC with chiral IG, OD, OX, AZ and AD columns with hexane and *i*-PrOH as solvents.

**UV/Vis:** Measurements were made with Agilent Cary 60 UV-Vis spectrophotometer.

**Stern-Volmer quenching studies:** Fluorescence spectra was collected on Agilent Fluorescence Spectrophotometer G9800AS24.

**Photoreactor:** The photoreactors used in this research were bought from GeAo Chem (Figure S1: purple LEDs, light intensity =  $15.2 \text{ mw/cm}^2$ , 1 W for every light bulb; every two Schlenk tube was irradiated by 6 light bulbs from the side). Gram-scale reaction was performed under irradiation of purple LEDs (Kessil PR160L-390 nm), which is bought from Anhui Kemi Machinery Technology Co., Ltd. (<http://www.kemiyiqi.com/>).



**Figure S1.** Photoreactor used in this research (4 x 6 W purple LEDs)

**Note:** All photos in this material were taken by the first author Guo-Qing Li.

## 2. Preparation of Materials

Reagents, unless otherwise stated, were used as supplied from commercial sources without further purification. Anhydrous solvent (DMF, DCM, CH<sub>3</sub>CN, MeOH, toluene and THF) were taken from JC-Meyer solvent purification system. Anhydrous DMA, DCE, EtOAc and 1,4-dioxane were purchased from J&K reagent company.

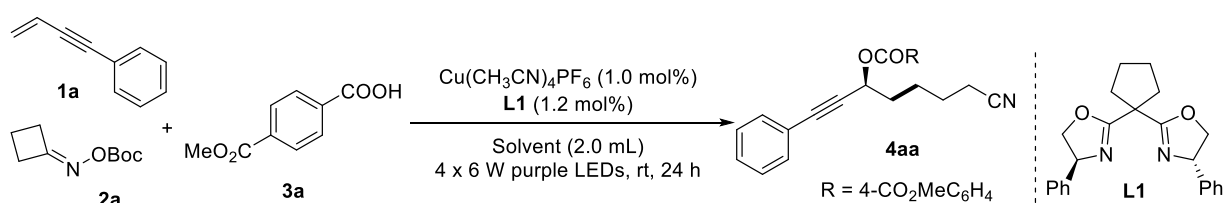
All 1,3-enynes were prepared from alkynes and vinyl bromide according to the reported literature.<sup>1</sup>

Oxime esters **2a-2f** were prepared from the corresponding ketones by following the literature report.<sup>2</sup>

Ligands **L1-L6**, **L8**, **L9** and **L12-L16** were purchased from Bide Pharmatech. **L7**<sup>3</sup>, **L10**<sup>4</sup>, **L11**<sup>4</sup> and **L17**<sup>5</sup> were prepared according to the reported literature.

## 3. Details for Condition Optimizations

**Table S1** The effect of solvents<sup>[a]</sup>

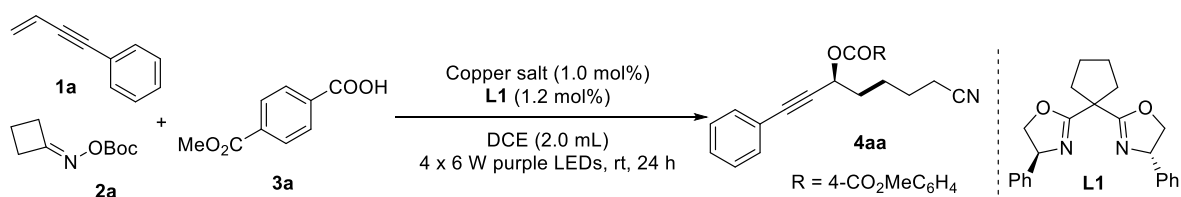


Entry	Solvent	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	THF	Trace	-
2	DCM	33	34
3	MeOH	43	8
4	CH <sub>3</sub> CN	53	31
5	DMF	24	7
6	Toluene	Trace	-
7	EtOAc	Trace	-
8	DME	13	0
9	DCE	<b>63</b>	<b>60</b>

<sup>[a]</sup> **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (1.0 equiv, 0.1 mmol), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (0.001 mmol, 1.0 mol%) and chiral ligand **L1** (0.0012 mmol, 1.2 mol%) in 2.0 mL solvent for 24h under the irradiation of 4 x 6 W purple LEDs. <sup>[b]</sup> NMR yield determined by using 1,3,5-trimethoxybenzene as an internal standard. <sup>[c]</sup> Determined by chiral HPLC.

As shown in **Table S1**, among all the tested, DCE (2.0 mL) gave the best results (63% yield, 60% ee), and was thus selected for further optimization studies.

**Table S2.** The effect of copper salts<sup>[a]</sup>



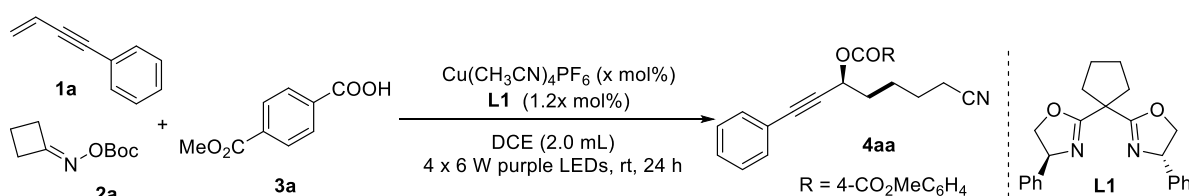


Entry	Copper Salt	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	CuOAc	10	12
2	CuCl	53	6
3	CuBr	48	31
4	CuOTf	5	29
5	CuCN	8	0
6	CuSCN	13	6
7	CuTc	50	0
8	Cu(OTf) <sub>2</sub>	54	58
<b>9</b>	<b>Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub></b>	<b>63</b>	<b>60</b>

<sup>[a]</sup> **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (1.0 equiv, 0.1 mmol), copper salt (0.001 mmol, 1.0 mol%) and chiral ligand **L1** (0.0012 mmol, 1.2 mol%) in 2.0 mL DCE for 8 h under the irradiation of 4 x 6 W purple LEDs. <sup>[b]</sup> NMR yield determined by using 1,3,5-trimethoxybenzene as an internal standard. <sup>[c]</sup> Determined by chiral HPLC.

As shown in **Table S2**, among all the tested, Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> gave the best results (63% yield, 60% ee), and was thus selected for further optimization studies..

**Table S3. The effect of temperature and catalyst loading<sup>[a]</sup>**

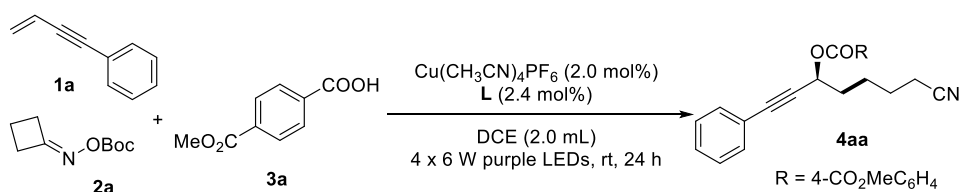


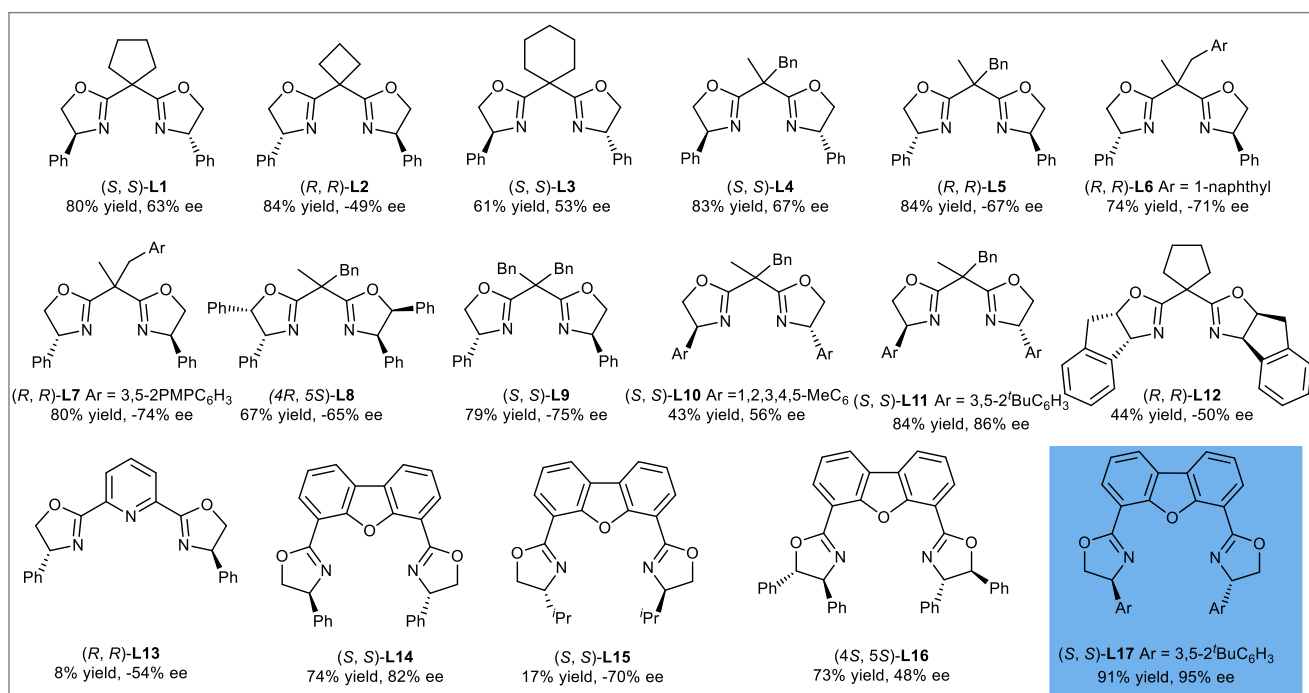
Entry	Conditions	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	with 1.0 mol% [Cu], 1.2 mol% <b>L1</b>	63	60
2	with 2.0 mol% [Cu], 2.4 mol% <b>L1</b>	<b>80</b>	<b>63</b>
3	with 5.0 mol% [Cu], 6.0 mol% <b>L1</b>	81	60

<sup>[a]</sup> **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (1.0 equiv, 0.1 mmol), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (0.00x mmol, x mol%) and chiral ligand **L1** (0.0012x mmol, 1.2x mol%) in 2.0 mL DCE for 24 h under the irradiation of 4 x 6 W purple LEDs. <sup>[b]</sup> NMR yield determined by using 1,3,5-trimethoxybenzene as an internal standard. <sup>[c]</sup> Determined by chiral HPLC.

As shown in **Table S3**, among all the tested, a combination of Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (2.0 mol%) and chiral ligand **L1** (2.4 mol%) gave the best results (80% yield, 63% ee), and was thus selected for further studies.

**Table S4. The effect of chiral ligands<sup>[a,b,c]</sup>**

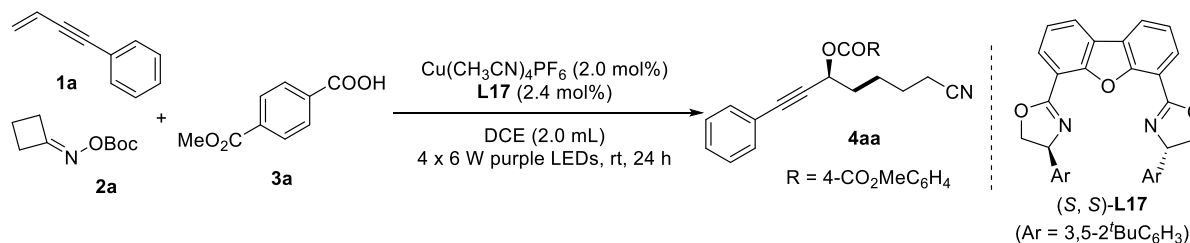




<sup>[a]</sup> **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (1.0 equiv, 0.1 mmol), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (0.002 mmol, 2.0 mol%) and chiral ligand **L** (0.0024 mmol, 2.4 mol%) in 2.0 mL DCE for 24 h under the irradiation of 4 x 6 W purple LEDs. <sup>[b]</sup> NMR yield determined by using 1,3,5-trimethoxybenzene as an internal standard. <sup>[c]</sup> Determined by chiral HPLC.

As shown in **Table S4**, among all the tested, chiral ligand **L17** (2.4 mol%) gave the best results (91% yield, 95% ee), and was thus selected for further optimization studies.

**Table S5. Control experiments**<sup>[a]</sup>



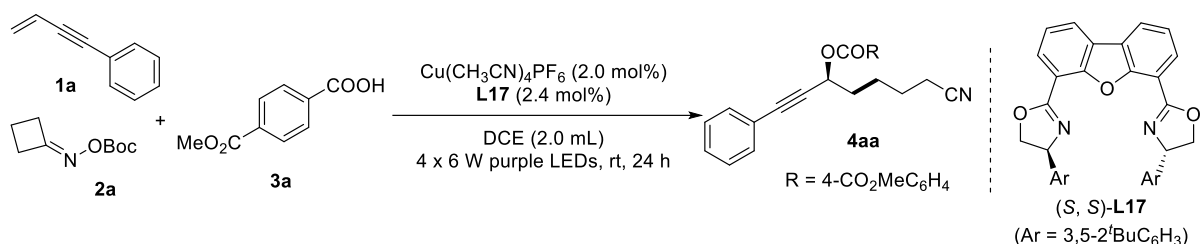
Entry	<i>hν</i>	Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub>	<b>L17</b>	Yield [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1 <sup>[d]</sup>	×	√	√	17	95
2 <sup>[e]</sup>	√	×	√	N.R.	-
3 <sup>[f]</sup>	√	√	×	11	-
<b>4</b>	√	√	√	<b>91 (90)</b>	<b>95</b>

<sup>[a]</sup> **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (1.0 equiv, 0.1 mmol), Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (0.005 mmol, 2.0 mol%) and chiral ligand **L17** (0.0024 mmol, 2.4 mol%) in 2.0 mL DCE for 24 h under the irradiation of 4 x 6 W purple LEDs. <sup>[b]</sup> NMR yield determined by using 1,3,5-trimethoxybenzene as an internal standard. Value in parentheses is isolated yield. <sup>[c]</sup> Determined by chiral HPLC. <sup>[d]</sup> Without the irradiation. <sup>[e]</sup> Without the copper salt. <sup>[f]</sup> Without the ligand. N.R. = no reaction.

The results of **Table S5** reveal that each component is essential for the reaction.

## 4. General Procedure and Characterization Data of Products

### 4.1 General procedure (with product **4aa** as an example)



In a flame-dried 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (0.75 mg, 0.002 mmol) and chiral ligand **L17** (1.64 mg, 0.0024 mmol), followed by the addition of DCE (2.0 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture, **3a** (18.0 mg, 0.10 mmol), **1a** (38.4 mg, 0.30 mmol) and **2a** (37.0 mg, 0.20 mmol) were added. Then, the resulting mixture was degassed (3 times) under argon atmosphere. At last, the mixture was stirred at a distance of ~1 cm from 4 x 6 W purple LEDs at room temperature for 24 h. The product was purified by flash column chromatography on silica gel to afford the desired product with petroleum ether and ethyl acetate (7:1, v/v) in 90% yield and 95% ee.

Note: The racemic samples were prepared according to the general procedure by replacing the chiral ligand with racemic ligand **L1** (by mixing equal parts *R*-**L1** and *S*-**L1**).

### 4.2 Characterization data of products

#### (*S*)-7-cyano-1-phenylhept-1-yn-3-yl methyl terephthalate **4aa**

90% isolated yield (33.8 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 63.44$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 19.38 min,  $t_{\text{R}}$  (minor) = 27.22 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.16 – 8.10 (m, 4H), 7.47 – 7.44 (m, 2H), 7.34 – 7.29 (m, 3H), 5.89 (t,  $J = 6.3$  Hz, 1H), 3.94 (s, 3H), 2.44 – 2.38 (m, 2H), 2.06 – 2.04 (m, 2H), 1.82 – 1.76 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 134.1, 133.5, 131.8, 129.7, 129.5, 128.8, 128.2, 121.8, 119.3, 86.2, 85.5, 65.0, 52.4, 34.0, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{21}\text{NNaO}_4$ : 398.1363, found: 398.1364.

#### (*S*)-7-cyano-1-(*p*-tolyl)hept-1-yn-3-yl methyl terephthalate **4ba**

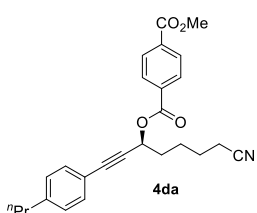
78% isolated yield (30.4 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 25.73$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 85% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 14.89 min,  $t_{\text{R}}$  (minor) = 22.24 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.17 – 8.09 (m, 4H), 7.35 (d,  $J = 7.9$  Hz, 2H), 7.11 (d,  $J = 7.9$  Hz, 2H), 5.88 (t,  $J = 6.3$  Hz, 1H), 3.94 (s, 3H), 2.49 – 2.38 (m, 2H), 2.33 (s, 3H), 2.05 – 2.04 (m, 2H), 1.83 – 1.75 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.7, 139.0, 134.1, 133.5, 131.8, 129.7, 129.5, 129.0, 119.3, 118.7, 86.3, 84.8, 65.1, 52.4, 34.1, 24.9, 24.2, 21.4, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_4$ : 412.1519, found: 412.1518.

#### (*S*)-7-cyano-1-(4-methoxyphenyl)hept-1-yn-3-yl methyl terephthalate **4ca**

90% isolated yield (36.5 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 63.00$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 89% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 29.83 min,  $t_{\text{R}}$  (minor) = 35.90 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.16 – 8.08 (m, 4H), 7.42 – 7.36 (m, 2H), 6.85 – 6.79 (m, 2H),

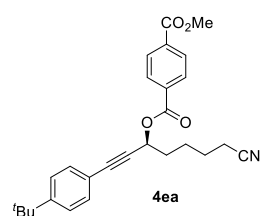
5.87 (t,  $J = 6.3$  Hz, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 2.42 – 2.39 (m, 2H), 2.09 – 1.99 (m, 2H), 1.83 – 1.73 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.7, 159.9, 134.0, 133.5, 133.4, 129.7, 129.5, 119.3, 113.9, 113.8, 86.2, 84.1, 65.1, 55.2, 52.4, 34.1, 24.9, 24.2, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_5$ : 428.1468, found: 428.1466.

**(S)-7-cyano-1-(4-propylphenyl)hept-1-yn-3-yl methyl terephthalate 4da**



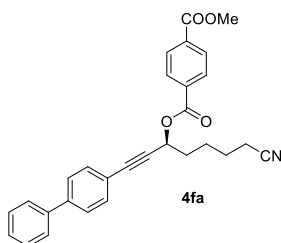
89% isolated yield (37.5 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 21.47$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 90% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 12.44 min,  $t_{\text{R}}$  (minor) = 18.36 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.17 – 8.07 (m, 4H), 7.37 (d,  $J = 8.0$  Hz, 2H), 7.11 (d,  $J = 7.9$  Hz, 2H), 5.88 (t,  $J = 6.3$  Hz, 1H), 3.94 (s, 3H), 2.56 (t,  $J = 7.6$  Hz, 2H), 2.40 – 2.39 (m, 2H), 2.07 – 2.02 (m, 2H), 1.84 – 1.74 (m, 4H), 1.64 – 1.58 (m, 2H), 0.91 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.7, 143.8, 134.1, 133.5, 131.8, 129.7, 129.5, 128.4, 119.3, 119.0, 86.4, 84.8, 65.1, 52.4, 37.9, 34.1, 25.0, 24.2, 17.1, 13.7. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{27}\text{NNaO}_4$ : 440.1832, found: 440.1831.

**(S)-1-(4-(tert-butyl)phenyl)-7-cyanohept-1-yn-3-yl methyl terephthalate 4ea**



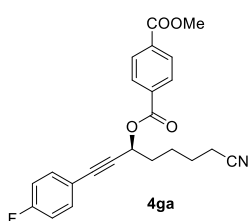
85% isolated yield (36.7 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 50.01$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 92% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 9.65 min,  $t_{\text{R}}$  (minor) = 11.51 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.17 – 8.09 (m, 4H), 7.39 (d,  $J = 8.5$  Hz, 2H), 7.35 – 7.30 (m, 2H), 5.88 (t,  $J = 6.3$  Hz, 1H), 3.95 (s, 3H), 2.40 (t,  $J = 4.4$  Hz, 2H), 2.09 – 1.98 (m, 2H), 1.83 – 1.79 (m, 4H), 1.29 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.2, 164.7, 152.1, 134.1, 133.5, 131.6, 129.7, 129.5, 125.8, 119.5, 118.8, 86.4, 84.8, 65.1, 52.4, 34.8, 34.1, 31.1, 25.0, 24.2, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{29}\text{NNaO}_4$ : 454.1989, found: 454.1986.

**(S)-1-([1,1'-biphenyl]-4-yl)-7-cyanohept-1-yn-3-yl methyl terephthalate 4fa**



81% isolated yield (36.5 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 77.30$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 20.61 min,  $t_{\text{R}}$  (minor) = 36.91 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.18 – 8.12 (m, 4H), 7.58 (d,  $J = 8.3$  Hz, 2H), 7.55 (s, 4H), 7.46 – 7.42 (m, 2H), 7.36 (t,  $J = 7.4$  Hz, 1H), 5.92 (t,  $J = 6.3$  Hz, 1H), 3.95 (s, 3H), 2.43 – 2.41 (m, 2H), 2.13 – 2.03 (m, 2H), 1.83–1.79 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 141.5, 140.0, 134.1, 133.4, 132.3, 129.7, 129.5, 128.8, 127.7, 126.9, 126.9, 120.7, 119.3, 86.1, 86.0, 65.0, 52.4, 34.0, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{29}\text{H}_{25}\text{NNaO}_4$ : 474.1676, found: 474.1673.

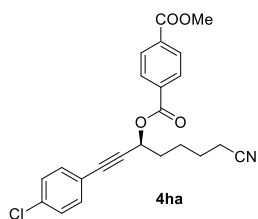
**(S)-7-cyano-1-(4-fluorophenyl)hept-1-yn-3-yl methyl terephthalate 4ga**



94% isolated yield (37.0 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 16.90$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 93% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 13.06 min,  $t_{\text{R}}$  (minor) = 22.43 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.15 – 8.08 (m, 4H), 7.43 (m, 2H), 6.99 (t,  $J = 8.7$  Hz, 2H), 5.85 (t,  $J = 6.3$  Hz, 1H), 3.93 (s, 3H), 2.41 (m, 2H), 2.07 – 1.96 (m, 2H), 1.81 – 1.75 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 162.7 (d,  $J = 250.2$  Hz), 134.1, 133.8 (d,  $J = 8.5$  Hz), 133.4, 129.6 (d,  $J = 15.9$  Hz), 119.3, 117.9, 117.9, 115.5 (d,  $J = 22.2$  Hz), 85.2, 85.1, 64.9, 52.4, 33.9, 24.9, 24.1, 17.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -109.9. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{ClNNaO}_4$ : 416.1269, found: 416.1266.

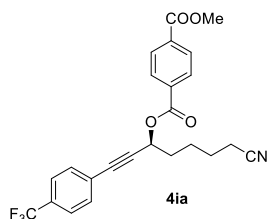
**(S)-1-(4-chlorophenyl)-7-cyanohept-1-yn-3-yl methyl terephthalate 4ha**

80% isolated yield (32.7 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 21.23$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis



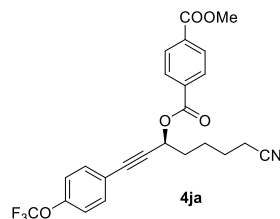
(Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 14.51 min,  $t_R$  (minor) = 23.91 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.18 – 8.13 (m, 4H), 7.44 – 7.38 (m, 2H), 7.32 – 7.29 (m, 2H), 5.89 (t,  $J = 6.3$  Hz, 1H), 3.97 (s, 3H), 2.47 – 2.42 (m, 2H), 2.10-2.05 (m, 2H), 1.83 - 1.79 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 134.8, 134.1, 133.3, 133.1, 129.67, 129.5, 128.6, 120.3, 119.3, 86.4, 85.0, 64.8, 52.4, 33.9, 24.9, 24.2, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{ClNNaO}_4$ : 432.0973, found: 432.0970.

**(S)-7-cyano-1-(4-(trifluoromethyl)phenyl)hept-1-yn-3-yl methyl terephthalate 4ia**



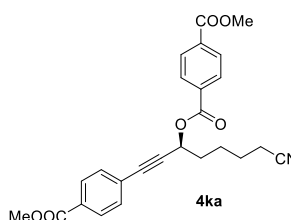
82% isolated yield (36.3 mg), colorless oil,  $[\alpha]_D^{25} = 20.03$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 220$  nm, 25 °C),  $t_R$  (minor) = 20.08 min,  $t_R$  (major) = 26.69 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.18 – 8.10 (m, 4H), 7.57 (s, 4H), 5.88 (t,  $J = 6.4$  Hz, 1H), 3.95 (s, 3H), 2.44 – 2.41 (m, 2H), 2.10 -2.04 (m, 2H), 1.84 – 1.76 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.4, 164.7, 134.3, 133.3, 132.1, 130.5 (d,  $J = 32.7$  Hz), 129.7 (d,  $J = 14.6$  Hz), 125.7, 125.2 (d,  $J = 4.0$  Hz), 119.3, 87.9, 84.8, 64.7, 52.5, 33.9, 24.9, 24.2, 17.1.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -62.89. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{20}\text{F}_3\text{N}_2\text{NaO}_4$ : 466.1237, found: 466.1235.

**(S)-7-cyano-1-(4-(trifluoromethoxy)phenyl)hept-1-yn-3-yl methyl terephthalate 4ja**



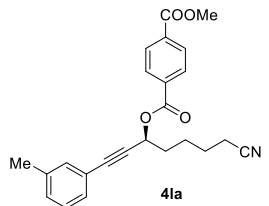
80% isolated yield (36.7 mg), colorless oil,  $[\alpha]_D^{25} = 71.00$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 92% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 10.28 min,  $t_R$  (minor) = 16.12 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.16 – 8.09 (m, 4H), 7.48 (d,  $J = 8.3$  Hz, 2H), 7.15 (d,  $J = 8.3$  Hz, 2H), 5.87 (t,  $J = 6.3$  Hz, 1H), 3.94 (s, 3H), 2.46 – 2.39 (m, 2H), 2.08 - 2.03 (m, 2H), 1.81 – 1.77 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.7, 149.3, 134.2, 133.4 (d,  $J = 11.0$  Hz), 129.7 (d,  $J = 14.5$  Hz), 120.8, 120.6, 119.3, 86.4, 84.8, 64.8, 52.4, 33.9, 24.9, 24.2, 17.1.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -57.80. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{20}\text{F}_3\text{NNaO}_5$ : 482.1186, found: 482.1187.

**(S)-7-cyano-1-(4-(methoxycarbonyl)phenyl)hept-1-yn-3-yl methyl terephthalate 4ka**



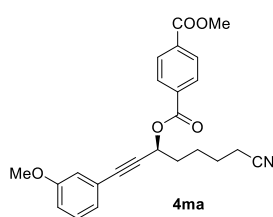
83% isolated yield (35.9 mg), colorless oil,  $[\alpha]_D^{25} = 17.77$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 90% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 22.76 min,  $t_R$  (minor) = 42.47 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.17 – 8.09 (m, 4H), 7.97 (d,  $J = 8.1$  Hz, 2H), 7.51 (d,  $J = 8.1$  Hz, 2H), 5.88 (t,  $J = 6.3$  Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 2.45 – 2.38 (m, 2H), 2.08 – 2.03 (m, 2H), 1.81 – 1.77 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.3, 166.1, 164.6, 134.2, 133.3, 131.8, 130.1, 129.7, 129.6, 129.4, 126.5, 119.3, 88.3, 85.3, 64.8, 52.5, 52.2, 33.9, 24.9, 24.2, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{23}\text{NNaO}_6$ : 456.1418, found: 456.1417.

**(S)-7-cyano-1-(*m*-tolyl)hept-1-yn-3-yl methyl terephthalate 4la**



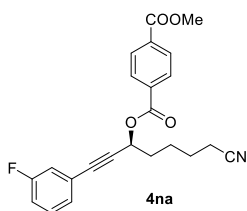
90% isolated yield (26.5 mg), colorless oil,  $[\alpha]_D^{25} = 15.47$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 93% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 18.07 min,  $t_R$  (minor) = 22.99 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.22 – 8.14 (m, 4H), 7.33 (s, 1H), 7.30 (d,  $J = 3.3$  Hz, 1H), 7.23 (d,  $J = 7.5$  Hz, 1H), 7.18 (d,  $J = 7.7$  Hz, 1H), 5.93 (t,  $J = 6.3$  Hz, 1H), 3.99 (s, 3H), 2.49 – 2.43 (m, 2H), 2.36 (s, 3H), 2.14 – 2.04 (m, 2H), 1.85 – 1.82 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 138.0, 134.1, 133.5, 132.4, 129.7, 129.7, 129.5, 128.9, 128.1, 121.6, 119.3, 86.3, 85.1, 65.0, 52.4, 34.0, 24.9, 24.2, 21.1, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_4$ : 412.1519, found: 412.1511.

**(S)-7-cyano-1-(3-methoxyphenyl)hept-1-yn-3-yl methyl terephthalate 4ma**



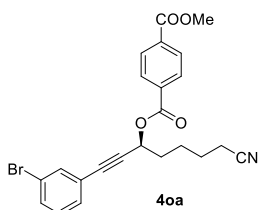
88% isolated yield (35.6 mg), colorless oil,  $[\alpha]_D^{25} = 14.53$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 18.03 min,  $t_R$  (minor) = 20.23 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.16 – 8.08 (m, 4H), 7.20 (t,  $J = 8.0$  Hz, 1H), 7.04 (d,  $J = 7.6$  Hz, 1H), 6.98 – 6.97 (m, 1H), 6.89 – 6.85 (m, 1H), 5.87 (t,  $J = 6.3$  Hz, 1H), 3.93 (s, 3H), 3.77 (s, 3H), 2.45 – 2.38 (m, 2H), 2.10 – 1.99 (m, 2H), 1.80 – 1.76 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.0, 164.6, 159.1, 134.1, 133.4, 129.7, 129.5, 129.3, 124.3, 122.7, 119.3, 116.5, 115.4, 86.0, 85.2, 64.9, 55.2, 52.4, 33.9, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_5$ : 428.1468, found: 428.1467.

**(S)-7-cyano-1-(3-fluorophenyl)hept-1-yn-3-yl methyl terephthalate 4na**



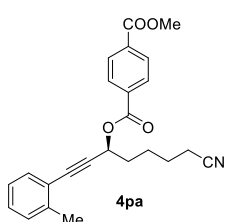
94% isolated yield (37.0 mg), colorless oil,  $[\alpha]_D^{25} = 20.57$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 250$  nm, 25 °C),  $t_R$  (major) = 14.13 min,  $t_R$  (minor) = 24.50 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.18 – 8.11 (m, 4H), 7.29 (d,  $J = 6.1$  Hz, 1H), 7.25 (d,  $J = 7.6$  Hz, 1H), 7.18 – 7.15 (m, 1H), 7.05 (t,  $J = 8.4$  Hz, 1H), 5.88 (t,  $J = 6.3$  Hz, 1H), 3.96 (s, 3H), 2.45 – 2.42 (m, 2H), 2.10 – 2.04 (m, 2H), 1.83 – 1.78 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 162.1 (d,  $J = 246.9$  Hz), 134.2, 133.3, 129.9 (d,  $J = 8.6$  Hz), 129.7, 129.5, 127.8, (d,  $J = 3.1$  Hz), 123.6 (d,  $J = 9.3$  Hz), 119.3, 118.9 (d,  $J = 22.9$  Hz), 116.2 (d,  $J = 21.1$  Hz), 86.4, 84.9, 84.8, 64.7, 52.4, 33.9, 24.98, 24.2, 17.1.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -113.93. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{FNNaO}_4$ : 416.1269, found: 416.1265.

**(S)-1-(3-bromophenyl)-7-cyanohept-1-yn-3-yl methyl terephthalate 4oa**



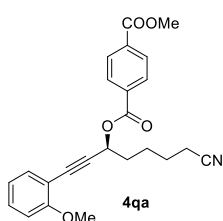
89% isolated yield (40.3 mg), colorless oil,  $[\alpha]_D^{25} = 46.13$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 13.49 min,  $t_R$  (major) = 16.18 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.15 – 8.09 (m, 4H), 7.59 (t,  $J = 1.8$  Hz, 1H), 7.46 – 7.43 (m, 1H), 7.39 – 7.36 (m, 1H), 7.17 (t,  $J = 7.9$  Hz, 1H), 5.85 (t,  $J = 6.3$  Hz, 1H), 3.94 (s, 3H), 2.41 (t,  $J = 6.4$  Hz, 2H), 2.07 – 2.02 (m, 2H), 1.79 – 1.76 (m, 4H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 134.5, 134.1, 133.3, 131.9, 130.4, 129.7, 129.5, 123.8, 122.0, 119.3, 86.8, 84.5, 64.7, 52.4, 33.9, 24.9, 24.2, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{20}\text{BrNNaO}_4$ : 476.0468, found: 476.0467.

**(S)-7-cyano-1-(2-methoxyphenyl)hept-1-yn-3-yl methyl terephthalate 4pa**



84% isolated yield (32.8 mg), colorless oil,  $[\alpha]_D^{25} = 47.37$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 98% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 14.09 min,  $t_R$  (minor) = 23.35 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.86 – 7.81 (m, 4H), 7.52 – 7.47 (m, 3H), 7.15 (d,  $J = 3.3$  Hz, 1H), 6.14 – 6.10 (m, 2H), 2.38 (s, 3H), 2.32 (t,  $J = 7.1$  Hz, 2H), 2.19 – 2.12 (m, 1H), 2.05 – 1.97 (m, 1H), 1.76 – 1.61 (m, 3H), 1.55 – 1.46 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.2, 164.7, 140.5, 134.1, 133.5, 132.1, 129.7, 129.6, 129.4, 128.8, 125.5, 121.6, 119.3, 89.3, 85.3, 65.2, 52.5, 34.1, 25.0, 24.3, 20.6, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{23}\text{NNaO}_4$ : 412.1519, found: 412.1513.

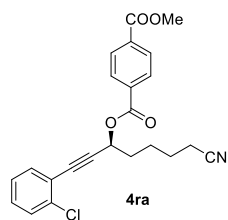
**(S)-7-cyano-1-(2-methoxyphenyl)hept-1-yn-3-yl methyl terephthalate 4qa**



83% isolated yield (33.6 mg), colorless oil,  $[\alpha]_D^{25} = 48.70$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 94% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 36.75 min,  $t_R$  (minor) = 46.26 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.16 – 8.10 (m, 4H), 7.43 – 7.40 (m, 1H), 7.33 – 7.27 (m, 1H), 6.92 – 6.84 (m, 2H), 5.96 (t,  $J = 6.2$  Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 2.44 – 2.36 (m, 2H), 2.09 –

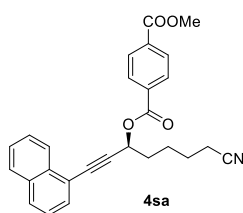
2.04 (m, 2H), 1.83 – 1.79 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.3, 164.8, 160.3, 134.1, 133.9, 133.7, 130.4, 129.8, 129.6, 120.4, 119.5, 111.1, 110.6, 65.4, 55.8, 52.5, 34.1, 25.1, 24.3, 17.2. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>NNaO<sub>5</sub>: 428.1468, found: 428.1463.

**(S)-1-(2-chlorophenyl)-7-cyanohept-1-yn-3-yl methyl terephthalate 4ra**



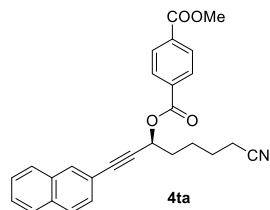
90% isolated yield (36.8 mg), colorless oil, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -4.00 (c = 0.5 in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C), t<sub>R</sub> (major) = 4.95 min, t<sub>R</sub> (minor) = 12.22 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.17 – 8.08 (m, 4H), 7.50 – 7.47 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.21 (m, 2H), 5.93 (t, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 2.42 (t, *J* = 6.3 Hz, 2H), 2.09 – 2.06 (m, 2H), 1.85 – 1.79 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.2, 164.7, 136.2, 134.2, 133.6, 133.4, 129.9, 129.8, 129.8, 129.6, 129.3, 126.4, 121.8, 119.4, 90.6, 65.0, 52.5, 33.9, 25.0, 24.2, 17.1. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>ClNNaO<sub>4</sub>: 432.0973, found: 432.0972.

**(S)-5-cyano-1-(naphthalen-2-yl)pentyl thiophene-3-carboxylate 4sa**



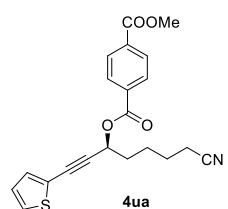
90% isolated yield (31.1 mg), colorless oil, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = 32.97 (c = 0.5 in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis (Chiralpak IC column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C), t<sub>R</sub> (minor) = 56.70 min, t<sub>R</sub> (major) = 63.79 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.20 – 8.11 (m, 4H), 8.01 (d, *J* = 1.5 Hz, 1H), 7.81 – 7.75 (m, 3H), 7.51 – 7.47 (m, 3H), 5.94 (t, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 2.45 – 2.39 (m, 2H), 2.12 – 2.07 (m, 2H), 1.83 – 1.79 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.1, 164.7, 134.1, 133.5, 132.9, 132.7, 132.0, 129.7, 129.5, 128.2, 127.9, 127.7, 127.7, 126.9, 126.6, 119.3, 119.1, 86.5, 85.7, 65.0, 52.4, 34.0, 24.9, 24.3, 17.1. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>27</sub>H<sub>23</sub>NNaO<sub>4</sub>: 448.1519, found: 448.1513.

**(S)-7-cyano-1-(naphthalen-2-yl)hept-1-yn-3-yl methyl terephthalate 4ta**



89% isolated yield (37.8 mg), colorless oil, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = 12.10 (c = 0.5 in CHCl<sub>3</sub>); 91% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C), t<sub>R</sub> (major) = 24.10 min, t<sub>R</sub> (minor) = 33.78 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.28 (d, *J* = 8.3 Hz, 1H), 8.21 – 8.11 (m, 4H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.71 – 7.60 (m, 1H), 7.60 – 7.56 (m, 1H), 7.54 – 7.50 (m, 1H), 7.44 – 7.40 (m, 1H), 6.03 (t, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 2.44 (t, *J* = 6.4 Hz, 2H), 2.18 – 2.14 (m, 2H), 1.89 – 1.83 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.2, 164.8, 134.2, 133.5, 133.3, 133.0, 131.0, 129.8, 129.6, 129.4, 128.3, 127.0, 126.5, 125.8, 125.1, 119.4, 119.4, 90.3, 84.4, 65.3, 52.5, 34.2, 25.0, 24.4 17.2. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>27</sub>H<sub>23</sub>NNaO<sub>4</sub>: 448.1519, found: 448.1520.

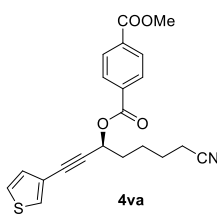
**(S)-7-cyano-1-(thiophen-2-yl)hept-1-yn-3-yl methyl terephthalate 4ua**



94% isolated yield (35.8 mg), colorless oil, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = 11.90 (c = 0.5 in CHCl<sub>3</sub>); 88% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C), t<sub>R</sub> (major) = 20.34 min, t<sub>R</sub> (minor) = 32.20 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.16 – 8.10 (m, 4H), 7.28 (d, *J* = 5.4 Hz, 1H), 7.26 (d, *J* = 3.8 Hz, 1H), 6.98 – 6.96 (m, 1H), 5.90 (t, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 2.42 (t, *J* = 6.5 Hz, 2H), 2.09 – 2.03 (m, 2H), 1.82 – 1.75 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.2, 164.7, 134.2, 133.4, 133.1, 129.8, 129.6, 127.9, 127.0, 121.7, 119.3, 89.4, 79.6, 65.0, 52.5, 33.9, 25.0, 24.3, 17.1. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>19</sub>NNaO<sub>4</sub>S: 404.0927, found: 404.0921.

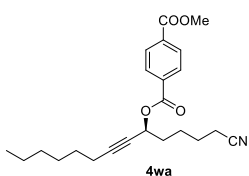
**(S)-7-cyano-1-(thiophen-3-yl)hept-1-yn-3-yl methyl terephthalate 4va**

80% isolated yield (31.6 mg), colorless oil, [ $\alpha$ ]<sub>D</sub><sup>25</sup> = 11.40 (c = 0.5 in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C), t<sub>R</sub> (major) = 20.37 min, t<sub>R</sub>



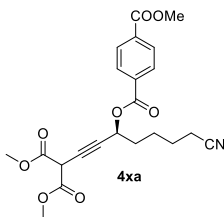
(minor) = 31.98 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.18 – 8.10 (m, 4H), 7.52 – 7.51 (m, 1H), 7.29 – 7.26 (m, 1H), 7.14 – 7.13 (m, 1H), 5.87 (t,  $J$  = 6.3 Hz, 1H), 3.96 (s, 3H), 2.42 (t,  $J$  = 4.4 Hz, 2H), 2.08 – 2.03 (m, 2H), 1.82 – 1.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 134.1, 133.4, 129.8, 129.7, 129.5, 125.4, 120.8, 119.3, 85.1, 81.3, 65.0, 52.4, 33.9, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{19}\text{NNaO}_4\text{S}$ : 404.0927, found: 404.0921.

#### (S)-1-cyanotridec-6-yn-5-yl methyl terephthalate 4wa



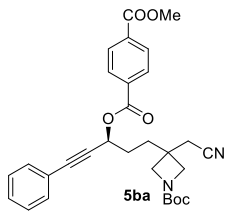
93% isolated yield (33.8 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 0.34$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 18% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 11.71 min,  $t_{\text{R}}$  (major) = 13.34 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.10 (s, 4H), 5.66 – 5.59 (m, 1H), 3.94 (s, 3H), 2.38 (t,  $J$  = 6.7 Hz, 2H), 2.23 – 2.19 (m, 2H), 1.92 (d,  $J$  = 6.9 Hz, 2H), 1.771– 1.69 (m, 4H), 1.53 – 1.46 (m, 2H), 1.39 – 1.33 (m, 2H), 1.30 – 1.24 (m, 4H), 0.86 (t,  $J$  = 6.7 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.2, 164.7, 134.0, 133.7, 129.7, 129.5, 119.4, 87.4, 65.0, 52.4, 34.2, 31.2, 28.4, 28.3, 25.0, 24.2, 22.5, 18.7, 17.1, 14.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{29}\text{NNaO}_4$ : 406.1989, found: 406.1994.

#### (S)-9-cyano-1-methoxy-2-(methoxycarbonyl)-1-oxonon-3-yn-5-yl methyl terephthalate 4xa



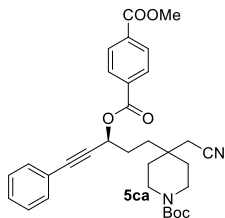
61% isolated yield (30.4 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 5.13$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 72% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 40.29 min,  $t_{\text{R}}$  (minor) = 52.71 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.07 (s, 4H), 5.57 – 5.53 (m, 1H), 3.92 (s, 3H), 3.71 (d,  $J$  = 3.6 Hz, 6H), 3.57 (t,  $J$  = 7.7 Hz, 1H), 2.81 – 2.79 (m, 2H), 2.38 (t,  $J$  = 6.9 Hz, 2H), 1.89 – 1.87 (m, 2H), 1.74 – 1.64 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 168.1, 168.0, 166.1, 164.5, 134.0, 133.4, 129.6, 129.5, 129.5, 119.3, 82.4, 79.0, 64.5, 52.7, 52.4, 50.7, 33.8, 24.8, 24.0, 18.7, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{23}\text{NNaO}_8$ : 452.1316, found: 452.1319.

#### (S)-5-(1-(tert-butoxycarbonyl)-3-(cyanomethyl)azetid-3-yl)-1-phenylpent-1-yn-3-yl methyl terephthalate 5ba



93% isolated yield (47.0 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 11.3$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 91% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 15.96 min,  $t_{\text{R}}$  (major) = 26.79 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.14– 8.08 (m, 4H), 7.44 (d,  $J$  = 7.0 Hz, 2H), 7.29 (d,  $J$  = 6.8 Hz, 3H), 5.87 (t,  $J$  = 5.5 Hz, 1H), 3.91 (d,  $J$  = 1.9 Hz, 3H), 3.80 – 3.72 (m, 4H), 2.68 (s, 2H), 2.02 (d,  $J$  = 9.7 Hz, 4H), 1.41 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 156.0, 134.2, 133.2, 131.9, 129.8, 129.6, 123.0, 128.3, 128.3, 128.2, 121.6, 116.7, 86.7, 84.9, 80.1, 64.8, 52.5, 42.6, 42.5, 35.1, 31.8, 31.6, 29.8, 28.3, 28.3, 27.7, 25.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_6$ : 539.2153, found: 539.2157.

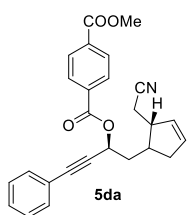
#### (S)-5-(1-(tert-butoxycarbonyl)-4-(cyanomethyl)piperidin-4-yl)-1-phenylpent-1-yn-3-yl methyl terephthalate 5ca



91% isolated yield (49.5 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = 112.63$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 87% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 13.38 min,  $t_{\text{R}}$  (major) = 26.63 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.17 – 8.10 (m, 4H), 7.49 – 7.43 (m, 2H), 7.34 – 7.29 (m, 3H), 5.86 (t,  $J$  = 6.0 Hz, 1H), 3.94 (s, 3H), 3.49 – 3.36 (m, 4H), 2.42 (s, 2H), 1.98 (d,  $J$  = 4.0 Hz, 2H), 1.87 (d,  $J$  = 3.3 Hz, 2H), 1.60 – 1.57 (m, 4H), 1.44 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.1, 166.2, 164.7, 154.6, 134.2, 133.3, 131.9, 129.8, 129.6, 128.9, 128.3, 121.7, 117.1, 86.4, 85.2, 65.2, 60.4, 52.5, 34.9, 33.9, 31.7, 28.7, 28.3, 25.9, 21.0, 14.2. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{32}\text{H}_{36}\text{N}_2\text{NaO}_6$ : 567.2466, found: 567.2460.

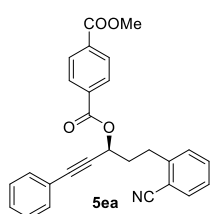


**(2S)-1-(2-(cyanomethyl)cyclopent-3-en-1-yl)-4-phenylbut-3-yn-2-yl methyl terephthalate 5da**



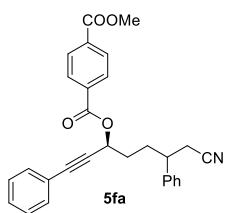
83% isolated yield (34.3 mg), 1:1.2 d.r., colorless oil,  $[\alpha]_D^{25} = 22.33$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee/53% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 49.34 min,  $t_R$  (minor) = 74.87 min;  $t_R$  (minor) = 56.83 min,  $t_R$  (major) = 87.02 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) (major + minor) 8.19 – 8.10 (m, 4H), 7.47 (m, 2H), 7.31 (d,  $J = 6.5$  Hz, 3H), 5.96 – 5.91 (m, 1H), 5.88 – 5.85 (m, 1H), 5.67 – 5.64 (m, 1H), 3.94 (s, 3H), 2.87 – 2.75 (m, 2H), 2.57 – 2.42 (m, 2H), 2.35 – 2.30 (m, 2H), 2.27 – 2.21 (m, 1H), 2.17 – 2.11 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) (major + minor) 166.1, 164.7, 164.6, 134.2, 133.4, 133.4, 132.5, 132.4, 131.9, 131.8, 130.6, 130.5, 129.7, 129.7, 129.6, 129.5, 128.8, 128.8, 128.3, 128.2, 121.8, 118.5, 118.4, 86.5, 86.3, 85.7, 85.4, 64.5, 64.2, 52.4, 48.2, 48.0, 40.4, 40.4, 40.2, 39.9, 39.1, 39.0, 22.7, 22.6. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{26}\text{H}_{23}\text{NNaO}_4$ : 436.1519, found: 436.1520.

**(S)-5-(2-cyanophenyl)-1-phenylpent-1-yn-3-yl methyl terephthalate 5ea**



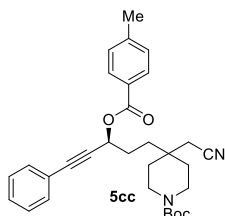
80% isolated yield (33.9 mg), colorless oil,  $[\alpha]_D^{25} = 55.40$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 39.14 min,  $t_R$  (minor) = 61.61 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.15 – 8.09 (m, 4H), 7.64 – 7.62 (m, 1H), 7.55 – 7.47 (m, 3H), 7.40 (d,  $J = 7.4$  Hz, 1H), 7.33 – 7.28 (m, 4H), 5.89 (t,  $J = 6.2$  Hz, 1H), 3.95 (s, 3H), 3.20 (t,  $J = 7.9$  Hz, 2H), 2.47 – 2.38 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 166.1, 164.6, 144.5, 134.1, 133.4, 133.0, 132.89, 131.9, 129.8, 129.6, 129.5, 128.8, 128.2, 126.9, 121.8, 117.7, 112.4, 86.6, 85.2, 64.7, 52.4, 35.5, 30.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{21}\text{NNaO}_4$ : 446.1363, found: 446.1367.

**(3S)-7-cyano-1,6-diphenylhept-1-yn-3-yl methyl terephthalate 5fa**



85% isolated yield (38.4 mg), 1:1.2 d.r., colorless oil,  $[\alpha]_D^{25} = 21.50$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 98% ee/96% ee, determined by HPLC analysis (Chiralpak AZ column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 44.73 min,  $t_R$  (major) = 62.35 min;  $t_R$  (minor) = 48.01 min,  $t_R$  (major) = 56.66 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) (major + minor) 8.11 (d,  $J = 3.7$  Hz, 4H), 7.46– 7.43 (m, 2H), 7.38 – 7.34 (m, 3H), 7.31 (d,  $J = 6.4$  Hz, 4H), 7.24 (s, 1H), 5.83 (t,  $J = 6.3$  Hz, 1H), 3.93 (d,  $J = 1.2$  Hz, 3H), 3.10 – 3.02 (m, 1H), 2.64 (d,  $J = 6.9$  Hz, 2H), 2.20 – 2.14 (m, 1H), 2.13 – 2.06 (m, 1H), 1.99 – 1.92 (m, 1H), 1.89 – 1.83 (m, 1H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) (major + minor) 166.1, 164.5, 164.5, 140.7, 134.0, 134.0, 133.4, 131.8, 131.8, 129.7, 129.6, 129.5, 129.5, 129.0, 128.8, 128.7, 128.2, 127.6, 127.1, 127.1, 121.7, 118.2, 86.2, 86.1, 85.4, 64.9, 64.9, 52.4, 41.7, 41.7, 32.5, 32.4, 30.1, 30.0, 25.3. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{29}\text{H}_{25}\text{NNaO}_4$ : 474.1676, found: 474.1682.

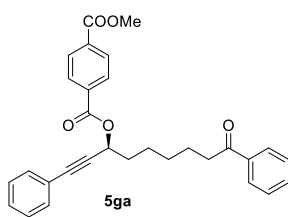
***tert*-butyl (S)-4-(cyanomethyl)-4-(3-((4-methylbenzoyl)oxy)-5-phenylpent-4-yn-1-yl)piperidine-1-carboxylate 5cc**



75% isolated yield (37.5 mg), white solid,  $[\alpha]_D^{25} = 21.50$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 86% ee, determined by HPLC analysis (Chiralpak OX column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 59.62 min,  $t_R$  (minor) = 64.01 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.99 (d,  $J = 8.2$  Hz, 2H), 7.48 – 7.44 (m, 2H), 7.31 (d,  $J = 5.7$  Hz, 3H), 7.26 (d,  $J = 7.9$  Hz, 2H), 5.86 (t,  $J = 5.9$  Hz, 1H), 3.42 (d,  $J = 6.1$  Hz, 4H), 2.41 (d,  $J = 3.1$  Hz, 5H), 2.00 – 1.94 (m, 2H), 1.89 – 1.82 (m, 2H), 1.61 – 1.54 (m, 4H), 1.45 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.4, 154.6, 144.0, 131.9, 129.8, 129.1, 128.7, 128.2, 126.8, 121.9, 117.1, 85.9, 85.7, 79.7, 64.4, 33.8, 31.5, 28.7, 28.3, 26.0, 21.6. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{31}\text{H}_{36}\text{N}_2\text{NaO}_4$ : 523.2567, found: 523.2570.

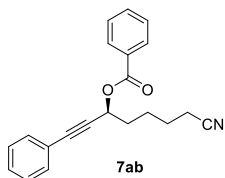
**(S)-methyl (9-oxo-1,9-diphenylnon-1-yn-3-yl) terephthalate 5ga**

70% isolated yield (32.8 mg), colorless oil,  $[\alpha]_D^{25} = 22.00$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 92% ee, determined by HPLC analysis (Chiralpak AZ column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 31.67 min,  $t_R$



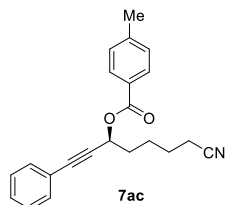
(major) = 38.19 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.23 – 8.06 (m, 4H), 7.95 (d,  $J$  = 7.0 Hz, 2H), 7.55 (t,  $J$  = 7.4 Hz, 1H), 7.50 – 7.39 (m, 4H), 7.30 (d,  $J$  = 6.9 Hz, 3H), 5.87 (t,  $J$  = 6.5 Hz, 1H), 3.95 (s, 3H), 2.99 (t,  $J$  = 7.3 Hz, 2H), 2.07 – 2.01 (m, 2H), 1.84 – 1.76 (m, 2H), 1.70 – 1.62 (m, 2H), 1.54 – 1.47 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 200.2, 166.3, 164.8, 136.9, 134.0, 133.7, 132.9, 131.9, 129.8, 129.5, 128.6, 128.6, 128.2, 128.0, 122.1, 65.5, 52.5, 38.3, 34.8, 28.8, 25.0, 24.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{30}\text{H}_{28}\text{NaO}_5$ : 491.1829, found: 491.1830.

#### (S)-7-cyano-1-phenylhept-1-yn-3-yl benzoate 7ab



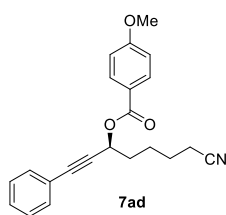
84% isolated yield (26.6 mg), colorless oil,  $[\alpha]_{\text{D}}^{25}$  = -9.23 ( $c$  = 0.5 in  $\text{CHCl}_3$ ); 94% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_{\text{R}}$  (minor) = 11.46 min,  $t_{\text{R}}$  (major) = 12.80 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.13 – 8.07 (m, 2H), 7.58 (t,  $J$  = 7.4 Hz, 1H), 7.48 – 7.44 (m, 4H), 7.36 – 7.29 (m, 3H), 5.89 (t,  $J$  = 6.3 Hz, 1H), 2.45 – 2.37 (m, 2H), 2.10 – 1.99 (m, 2H), 1.80 – 1.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.4, 133.2, 131.8, 129.7, 128.7, 128.4, 128.2, 122.0, 119.3, 85.8, 64.4, 34.0, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{19}\text{NNaO}_2$ : 340.1308, found: 340.1306.

#### (S)-7-cyano-1-phenylhept-1-yn-3-yl 4-methylbenzoate 7ac



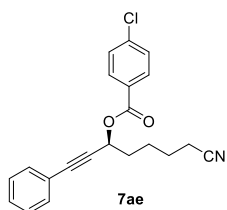
89% isolated yield (29.5 mg), colorless oil,  $[\alpha]_{\text{D}}^{25}$  = 7.03 ( $c$  = 0.5 in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_{\text{R}}$  (minor) = 10.87 min,  $t_{\text{R}}$  (major) = 12.01 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.98 (d,  $J$  = 8.0 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.36 – 7.29 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 5.88 (t,  $J$  = 6.3 Hz, 1H), 2.41 (s, 3H), 2.41 – 2.37 (m, 2H), 2.09 – 1.98 (m, 2H), 1.80 – 1.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.5, 143.9, 131.8, 129.8, 129.7, 129.1, 129.0, 128.6, 128.2, 126.9, 122.0, 119.3, 86.0, 85.7, 64.2, 34.0, 24.9, 24.2, 21.6, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{21}\text{NNaO}_2$ : 354.1465, found: 354.1458.

#### (S)-7-cyano-1-phenylhept-1-yn-3-yl 4-methoxybenzoate 7ad



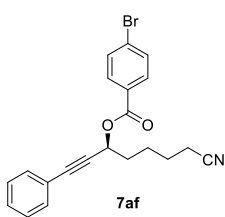
89% isolated yield (30.9 mg), colorless oil,  $[\alpha]_{\text{D}}^{25}$  = 20.53 ( $c$  = 0.5 in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_{\text{R}}$  (minor) = 37.49 min,  $t_{\text{R}}$  (major) = 40.04 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.07 – 8.03 (m, 2H), 7.48 – 7.43 (m, 2H), 7.33 – 7.28 (m, 3H), 6.96 – 6.91 (m, 2H), 5.86 (t,  $J$  = 6.3 Hz, 1H), 3.85 (s, 3H), 2.42 – 2.37 (m, 2H), 2.05 – 2.02 (m, 2H), 1.80 – 1.76 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.1, 163.5, 131.8, 131.8, 131.8, 131.6, 128.6, 128.2, 128.1, 122.0, 119.4, 113.6, 113.6, 86.1, 85.6, 64.0, 55.4, 34.1, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{21}\text{NNaO}_3$ : 370.1414, found: 370.1409.

#### (S)-7-cyano-1-phenylhept-1-yn-3-yl 4-chlorobenzoate 7ae



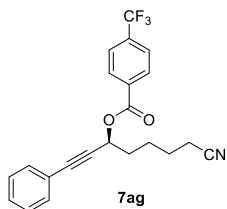
80% isolated yield (28.1 mg), colorless oil,  $[\alpha]_{\text{D}}^{25}$  = 11.57 ( $c$  = 0.5 in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_{\text{R}}$  (minor) = 18.97 min,  $t_{\text{R}}$  (major) = 21.72 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.09 – 7.95 (m, 2H), 7.50 – 7.40 (m, 4H), 7.31 (d,  $J$  = 6.5 Hz, 3H), 5.87 (t,  $J$  = 6.3 Hz, 1H), 2.45 – 2.35 (m, 2H), 2.06 – 2.01 (m, 2H), 1.80 – 1.76 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 164.6, 139.7, 131.8, 131.1, 128.7, 128.7, 128.2, 128.1, 121.9, 119.3, 86.0, 85.6, 64.7, 34.0, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{18}\text{ClNNaO}_2$ : 374.0918, found: 374.0913.

#### (S)-7-cyano-1-phenylhept-1-yn-3-yl 4-bromobenzoate 7af



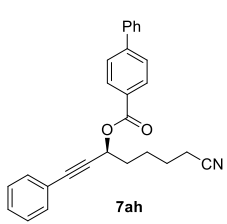
80% isolated yield (31.6 mg), colorless oil,  $[\alpha]_D^{25} = 46.74$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 26.39 min,  $t_R$  (major) = 29.01 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.94 (d,  $J = 8.2$  Hz, 2H), 7.59 (d,  $J = 8.3$  Hz, 2H), 7.47 – 7.44 (m, 2H), 7.31 (d,  $J = 6.4$  Hz, 3H), 5.86 (t,  $J = 6.3$  Hz, 1H), 2.43 – 2.36 (m, 2H), 2.09 – 1.98 (m, 2H), 1.79 – 1.75 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 164.7, 131.8, 131.7, 131.2, 128.7, 128.5, 128.3, 128.2, 121.8, 119.3, 86.0, 85.5, 64.7, 33.9, 24.9, 24.1, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{18}\text{BrNNaO}_2$ : 418.0413, found: 418.0418.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 4-(trifluoromethyl)benzoate 7ag**



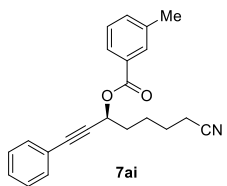
81% isolated yield (31.2 mg), colorless oil,  $[\alpha]_D^{25} = -12.70$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 10.95 min,  $t_R$  (major) = 12.08 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.02 (d,  $J = 8.5$  Hz, 2H), 7.49 – 7.41 (m, 4H), 7.31 (d,  $J = 6.6$  Hz, 3H), 5.87 (t,  $J = 6.3$  Hz, 1H), 2.43 – 2.36 (m, 2H), 2.07 – 2.04 (m, 2H), 1.81 – 1.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 164.2, 134.6 (q,  $J = 32.6$  Hz), 132.9, 131.8, 130.1, 128.8, 128.3, 125.4 (q,  $J = 3.7$  Hz), 124.9, 122.0 (d,  $J = 37.8$  Hz), 119.3, 86.2, 85.3, 65.1, 34.0, 24.9, 24.2, 17.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -63.09. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{18}\text{F}_3\text{NNaO}_2$ : 408.1182, found: 408.1180.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl [1,1'-biphenyl]-4-carboxylate 7ah**



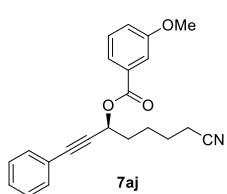
75% isolated yield (29.5 mg), colorless oil,  $[\alpha]_D^{25} = 17.20$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 16.69 min,  $t_R$  (major) = 20.28 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.19 (d,  $J = 8.1$  Hz, 2H), 7.70 (d,  $J = 8.2$  Hz, 2H), 7.66 – 7.63 (m, 2H), 7.49 (t,  $J = 7.8$  Hz, 4H), 7.42 (d,  $J = 7.2$  Hz, 1H), 7.35 – 7.31 (m, 3H), 5.94 (t,  $J = 6.3$  Hz, 1H), 2.44 – 2.38 (m, 2H), 2.11 – 2.05 (m, 2H), 1.86 – 1.78 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.6, 138.2, 134.0, 131.8, 130.2, 129.6, 128.7, 128.3, 128.2, 126.9, 122.0, 119.3, 85.9, 85.8, 64.3, 34.0, 25.0, 24.2, 21.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{23}\text{NNaO}_2$ : 416.1621, found: 416.1617.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3-methylbenzoate 7ai**



95% isolated yield (31.4 mg), colorless oil,  $[\alpha]_D^{25} = -25.83$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 10.35 min,  $t_R$  (major) = 11.56 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.90 (d,  $J = 7.4$  Hz, 2H), 7.48 – 7.45 (m, 2H), 7.39 (d,  $J = 7.6$  Hz, 1H), 7.36 (d,  $J = 7.4$  Hz, 1H), 7.34 – 7.30 (m, 3H), 5.89 (t,  $J = 6.3$  Hz, 1H), 2.42 (s, 3H), 2.40 – 2.38 (m, 2H), 2.07 – 2.02 (m, 2H), 1.81 – 1.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 174.4, 141.5, 141.5, 137.5, 133.1, 128.5, 128.0, 127.7, 126.6, 126.3, 126.2, 125.6, 124.3, 123.9, 119.4, 75.7, 43.8, 36.2, 36.1, 35.4, 25.1, 24.6, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{22}\text{H}_{21}\text{NNaO}_2$ : 354.1465, found: 354.1470.

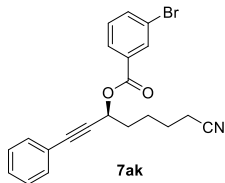
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3-methoxybenzoate 7aj**



90% isolated yield (31.2 mg), colorless oil,  $[\alpha]_D^{25} = -21.53$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 26.55 min,  $t_R$  (major) = 31.17 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.70 – 7.68 (m, 1H), 7.60 (t,  $J = 1.9$  Hz, 1H), 7.47 – 7.45 (m, 2H), 7.37 (t,  $J = 8.0$  Hz, 1H), 7.34 – 7.29 (m, 3H), 7.14 – 7.11 (m, 1H), 5.88 (t,  $J = 6.3$  Hz, 1H), 3.86 (s, 3H), 2.43 – 2.41 – 2.38 (m, 2H), 2.07 – 2.02 (m, 2H), 1.81 – 1.77 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 165.3, 159.5, 131.8, 131.0, 129.4, 128.7, 128.2, 122.1, 122.0, 119.6, 119.3, 114.2, 85.9, 85.8, 64.5, 55.4, 34.0, 24.9, 24.2, 17.0. HRMS (EI):

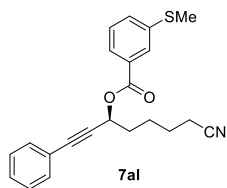
m/z [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>21</sub>NNaO<sub>3</sub>: 370.1414, found: 370.1412.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3-bromobenzoate 7ak**



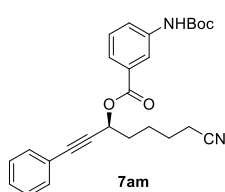
80% isolated yield (31.6 mg), colorless oil,  $[\alpha]_D^{25} = -23.10$  ( $c = 0.5$  in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 11.62 min,  $t_R$  (major) = 14.67 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.21 (d,  $J = 1.8$  Hz, 1H), 8.02 (d,  $J = 7.8$  Hz, 1H), 7.74 – 7.67 (m, 1H), 7.47 – 7.45 (m, 2H), 7.36 – 7.30 (m, 4H), 5.87 (t,  $J = 6.3$  Hz, 1H), 2.44 – 2.38 (m, 2H), 2.10 – 2.00 (m, 2H), 1.80 – 1.75 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 164.1, 136.1, 132.6, 131.8, 131.6, 130.0, 128.8, 128.3, 128.2, 122.4, 121.8, 119.3, 86.2, 85.4, 65.0, 34.0, 24.9, 24.2, 17.0. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>BrNNaO<sub>2</sub>: 418.0413, found: 418.0412.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3-(methylthio)benzoate 7al**



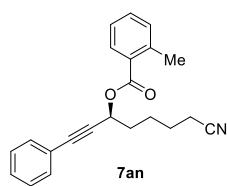
90% isolated yield (32.7 mg), colorless oil,  $[\alpha]_D^{25} = -21.13$  ( $c = 0.5$  in CHCl<sub>3</sub>); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 15.28 min,  $t_R$  (major) = 18.08 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.95 (d,  $J = 1.9$  Hz, 1H), 7.84 (d,  $J = 7.6$  Hz, 1H), 7.47 – 7.44 (m, 3H), 7.38 (d,  $J = 7.7$  Hz, 1H), 7.34 – 7.29 (m, 3H), 5.87 (t,  $J = 6.3$  Hz, 1H), 2.53 (s, 3H), 2.40 (t,  $J = 4.4$  Hz, 2H), 2.07 – 2.02 (m, 2H), 1.80 – 1.77 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 165.1, 139.4, 131.8, 131.0, 130.3, 128.7, 128.7, 128.2, 127.3, 126.2, 121.9, 119.3, 86.0, 85.7, 64.6, 34.0, 25.0, 24.2, 17.1, 15.6. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>NaO<sub>2</sub>S: 386.1185, found: 386.1183.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3-((tert-butoxycarbonyl)amino)benzoate 7am**



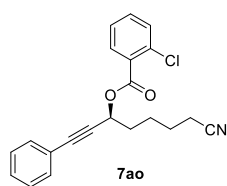
88% isolated yield (38.0 mg), colorless oil,  $[\alpha]_D^{25} = 9.37$  ( $c = 0.5$  in CHCl<sub>3</sub>); 96% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (major) = 10.47 min,  $t_R$  (minor) = 12.51 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.93 (t,  $J = 1.9$  Hz, 1H), 7.76 (t,  $J = 8.9$  Hz, 2H), 7.46 – 7.44 (m, 2H), 7.39 (t,  $J = 8.0$  Hz, 1H), 7.33 – 7.29 (m, 3H), 6.70 (s, 1H), 5.86 (t,  $J = 6.2$  Hz, 1H), 2.45 – 2.38 (m, 2H), 2.06 – 2.01 (m, 2H), 1.81 – 1.78 (m, 4H), 1.52 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 165.2, 152.6, 138.8, 131.9, 130.5, 129.2, 128.8, 128.3, 124.3, 123.3, 122.1, 119.6, 119.5, 86.0, 85.8, 80.9, 64.6, 34.0, 28.3, 25.0, 24.2, 17.1. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>26</sub>H<sub>28</sub>NNaO<sub>4</sub>: 455.1941, found: 455.1936.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 2-methylbenzoate 7an**



88% isolated yield (29.1 mg), colorless oil,  $[\alpha]_D^{25} = -29.17$  ( $c = 0.5$  in CHCl<sub>3</sub>); 94% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 18.76 min,  $t_R$  (major) = 20.65 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.97 (d,  $J = 7.3$  Hz, 1H), 7.48 (d,  $J = 2.0$  Hz, 1H), 7.45 (t,  $J = 2.4$  Hz, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.37 – 7.31 (m, 3H), 7.27 (d,  $J = 4.9$  Hz, 2H), 5.88 (t,  $J = 6.3$  Hz, 1H), 2.65 (s, 3H), 2.44 – 2.38 (m, 2H), 2.04 (t,  $J = 7.0$  Hz, 2H), 1.82 – 1.78 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 166.4, 140.4, 132.2, 131.8, 131.7, 130.7, 129.1, 128.7, 128.2, 128.1, 125.7, 122.1, 119.4, 86.0, 85.8, 64.1, 34.1, 25.0, 24.3, 21.8, 17.1. HRMS (EI): m/z [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>21</sub>NNaO<sub>2</sub>: 354.1465, found: 354.1461.

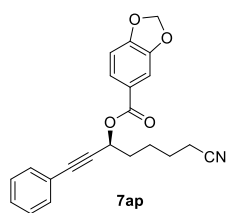
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 2-chlorobenzoate 7ao**



80% isolated yield (28.1 mg), colorless oil,  $[\alpha]_D^{25} = -33.17$  ( $c = 0.5$  in CHCl<sub>3</sub>); 93% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 30.91 min,  $t_R$  (major) = 34.11 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.89 – 7.87 (m, 1H), 7.51 – 7.42 (m, 4H), 7.36 – 7.29 (m, 4H), 5.89 (t,  $J = 6.3$  Hz, 1H), 2.47 – 2.37 (m, 2H), 2.12 – 2.00 (m, 2H), 1.87 – 1.76 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$

(ppm) 164.6, 133.8, 132.8, 131.8, 131.5, 131.1, 129.6, 128.7, 128.2, 126.6, 121.9, 119.4, 86.1, 85.4, 65.1, 33.9, 24.9, 24.2, 17.1. HRMS (EI):  $m/z$   $[M + Na]^+$  calcd for  $C_{21}H_{18}ClNNaO_2$ : 374.0918, found: 374.0915.

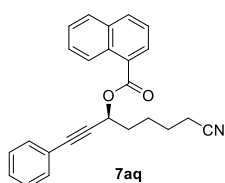
**(S)-7-cyano-1-phenylhept-1-yn-3-yl benzo[d][1,3]dioxole-4-carboxylate 7ap**



83% isolated yield (30.0 mg), colorless oil,  $[\alpha]_D^{25} = -55.60$  ( $c = 0.5$  in  $CHCl_3$ ); 95% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 21.69 min,  $t_R$  (major) = 24.78 min.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.71 – 7.69 (m, 1H), 7.53 – 7.48 (m, 1H), 7.47 – 7.43 (m, 2H), 7.35 – 7.28 (m, 3H), 6.85 (d,  $J = 8.2$  Hz, 1H), 6.03 (s, 2H), 5.84 (t,  $J = 6.3$  Hz, 1H), 2.38 (d,  $J = 6.5$  Hz, 2H), 2.04 – 1.99 (m, 2H), 1.79 – 1.75 (m, 4H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 164.7, 151.8, 147.7,

131.8, 128.6, 128.2, 125.6, 123.6, 122.0, 119.3, 109.5, 108.0, 101.8, 85.9, 85.8, 64.3, 34.0, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[M + Na]^+$  calcd for  $C_{22}H_{19}NNaO_4$ : 384.1206, found: 384.1204.

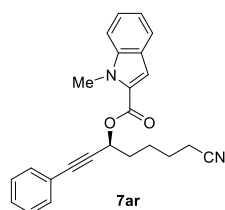
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 1-naphthoate 7aq**



85% isolated yield (31.2 mg), colorless oil,  $[\alpha]_D^{25} = -58.20$  ( $c = 0.5$  in  $CHCl_3$ ); 99% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 39.13 min,  $t_R$  (major) = 43.33 min.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 8.98 (d,  $J = 8.7$  Hz, 1H), 8.26 (d,  $J = 7.2$  Hz, 1H), 8.05 (d,  $J = 8.2$  Hz, 1H), 7.90 (d,  $J = 8.1$  Hz, 1H), 7.67 – 7.63 (m, 1H), 7.58 – 7.55 (m, 1H), 7.54 – 7.48 (m, 3H), 7.35 – 7.31

(m, 3H), 6.00 (t,  $J = 6.3$  Hz, 1H), 2.44 – 2.38 (m, 2H), 2.16 – 2.07 (m, 2H), 1.85 – 1.81 (m, 4H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 166.3, 133.8, 133.7, 131.9, 131.4, 130.5, 128.7, 128.6, 128.3, 127.9, 126.5, 126.3, 125.6, 124.5, 122.0, 119.4, 86.0, 86.0, 64.5, 34.1, 25.0, 24.4, 17.1. HRMS (EI):  $m/z$   $[M + Na]^+$  calcd for  $C_{25}H_{21}NNaO_2$ : 390.1465, found: 390.1462.

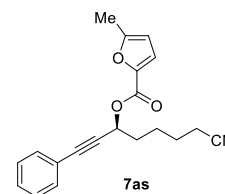
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 1-methyl-1H-indole-2-carboxylate 7ar**



80% isolated yield (29.6 mg), colorless oil,  $[\alpha]_D^{25} = 78.17$  ( $c = 0.5$  in  $CHCl_3$ ); 89% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 9.59 min,  $t_R$  (major) = 13.02 min.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.70 (d,  $J = 7.9$  Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 – 7.37 (m, 3H), 7.35 – 7.30 (m, 3H), 7.19 – 7.15 (m, 1H), 5.88 (t,  $J = 6.3$  Hz, 1H), 4.11 (s, 3H), 2.45 – 2.39 (m, 2H), 2.10 – 2.01 (m, 2H), 1.83 – 1.80 (m, 4H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 161.0, 139.8, 131.9,

128.7, 128.2, 127.1, 125.7, 125.2, 122.6, 122.0, 120.6, 119.4, 110.8, 110.2, 85.9, 63.9, 34.1, 31.6, 25.0, 24.3, 17.1. HRMS (EI):  $m/z$   $[M + Na]^+$  calcd for  $C_{24}H_{22}N_2NaO_2$ : 393.1573, found: 393.1572.

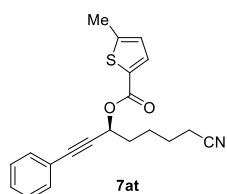
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 5-methylfuran-2-carboxylate 7as**



80% isolated yield (25.7mg), colorless oil,  $[\alpha]_D^{25} = 9.17$  ( $c = 0.5$  in  $CHCl_3$ ); 86% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 12.28 min,  $t_R$  (major) = 15.64 min.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 7.46 – 7.43 (m, 2H), 7.30 (d,  $J = 6.6$  Hz, 3H), 7.15 (d,  $J = 3.4$  Hz, 1H), 6.13 (d,  $J = 3.4$  Hz, 1H), 5.83 (t,  $J = 6.3$  Hz, 1H), 2.38 (s, 5H), 2.03 – 1.98 (m, 2H), 1.80 – 1.70 (m, 4H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 157.7, 157.6, 142.4, 131.8, 128.7, 128.2, 122.0, 120.1, 119.4, 108.5,

86.0, 85.6, 64.1, 34.0, 24.9, 24.2, 17.0, 14.0. HRMS (EI):  $m/z$   $[M + Na]^+$  calcd for  $C_{20}H_{19}NNaO_3$ : 344.1257, found: 344.1253.

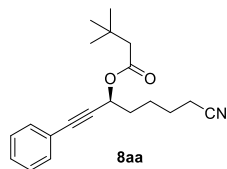
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 5-methylthiophene-2-carboxylate 7at**



77% isolated yield (25.9 mg), colorless oil,  $[\alpha]_D^{25} = 20.53$  ( $c = 0.5$  in  $CHCl_3$ ); 91% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_R$  (minor) = 13.86 min,  $t_R$  (major) = 15.86 min.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$

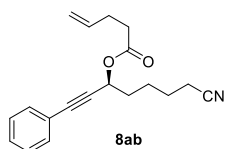
(ppm) 7.67 (d,  $J = 3.7$  Hz, 1H), 7.46 – 7.44 (m, 2H), 7.33 – 7.28 (m, 3H), 6.81 – 6.76 (m, 1H), 5.81 (t,  $J = 6.2$  Hz, 1H), 2.53 (s, 3H), 2.39 (t,  $J = 6.6$  Hz, 2H), 2.03 - 1.98 (m, ), 1.80 – 1.74 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 161.1, 148.6, 134.4, 131.9, 130.4, 128.7, 128.2, 126.4, 122.0, 119.4, 85.9, 85.8, 64.4, 34.0, 25.0, 24.2, 17.1, 15.8. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{19}\text{NNaO}_2\text{S}$ : 360,1029, found: 360,1028.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3,3-dimethylbutanoate 8aa**



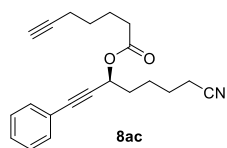
84% isolated yield (26.1 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -20.23$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 88% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 11.74 min,  $t_{\text{R}}$  (minor) = 13.20 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.43 – 7.41 (m, 2H), 7.33 – 7.28 (m, 3H), 5.61 (t,  $J = 6.3$  Hz, 1H), 2.38 (t,  $J = 6.7$  Hz, 2H), 2.25 (d,  $J = 3.2$  Hz, 2H), 1.94 – 1.83 (m, 2H), 1.78 – 1.67 (m, 4H), 1.06 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.2, 131.7, 128.6, 128.2, 122.0, 119.4, 86.0, 85.4, 63.3, 47.8, 33.8, 31.0, 29.6, 24.9, 24.2, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{20}\text{H}_{25}\text{NNaO}_2$ : 334.1778, found: 334.1776.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl pent-4-enoate 8ab**



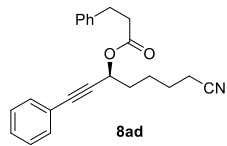
83% isolated yield (24.5 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -30.60$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 12.94 min,  $t_{\text{R}}$  (major) = 14.93 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.44 – 7.42 (m, 2H), 7.34 – 7.27 (m, 3H), 5.89 – 5.76 (m, 1H), 5.64 (t,  $J = 6.4$  Hz, 1H), 5.13 – 4.99 (m, 2H), 2.52 – 2.45 (m, 2H), 2.43 – 2.35 (m, 4H), 1.91 – 1.86 (m, , 2H), 1.78 – 1.67 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.9, 136.3, 131.8, 128.7, 128.2, 121.9, 119.4, 115.6, 85.8, 85.6, 63.7, 33.9, 33.4, 28.7, 24.9, 24.1, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{21}\text{NNaO}_2$ : 318.1465, found: 318.1466.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl hept-6-ynoate 8ac**



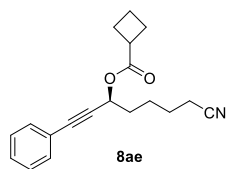
83% isolated yield (26.7 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -40.83$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 95% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 17.82 min,  $t_{\text{R}}$  (major) = 22.11 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.45 – 7.42 (m, 2H), 7.31 (d,  $J = 6.6$  Hz, 3H), 5.63 (t,  $J = 6.4$  Hz, 1H), 2.41 – 2.37 (m, 4H), 2.24 – 2.20 (m, 2H), 1.95 (t,  $J = 2.7$  Hz, 1H), 1.92 – 1.86 (m, 2H), 1.80 - 1.68 (m, 6H), 1.62 – 1.55 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 172.3, 131.8, 128.7, 128.2, 121.9, 119.4, 85.8, 85.6, 83.8, 77.3, 77.0, 76.7, 68.6, 63.7, 33.9, 33.7, 27.7, 24.9, 24.2, 23.9, 18.1, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{23}\text{N}_2\text{NaO}_2$ : 344.1621, found: 344.1618.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 3-phenylpropanoate 8ad**



75% isolated yield (35.4 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -60.73$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 90% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 7.92 min,  $t_{\text{R}}$  (major) = 8.64 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.37 – 7.35 (m, 2H), 7.26 - 7.22 (m, 3H), 7.21 - 7.20 (m, 1H), 7.19 (d,  $J = 2.3$  Hz, 1H), 7.17 – 7.10 (m, 3H), 5.55 (t,  $J = 6.3$  Hz, 1H), 2.91 (t,  $J = 7.7$  Hz, 2H), 2.65 - 2.60 (m, 2H), 2.26 (t,  $J = 7.0$  Hz, 2H), 1.79 - 1.74 (m, 2H), 1.65 – 1.58 (m, 2H), 1.57 – 1.50 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 171.8, 140.2, 131.8, 128.7, 128.4, 128.3, 128.2, 126.2, 121.9, 119.4, 85.8, 85.7, 63.8, 35.8, 33.9, 30.8, 24.9, 24.1, 17.0. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{23}\text{NNaO}_2$ : 368.1621, found: 368.1620.

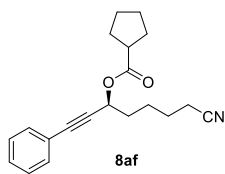
**(S)-7-cyano-1-phenylhept-1-yn-3-yl cyclobutanecarboxylate 8ae**



85% isolated yield (25.1 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -22.30$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 98% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 8.63 min,  $t_{\text{R}}$  (major) = 9.37 min.  $^1\text{H}$  NMR (400 MHz,

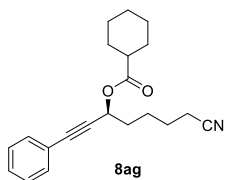
CDCl<sub>3</sub>)  $\delta$  (ppm) 7.45 - 7.42 (m, 2H), 7.33 - 7.28 (m, 3H), 5.62 (t,  $J$  = 6.4 Hz, 1H), 3.23 - 3.13 (m, 1H), 2.38 (t,  $J$  = 6.8 Hz, 2H), 2.35 - 2.27 (m, 2H), 2.25 - 2.20 (m, 2H), 2.00 - 1.86 (m, 4H), 1.79 - 1.67 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 174.3, 131.8, 128.6, 128.2, 122.0, 119.4, 86.0, 85.5, 63.6, 37.9, 33.9, 25.2, 25.0, 24.9, 24.1, 18.3, 17.0. HRMS (EI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>19</sub>H<sub>21</sub>NNaO<sub>2</sub>: 318.1465, found: 318.1466.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl cyclopentanecarboxylate 8af**



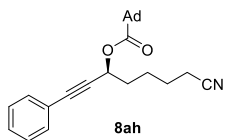
87% isolated yield (26.9 mg), colorless oil,  $[\alpha]_D^{25}$  = -16.50 ( $c$  = 0.5 in CHCl<sub>3</sub>); 92% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_R$  (minor) = 17.67 min,  $t_R$  (major) = 19.57 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.44 - 7.42 (m, 2H), 7.35 - 7.28 (m, 3H), 5.62 (t,  $J$  = 6.4 Hz, 1H), 2.82 - 2.74 (m, 1H), 2.38 (t,  $J$  = 6.8 Hz, 2H), 1.93 - 1.83 (m, 6H), 1.76 - 1.67 (m, 6H), 1.60 - 1.56 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 175.6, 131.8, 128.6, 128.2, 122.0, 119.4, 86.0, 85.4, 77.3, 77.0, 76.7, 63.5, 43.6, 33.9, 30.0, 29.8, 25.8, 25.7, 24.9, 24.1, 17.0. HRMS (EI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>23</sub>NNaO<sub>2</sub>: 332.1621, found: 332.1615.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl cyclohexanecarboxylate 8ag**



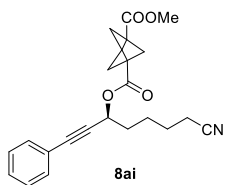
82% isolated yield (26.5 mg), colorless oil,  $[\alpha]_D^{25}$  = -22.43 ( $c$  = 0.5 in CHCl<sub>3</sub>); 96% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_R$  (minor) = 12.40 min,  $t_R$  (major) = 14.28 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.44 - 7.42 (m, 2H), 7.33 - 7.28 (m, 3H), 5.62 (t,  $J$  = 6.3 Hz, 1H), 2.38 (t,  $J$  = 6.8 Hz, 3H), 1.96 - 1.85 (m, 4H), 1.80 - 1.73 (m, 3H), 1.73 - 1.68 (m, 2H), 1.68 - 1.61 (m, 2H), 1.52 - 1.42 (m, 2H), 1.35 - 1.22 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 174.9, 131.8, 128.6, 128.2, 122.0, 119.4, 86.0, 85.4, 63.3, 43.0, 33.9, 28.9, 28.7, 25.6, 25.3, 25.2, 24.9, 24.1, 17.0. HRMS (EI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>25</sub>NNaO<sub>2</sub>: 346.1778, found: 346.1780.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl (3S,5S,7S)-adamantane-1-carboxylate 8ah**



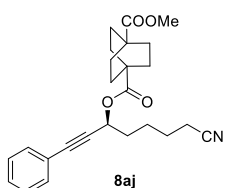
81% isolated yield (30.4 mg), colorless oil,  $[\alpha]_D^{25}$  = 25.14 ( $c$  = 0.5 in CHCl<sub>3</sub>); 90% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_R$  (minor) = 19.24 min,  $t_R$  (major) = 20.78 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.45 - 7.42 (m, 2H), 7.32 - 7.30 (m, 3H), 5.61 (t,  $J$  = 6.3 Hz, 1H), 2.38 (t,  $J$  = 6.8 Hz, 2H), 2.04 - 2.01 (m, 3H), 1.93 (d,  $J$  = 2.9 Hz, 6H), 1.79 - 1.63 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 176.4, 131.8, 128.6, 128.2, 128.1, 128.1, 122.1, 119.4, 86.2, 85.2, 77.3, 77.0, 76.7, 63.2, 40.7, 38.6, 36.4, 33.8, 27.8, 24.9, 24.1, 17.1. HRMS (EI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>29</sub>N<sub>2</sub>NaO<sub>2</sub>: 398.2091, found: 398.2098.

**3-((S)-7-cyano-1-phenylhept-1-yn-3-yl) 5-methyl tricyclo[3.1.0.0<sup>1,3</sup>]hexane-3,5-dicarboxylate 8ai**



85% isolated yield (32.0 mg), colorless oil,  $[\alpha]_D^{25}$  = -31.90 ( $c$  = 0.5 in CHCl<sub>3</sub>); 96% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_R$  (minor) = 25.09 min,  $t_R$  (major) = 32.21 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.45 - 7.42 (m, 2H), 7.35 - 7.27 (m, 3H), 5.60 (t,  $J$  = 6.4 Hz, 1H), 3.68 (s, 3H), 2.40 - 2.35 (m, 8H), 1.90 (d,  $J$  = 7.5 Hz, 2H), 1.76 - 1.68 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 169.5, 168.1, 131.8, 128.8, 128.2, 121.8, 119.3, 85.9, 85.4, 64.3, 52.8, 51.8, 37.6, 37.5, 33.8, 29.6, 24.8, 24.1, 17.0. HRMS (EI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>23</sub>NNaO<sub>4</sub>: 400.1519, found: 400.1517.

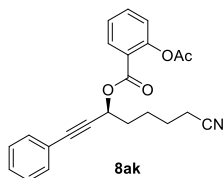
**(S)-1-(7-cyano-1-phenylhept-1-yn-3-yl) 4-methyl bicyclo[2.2.2]octane-1,4-dicarboxylate 8aj**



88% isolated yield (35.8 mg), colorless oil,  $[\alpha]_D^{25}$  = -34.87 ( $c$  = 0.5 in CHCl<sub>3</sub>); 98% ee, determined by HPLC analysis (Chiralpak OD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 1.0 mL/min,  $\lambda$  = 254 nm, 25 °C),  $t_R$  (minor) = 38.77 min,  $t_R$  (major) = 41.71 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.45 - 7.43 (m, 2H), 7.33 - 7.30 (m, 3H), 5.60 (t,  $J$  = 6.4 Hz, 1H), 3.69 (s,

3H), 2.37 (d,  $J = 13.9$  Hz, 8H), 1.93 – 1.87 (m, 2H), 1.79 – 1.63 (m, 5H), 1.25 (s, 2H), 0.89 – 0.85 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.6, 168.1, 131.9, 128.8, 128.3, 121.9, 119.3, 86.0, 85.4, 64.3, 52.8, 51.8, 37.6, 37.5, 33.8, 24.8, 24.1, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{29}\text{NNaO}_4$ : 430.1989, found: 430.1985.

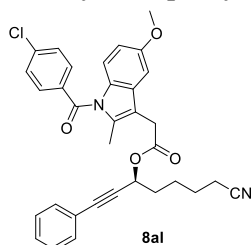
**(S)-7-cyano-1-phenylhept-1-yn-3-yl methyl isophthalate 8ak**



81% isolated yield, (30.4 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -31.90$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 92% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 18.05 min,  $t_{\text{R}}$  (minor) = 20.90 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.08 – 8.06 (m, 1H), 7.61 – 7.56 (m, 1H), 7.47 – 7.45 (m, 2H), 7.36 – 7.31 (m, 4H), 7.13 – 7.31 (m, 1H), 5.86 (t,  $J = 6.3$  Hz, 1H), 2.41 – 2.37 (m, 5H), 2.02 – 1.97 (m, 2H), 1.80 – 1.72 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.6, 163.4, 150.6, 134.1,

131.9, 131.8, 128.8, 128.3, 126.1, 123.8, 122.9, 121.9, 119.4, 86.1, 85.5, 64.6, 34.0, 24.9, 24.1, 21.1, 17.1. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{21}\text{NNaO}_4$ : 398.1363, found: 398.1372.

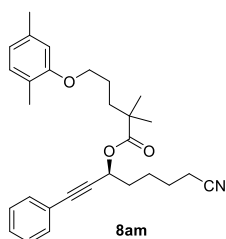
**(S)-7-cyano-1-phenylhept-1-yn-3-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-1*H*-indol-3-yl)acetate 8al**



85% isolated yield (40.4 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -54.34$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 96% ee, determined by HPLC analysis (Chiralpak AD column, hexane/*i*-PrOH, 80:20 v/v, flow rate 1.0 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (major) = 33.42 min,  $t_{\text{R}}$  (minor) = 37.61 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.66 – 7.61 (m, 2H), 7.45 – 7.43 (m, 2H), 7.39 – 7.37 (m, 2H), 7.33 – 7.27 (m, 3H), 7.00 (d,  $J = 2.5$  Hz, 1H), 6.90 (d,  $J = 8.9$  Hz, 1H), 6.69 – 6.66 (m, 1H), 5.63 (t,  $J = 6.3$  Hz, 1H), 3.80 (s, 3H), 3.73 (d,  $J = 1.5$  Hz, 2H), 2.40 (s, 3H), 2.27 (t,  $J = 6.7$  Hz, 2H), 1.90

– 1.85 (m, 2H), 1.68 – 1.56 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 169.7, 168.2, 155.9, 139.2, 135.9, 133.7, 131.7, 131.1, 130.7, 130.4, 129.0, 128.7, 128.2, 121.8, 119.3, 114.9, 112.2, 111.5, 101.3, 85.8, 85.5, 64.5, 55.5, 33.8, 30.4, 26.8, 24.8, 24.0, 16.9, 13.3. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{32}\text{H}_{27}\text{ClNNaO}_4$ : 561.1552, found: 561.1553.

**(S)-7-cyano-1-phenylhept-1-yn-3-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate 8am**



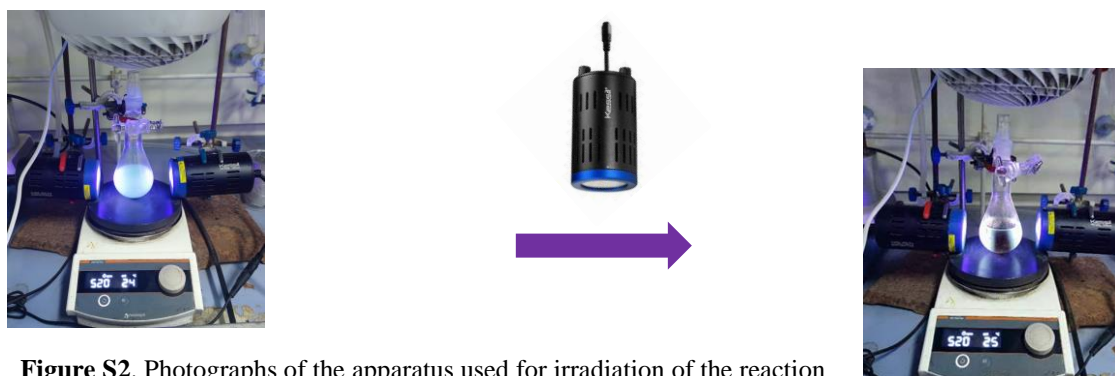
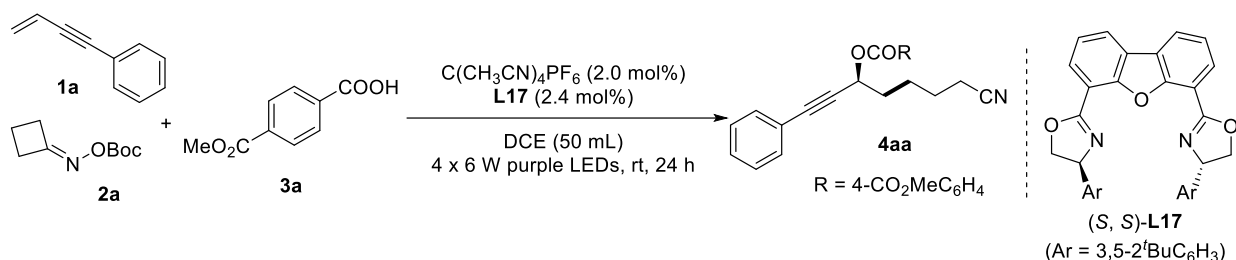
86% isolated yield (33.6 mg), colorless oil,  $[\alpha]_{\text{D}}^{25} = -29.37$  ( $c = 0.5$  in  $\text{CHCl}_3$ ); 90% ee, determined by HPLC analysis (Chiralpak IG column, hexane/*i*-PrOH, 80:20 v/v, flow rate 0.5 mL/min,  $\lambda = 254$  nm, 25 °C),  $t_{\text{R}}$  (minor) = 15.97 min,  $t_{\text{R}}$  (major) = 18.50 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.45 – 7.40 (m, 2H), 7.32 – 7.26 (m, 3H), 7.01 (d,  $J = 7.5$  Hz, 1H), 6.67 (d,  $J = 7.5$  Hz, 1H), 6.60 (s, 1H), 5.63 (t,  $J = 6.4$  Hz, 1H), 3.95 – 3.91 (m, 2H), 2.37 (t,  $J = 6.7$  Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 1.94 – 1.89 (m, 2H), 1.83 – 1.68 (m, 8H), 1.28 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 176.6, 156.8, 136.4, 131.7, 130.2, 128.6, 128.2, 123.4, 122.1, 120.6,

119.3, 111.8, 86.0, 85.5, 67.8, 63.7, 42.1, 37.1, 33.8, 25.2, 25.1, 24.9, 24.8, 24.2, 21.3, 17.0, 15.7. HRMS (EI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{29}\text{H}_{35}\text{NNaO}_3$ : 468.2509, found: 468.2505.



## 5. Synthetic Applications of the Reaction

### 5.1 Gram-scale reaction



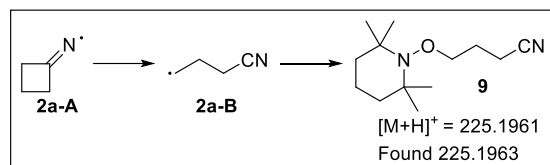
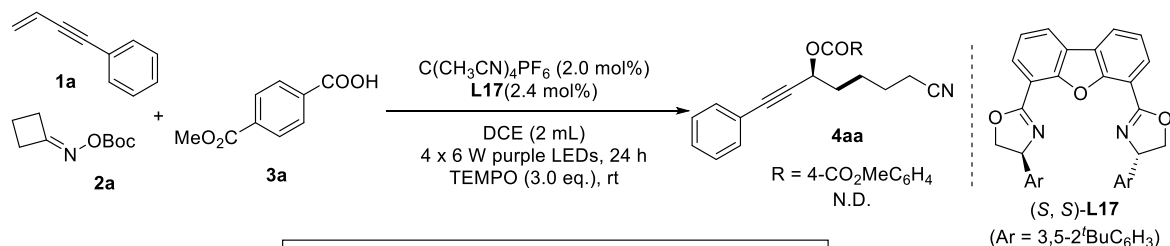
**Figure S2.** Photographs of the apparatus used for irradiation of the reaction

system.

In a flame-dried 100 mL Shrek bottle equipped with a magnetic stirrer bar was charged sequentially with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (37.3 mg, 0.10 mmol) and chiral ligand **L17** (81.9 mg, 0.12 mmol), followed by the addition of DCE (50.0 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture, **3a** (900 mg, 5.0 mmol), **1a** (1.92 g, 15.0 mmol) and **2a** (1.85g, 10.0 mmol) were added. Then, the resulting mixture was degassed (3 times) under argon atmosphere. At last, the mixture was stirred at a distance of ~4 cm from a 20 W Kessil purple LEDs at room temperature for 36 h. The product was purified by flash column chromatography on silica gel to afford the desired product **4aa** (1.69 g, 90% yield, 93% ee) with petroleum ether and ethyl acetate (7:1, v/v).

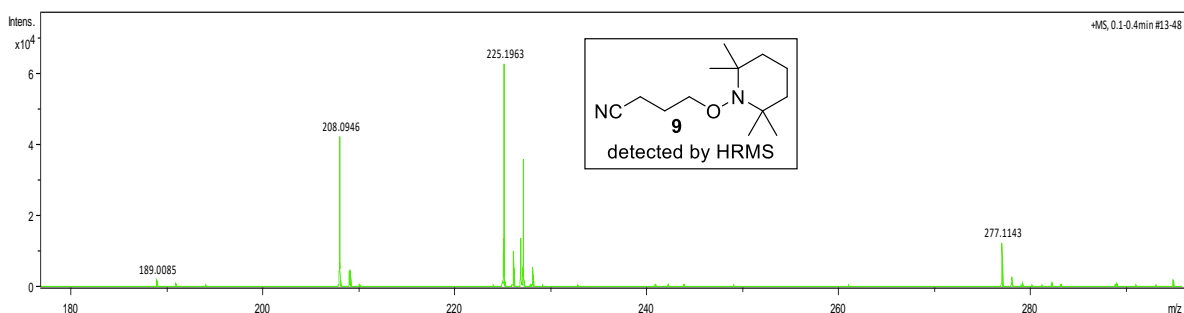
## 6. Mechanistic Investigation

### 6.1 Radical trapping experiments

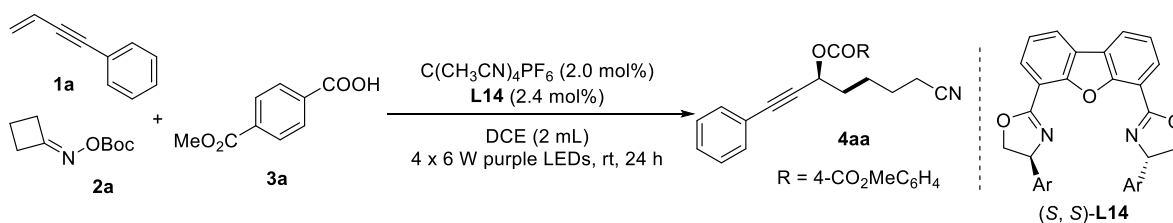


In a flame-dried 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (0.75mg, 0.0020 mmol) and chiral ligand **L17** (1.64 mg, 0.0024 mmol), followed by the addition of DCE (2.0 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture, **3a** (18.0 mg, 0.10

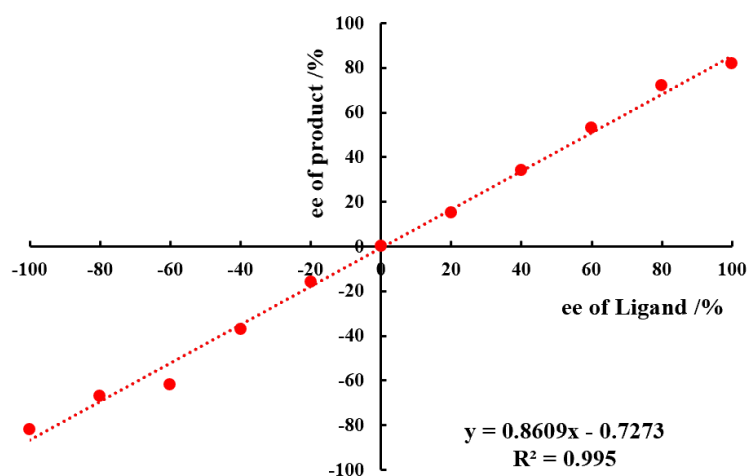
mmol), **1a** (30.4 mg, 0.30 mmol), **2a** (37.0 mg, 0.20 mmol) and TEMPO (46.9 mg, 0.3 mmol) were added. Then, the resulting mixture was degassed (3 times) under argon atmosphere. At last, the mixture was stirred at a distance of ~1 cm from 4 x 6 W purple LEDs at room temperature for 24 h.



## 6.2 Non-linear effect experiments



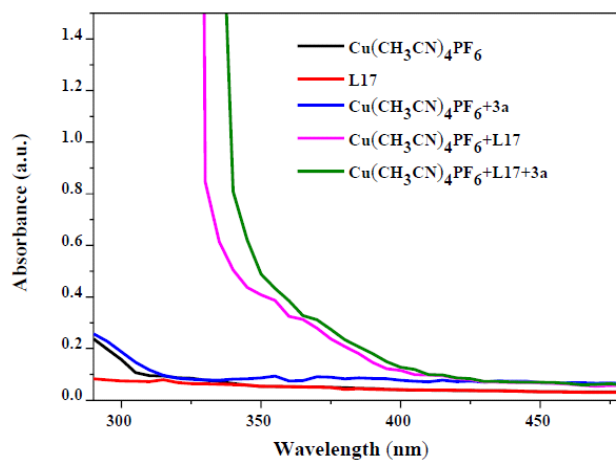
In a flame-dried 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged sequentially with  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (0.75mg, 0.0020 mmol) and chiral ligand **L14** (1.64 mg, 0.0024 mmol), followed by the addition of DCE (2.0 mL). Then the mixture was stirred at room temperature for 30 min. To the resulting mixture, **3a** (18.0 mg, 0.10 mmol), **1a** (30.4 mg, 0.30 mmol) and **2a** (37.0 mg, 0.20 mmol) were added. Then, the resulting mixture was degassed (3 times) under argon atmosphere. At last, the mixture was stirred at a distance of ~1 cm from 4 x 6 W purple LEDs at 0 °C for 24 h. The product was purified by flash column chromatography on silica gel to afford the desired product with petroleum ether and ethyl acetate (7:1, v/v).



**Figure S3.** Relationship between ee values of ligand and product **4aa**

### 6.3 UV-Vis absorption spectra of the reaction components

UV vis absorption studies were conducted to probe the role of the copper salt, chiral ligand and acid under this photocatalytic system. Absorption experiments were performed on a Agilent Cary 60 UV-Vis spectrophotometer.



**Figure S4.** UV-Vis spectra of substrate  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ , chiral ligand **L17**, chiral copper complexes [ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + p\text{-COOMeC}_6\text{H}_4\text{COOH}$ ] (1:2), [ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + \text{L17}$ ] (1:1), [ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + \text{L17} + p\text{-COOMeC}_6\text{H}_4\text{COOH}$ ] (1:1:2) in DCE. All the samples were prepared as a 1.0 mM solution and used freshly for the measurement. All solutions were scanned from 200 to 800 nm.

**Preparation of the samples for UV-Vis spectra measurement** (All the samples were used freshly for UV-Vis spectra measurement):

**$\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  in DCE (1.0 mM):**  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (2.68 mg, 0.0072 mmol) was dissolved in anhydrous DCE (6.0 mL).

**chiral ligand L17 in DCE (1.0 mM):** chiral ligand **L17** (4.91 mg, 0.0072 mmol) was dissolved in anhydrous DCE (6.0 mL).

**[ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + p\text{-COOMeC}_6\text{H}_4\text{COOH}$ ] (1:2) in DCE (1.0 mM):**  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (2.68 mg, 0.0072 mmol),  $p\text{-COOMeC}_6\text{H}_4\text{COOH}$  (2.59 mg, 0.0144 mmol) was dissolved in anhydrous DCE (6.0 mL) and stirred at room temperature for 1 h.

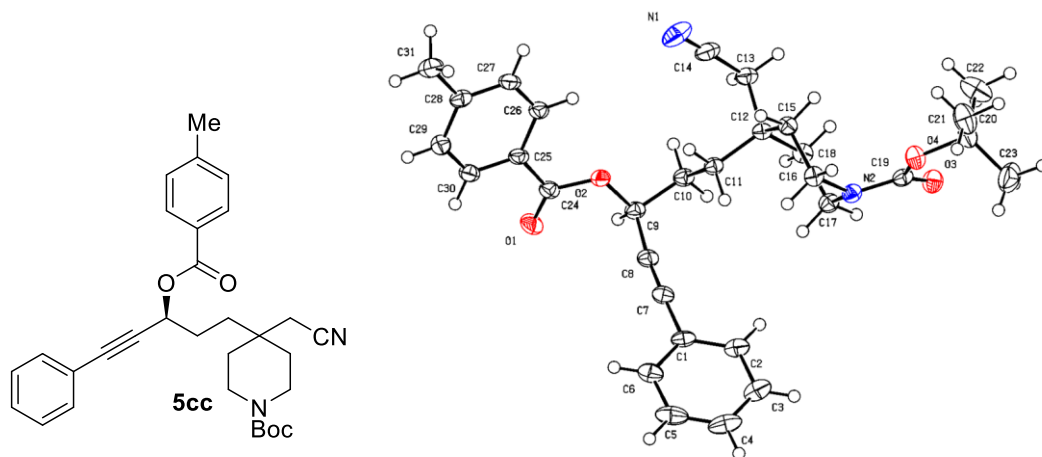
**copper complexes [ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + \text{L17}$ ] (1:1) in DCE (1.0 mM):**  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (2.68 mg, 0.0072 mmol) and chiral ligand **L17** (4.91 mg, 0.0072 mmol) was dissolved in anhydrous DCE (6.0 mL) and stirred at room temperature for 1 h.

**[ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + \text{L17} + p\text{-COOMeC}_6\text{H}_4\text{COOH}$ ] (1:1:2) in DCE (1.0 mM):**  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (2.68 mg, 0.0072 mmol), chiral ligand **L17** (4.91 mg, 0.0072 mmol) and  $p\text{-COOMeC}_6\text{H}_4\text{COOH}$  (2.59 mg, 0.0144 mmol) was dissolved in anhydrous DCE (6.0 mL) and stirred at room temperature for 1 h.

**Remarks:** All of the individual  $p\text{-COOMeC}_6\text{H}_4\text{COOH}$ ,  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ , chiral ligand **L17** showed no spectra feature in the visible light region. However, in situ generated chiral copper complex with acid ([ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + \text{L17}$ ] (1:1) and [ $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6 + \text{L17} + p\text{-COOMeC}_6\text{H}_4\text{COOH}$ ](1:1:2)) exhibited significant absorption enhancement in the range of 350-450 nm.

## 7. Determination of the Absolute Configuration of Product **5cc**

Single crystals of  $\text{C}_{31}\text{H}_{36}\text{N}_2\text{O}_4$  (**5cc**). A suitable crystal was selected on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.



**Figure S5.** X-ray crystal structure of **5cc**

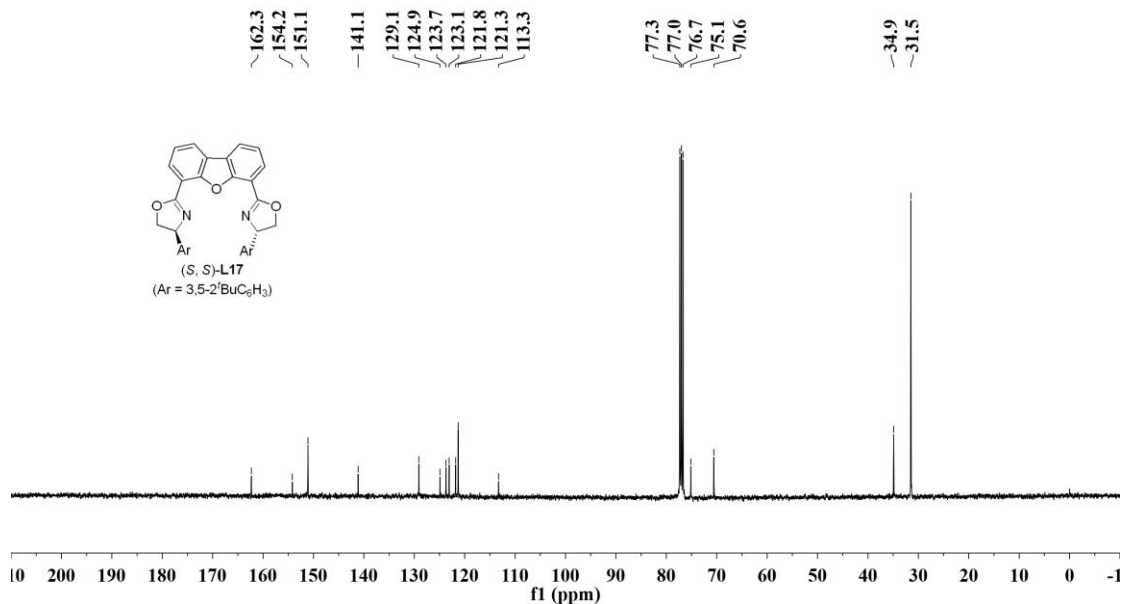
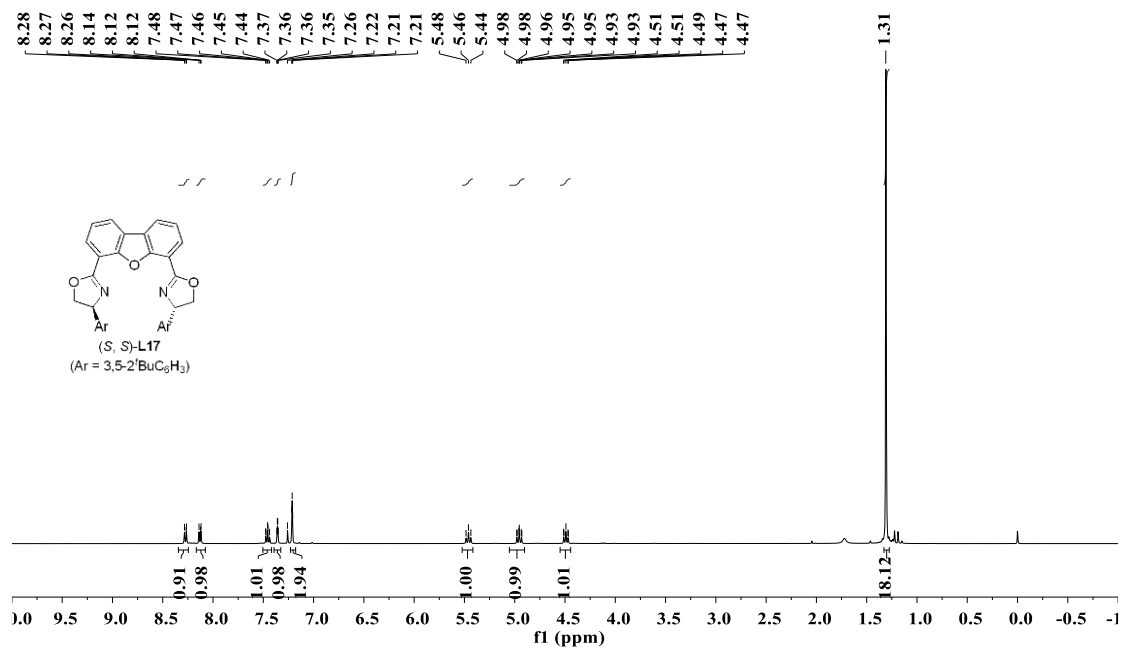
Crystal Data for  $C_{31}H_{36}N_2O_4$  ( $M = 500.62$  g/mol): monoclinic, space group  $P2_1$  (no. 4),  $a = 15.3918(2)$  Å,  $b = 5.81640(10)$  Å,  $c = 15.5214(2)$  Å,  $\beta = 94.6890(10)^\circ$ ,  $V = 1384.90(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 108(12)$  K,  $\mu(\text{Cu K}\alpha) = 0.631$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.201$  g/cm<sup>3</sup>, 6414 reflections measured ( $5.714^\circ \leq 2\theta \leq 143.062^\circ$ ), 3681 unique ( $R_{\text{int}} = 0.0296$ ,  $R_{\text{sigma}} = 0.0467$ ) which were used in all calculations. The final  $R_1$  was 0.0340 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0892 (all data).

## References

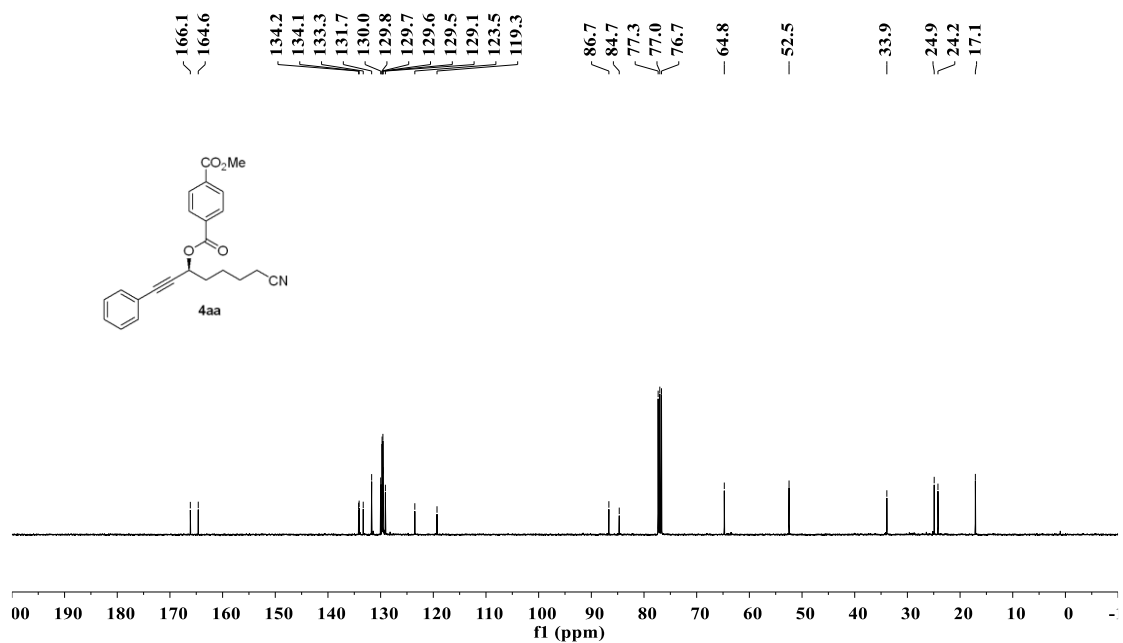
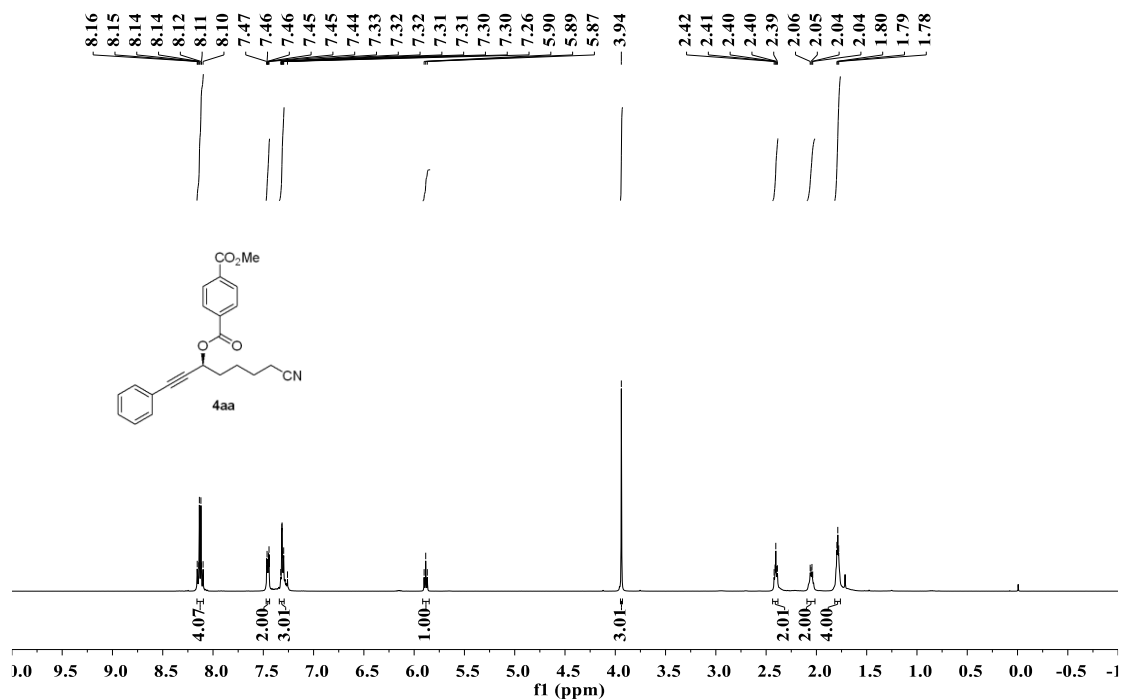
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## 8. Copies of NMR Spectra

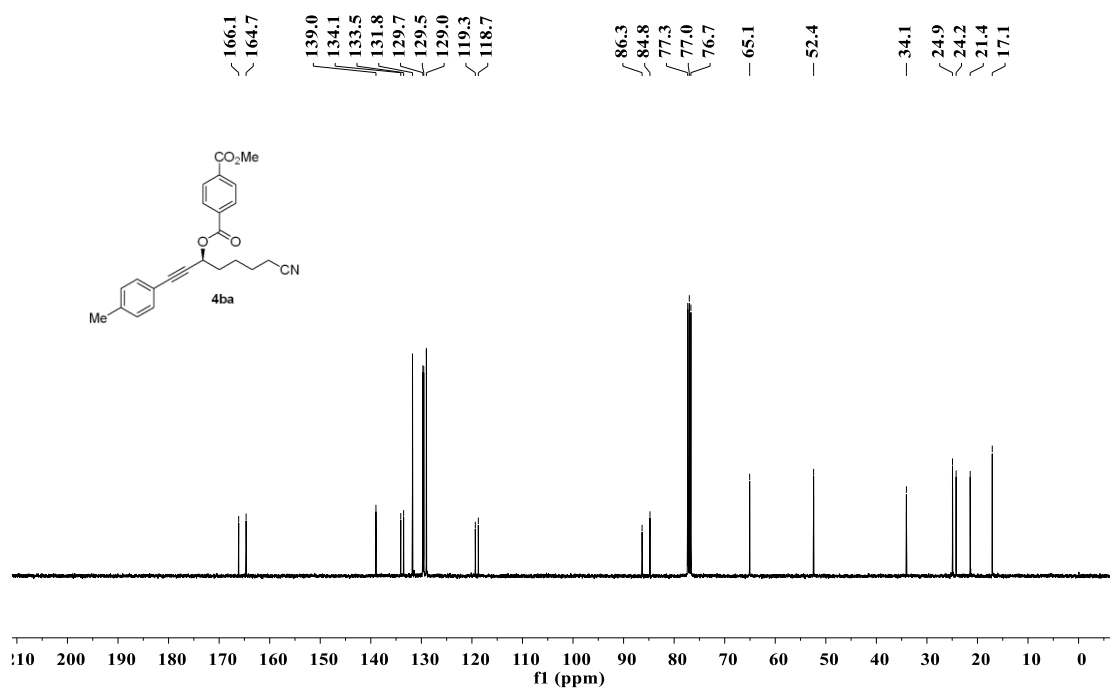
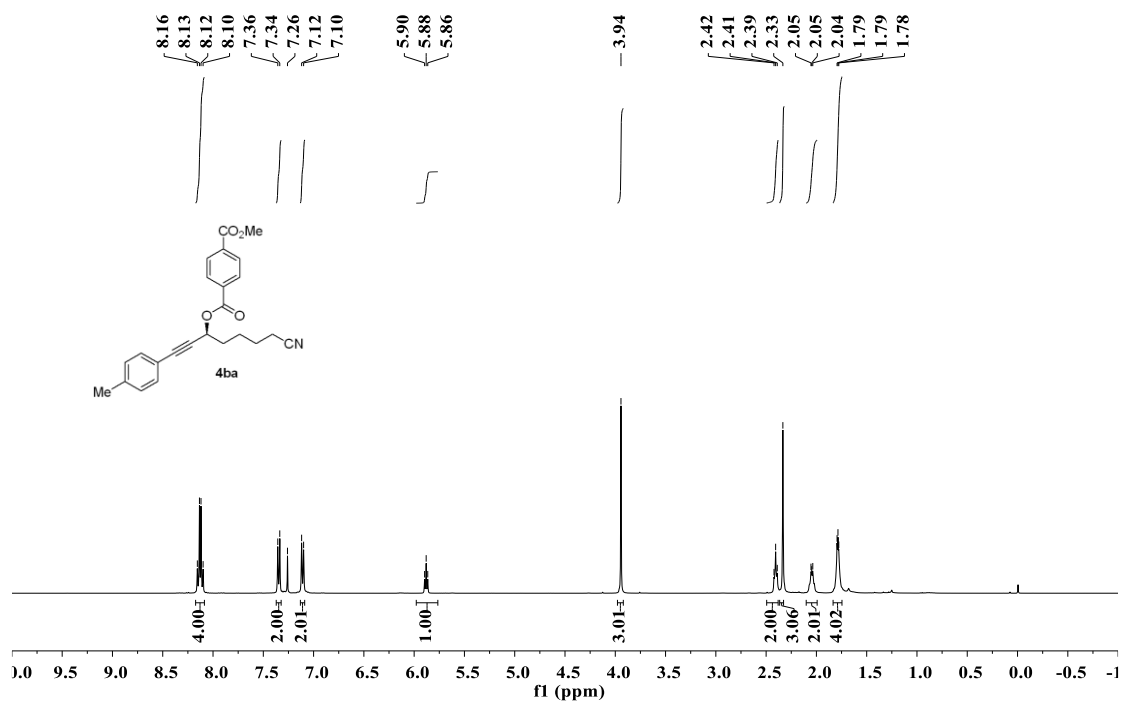
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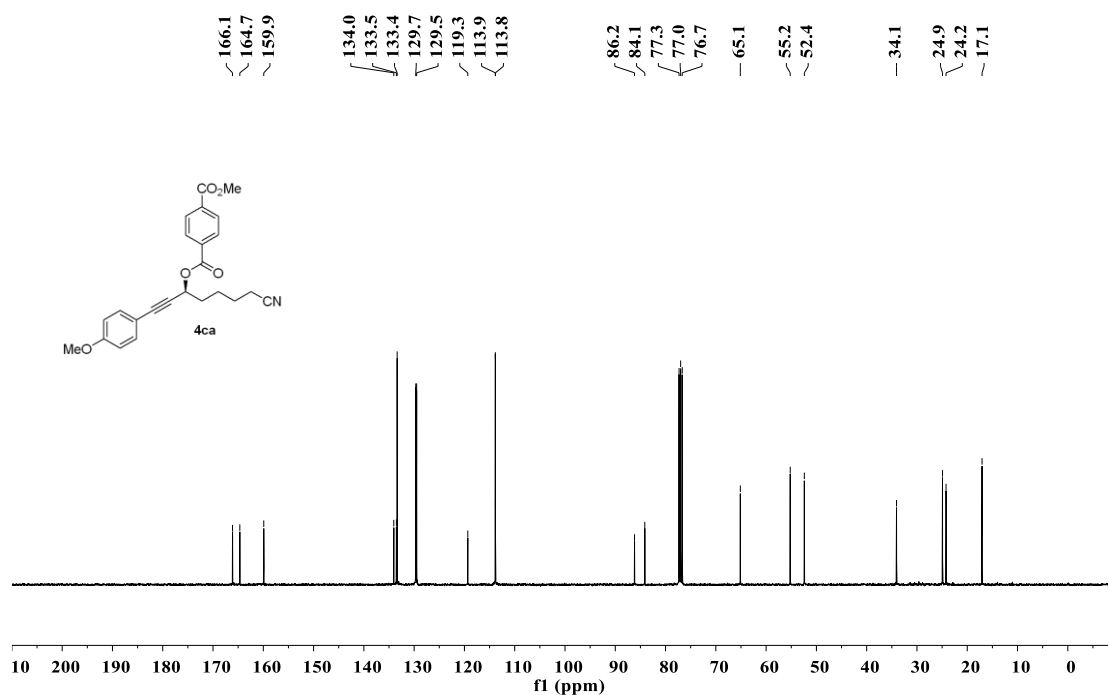
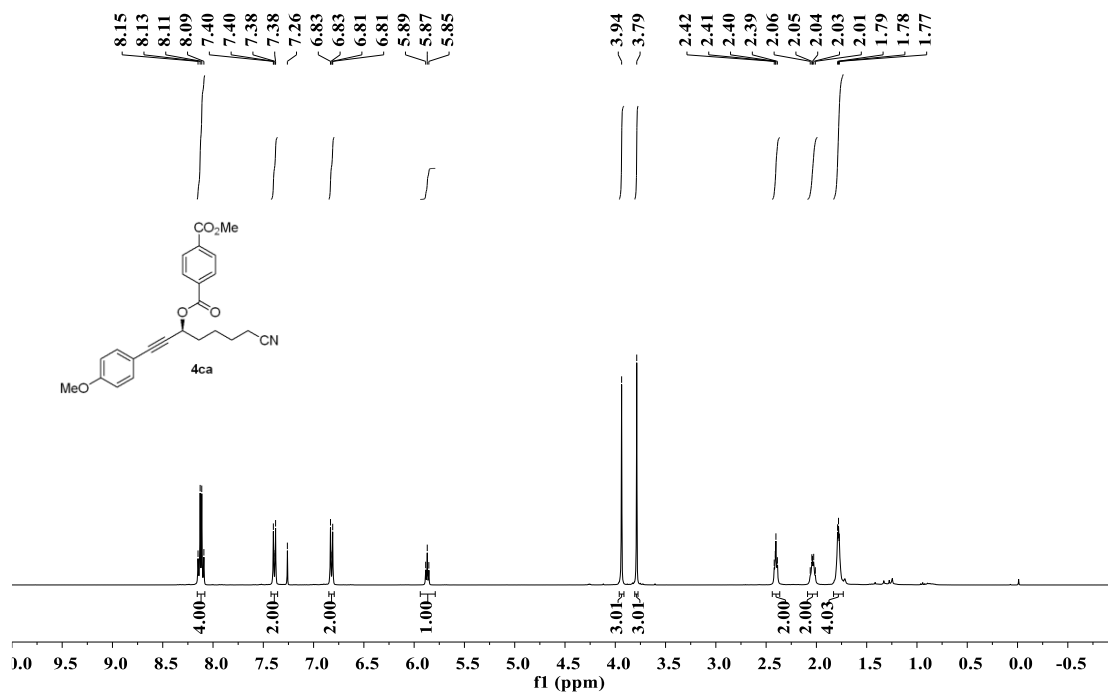
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<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 4ba

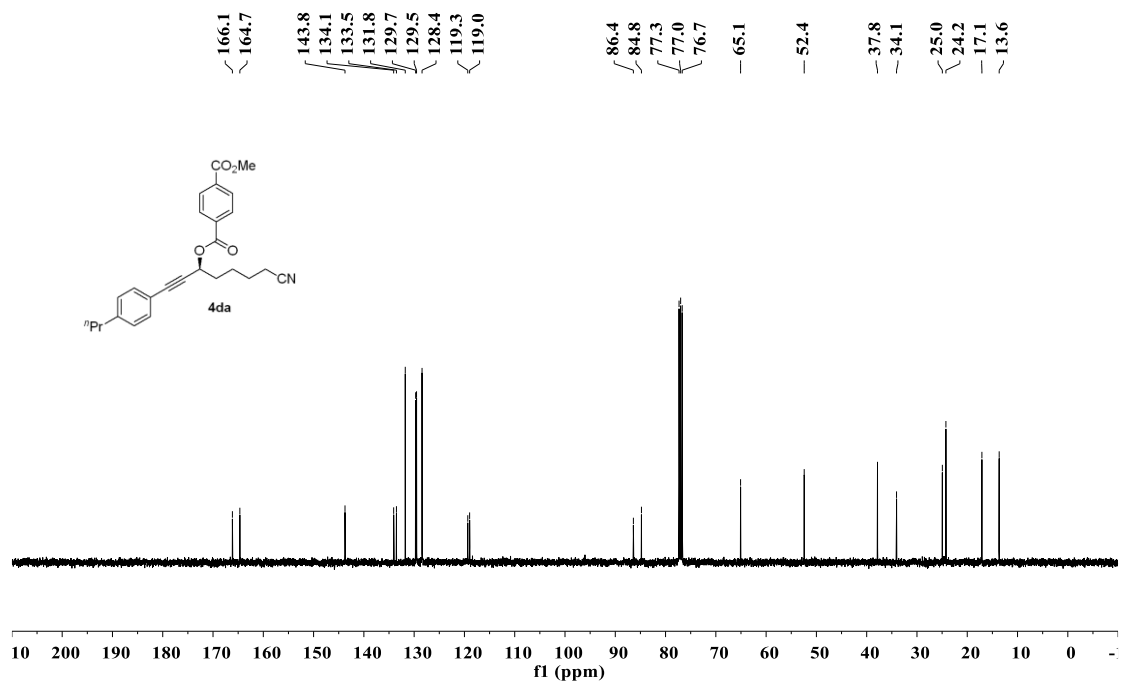
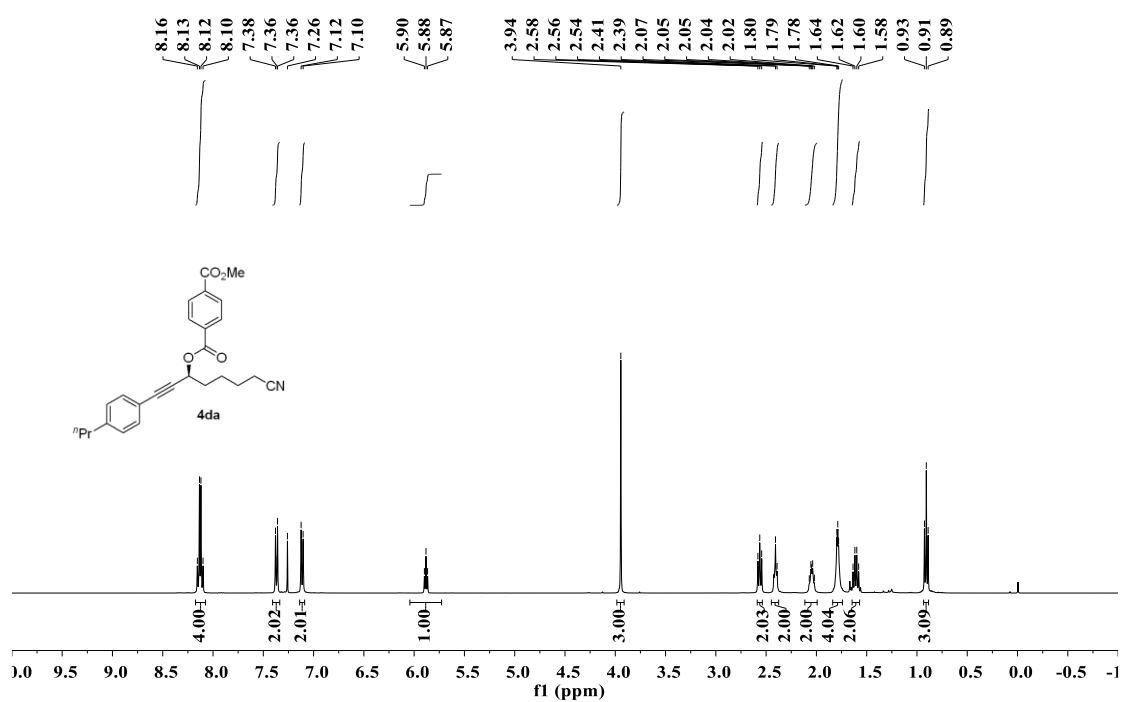


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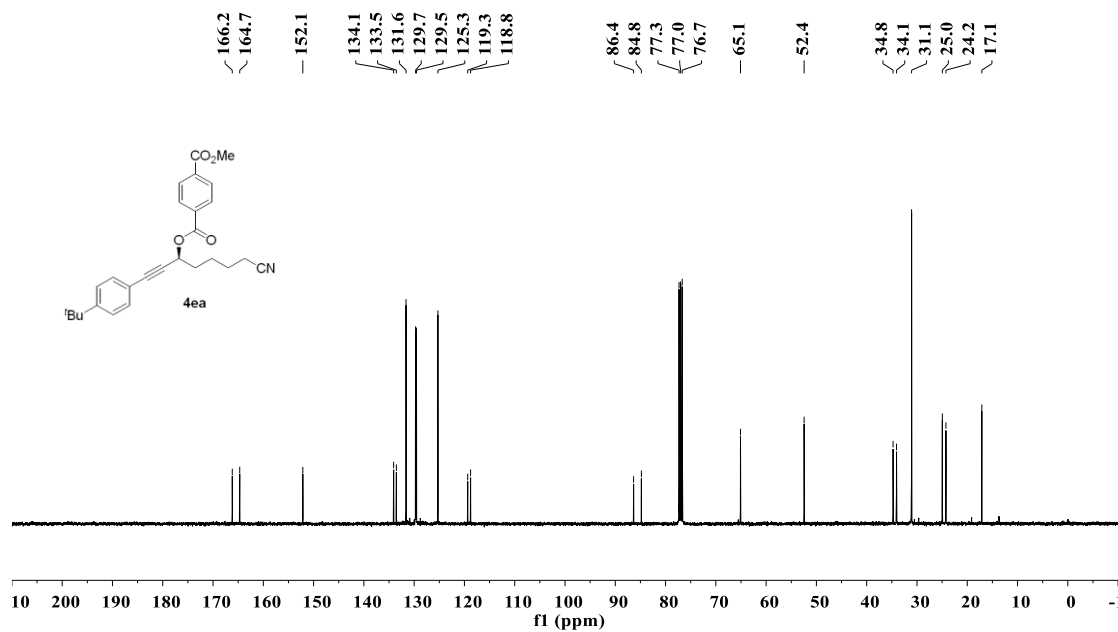
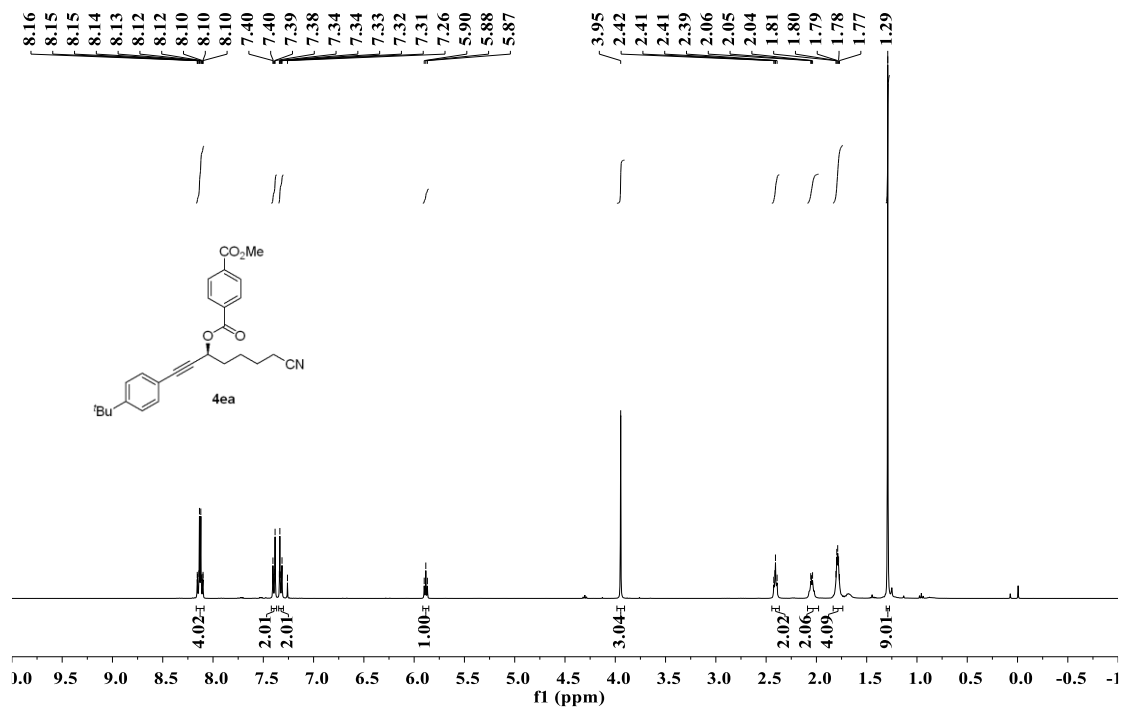




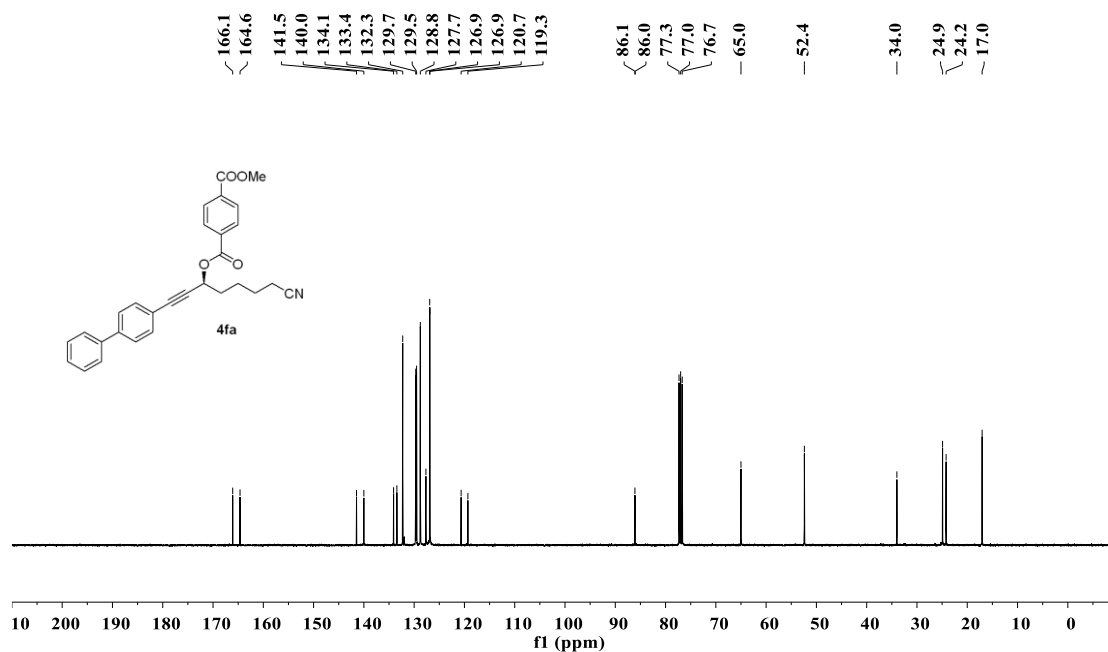
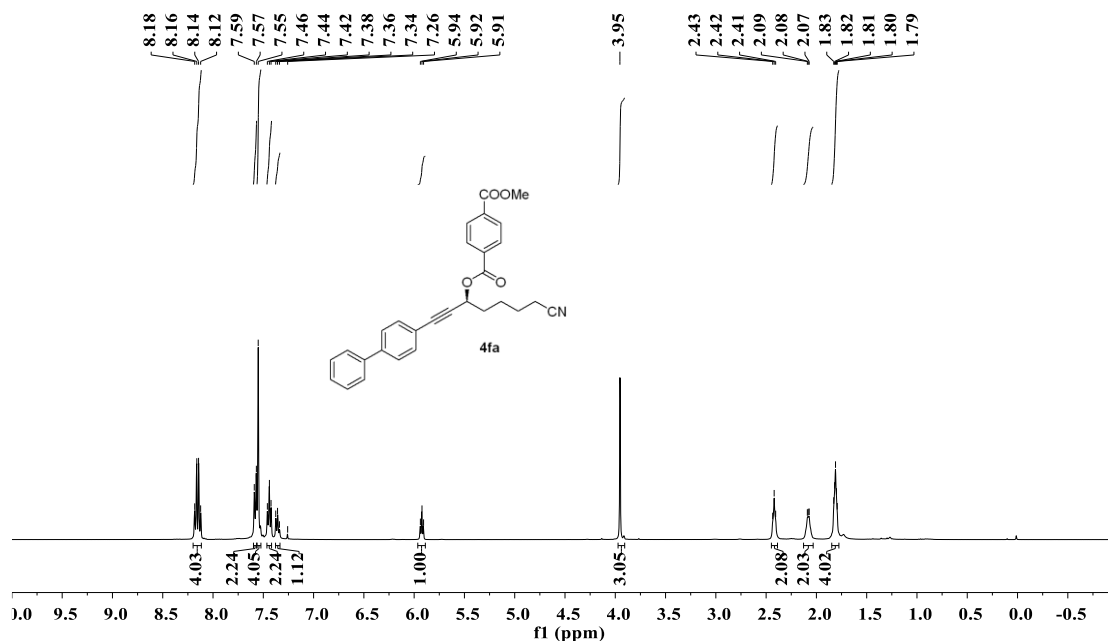
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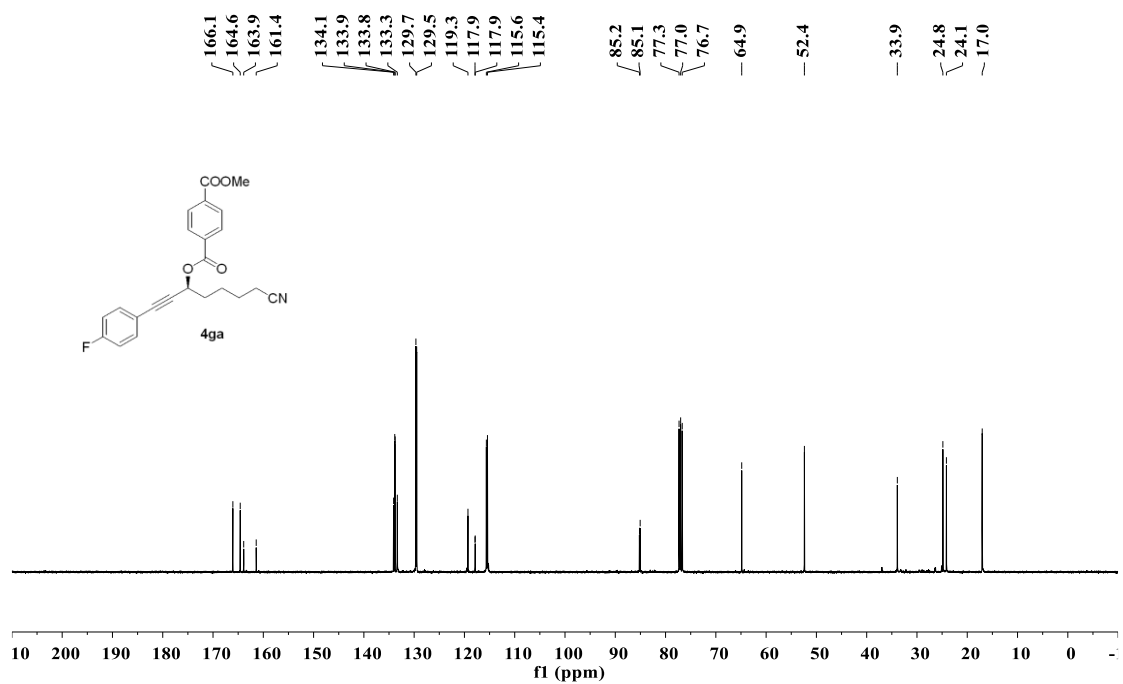
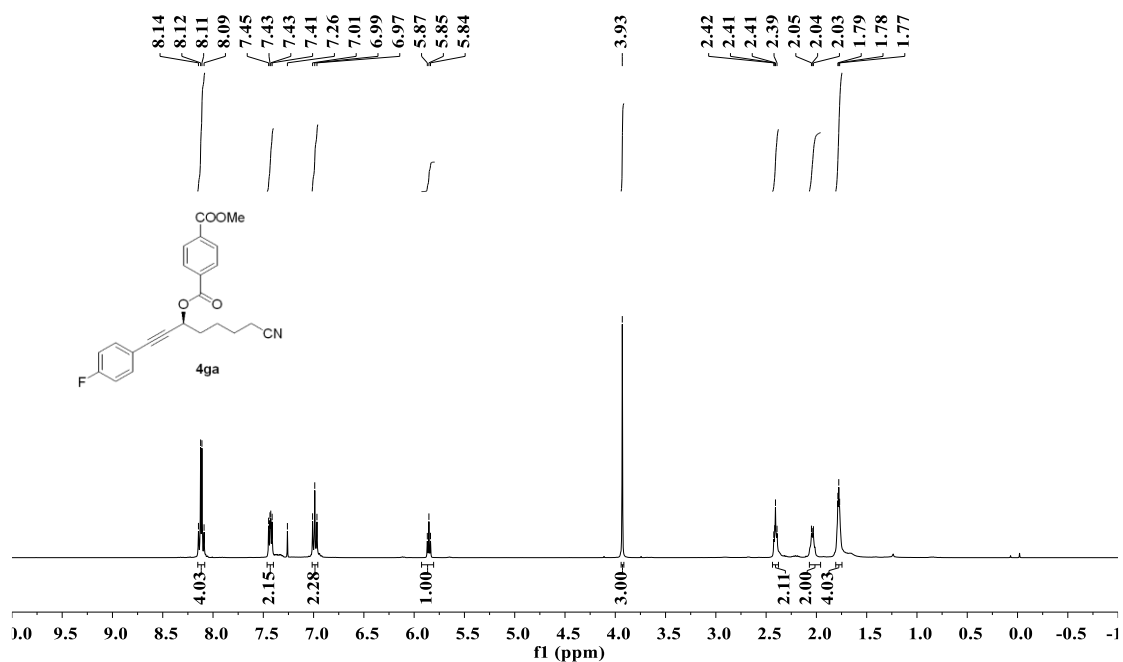
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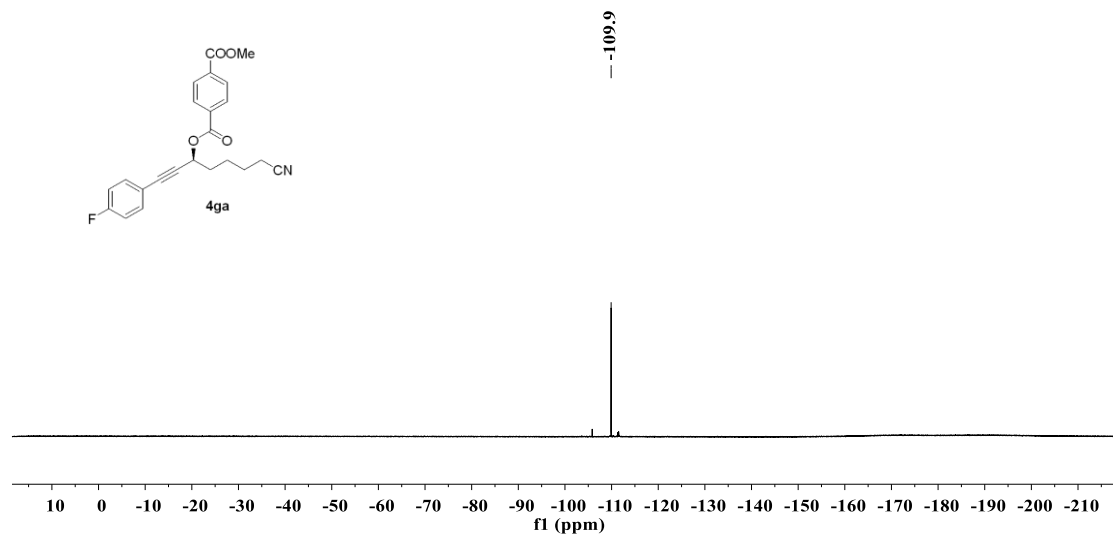


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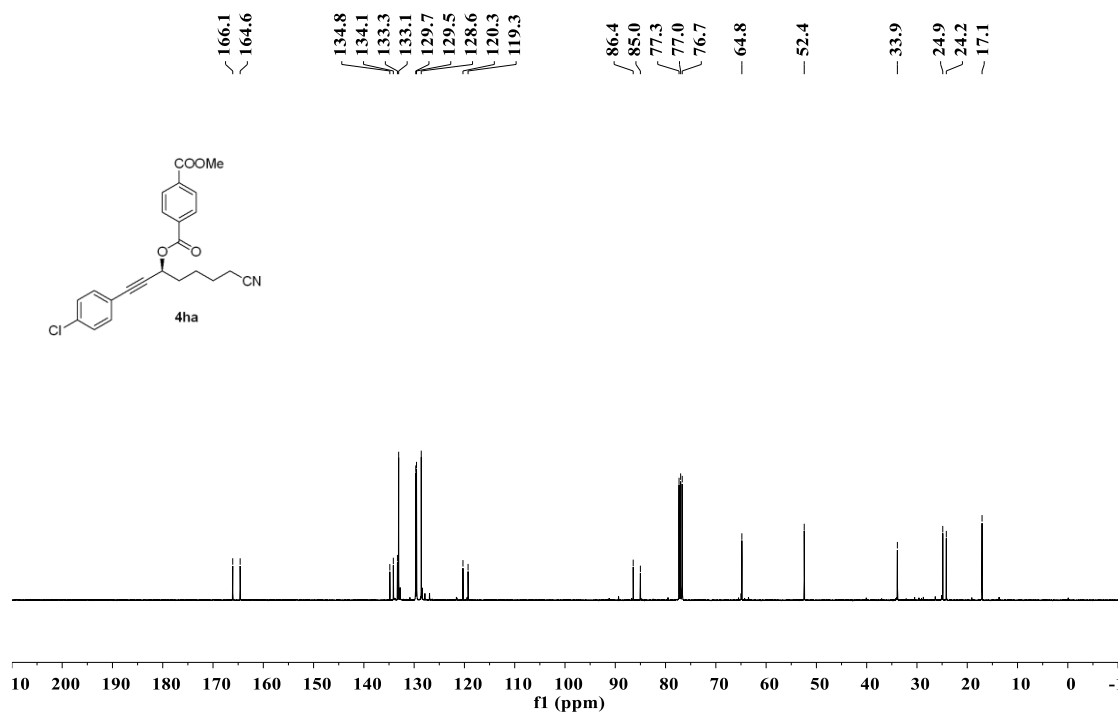
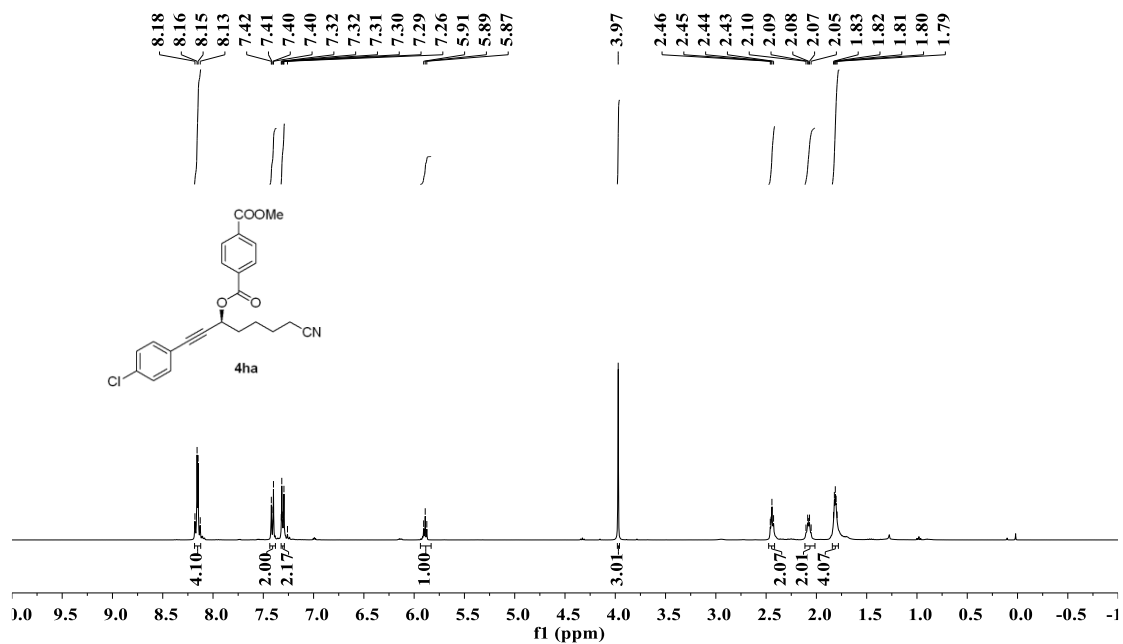


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F (376 MHz) spectra of product **4ga**

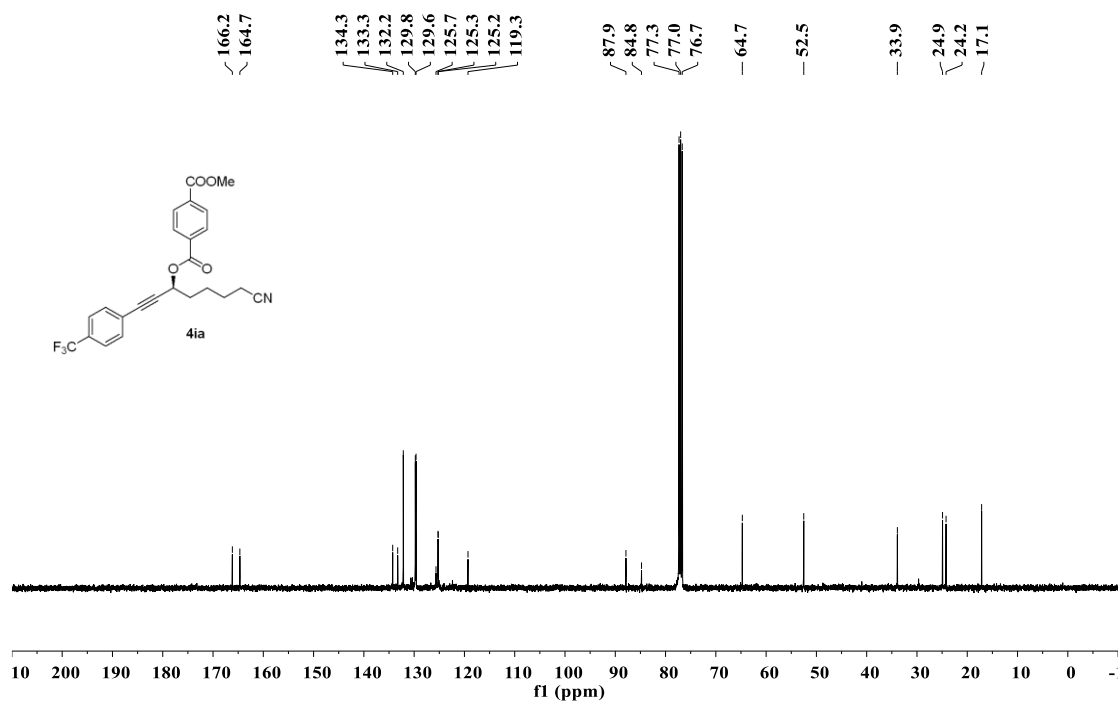
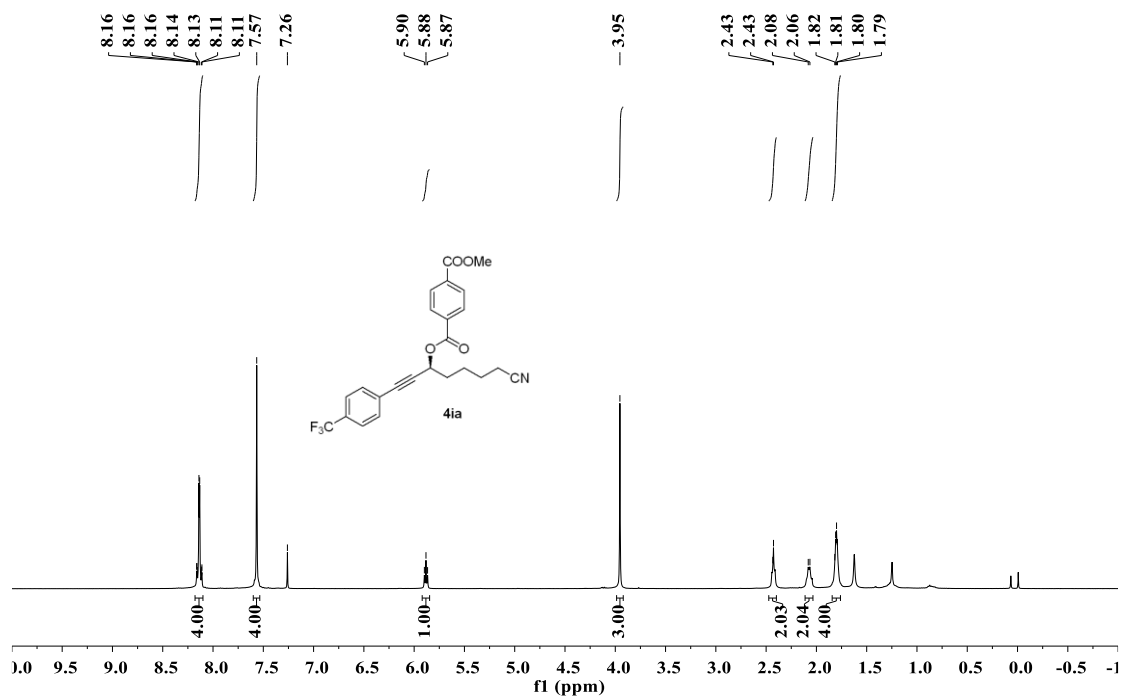


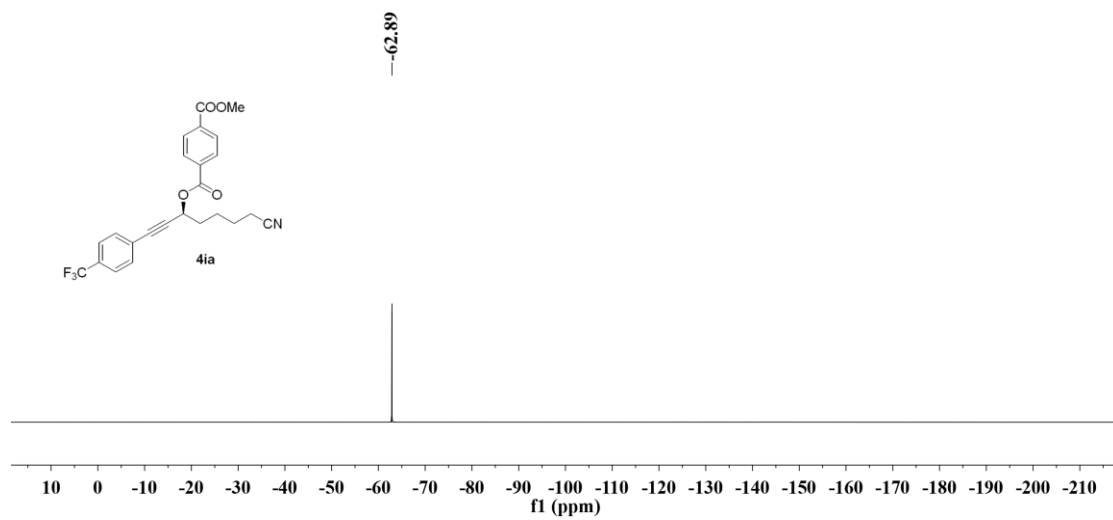


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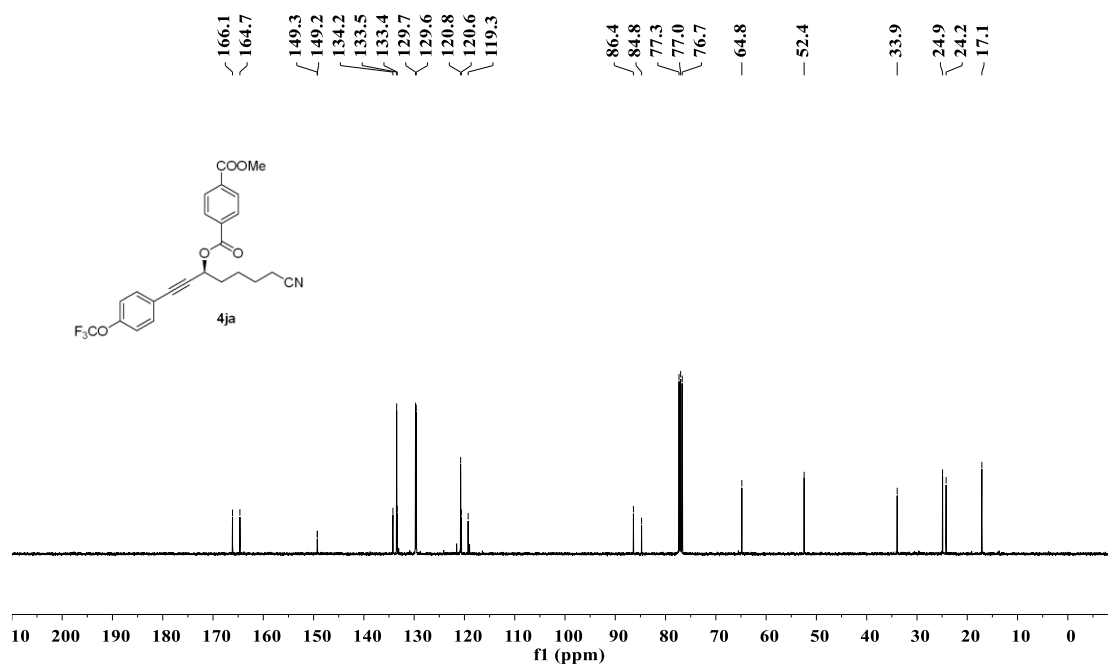
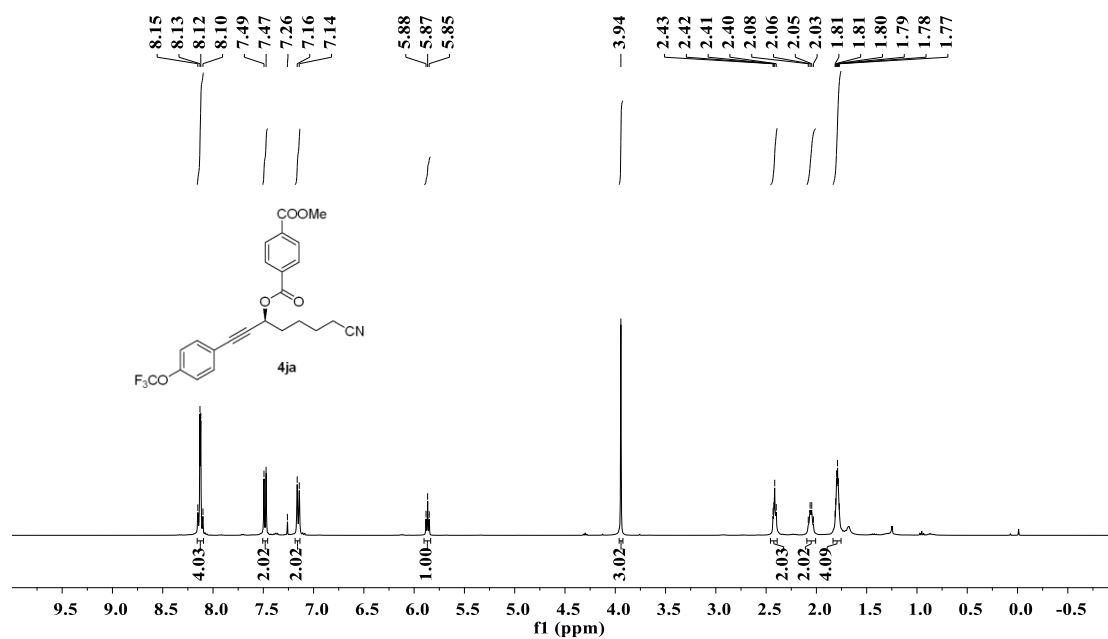
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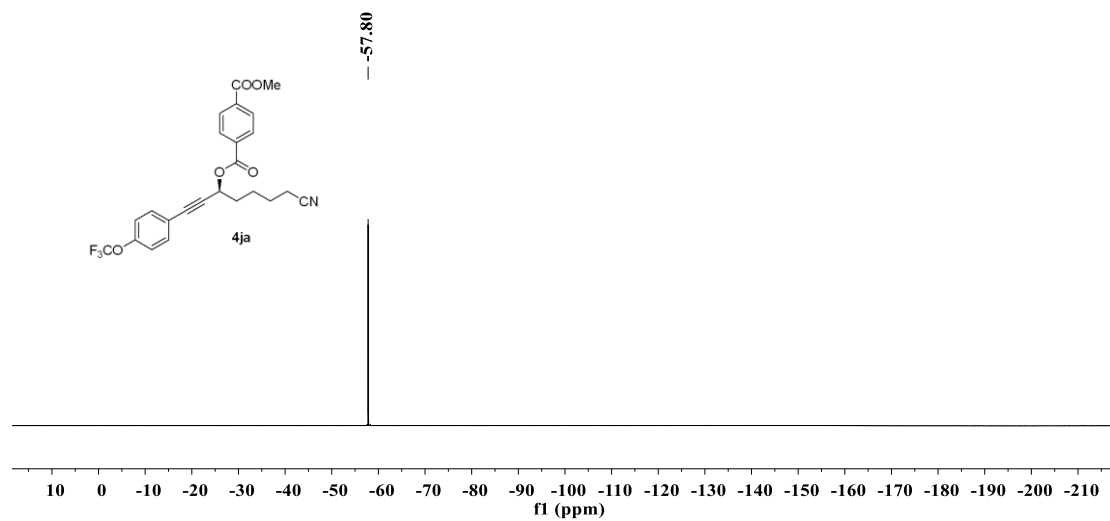




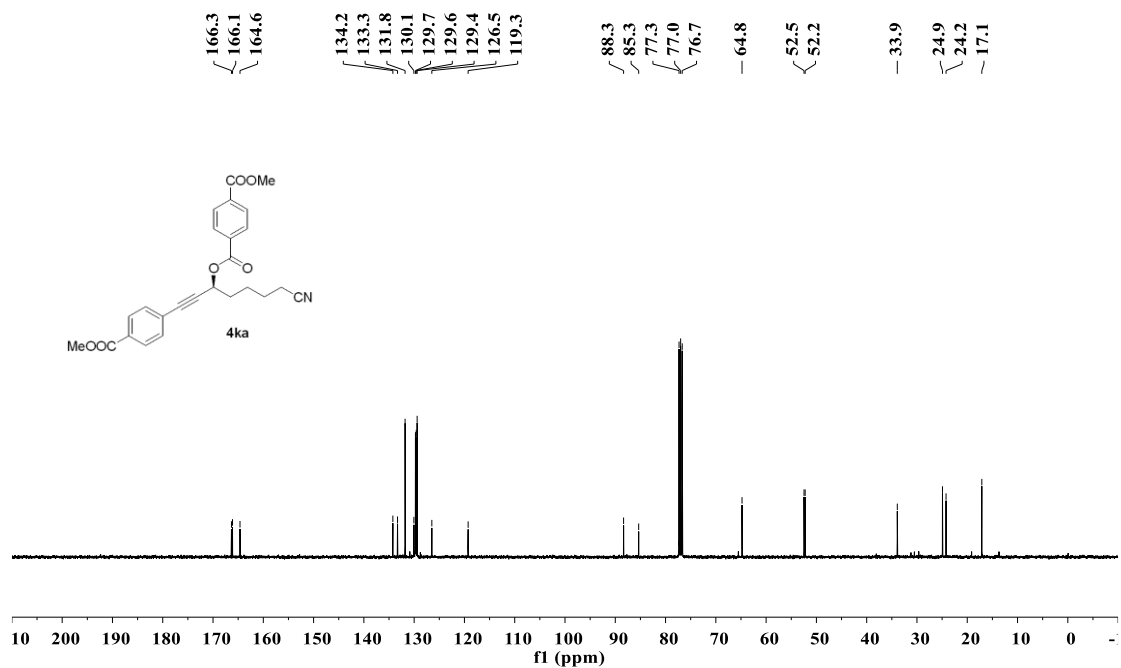
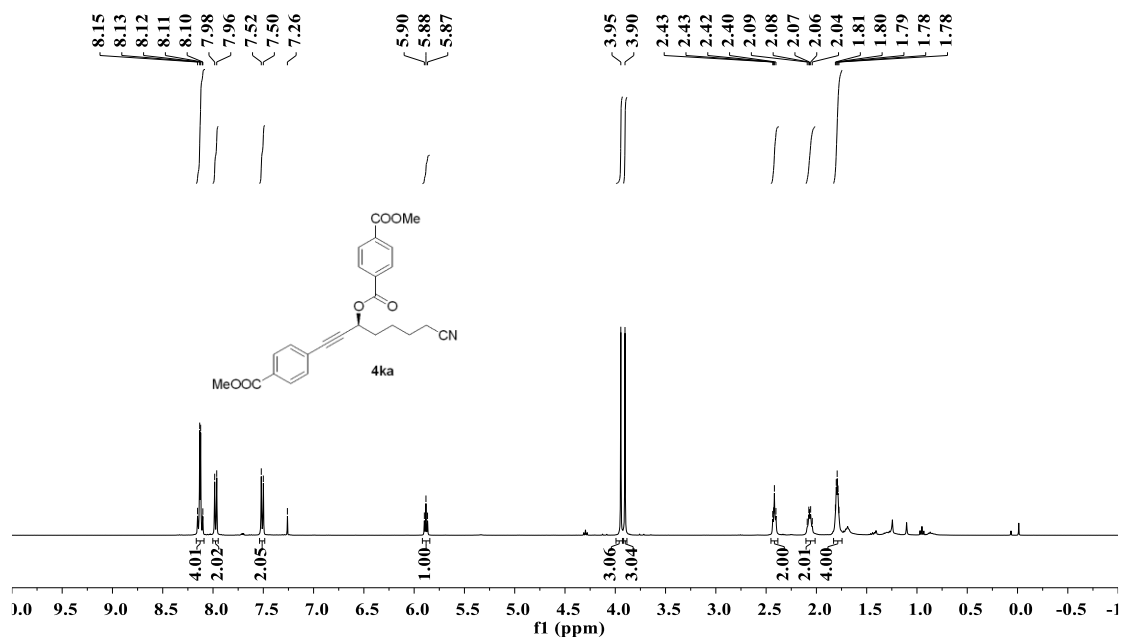


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F (376 MHz) spectra of product 4ja

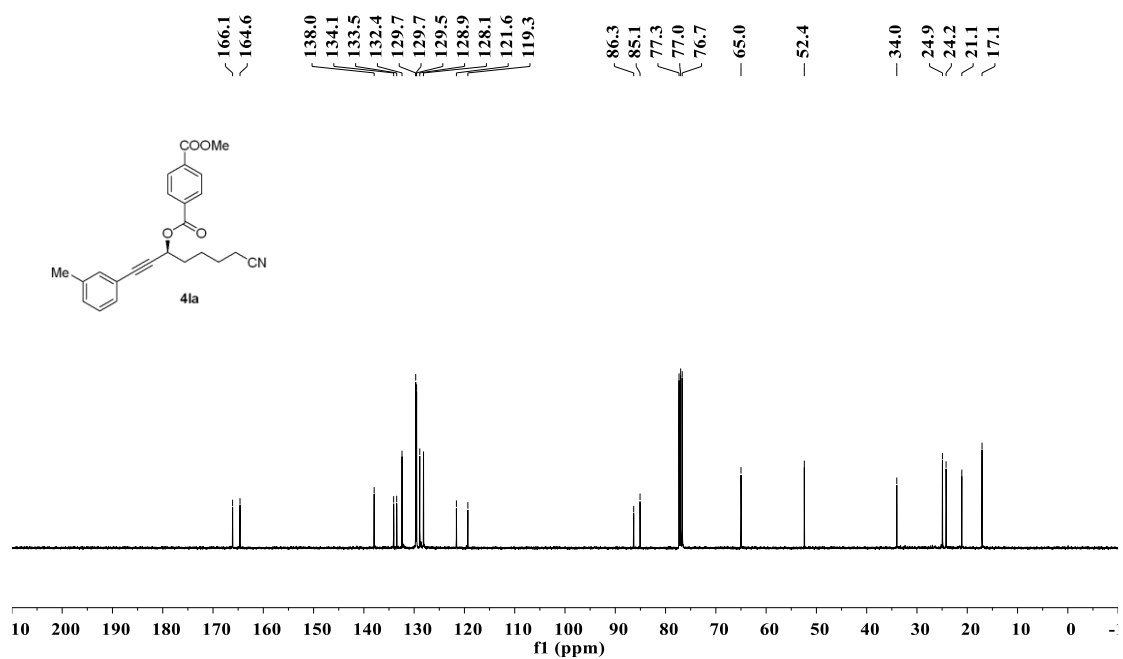
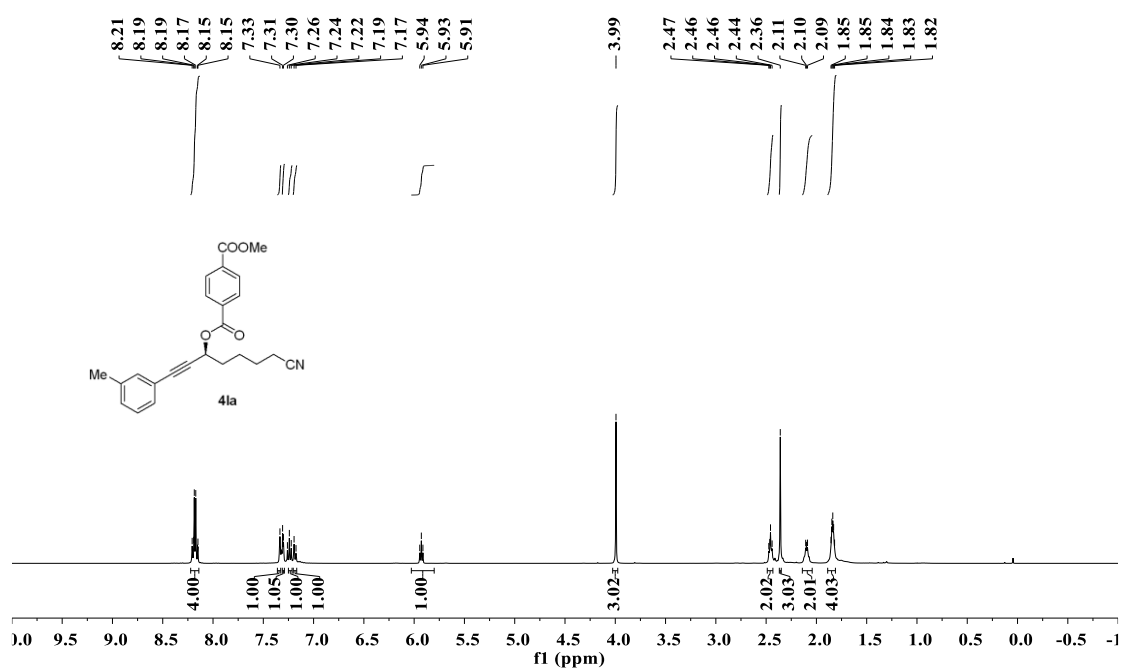




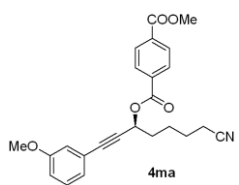
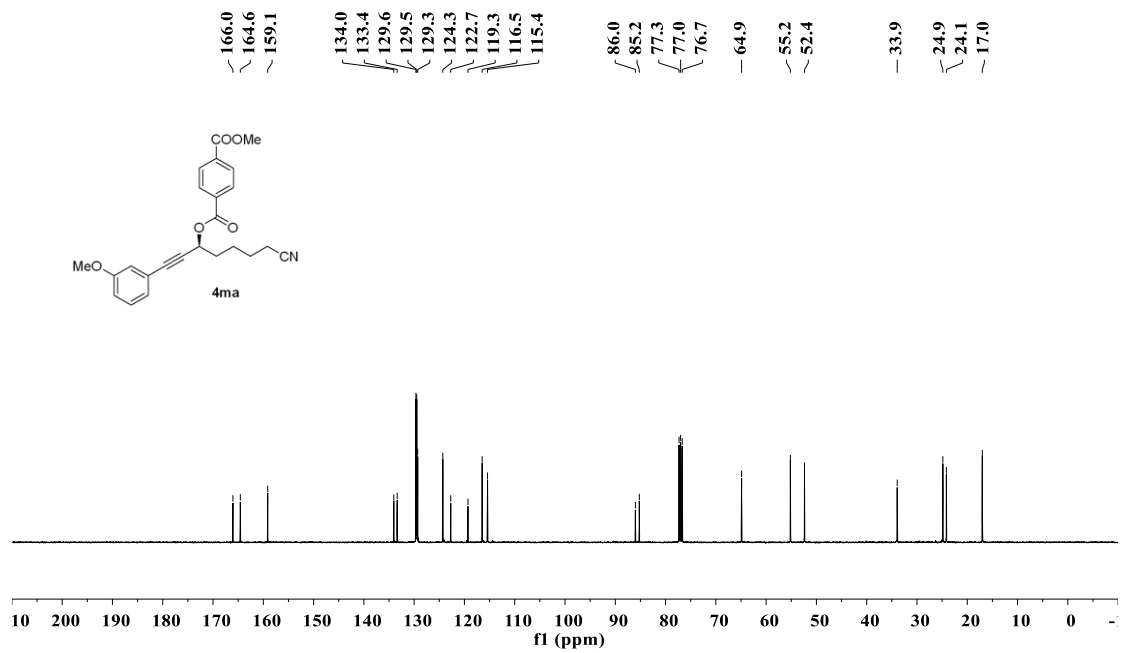
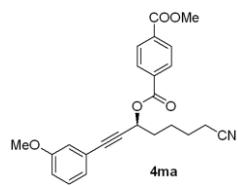
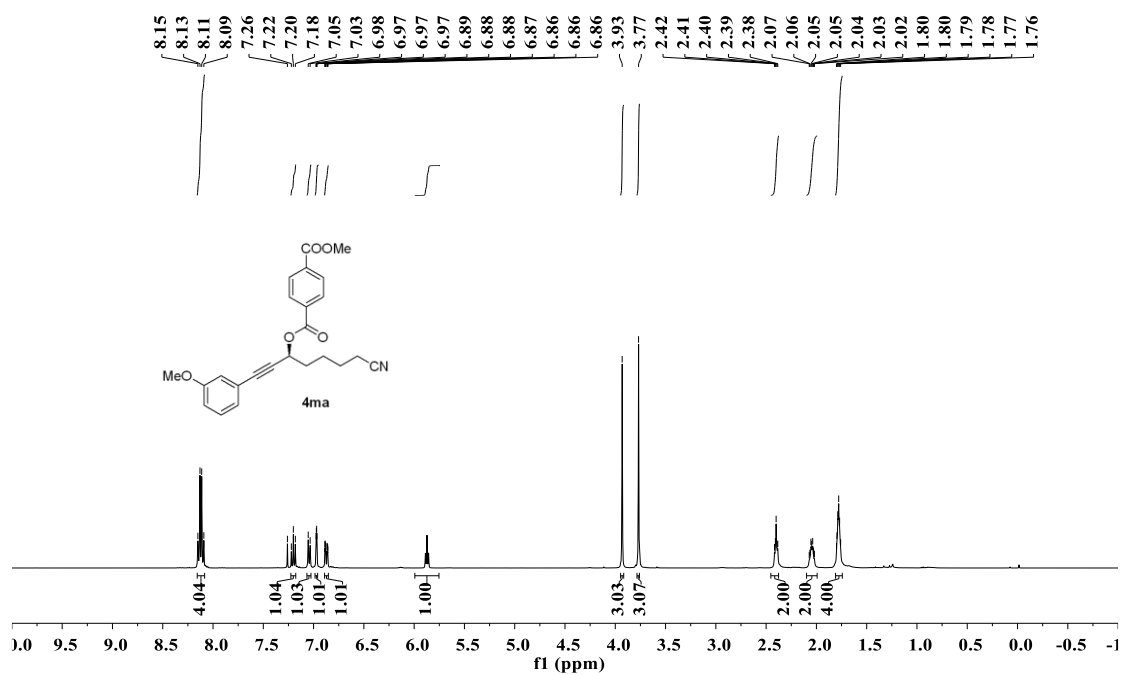
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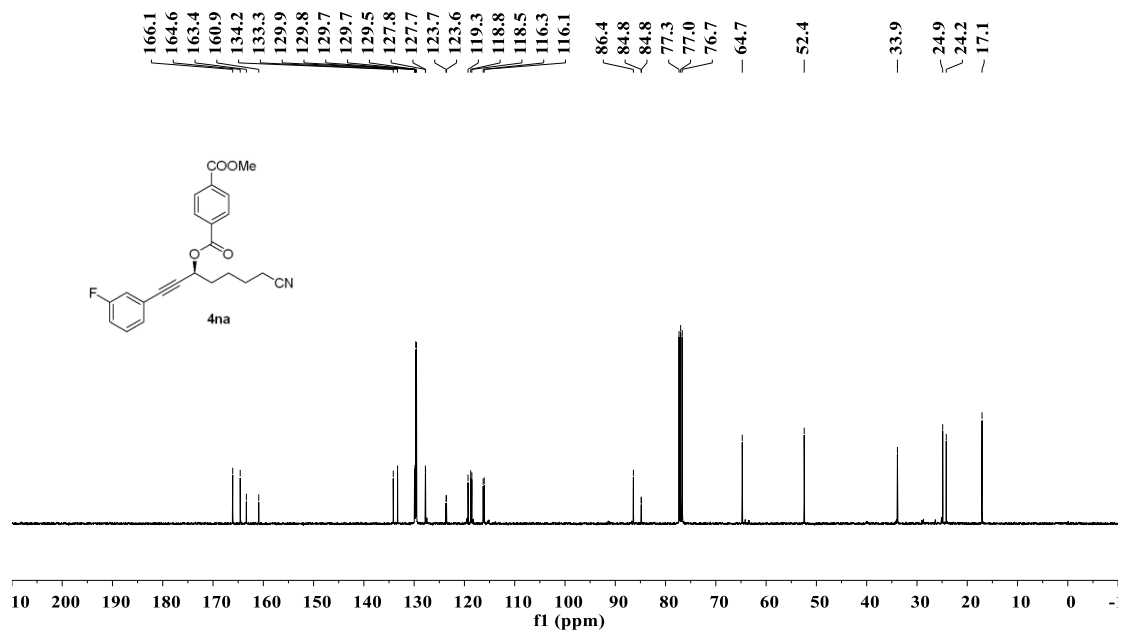
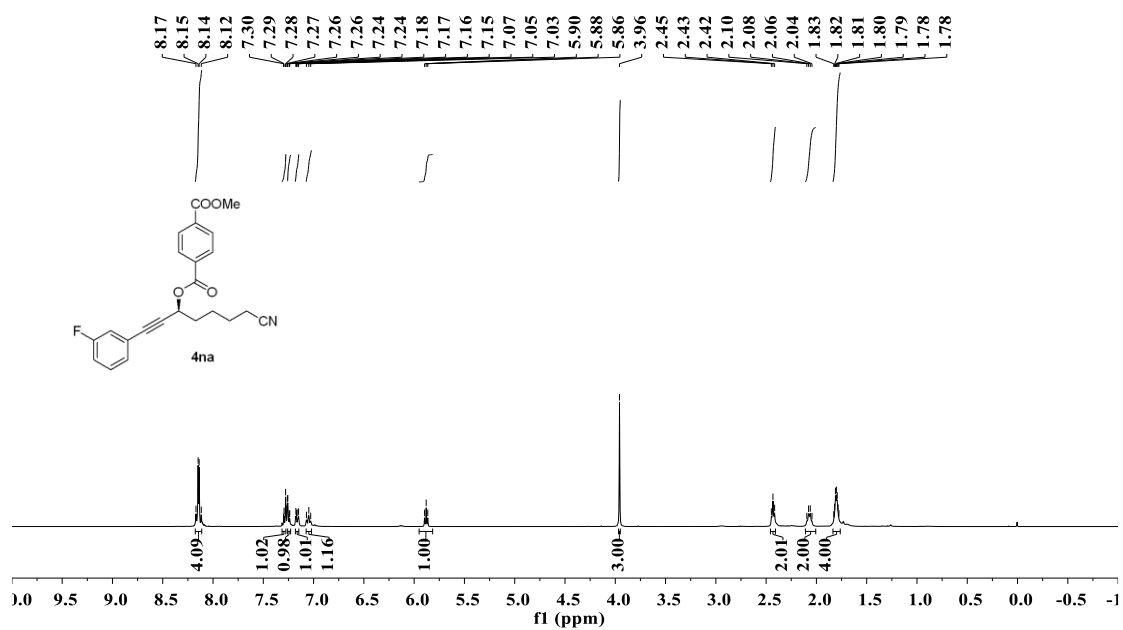
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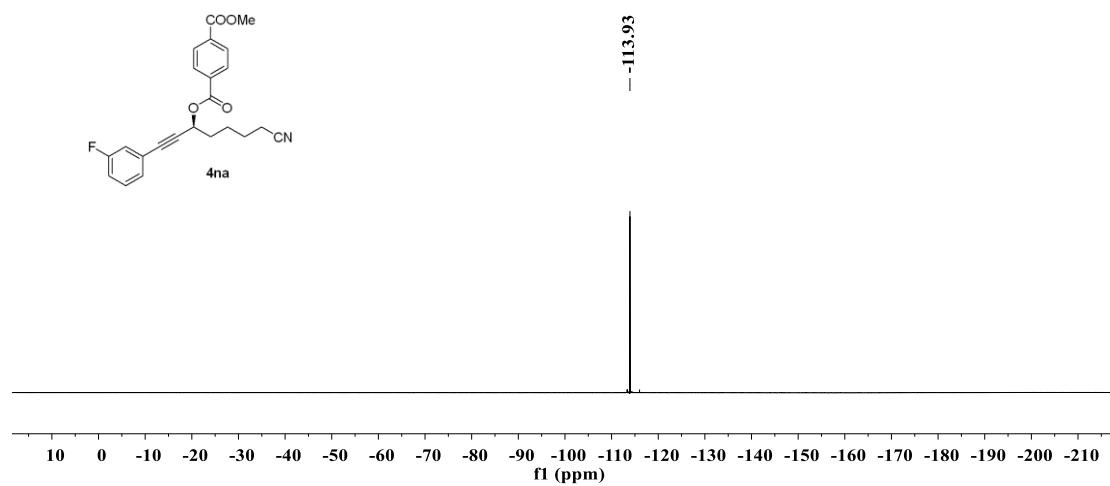


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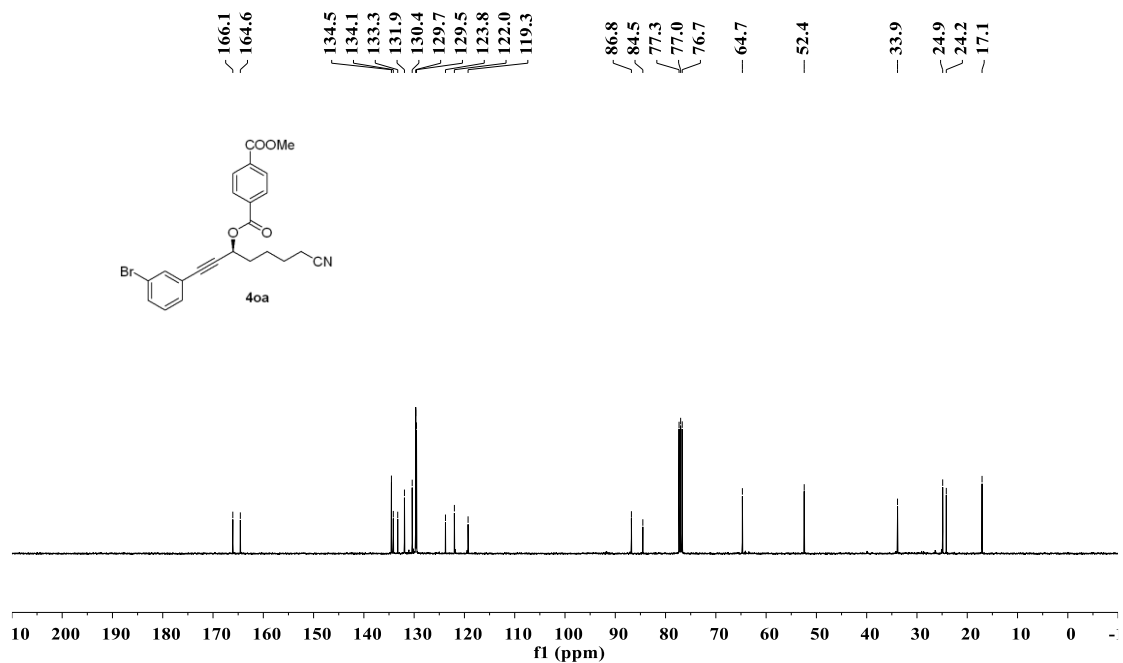
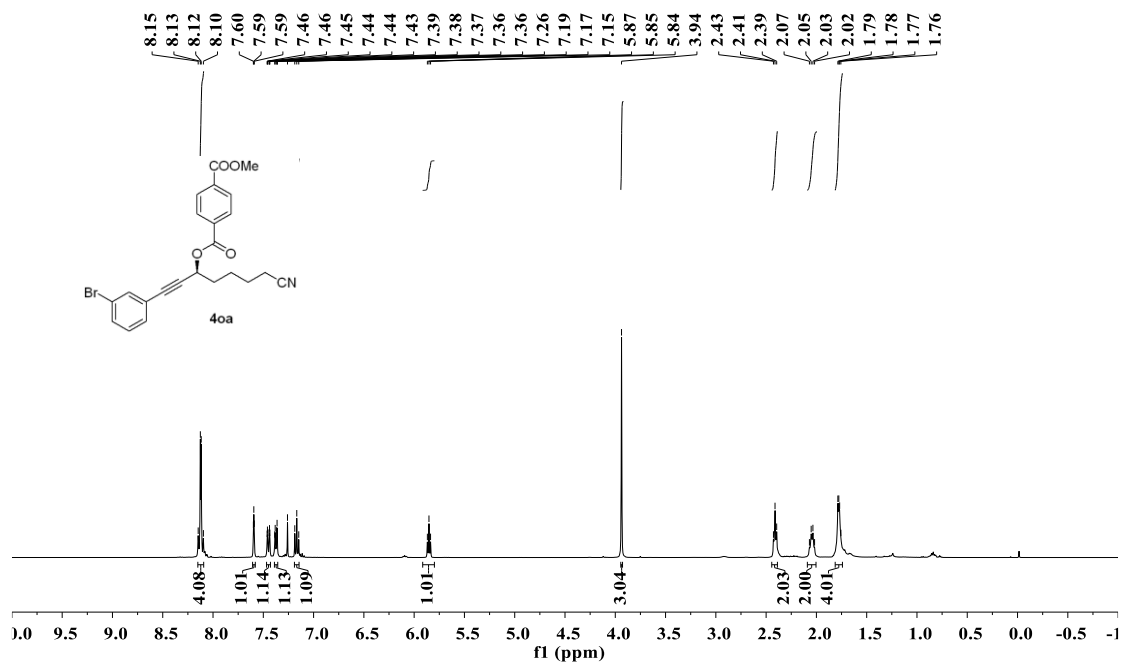


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) of product 4na



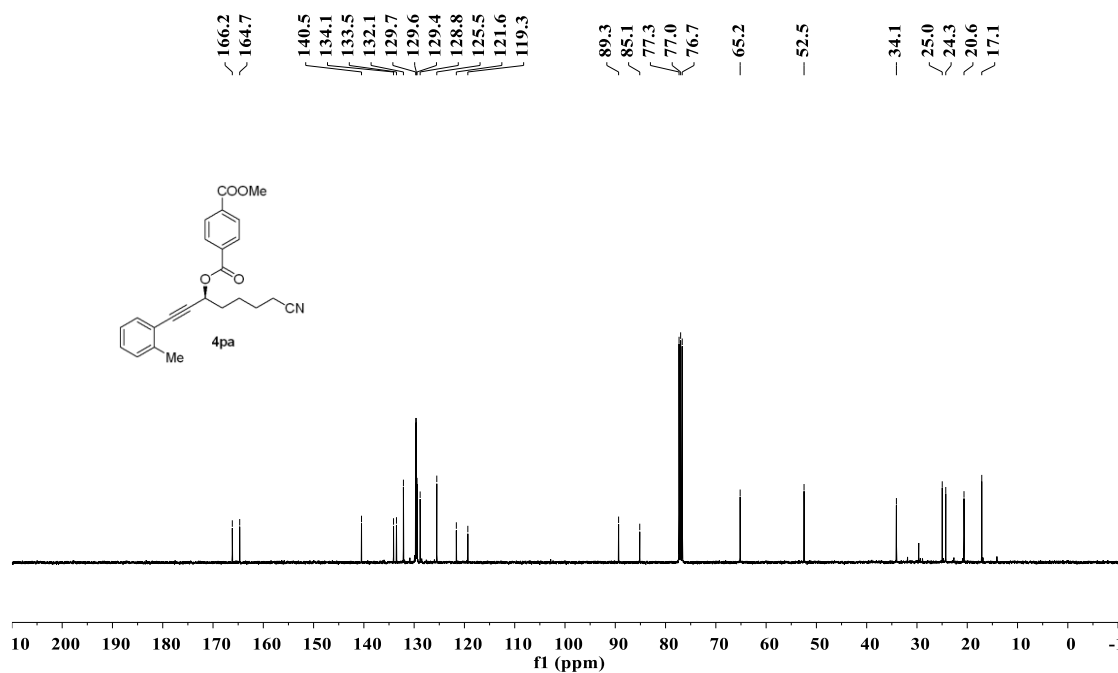
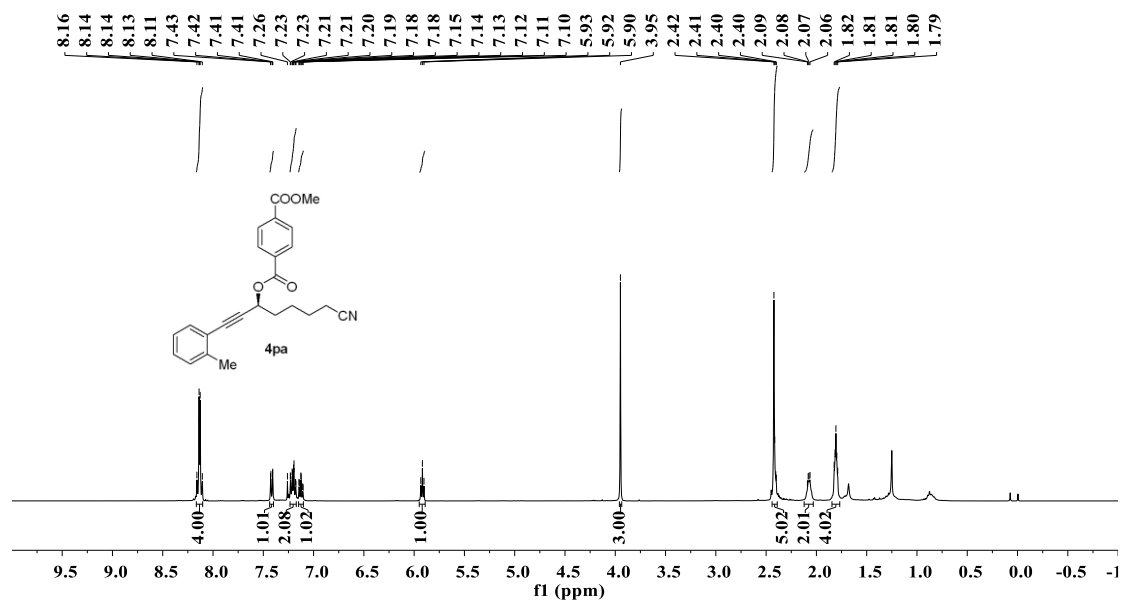


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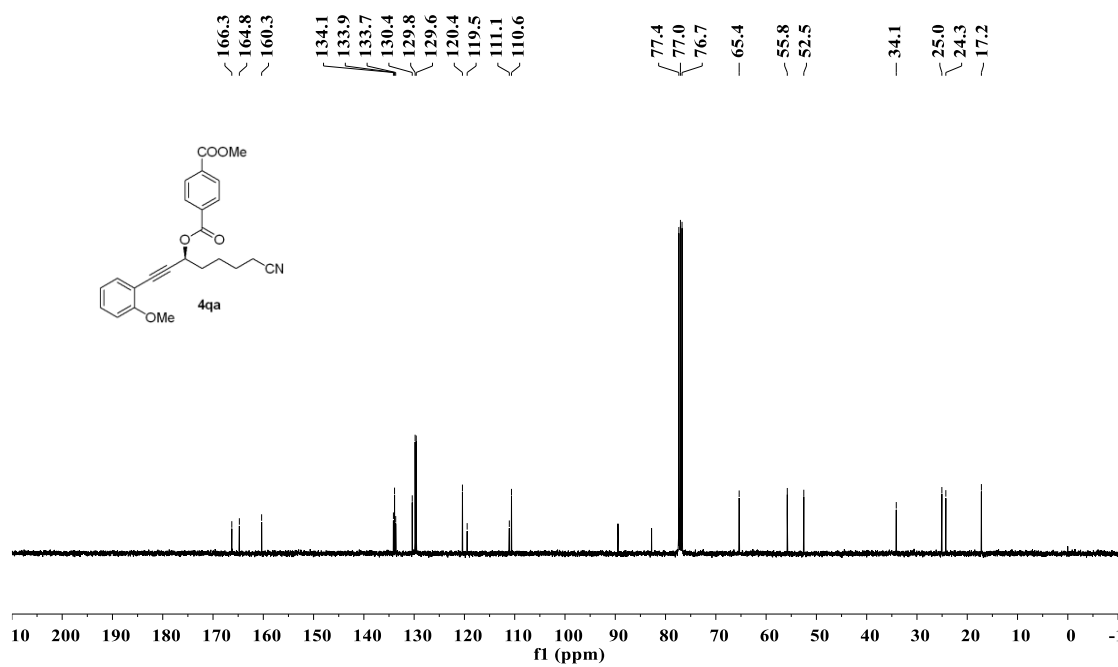
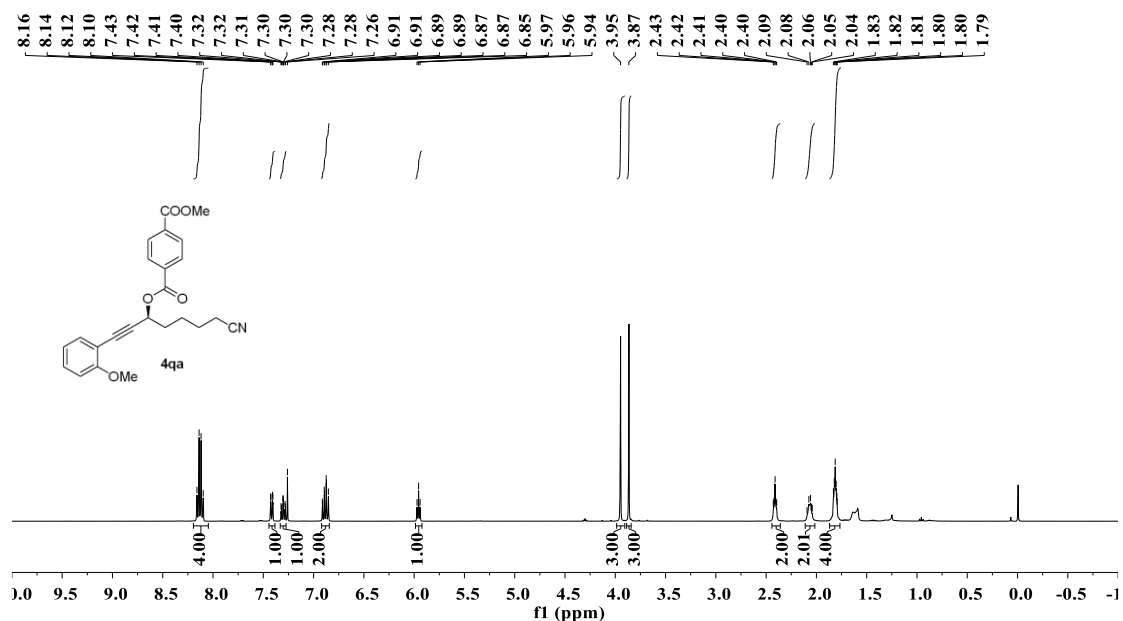




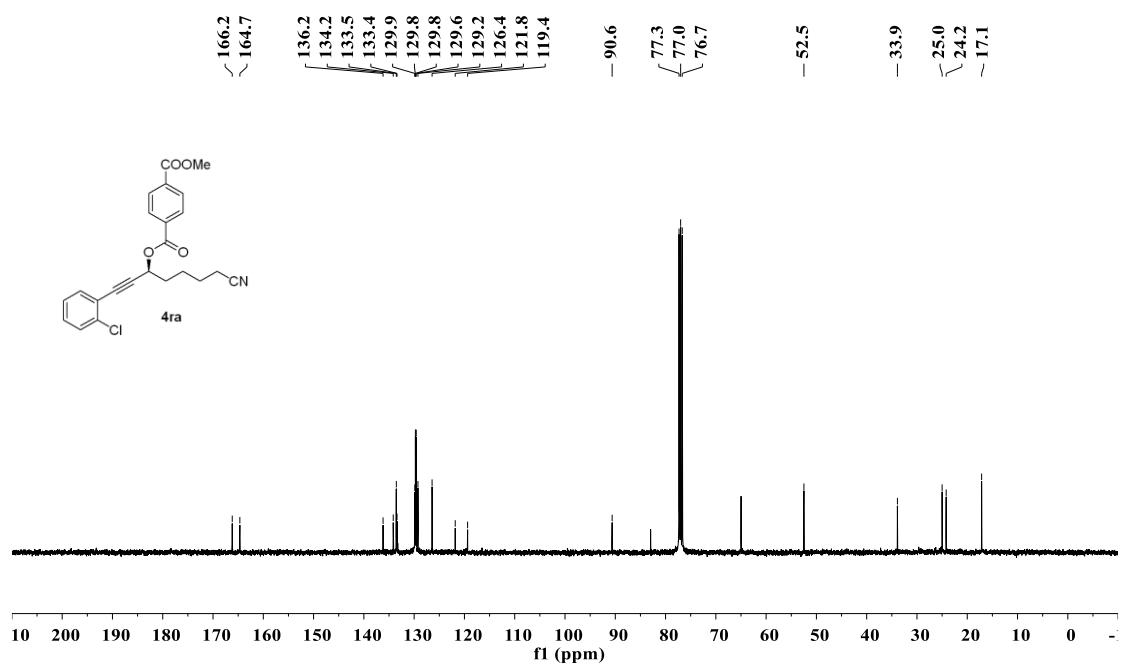
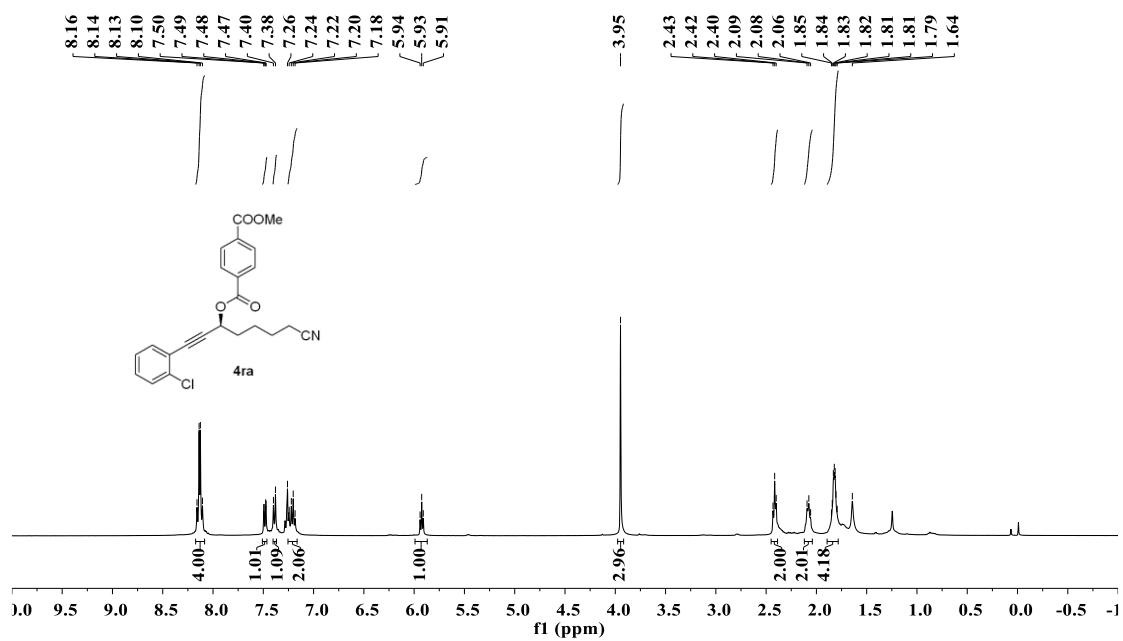
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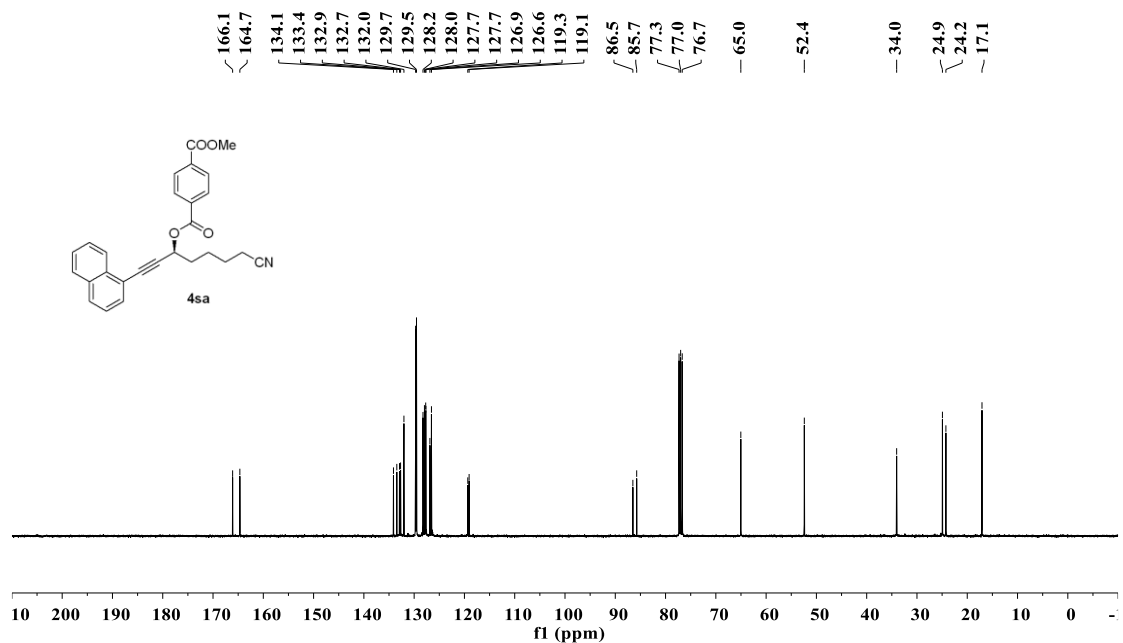
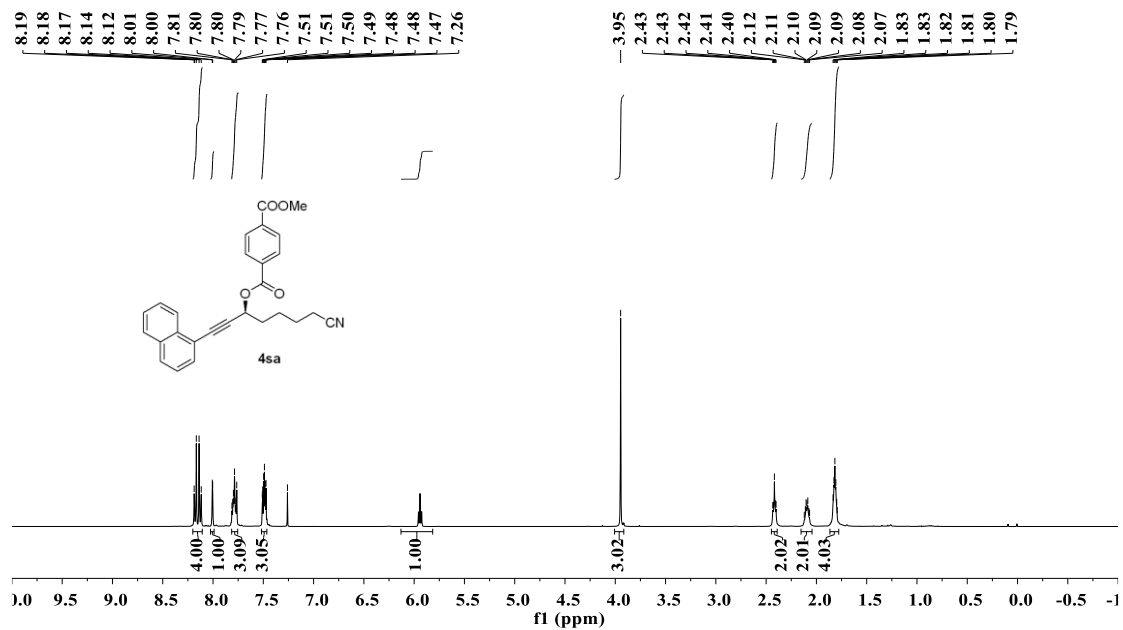
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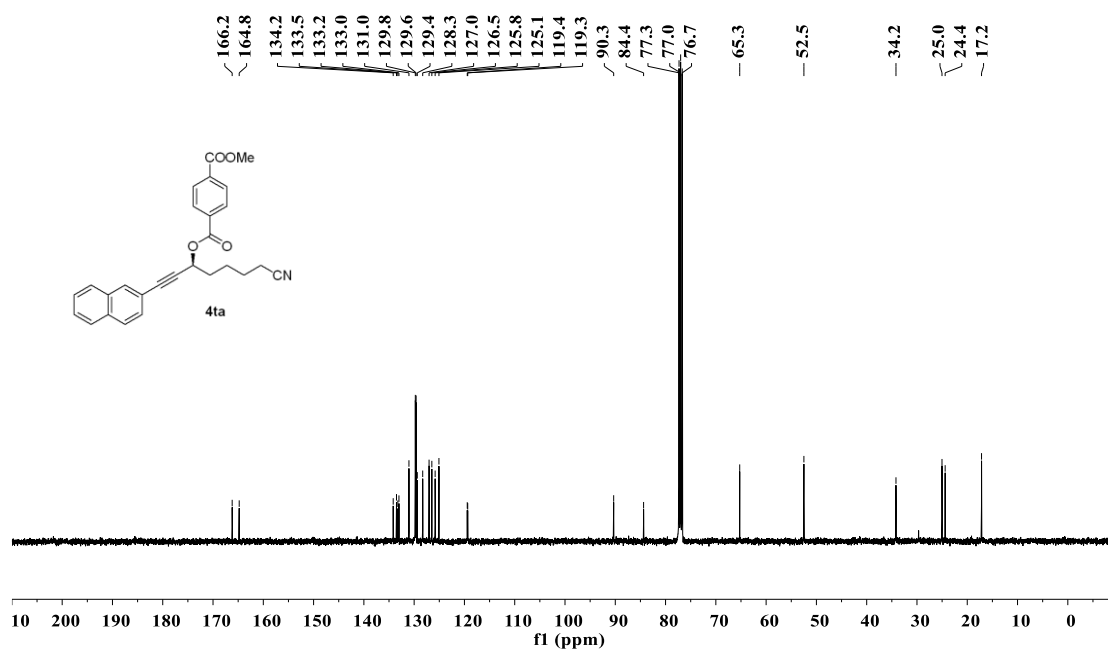
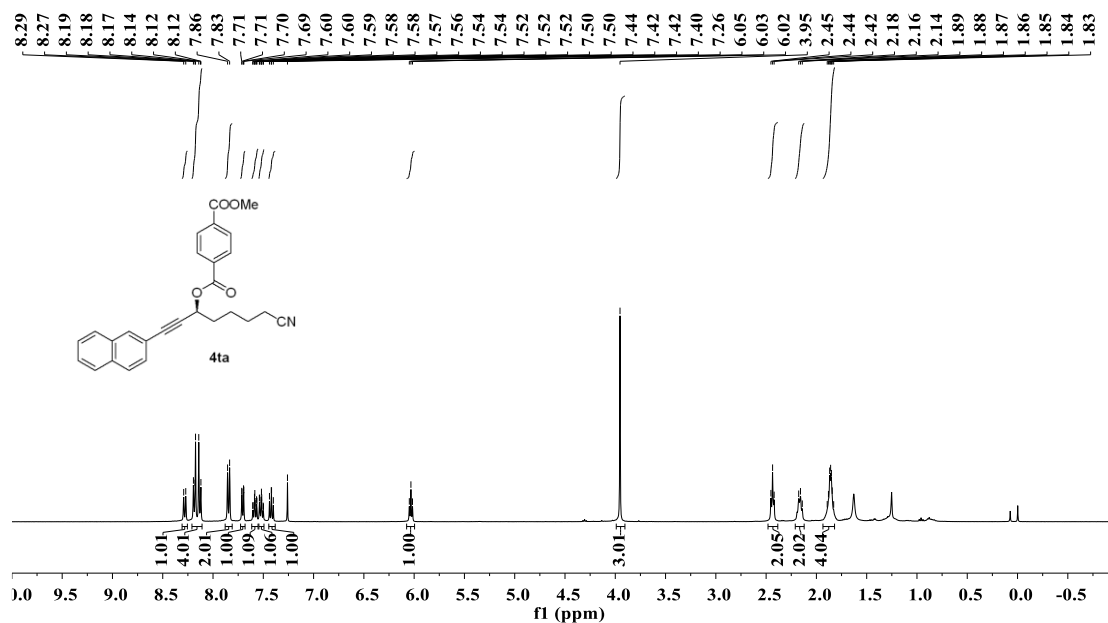
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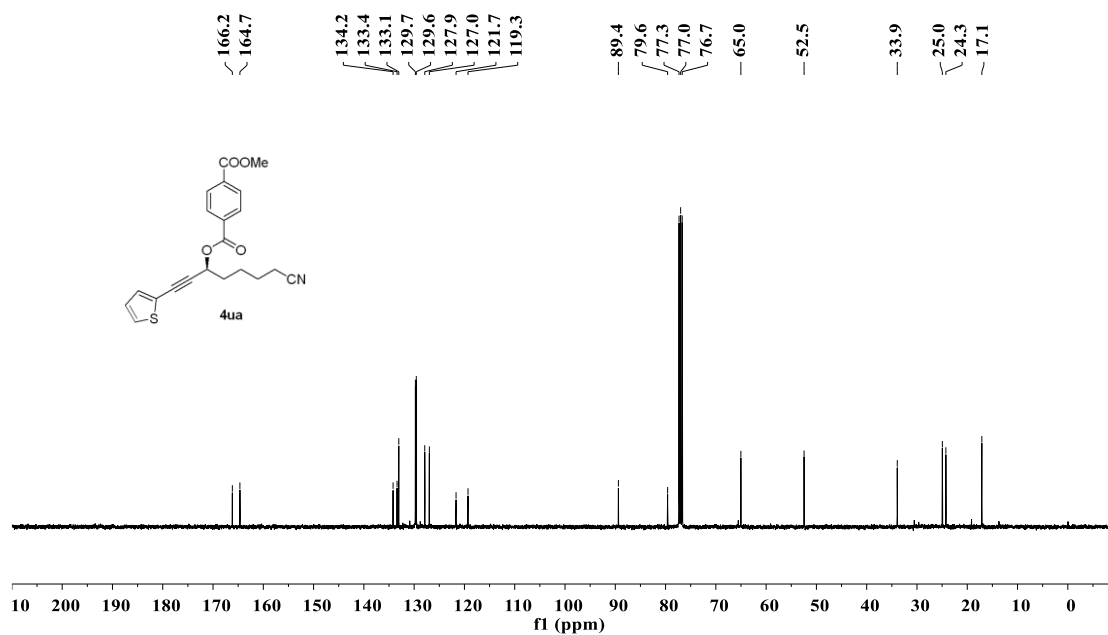
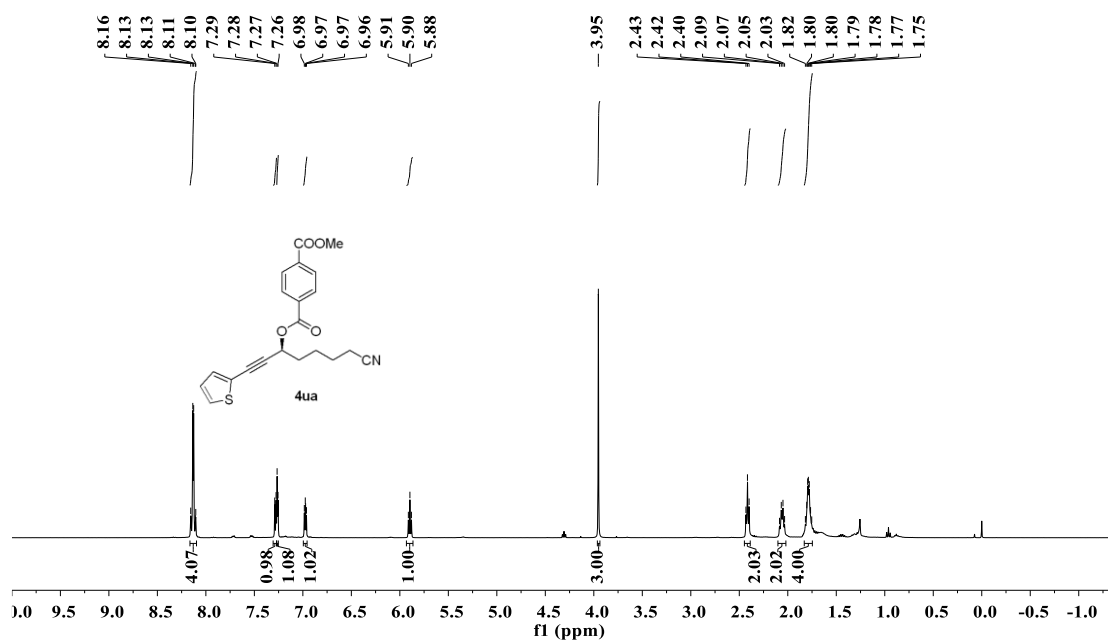
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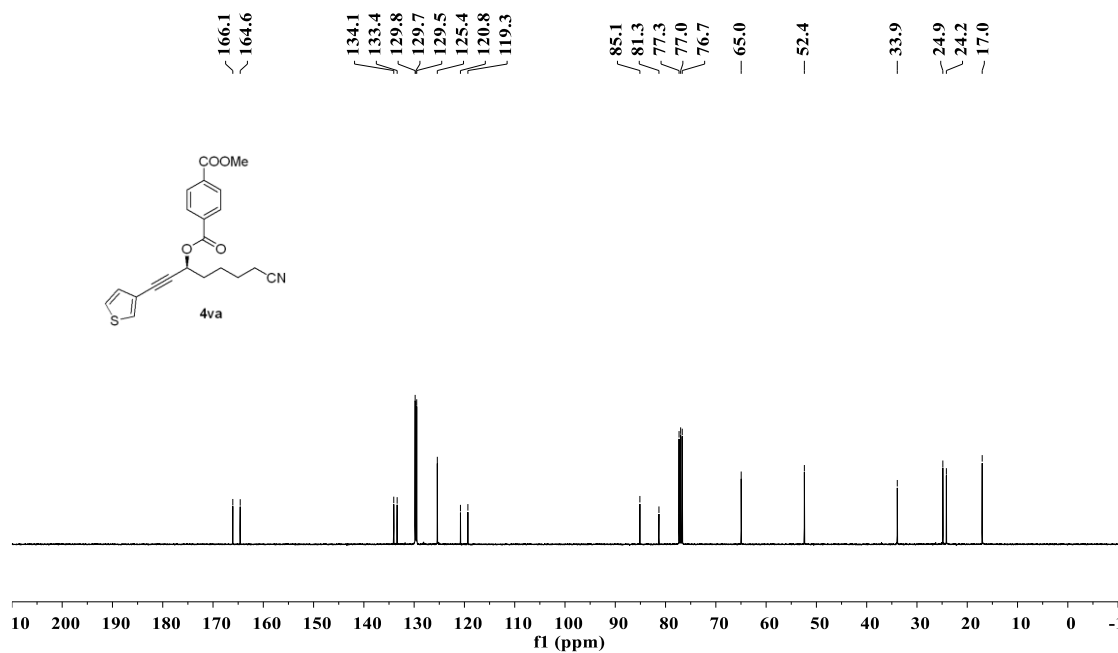
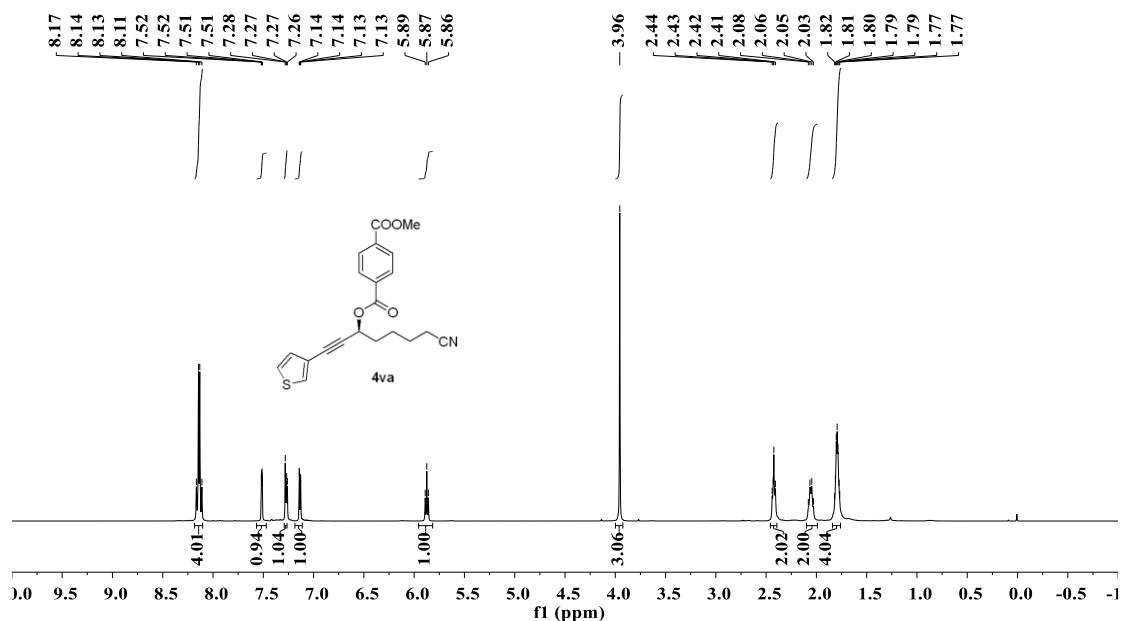
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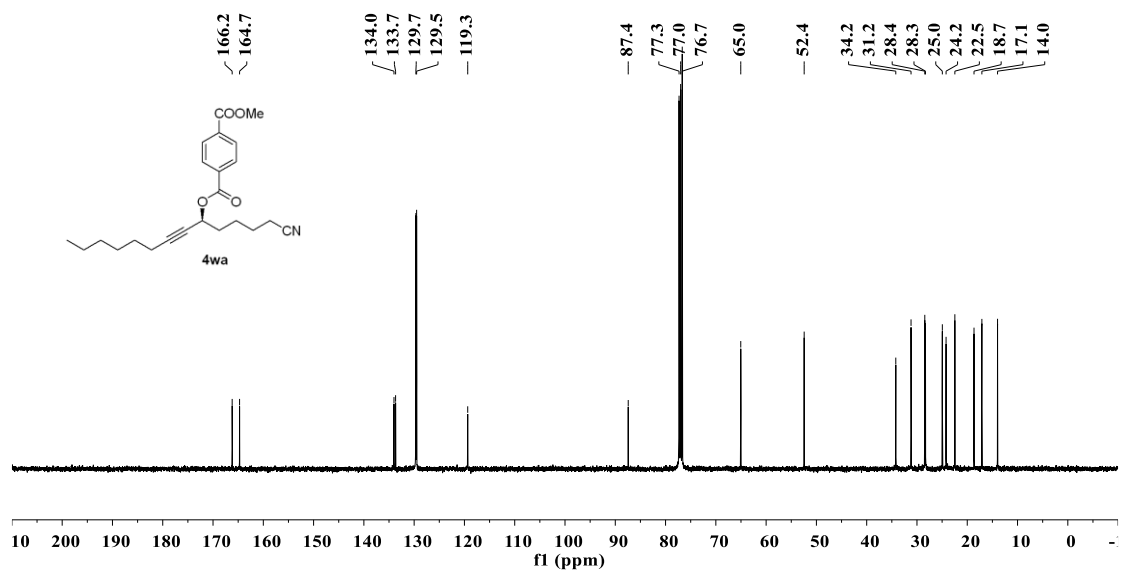
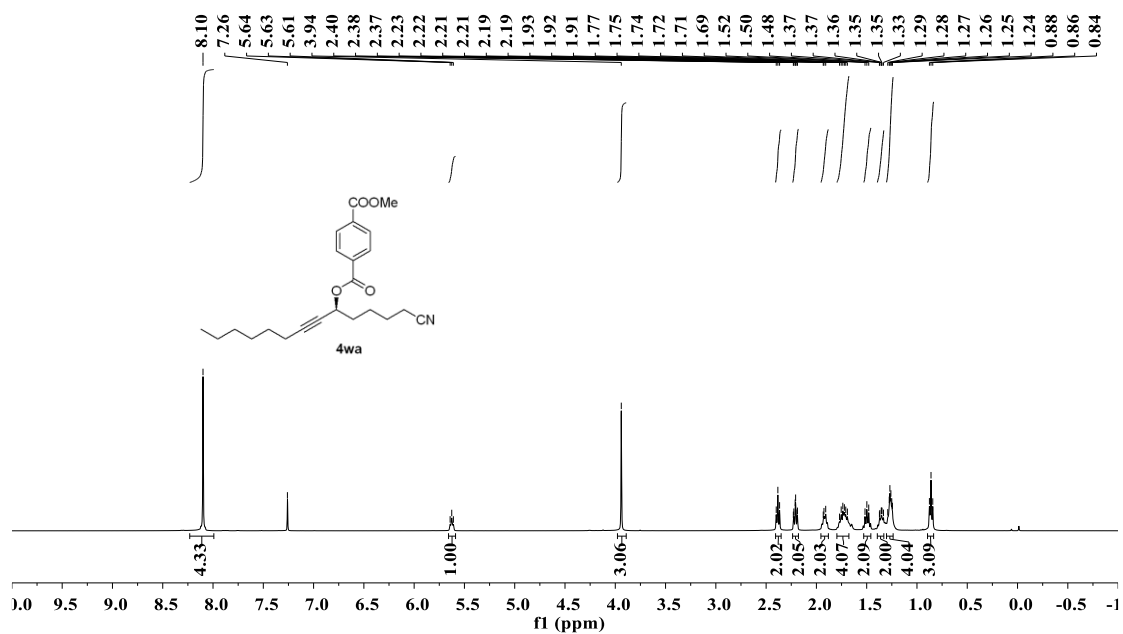
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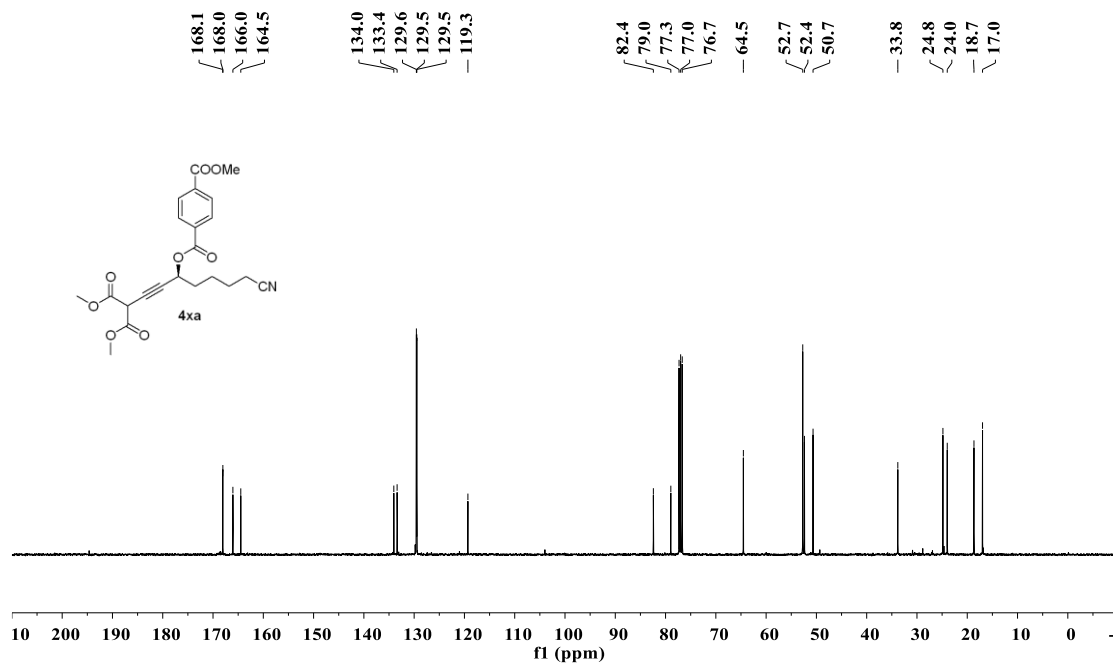
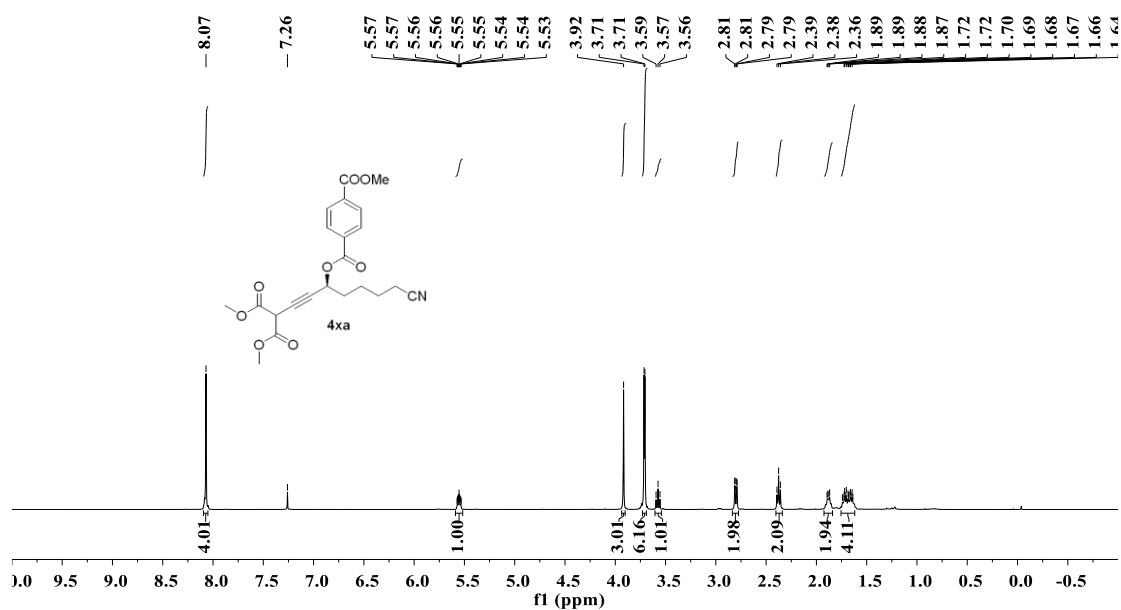


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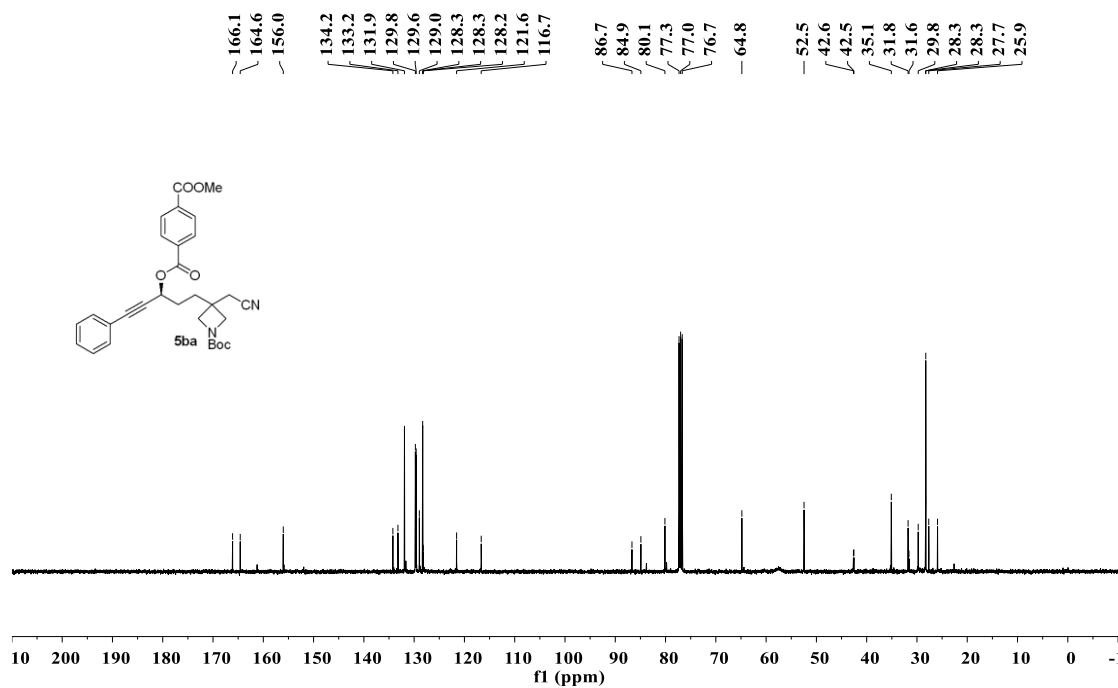
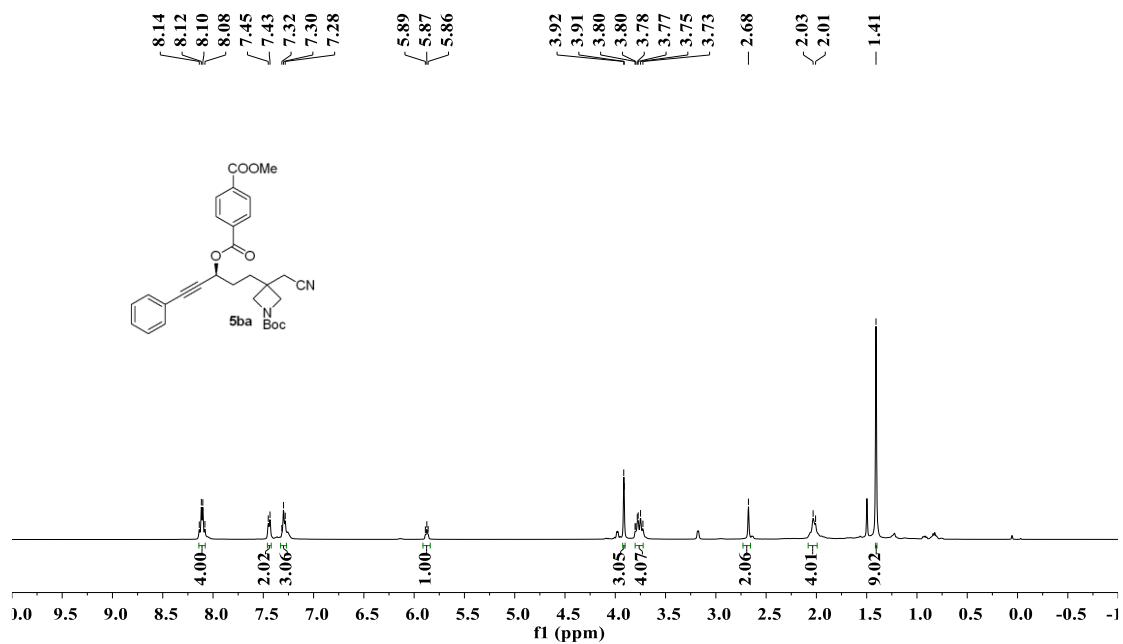




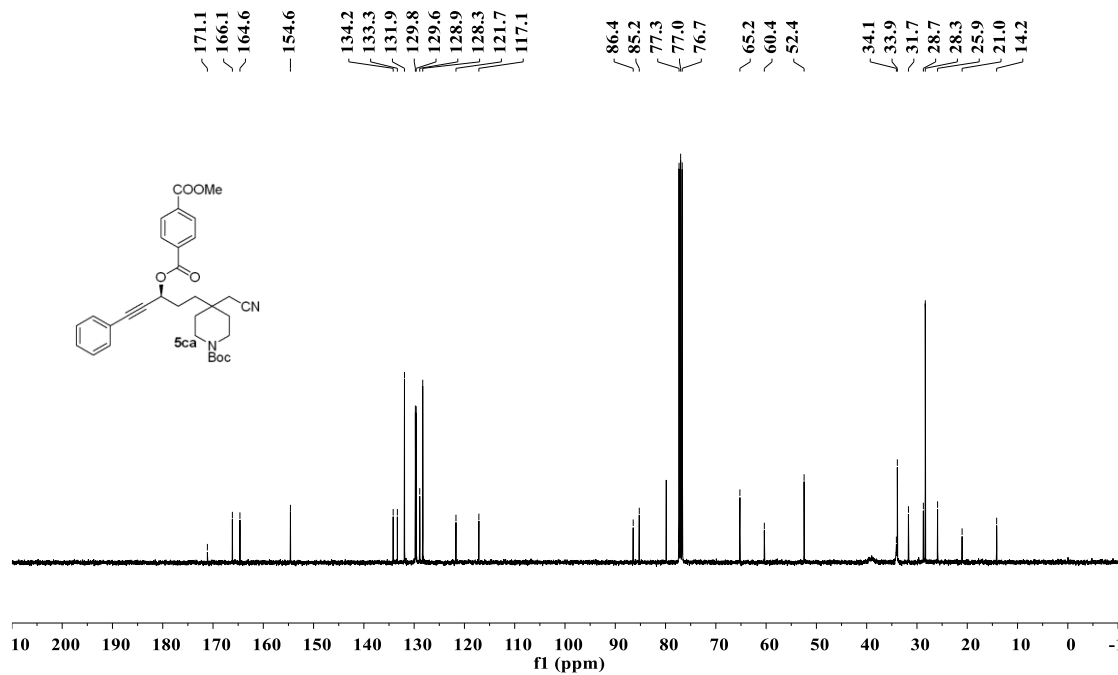
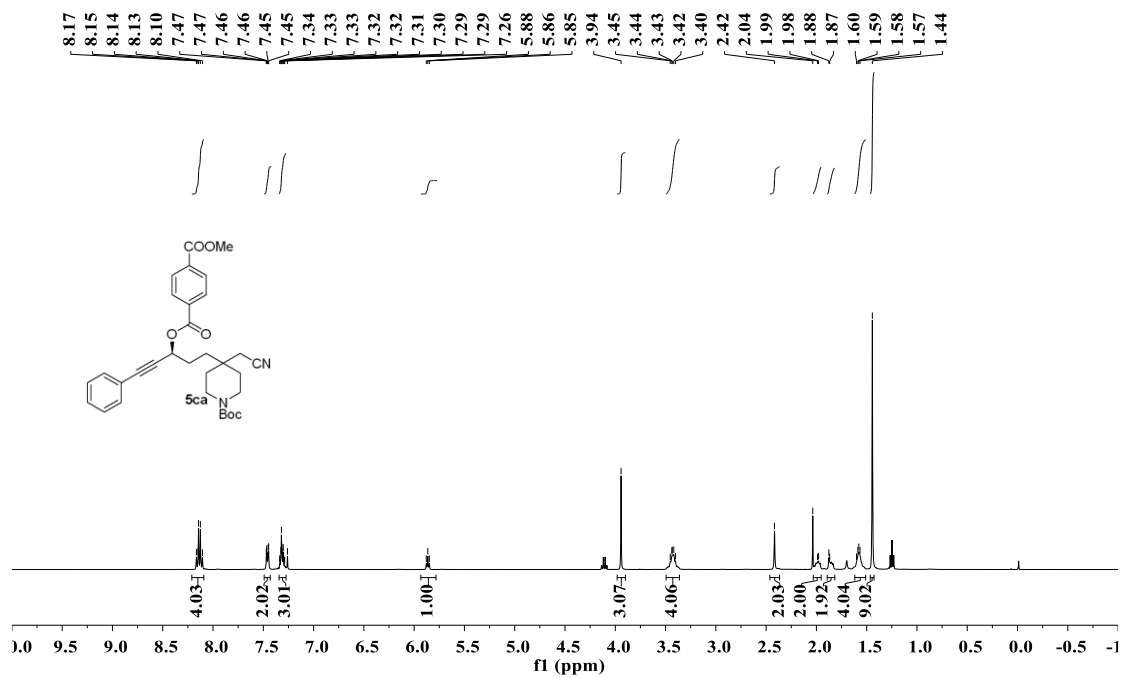
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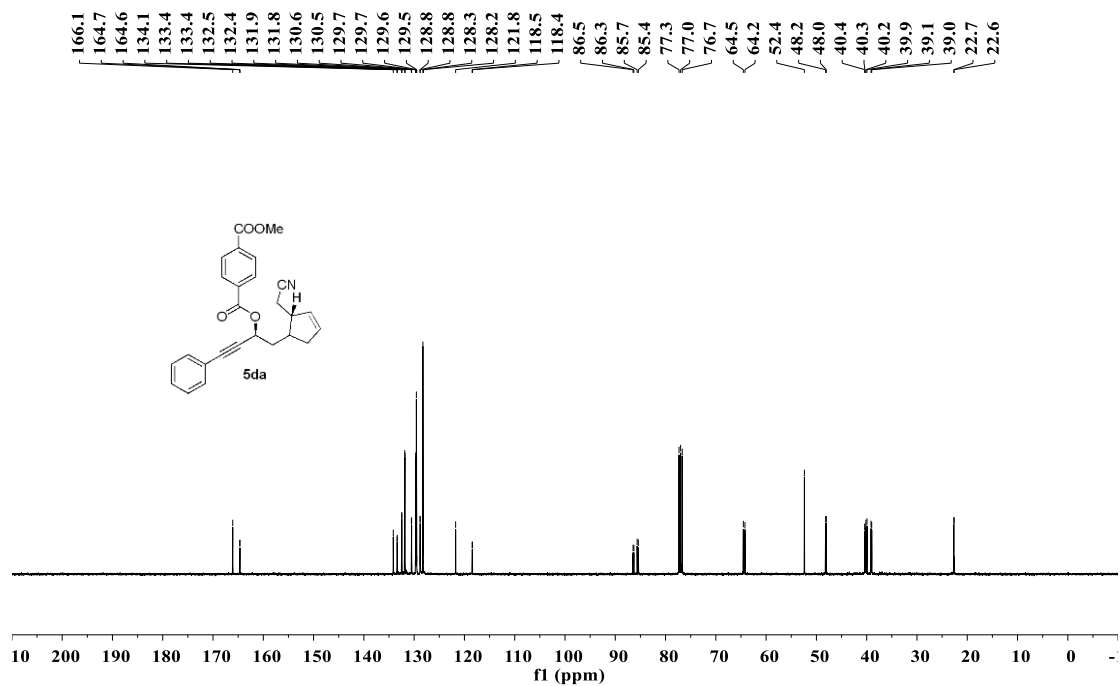
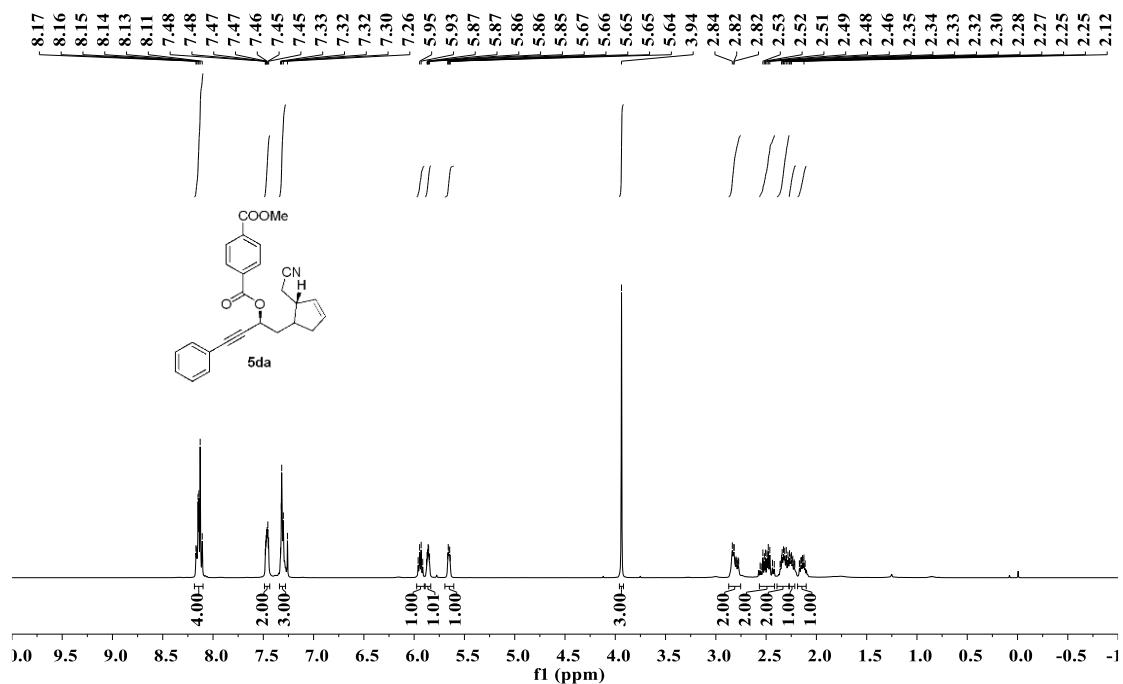
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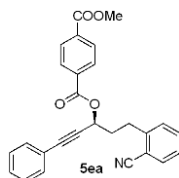
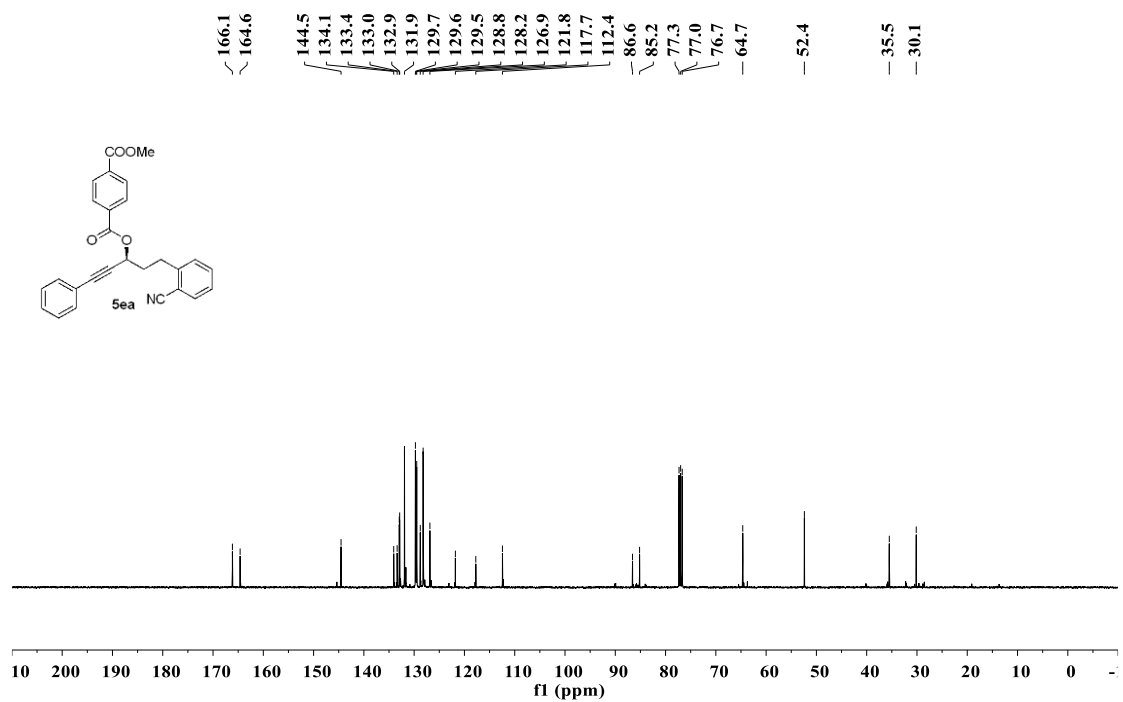
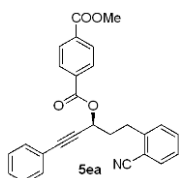
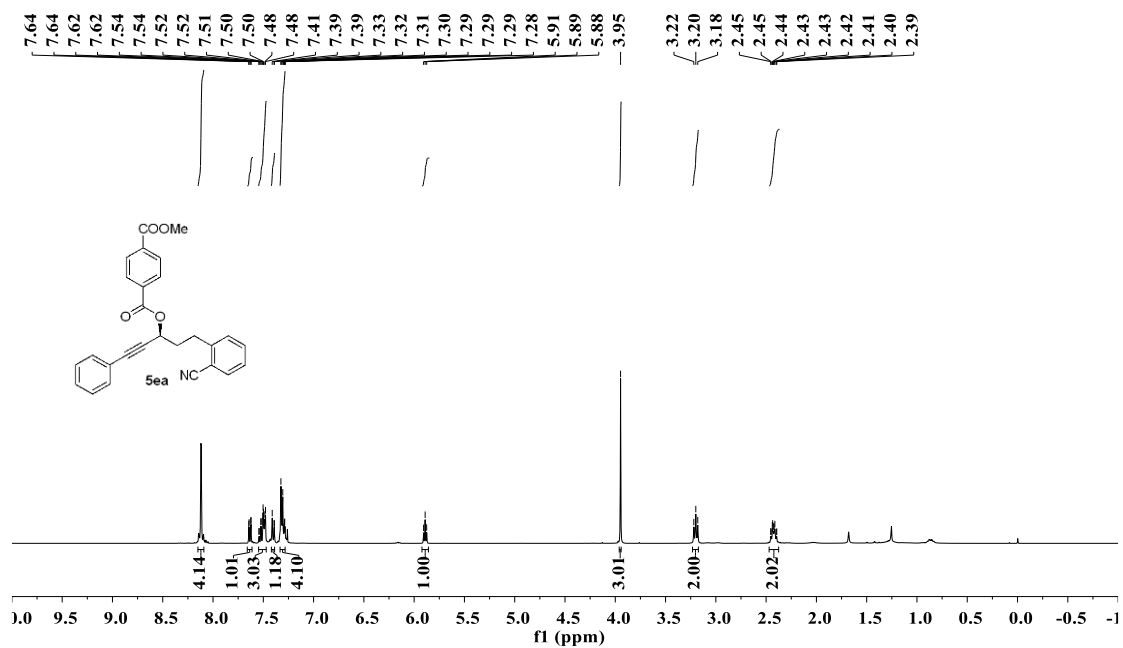
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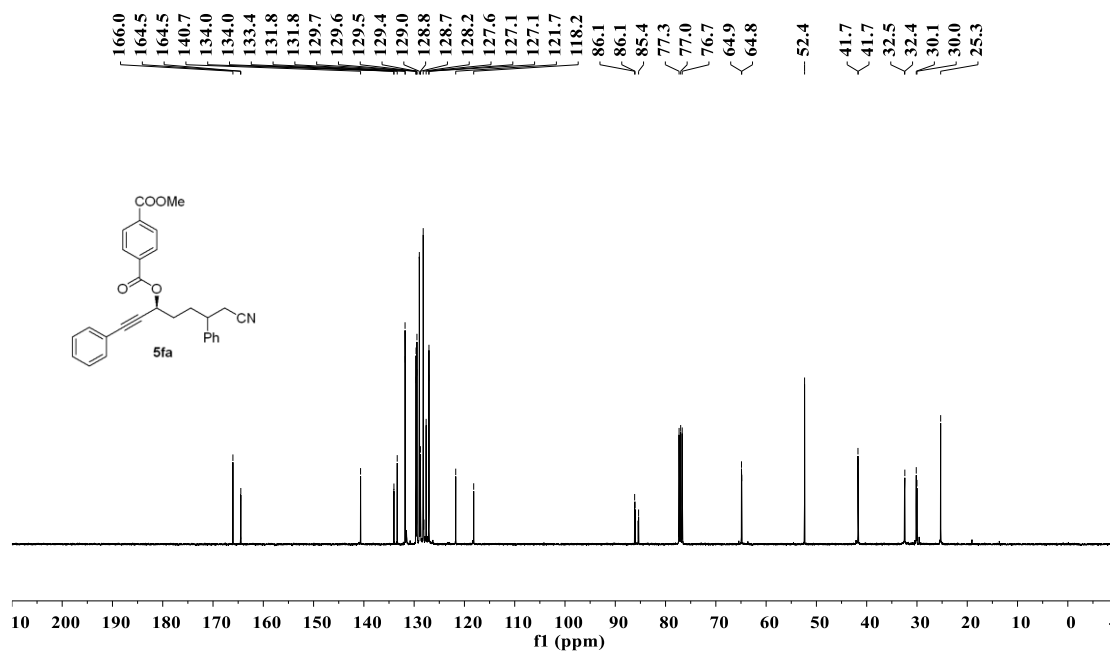
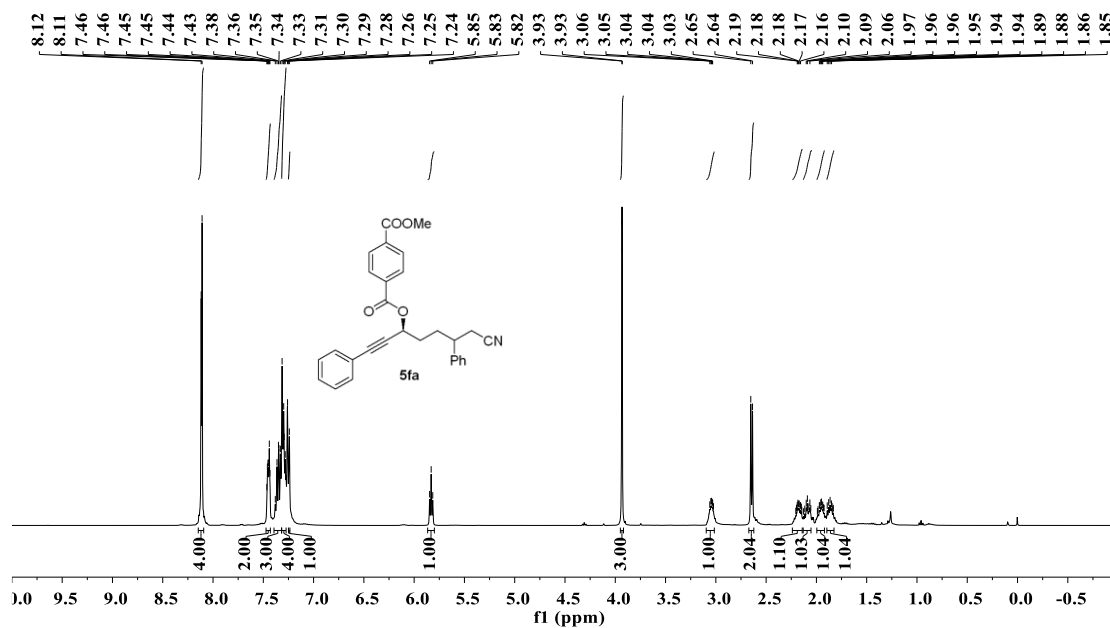
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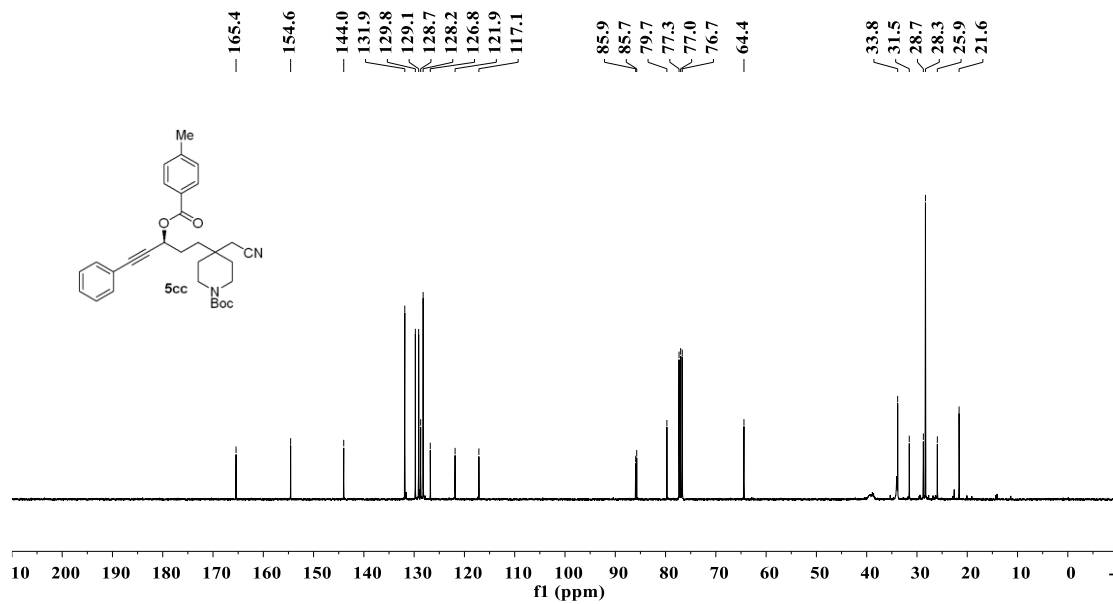
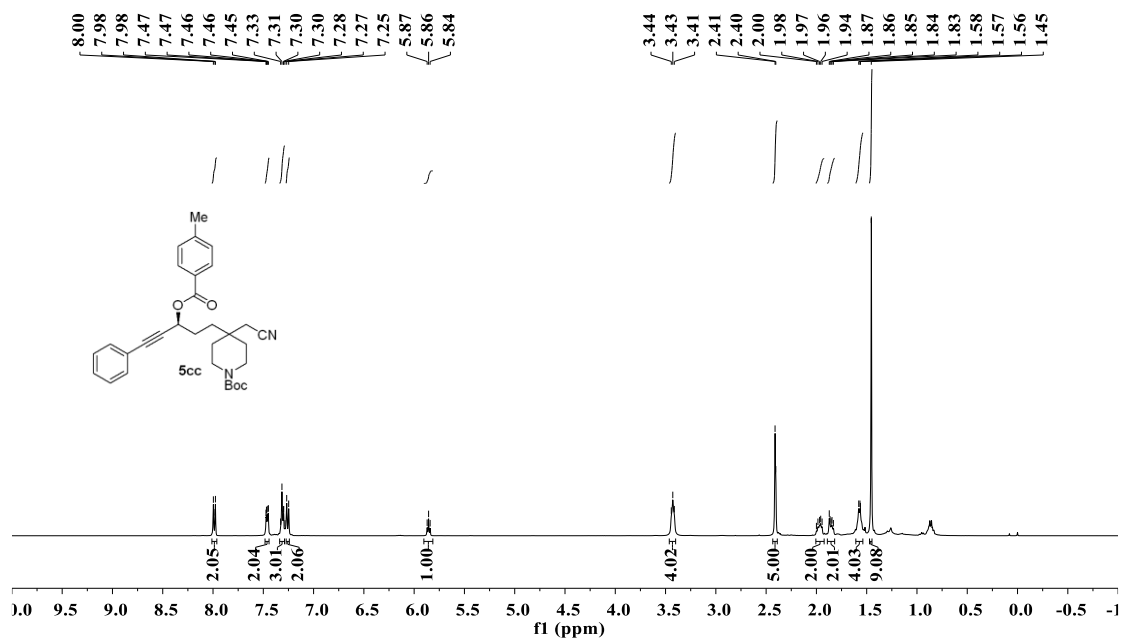
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 5ea



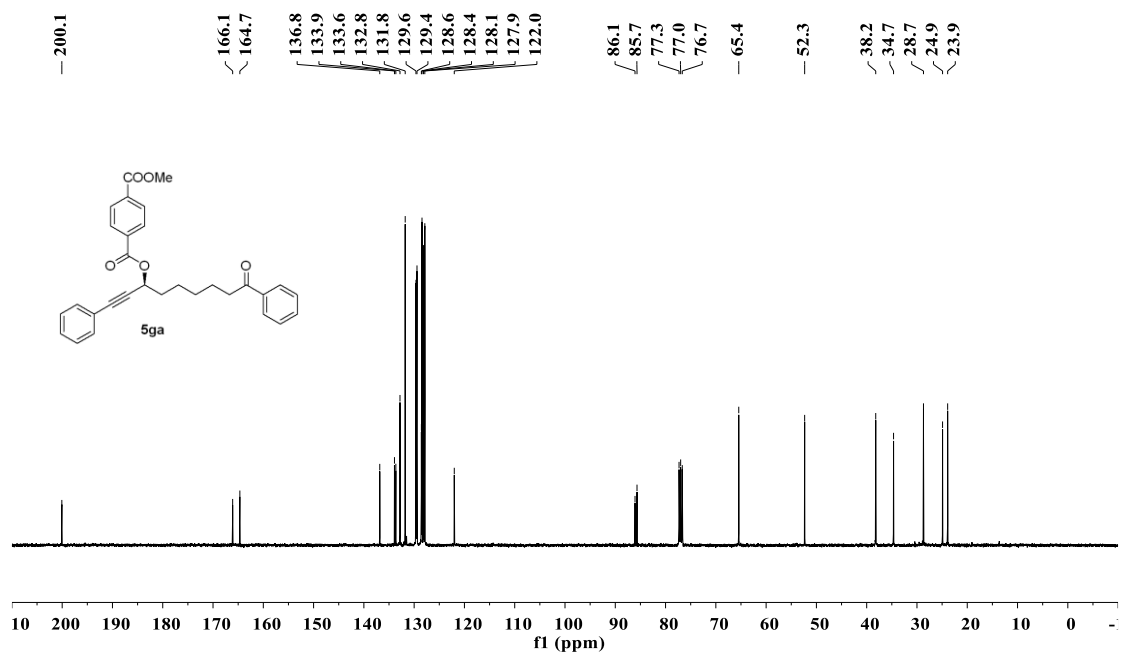
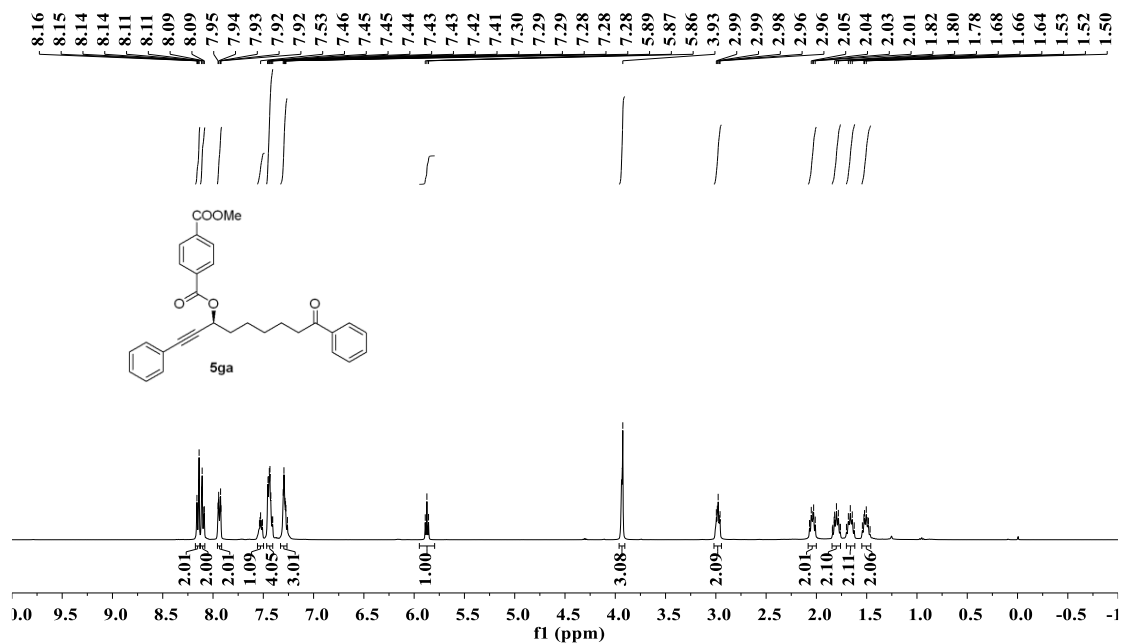
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 5fa



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of product **5cc**

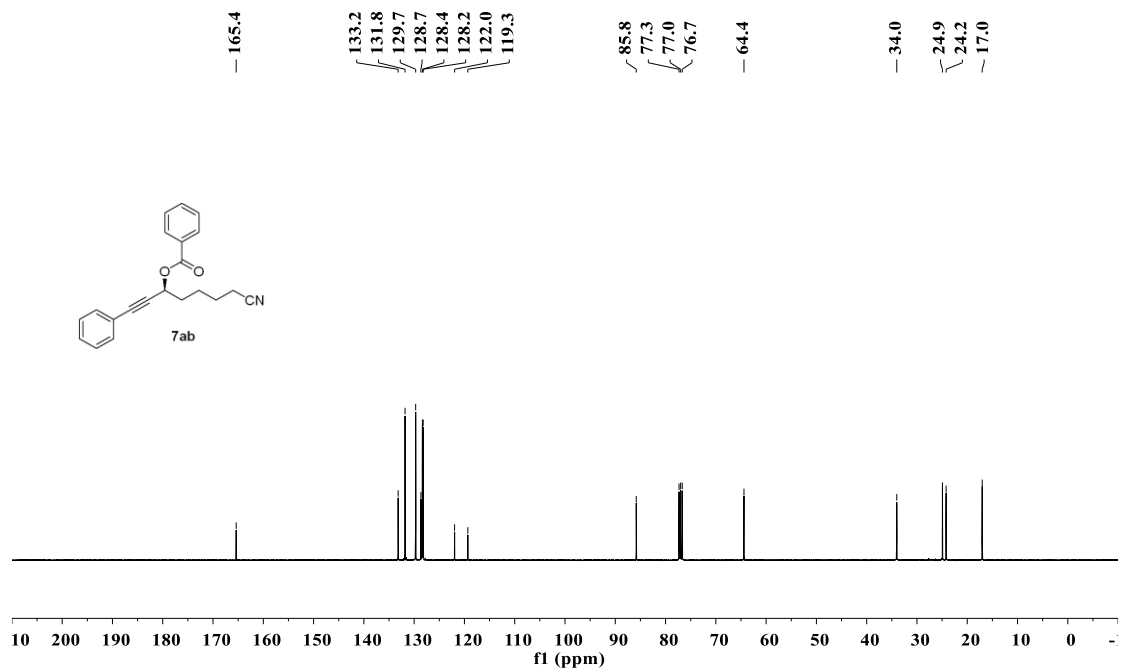
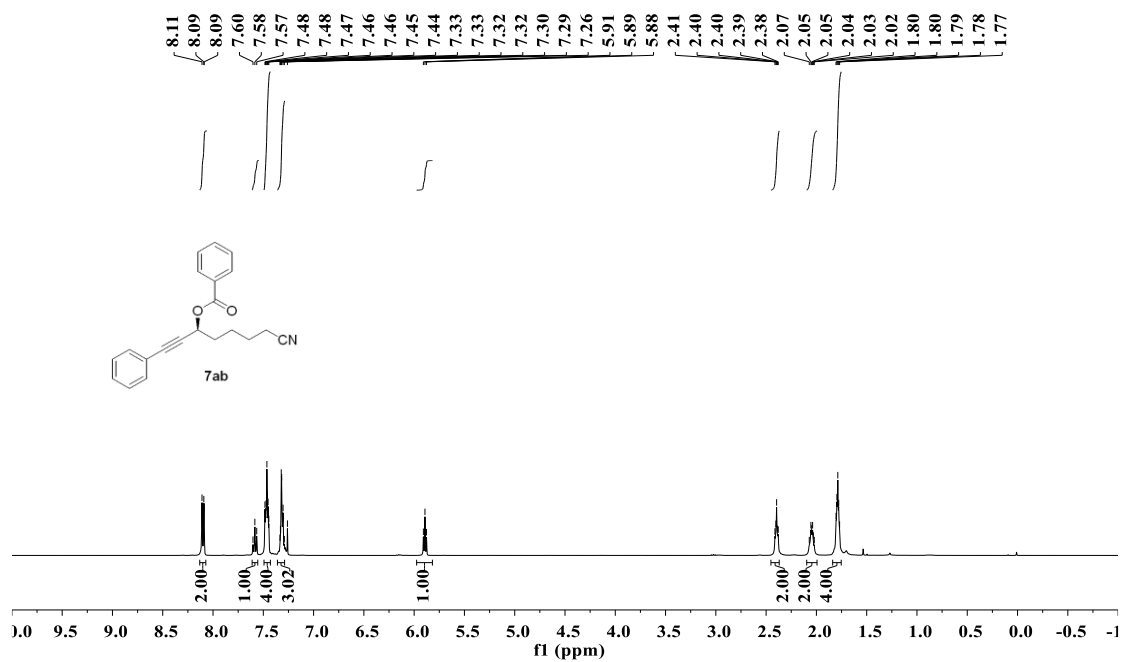


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 5ga

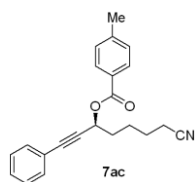
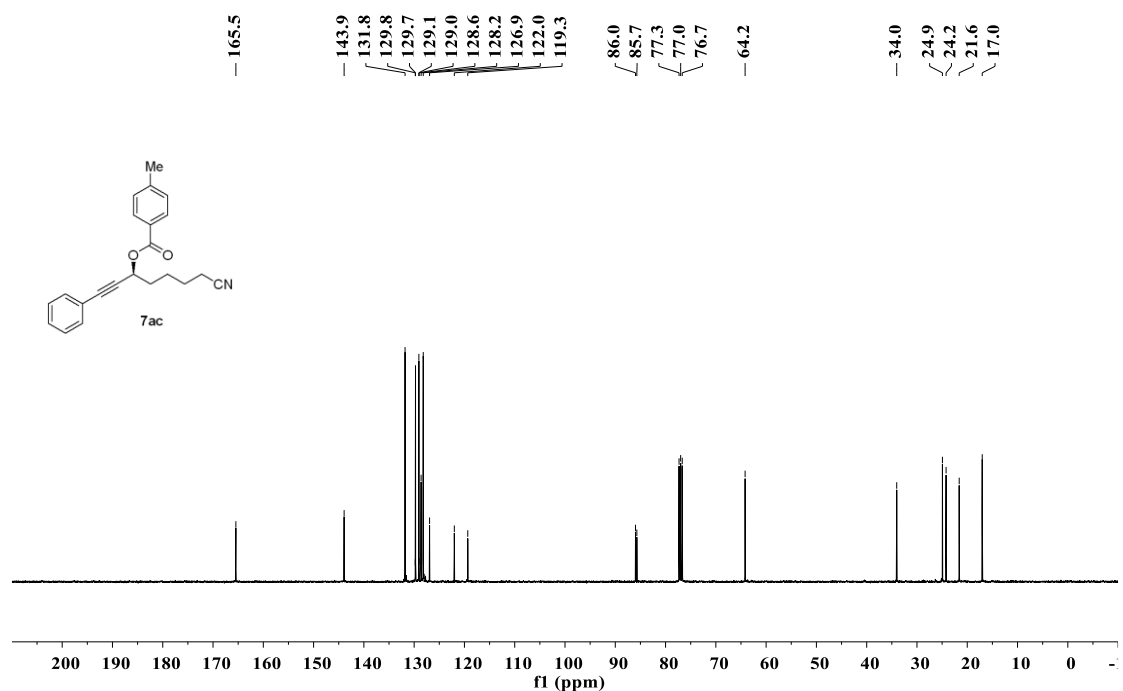
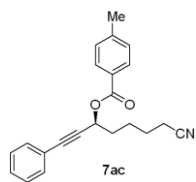
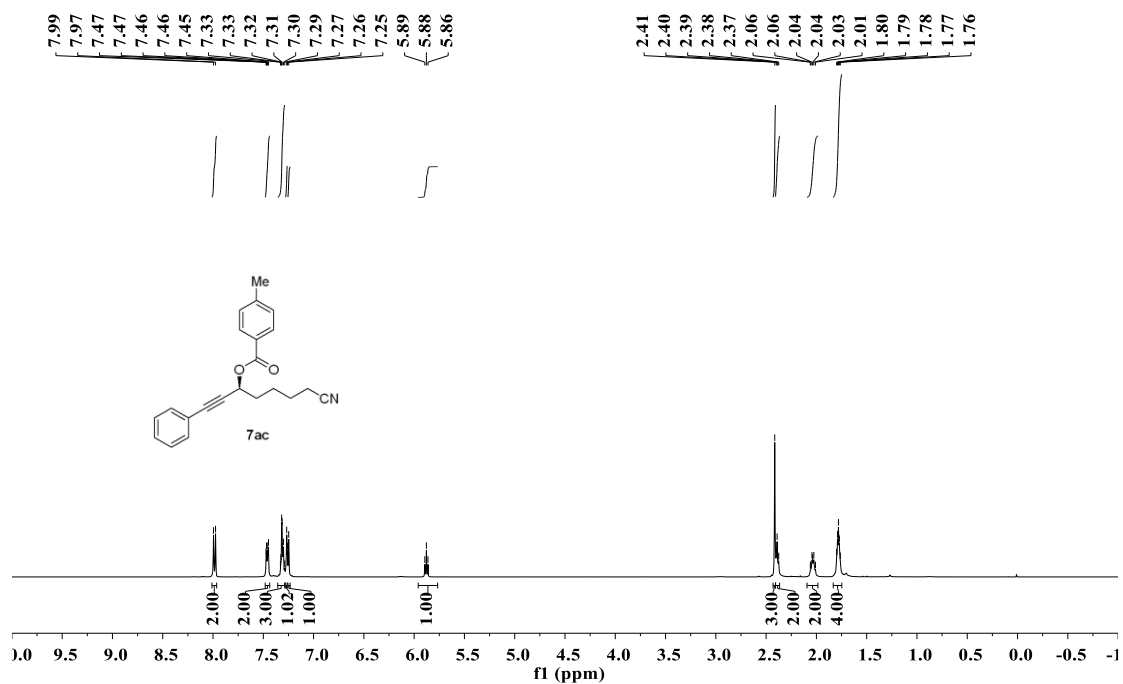




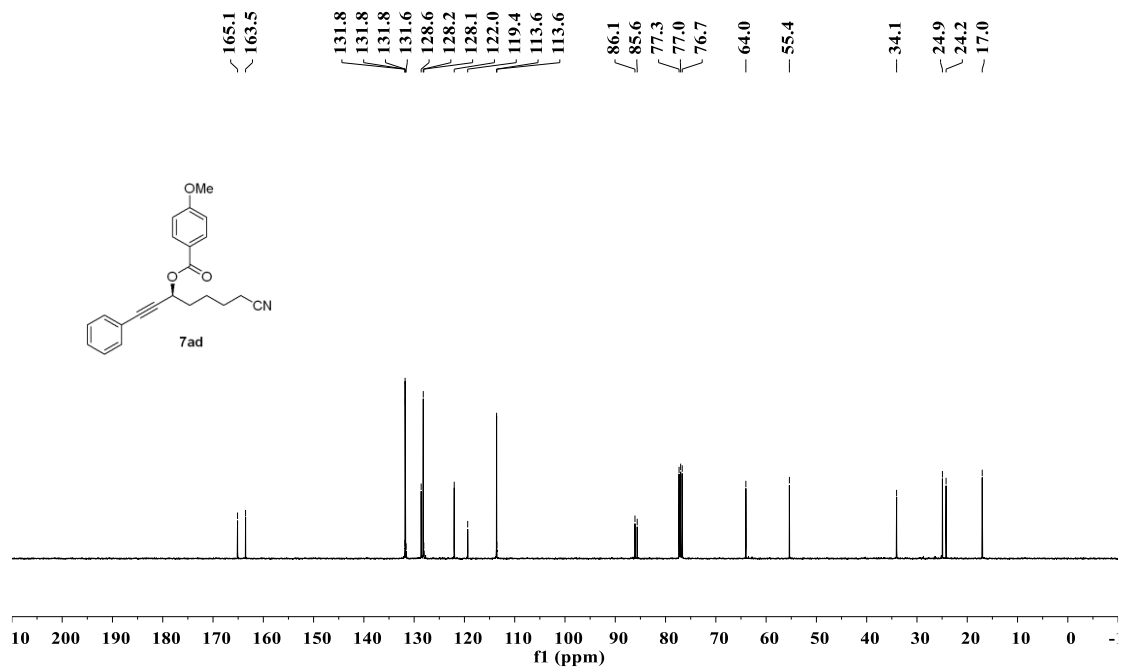
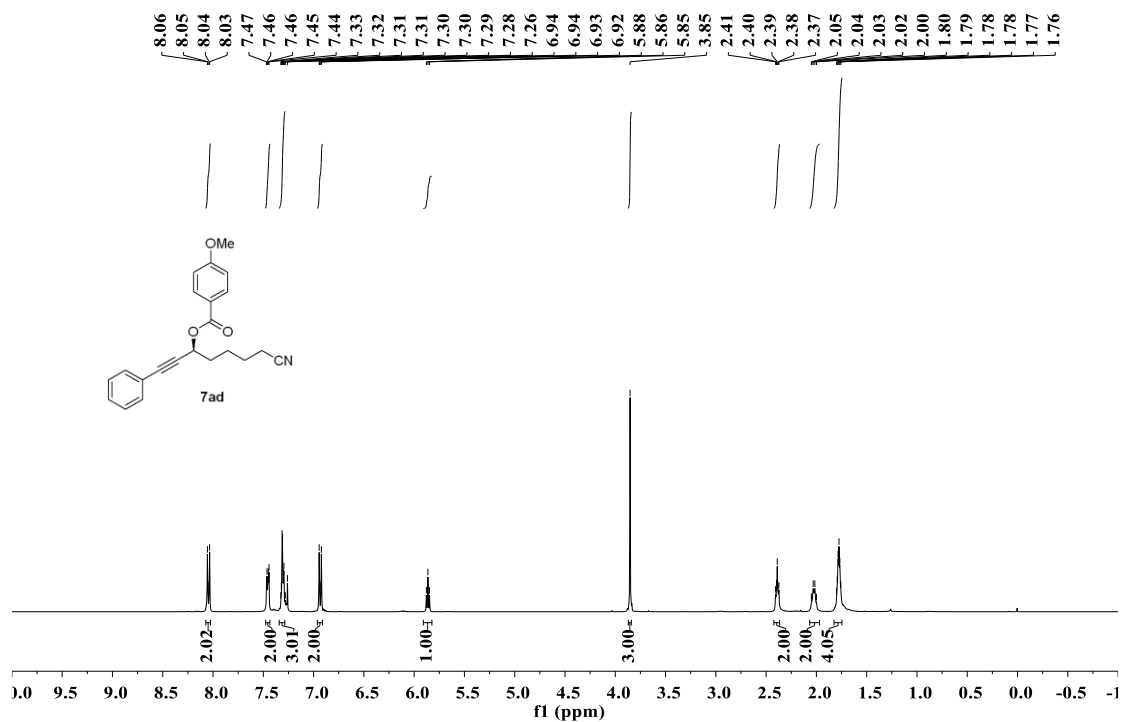
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7ab



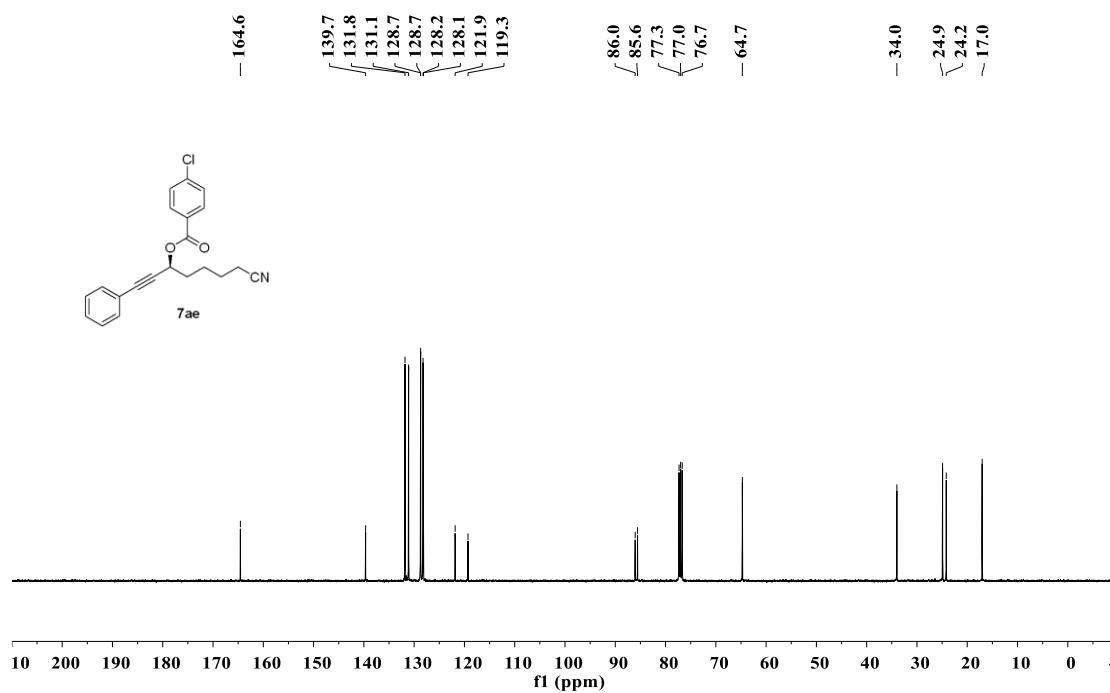
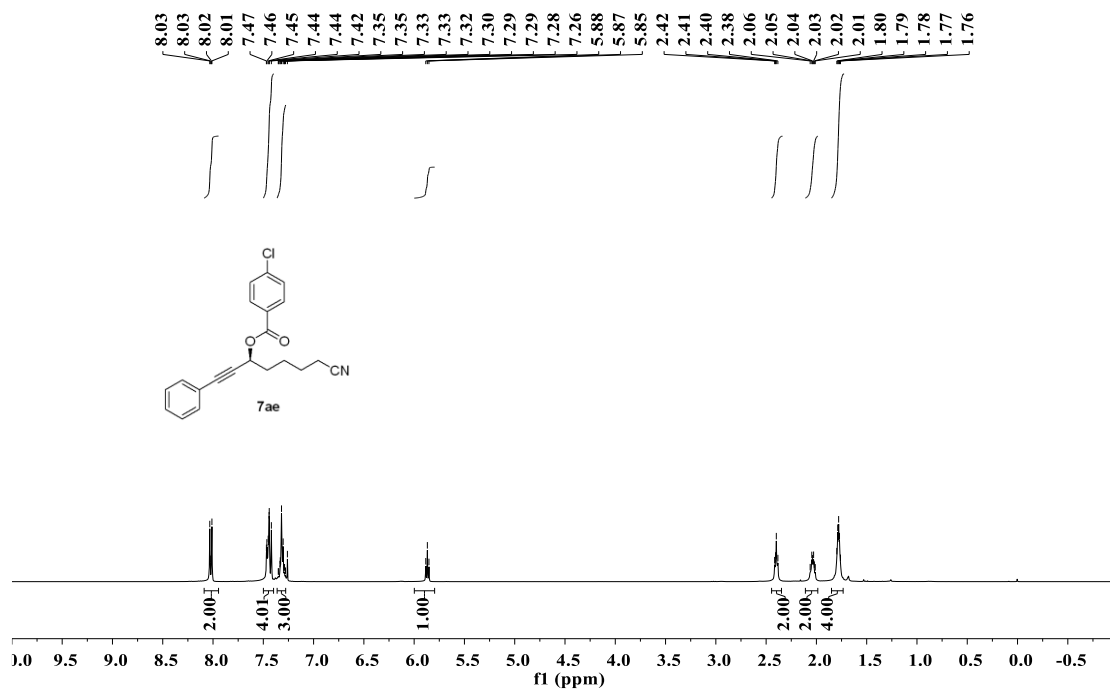
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of product **7ac**



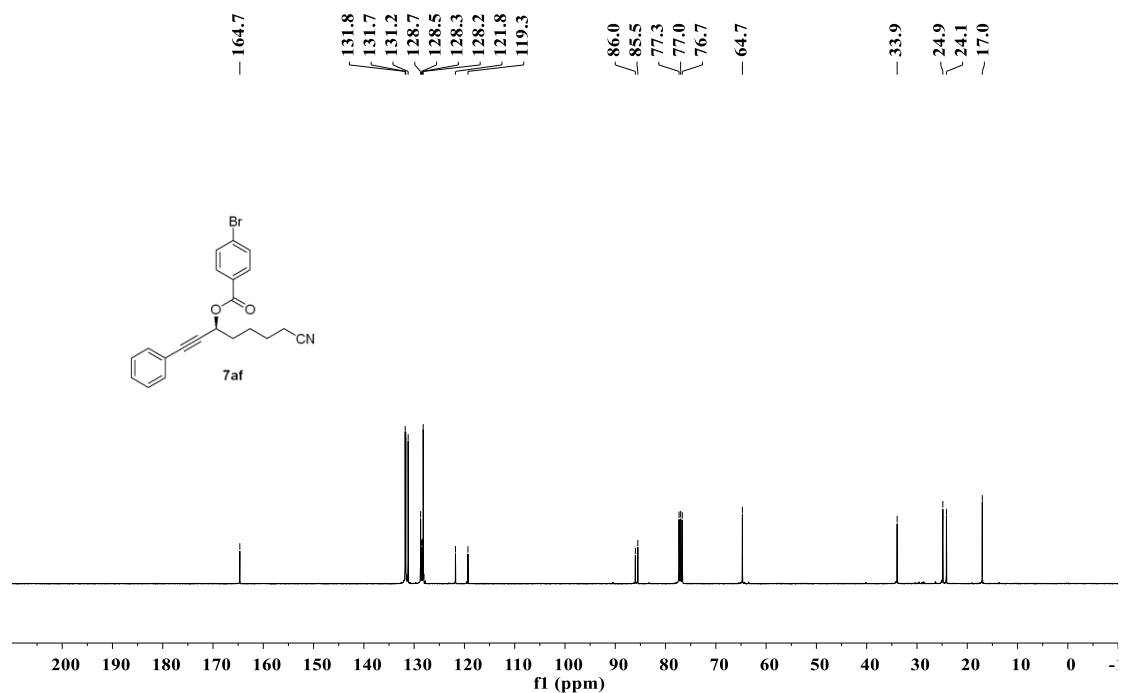
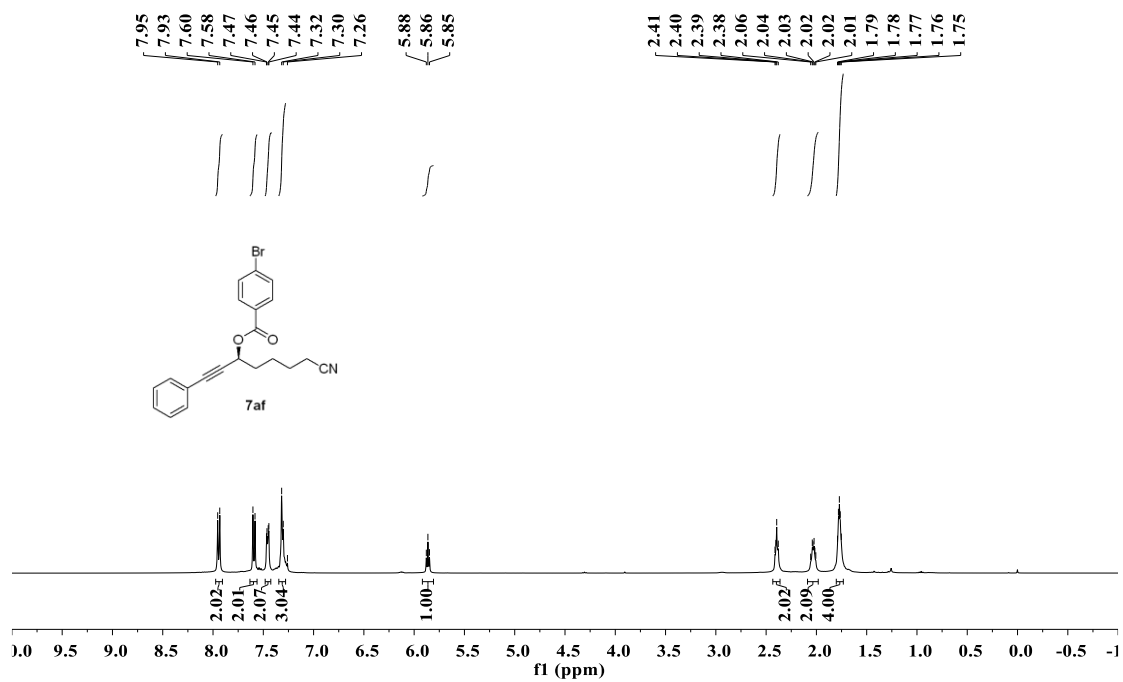
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7ad



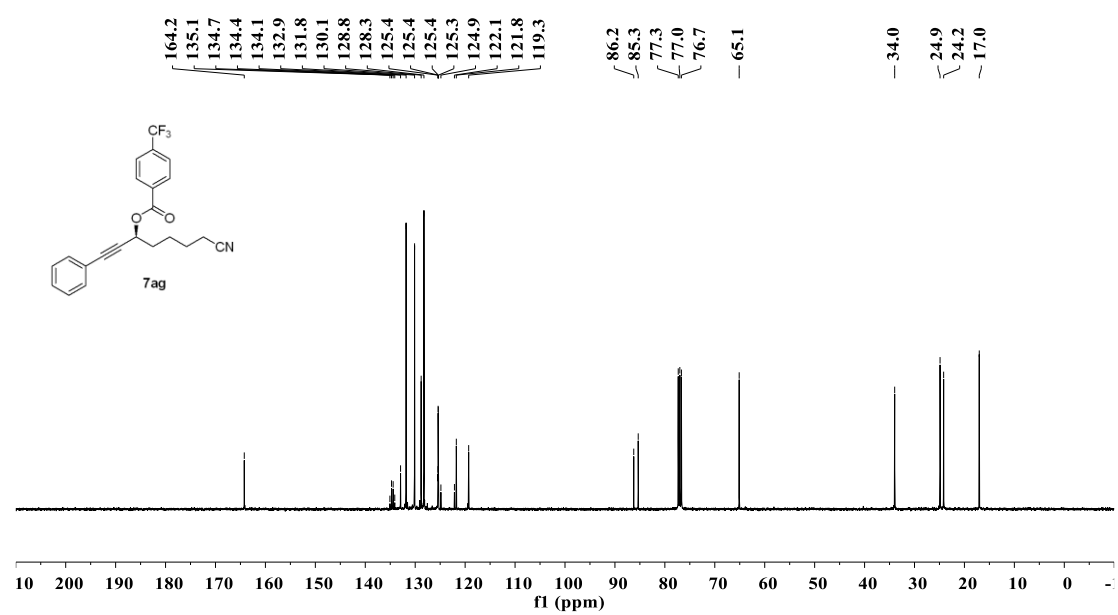
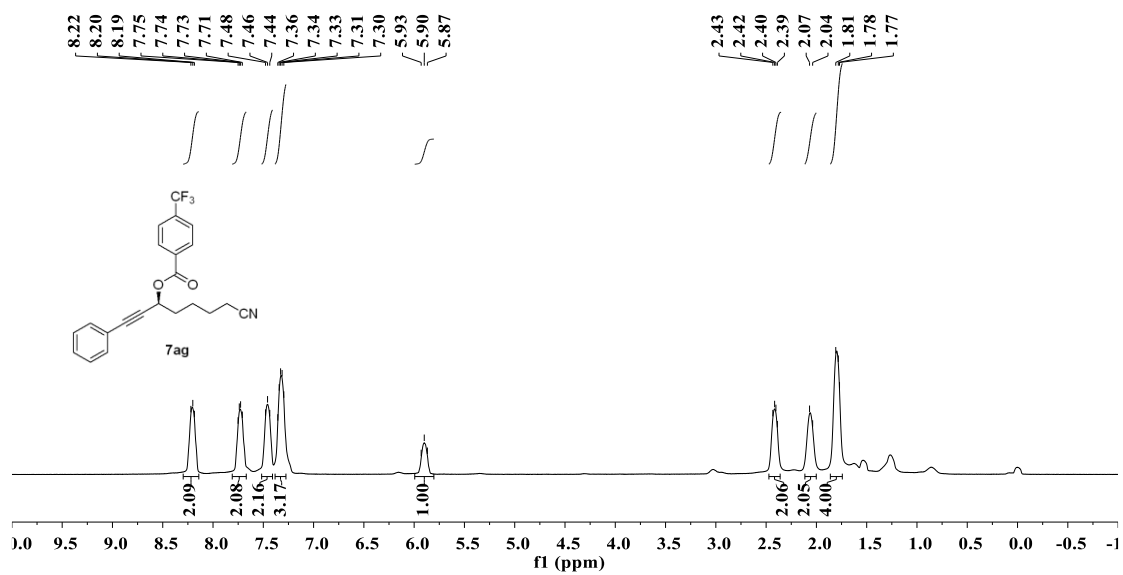
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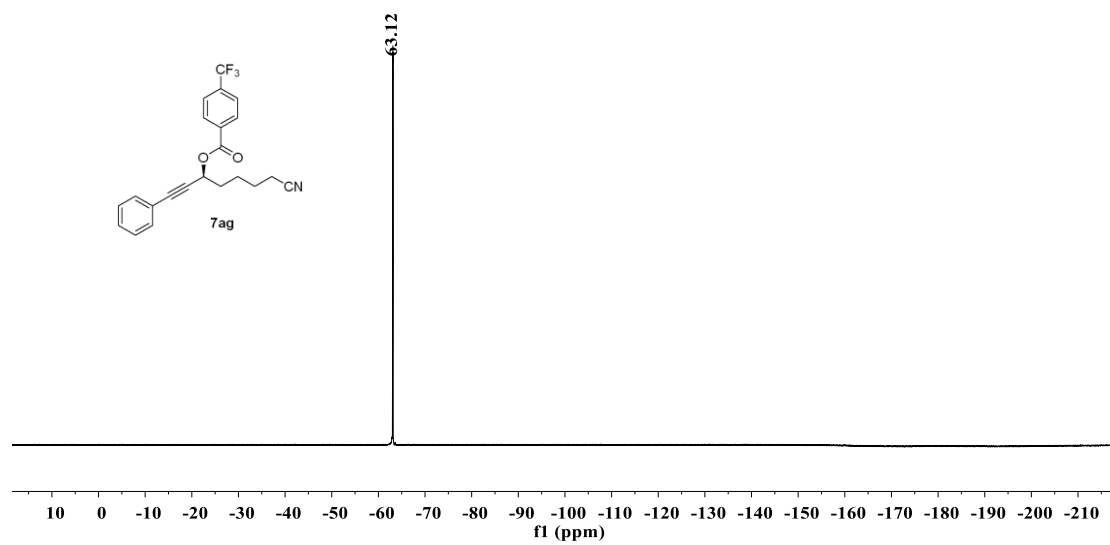


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7af

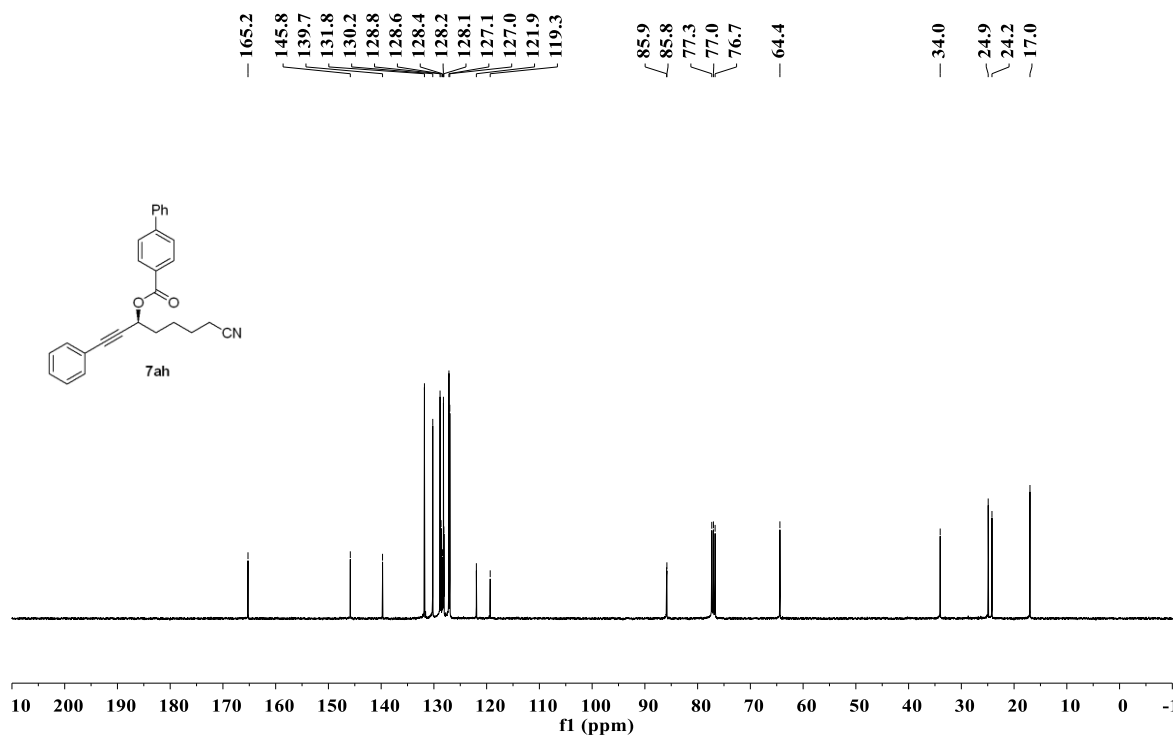
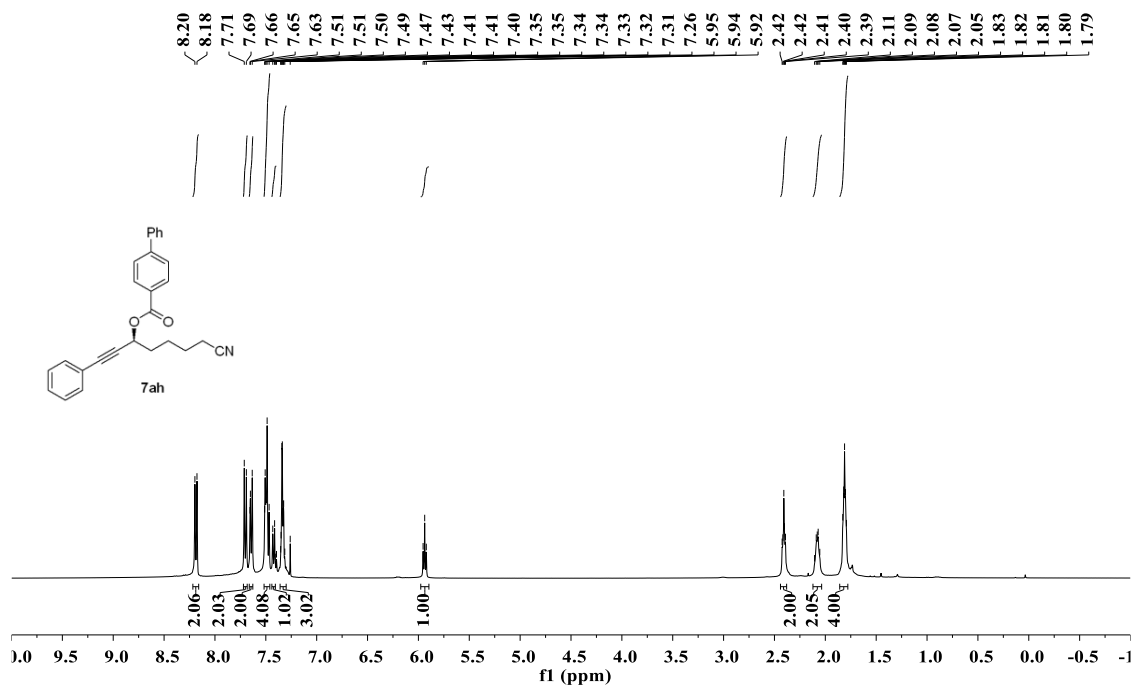


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F (376 MHz) spectra of product 7ag



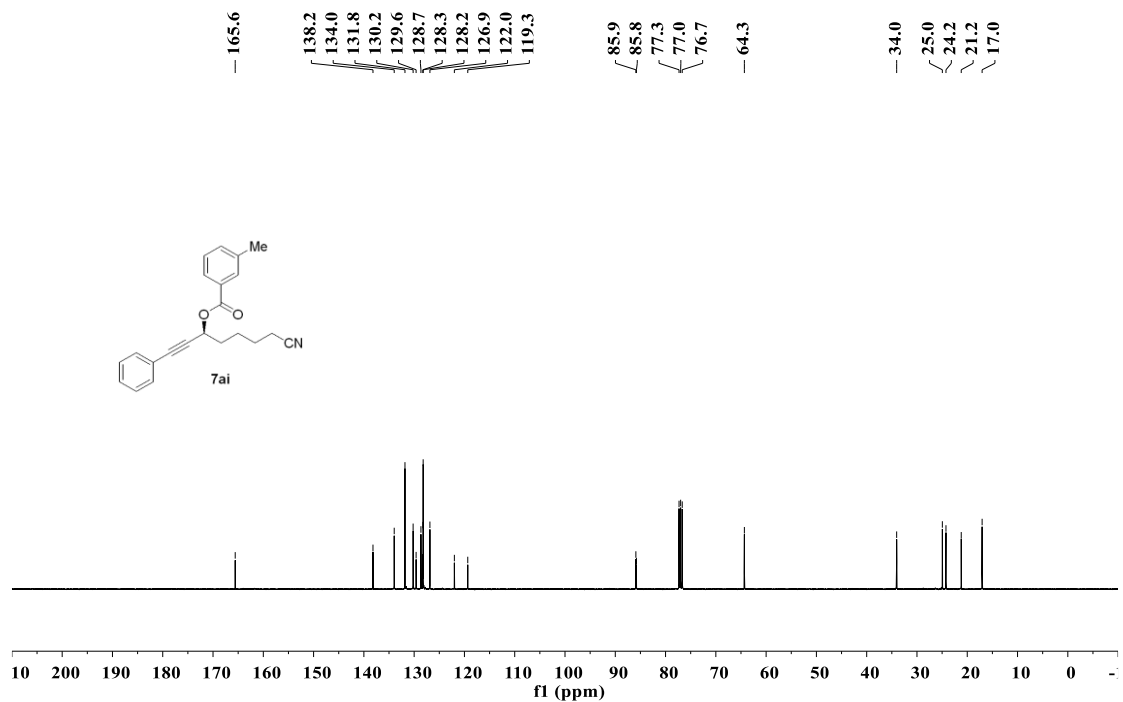
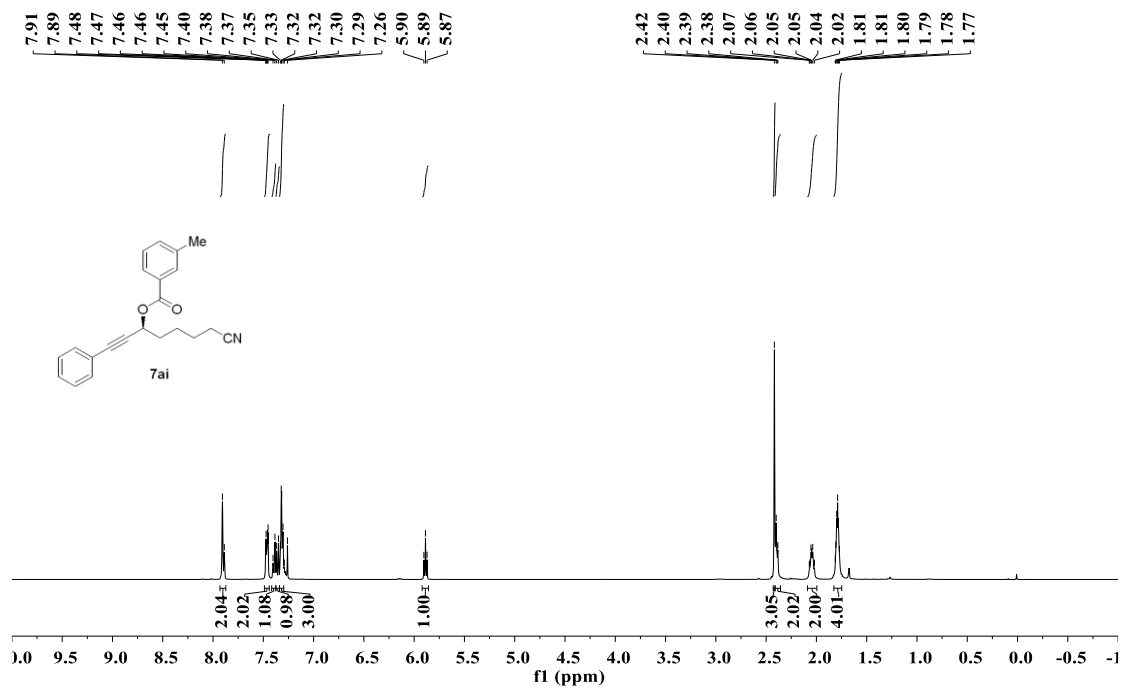


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7ah

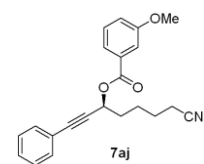
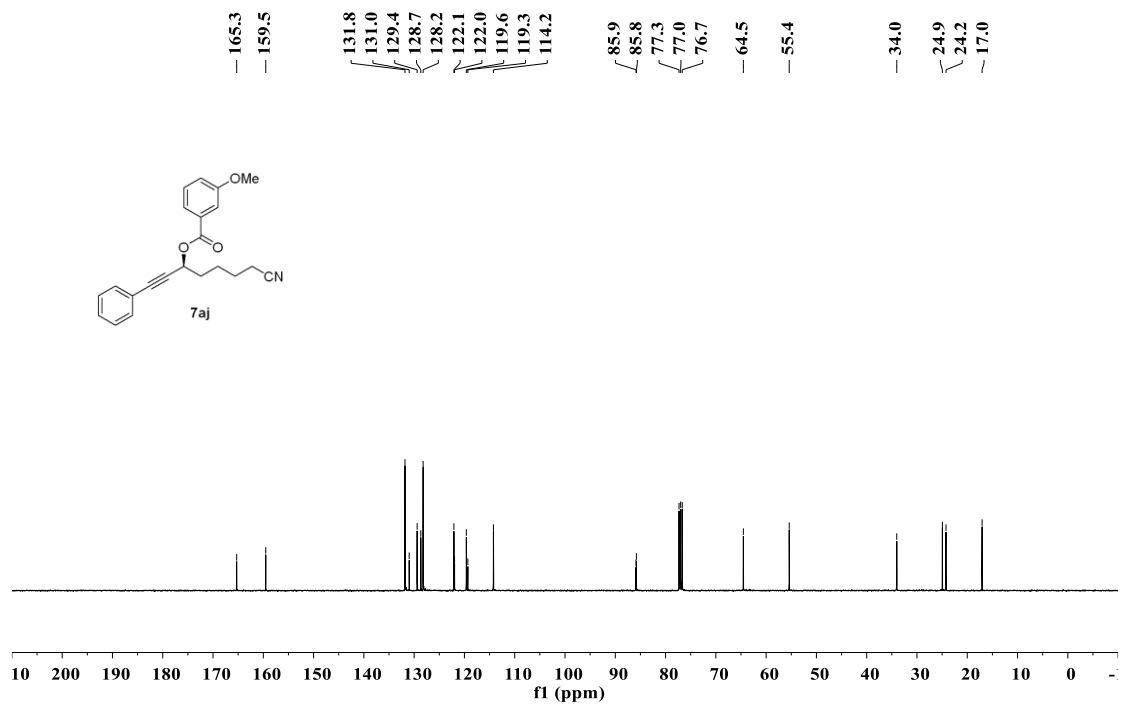
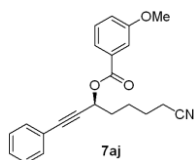
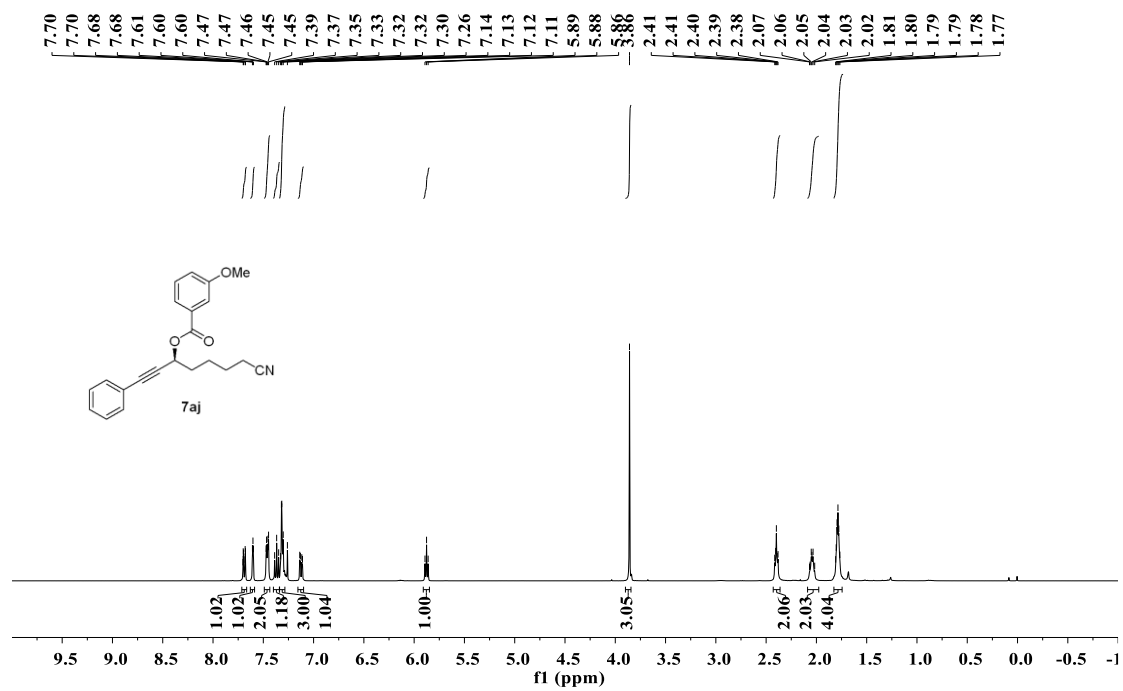




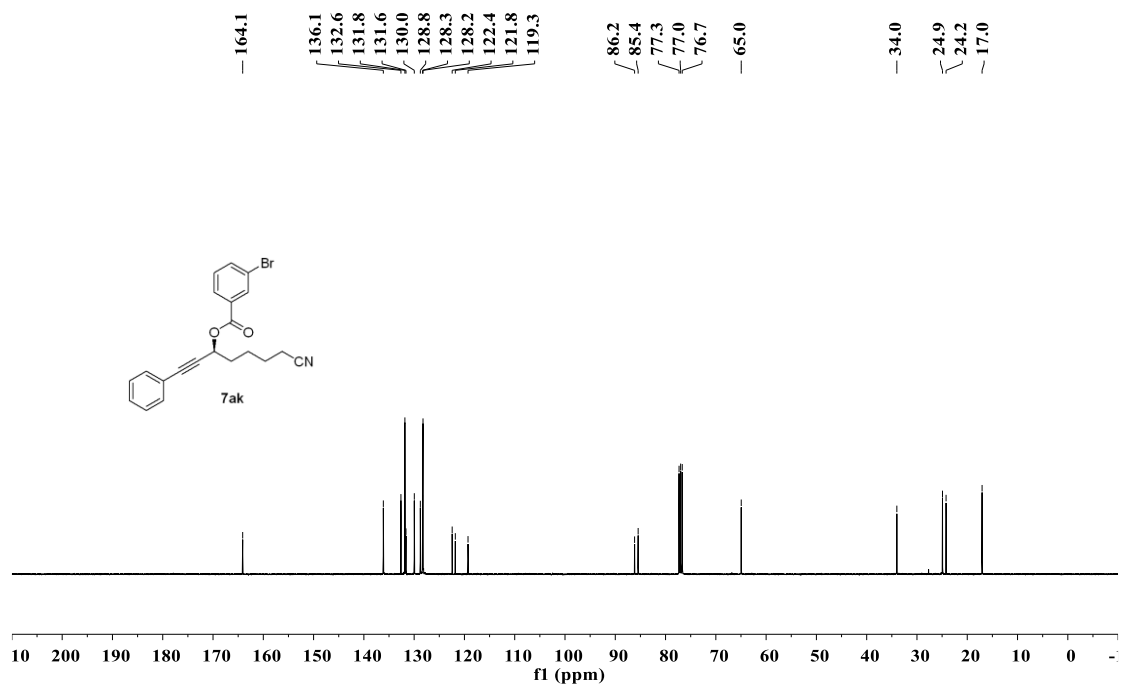
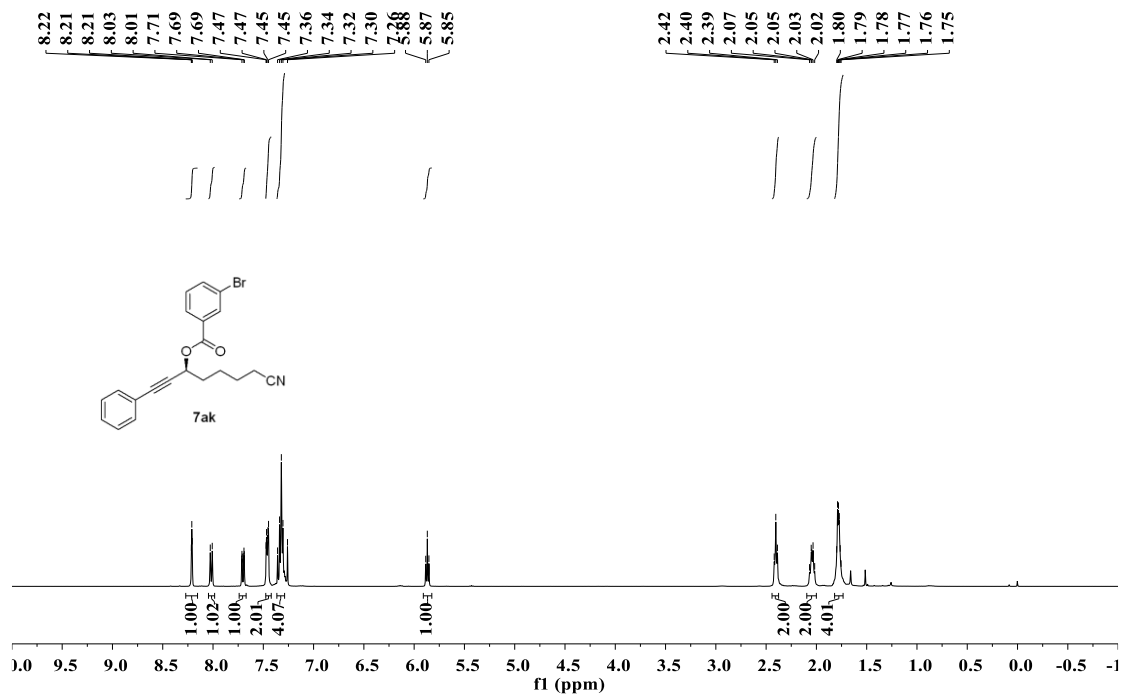
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7ai



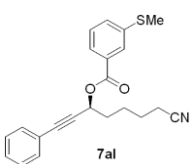
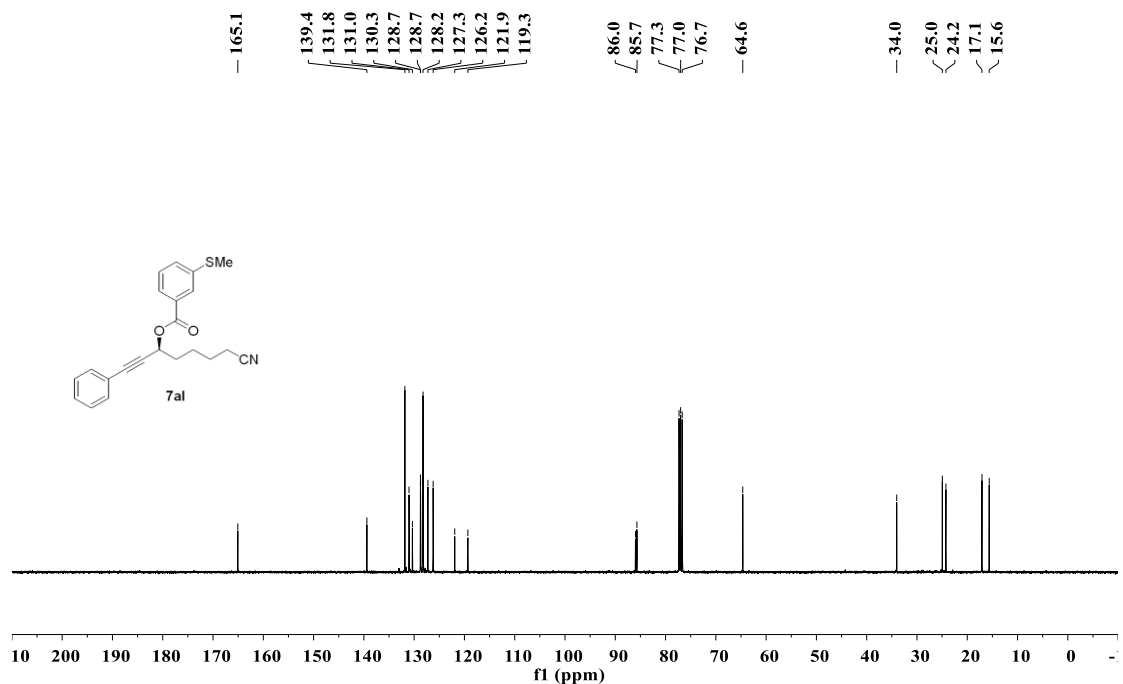
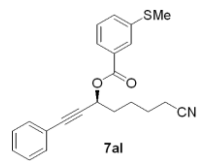
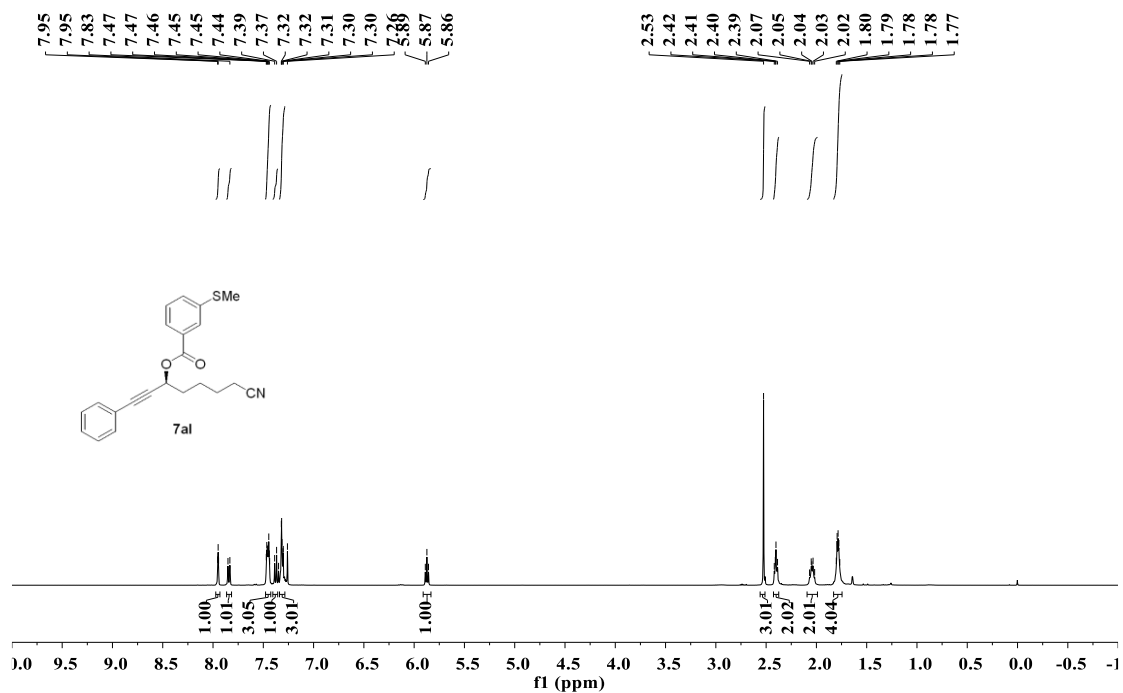
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of product 7aj



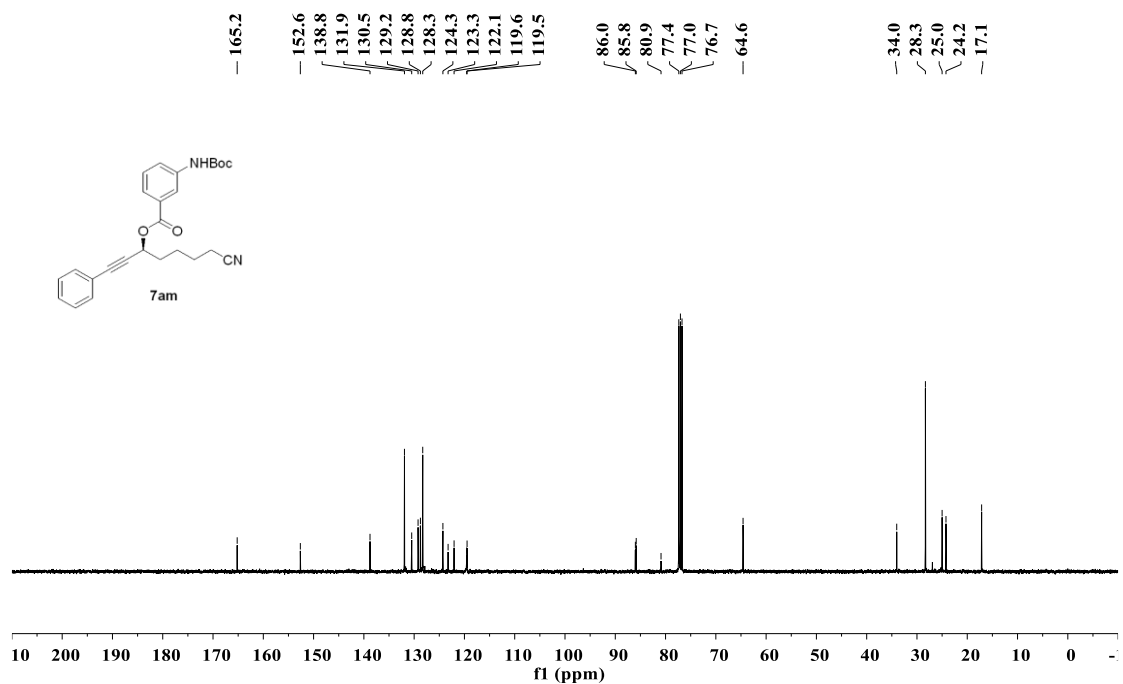
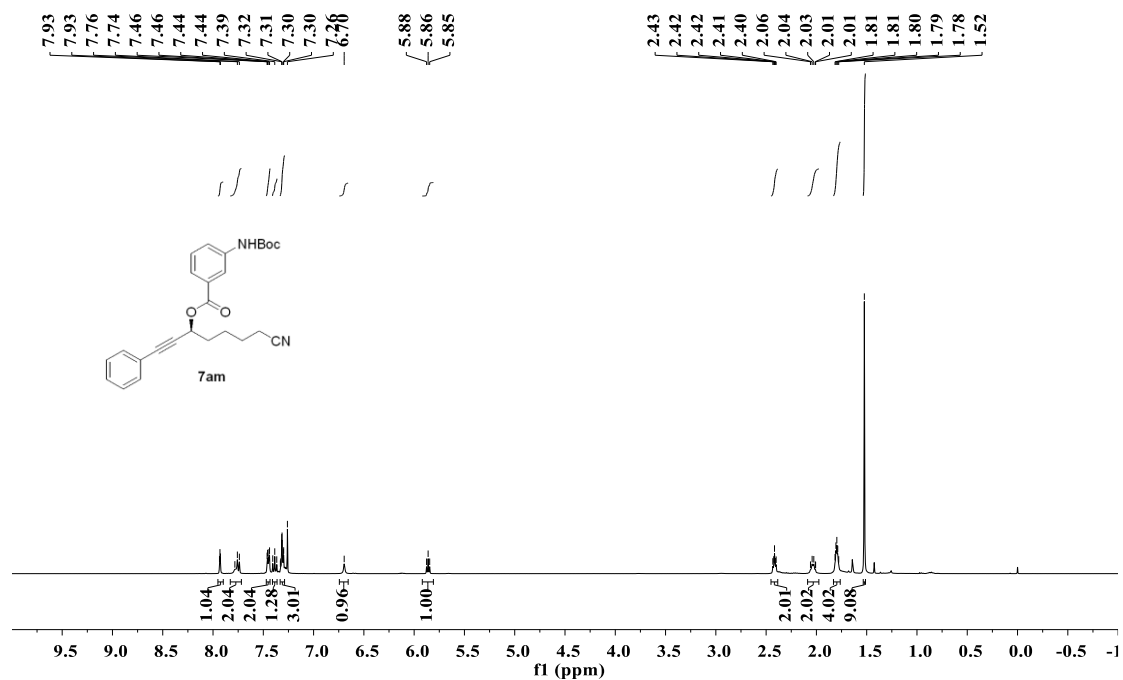
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7ak



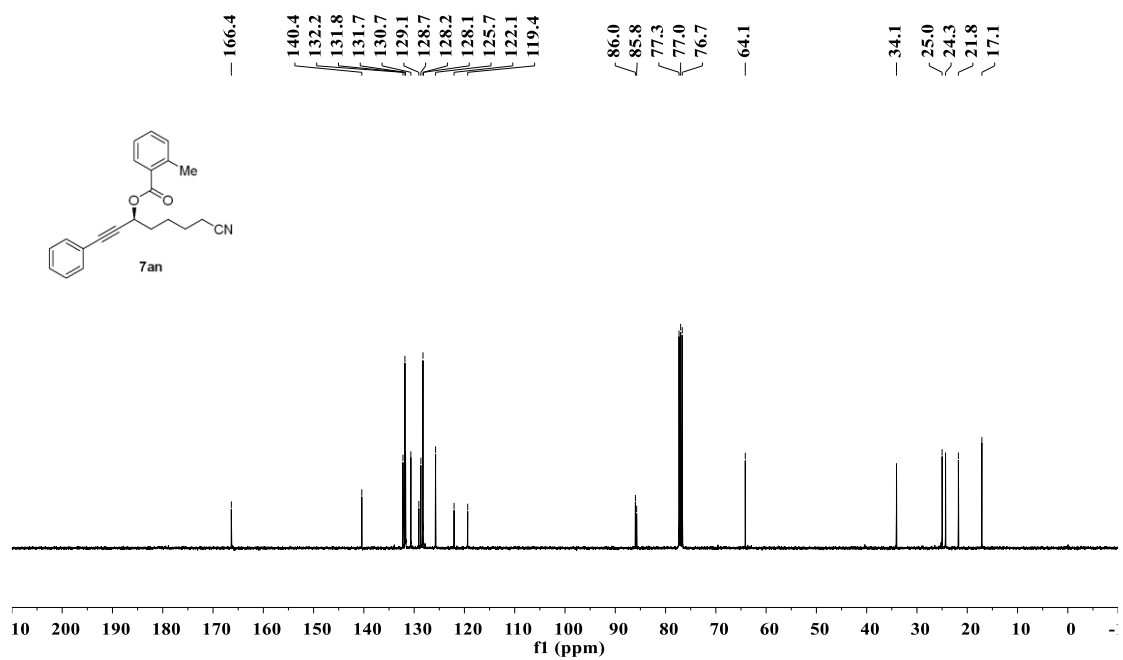
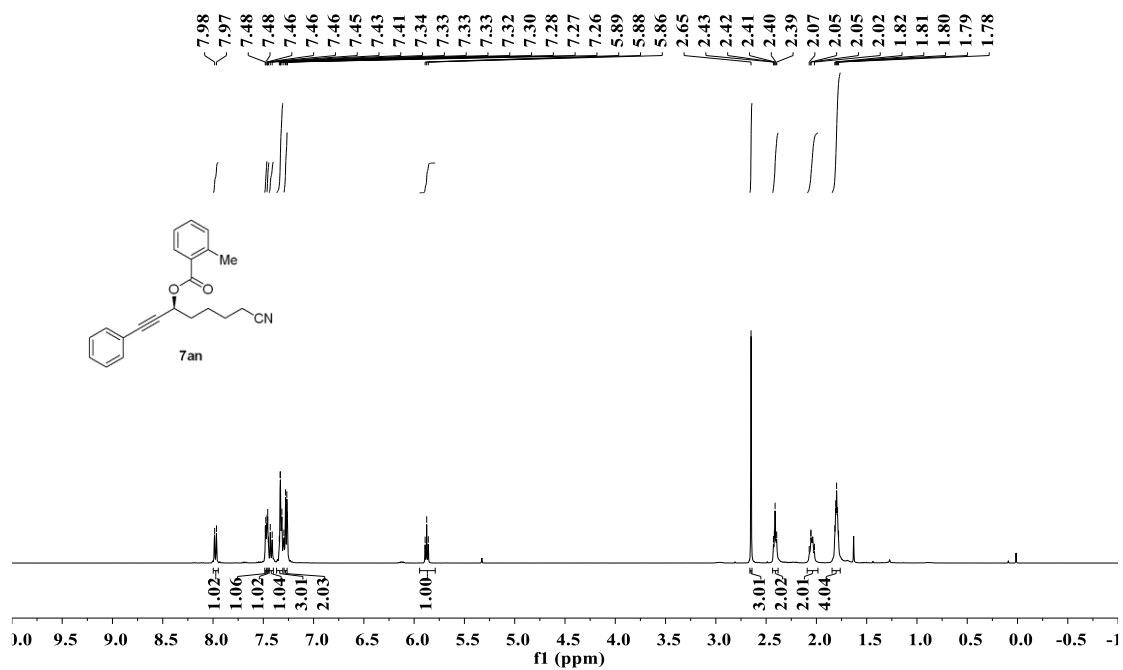
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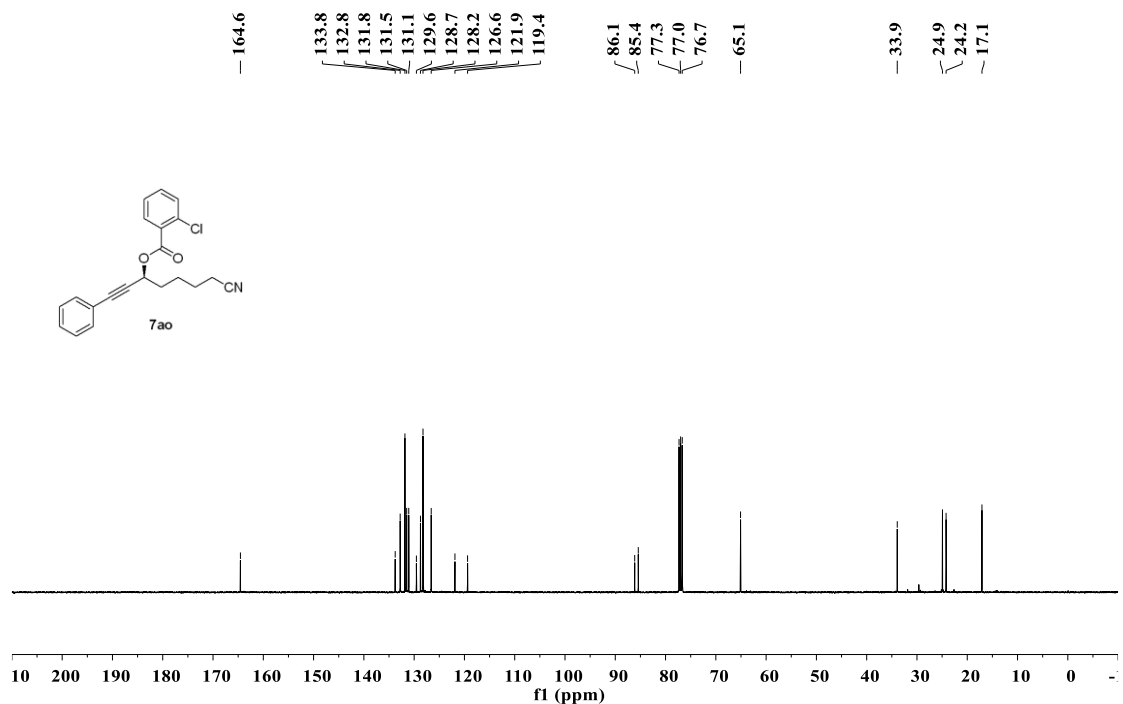
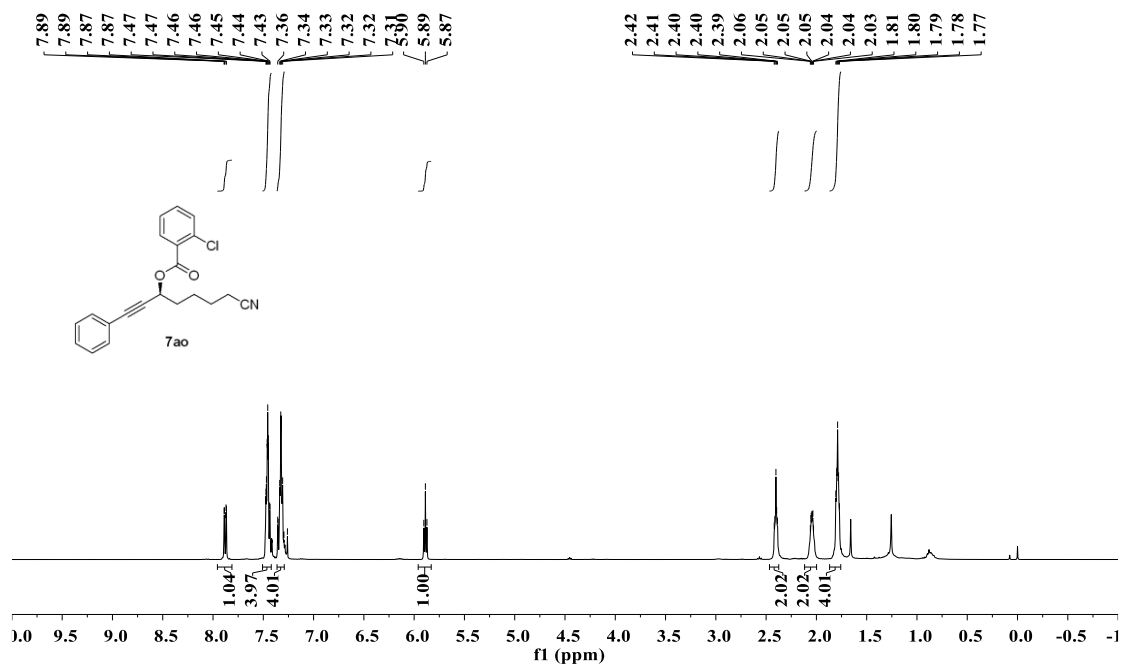
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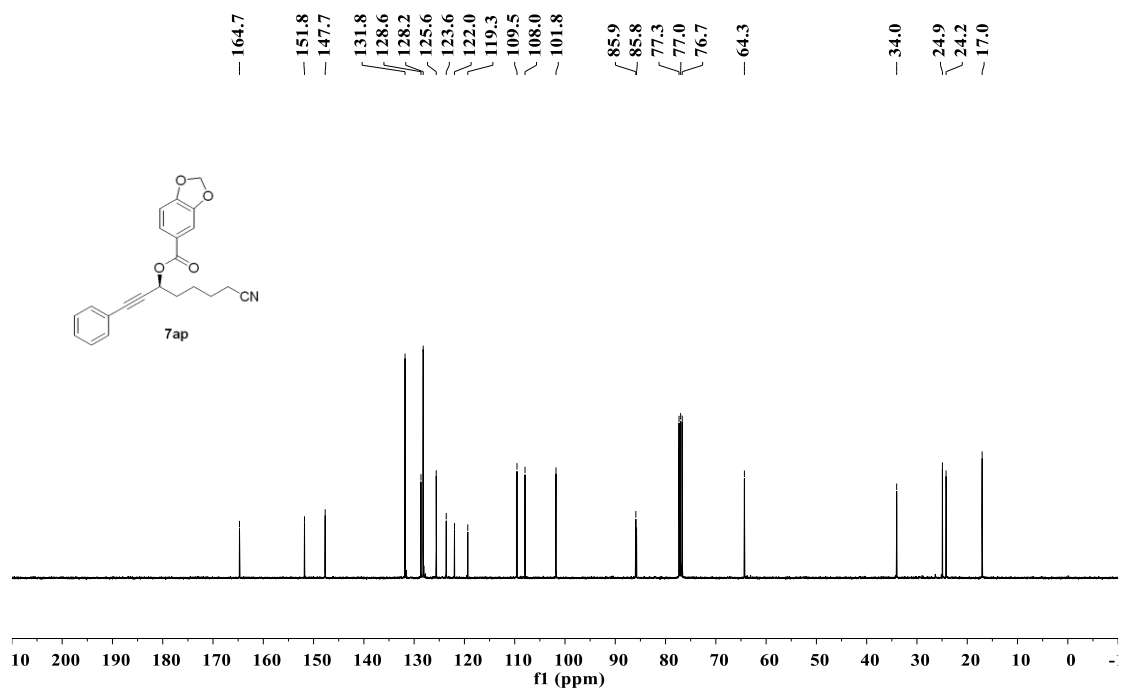
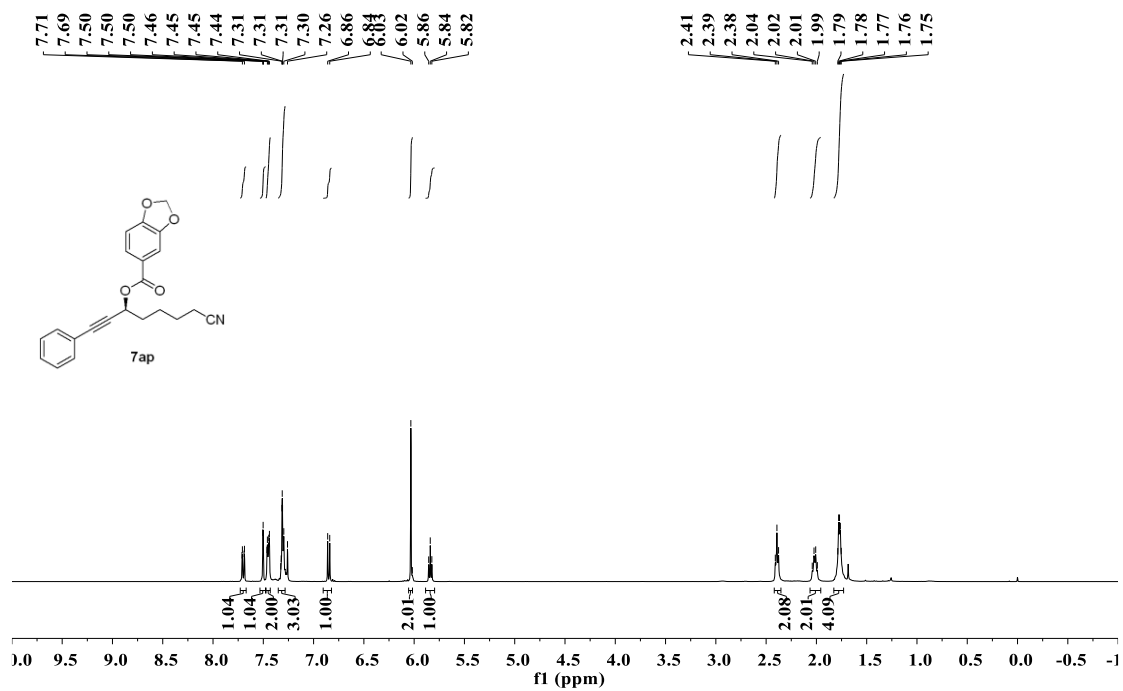
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7an



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra of product 7ao

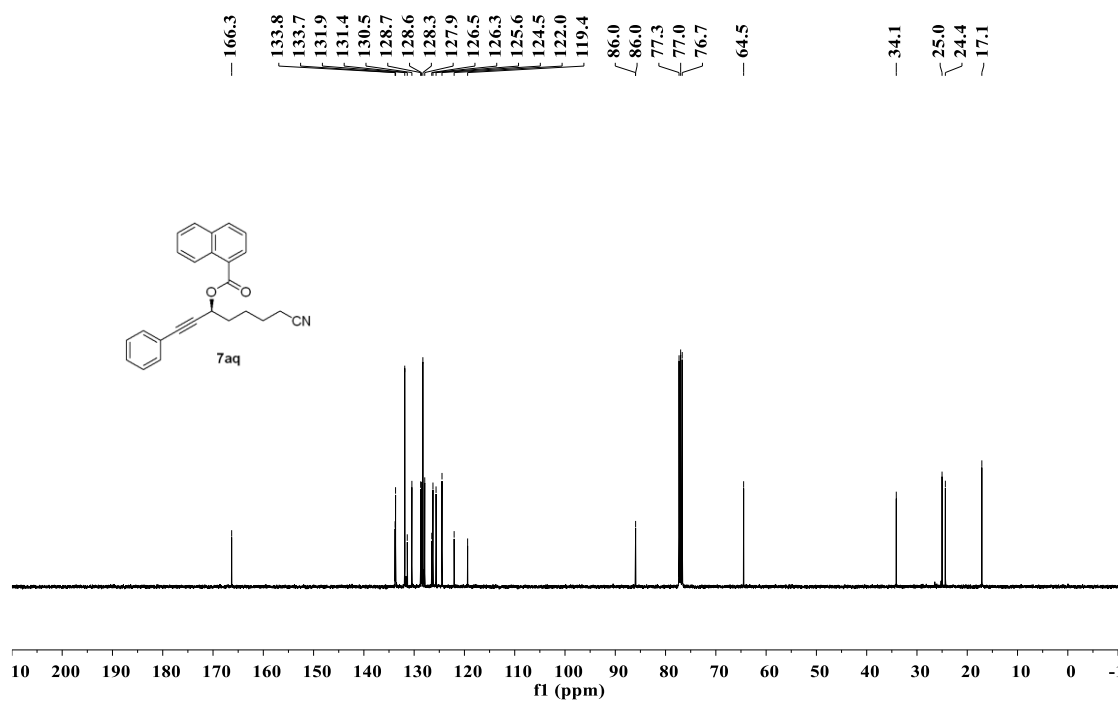
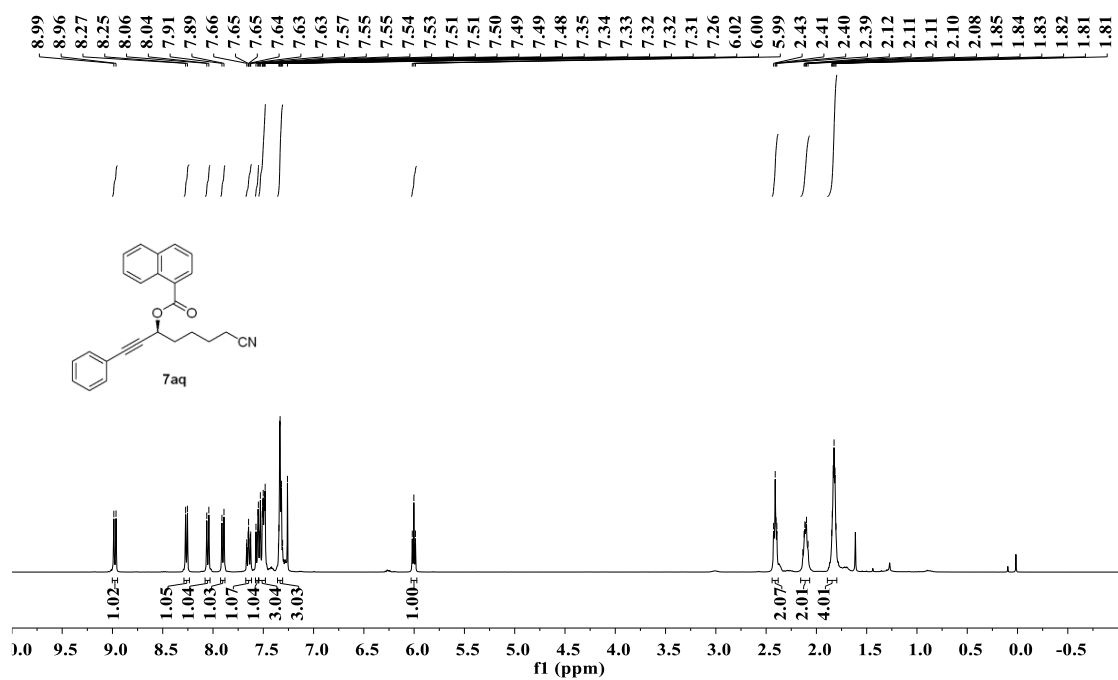


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7ap

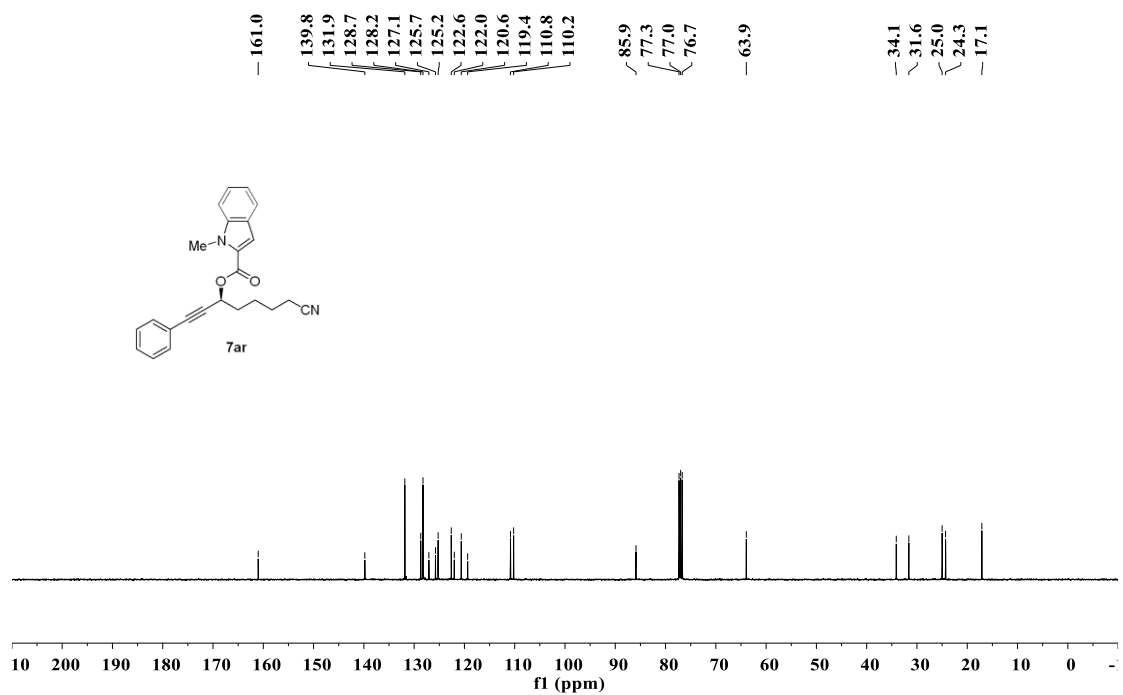
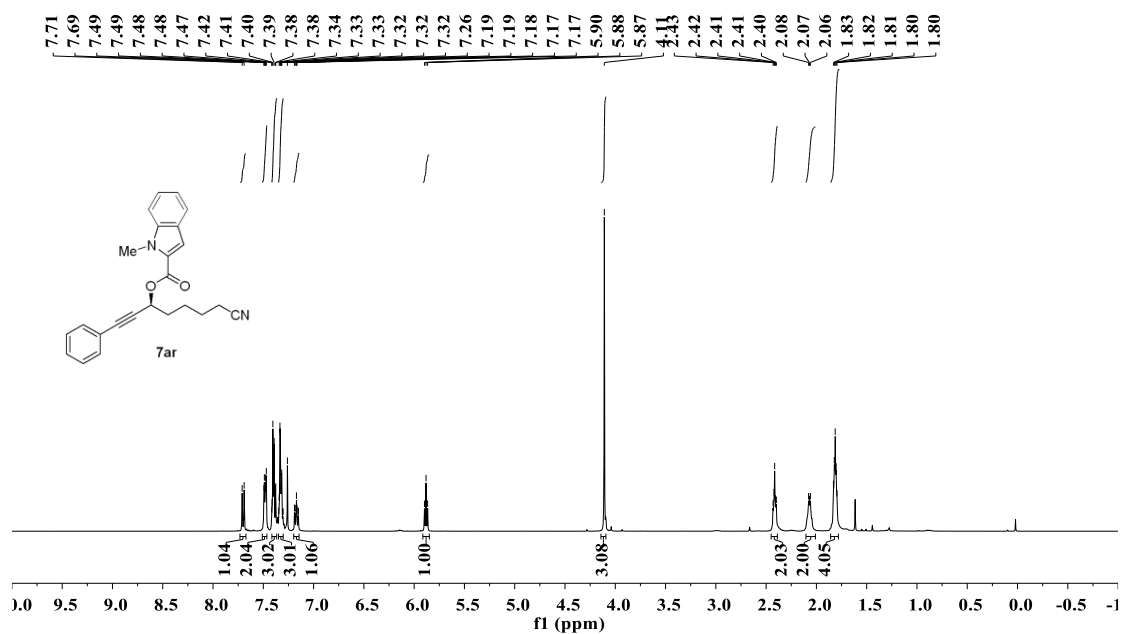




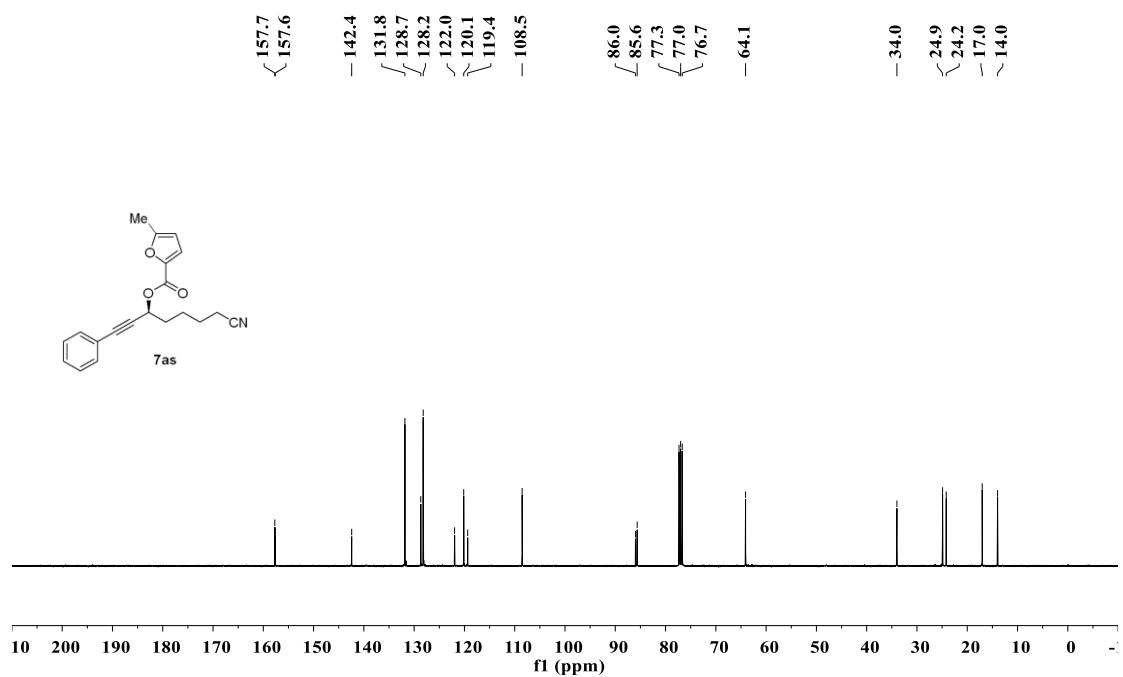
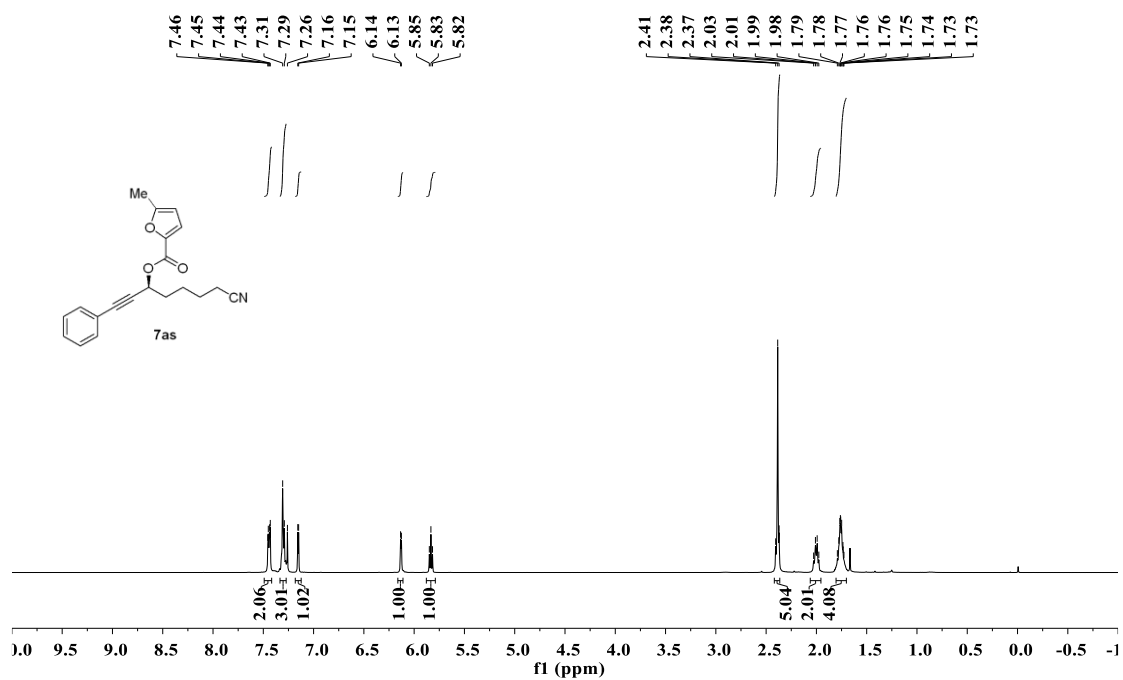
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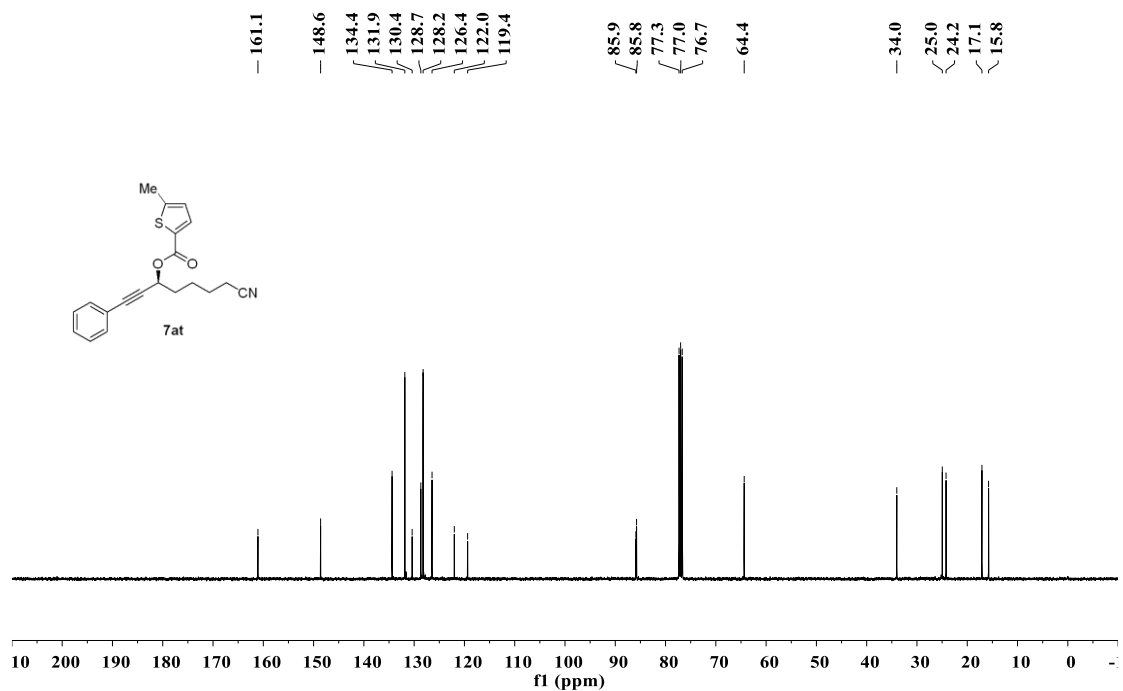
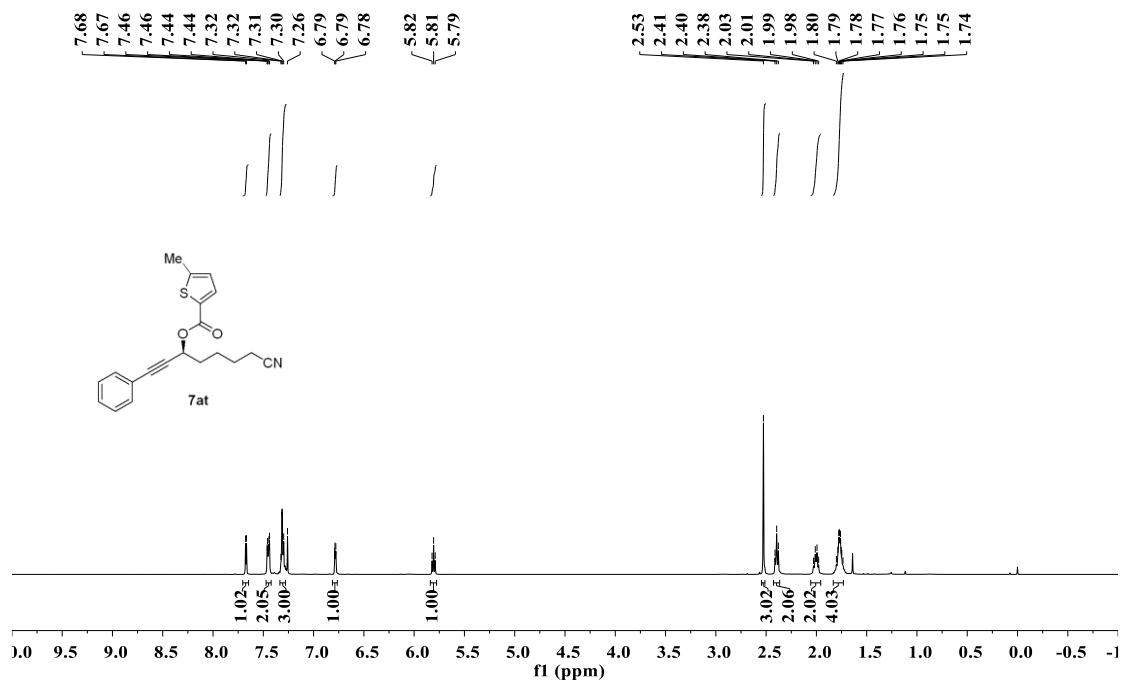
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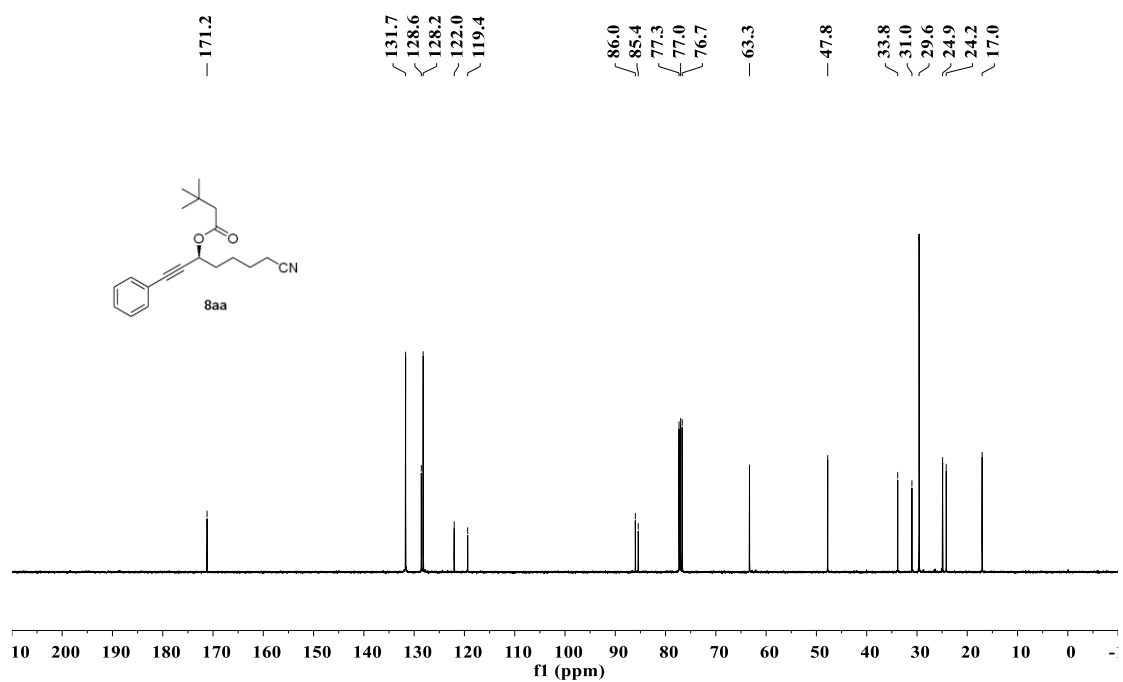
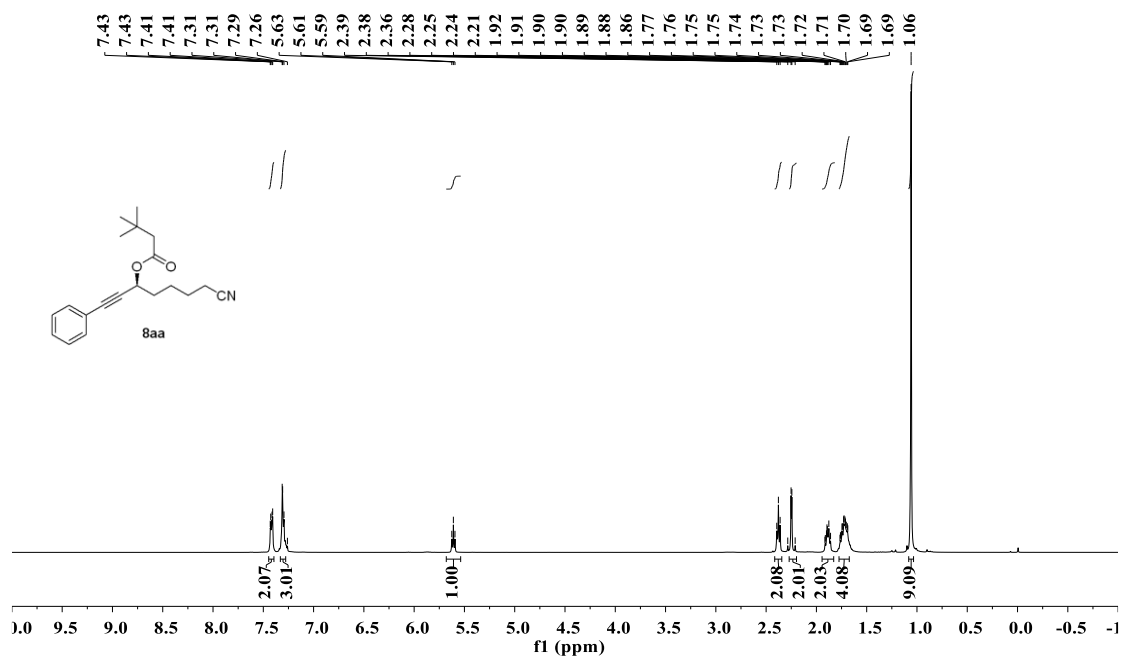
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7as



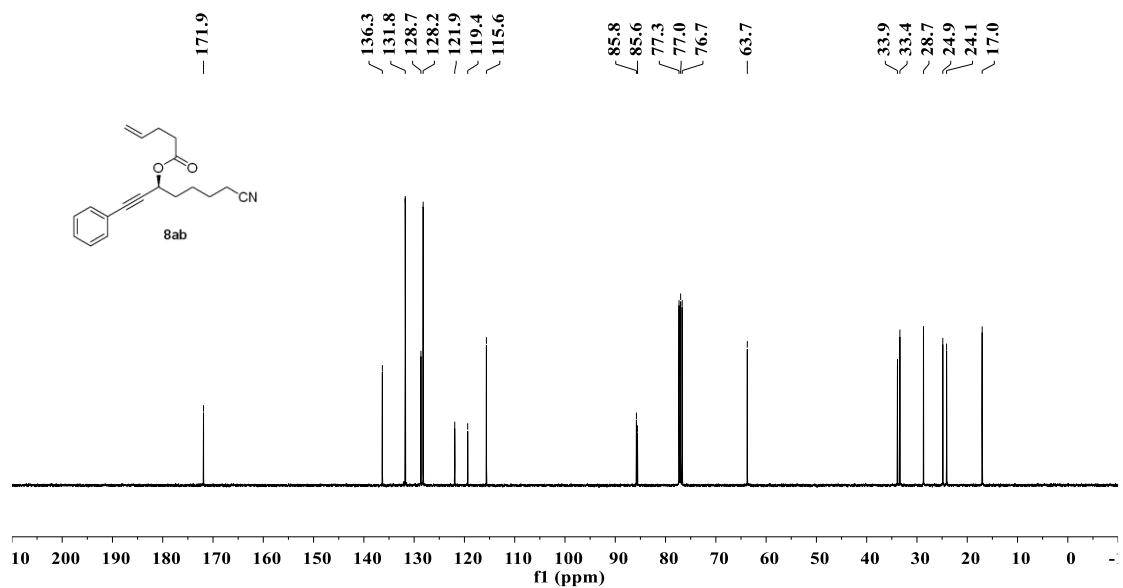
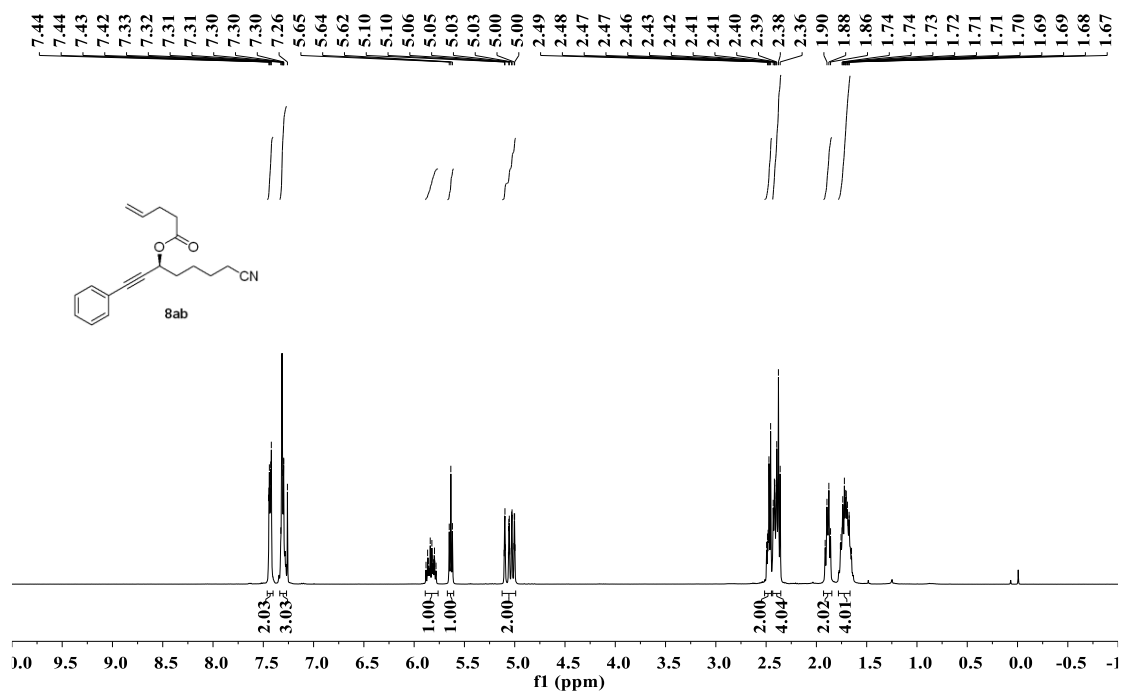
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 7at



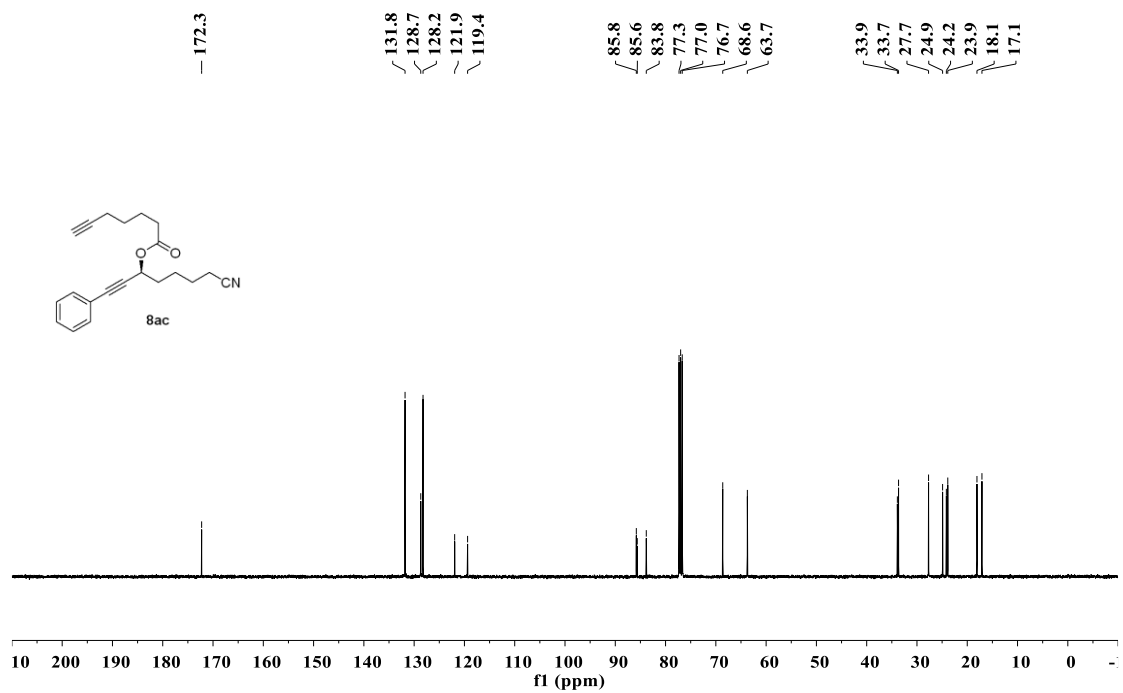
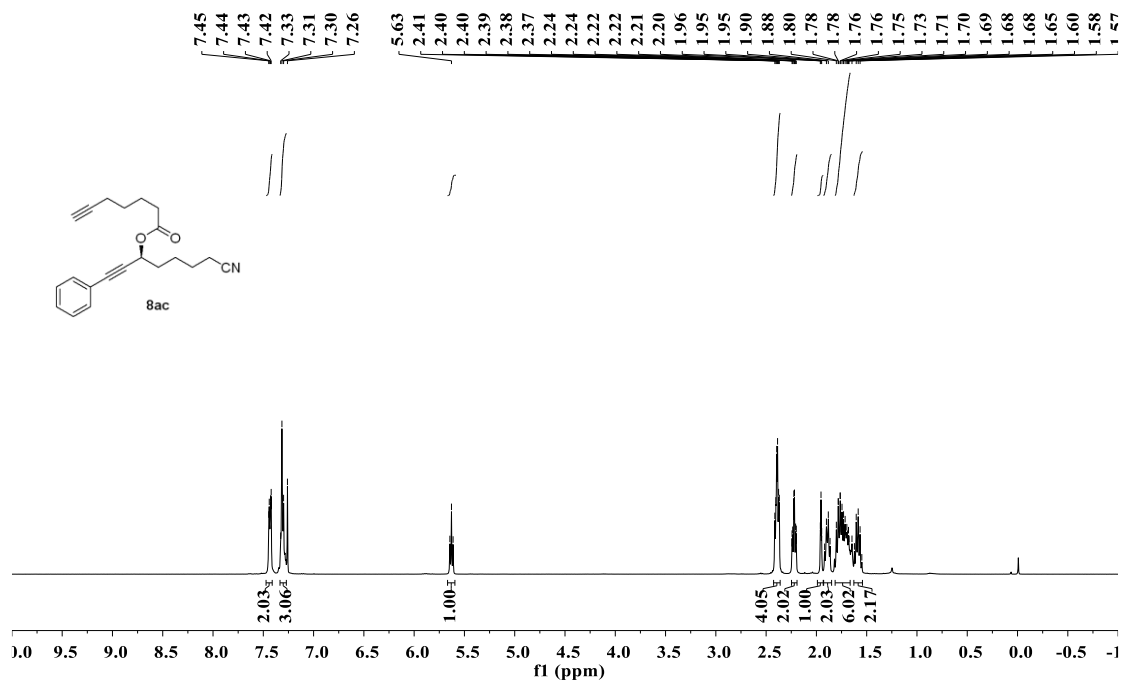
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8aa



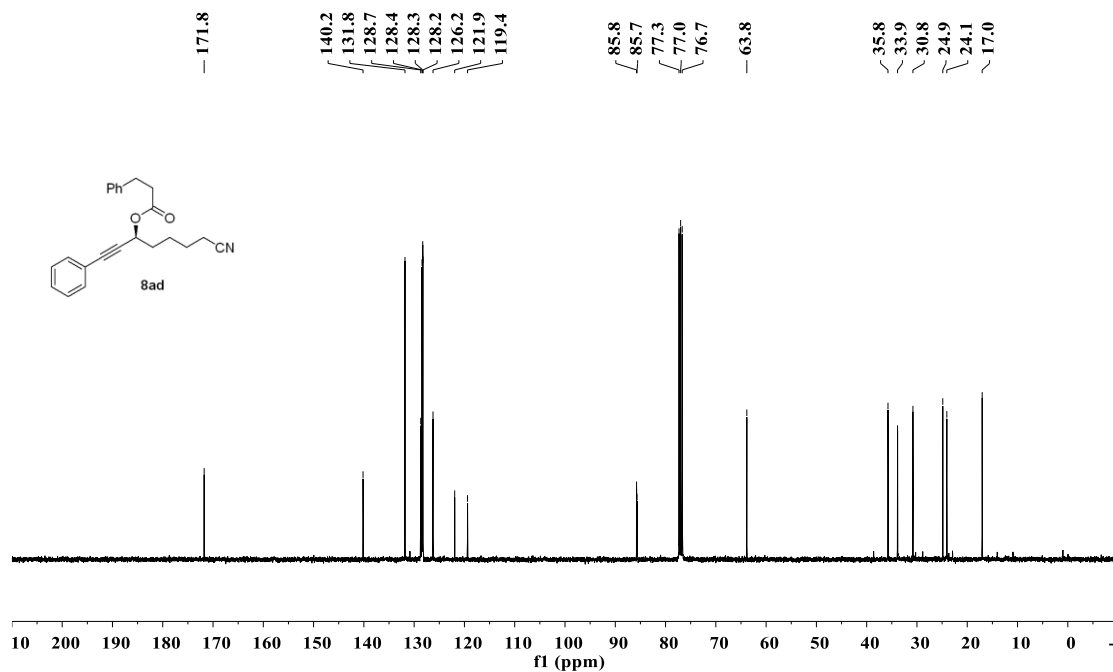
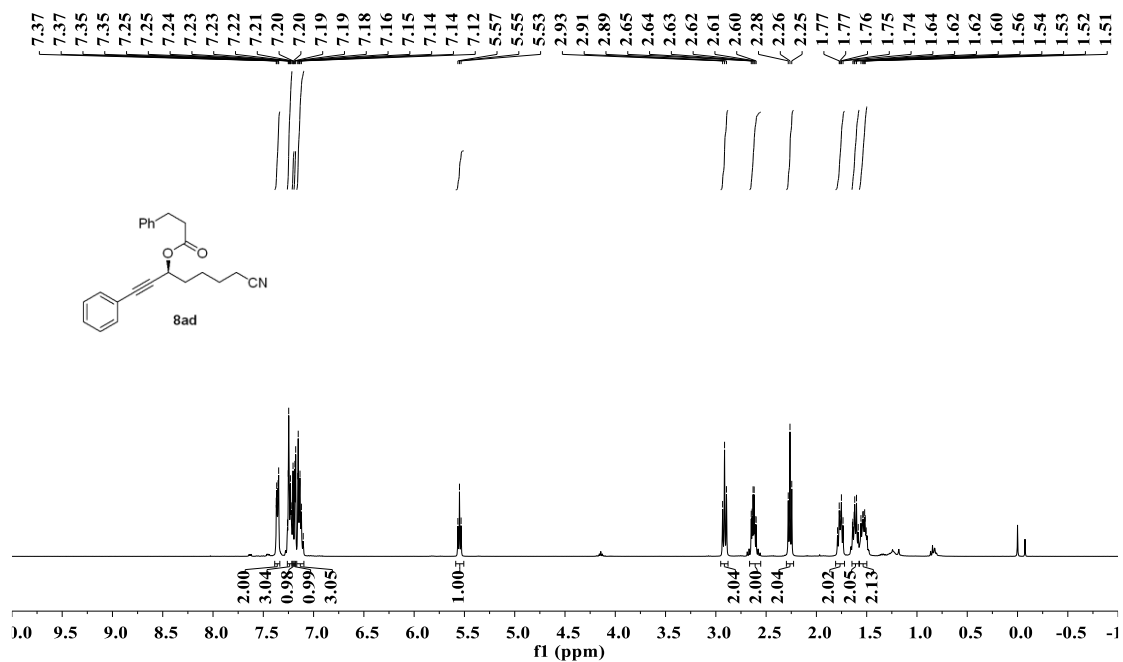
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8ab



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8ac

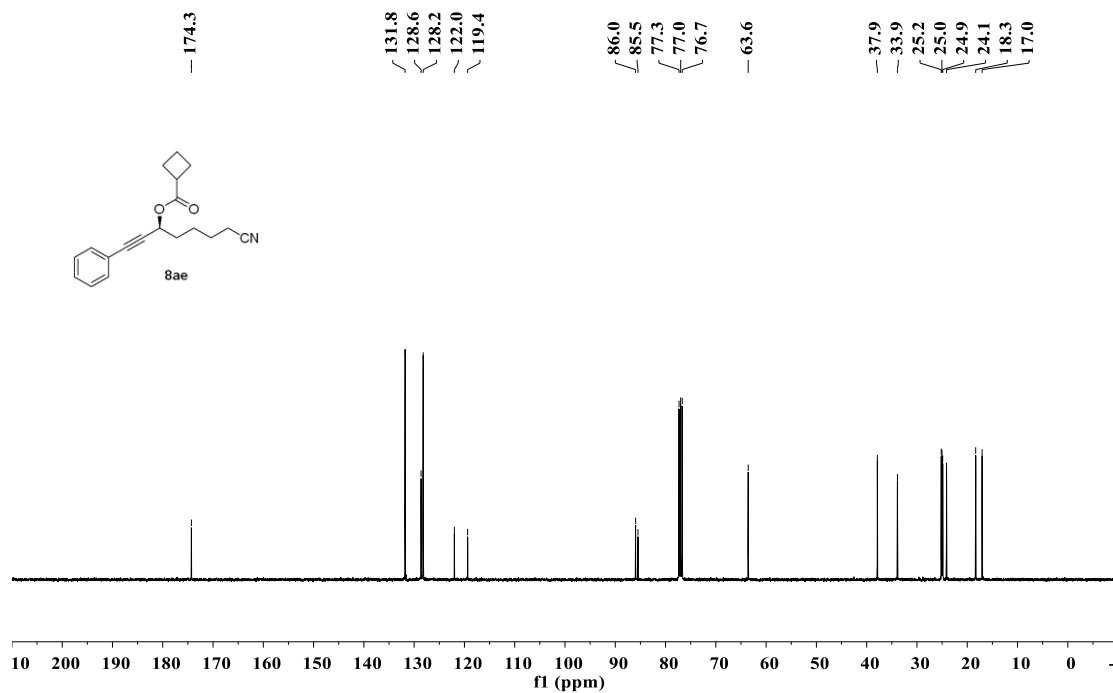
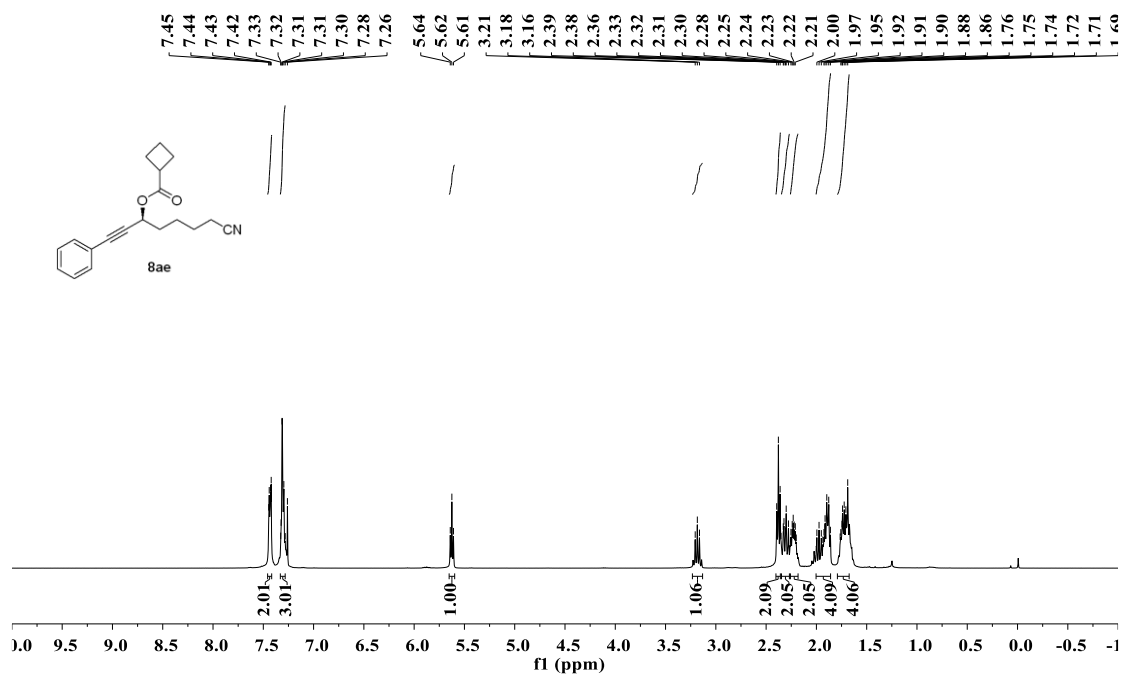


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8ad

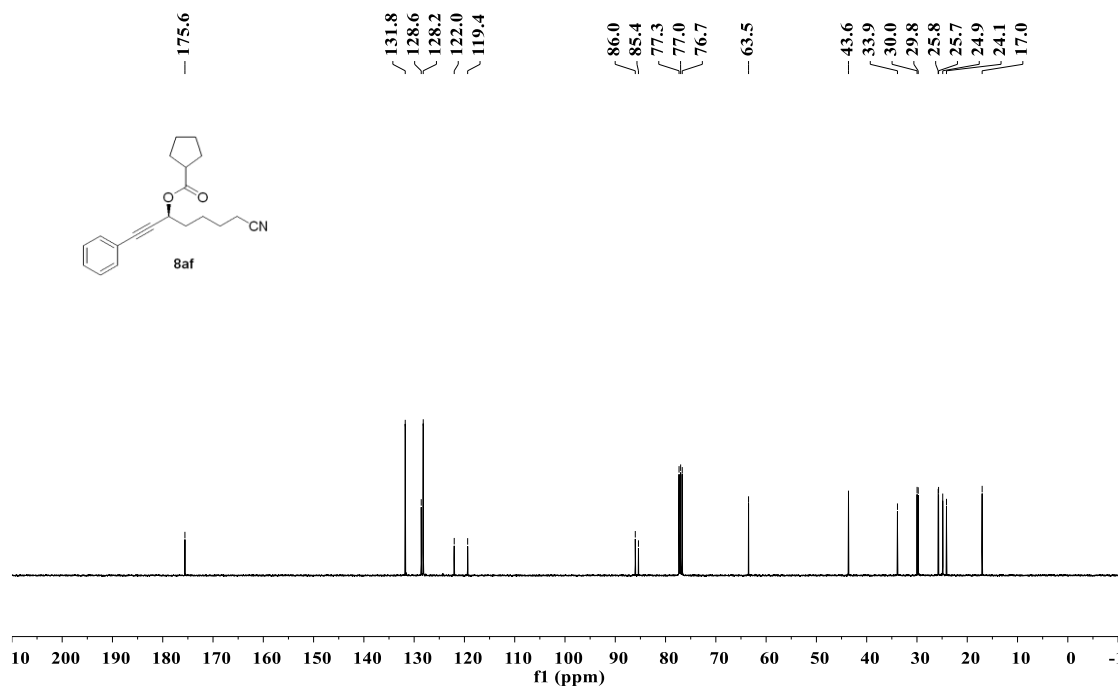
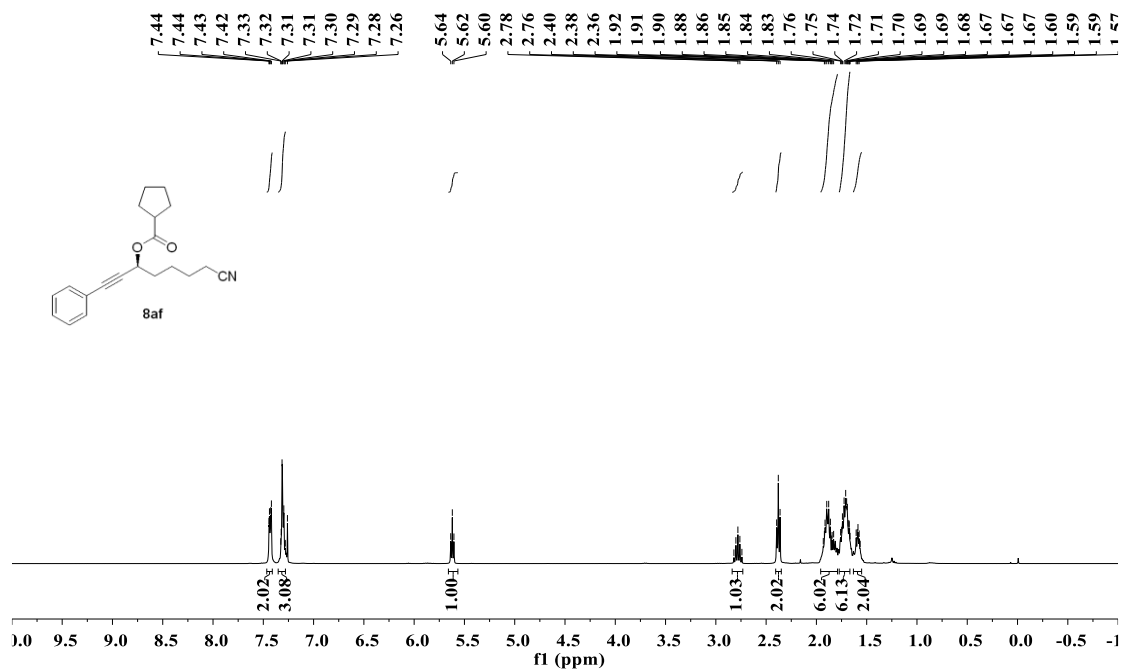




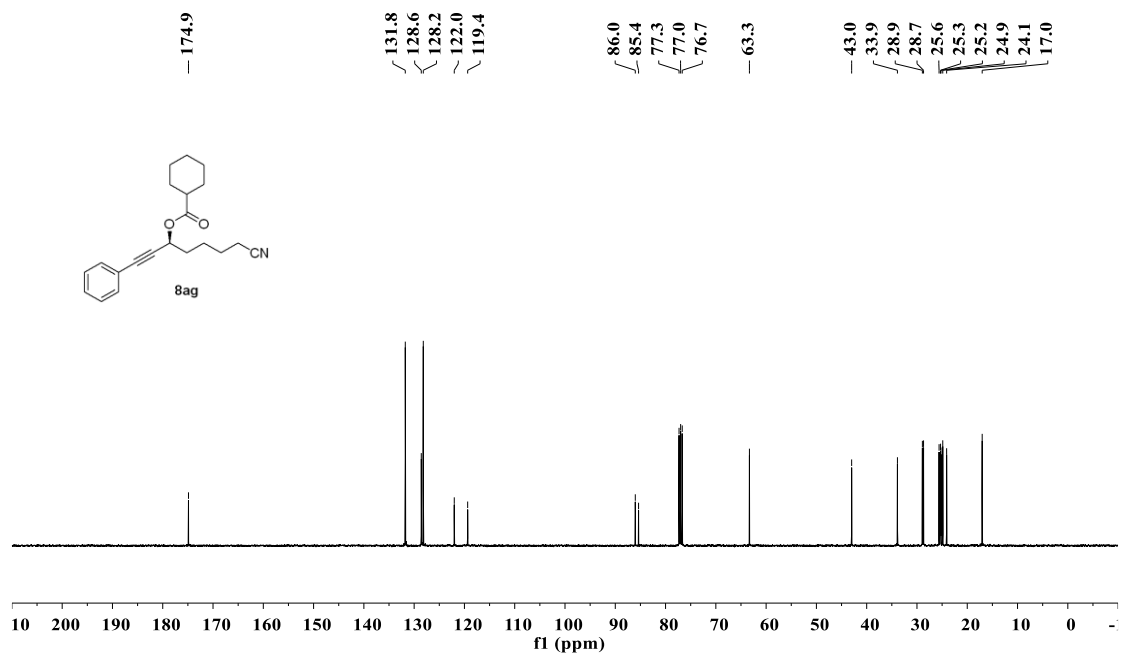
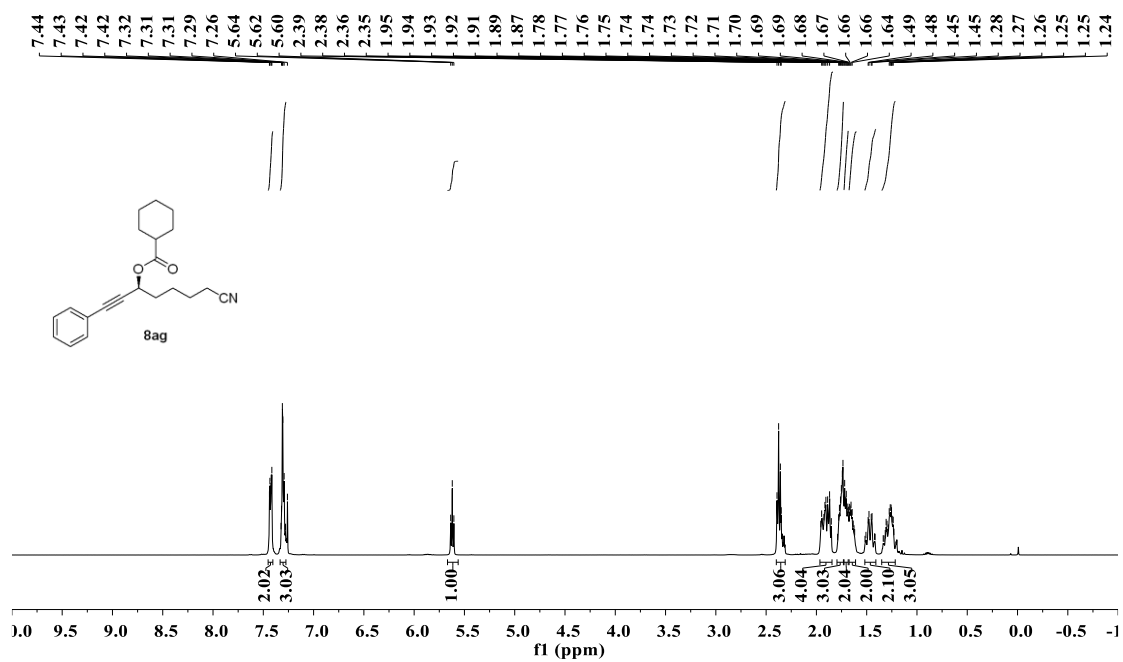
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8ae



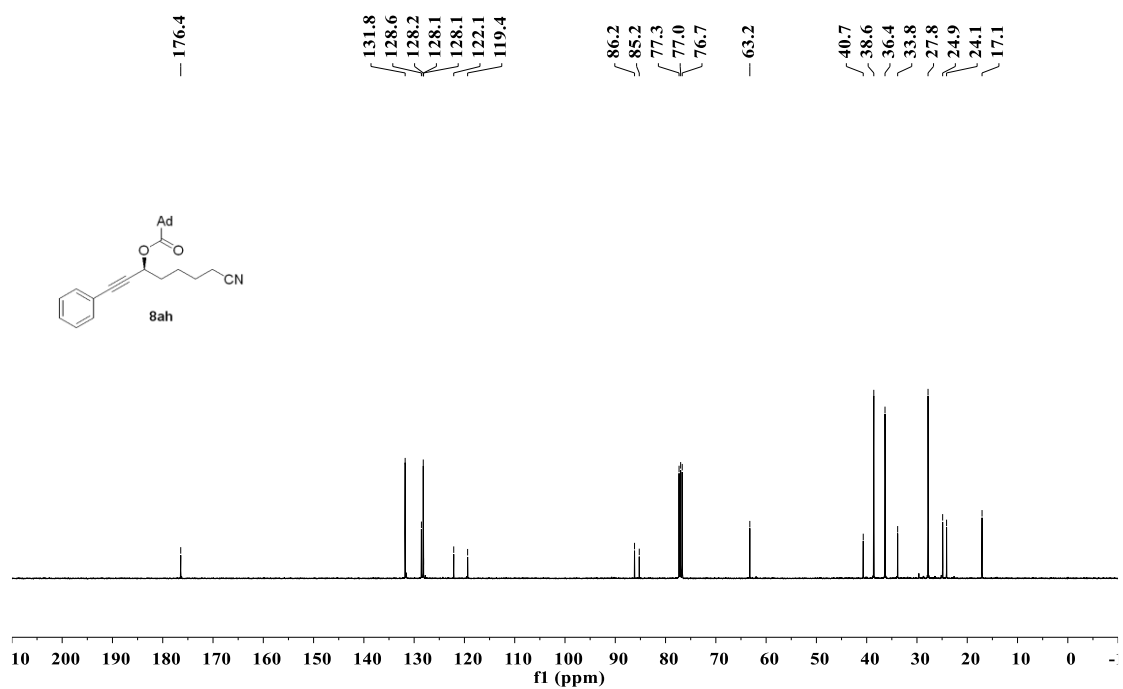
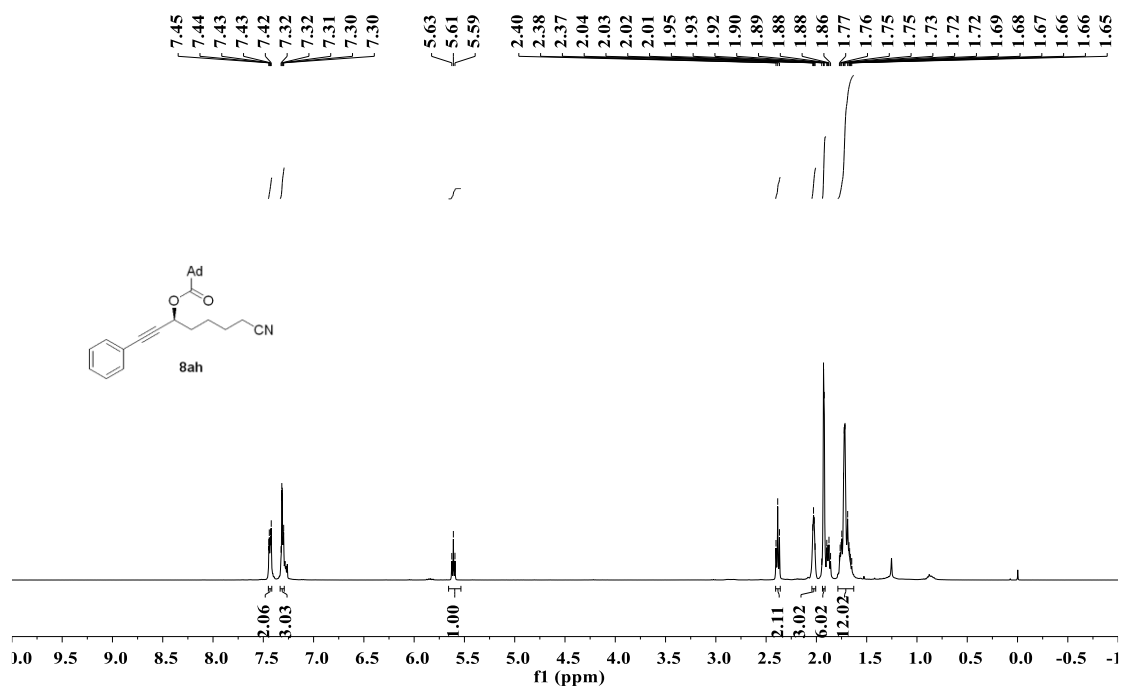
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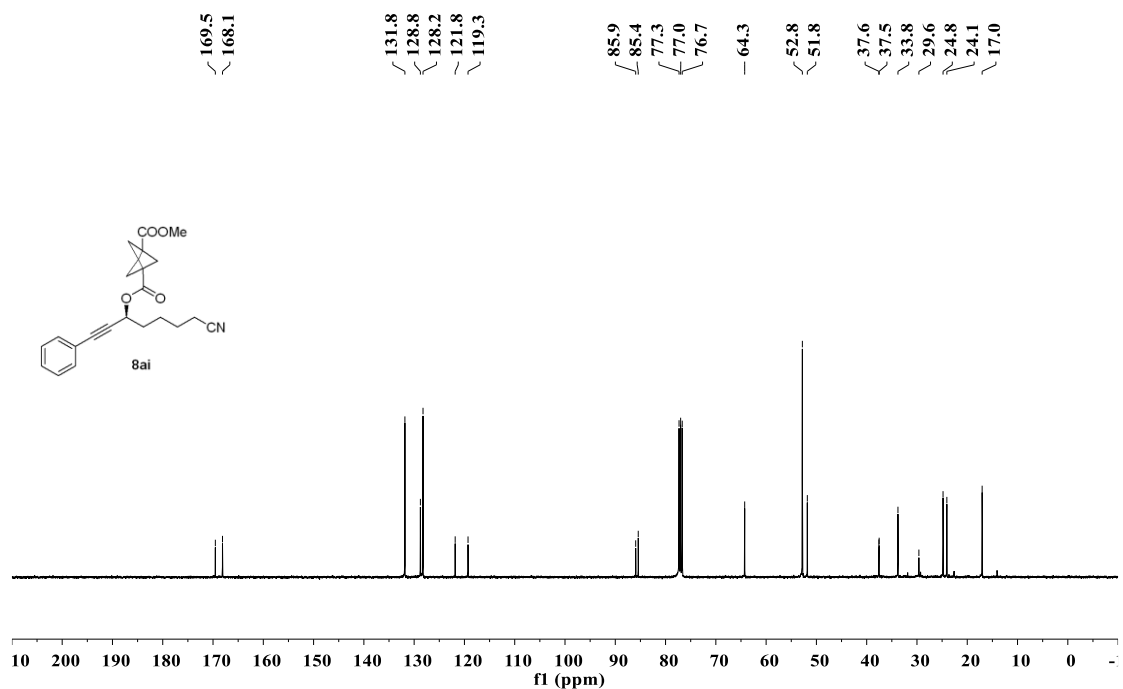
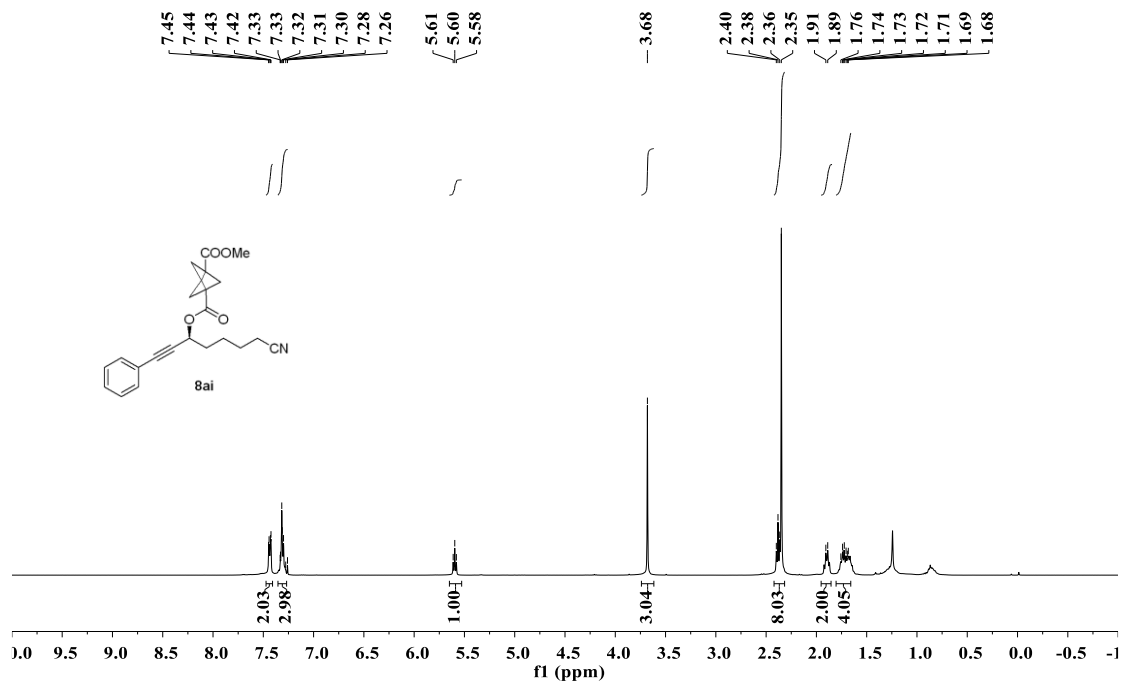
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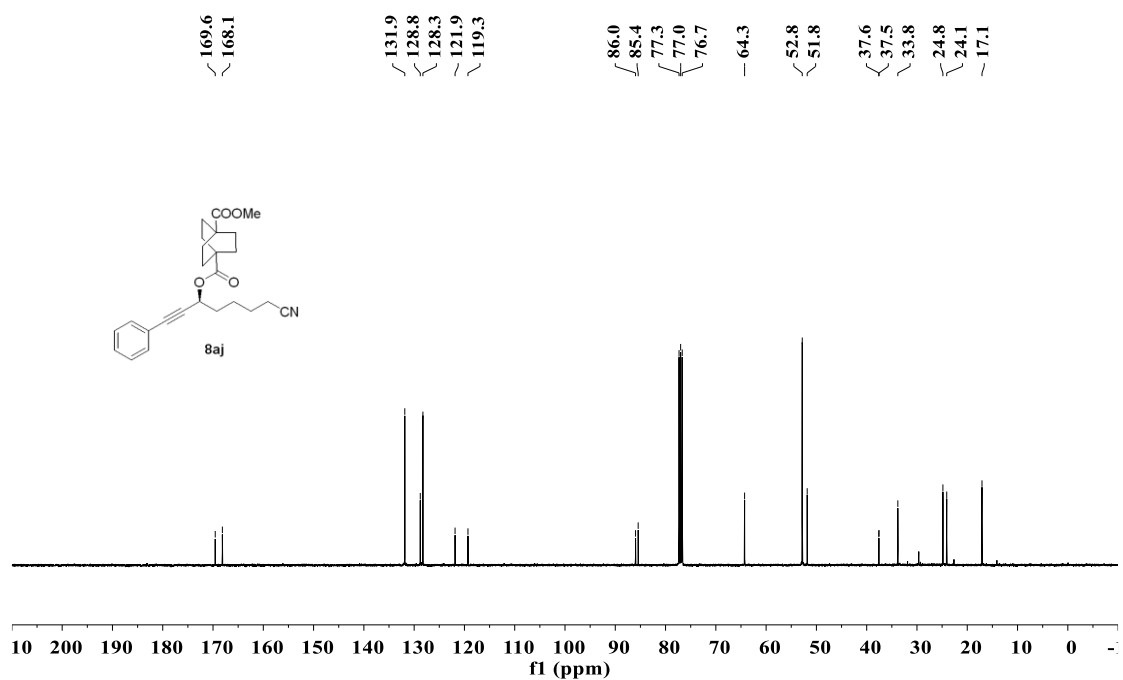
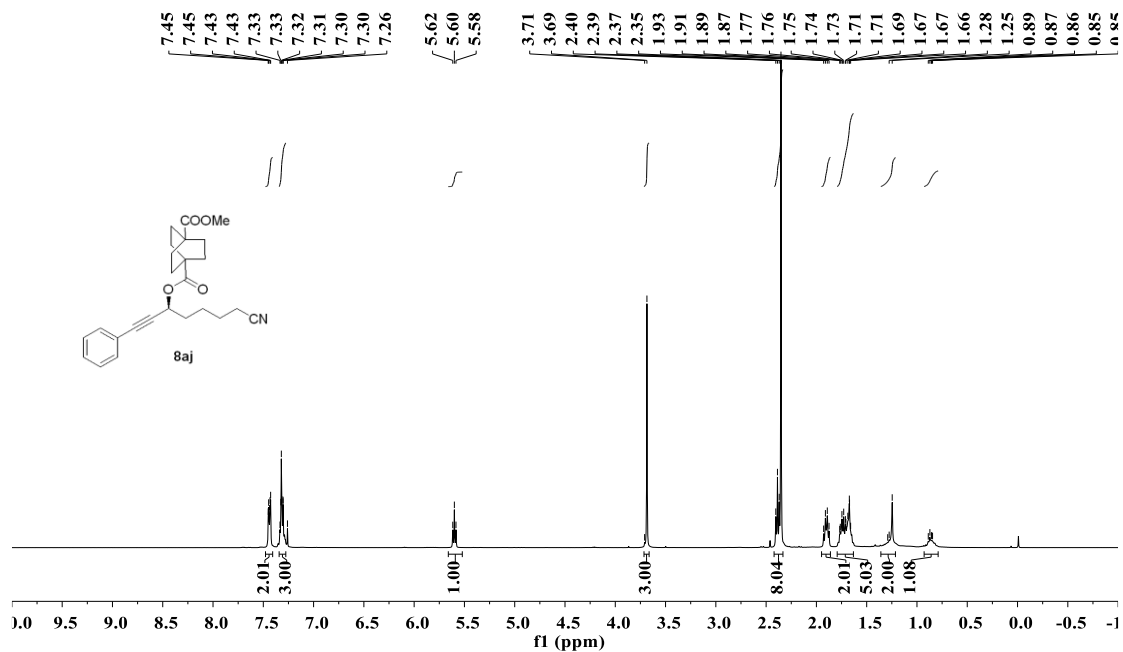
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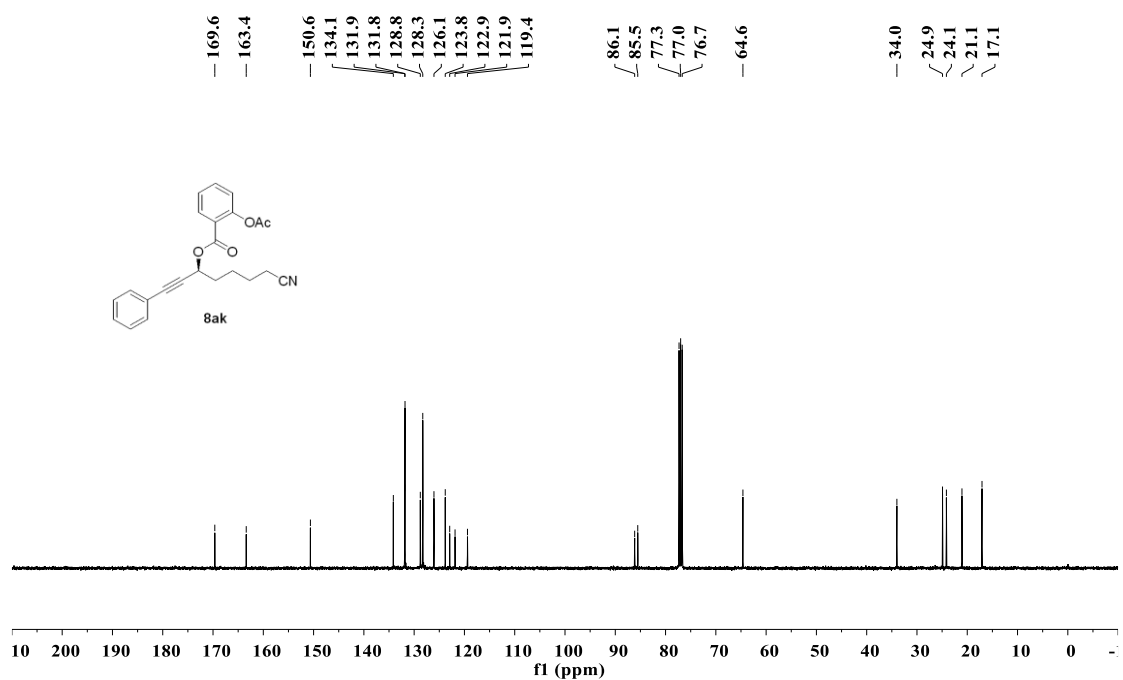
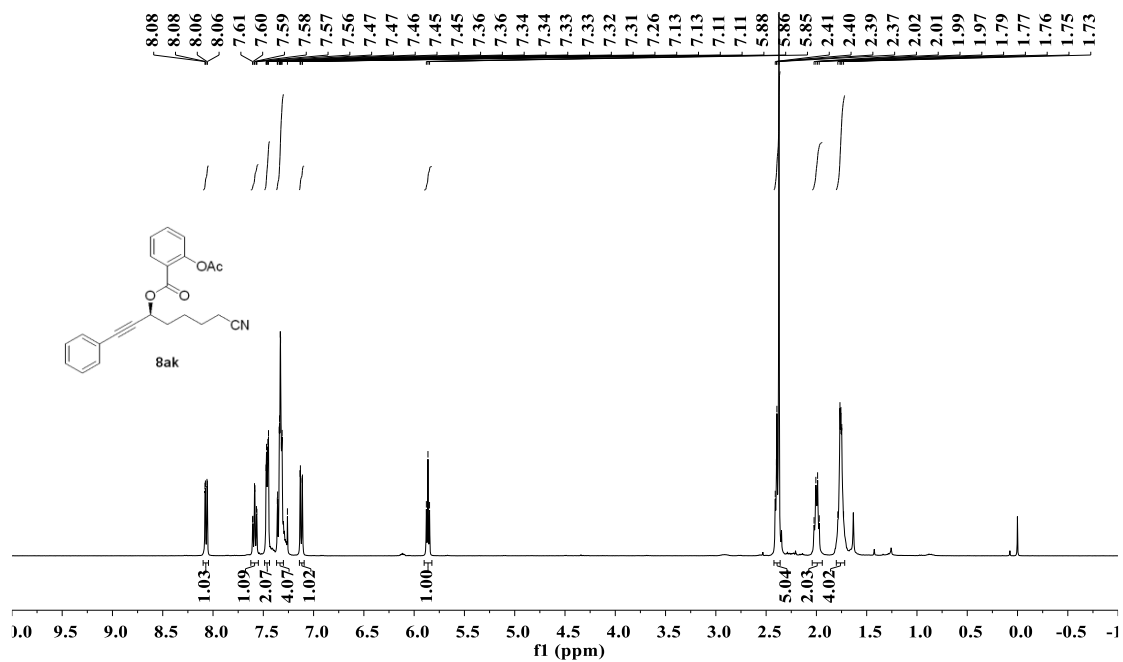
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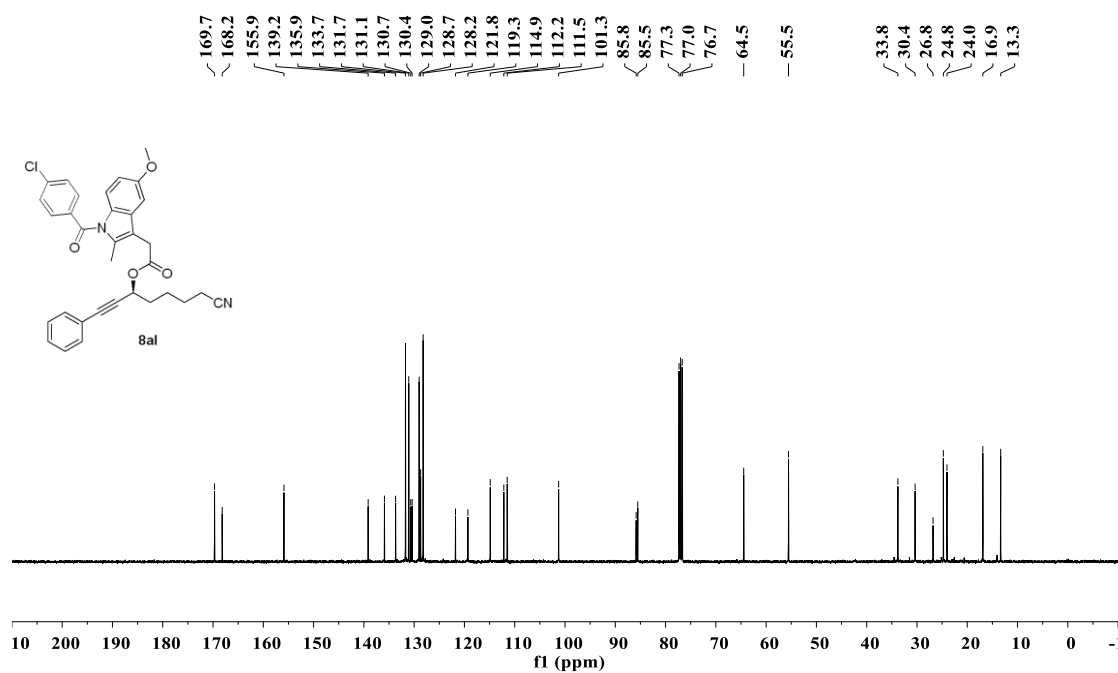
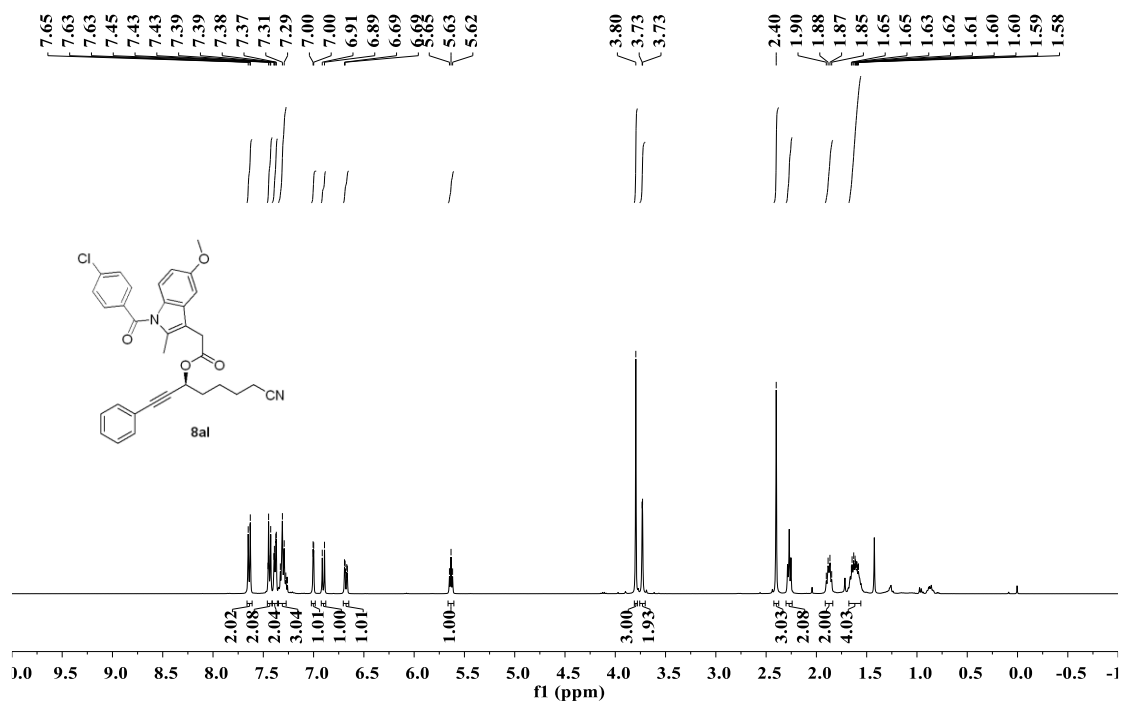
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8aj



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8ak

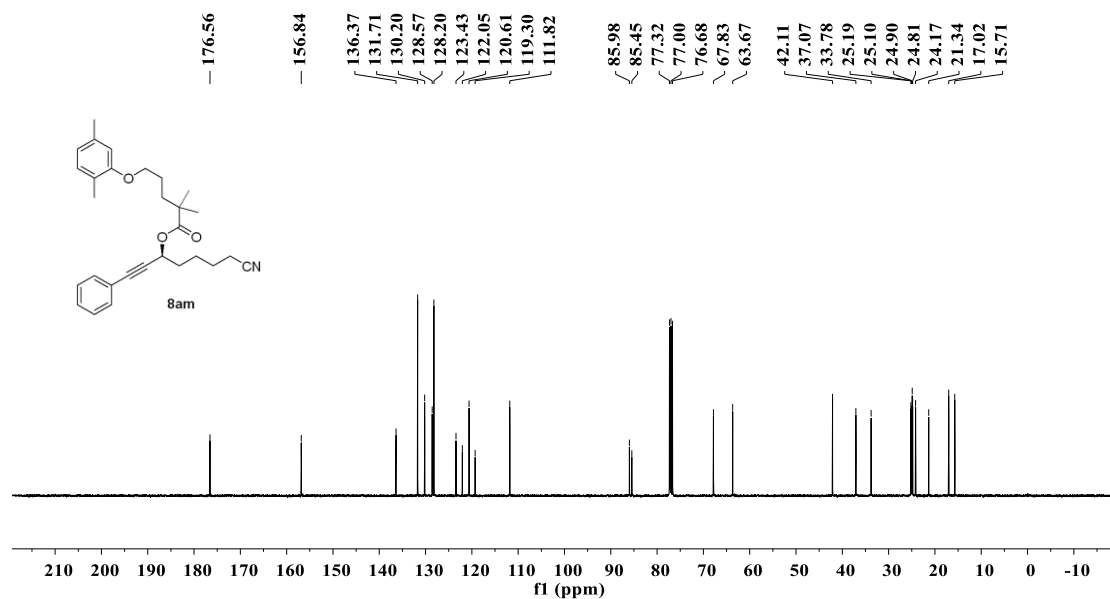
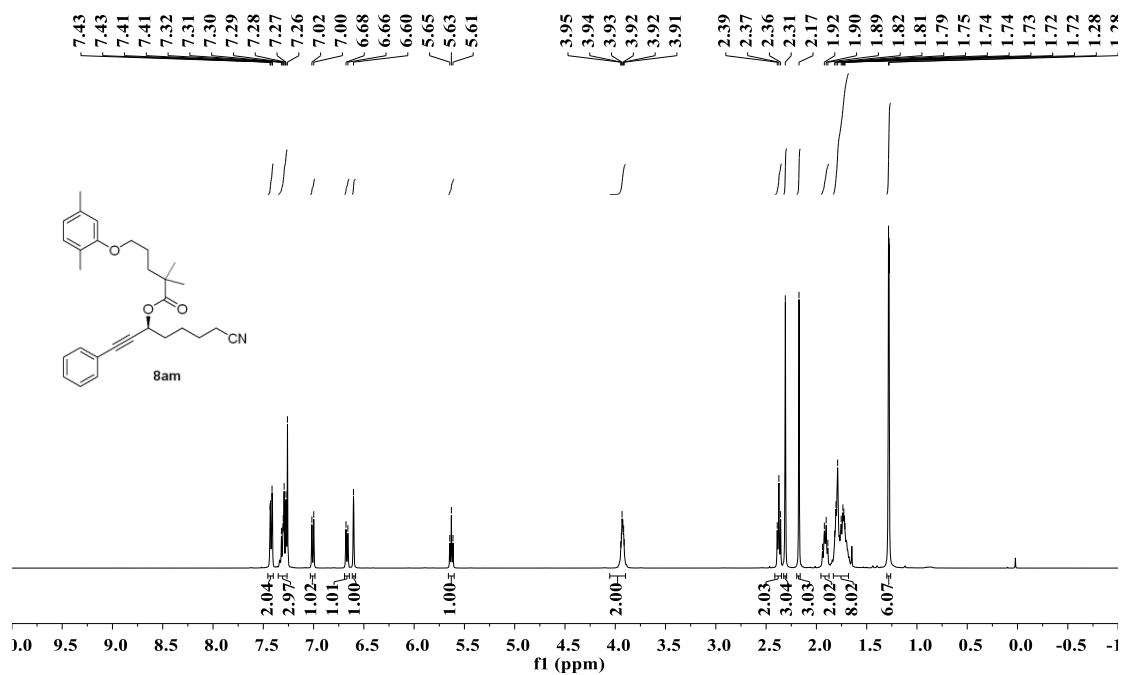


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8al

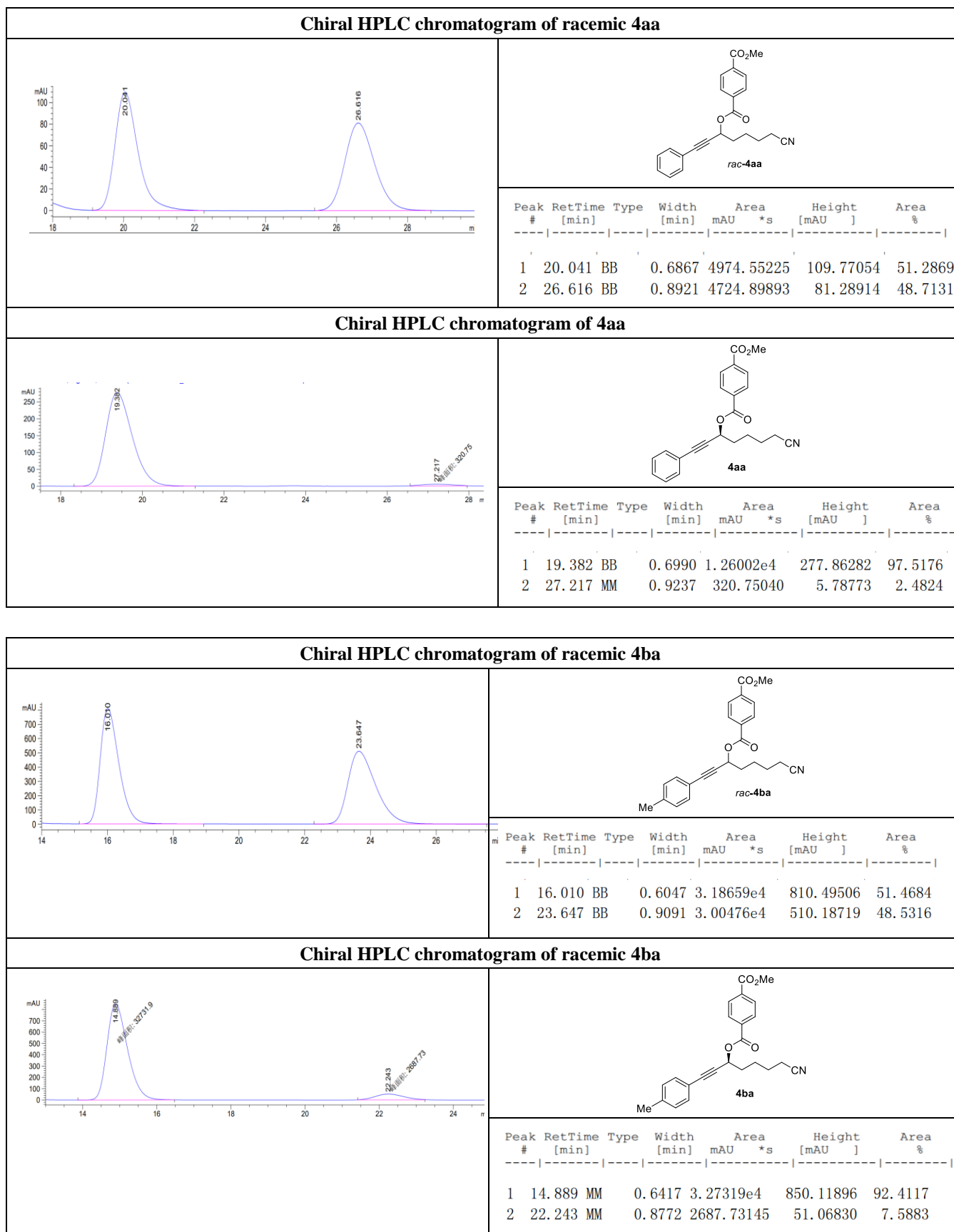




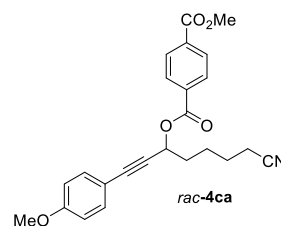
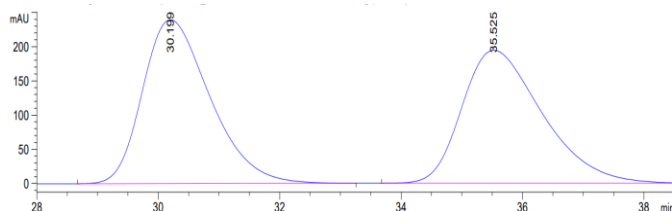
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectra of product 8am



## 9. Copies of HPLC chromatograms

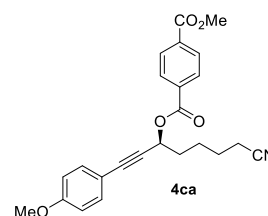
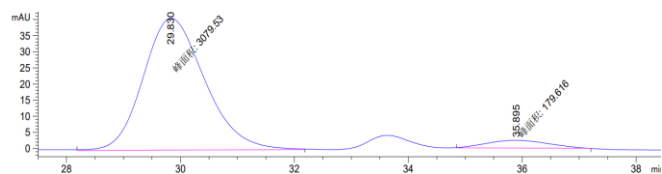


### Chiral HPLC chromatogram of racemic 4ca



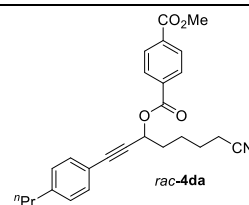
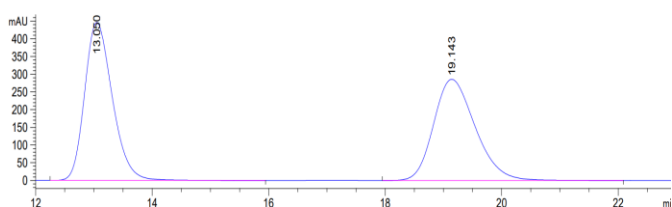
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.199	BB	1.1747	1.84832e4	239.40404	50.8421
2	35.525	BB	1.3588	1.78709e4	194.34470	49.1579

### Chiral HPLC chromatogram of 4ca



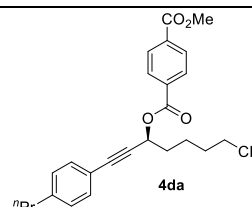
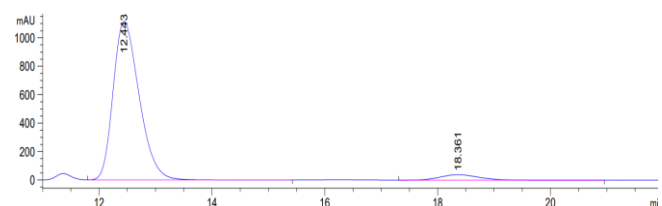
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.830	MM	1.2522	3079.53418	40.98910	94.4889
2	35.895	MM	1.2545	179.61600	2.38637	5.5111

### Chiral HPLC chromatogram of racemic 4da



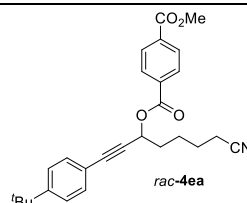
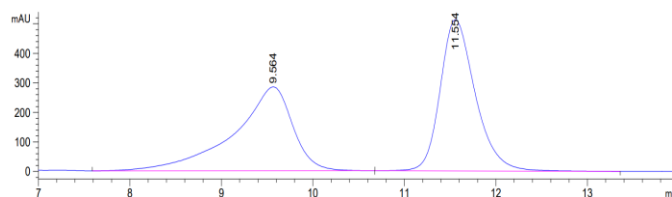
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.050	BB	0.5078	1.46754e4	446.09244	50.9722
2	19.143	BB	0.7650	1.41156e4	285.42587	49.0278

### Chiral HPLC chromatogram of 4da



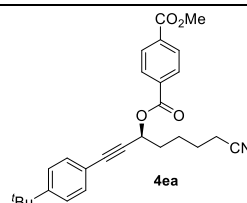
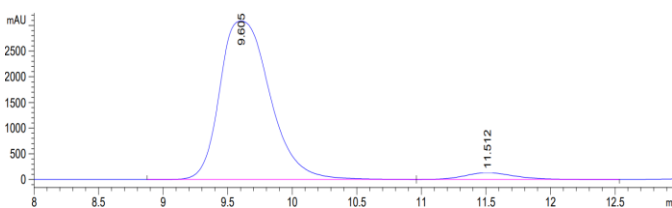
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.443	VB	0.4984	3.57641e4	1114.42578	95.1685
2	18.361	BB	0.7429	1815.68286	37.76916	4.8315

### Chiral HPLC chromatogram of racemic 4ea



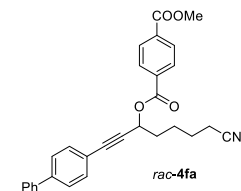
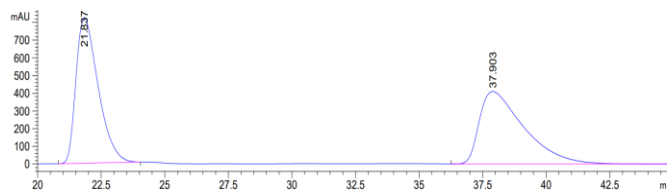
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.564	BB	0.6164	1.26737e4	284.11975	48.1496
2	11.554	BB	0.4049	1.36478e4	512.19775	51.8504

### Chiral HPLC chromatogram of 4ea



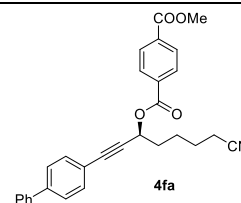
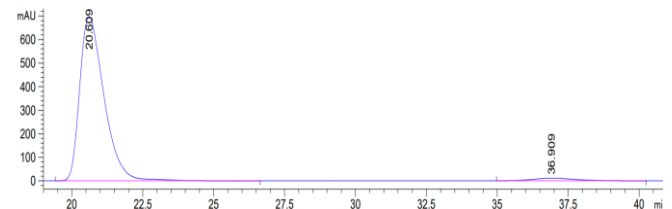
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.605	BV	0.4202	8.31102e4	3085.54541	95.9768
2	11.512	VB	0.4076	3483.81567	130.42270	4.0232

### Chiral HPLC chromatogram of racemic 4fa



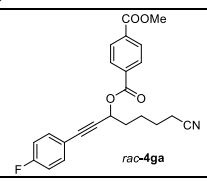
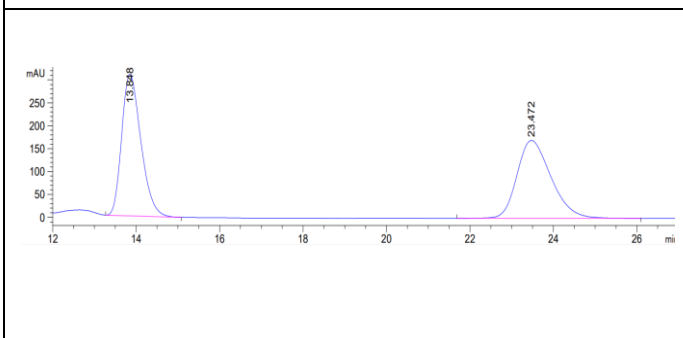
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.837	BB	0.9286	4.98662e4	823.32178	50.0940
2	37.903	BB	1.7661	4.96791e4	409.29633	49.9060

### Chiral HPLC chromatogram of 4fa



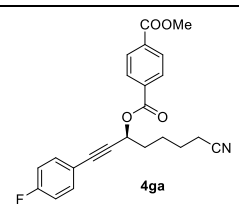
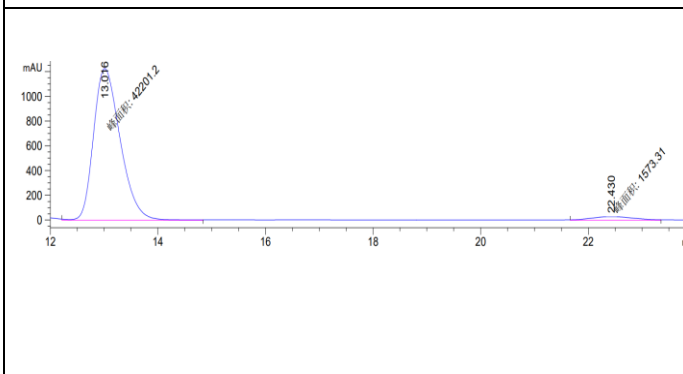
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.609	BB	0.9235	4.14188e4	696.81696	97.2989
2	36.909	BB	1.2859	1149.82227	10.51407	2.7011

### Chiral HPLC chromatogram of racemic 4ga



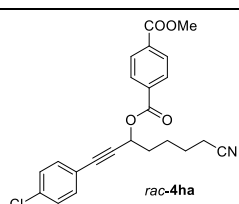
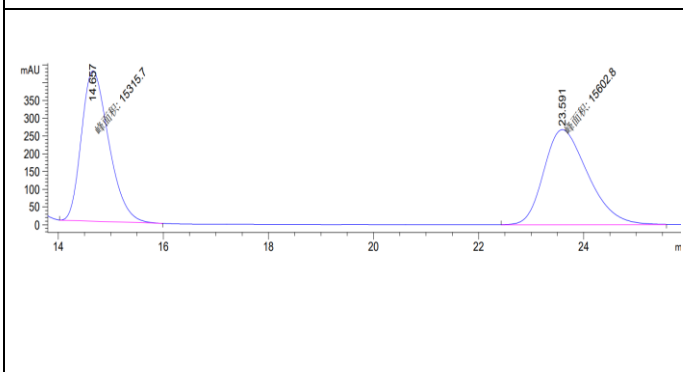
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.848	BB	0.4945	9876.67969	309.30194	50.7889
2	23.472	BB	0.8638	9569.84668	169.73198	49.2111

### Chiral HPLC chromatogram of 4ga



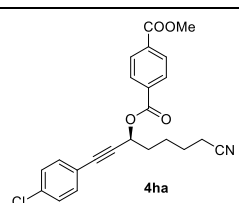
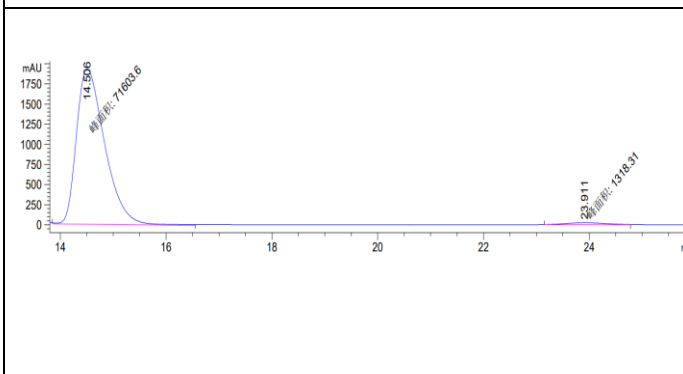
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.016	MM	0.5736	4.22012e4	1226.16785	96.4059
2	22.430	MM	0.9172	1573.30579	28.58913	3.5941

### Chiral HPLC chromatogram of racemic 4ha



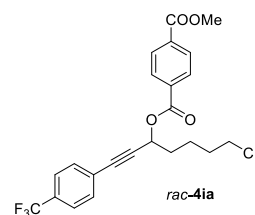
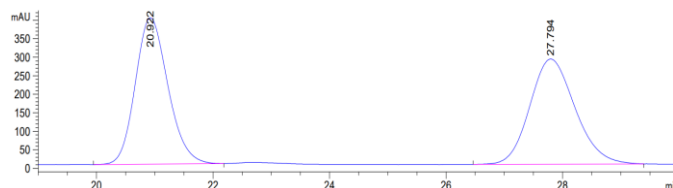
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.657	MM	0.6029	1.53157e4	423.39148	49.5357
2	23.591	MM	0.9722	1.56028e4	267.49545	50.4643

### Chiral HPLC chromatogram of 4ha



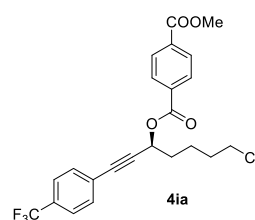
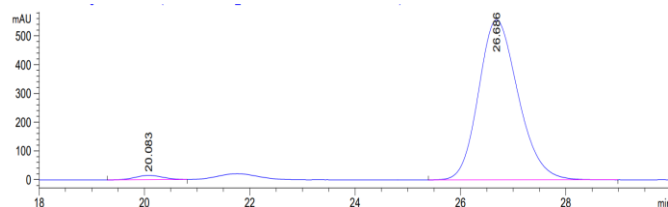
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.506	MM	0.6184	7.16036e4	1929.66187	98.1922
2	23.911	MM	0.9116	1318.30750	24.10193	1.8078

### Chiral HPLC chromatogram of racemic 4ia



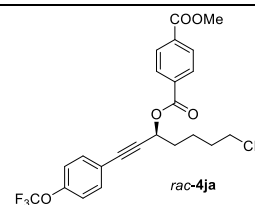
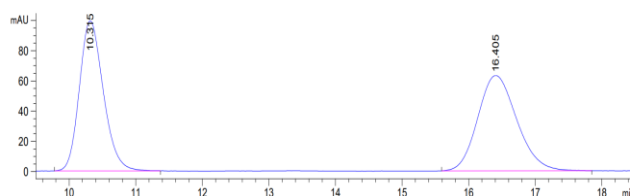
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.922	BB	0.5971	1.53239e4	394.60956	50.0677
2	27.794	BB	0.8225	1.52825e4	283.70477	49.9323

### Chiral HPLC chromatogram of 4ia



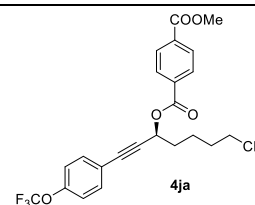
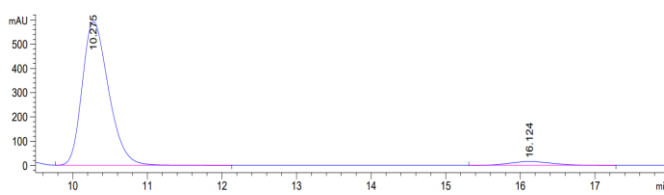
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.083	BB	0.5234	538.44165	14.97637	1.8220
2	26.686	BB	0.8048	2.90136e4	555.97205	98.1780

### Chiral HPLC chromatogram of racemic 4ja



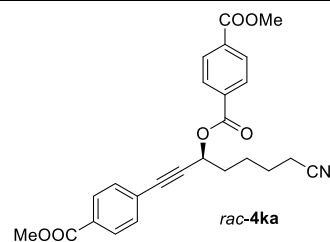
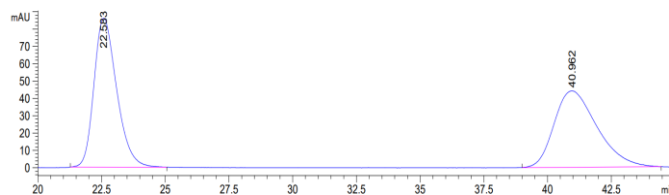
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.315	BB	0.3868	2474.82813	99.29336	49.1357
2	16.405	BB	0.6160	2561.89136	63.05993	50.8643

### Chiral HPLC chromatogram of 4ja



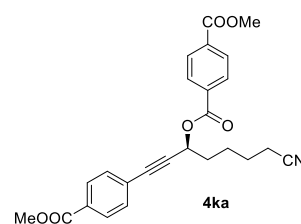
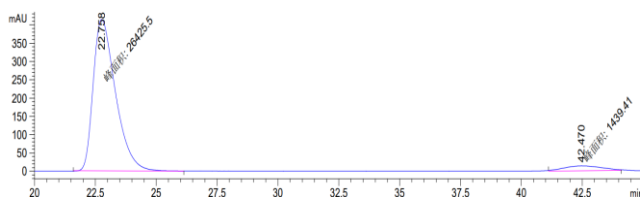
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.275	VB	0.3798	1.45113e4	592.32416	95.9824
2	16.124	BB	0.5657	607.41559	15.48215	4.0176

### Chiral HPLC chromatogram of racemic 4ka



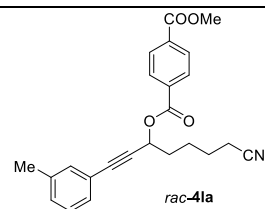
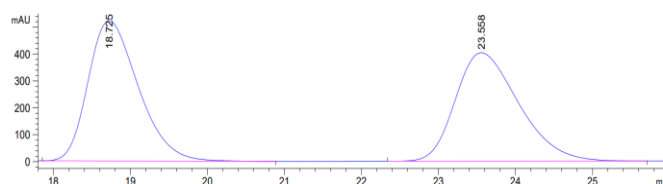
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.583	BB	0.8737	5311.14941	85.86082	50.7871
2	40.962	BB	1.3663	5146.51953	44.07512	49.2129

### Chiral HPLC chromatogram of 4ka



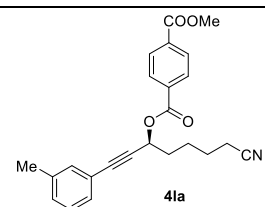
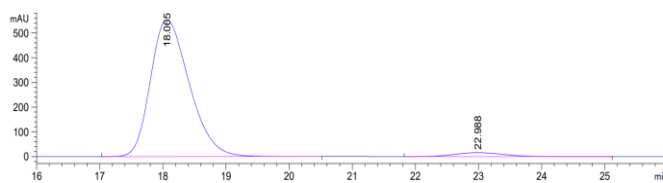
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.758	MM	1.0647	2.64255e4	413.66782	94.8343
2	42.470	MM	1.7867	1439.40649	13.42674	5.1657

### Chiral HPLC chromatogram of racemic 4la



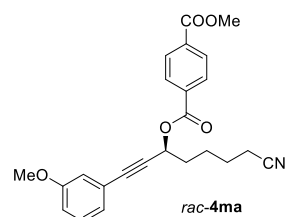
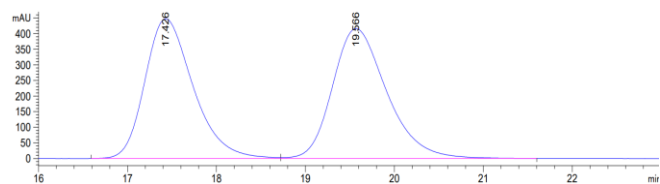
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.725	BB	0.7018	2.35732e4	521.05475	50.6562
2	23.558	BB	0.8829	2.29624e4	402.93149	49.3438

### Chiral HPLC chromatogram of 4la



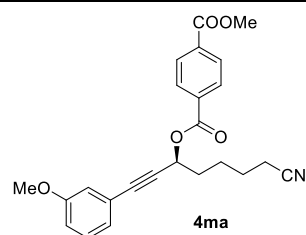
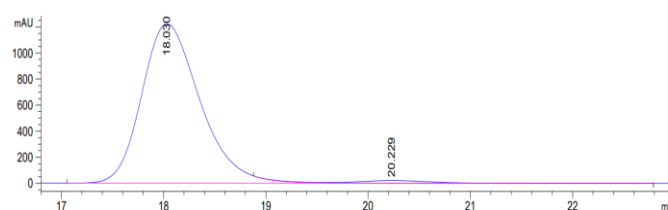
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.065	BB	0.6585	2.35906e4	554.30634	96.5560
2	22.988	BB	0.8083	841.43146	15.67513	3.4440

### Chiral HPLC chromatogram of racemic 4ma



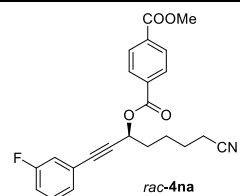
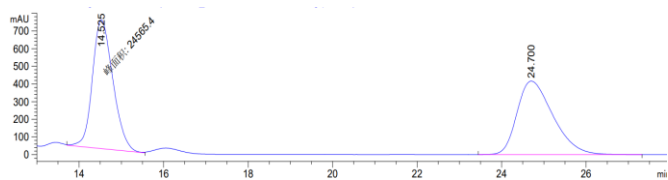
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.426	BV	0.5707	1.68262e4	447.43515	48.8640
2	19.566	VB	0.6418	1.76086e4	416.04367	51.1360

### Chiral HPLC chromatogram of 4ma



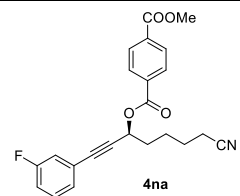
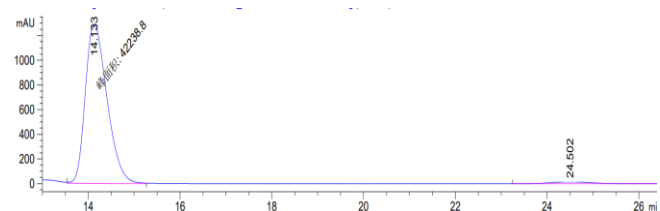
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.030	BV R	0.6100	4.84343e4	1223.04114	97.8885
2	20.229	VB E	0.7509	1044.74805	20.42156	2.1115

### Chiral HPLC chromatogram of racemic 4na



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.525	MM	0.5619	2.45654e4	728.65869	50.0741
2	24.700	BB	0.9037	2.44927e4	415.49844	49.9259

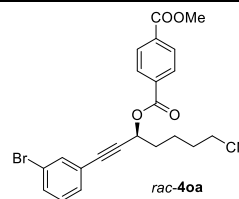
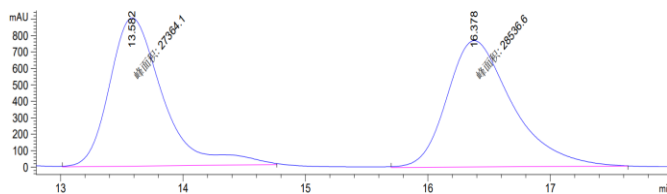
### Chiral HPLC chromatogram of 4na



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.133	MM	0.5449	4.22388e4	1291.89673	98.1082
2	24.502	BB	0.8139	814.50043	14.75689	1.8918

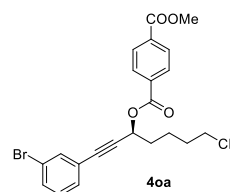
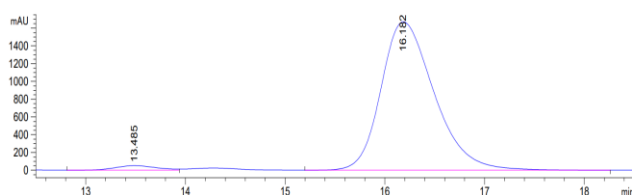


### Chiral HPLC chromatogram of racemic 4oa



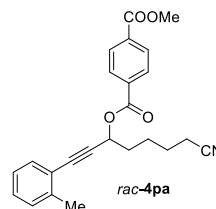
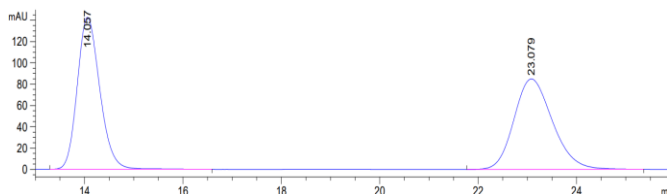
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.582	MM	0.5058	2.73641e4	901.73438	48.9513
2	16.378	MM	0.6191	2.85366e4	768.20776	51.0487

### Chiral HPLC chromatogram of 4oa



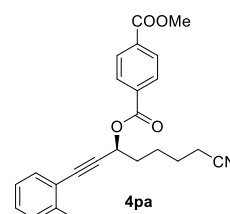
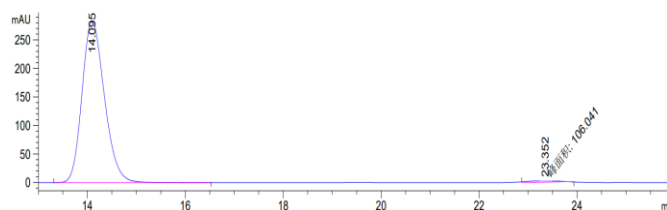
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.485	BV	0.4432	1464.42297	50.67054	2.3118
2	16.182	BB	0.5683	6.18798e4	1669.92505	97.6882

### Chiral HPLC chromatogram of racemic 4pa



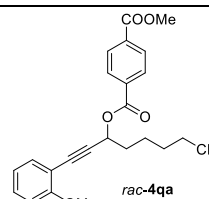
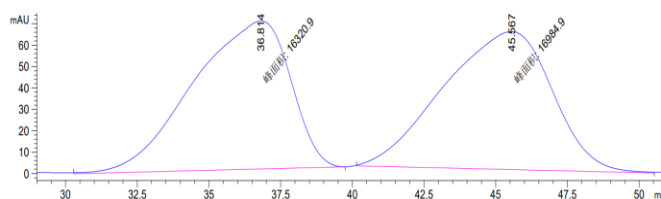
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.057	BB	0.4905	4525.12842	142.50616	49.6560
2	23.079	BB	0.8416	4587.81738	84.73967	50.3440

### Chiral HPLC chromatogram of 4pa



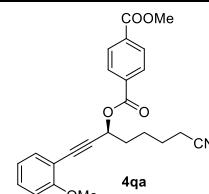
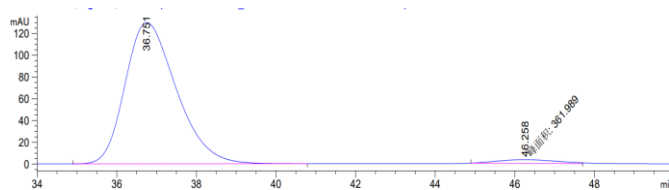
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.095	BB	0.4889	8983.24902	284.08578	98.8333
2	23.352	MM	0.6830	106.04147	2.58774	1.1667

### Chiral HPLC chromatogram of racemic 4qa



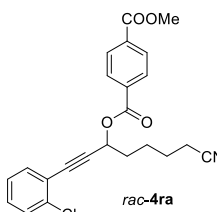
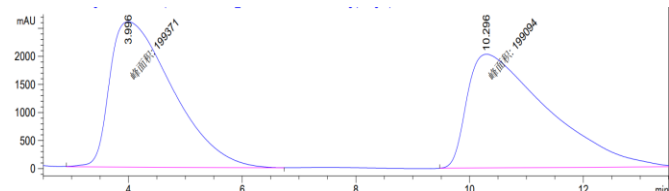
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.814	MM	3.9308	1.63209e4	69.20119	49.0032
2	45.567	MM	4.3893	1.69849e4	64.49287	50.9968

### Chiral HPLC chromatogram of 4qa



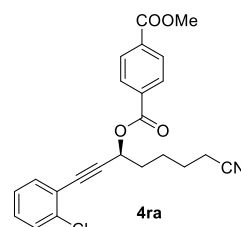
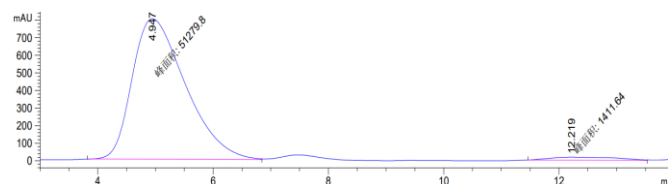
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.751	BB	1.3423	1.15966e4	129.79819	96.9730
2	46.258	MM	1.7299	361.98923	3.48767	3.0270

### Chiral HPLC chromatogram of racemic 4ra



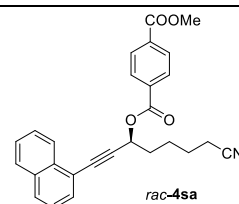
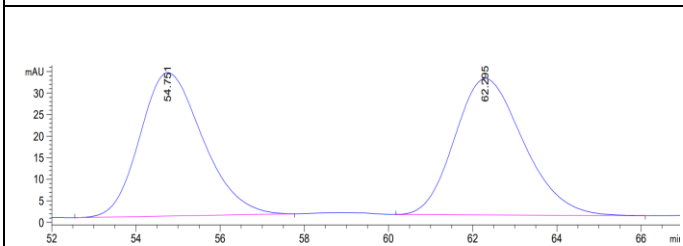
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	3.996	MM	1.2820	1.99371e5	2592.02002	50.0348
2	10.296	MM	1.6367	1.99094e5	2027.34521	49.9652

### Chiral HPLC chromatogram of 4ra



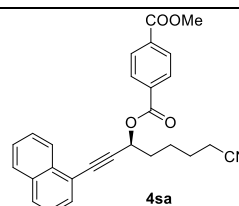
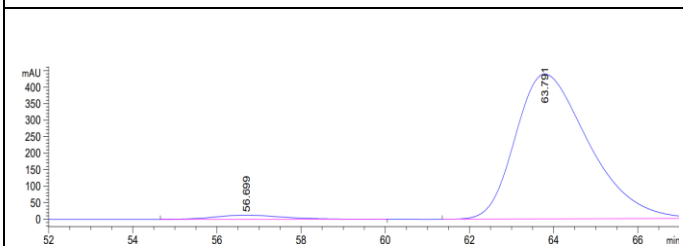
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.947	MM	1.0700	5.12798e4	798.71747	97.3209
2	12.219	MM	1.3687	1411.63855	17.18926	2.6791

### Chiral HPLC chromatogram of racemic 4sa



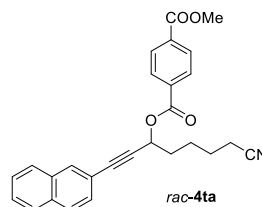
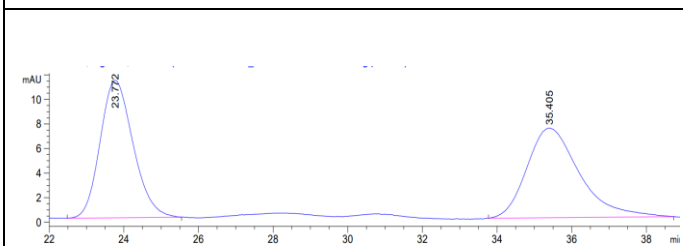
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	54.751	BB	1.4664	3451.58813	33.26871	49.0084
2	62.295	BB	1.4183	3591.26489	31.68695	50.9916

### Chiral HPLC chromatogram of 4sa



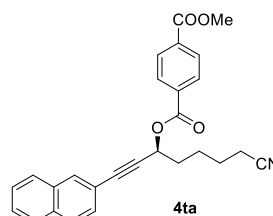
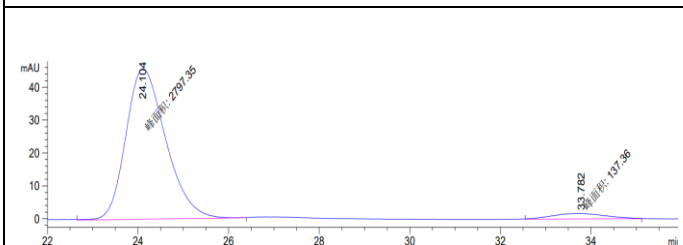
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	56.699	BB	1.3067	1373.43628	12.43390	2.5197
2	63.791	BB	1.8548	5.31337e4	438.77386	97.4803

### Chiral HPLC chromatogram of racemic 4ta



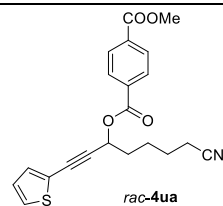
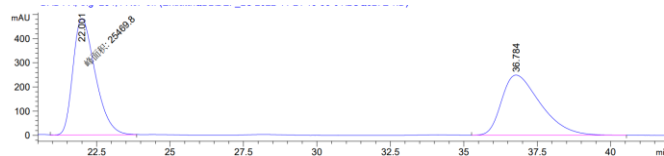
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.772	BB	0.8455	686.08771	11.18645	49.0262
2	35.405	BB	1.1574	713.34418	7.29105	50.9738

### Chiral HPLC chromatogram of 4ta



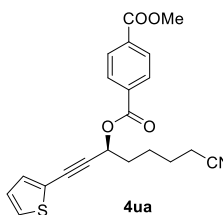
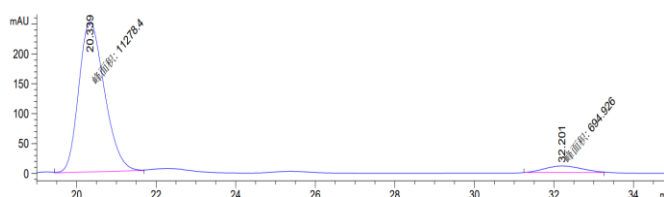
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.104	MM	1.0185	2797.35303	45.77496	95.3195
2	33.782	MM	1.3567	137.36012	1.68747	4.6805

### Chiral HPLC chromatogram of racemic 4ua



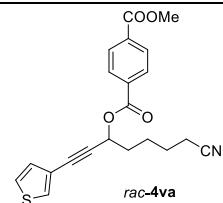
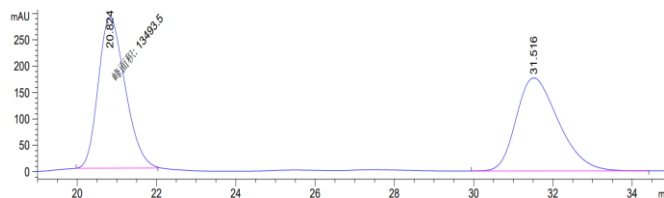
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.001	MM	0.8803	2.54698e4	482.20126	52.7385
2	36.784	BB	1.3244	2.28247e4	248.78468	47.2615

### Chiral HPLC chromatogram of 4ua



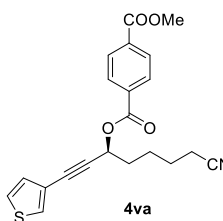
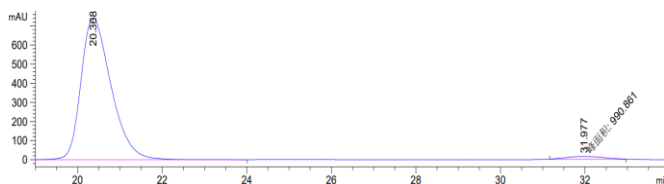
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.339	MM	0.7485	1.12784e4	251.13148	94.1960
2	32.201	MM	1.0717	694.92627	10.80742	5.8040

### Chiral HPLC chromatogram of racemic 4va



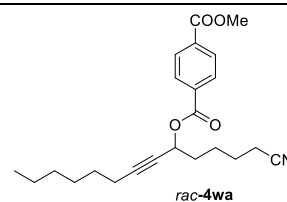
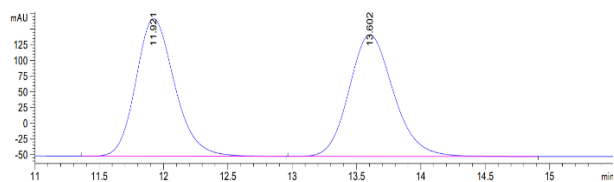
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.824	MM	0.7866	1.34935e4	285.91623	50.8143
2	31.516	BB	1.1378	1.30610e4	176.39807	49.1857

### Chiral HPLC chromatogram of 4va



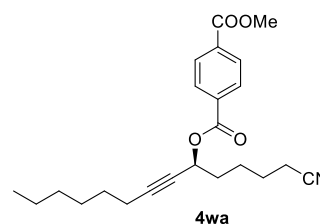
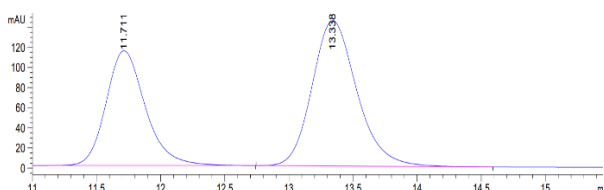
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.368	BB	0.7586	3.65592e4	742.23889	97.3612
2	31.977	MM	1.0813	990.86139	15.27252	2.6388

### Chiral HPLC chromatogram of racemic 4wa



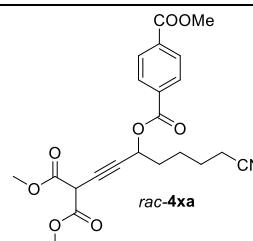
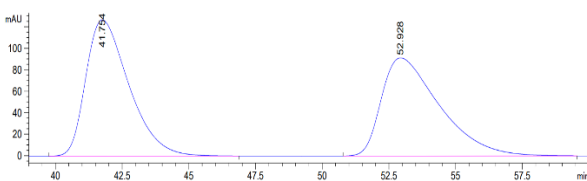
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	11.921	BB	0.3204	4595.84473		219.38791	49.6284
2	13.602	BB	0.3706	4664.67480		193.91878	50.3716

### Chiral HPLC chromatogram of 4wa



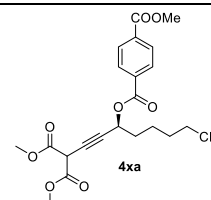
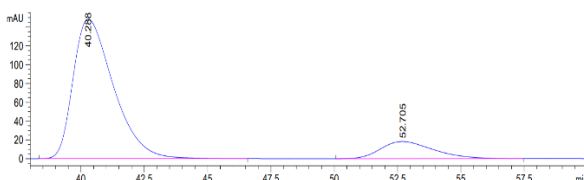
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	11.711	BB	0.3282	2450.10571		114.23812	41.0626
2	13.338	BB	0.3736	3516.65503		144.64700	58.9374

### Chiral HPLC chromatogram of racemic 4xa



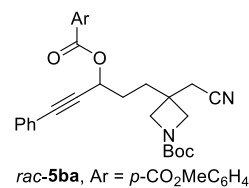
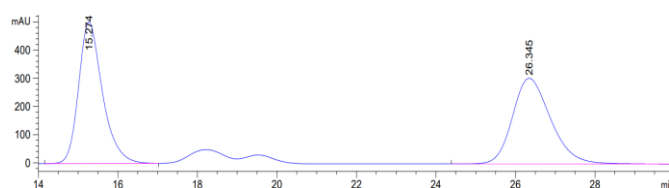
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	41.754	BB	1.6666	1.42450e4		126.80149	50.8158
2	52.928	BB	2.0969	1.37876e4		91.14021	49.1842

### Chiral HPLC chromatogram of 4xa



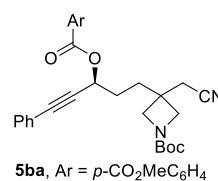
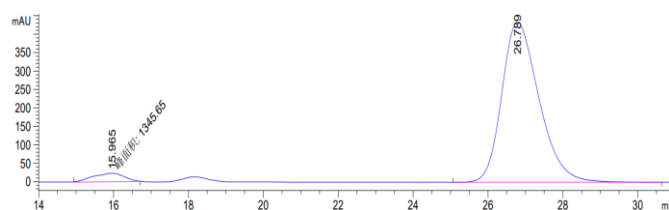
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	40.288	BB	1.6209	1.64002e4		148.22200	86.1691
2	52.705	BB	1.6989	2632.36353		18.18356	13.8309

### Chiral HPLC chromatogram of racemic 5ba



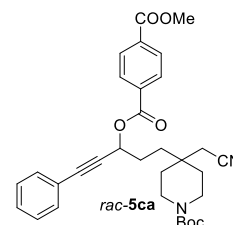
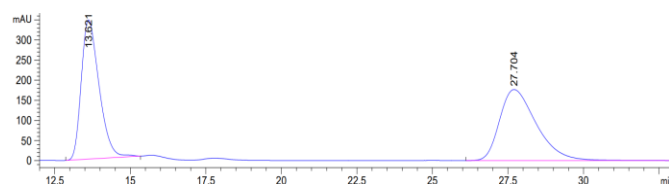
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	15.274	BB	0.6304	2.09303e4		502.00470	50.7278
2	26.345	BB	1.0208	2.03298e4		303.77676	49.2722

### Chiral HPLC chromatogram of 7a



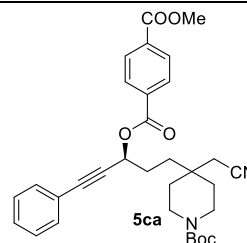
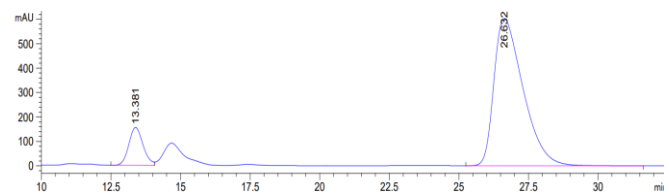
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	15.965	MM	0.9703	1345.65027		23.11349	4.3056
2	26.789	BB	1.0616	2.99075e4		434.19070	95.6944

### Chiral HPLC chromatogram of racemic 5ca



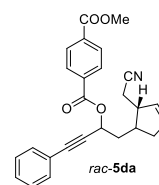
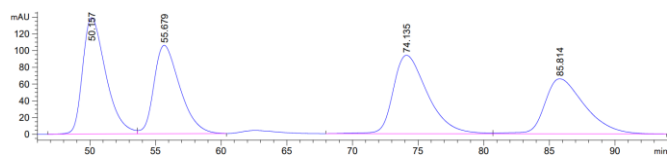
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	13.621	BB	0.6253	1.41594e4		346.07959	48.7762
2	27.704	BB	1.2982	1.48699e4		176.61806	51.2238

### Chiral HPLC chromatogram of 5ca



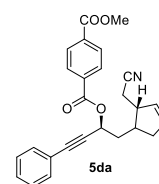
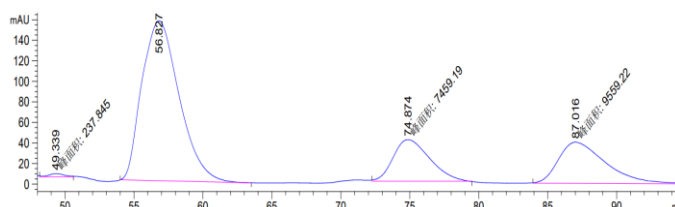
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	13.381	BV	0.5444	5508.02197		155.07568	11.1726
2	26.632	BB	1.1115	4.37914e4		602.82513	88.8274

### Chiral HPLC chromatogram of racemic 5da



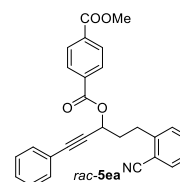
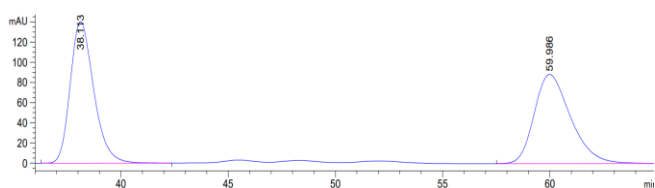
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	50.157	BV	1.9136	1.70333e4	138.61842	27.2812
2	55.679	VB	2.1181	1.45069e4	105.37676	23.2348
3	74.135	BV	2.7899	1.69884e4	93.58150	27.2092
4	85.814	VB	3.2053	1.39076e4	65.70885	22.2749

### Chiral HPLC chromatogram of 5da



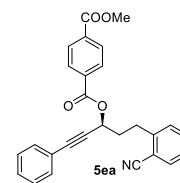
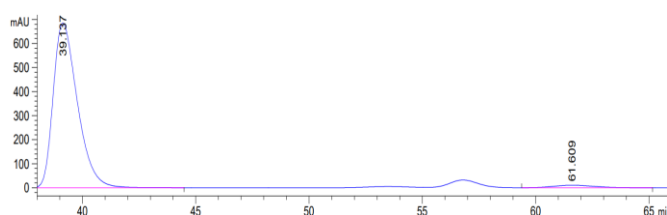
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.339	MM	1.3065	237.84451	3.03415	0.5109
2	56.827	BB	2.5600	2.92977e4	155.79420	62.9328
3	74.874	MM	3.0733	7459.18994	40.45102	16.0227
4	87.016	MM	3.9644	9559.22168	40.18769	20.5336

### Chiral HPLC chromatogram of racemic 5ea



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.113	BB	1.1524	1.07120e4	140.35490	50.7248
2	59.986	BBA	1.7168	1.04059e4	88.30840	49.2752

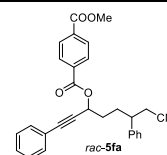
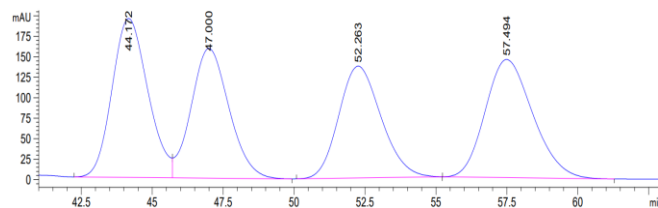
### Chiral HPLC chromatogram of 5ea



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.137					
2	61.609					

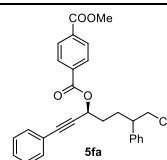
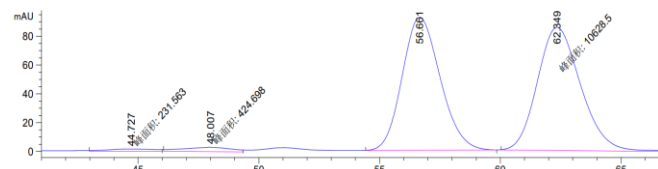
1	39.137	BB	1.1364	5.07272e4	684.61877	97.5723
2	61.609	BB	1.4450	1262.16284	10.33315	2.4277

### Chiral HPLC chromatogram of racemic 5fa



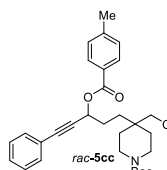
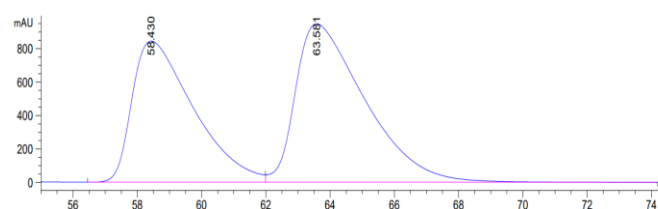
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.172	BV	1.3178	1.69954e4	194.04349	27.1038
2	47.000	VB	1.3892	1.47144e4	158.48764	23.4661
3	52.263	BB	1.5369	1.41718e4	136.53653	22.6008
4	57.494	BB	1.7231	1.68234e4	144.20512	26.8294

### Chiral HPLC chromatogram of 5fa



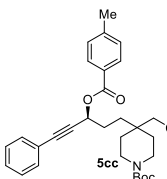
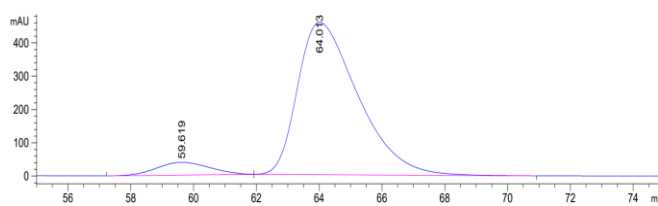
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.727	MM	2.3402	231.56281	1.64920	1.0839
2	48.007	MM	2.3329	424.69827	3.03411	1.9879
3	56.661	BB	1.5470	1.00799e4	92.37705	47.1803
4	62.349	MM	2.0692	1.06285e4	85.60879	49.7480

### Chiral HPLC chromatogram of racemic 5cc



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	58.430	BV	1.9508	1.11841e5	843.55957	48.8640
2	63.581	VB	2.1791	1.42336e5	947.20911	51.1360

### Chiral HPLC chromatogram of 5cc

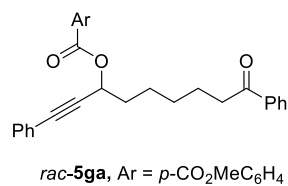
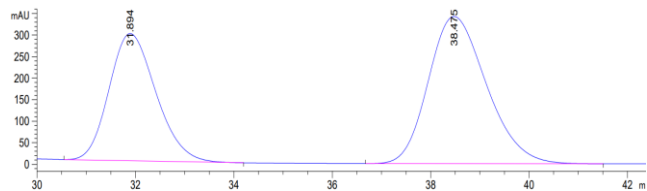


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	58.619					
2	64.033					



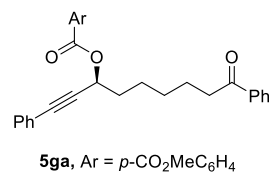
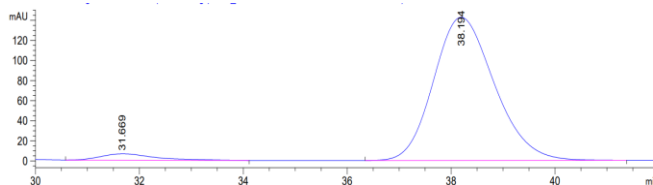
	1	59.619	BB	1.5723	4504.42236	38.46289	6.8685
	2	64.013	BB	2.0048	6.10768e4	457.71579	93.1315

### Chiral HPLC chromatogram of racemic 5ga



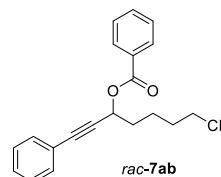
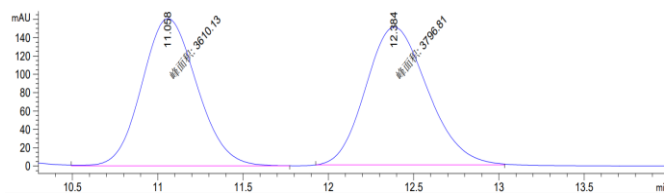
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.894	BB	1.0246	1.95534e4	295.26044	50.6562
2	38.475	BB	1.2720	2.80759e4	341.90616	49.3438

### Chiral HPLC chromatogram of 5ga



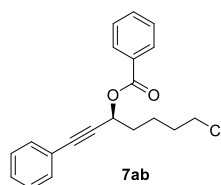
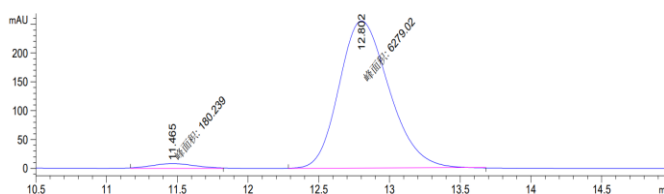
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.669	BB	0.8617	456.60013	6.32899	3.7954
2	38.194	BB	1.2317	1.15739e4	142.48247	96.2046

### Chiral HPLC chromatogram of racemic 7ab



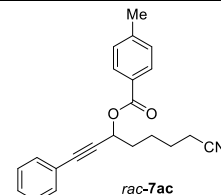
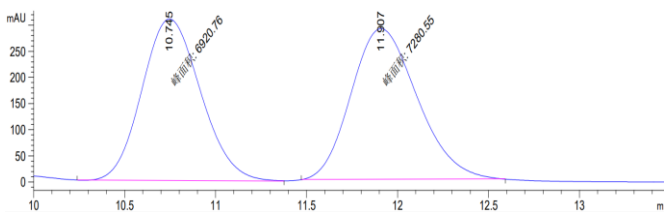
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.058	MM	0.3747	3610.12598	160.56847	48.7398
2	12.384	MM	0.4214	3796.81274	150.17322	51.2602

### Chiral HPLC chromatogram of 7ab



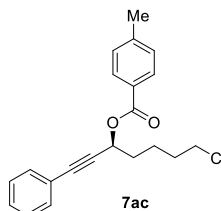
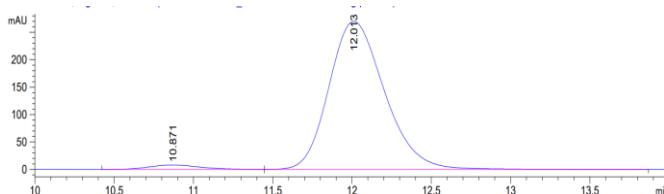
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.465	MM	0.3582	180.23946	8.38562	2.7904
2	12.802	MM	0.4099	6279.02344	255.29530	97.2096

### Chiral HPLC chromatogram of racemic 7ac



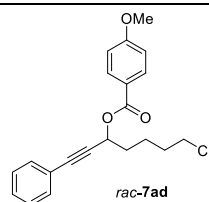
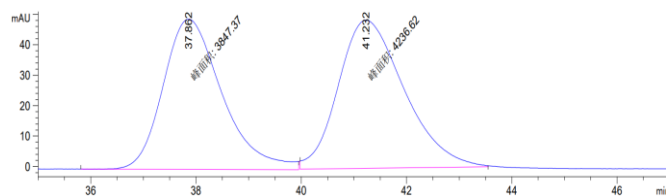
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.745	MM	0.3735	6920.76318	308.84390	48.7333
2	11.907	MM	0.4214	7280.54590	287.93240	51.2667

### Chiral HPLC chromatogram of 7ac



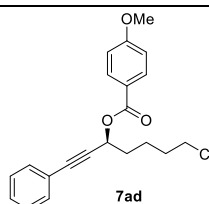
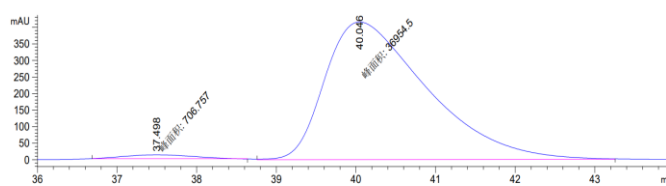
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.871	BB	0.3308	172.64874	8.03257	2.5630
2	12.013	BB	0.3756	6563.44775	270.04062	97.4370

### Chiral HPLC chromatogram of racemic 7ad



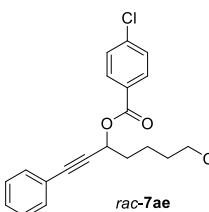
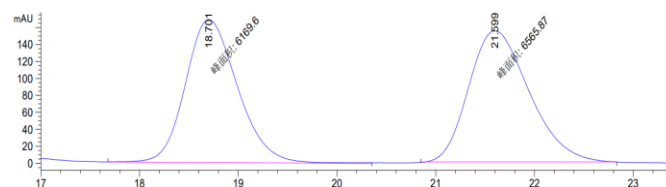
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.862	MM	1.2982	3847.36646	49.39214	47.5924
2	41.232	MM	1.4500	4236.62354	48.69737	52.4076

### Chiral HPLC chromatogram of 7ad



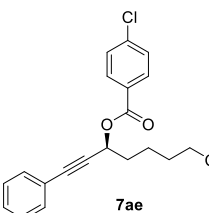
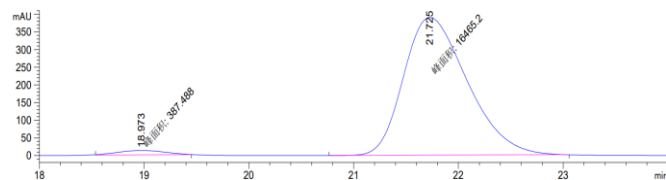
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	37.498	MM	0.9972	706.75677	11.81195	1.8766
2	40.046	MM	1.4813	3.69545e4	415.80258	98.1234

### Chiral HPLC chromatogram of racemic 7ae



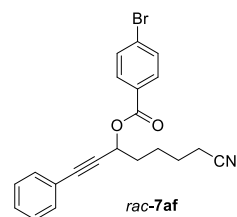
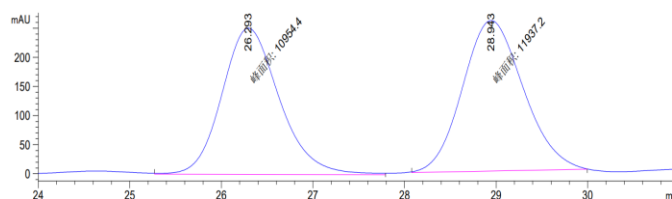
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.701	MM	0.6109	6169.59619	168.31406	48.4442
2	21.599	MM	0.7077	6565.86865	154.62335	51.5558

### Chiral HPLC chromatogram of 7ae



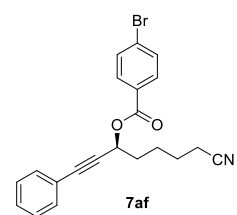
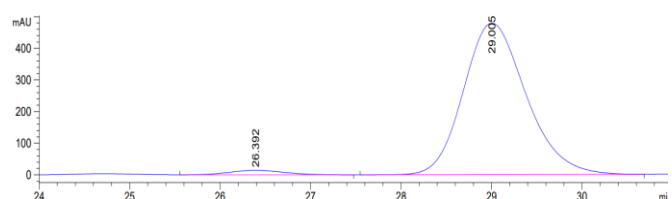
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.973	MM	0.5167	387.48828	12.49762	2.2993
2	21.725	MM	0.7034	1.64652e4	390.14963	97.7007

### Chiral HPLC chromatogram of racemic 7af



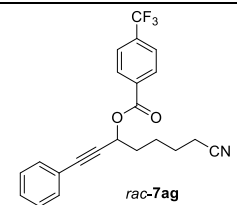
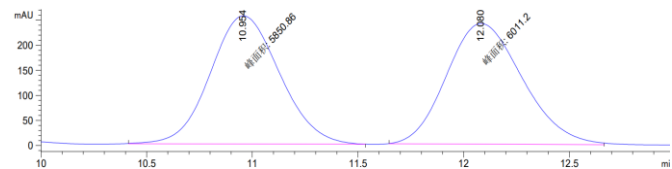
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.293	MM	0.7272	1.09544e4	251.05565	47.8534
2	28.943	MM	0.7692	1.19372e4	258.64316	52.1466

### Chiral HPLC chromatogram of 7af



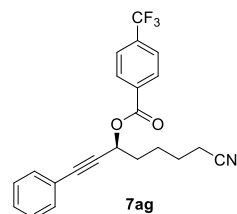
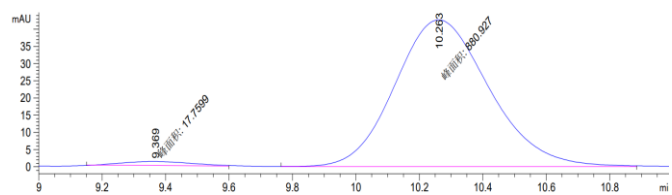
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.392	BB	0.6339	593.08472	14.18254	2.5113
2	29.005	BB	0.7391	2.30239e4	478.73273	97.4887

### Chiral HPLC chromatogram of racemic 7ag



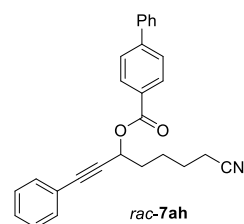
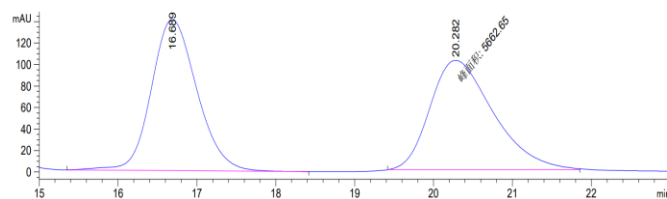
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.954	MM	0.3815	5850.86133	255.57797	49.3242
2	12.080	MM	0.4165	6011.19580	240.55594	50.6758

### Chiral HPLC chromatogram of 7ag



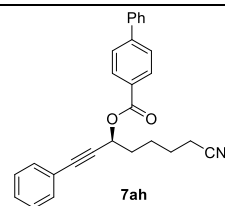
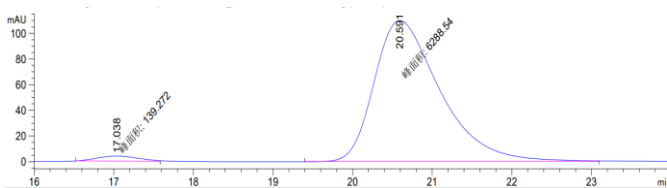
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.369	MM	0.2527	17.75990	1.17117	1.9762
2	10.263	MM	0.3444	880.92743	42.63631	98.0238

### Chiral HPLC chromatogram of racemic 7ah



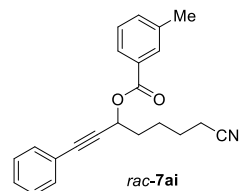
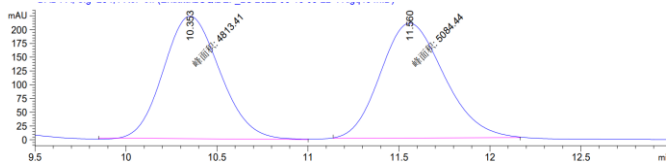
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	16.689	BB	0.6185	5651.55371		140.72766	49.9510
2	20.282	MM	0.9270	5662.65039		101.80650	50.0490

### Chiral HPLC chromatogram of 7ah



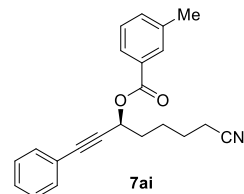
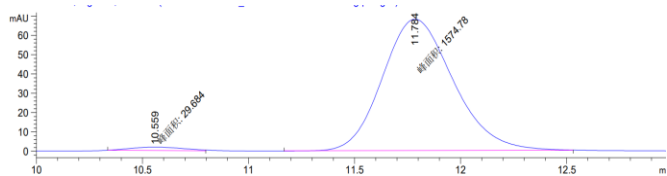
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	17.038	MM	0.5923	139.27184		3.91920	2.1667
2	20.591	MM	0.9553	6288.53906		109.71644	97.8333

### Chiral HPLC chromatogram of racemic 7ai



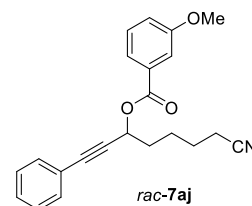
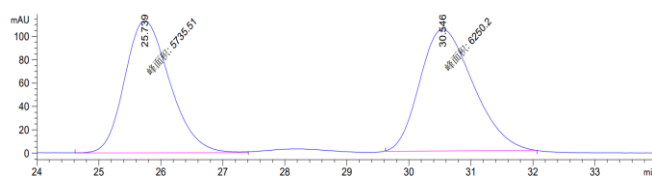
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.353	MM	0.3603	4813.41455		222.68799	48.6309
2	11.560	MM	0.4059	5084.44189		208.74883	51.3691

### Chiral HPLC chromatogram of 7ai



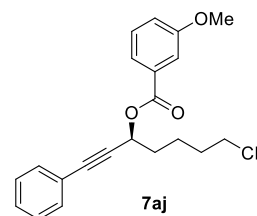
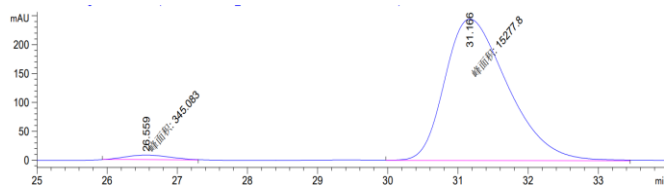
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.559	MM	0.2814	29.68396		1.75832	1.8501
2	11.784	MM	0.3863	1574.78076		67.93993	98.1499

### Chiral HPLC chromatogram of racemic 7aj



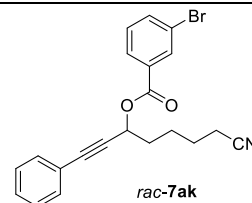
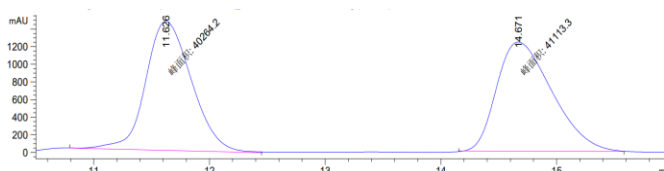
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.739	MM	0.8438	5735.50635	113.28175	47.8529
2	30.546	MM	0.9974	6250.19678	104.44579	52.1471

### Chiral HPLC chromatogram of 7aj



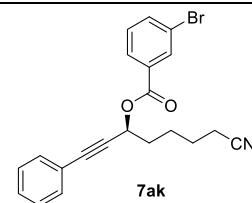
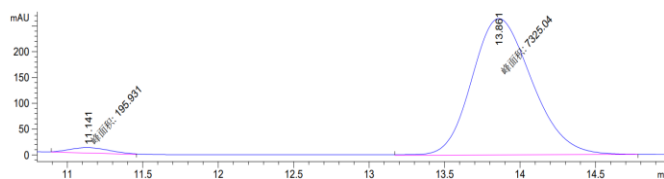
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.559	MM	0.7191	345.08292	7.99793	2.2088
2	31.166	MM	1.0392	1.52778e4	245.01814	97.7912

### Chiral HPLC chromatogram of racemic 7ak



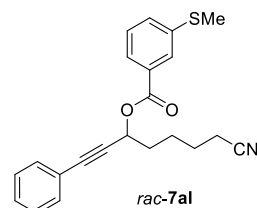
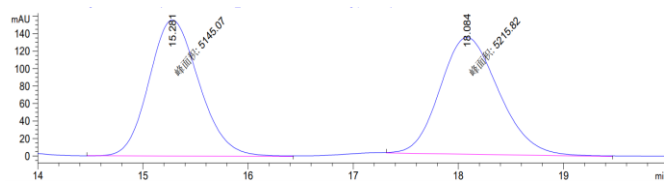
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.626	MM	0.4589	4.02642e4	1462.49927	49.4783
2	14.671	MM	0.5535	4.11133e4	1238.08875	50.5217

### Chiral HPLC chromatogram of 7ak



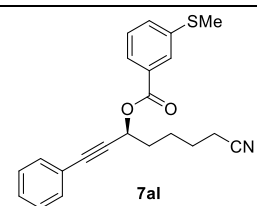
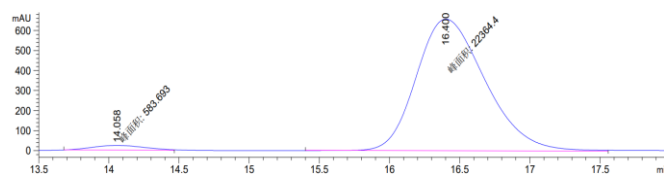
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.141	MM	0.3093	195.93074	10.55700	2.6051
2	13.861	MM	0.4615	7325.03662	264.54074	97.3949

### Chiral HPLC chromatogram of racemic 7al



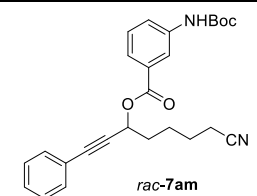
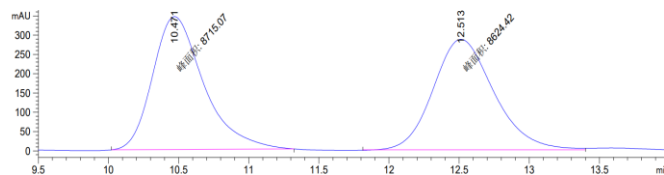
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	15.281	MM	0.5514	5145.07178	155.52129	49.6586	
2	18.084	MM	0.6508	5215.82178	133.57709	50.3414	

### Chiral HPLC chromatogram of 7al



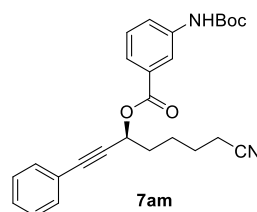
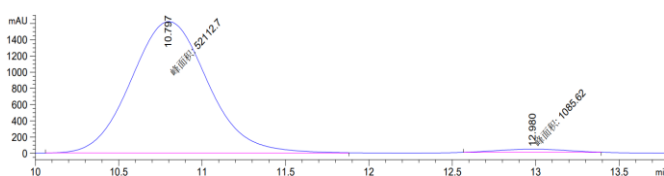
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	14.058	MM	0.4243	583.69330	22.93003	2.5435	
2	16.400	MM	0.5675	2.23644e4	656.82703	97.4565	

### Chiral HPLC chromatogram of racemic 7am



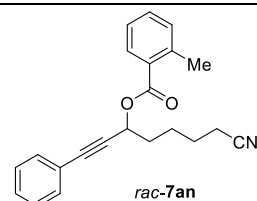
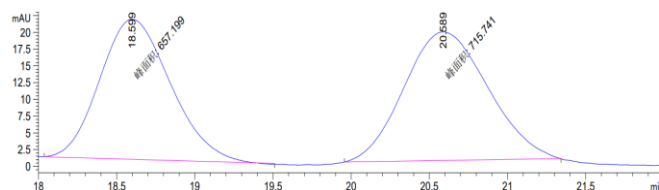
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.471	MM	0.4214	8715.07324	344.68573	50.2614	
2	12.513	MM	0.5016	8624.41504	286.58902	49.7386	

### Chiral HPLC chromatogram of 7am



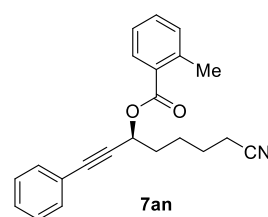
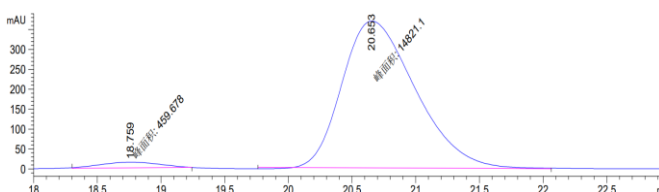
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	10.797	MM	0.5358	5.21127e4	1620.93616	97.9593	
2	12.980	MM	0.4599	1085.61560	39.34563	2.0407	

### Chiral HPLC chromatogram of racemic 7an



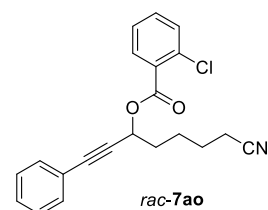
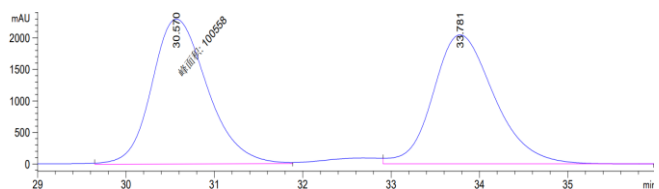
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.599	MM	0.5241	657.19891	20.89902	47.8680
2	20.589	MM	0.6219	715.74078	19.18149	52.1320

### Chiral HPLC chromatogram of 7an



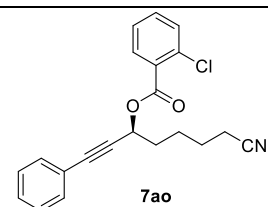
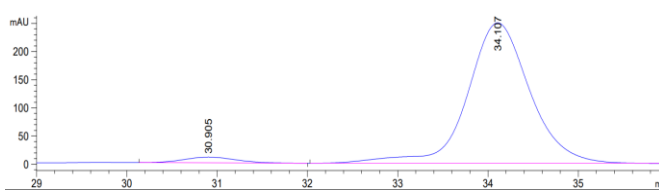
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.759	MM	0.5355	459.67822	14.30752	3.0082
2	20.653	MM	0.6691	1.48211e4	369.17059	96.9918

### Chiral HPLC chromatogram of racemic 7ao



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.570	MM	0.7298	1.00558e5	2296.44360	50.4451
2	33.781	VB	0.7411	9.87833e4	2046.57312	49.5549

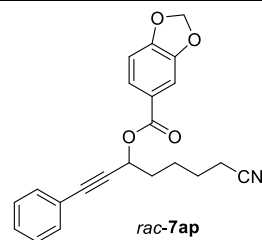
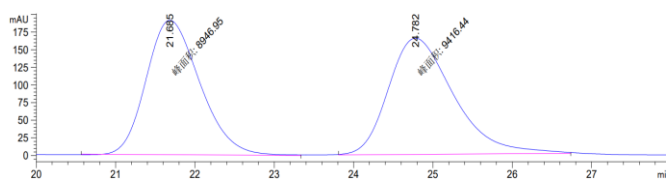
### Chiral HPLC chromatogram of 7ao



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.905	BB	0.5914	411.18039	10.30792	3.3147
2	34.107	BB	0.7271	1.19937e4	249.37199	96.6853

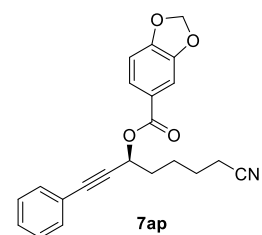
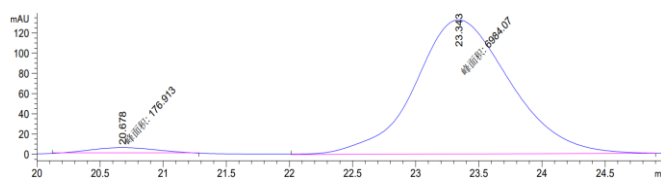


### Chiral HPLC chromatogram of racemic 7ap



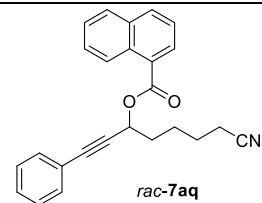
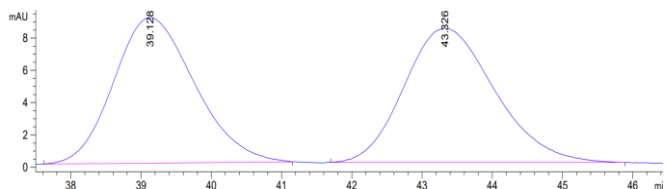
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.685	MM	0.7826	8946.94531	190.54466	48.7216
2	24.782	MM	0.9522	9416.44434	164.82524	51.2784

### Chiral HPLC chromatogram of 7ap



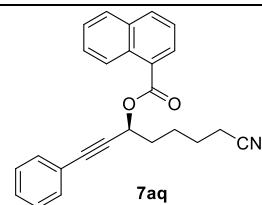
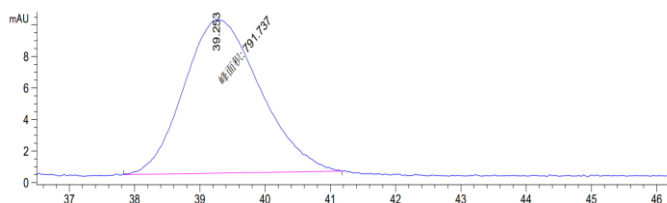
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.678	MM	0.5726	176.91281	5.14923	2.4705
2	23.343	MM	0.8767	6984.07275	132.76654	97.5295

### Chiral HPLC chromatogram of racemic 7aq



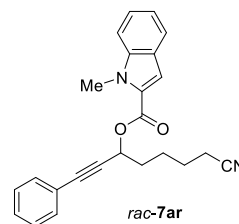
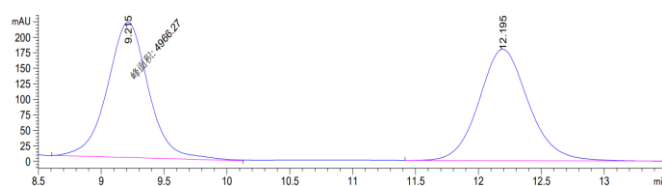
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.128	BB	0.9835	723.08197	9.01778	49.2531
2	43.326	BB	1.0697	745.01105	8.31204	50.7469

### Chiral HPLC chromatogram of 7aq



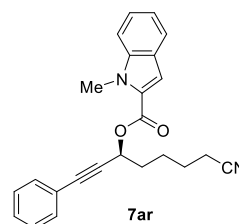
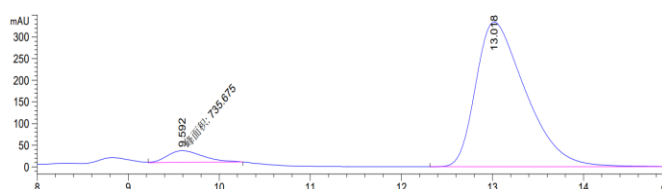
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.253	MM	1.3544	791.73676	9.74245	100.0000

### Chiral HPLC chromatogram of racemic 7ar



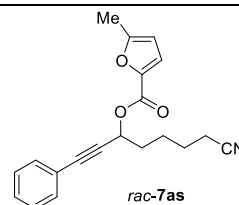
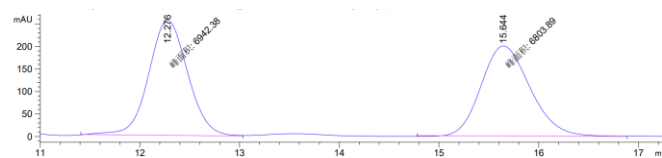
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.215	MM	0.3791	4966.26855	218.34009	50.1966
2	12.195	BB	0.4178	4927.36523	179.76183	49.8034

### Chiral HPLC chromatogram of 7ar



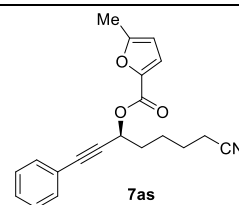
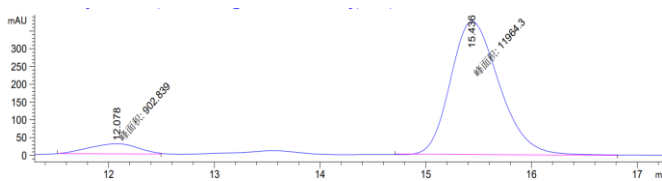
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.592	MM	0.4498	735.67480	27.26163	5.4643
2	13.018	BB	0.5765	1.27277e4	334.03625	94.5357

### Chiral HPLC chromatogram of racemic 7as



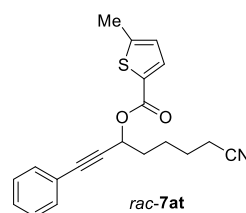
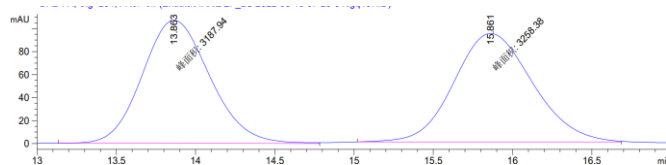
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.276	MM	0.4516	6942.37939	256.18973	50.5037
2	15.644	MM	0.5668	6803.88965	200.06252	49.4963

### Chiral HPLC chromatogram of 7as



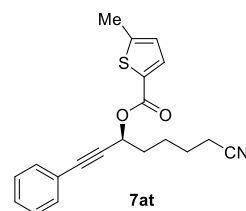
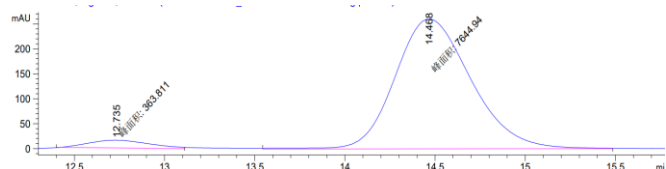
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.078	MM	0.5319	902.83875	28.29081	7.0166
2	15.436	MM	0.5321	1.19643e4	374.72519	92.9834

### Chiral HPLC chromatogram of racemic 7at



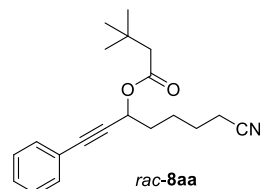
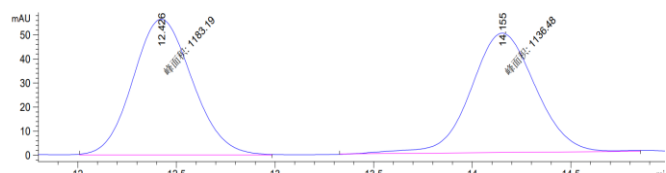
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.863	MM	0.4959	3187.93848	107.13504	49.4536
2	15.861	MM	0.5755	3258.38452	94.35612	50.5464

### Chiral HPLC chromatogram of 7at



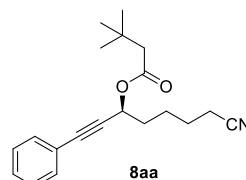
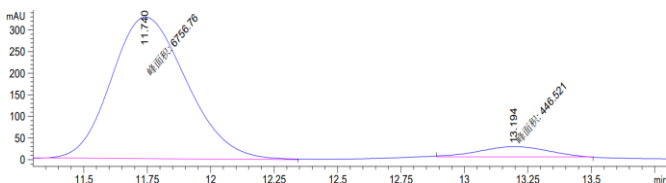
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.735	MM	0.3902	363.81088	15.54080	4.5427
2	14.468	MM	0.4890	7644.94287	260.55466	95.4573

### Chiral HPLC chromatogram of racemic 8aa



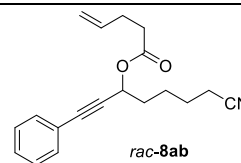
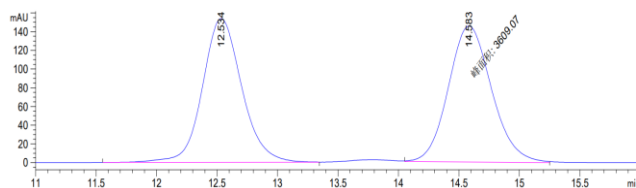
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.426	MM	0.3497	1183.19360	56.39409	51.0068
2	14.155	MM	0.3817	1136.48376	49.62833	48.9932

### Chiral HPLC chromatogram of 8aa



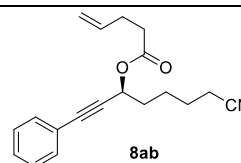
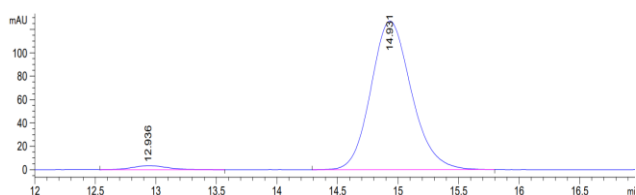
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.740	MM	0.3439	6756.75977	327.43231	93.8011
2	13.194	MM	0.3141	446.52109	23.69547	6.1989

### Chiral HPLC chromatogram of racemic 8ab



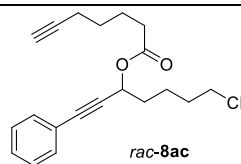
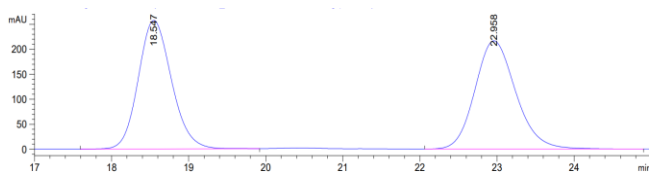
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.534	BB	0.3447	3459.84814	153.67183	48.9445
2	14.583	MM	0.4135	3609.06934	145.47578	51.0555

### Chiral HPLC chromatogram of 8ab



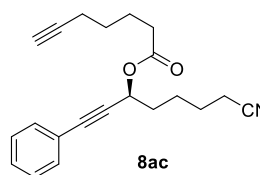
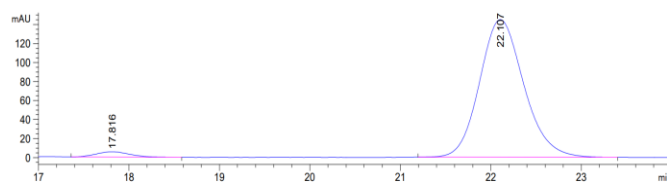
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.936	BB	0.2725	67.93878	3.37998	2.2541
2	14.931	BB	0.3566	2946.12598	126.99804	97.7459

### Chiral HPLC chromatogram of racemic 8ac



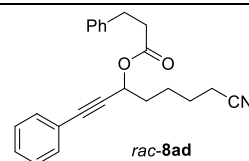
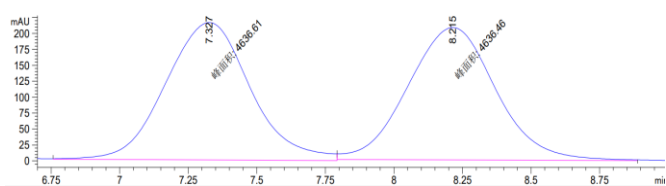
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.547	BB	0.4609	7687.93359	257.09119	49.1075
2	22.958	BB	0.5632	7967.37744	216.57588	50.8925

### Chiral HPLC chromatogram of 8ac



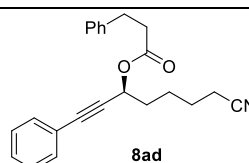
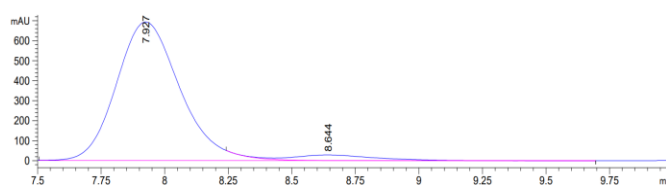
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.816	BB	0.3316	146.14143	5.61608	2.8823
2	22.107	BB	0.5264	4924.20850	144.93526	97.1177

### Chiral HPLC chromatogram of racemic 8ad



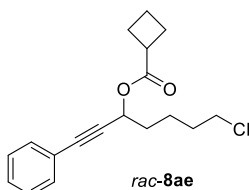
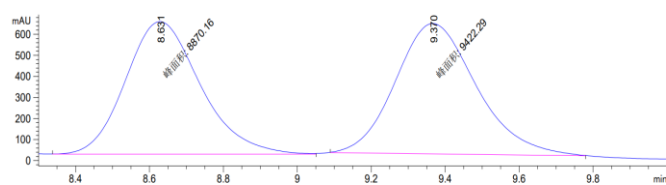
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.327	MM	0.3585	4636.60938	215.55452	50.0008
2	8.215	MM	0.3719	4636.46045	207.77258	49.9992

### Chiral HPLC chromatogram of 8ad



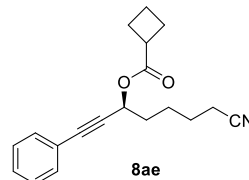
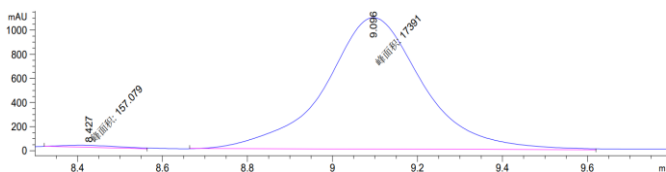
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.927	VV R	0.2673	1.20724e4	692.95215	94.9988
2	8.644	VB E	0.3304	635.54791	27.82935	5.0012

### Chiral HPLC chromatogram of racemic 8ae



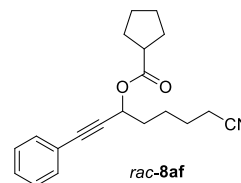
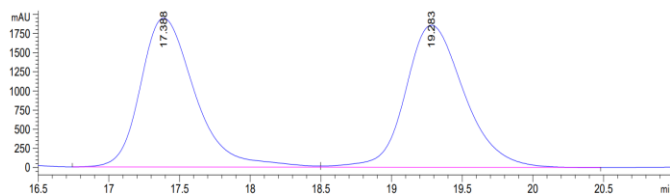
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.631	MM	0.2347	8870.16113	629.81329	48.4908
2	9.370	MM	0.2534	9422.28613	619.62085	51.5092

### Chiral HPLC chromatogram of 8ae



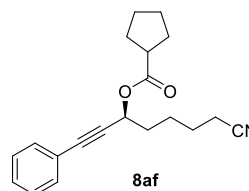
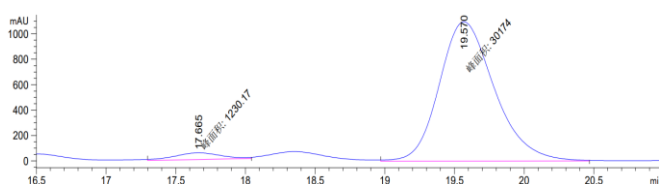
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.427	MM	0.1584	157.07950	16.53003	0.8951
2	9.096	MM	0.2660	1.73910e4	1089.86670	99.1049

### Chiral HPLC chromatogram of racemic 8af



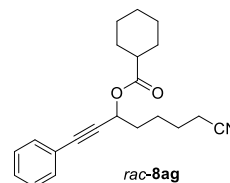
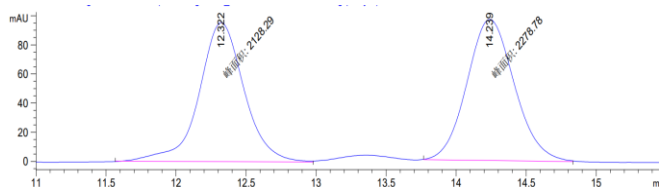
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	17.388	BV	0.4099	5.19097e4	1941.71399	49.2249	
2	19.283	VB	0.4428	5.35444e4	1854.62769	50.7751	

### Chiral HPLC chromatogram of 8af



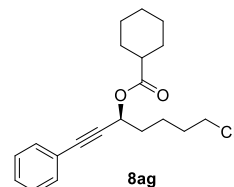
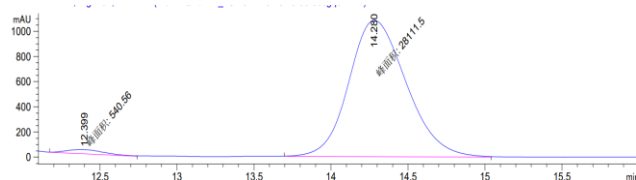
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	17.665	MM	0.3910	1230.17249	52.44139	3.9172	
2	19.570	MM	0.4586	3.01740e4	1096.54919	96.0828	

### Chiral HPLC chromatogram of racemic 8ag



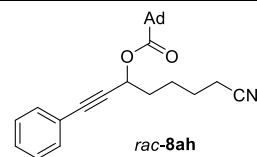
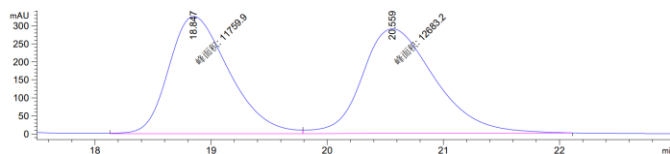
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	12.322	MM	0.3717	2128.29297	95.43626	48.2927	
2	14.239	MM	0.3919	2278.77881	96.92269	51.7073	

### Chiral HPLC chromatogram of 8ag



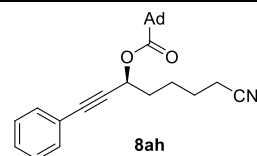
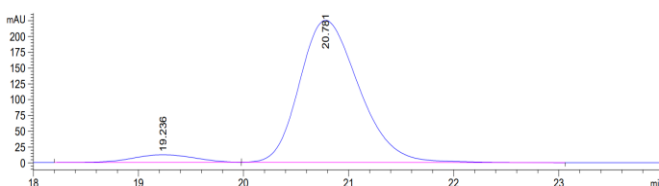
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	12.399	MM	0.2713	540.56030	33.20974	1.8866	
2	14.280	MM	0.4323	2.81115e4	1083.74011	98.1134	

### Chiral HPLC chromatogram of racemic 8ah



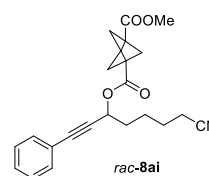
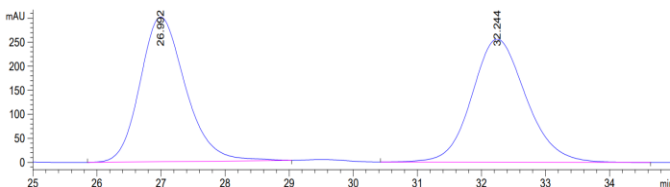
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.847	MM	0.6019	1.17599e4	325.62805	48.1113
2	20.559	MM	0.7280	1.26832e4	290.38092	51.8887

### Chiral HPLC chromatogram of 8ah



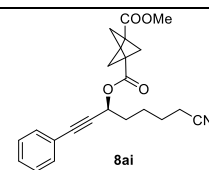
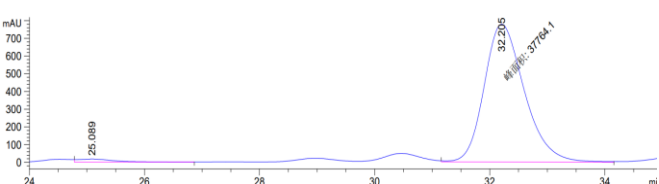
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.236	BB	0.6274	475.99701	11.78153	5.1378
2	20.781	BB	0.6104	8788.65918	224.66734	94.8622

### Chiral HPLC chromatogram of racemic 8ai



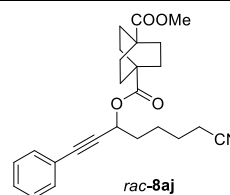
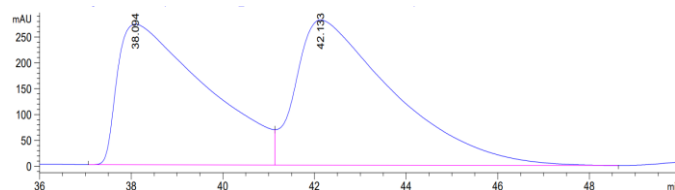
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.992	BB	0.7555	1.48022e4	301.13348	49.5401
2	32.244	BB	0.9083	1.50770e4	256.29480	50.4599

### Chiral HPLC chromatogram of 8ai



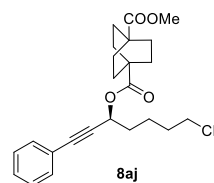
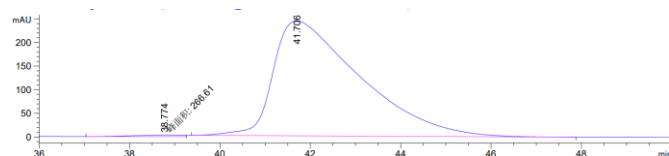
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.089	VB	0.6244	761.21735	17.46788	1.9759
2	32.205	MM	0.8092	3.77641e4	777.83673	98.0241

### Chiral HPLC chromatogram of racemic 8aj



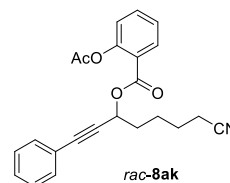
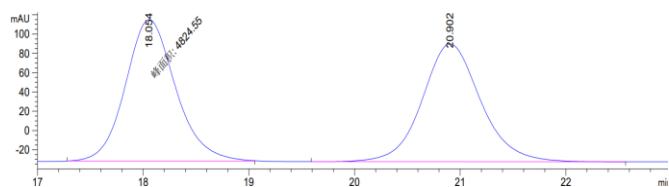
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.094	BV	1.8621	3.65659e4	271.70401	46.9454
2	42.133	VB	1.9985	4.13245e4	280.54694	53.0546

### Chiral HPLC chromatogram of 8aj



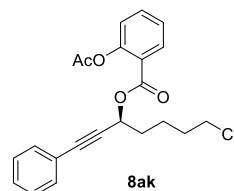
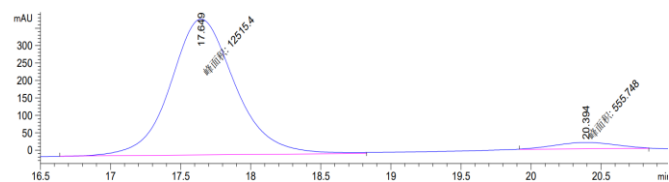
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.774	MM	1.3073	266.61023	3.39895	0.8164
2	41.706	BB	1.8562	3.23909e4	243.76732	99.1836

### Chiral HPLC chromatogram of racemic 8ak



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.054	MM	0.5485	4824.55420	146.59010	50.6431
2	20.902	BB	0.5872	4702.01660	122.12465	49.3569

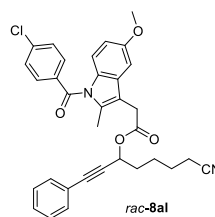
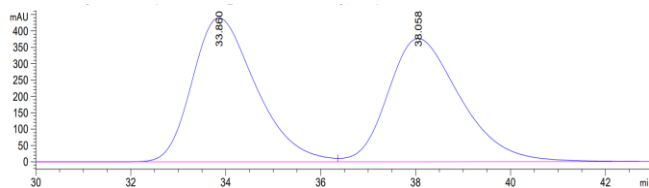
### Chiral HPLC chromatogram of 8ak



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.649	MM	0.5355	1.25154e4	389.52802	95.7483
2	20.394	MM	0.5067	555.74762	18.27933	4.2517

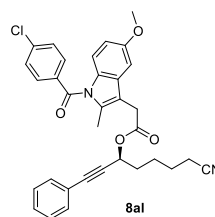
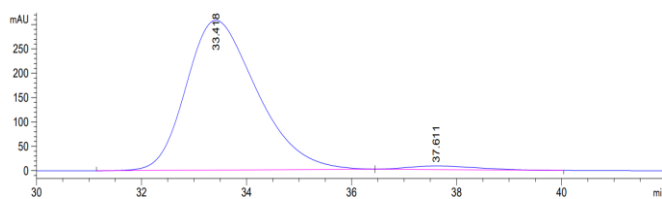


### Chiral HPLC chromatogram of racemic 8al



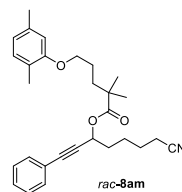
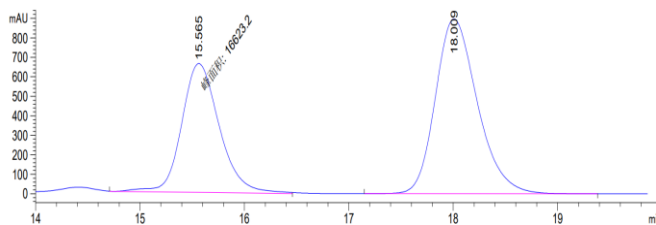
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.860	BV	1.4253	4.10386e4	439.52249	50.6983
2	38.058	VBA	1.6213	3.99081e4	376.28818	49.3017

### Chiral HPLC chromatogram of 8al



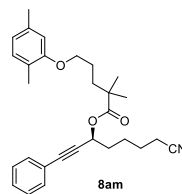
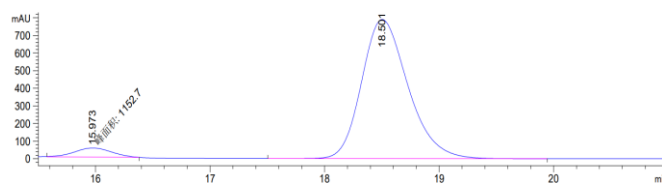
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.418	BB	1.4282	2.87295e4	307.43829	97.7558
2	37.611	BB	1.1079	659.53448	7.21876	2.2442

### Chiral HPLC chromatogram of racemic 8am



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.565	MM	0.4191	1.66232e4	661.09570	49.1716
2	18.009	BB	0.4291	2.49698e4	896.16803	50.8284

### Chiral HPLC chromatogram of 8am



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.973	MM	0.3731	1152.70422	51.49614	4.9364
2	18.501	BB	0.4320	2.21983e4	789.67834	95.0636