

Supporting Information to

**Copper-catalyzed cascade annulation between α -bromocarbonyls and biaryl or
(*Z*)-arylvinyllacetylenes enabling a direct synthesis of dibenzocycloheptanes and
related compounds**

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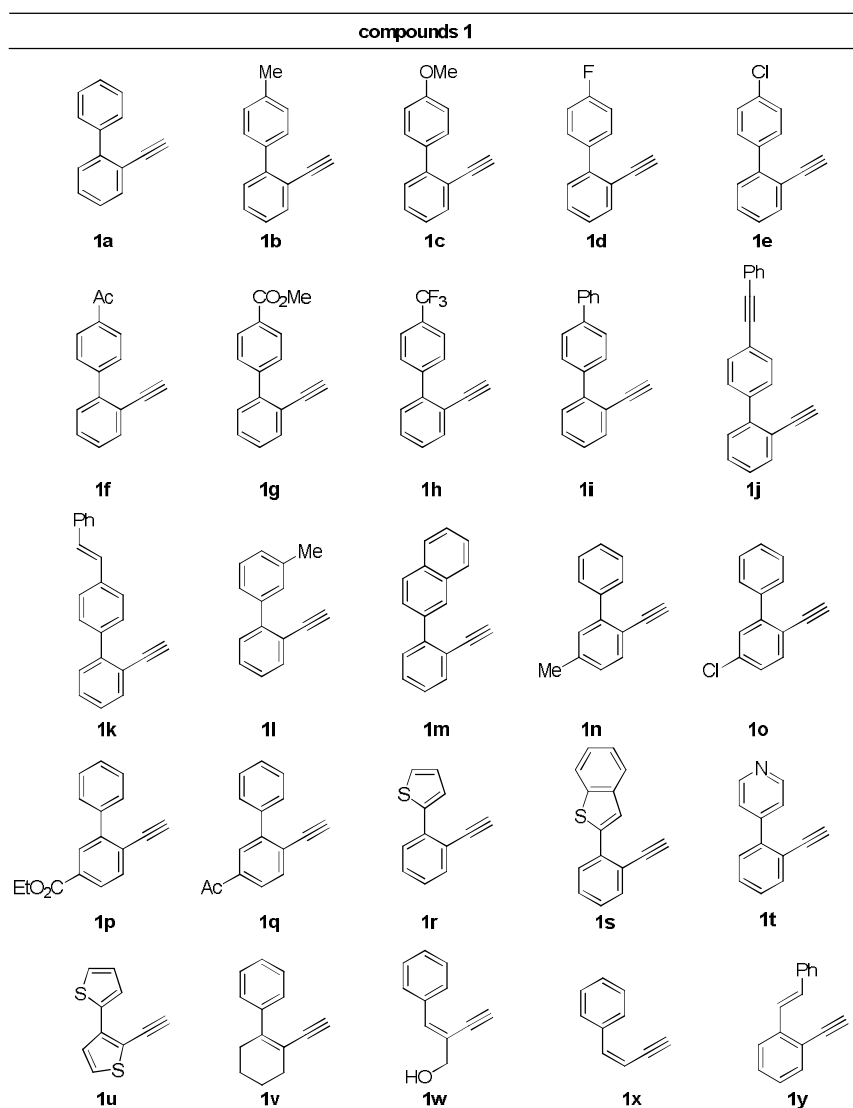
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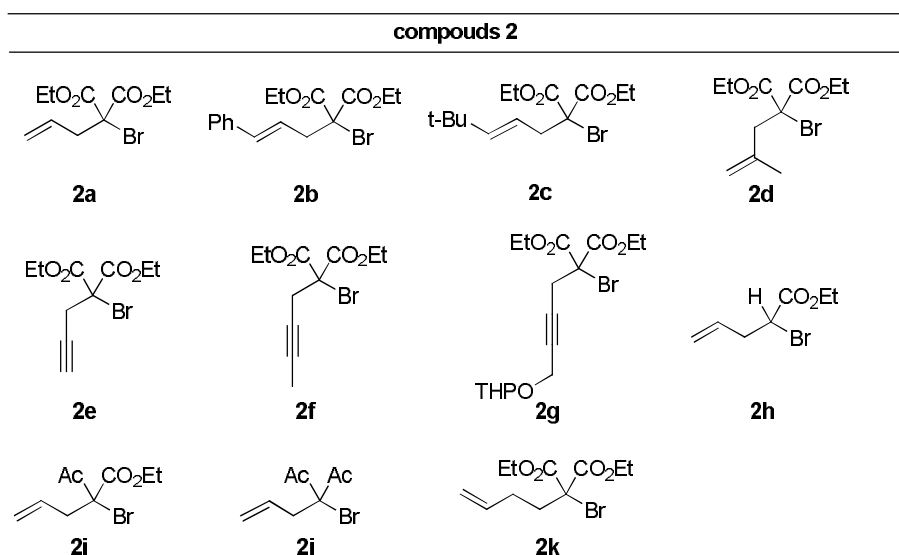
General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. ^1H , ^{13}C , and ^{19}F NMR spectra were measured on a 600 or 400 MHz NMR spectrometer using CDCl_3 as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relative to TMS, and the coupling constants are given in hertz. High-resolution mass spectrometry (HRMS) analyses were carried out using a TOF MS instrument with ESI source. Column chromatography was performed using silica gel (300–400 mesh). The starting materials **1a–1v**^{1,2} were prepared from *ortho*-bromophenylacetylene compounds via the Suzuki-Miyaura coupling,² exemplified by the synthesis of **1a**. The starting materials **2** were prepared from γ,δ -unsaturated carbonyls via the $\text{Mg}(\text{ClO}_4)_2$ -catalyzed α -bromination.³



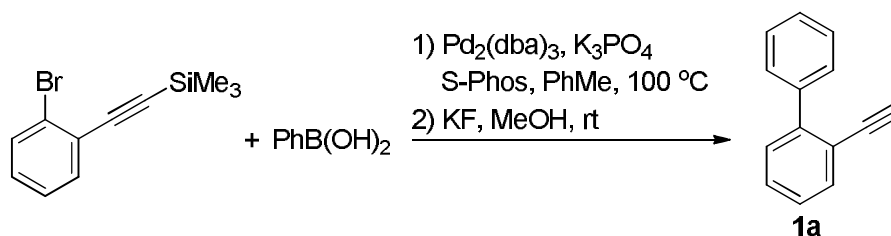
¹ (a) M. L. Hossain, F. Ye, Z. Liu, Y. Xia, Y. Shi, L. Zhou, Y. Zhang and J. Wang, *J. Org. Chem.*, 2014, **79**, 8689; (b) B. Seo, W. H. Jeon, J. Kim, S. Kim and P. H. Lee, *J. Org. Chem.*, 2015, **80**, 722.

² J. Panteleev, K. Geyer, A. Aguilar-Aguilar, L. Wang and M. Lautens, *Org. Lett.*, 2010, **12**, 5092.

³ (a) D. Yang, Y.-L. Yan and B. Lui, *J. Org. Chem.*, 2002, **67**, 7429; (b) W. Yang, L. Huang, H. Liu, W. Wang and H. Li, *Chem. Commun.*, 2013, **49**, 4667.

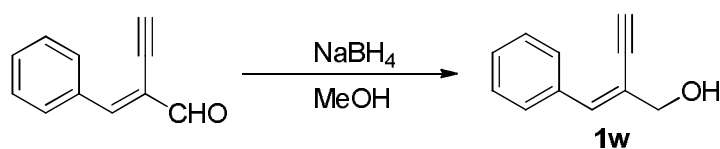


Experimental procedure² for the preparation of biarylacetylene **1a**:



To a mixture of $\text{Pd}_2(\text{dba})_3$ (22.9 mg, 0.05 mmol), S-Phos (41 mg, 0.2 mmol), K_3PO_4 (2.1 g, 10 mmol), and $\text{PhB}(\text{OH})_2$ (732 mg, 6.0 mmol) in 10 mL of toluene was added 1-(trimethylsilyl)ethynyl-2-bromobenzene⁴ (1.27 g, 5.0 mmol). After stirring at 100 °C under N_2 for 5 h, the reaction mixture was quenched with water, then extracted with EtOAc, washed with brine, dried over Na_2SO_4 , and concentrated. To the residue thus obtained in 10 mL of MeOH was added KF (320 mg, 5.5 mmol). After stirring at room temperature for 3 h, the reaction mixture was quenched with water, then extracted with EtOAc, washed with brine, dried over Na_2SO_4 and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:100) provided 710 mg of **1a**^{1a} (yield: 80%) as a colorless oil. ^1H NMR (600 MHz, CDCl_3): δ 7.62–7.60 (m, 1H), 7.59–7.57 (m, 2H), 7.44–7.37 (m, 5H), 7.31–7.28 (m, 1H), 3.03 (s, 1H); ^{13}C NMR (151 MHz, CDCl_3): δ 144.4, 140.2, 133.8, 129.6, 129.2, 128.9, 128.0, 127.5, 127.0, 120.4, 83.1, 80.1.

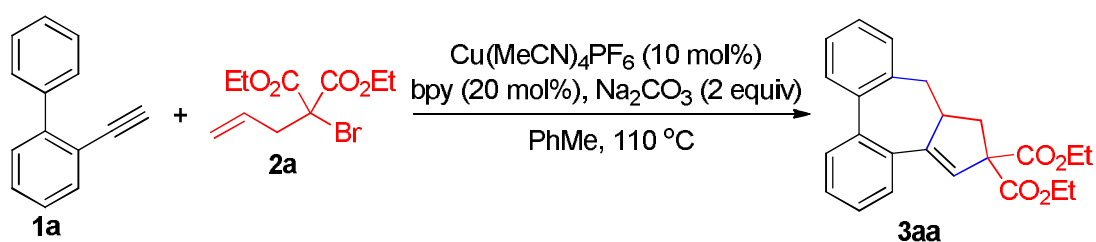
Experimental procedure for the preparation of **1w**:



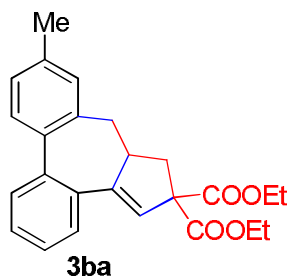
⁴ A. Odedra, C.-J. Wu, T. B. Pratap, C.-W. Huang, Y.-F. Ran and R.-S. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 3406.

To a solution of (*E*)-2-benzylidenebut-3-ynal⁵ (780 mg, 5.0 mmol) in 10 mL of MeOH was added NaBH₄ (228 mg, 6.0 mmol) at 0 °C. After stirring at 0 °C for 1 h, the reaction mixture was quenched with saturated NaHCO₃ solution, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:10) gave 750 mg of **1w** (yield: 95%) as a colorless oil. ¹H NMR (600 MHz, CDCl₃): δ 7.83–7.81 (m, 2H), 7.36–7.33 (m, 2H), 7.31–7.28 (m, 1H), 6.84 (s, 1H), 4.29 (s, 2H), 3.40 (s, 1H); ¹³C NMR (151 MHz, CDCl₃): δ 135.8, 135.4, 128.7, 128.6, 128.3, 120.1, 85.2, 81.4, 67.2; HRMS (ESI) calcd for C₁₁H₁₁O (M + H)⁺ 159.0810, found 159.0805.

General procedure for the copper-catalyzed cascade annulation between α-bromocarbonyls and biaryl or (*Z*)-arylvinylnacetylenes:



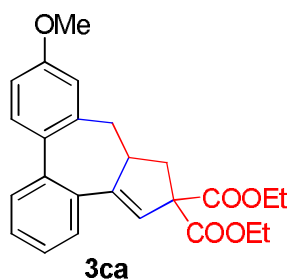
To a mixture of Cu(MeCN)₄PF₆ (9.0 mg, 0.025 mmol), bpy (7.8 mg, 0.05 mmol) and Na₂CO₃ (53.0 mg, 0.5 mmol) was added a solution of **1a** (44.5 mg, 0.25 mmol) and **2a** (83.4 mg, 0.30 mmol) in 5 mL of PhMe under a nitrogen atmosphere. After stirring at 110 °C for 12 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:10) gave 77 mg of **3aa** (yield: 82%) as a white solid, mp 86–88 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.46–7.40 (m, 2H), 7.34–7.28 (m, 4H), 7.25–7.21 (m, 1H), 7.18–7.14 (m, 1H), 5.67–5.64 (m, 1H), 4.24–4.17 (m, 2H), 4.09–4.02 (m, 2H), 3.81–3.74 (m, 1H), 3.04–2.98 (m, 1H), 2.75–2.71 (m, 1H), 2.53–2.48 (m, 1H), 2.13–2.07 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 170.9, 170.5, 151.3, 140.9, 139.7, 136.1, 135.9, 130.3, 130.0, 128.6, 128.5, 127.4, 127.2, 127.0, 127.0, 125.5, 65.3, 61.4, 61.2, 53.9, 37.4, 35.2, 14.0, 13.8; HRMS (ESI) calcd for C₂₄H₂₅O₄ (M + H)⁺ 377.1753, found 377.1745.



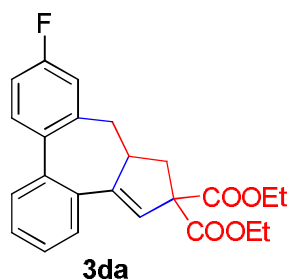
Compound 3ba. 63 mg, 65% yield; colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 7.44–7.39 (m, 2H), 7.32–7.26 (m, 2H), 7.21–7.18 (m, 1H), 7.12–7.09 (m, 1H), 6.99–6.96 (m, 1H), 5.68–5.63 (m,

⁵ W. Li and J. Zhang, *Org. Lett.*, 2014, **16**, 162.

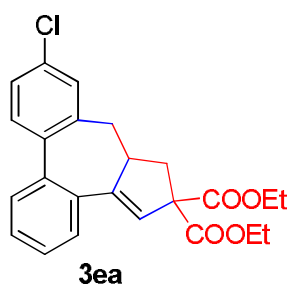
1H), 4.24–4.18 (m, 2H), 4.12–4.04 (m, 2H), 3.79–3.73 (m, 1H), 3.02–2.97 (m, 1H), 2.74–2.70 (m, 1H), 2.49–2.45 (m, 1H), 2.35 (s, 3H), 2.14–2.08 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 171.0, 170.6, 151.5, 139.7, 138.0, 136.9, 136.0, 135.9, 131.1, 129.9, 128.6, 128.5, 127.7, 127.1, 127.0, 125.3, 65.3, 61.5, 61.2, 53.7, 37.5, 35.2, 21.1, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 391.1909, found 391.1905.



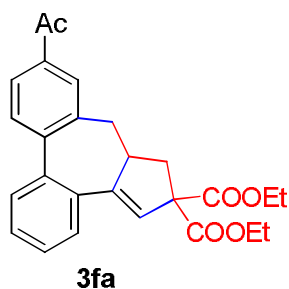
Compound 3ca. 74 mg, 73% yield; white solid, mp 102–104 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.41–7.38 (m, 2H), 7.30–7.26 (m, 2H), 7.24–7.20 (m, 1H), 6.85–6.81 (m, 1H), 6.74–6.71 (m, 1H), 5.67–5.65 (m, 1H), 4.24–4.18 (m, 2H), 4.12–4.05 (m, 2H), 3.82 (s, 3H), 3.78–3.74 (m, 1H), 3.03–2.98 (m, 1H), 2.76–2.71 (m, 1H), 2.50–2.45 (m, 1H), 2.13–2.07 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.9, 170.5, 158.6, 151.4, 139.4, 137.6, 135.7, 133.5, 131.1, 128.5, 128.4, 127.0, 126.9, 125.2, 116.1, 111.7, 65.2, 61.4, 61.2, 55.2, 53.5, 37.6, 35.4, 14.0, 13.8; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 407.1858, found 407.1850.



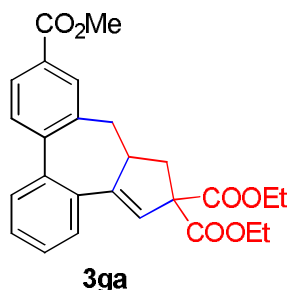
Compound 3da. 70 mg, 71% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.44–7.39 (m, 2H), 7.34–7.31 (m, 1H), 7.29–7.26 (m, 2H), 7.01–6.97 (m, 1H), 6.92–6.89 (m, 1H), 5.68–5.65 (m, 1H), 4.25–4.18 (m, 2H), 4.13–4.06 (m, 2H), 3.81–3.73 (m, 1H), 3.02–2.97 (m, 1H), 2.77–2.73 (m, 1H), 2.52–2.46 (m, 1H), 2.10–2.04 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.8, 170.4, 161.2 (d, $J = 246.7$ Hz), 150.9, 138.8, 138.4 (d, $J = 7.6$ Hz), 137.0 (d, $J = 3.1$ Hz), 135.8, 131.5 (d, $J = 8.2$ Hz), 128.6, 128.6, 127.5, 127.1, 125.7, 117.0 (d, $J = 21.1$ Hz), 113.7 (d, $J = 20.9$ Hz), 65.3, 61.5, 61.3, 53.6, 37.4, 35.2, 14.1, 13.9; ^{19}F NMR (565 MHz, CDCl_3): δ -115.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4\text{F}$ ($\text{M} + \text{H}$) $^+$ 395.1659, found 395.1649.



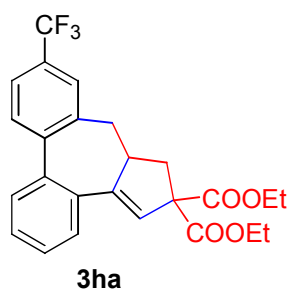
Compound 3ea. 75 mg, 73% yield; white solid, mp 100–102 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.45–7.39 (m, 2H), 7.36–7.33 (m, 1H), 7.29–7.27 (m, 2H), 7.24–7.21 (m, 1H), 7.19–7.15 (m, 1H), 5.70–5.65 (m, 1H), 4.26–4.18 (m, 2H), 4.15–4.05 (m, 2H), 3.83–3.76 (m, 1H), 3.01–2.95 (m, 1H), 2.79–2.74 (m, 1H), 2.51–2.46 (m, 1H), 2.09–2.03 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.16 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.3, 150.7, 139.4, 138.5, 138.0, 135.8, 132.7, 131.2, 130.0, 128.6, 128.5, 127.7, 127.1, 127.0, 125.8, 65.2, 61.5, 61.3, 53.6, 37.3, 35.0, 14.0, 13.8; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4\text{Cl}$ ($\text{M} + \text{H}$) $^+$ 411.1363, found 411.1358.



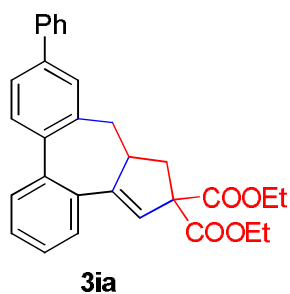
Compound 3fa. 73 mg, 70% yield; white solid, mp 111–113 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.92–7.86 (m, 1H), 7.81–7.72 (m, 1H), 7.49–7.44 (m, 2H), 7.41–7.37 (m, 2H), 7.32–7.29 (m, 1H), 5.71–5.67 (m, 1H), 4.26–4.20 (m, 2H), 4.13–4.01 (m, 2H), 3.88–3.77 (m, 1H), 3.07–3.00 (m, 1H), 2.79–2.72 (m, 1H), 2.63 (s, 3H), 2.63–2.59 (m, 1H), 2.10–2.03 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 198.0, 170.7, 170.3, 150.6, 146.1, 138.6, 136.7, 136.0, 135.7, 130.3, 129.9, 128.8, 128.7, 128.3, 127.4, 127.2, 126.2, 65.2, 61.5, 61.3, 53.7, 37.4, 35.2, 26.7, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 419.1858, found 419.1844.



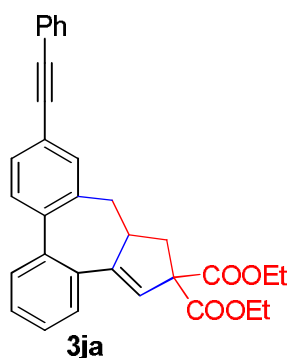
Compound 3ga. 76 mg, 70% yield; white solid, mp 96–98 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.99–7.95 (m, 1H), 7.86–7.84 (m, 1H), 7.47–7.44 (m, 2H), 7.38–7.36 (m, 2H), 7.31–7.29 (m, 1H), 5.69–5.67 (m, 1H), 4.24–4.19 (m, 2H), 4.10–4.02 (m, 2H), 3.93 (s, 3H), 3.83–3.79 (m, 1H), 3.05–3.01 (m, 1H), 2.77–2.73 (m, 1H), 2.62–2.59 (m, 1H), 2.05–2.10 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.4, 167.0, 150.7, 145.8, 138.6, 136.4, 136.0, 131.3, 130.1, 128.8, 128.7, 128.6, 128.3, 128.2, 127.2, 126.1, 65.2, 61.5, 61.3, 53.7, 52.1, 37.3, 35.1, 14.0, 13.8; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{O}_6$ ($\text{M} + \text{H}$) $^+$ 435.1808, found 435.1804.



Compound 3ha. 84 mg, 76% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.57–7.54 (m, 1H), 7.47–7.44 (m, 2H), 7.43–7.37 (m, 3H), 7.32–7.30 (m, 1H), 5.72–5.65 (m, 1H), 4.26–4.18 (m, 2H), 4.11–4.03 (m, 2H), 3.85–3.79 (m, 1H), 3.06–3.02 (m, 1H), 2.82–2.77 (m, 1H), 2.61–2.57 (m, 1H), 2.07–2.01 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.11 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.3, 150.3, 144.7, 138.3, 137.1, 136.0, 130.3, 129.1 (q, $J = 32.3$ Hz), 128.8, 128.7, 128.3, 127.2, 126.8 (q, $J = 4.0$ Hz), 126.2, 124.1 (q, $J = 272.2$ Hz), 123.9 (q, $J = 4.2$ Hz), 65.3, 61.6, 61.3, 53.7, 37.3, 35.2, 14.0, 13.8; ^{19}F NMR (565 MHz, CDCl_3): δ -62.2; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_4\text{F}_3$ ($\text{M} + \text{H}$) $^+$ 445.1627, found 445.1624.

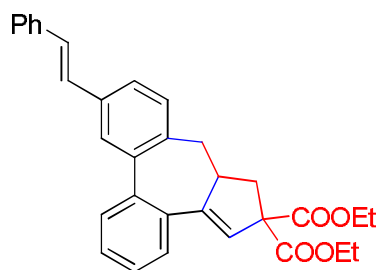


Compound 3ia. 87 mg, 77% yield; white solid, mp 153–155 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 7.66–7.60 (m, 2H), 7.56–7.52 (m, 1H), 7.51–7.47 (m, 1H), 7.47–7.42 (m, 3H), 7.42–7.32 (m, 4H), 7.32–7.28 (m, 1H), 5.72–5.65 (m, 1H), 4.27–4.17 (m, 2H), 4.10–4.00 (m, 2H), 3.85–3.78 (m, 1H), 3.11–3.02 (m, 1H), 2.79–2.73 (m, 1H), 2.65–2.55 (m, 1H), 2.17–2.10 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.10 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.9, 170.5, 151.2, 140.7, 140.0, 140.0, 139.3, 136.6, 136.0, 130.5, 128.9, 128.7, 128.7, 128.6, 127.5, 127.3, 127.1, 127.1, 125.7, 125.6, 65.3, 61.5, 61.2, 53.8, 37.5, 35.5, 14.1, 13.8; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{29}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 453.2066, found 453.2062.



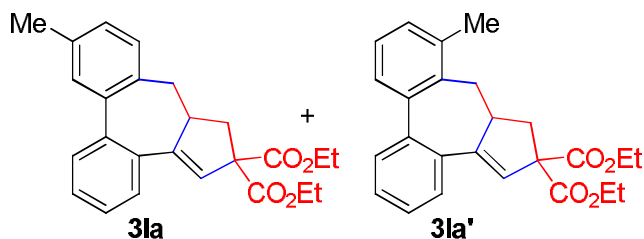
Compound 3ja. 62 mg, 52% yield; white solid, mp 152–154 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3): δ 7.56–7.54 (m, 2H), 7.48–7.43 (m, 3H), 7.37–7.34 (m, 5H), 7.30–7.28 (m, 2H), 5.70–5.67 (m, 1H),

4.24–4.18 (m, 2H), 4.12–4.04 (m, 2H), 3.83–3.78 (m, 1H), 3.03–2.98 (m, 1H), 2.80–2.73 (m, 1H), 2.56–2.51 (m, 1H), 2.14–2.07 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.8, 170.5, 150.9, 141.2, 139.0, 136.4, 136.0, 133.3, 131.6, 130.3, 130.1, 128.7, 128.6, 128.3, 128.2, 127.8, 127.1, 125.9, 123.3, 122.0, 89.7, 89.4, 65.3, 61.5, 61.3, 53.7, 37.5, 35.1, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{29}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 477.2066, found 477.2043.

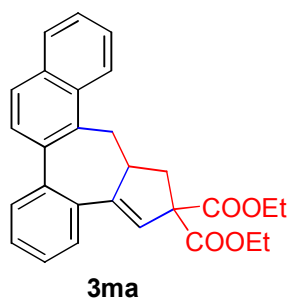


3ka

Compound 3ka. 68 mg, 57% yield; white solid, mp 107–119 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.54–7.52 (m, 2H), 7.47–7.45 (m, 2H), 7.44–7.41 (m, 1H), 7.39–7.34 (m, 4H), 7.32–7.28 (m, 3H), 7.14–7.10 (m, 2H), 5.71–5.66 (m, 1H), 4.23–4.19 (m, 2H), 4.09–4.02 (m, 2H), 3.82–3.77 (m, 1H), 3.06–3.02 (m, 1H), 2.80–2.75 (m, 1H), 2.57–2.53 (m, 1H), 2.16–2.11 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.9, 170.5, 151.2, 140.4, 139.4, 137.3, 136.5, 136.3, 135.9, 130.4, 128.7, 128.7, 128.6, 128.6, 128.5, 128.3, 127.6, 127.5, 127.1, 126.5, 125.6, 125.1, 65.3, 61.5, 61.2, 53.7, 37.6, 35.4, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{31}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 479.2222, found 479.2213.

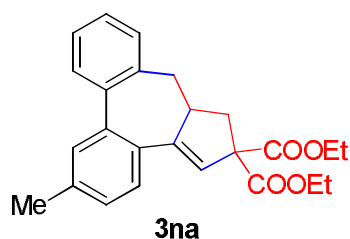


Compound 3la and 3la'. 75 mg, 77% yield (**3la:3la'** = 2.3:1); colorless oil; ^1H NMR (600 MHz, CDCl_3) data of **3la**: δ 7.44–7.40 (m, 2H), 7.33–7.31 (m, 1H), 7.28–7.26 (m, 1H), 7.18–7.15 (m, 1H), 7.14–7.11 (m, 2H), 5.68–5.66 (m, 1H), 4.23–4.20 (m, 2H), 4.08–4.05 (m, 2H), 3.81–3.76 (m, 1H), 2.92–2.87 (m, 1H), 2.75–2.73 (m, 1H), 2.73–2.71 (m, 1H), 2.37 (s, 3H), 2.03–1.98 (m, 1H), 1.28–1.26 (m, 3H), 1.14–1.12 (m, 3H); ^{13}C NMR (151 MHz, CDCl_3) data of **3la**: δ 170.9, 170.5, 151.6, 141.5, 140.3, 136.0, 135.8, 134.5, 129.3, 128.9, 128.4, 128.2, 127.3, 126.7, 126.5, 124.9, 65.3, 61.5, 61.2, 54.2, 37.3, 29.3, 20.8, 14.1, 13.8; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 391.1909, found 391.1901.

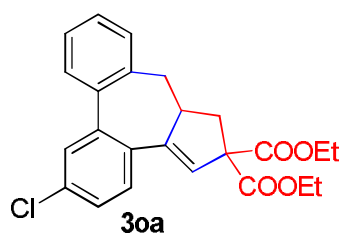


Compound 3ma. 75 mg, 70% yield; white solid, mp 107–119 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.12–8.09 (m, 1H), 7.84–7.82 (m, 1H), 7.79–7.77 (m, 1H), 7.56–7.52 (m, 2H), 7.48–7.44 (m, 3H), 7.37–7.32 (m, 2H), 5.68–5.64 (m, 1H), 4.24–4.18 (m, 2H), 4.00–3.96 (m, 1H), 3.93–3.85 (m, 2H), 3.53–3.47 (m, 1H), 3.03–2.98 (m, 1H), 2.85–2.81 (m, 1H), 1.96–1.91 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 0.92 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.4, 151.5, 140.3, 138.5, 136.4, 132.8, 132.8, 132.3, 129.2, 128.5, 128.5, 128.1, 127.5, 127.1, 126.9, 126.4, 125.4, 124.8, 123.8, 65.5, 61.4, 61.0, 55.8, 37.7, 28.1, 14.0, 13.6; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{26}\text{O}_4\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 449.1729, found 449.1723.

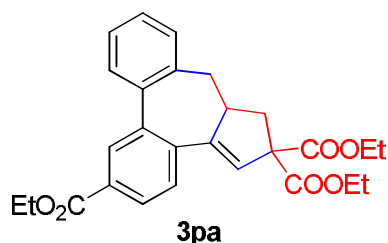
Crystal data for **3ma** ($\text{C}_{28}\text{H}_{26}\text{O}_4$, 426.49): monoclinic, space group $P2_1/c$, $a = 31.220(4)$ Å, $b = 10.5893(12)$ Å, $c = 13.5925(15)$ Å, $U = 4493.6(9)$ Å 3 , $Z = 4$, $T = 296(2)$ K, absorption coefficient 0.042 mm^{-1} , reflections collected 82914, independent reflections 7873 [$R(\text{int}) = 0.0842$], refinement by full-matrix least-squares on F^2 , data/restraints/parameters 7873/0/289, goodness-of-fit on $F^2 = 2.859$, final R indices [$I > 2s(I)$] $R_1 = 0.1764$, $wR_2 = 0.4273$, R indices (all data) $R_1 = 0.1945$, $wR_2 = 0.4324$, largest diff peak and hole 0.462 and -0.605 $\text{e} \cdot \text{\AA}^{-3}$. Crystallographic data for the structure **3ma** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1498312.



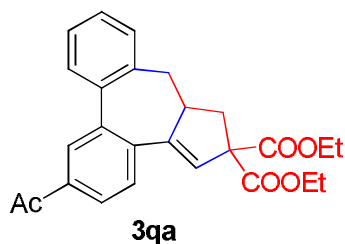
Compound 3na. 76 mg, 78% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.30–7.27 (m, 3H), 7.23–7.20 (m, 1H), 7.19–7.17 (m, 1H), 7.16–7.13 (m, 2H), 5.64–5.61 (m, 1H), 4.24–4.17 (m, 2H), 4.09–4.03 (m, 2H), 3.76–3.71 (m, 1H), 3.02–2.98 (m, 1H), 2.74–2.70 (m, 1H), 2.52–2.49 (m, 1H), 2.42 (s, 3H), 2.10–2.05 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.9, 170.6, 151.3, 141.0, 139.5, 138.2, 136.2, 133.1, 130.2, 129.9, 129.4, 128.1, 127.1, 127.0, 126.9, 125.2, 65.2, 61.4, 61.1, 53.7, 37.4, 35.2, 21.3, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{27}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 391.1909, found 391.1905.



Compound 3oa. 79 mg, 77% yield; white solid, mp 99–101 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.45–7.43 (m, 1H), 7.32–7.28 (m, 3H), 7.28–7.26 (m, 1H), 7.23–7.20 (m, 1H), 7.18–7.15 (m, 1H), 5.67–5.64 (m, 1H), 4.23–4.18 (m, 2H), 4.10–4.04 (m, 2H), 3.78–3.72 (m, 1H), 3.01–2.96 (m, 1H), 2.75–2.70 (m, 1H), 2.54–2.50 (m, 1H), 2.10–2.04 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.4, 150.2, 141.5, 139.7, 136.2, 134.4, 134.3, 130.4, 129.9, 128.6, 128.3, 127.8, 127.3, 127.2, 126.1, 65.3, 61.5, 61.3, 53.7, 37.4, 35.1, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4\text{Cl}$ ($\text{M} + \text{H}$) $^+$ 411.1363, found 411.1357.

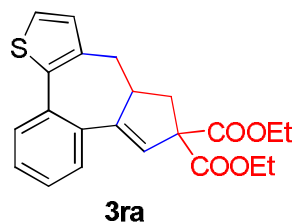


Compound 3pa. 90 mg, 80% yield; white solid, mp 97–109 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.16–8.11 (m, 1H), 8.02–7.99 (m, 1H), 7.37–7.33 (m, 3H), 7.28–7.26 (m, 1H), 7.20–7.15 (m, 1H), 5.74–5.69 (m, 1H), 4.43–4.38 (m, 2H), 4.24–4.19 (m, 2H), 4.11–4.05 (m, 2H), 3.83–3.75 (m, 1H), 3.00–2.95 (m, 1H), 2.78–2.72 (m, 1H), 2.55–2.50 (m, 1H), 2.14–2.09 (m, 1H), 1.41 (t, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.7, 170.3, 166.4, 150.5, 140.4, 140.0, 140.0, 136.0, 130.7, 130.3, 130.2, 129.8, 128.5, 127.7, 127.2, 126.4, 65.4, 61.6, 61.3, 61.1, 53.8, 37.5, 35.1, 14.3, 14.1, 13.9; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{28}\text{O}_6\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 471.1784, found 471.1788.

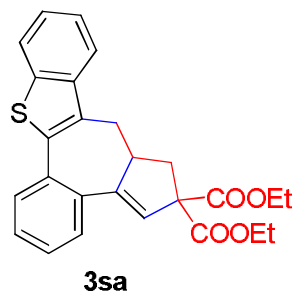


Compound 3qa. 75 mg, 72% yield; white solid, mp 109–111 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.05–8.03 (m, 1H), 7.93–7.91 (m, 1H), 7.40–7.38 (m, 1H), 7.35–7.32 (m, 2H), 7.29–7.27 (m, 1H), 7.20–7.16 (m, 1H), 5.73–5.70 (m, 1H), 4.24–4.20 (m, 2H), 4.10–4.04 (m, 2H), 3.82–3.76 (m, 1H), 3.00–2.96 (m, 1H), 2.78–2.73 (m, 1H), 2.65 (s, 3H), 2.56–2.52 (m, 1H), 2.14–2.09 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 197.7, 170.6, 170.3, 150.4, 140.7, 140.2, 134.0, 137.3, 136.0, 130.4, 130.1, 128.7, 127.8, 127.4, 127.3, 127.2, 126.5,

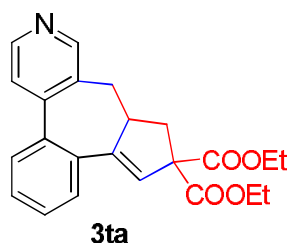
65.4, 61.6, 61.3, 53.8, 37.5, 35.0, 26.7, 14.0, 13.9; HRMS (ESI) calcd for $C_{26}H_{27}O_5$ ($M + H$)⁺ 419.1858, found 419.1851.



Compound 3ra. 67 mg, 70% yield; white solid, mp 106–108 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.61–7.59 (m, 1H), 7.54–7.51 (m, 1H), 7.32–7.29 (m, 1H), 7.23–7.20 (m, 1H), 7.17–7.13 (m, 1H), 6.88–6.85 (m, 1H), 6.00–5.97 (m, 1H), 4.23–4.15 (m, 4H), 3.54–3.48 (m, 1H), 3.03–2.99 (m, 1H), 2.84–2.80 (m, 1H), 2.76–2.72 (m, 1H), 2.30–2.25 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 170.9, 170.7, 151.7, 138.4, 137.5, 133.4, 132.6, 130.9, 128.8, 128.6, 126.9, 125.5, 123.6, 64.8, 61.6, 61.5, 49.3, 39.5, 33.3, 14.1, 14.0; HRMS (ESI) calcd for $C_{22}H_{23}O_4$ S ($M + H$)⁺ 383.1317, found 383.1311.

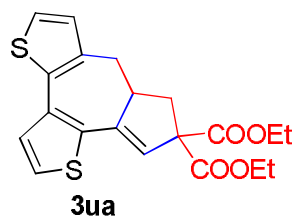


Compound 3sa. 86 mg, 80% yield; white solid, mp 134–136 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.86–7.83 (m, 1H), 7.76–7.71 (m, 2H), 7.61–7.57 (m, 1H), 7.43–7.38 (m, 2H), 7.37–7.35 (m, 1H), 7.34–7.30 (m, 1H), 6.05–6.02 (m, 1H), 4.29–4.23 (m, 2H), 4.19–4.13 (m, 2H), 3.70–3.63 (m, 1H), 3.26–3.22 (m, 1H), 3.02–2.96 (m, 1H), 2.94–2.89 (m, 1H), 2.36–2.30 (m, 1H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 170.8, 170.7, 151.5, 140.9, 138.6, 138.6, 134.5, 132.7, 131.6, 129.5, 128.9, 128.7, 127.7, 125.7, 124.5, 124.2, 122.0, 121.7, 65.0, 61.6, 61.5, 49.5, 39.7, 30.5, 14.1, 13.9; HRMS (ESI) calcd for $C_{26}H_{25}O_4$ S ($M + H$)⁺ 433.1474, found 433.1468.

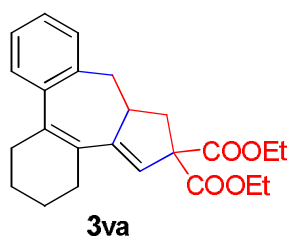


Compound 3ta. 76 mg, 81% yield; white solid, mp 104–106 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.57–8.54 (m, 1H), 8.42–8.39 (m, 1H), 7.49–7.46 (m, 2H), 7.43–7.40 (m, 1H), 7.35–7.32 (m, 1H), 7.24–7.22 (m, 1H), 5.73–5.70 (m, 1H), 4.26–4.18 (m, 2H), 4.12–4.05 (m, 2H), 3.90–3.84 (m, 1H), 2.98–2.94 (m, 1H), 2.82–2.77 (m, 1H), 2.60–2.56 (m, 1H), 2.08–2.03 (m, 1H), 1.27 (t, $J = 7.1$ Hz,

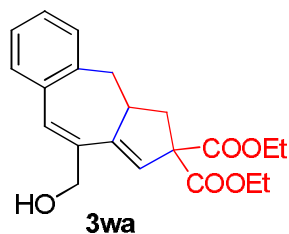
3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.5, 170.2, 150.5, 150.0, 148.8, 148.8, 136.9, 136.1, 131.4, 128.9, 128.8, 128.5, 127.5, 126.9, 123.9, 65.2, 61.6, 61.3, 53.8, 37.4, 32.0, 14.0, 13.9; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{O}_4\text{N}$ ($\text{M} + \text{H}$) $^+$ 378.1705, found 378.1700.



Compound 3ua. 41 mg, 42% yield; white solid, mp 109–111 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.20–7.17 (m, 1H), 7.16–7.12 (m, 1H), 7.11–7.08 (m, 1H), 6.84–6.79 (m, 1H), 6.13–6.09 (m, 1H), 4.26–4.22 (m, 2H), 4.21–4.13 (m, 2H), 3.29–3.22 (m, 1H), 3.09–3.00 (m, 2H), 2.75–2.67 (m, 1H), 2.14–2.07 (m, 1H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.9, 170.4, 144.6, 137.7, 134.1, 132.7, 131.6, 130.5, 128.2, 125.3, 122.7, 122.4, 64.7, 61.7, 61.6, 44.5, 40.3, 34.9, 14.1, 14.0; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{O}_4\text{S}_2$ ($\text{M} + \text{H}$) $^+$ 389.0881, found 389.0898.

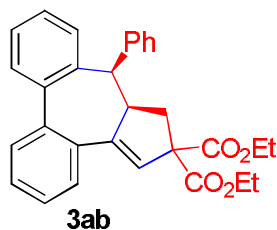


Compound 3va. 84 mg, 88% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.36–7.31 (m, 1H), 7.20–7.15 (m, 1H), 7.11–7.04 (m, 2H), 5.72–5.69 (m, 1H), 4.18–4.07 (m, 4H), 3.27–3.16 (m, 1H), 2.82–2.73 (m, 2H), 2.67–2.60 (m, 2H), 2.55–2.48 (m, 1H), 2.44–2.36 (m, 2H), 2.01–1.92 (m, 1H), 1.84–1.77 (m, 2H), 1.74–1.67 (m, 1H), 1.64–1.58 (m, 1H), 1.23–1.18 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3): δ 171.3, 170.4, 152.4, 141.9, 138.5, 134.8, 129.8, 128.5, 127.3, 126.3, 126.1, 122.7, 64.3, 61.3, 61.2, 51.4, 39.8, 38.1, 32.4, 29.5, 23.0, 22.8, 14.0; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{29}\text{O}_4$ ($\text{M} + \text{H}$) $^+$ 381.2066, found 381.2055.

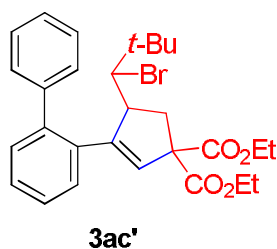


Compound 3wa. 66 mg, 74% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.25–7.22 (m, 1H), 7.21–7.14 (m, 2H), 7.14–7.10 (m, 1H), 6.80–6.68 (m, 1H), 6.02–5.92 (m, 1H), 4.55–4.46 (m, 2H), 4.25–4.21 (m, 2H), 4.19–4.09 (m, 2H), 3.17–3.06 (m, 1H), 3.03–2.97 (m, 1H), 2.89–2.80 (m, 2H), 2.14–2.06 (m, 1H), 2.06–2.00 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 171.0, 170.3, 147.8, 139.5, 135.2, 133.2, 132.4, 130.9, 129.2, 127.8,

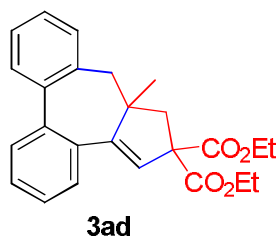
126.4, 124.0, 66.1, 64.7, 61.6, 61.6, 45.7, 41.0, 40.6, 14.0, 14.0; HRMS (ESI) calcd for $C_{21}H_{25}O_5$ ($M + H$)⁺ 357.1702, found 357.1696.



Compound 3ab. 79 mg, 70% yield; *cis/trans* = 6.7:1; white solid, mp 108–110 °C; ¹H NMR (600 MHz, CDCl₃) data of *cis*-isomer: δ 7.46–7.42 (m, 3H), 7.39–7.36 (m, 3H), 7.35–7.32 (m, 3H), 7.12–7.10 (m, 2H), 6.98–6.95 (m, 2H), 6.11–6.07 (m, 1H), 4.76–4.71 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.22–4.18 (m, 2H), 2.85–2.80 (m, 1H), 2.74–2.69 (m, 1H), 2.35–2.31 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) data of *cis*-isomer: δ 170.7, 170.4, 150.7, 141.0, 140.1, 139.4, 133.7, 131.7, 129.7, 129.7, 129.2, 129.0, 128.4, 128.3, 128.1, 128.1, 127.7, 127.6, 127.5, 127.4, 64.8, 61.6, 61.6, 58.6, 52.8, 34.0, 14.1, 14.1; HRMS (ESI) calcd for $C_{30}H_{29}O_4$ ($M + H$)⁺ 453.2066, found 453.2062. The *cis*-diastereoselectivity of major isomer was determined by NOE analysis.



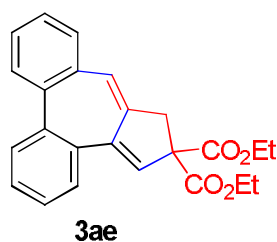
Compound 3ac'. 78 mg, 92% yield; white solid, mp 98–100 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.48–7.45 (m, 1H), 7.42–7.39 (m, 3H), 7.37–7.31 (m, 5H), 5.99–5.97 (m, 1H), 4.29–4.22 (m, 4H), 3.54–3.49 (m, 1H), 3.02–2.95 (m, 1H), 2.56–2.48 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H), 0.69 (s, 9H); ¹³C NMR (151 MHz, CDCl₃): δ 170.8, 170.6, 152.1, 140.8, 139.1, 133.9, 132.1, 129.8, 129.1, 128.4, 128.3, 127.4, 127.3, 72.1, 65.7, 61.6, 61.4, 47.5, 36.2, 34.8, 28.1, 14.1, 14.1; HRMS (ESI) calcd for $C_{28}H_{33}O_4BrNa$ ($M + Na$)⁺ 535.1460, found 535.1452.



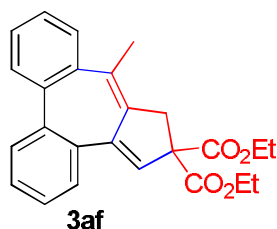
Compound 3ad. 74% yield (72 mg); white solid, mp 85–87 °C; ¹H NMR (600 MHz, CDCl₃): δ 7.48–7.45 (m, 1H), 7.44–7.41 (m, 1H), 7.34–7.32 (m, 1H), 7.31–7.28 (m, 2H), 7.27–7.23 (m, 2H), 7.18–7.14 (m, 1H), 5.43–5.38 (m, 1H), 4.25–4.20 (m, 2H), 4.00–3.93 (m, 2H), 2.61–2.45 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 171.5, 171.0, 154.7, 141.0, 139.8, 136.8, 135.2, 130.0, 129.5, 128.3, 128.0, 127.4, 127.2, 127.1,

126.9, 123.7, 64.9, 61.5, 61.2, 59.4, 44.1, 41.9, 26.7, 14.0, 13.7; HRMS (ESI) calcd for $C_{25}H_{27}O_4$ ($M + H$)⁺ 391.1909, found 391.1901.

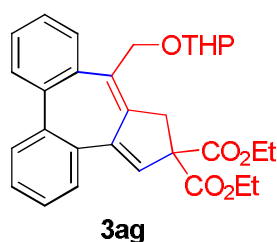
Crystal data for **3ad** ($C_{25}H_{26}O_4$, 390.46): monoclinic, space group $P2_1$, $a = 8.8392(5)$ Å, $b = 12.7460(7)$ Å, $c = 9.5979(5)$ Å, $U = 1066.00(10)$ Å³, $Z = 2$, $T = 296(2)$ K, absorption coefficient 0.081 mm⁻¹, reflections collected 17528, independent reflections 4929 [$R(\text{int}) = 0.0782$], refinement by full-matrix least-squares on F^2 , data/restraints/parameters 4929/1/262, goodness-of-fit on $F^2 = 0.896$, final R indices [$I > 2s(I)$] $R_1 = 0.0637$, $wR_2 = 0.1444$, R indices (all data) $R_1 = 0.1355$, $wR_2 = 0.1847$, largest diff peak and hole 0.164 and -0.178 e Å⁻³. Crystallographic data for the structure **3ad** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1498313.



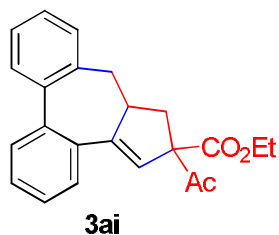
Compound 3ae. 42 mg, 45% yield; colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 7.59–7.53 (m, 2H), 7.49–7.46 (m, 1H), 7.39–7.32 (m, 2H), 7.27–7.23 (m, 2H), 7.14–7.08 (m, 1H), 6.43–6.39 (m, 1H), 6.38–6.35 (m, 1H), 4.25–4.16 (m, 4H), 3.37–3.25 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 6H); ¹³C NMR (151 MHz, CDCl₃): δ 170.1, 147.7, 147.6, 138.3, 137.5, 136.3, 134.3, 131.9, 131.5, 130.5, 129.6, 129.2, 128.9, 128.2, 127.9, 126.9, 123.7, 62.9, 61.8, 42.4, 14.0; HRMS (ESI) calcd for $C_{24}H_{22}O_4Na$ ($M + Na$)⁺ 397.1416, found 397.1412.



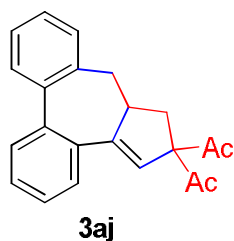
Compound 3af. 57 mg, 58% yield; colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 7.52–7.49 (m, 1H), 7.4–7.41 (m, 3H), 7.38–7.36 (m, 1H), 7.33–7.28 (m, 2H), 7.26–7.24 (m, 1H), 6.46–6.45 (m, 1H), 4.17–4.23 (m, 4H), 3.32 (s, 2H), 2.23 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 6H); ¹³C NMR (151 MHz, CDCl₃): δ 170.2, 147.7, 146.5, 139.7, 139.0, 137.5, 135.4, 132.1, 131.4, 129.2, 128.7, 128.5, 127.8, 127.5, 127.3, 126.5, 125.8, 62.8, 61.7, 42.6, 20.3, 14.0; HRMS (ESI) calcd for $C_{25}H_{24}O_4Na$ ($M + Na$)⁺ 411.1572, found 411.1581.



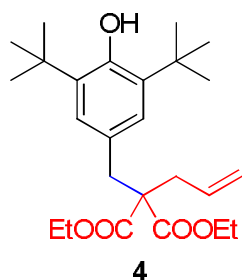
Compound 3ag. 73 mg, 60% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.58–7.55 (m, 1H), 7.53–7.50 (m, 1H), 7.46–7.43 (m, 1H), 7.41–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.26–7.23 (m, 1H), 6.56–6.51 (m, 1H), 4.82–4.79 (m, 1H), 4.79–4.77 (m, 1H), 4.39–4.34 (m, 1H), 4.24–4.18 (m, 4H), 3.99–3.93 (m, 1H), 3.62–3.58 (m, 1H), 3.46 (s, 2H), 1.88–1.81 (m, 1H), 1.77–1.71 (m, 1H), 1.66–1.56 (m, 4H), 1.27–1.23 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3): δ 170.1, 170.0, 150.9, 147.9, 139.1, 138.1, 137.6, 135.3, 132.1, 131.4, 130.5, 129.4, 128.8, 128.5, 127.8, 127.6, 126.6, 126.5, 98.9, 68.3, 63.2, 62.5, 61.8, 61.8, 41.9, 30.7, 25.5, 19.4, 14.0, 14.0; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{33}\text{O}_6$ ($\text{M} + \text{H}$) $^+$ 489.2277, found 489.2270.



Compound 3ai. 61 mg, 70% yield; dr = 1.4:1; white solid, mp 89–91 °C; ^1H NMR (600 MHz, CDCl_3) data of the major isomer: δ 7.48–7.45 (m, 2H), 7.31–7.29 (m, 3H), 7.25–7.23 (m, 2H), 7.18–7.16 (m, 1H), 5.72–5.69 (m, 1H), 4.09–4.03 (m, 2H), 3.66–3.59 (m, 1H), 3.02–2.99 (m, 1H), 2.76–2.73 (m, 1H), 2.52–2.50 (m, 1H), 2.24 (s, 3H), 2.08–2.04 (m, 1H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) data of the major isomer: δ 202.3, 171.3, 152.0, 140.9, 139.7, 136.1, 135.9, 130.3, 129.9, 128.6, 128.5, 127.4, 127.3, 127.0, 126.8, 125.4, 72.3, 61.3, 53.8, 35.9, 35.2, 26.7, 13.9; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{O}_3$ ($\text{M} + \text{H}$) $^+$ 347.1647, found 347.1632.

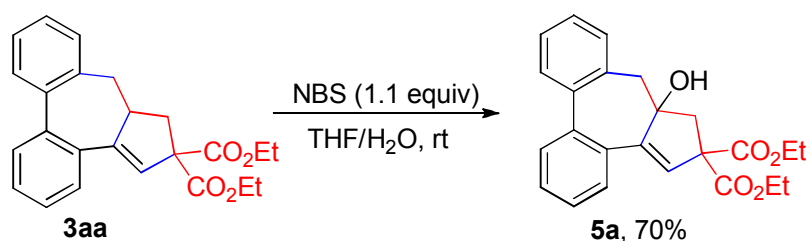


Compound 3aj. 58% yield (46 mg); white solid, mp 91–93 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.48–7.44 (m, 2H), 7.36–7.34 (m, 1H), 7.33–7.30 (m, 2H), 7.28–7.26 (m, 1H), 7.24–7.22 (m, 1H), 7.20–7.17 (m, 1H), 5.75–5.67 (m, 1H), 3.68–3.62 (m, 1H), 3.03–2.99 (m, 1H), 2.90–2.86 (m, 1H), 2.53–2.50 (m, 1H), 2.17 (s, 3H), 1.89–1.85 (m, 1H), 1.75 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 207.2, 203.6, 153.1, 140.9, 139.7, 135.9, 135.8, 130.3, 130.0, 128.7, 128.6, 127.5, 127.4, 127.2, 126.5, 125.3, 79.2, 53.9, 35.2, 34.5, 27.4, 26.2; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 317.1542, found 317.1535.



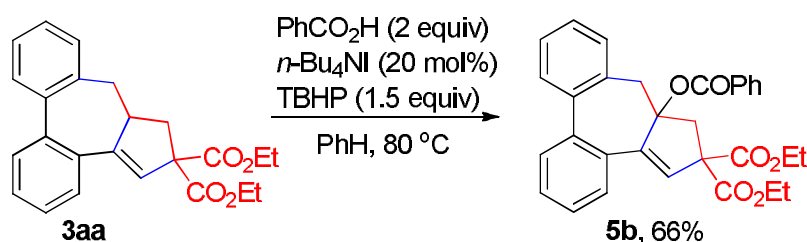
Compound 4. 85 mg, 81% yield; colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 6.92–6.86 (m, 2H), 5.84–5.67 (m, 1H), 5.19–5.12 (m, 2H), 5.10–5.06 (m, 1H), 4.23–4.13 (m, 4H), 3.15 (s, 2H), 2.58–2.52 (m, 2H), 1.40 (s, 18H), 1.24 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3): δ 171.0, 152.6, 135.5, 132.9, 126.5, 126.4, 118.9, 61.1, 58.9, 37.8, 36.2, 34.2, 30.3, 14.0; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{39}\text{O}_5$ ($\text{M} + \text{H}$) $^+$ 419.2797, found 419.2809.

Experimental procedure for the preparation of compound 5a:



To a solution of **3aa** (94 mg, 0.25 mmol) in 1 mL of THF and 0.7 mL of H_2O was added NBS (49 mg, 0.28 mmol). After stirring at room temperature for 8 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 , and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:10) gave 65 mg of **5a** (yield: 70%) as a colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.49–7.44 (m, 2H), 7.37–7.34 (m, 1H), 7.32–7.29 (m, 3H), 7.25–7.22 (m, 1H), 7.22–7.19 (m, 1H), 5.73 (s, 1H), 4.31–4.25 (m, 2H), 4.12–4.06 (m, 2H), 4.05 (s, 1H), 3.01–2.95 (m, 1H), 2.92–2.86 (m, 1H), 2.57–2.53 (m, 1H), 2.51–2.46 (m, 1H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 173.4, 169.8, 153.8, 141.0, 139.3, 134.8, 133.9, 130.1, 129.8, 128.9, 128.4, 128.1, 127.6, 127.5, 127.4, 126.9, 92.1, 64.5, 62.8, 61.4, 43.3, 42.3, 13.9, 13.8; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{O}_5\text{Na}$ ($\text{M} + \text{Na}$) $^+$ 415.1521, found 415.1512.

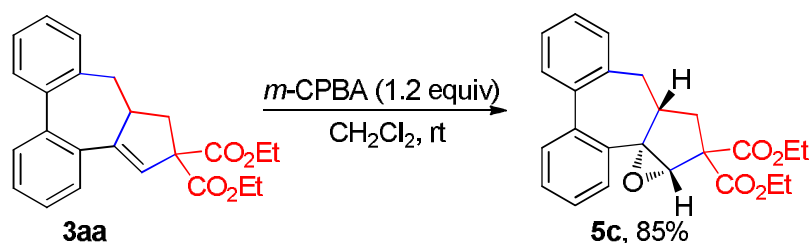
Experimental procedure for the preparation of compound 5b:⁶



- ⁶ E. Shi, Y. Shao, S. Chen, H. Hu, Z. Liu, J. Zhang and X. Wan, *Org. Lett.*, 2012, **14**, 3384.

To a mixture of **3aa** (94 mg, 0.25 mmol), PhCO₂H (61 mg, 0.5 mmol), and *n*-Bu₄NI (18 mg, 0.05 mmol) in 2 mL of benzene was added TBHP (1.5 equiv, 70% aqueous solution, 50 μ L). After stirring at 80 °C for 12 h, the reaction mixture was quenched with saturated Na₂SO₃ solution, extracted with ethyl acetate, dried over Na₂SO₄ and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:5) gave 82 mg of **5b** (yield: 66%) as a colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 8.18–8.08 (m, 2H), 7.97–7.87 (m, 2H), 7.53–7.46 (m, 6H), 7.41–7.38 (m, 2H), 7.35–7.34 (m, 1H), 6.03 (s, 1H), 4.07–3.96 (m, 3H), 3.94–3.88 (m, 2H), 3.67–3.62 (m, 1H), 3.07–3.03 (m, 1H), 2.73–2.66 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 169.8, 169.6, 165.7, 148.4, 141.0, 139.4, 134.3, 133.9, 133.7, 132.8, 131.9, 130.6, 130.2, 129.7, 129.5, 129.1, 128.5, 128.3, 128.3, 128.2, 127.7, 100.3, 64.8, 61.8, 61.7, 40.5, 38.9, 13.8, 13.8; HRMS (ESI) calcd for C₃₁H₂₉O₆ (M + H)⁺ 497.1964, found 497.1959.

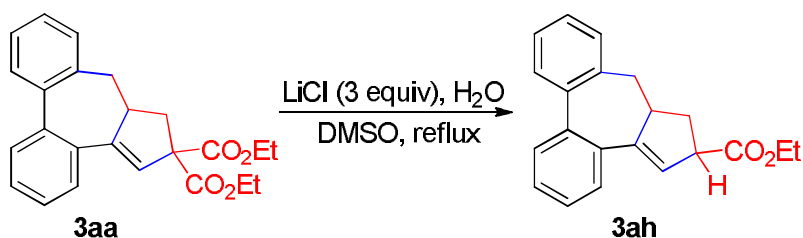
Experimental procedure for the preparation of compound **5c**:



To a mixture of **3aa** (94 mg, 0.25 mmol) and NaHCO₃ (42 mg, 0.5 mmol) in 2 mL of DCM was added *m*-CPBA (52 mg, 0.3 mmol) at 0 °C. After stirring at 25 °C for 24 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:5) gave 83 mg of **5c** (yield: 85%) as a white solid, mp 160–162 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.52–7.50 (m, 1H), 7.48–7.44 (m, 1H), 7.40–7.38 (m, 1H), 7.37–7.32 (m, 3H), 7.26–7.29 (m, 1H), 7.25–7.22 (m, 1H), 4.33–4.24 (m, 2H), 4.21–4.14 (m, 2H), 4.13 (s, 1H), 3.06–3.00 (m, 1H), 2.97–2.91 (m, 1H), 2.57–2.52 (m, 1H), 2.14–2.06 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 169.4, 168.5, 142.3, 140.6, 137.5, 133.3, 130.1, 129.9, 129.3, 128.9, 127.6, 127.3, 127.2, 125.5, 68.3, 61.9, 61.7, 61.4, 60.8, 47.3, 32.4, 31.1, 14.1, 13.9; HRMS (ESI) calcd for C₂₄H₂₅O₅ (M + H)⁺ 393.1702, found 393.1689.

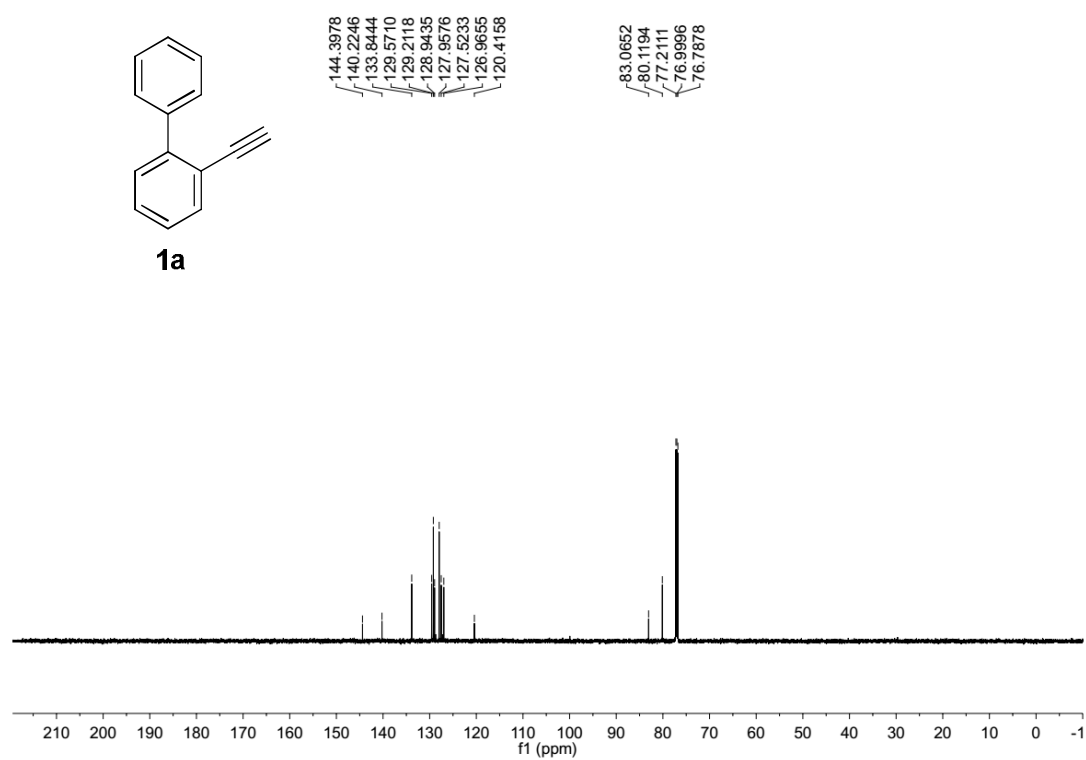
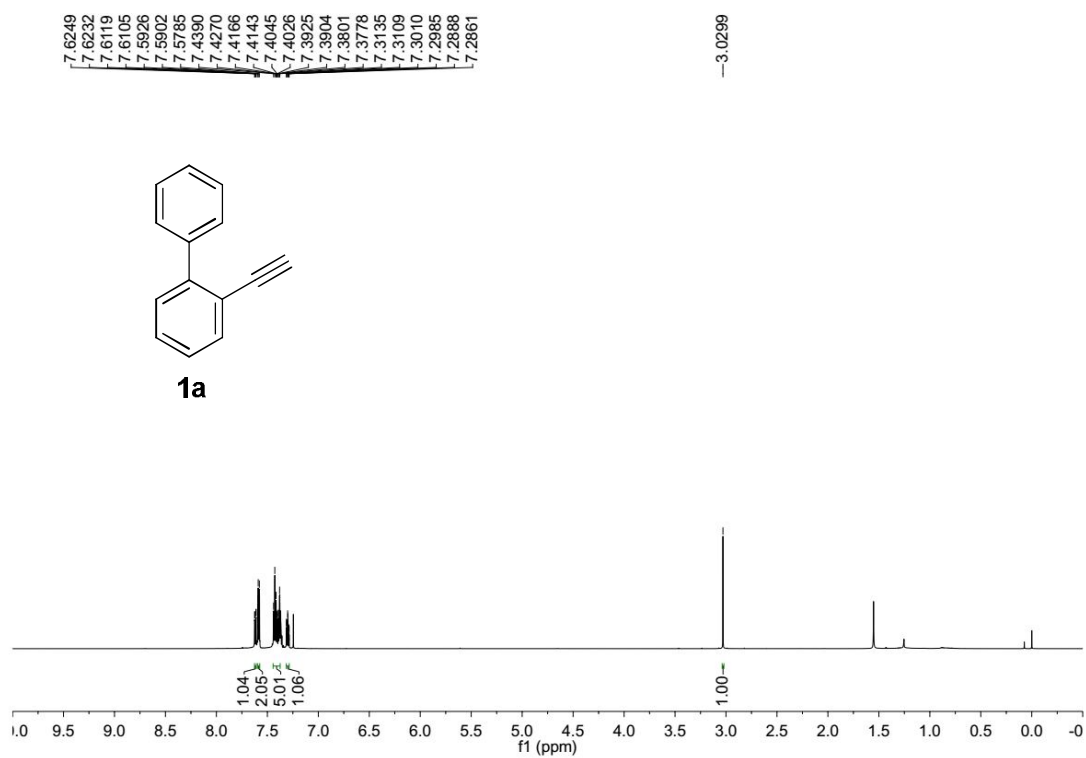
Crystal data for **5c** (C₂₄H₂₄O₅, 392.43): monoclinic, space group *P*2₁/*c*, *a* = 12.7888(4) Å, *b* = 15.5970(5) Å, *c* = 11.0139(4) Å, *U* = 2061.73(12) Å³, *Z* = 4, *T* = 296(2) K, absorption coefficient 0.088 mm^{−1}, reflections collected 72628, independent reflections 4736 [*R*(int) = 0.1094], refinement by full-matrix least-squares on *F*², data/restraints/parameters 4736/0/262, goodness-of-fit on *F*² = 1.359, final *R* indices [*I* > 2σ(*I*)] *R*₁ = 0.0729, *wR*₂ = 0.1911, *R* indices (all data) *R*₁ = 0.1245, *wR*₂ = 0.2224, largest diff peak and hole 0.636 and −0.333 e Å^{−3}. Crystallographic data for the structure **5c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1498314.

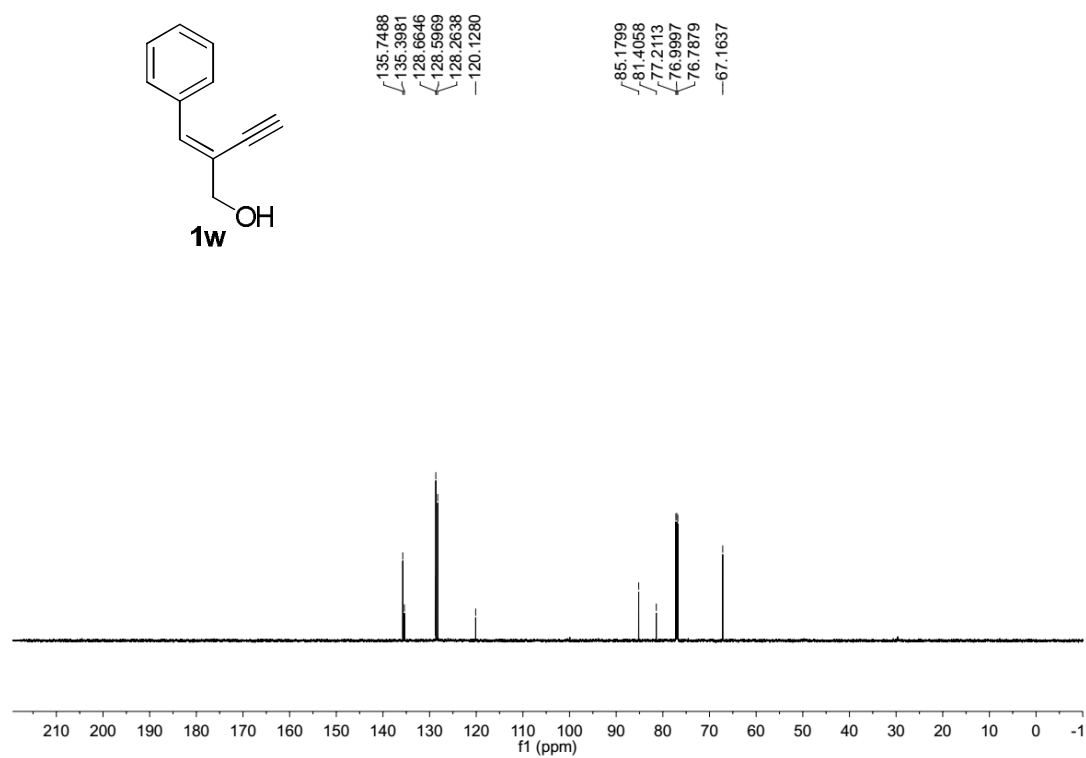
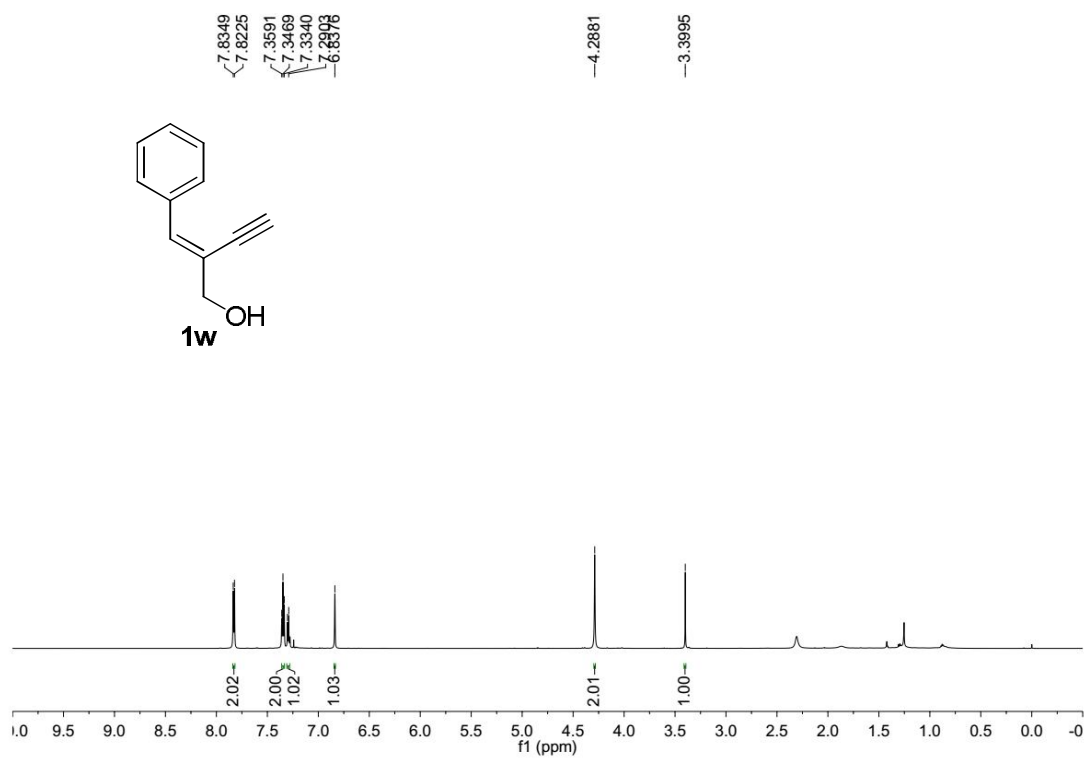
Experimental procedure for the preparation of compound **3ah:**⁷

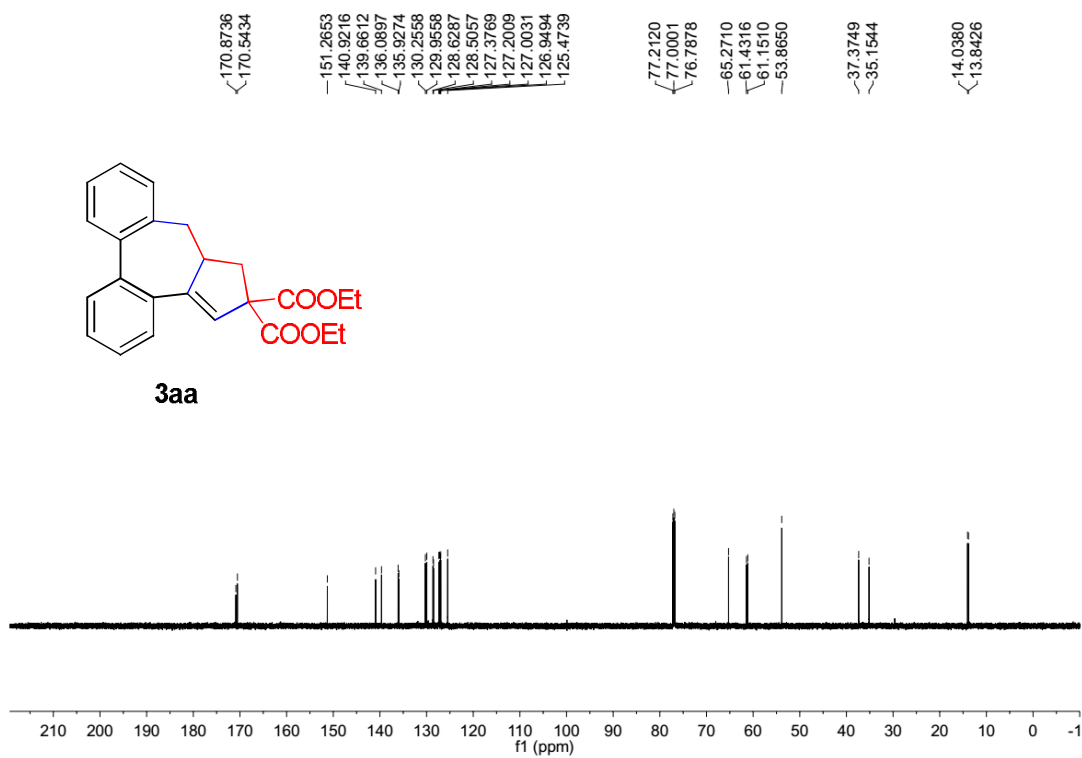
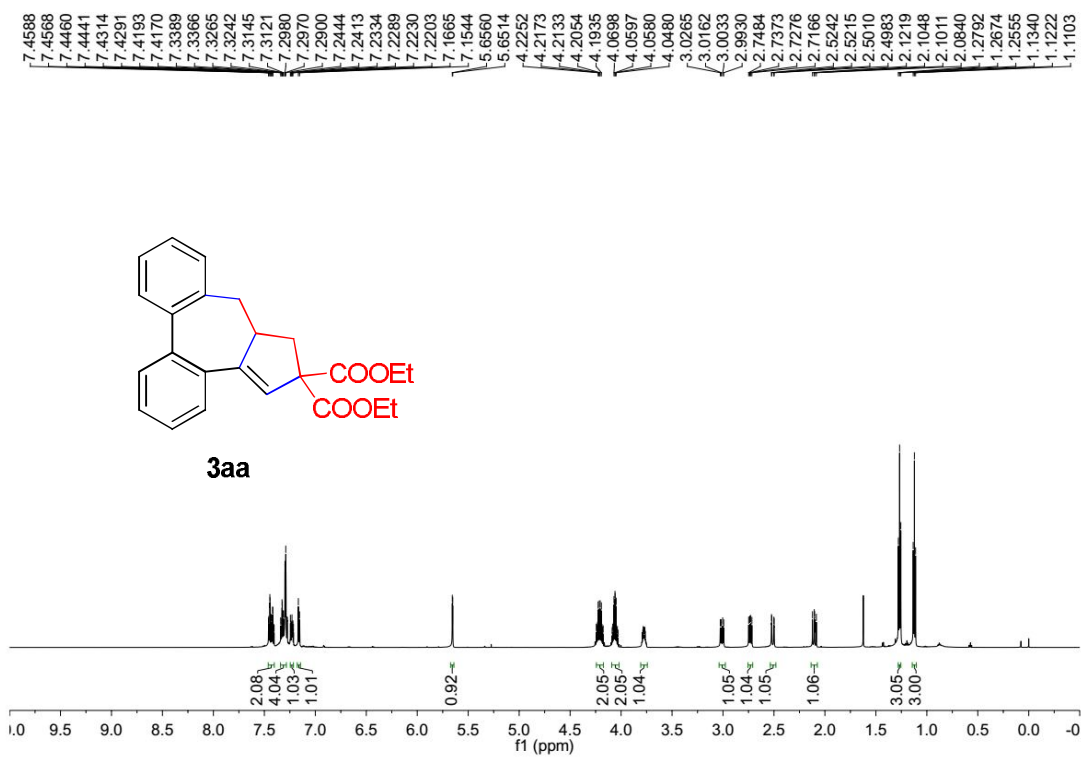


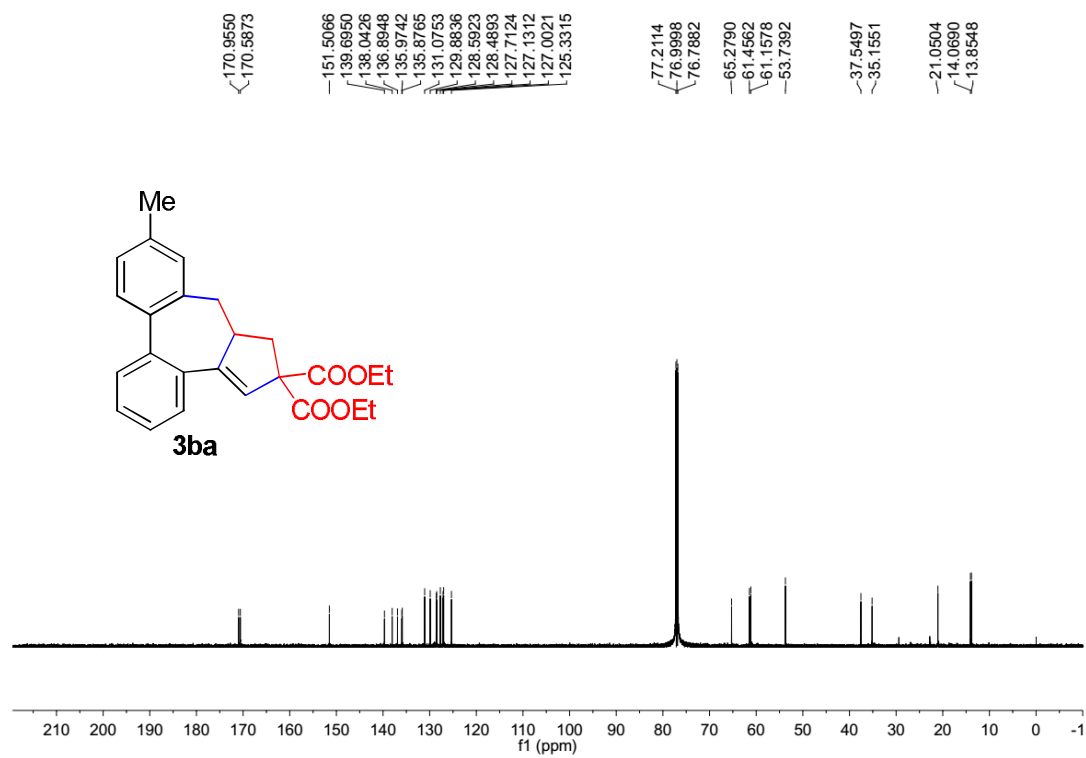
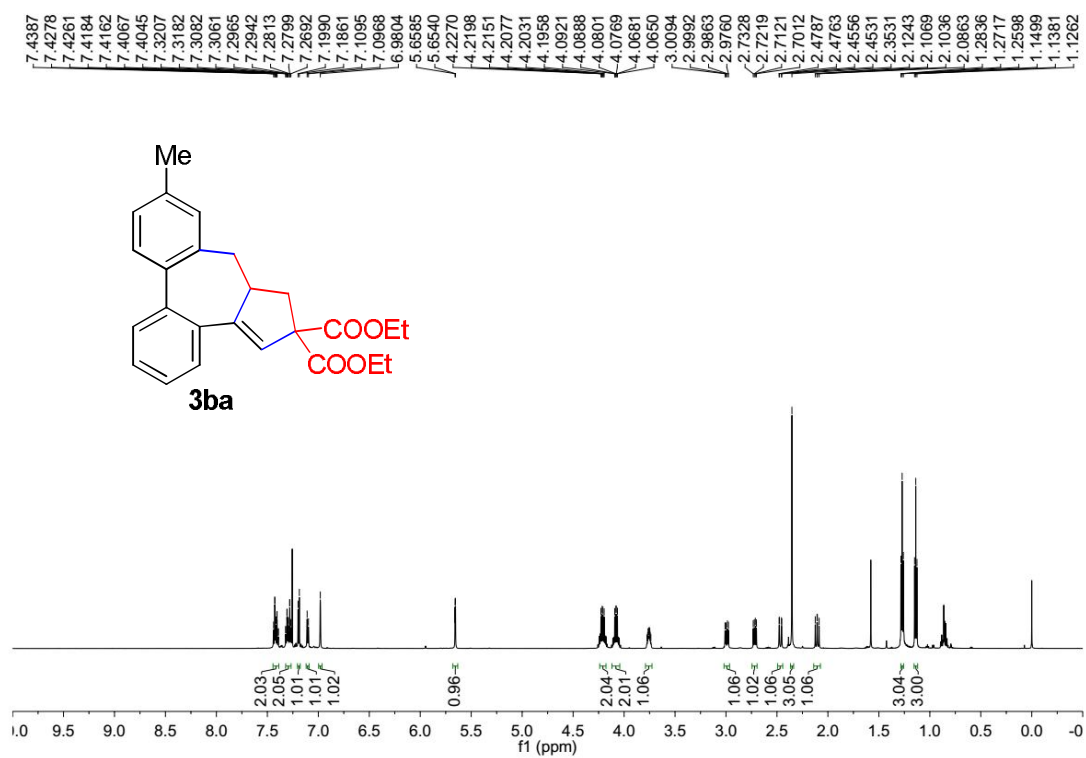
To a solution of **3aa** (188 mg, 0.5 mmol) in 0.25 mL of H₂O and 1 mL of DMSO was added LiCl (63 mg, 1.5 mmol). After refluxing for 6 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:15) gave 116 mg of **3ah** (yield: 76%) as a colorless oil; dr = 87:13. ¹H NMR (600 MHz, CDCl₃) data of major isomer: δ 7.46–7.44 (m, 1H), 7.42–7.39 (m, 1H), 7.33–7.27 (m, 4H), 7.24–7.23 (m, 1H), 7.19–7.17 (m, 1H), 5.65–5.59 (m, 1H), 4.03 (q, J = 7.1 Hz, 2H), 3.58–3.49 (m, 2H), 3.05–3.01 (m, 1H), 2.55–2.51 (m, 1H), 2.34–2.26 (m, 1H), 1.93–1.86 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) data of major isomer: δ 173.9, 149.0, 141.1, 139.8, 136.8, 136.7, 130.4, 130.0, 128.8, 128.3, 127.4, 127.2, 127.1, 126.9, 126.1, 60.4, 54.7, 49.8, 35.5, 33.0, 14.1; HRMS (ESI) calcd for C₂₁H₂₀O₂Na (M + Na)⁺ 327.1361, found 327.1369.

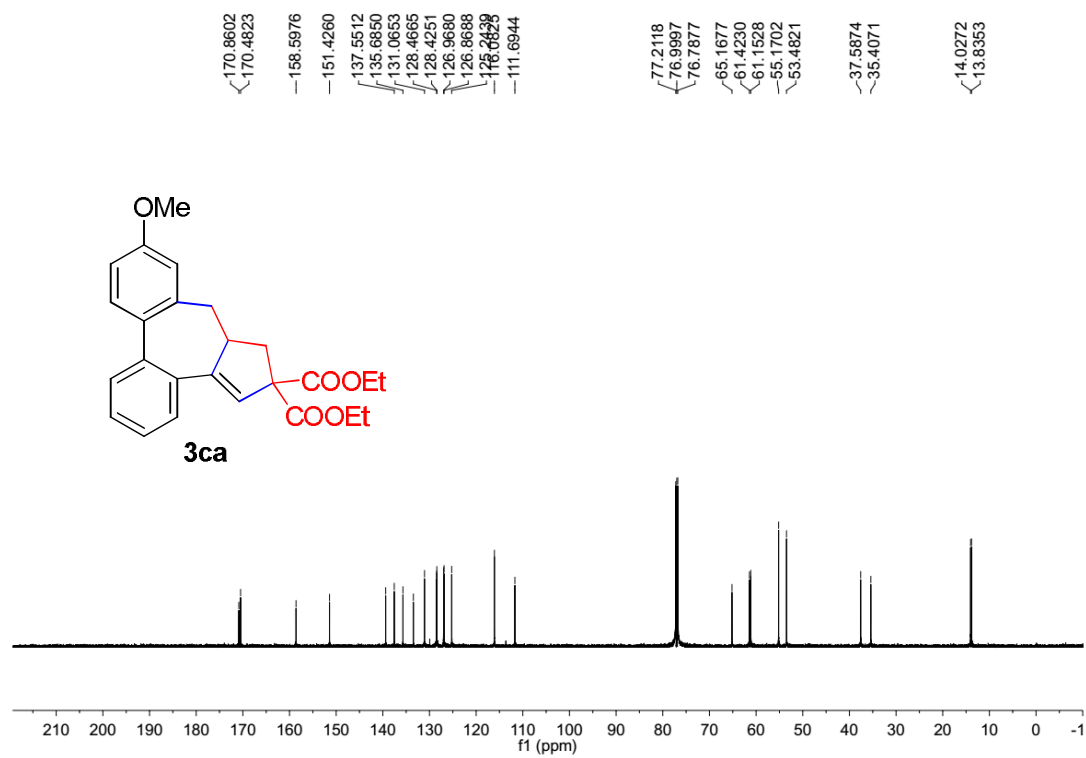
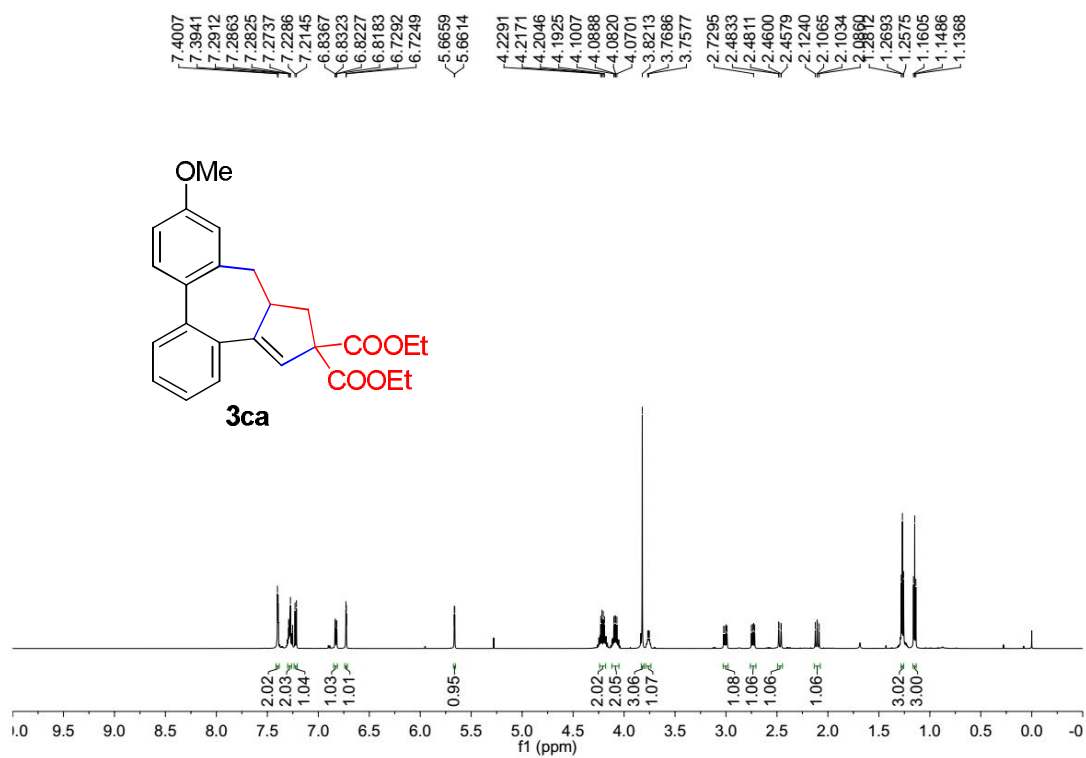
⁷ C. Che, Q. Huang, H. Zheng and G. Zhu, *Chem. Sci.*, 2016, **7**, 4134.

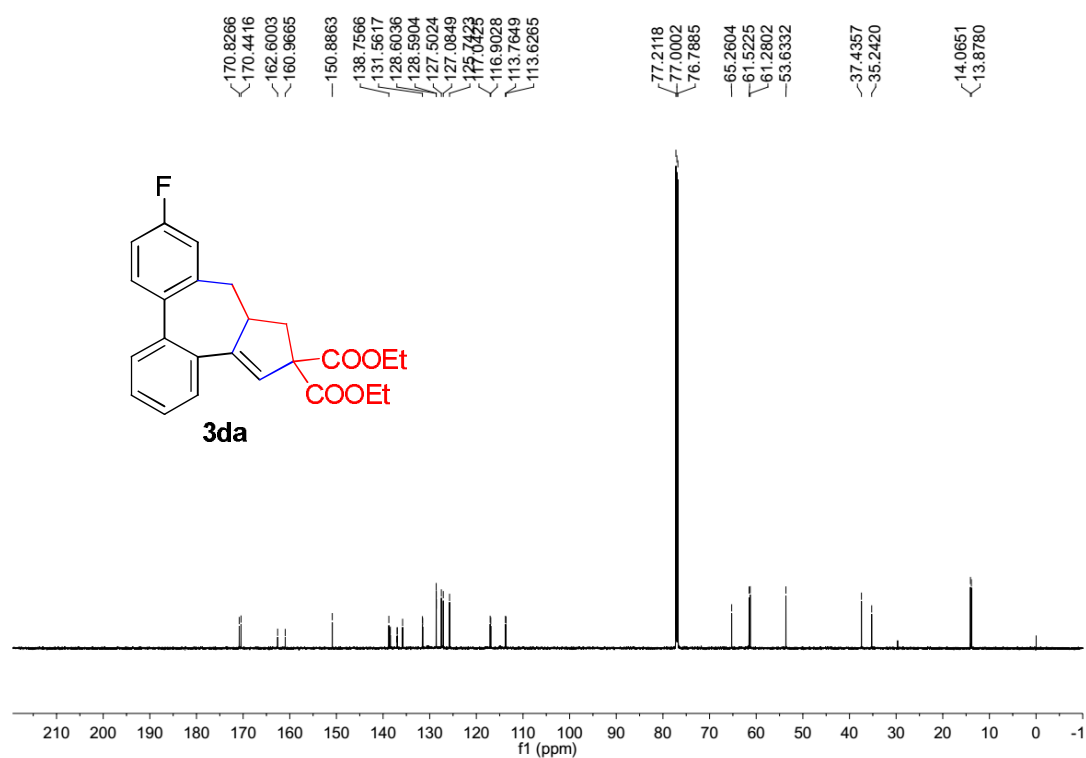
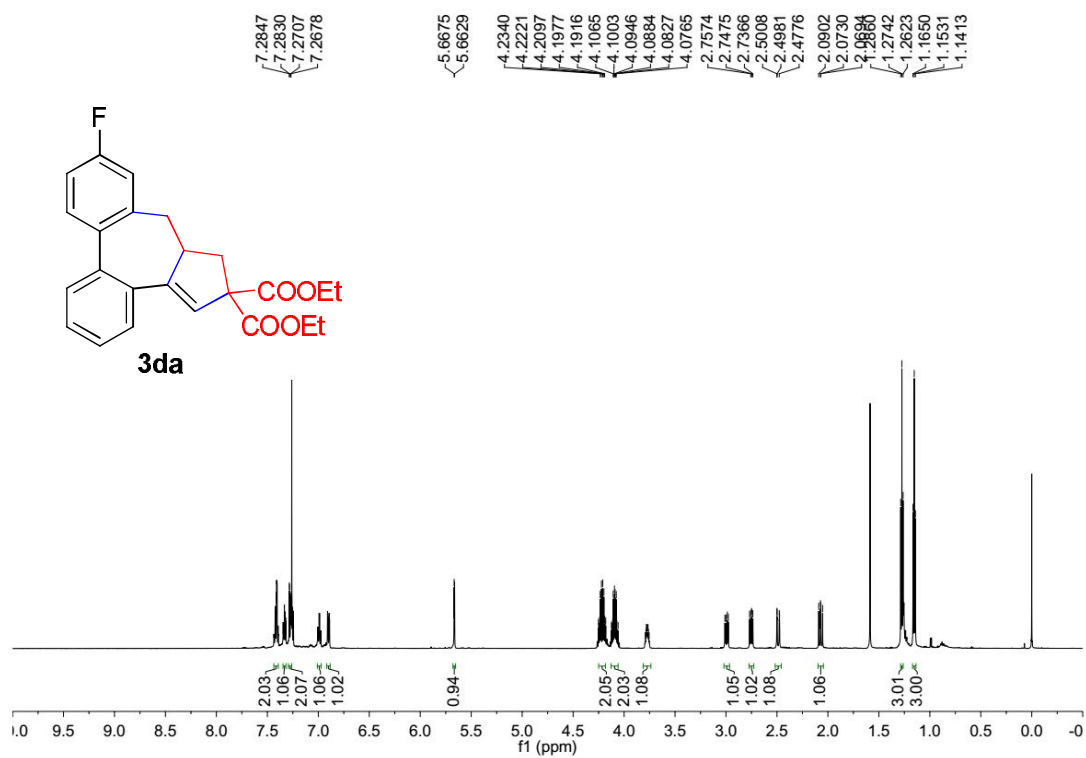


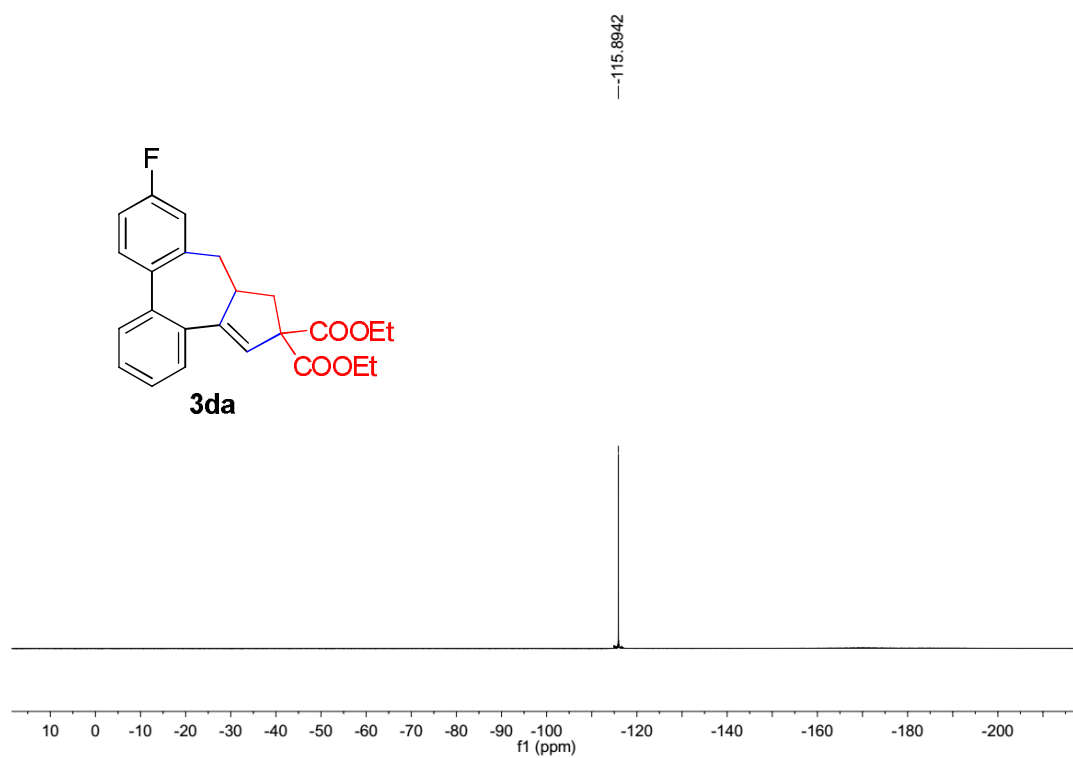


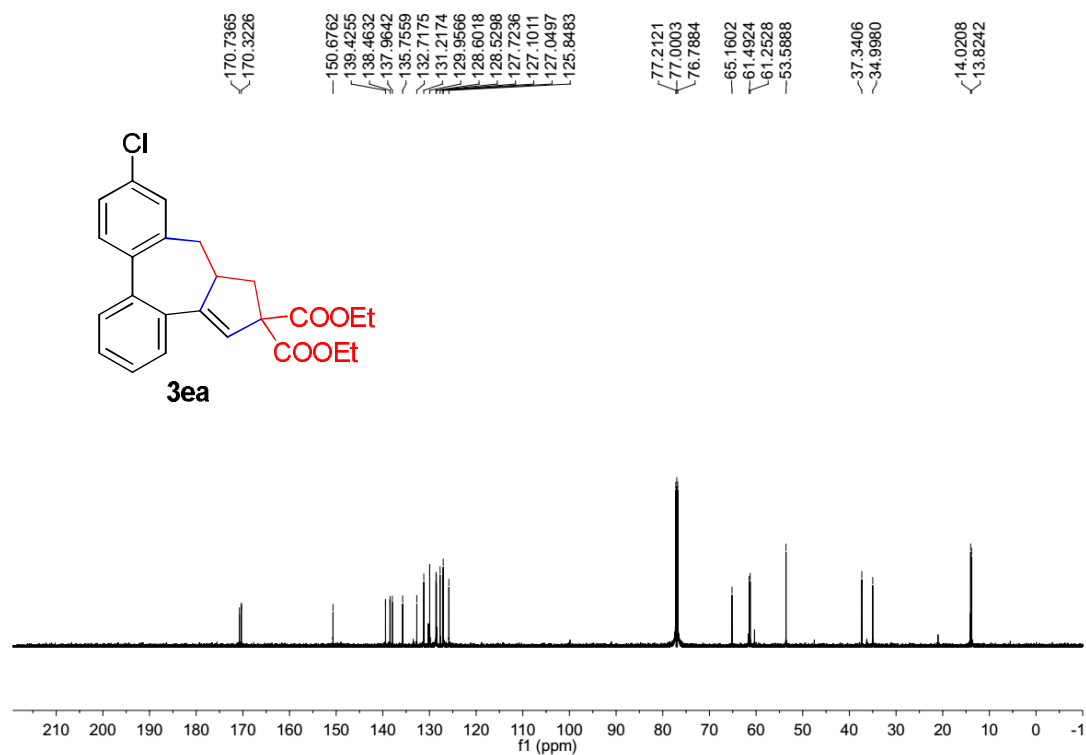
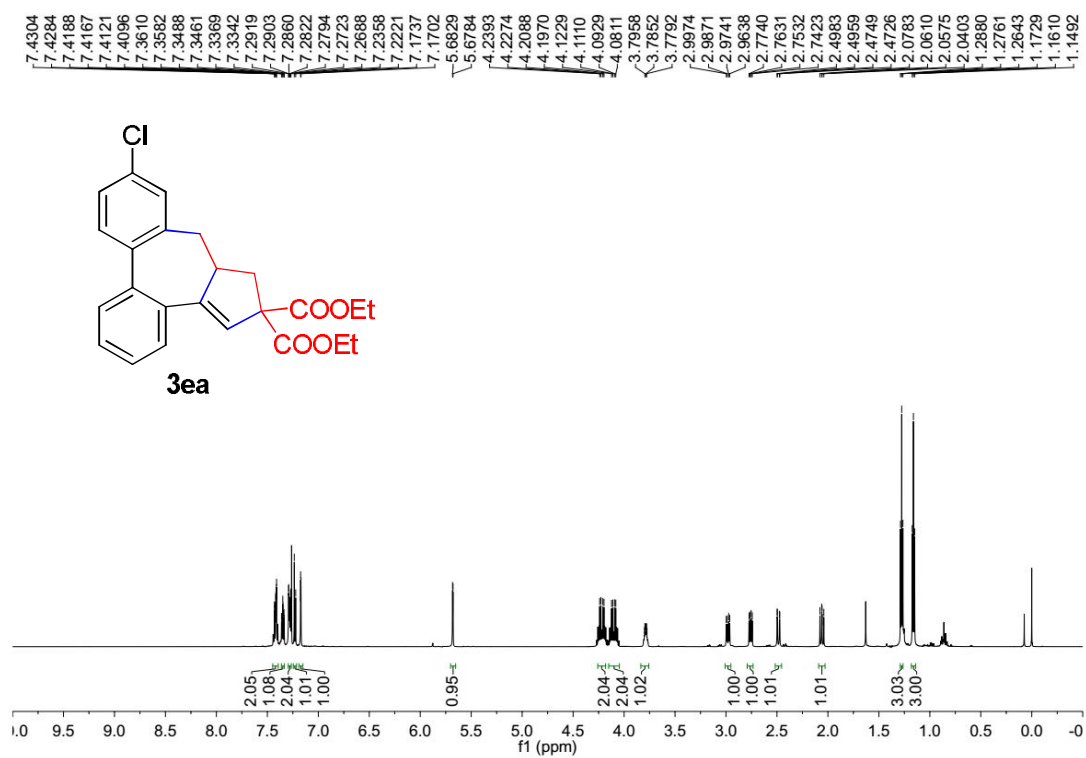


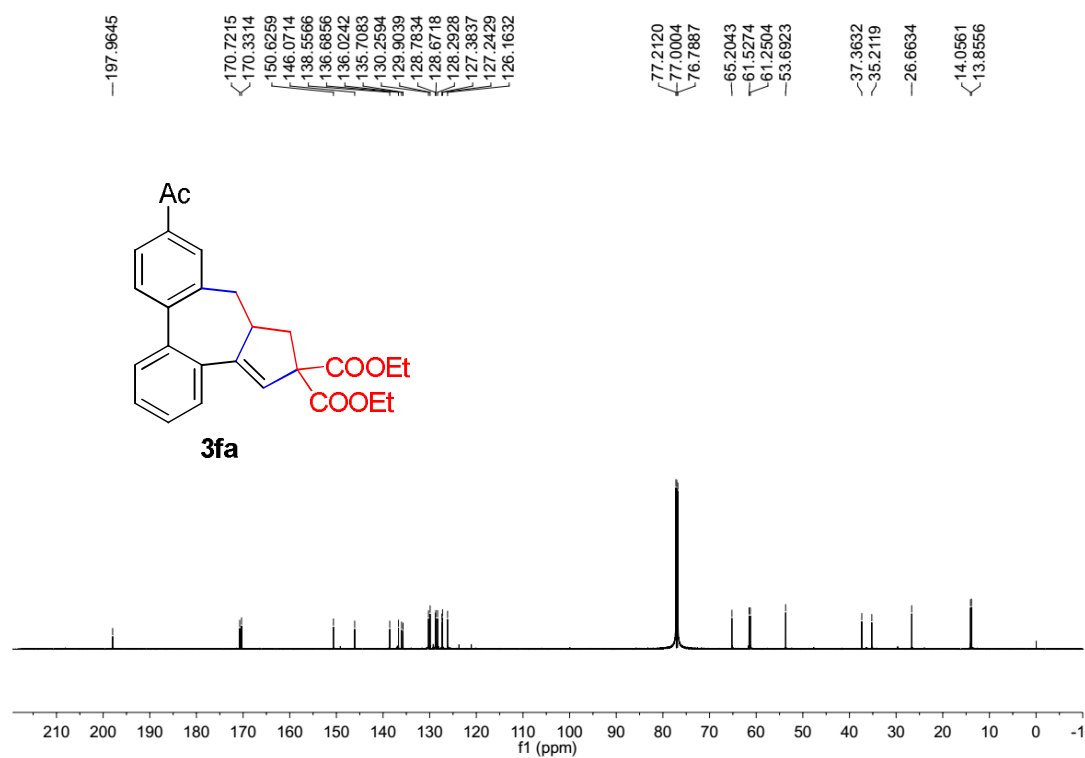
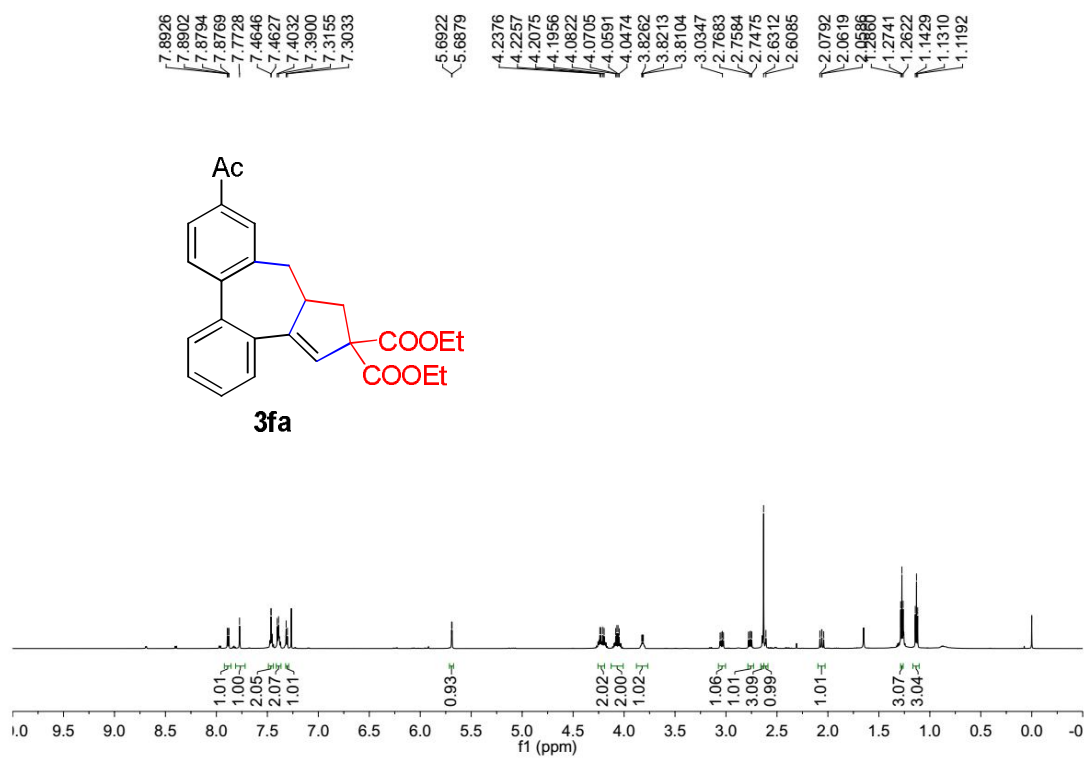


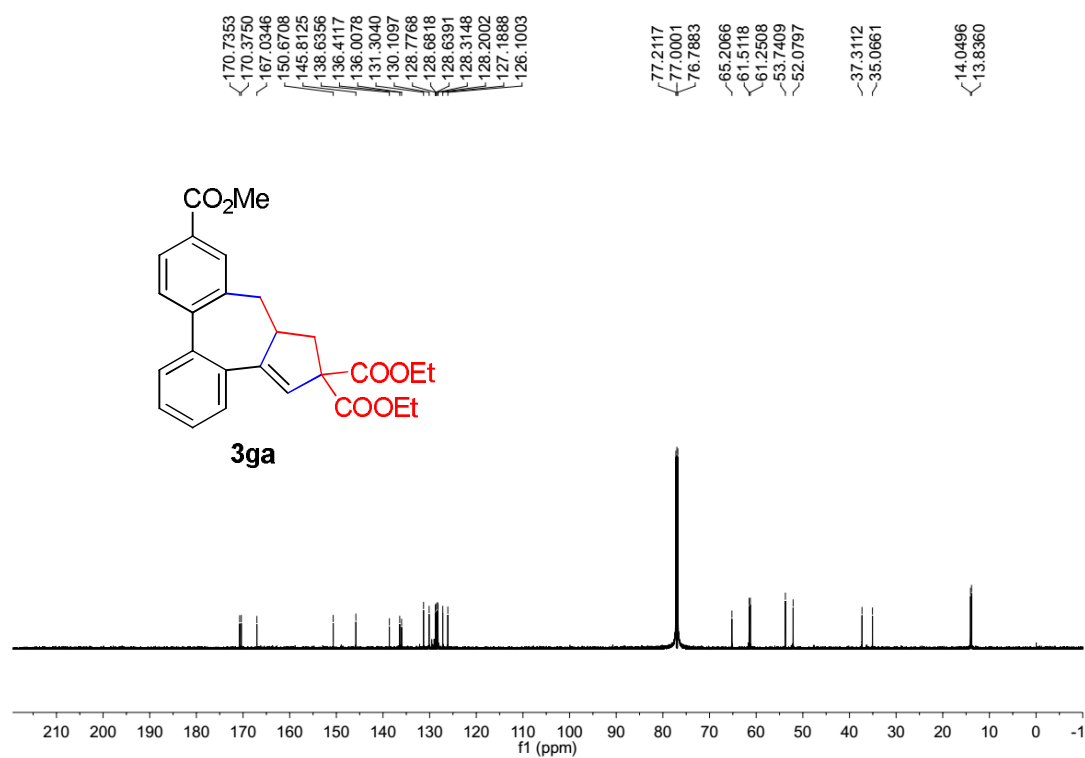
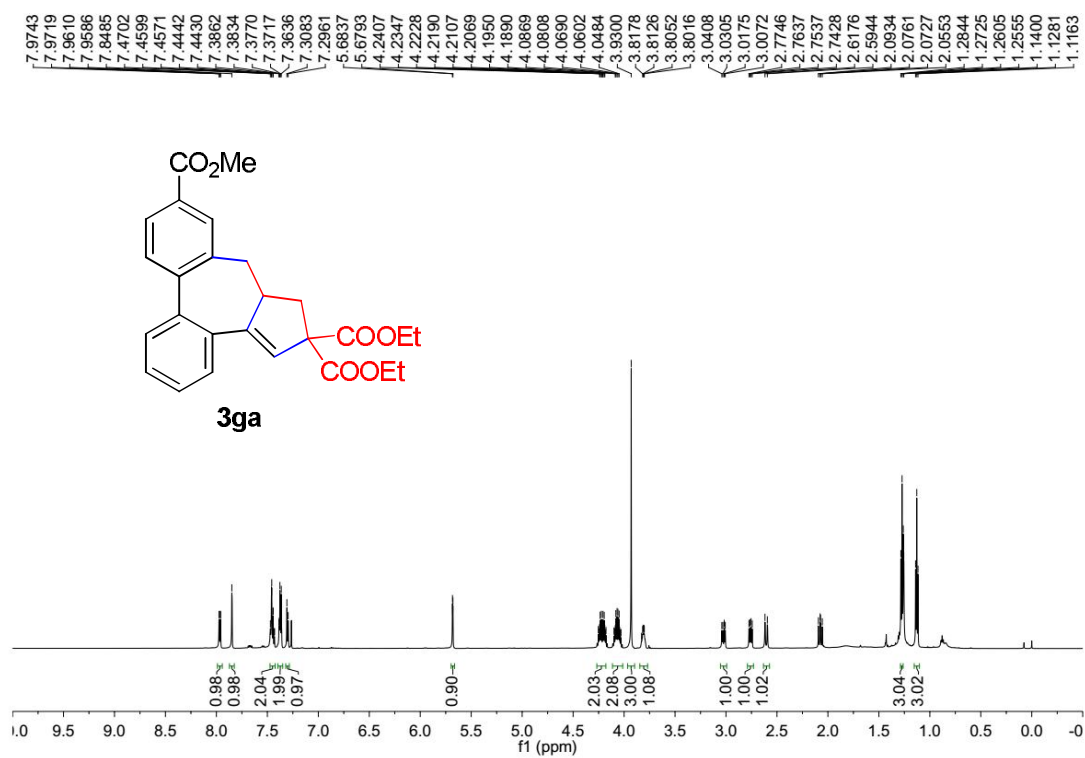


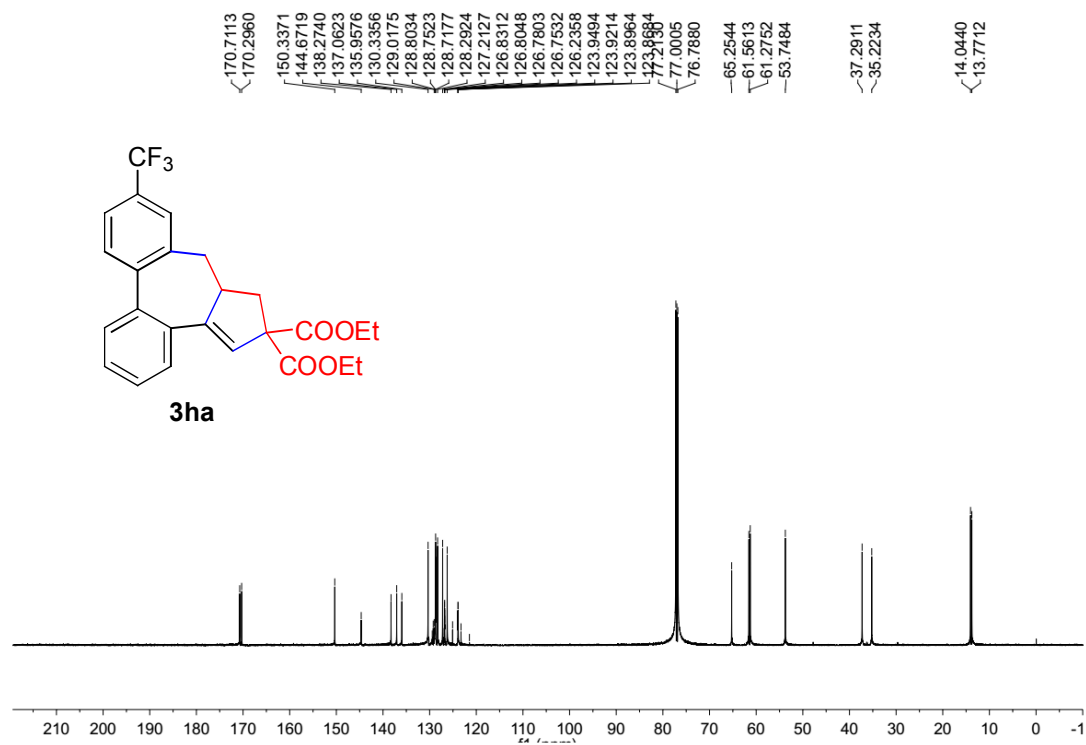
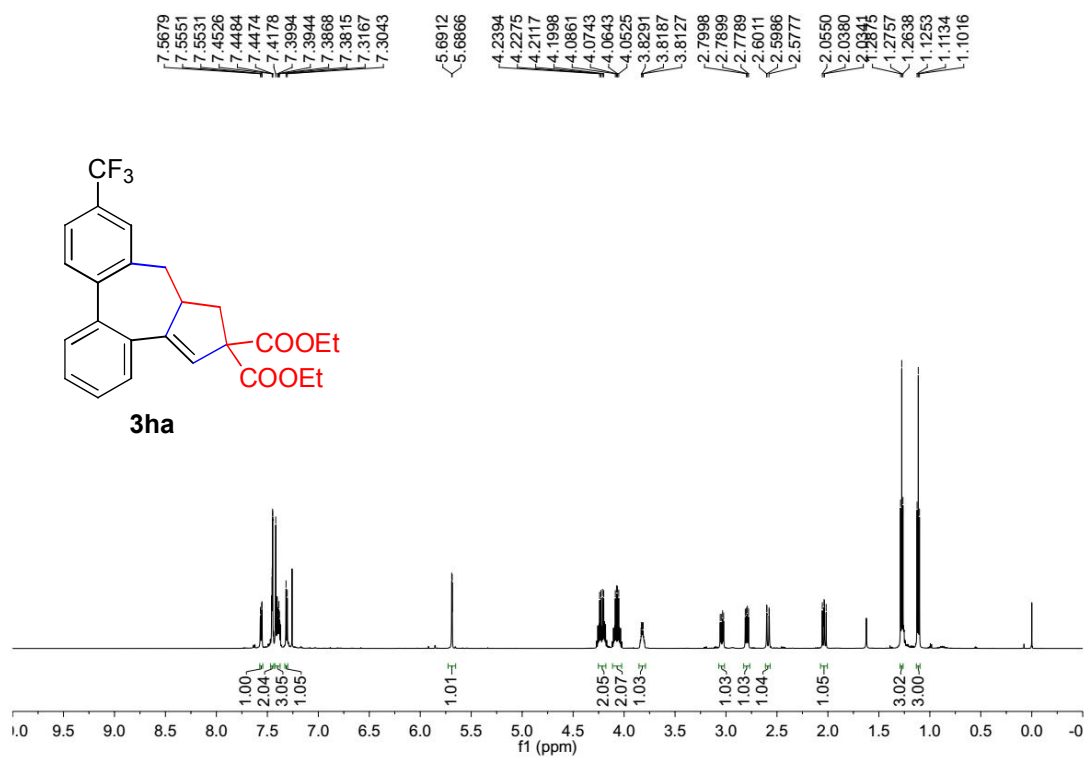


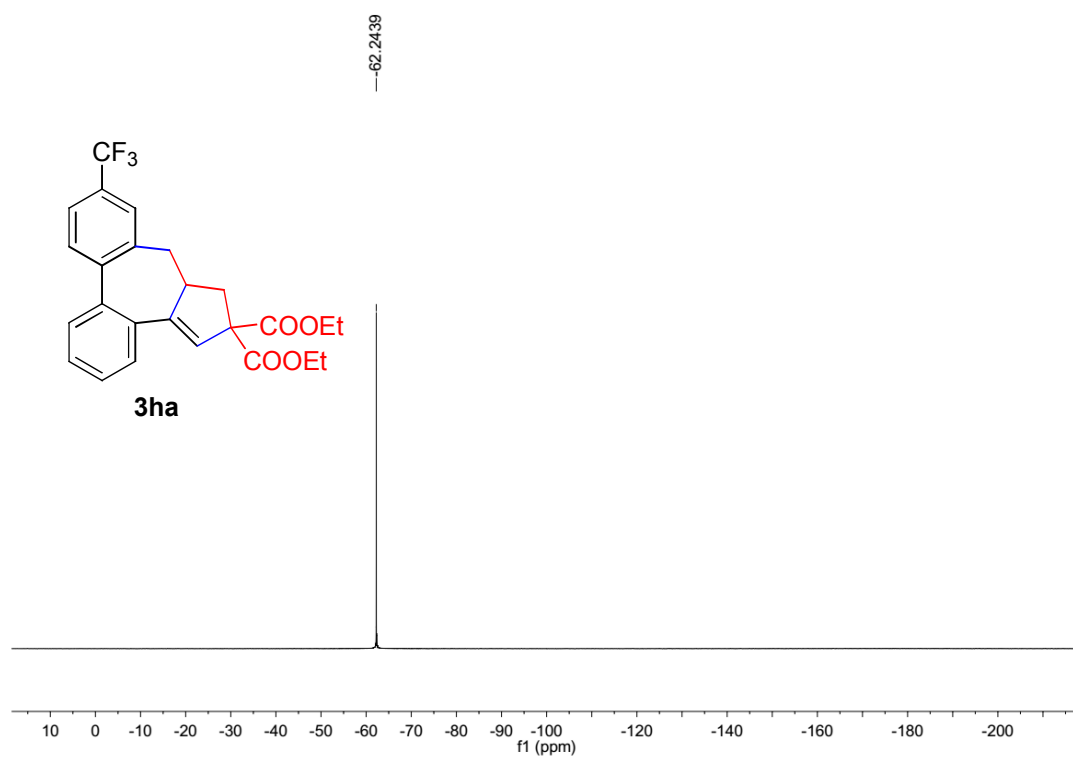


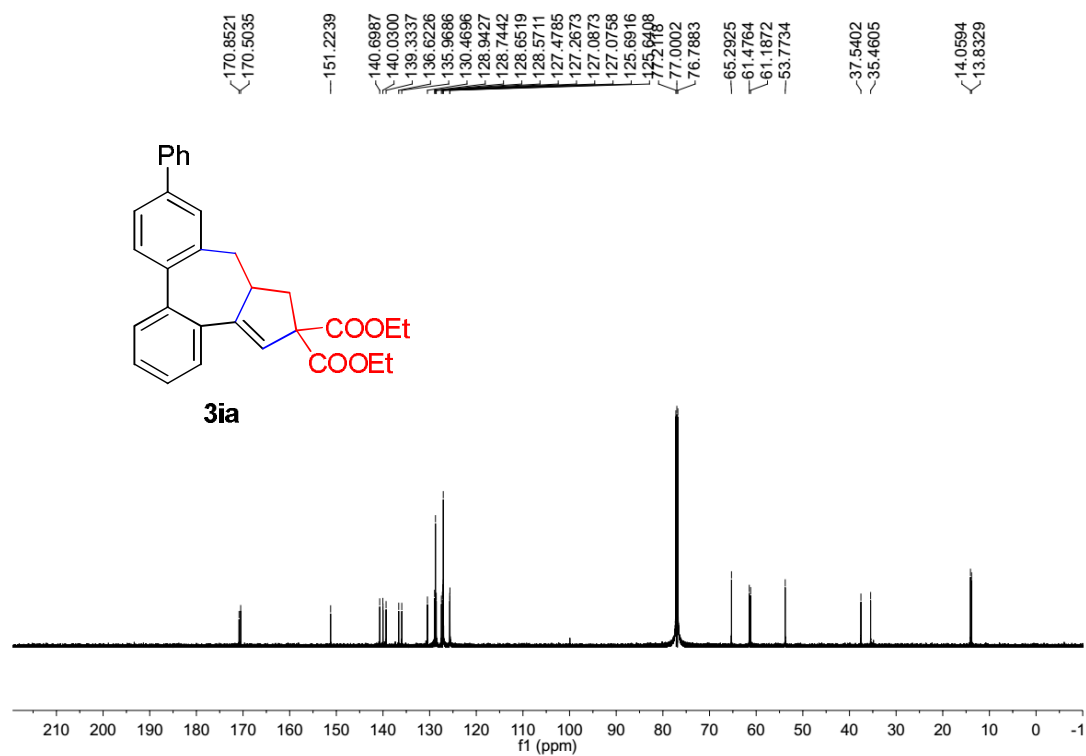
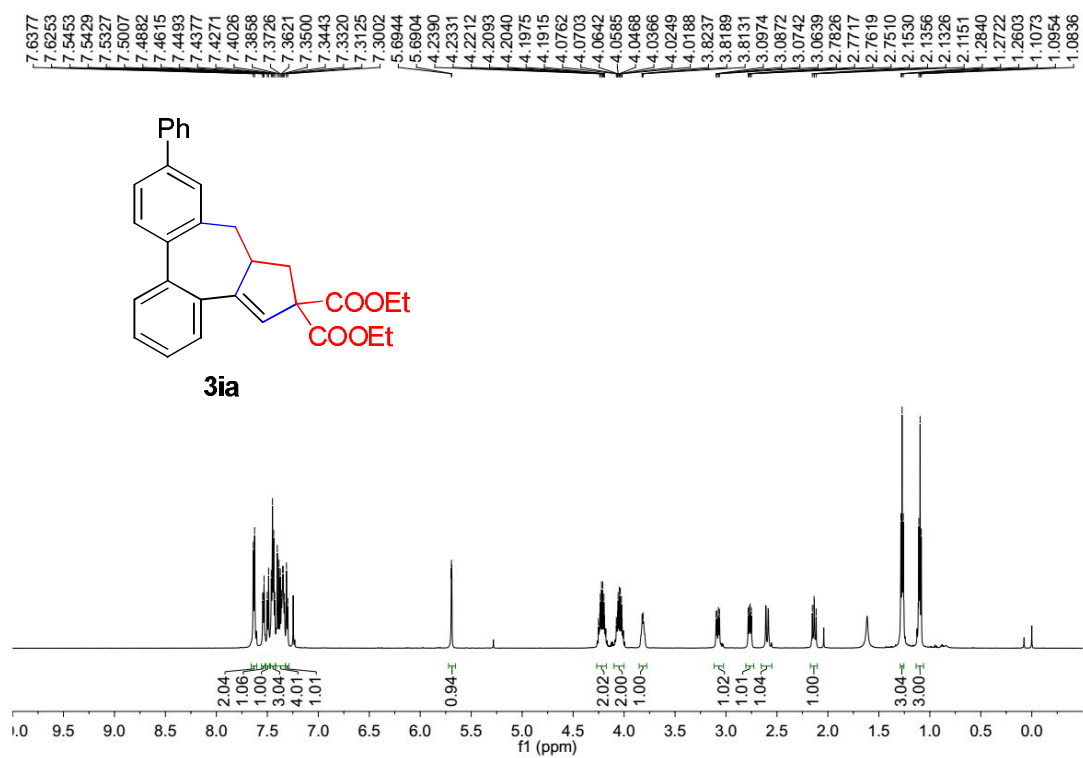


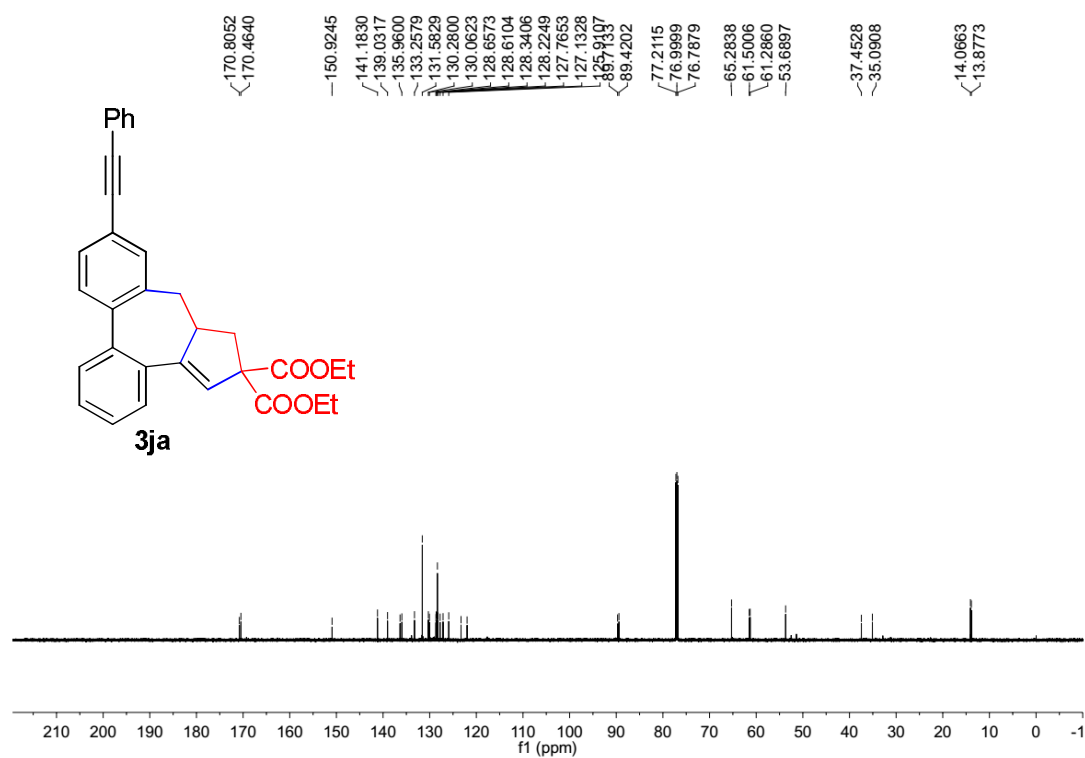
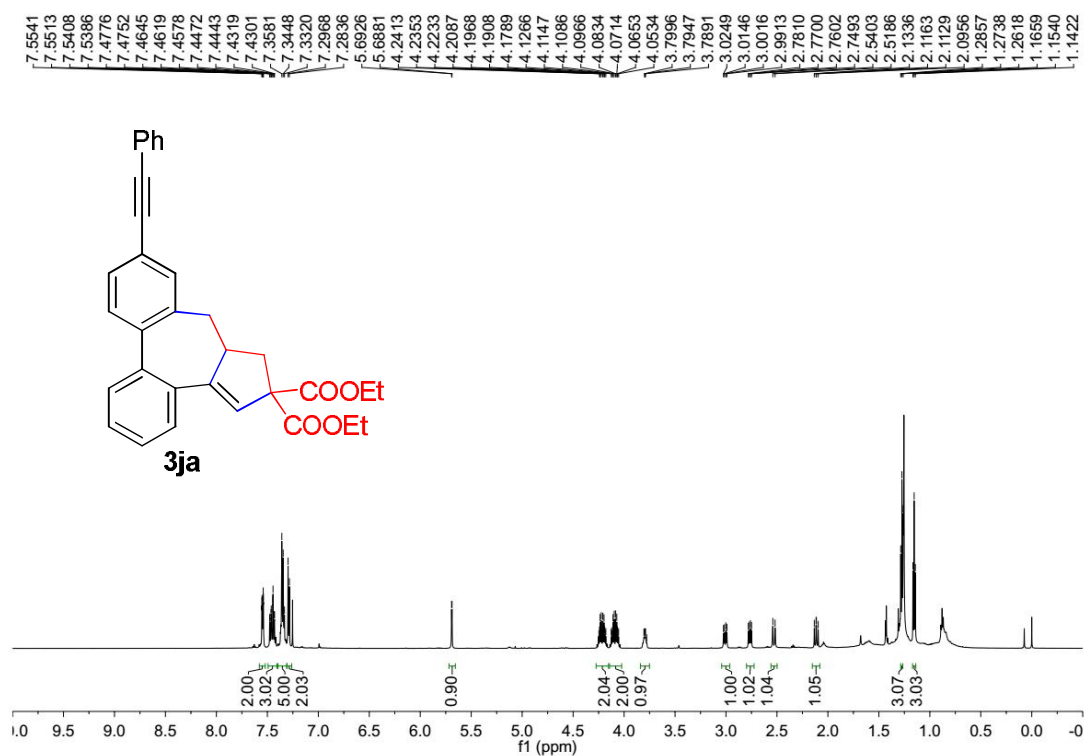


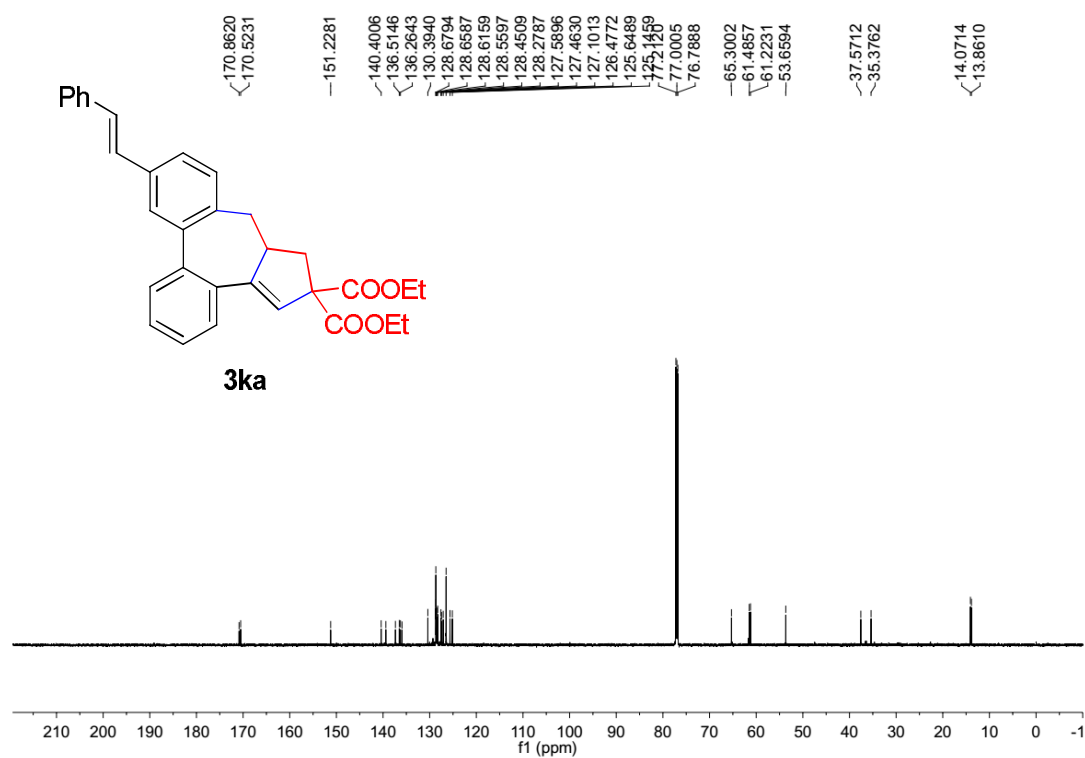
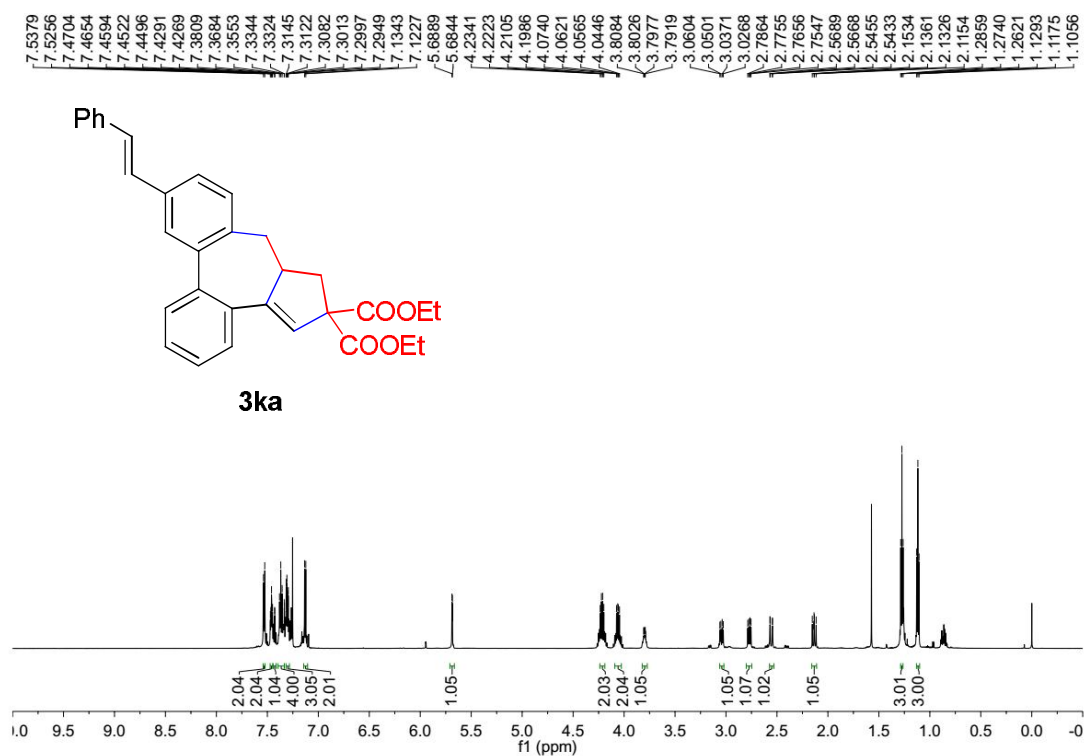


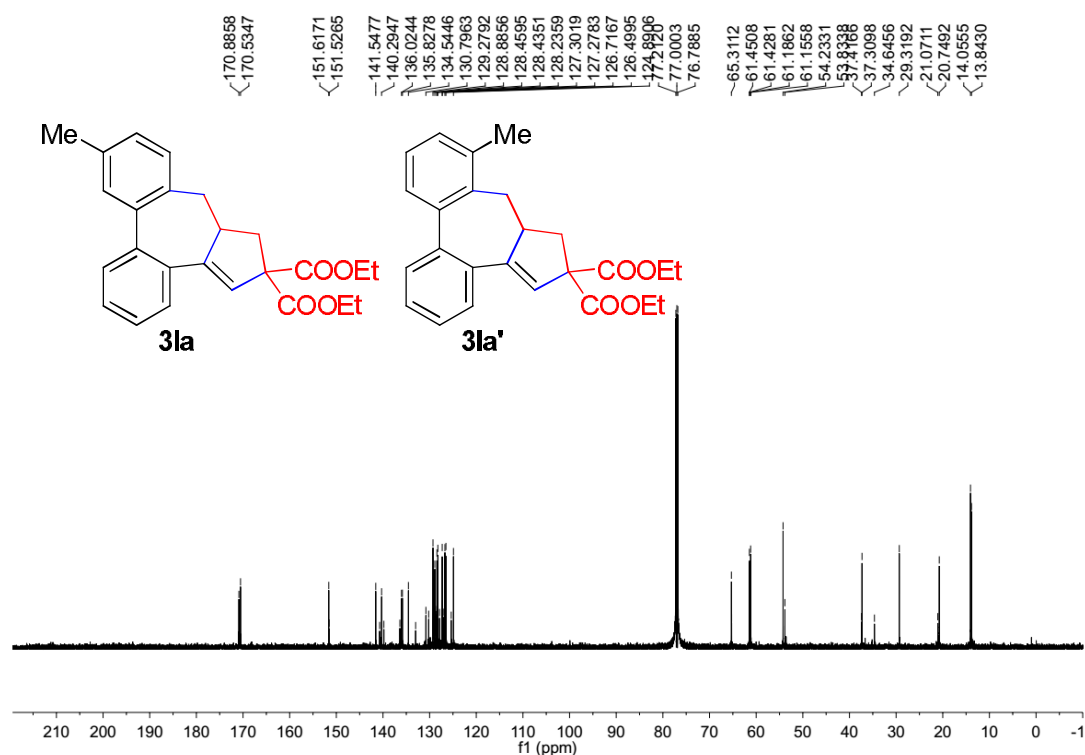
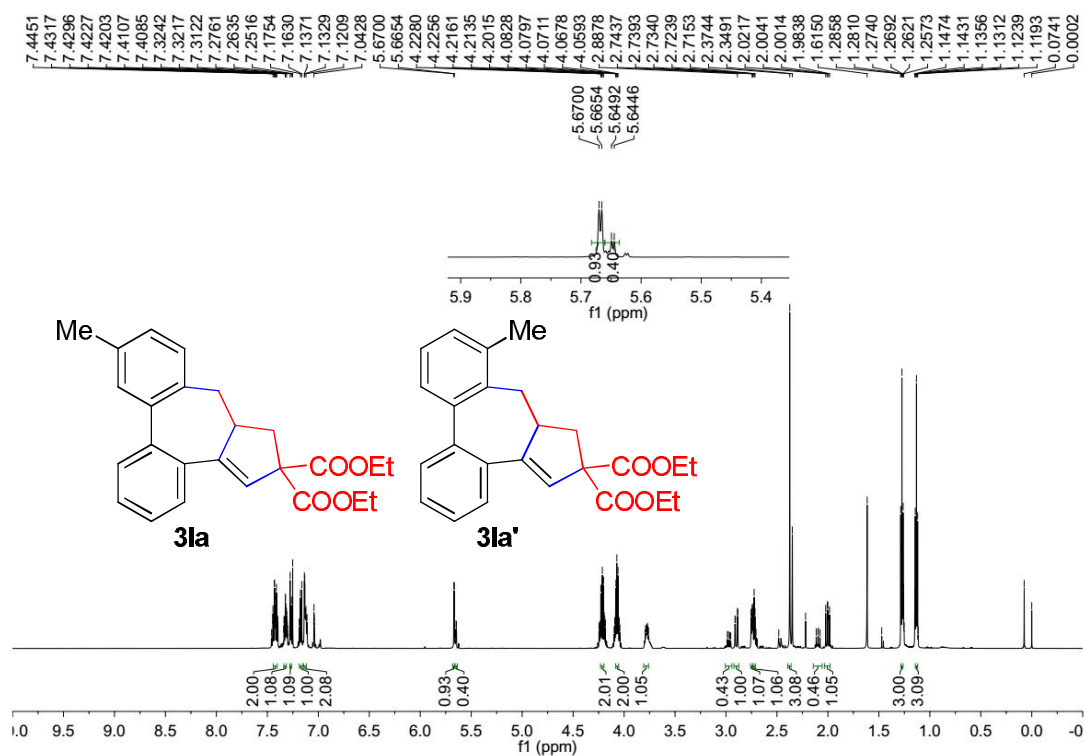


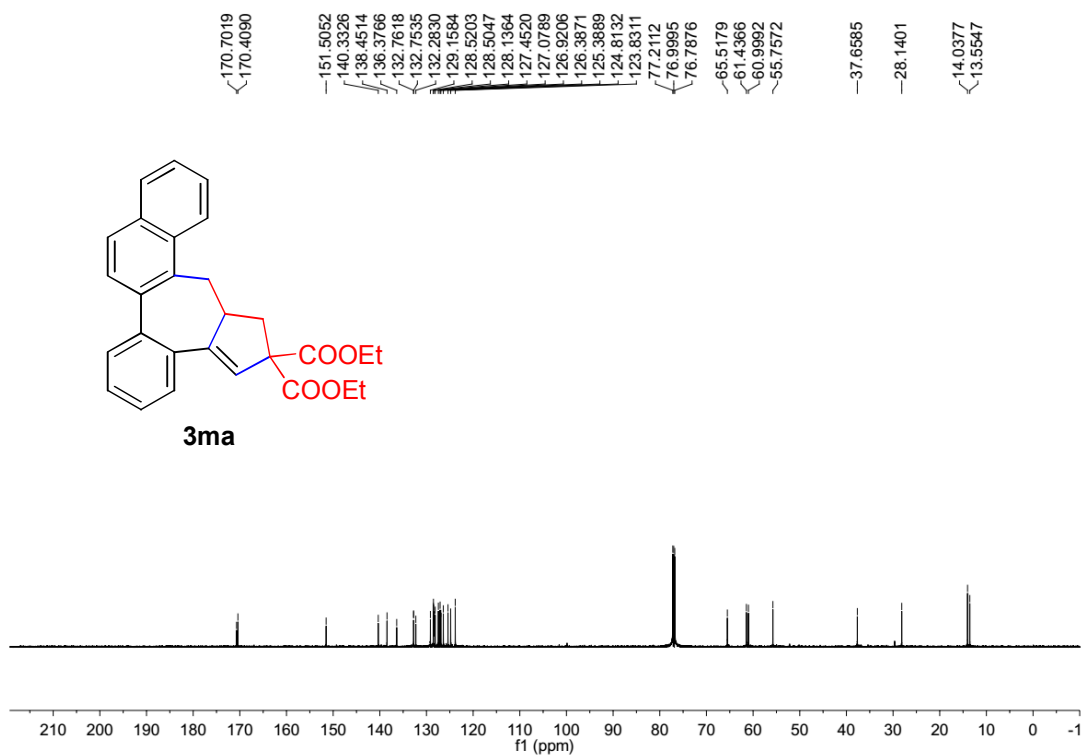
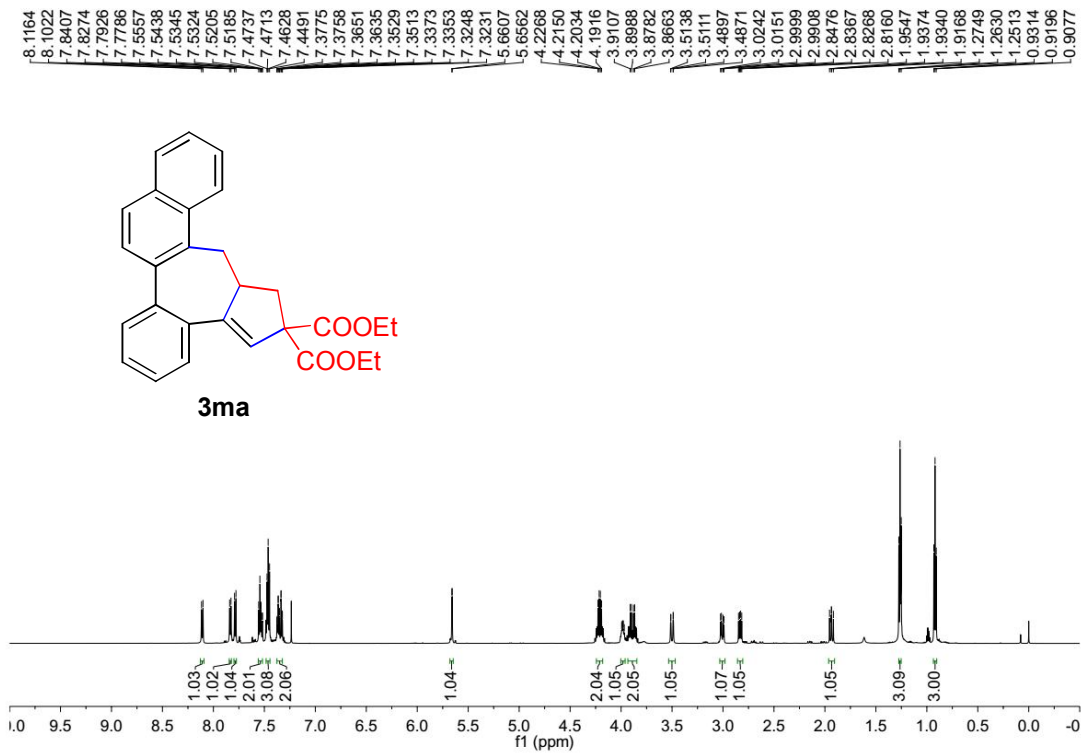


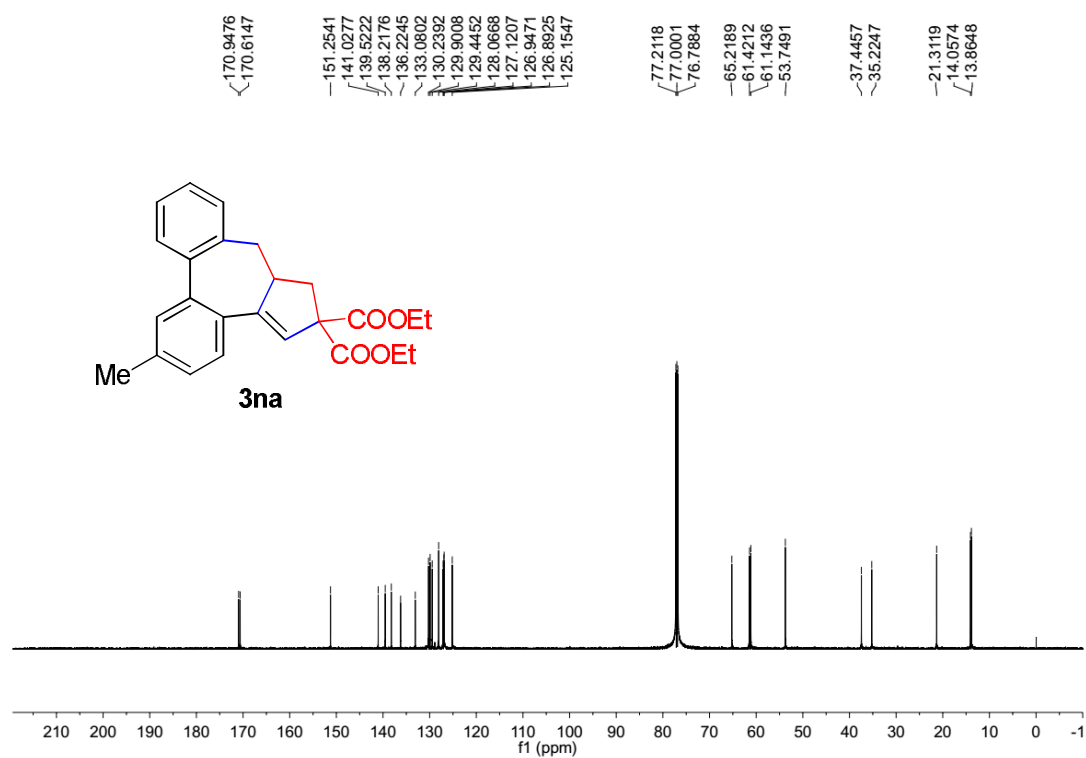
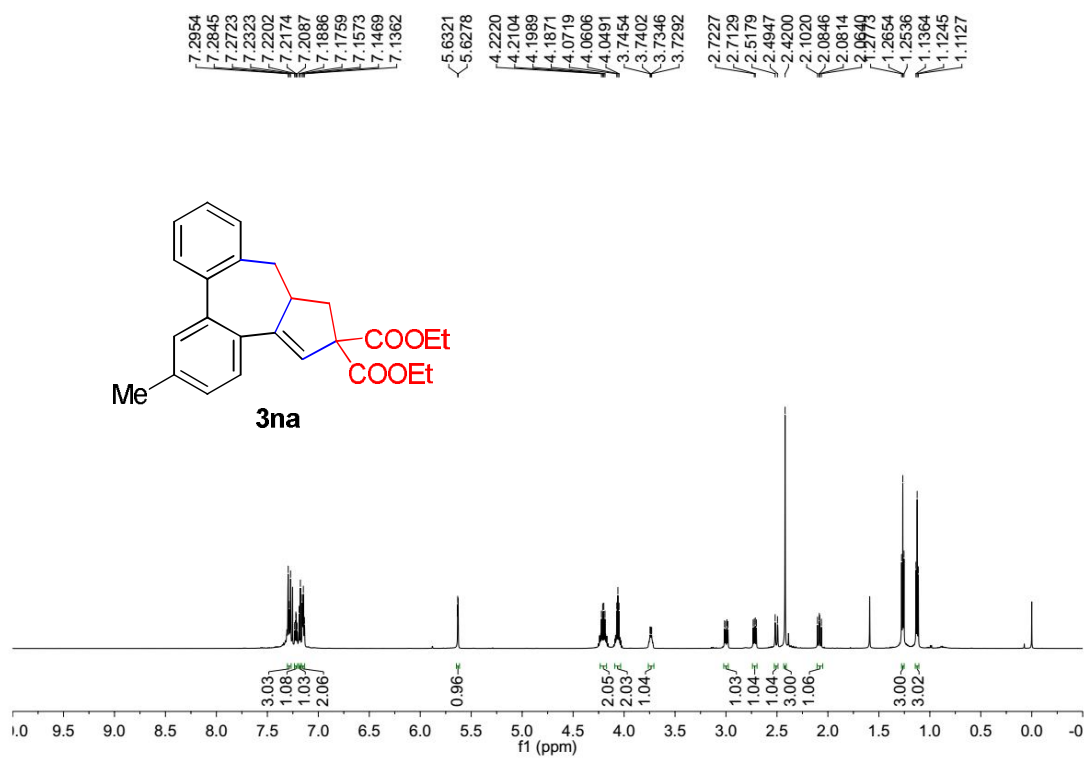


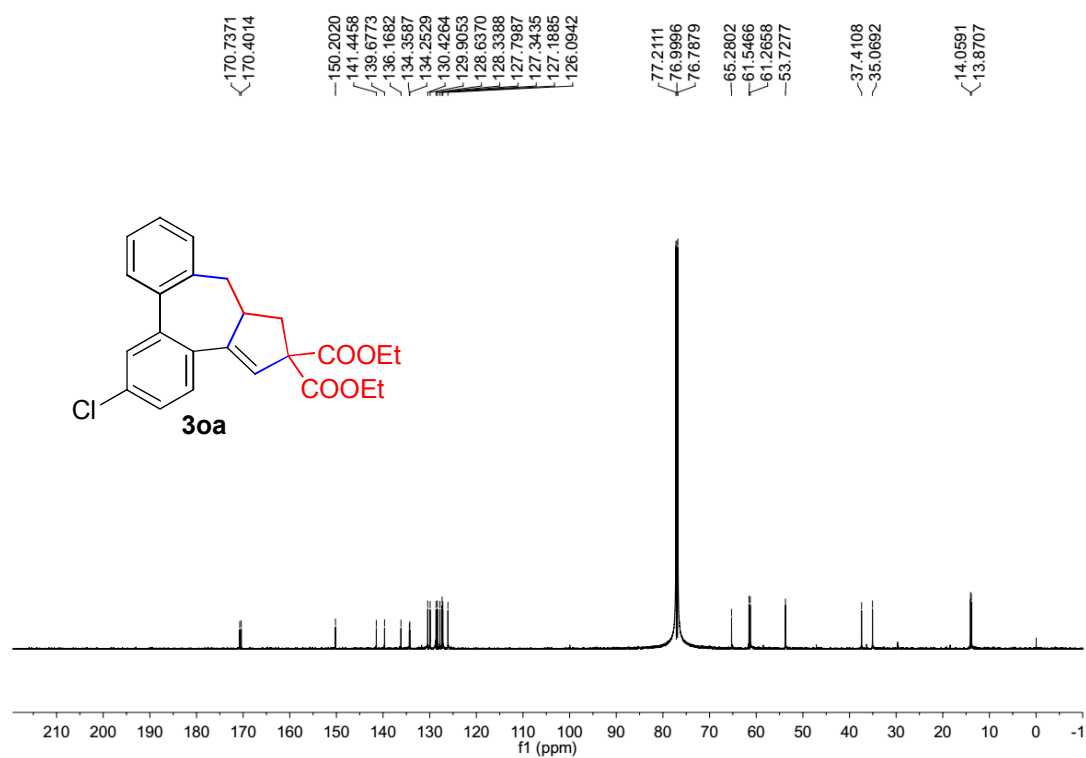
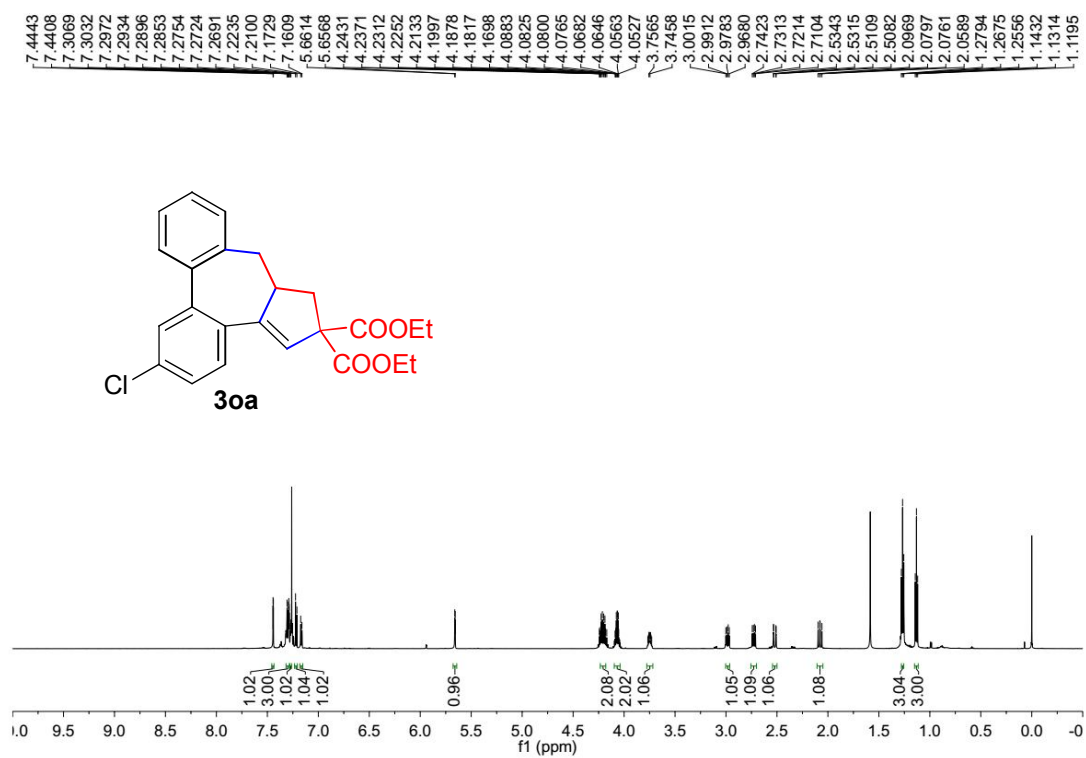


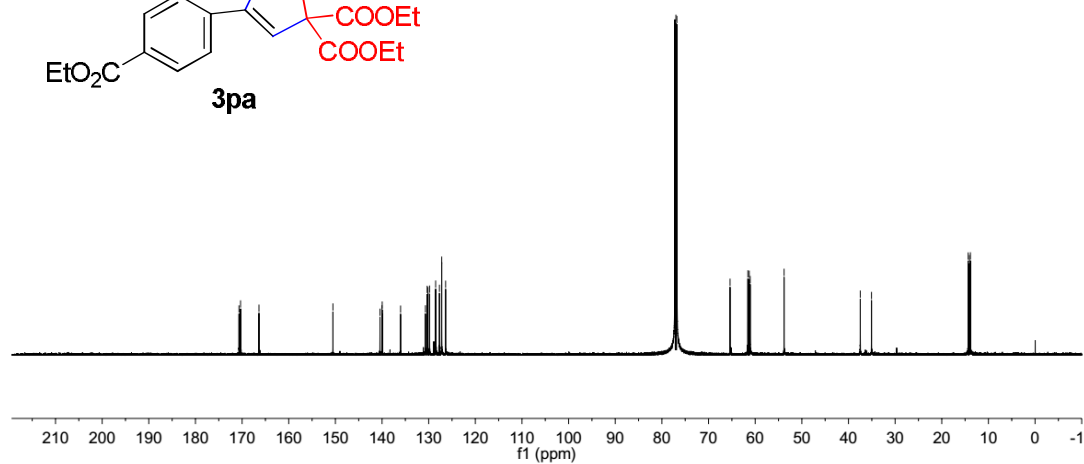
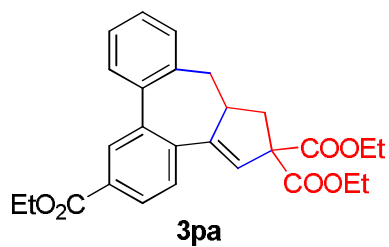
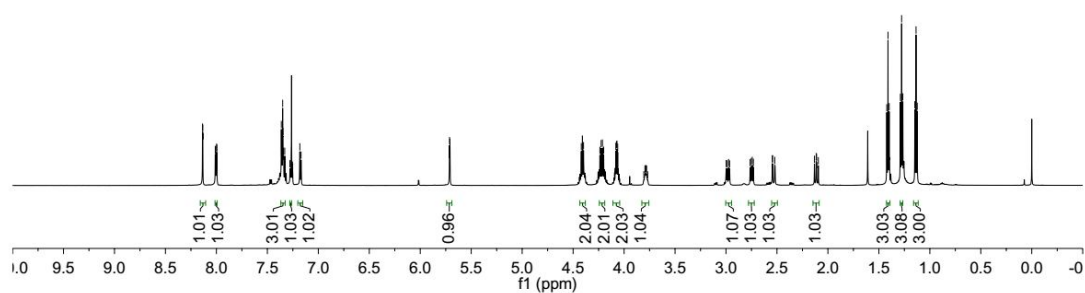
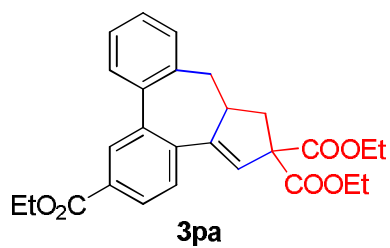


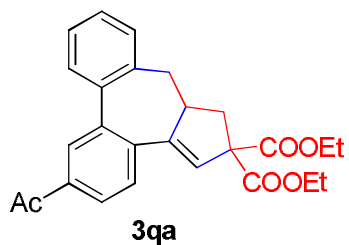
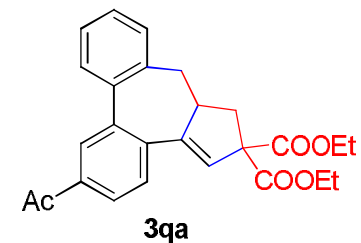


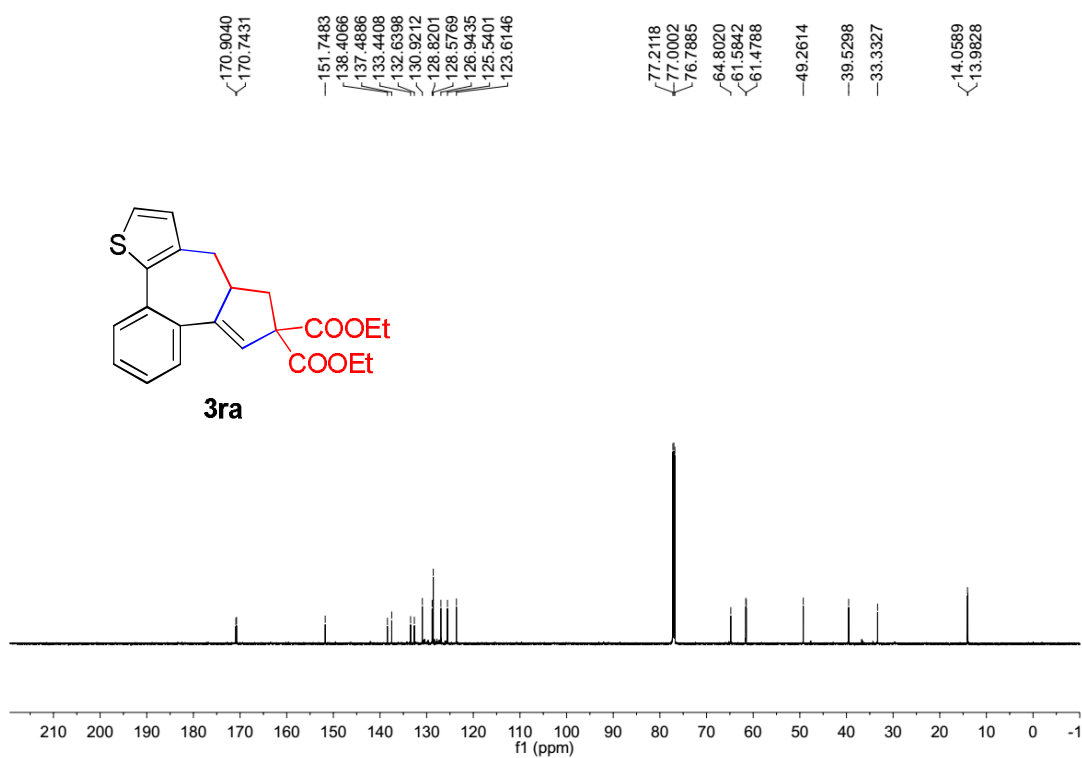
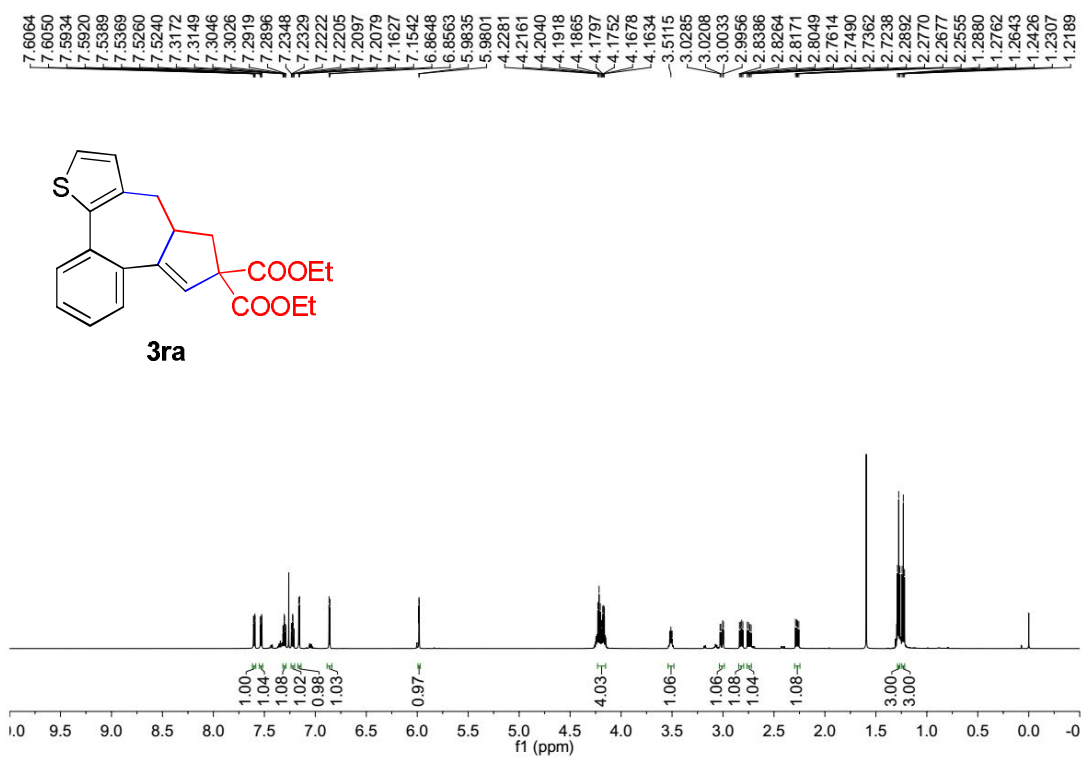


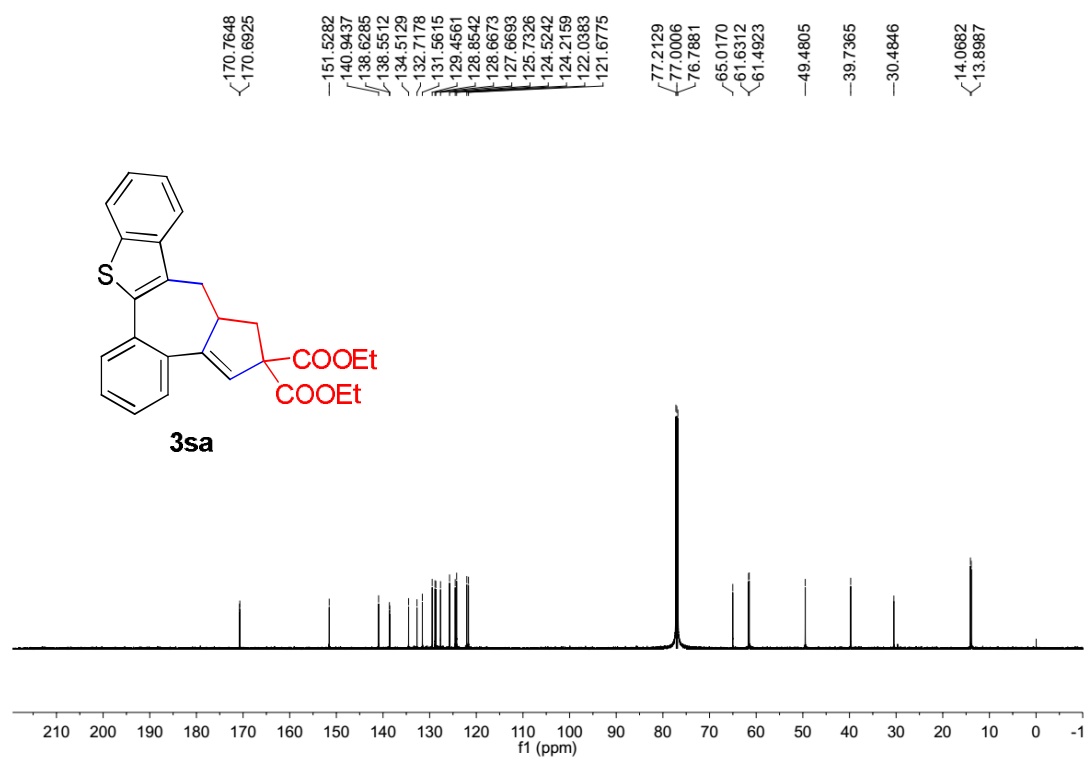
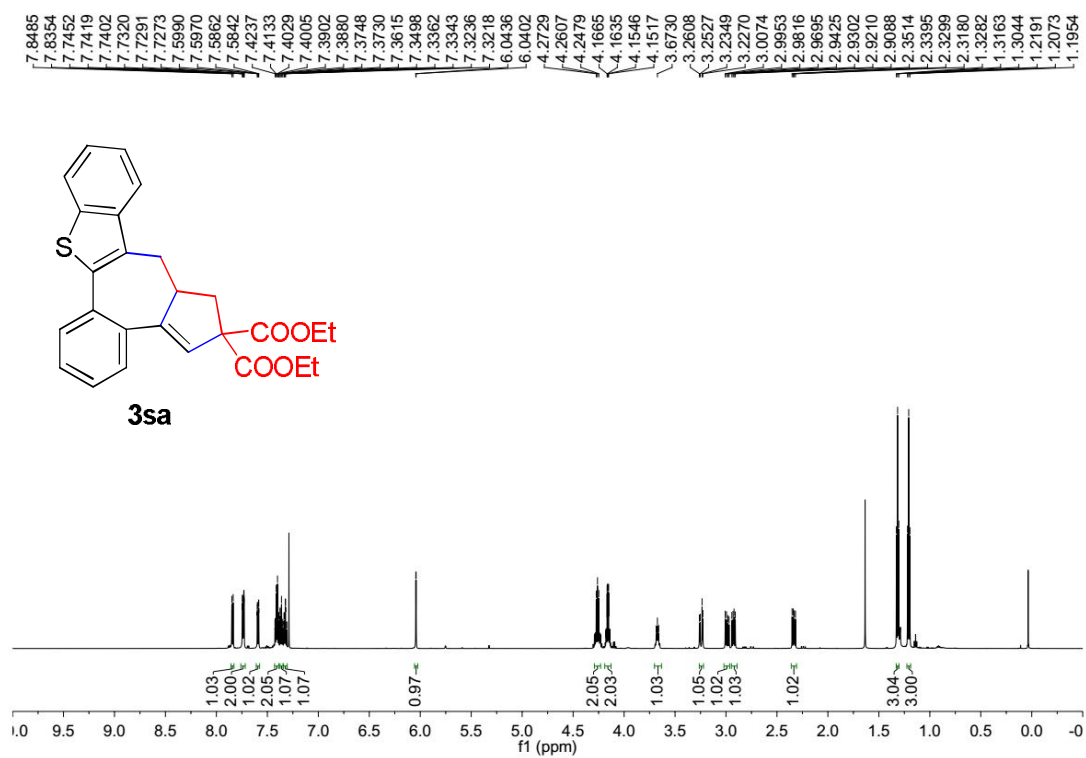


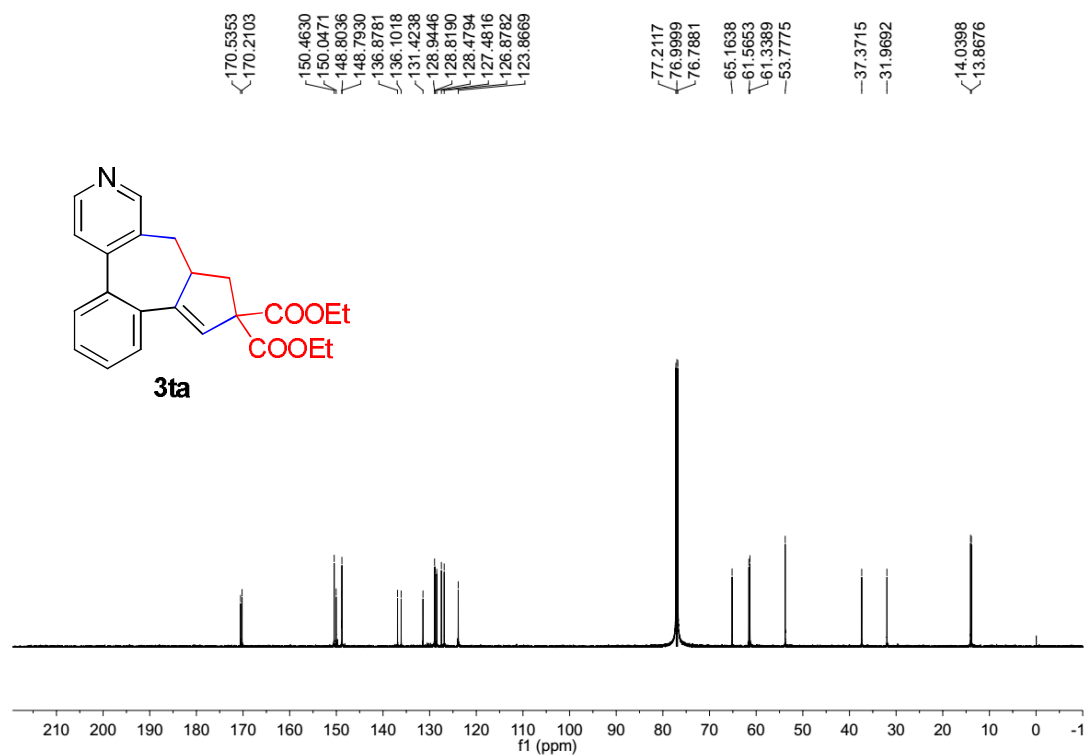
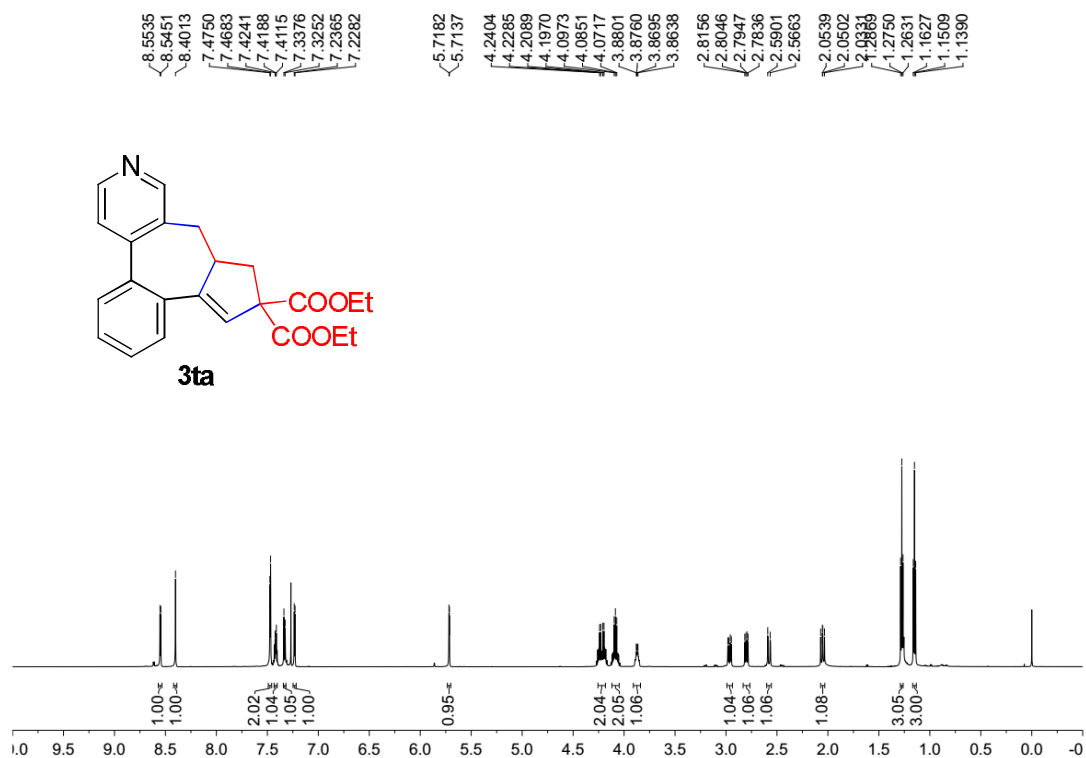


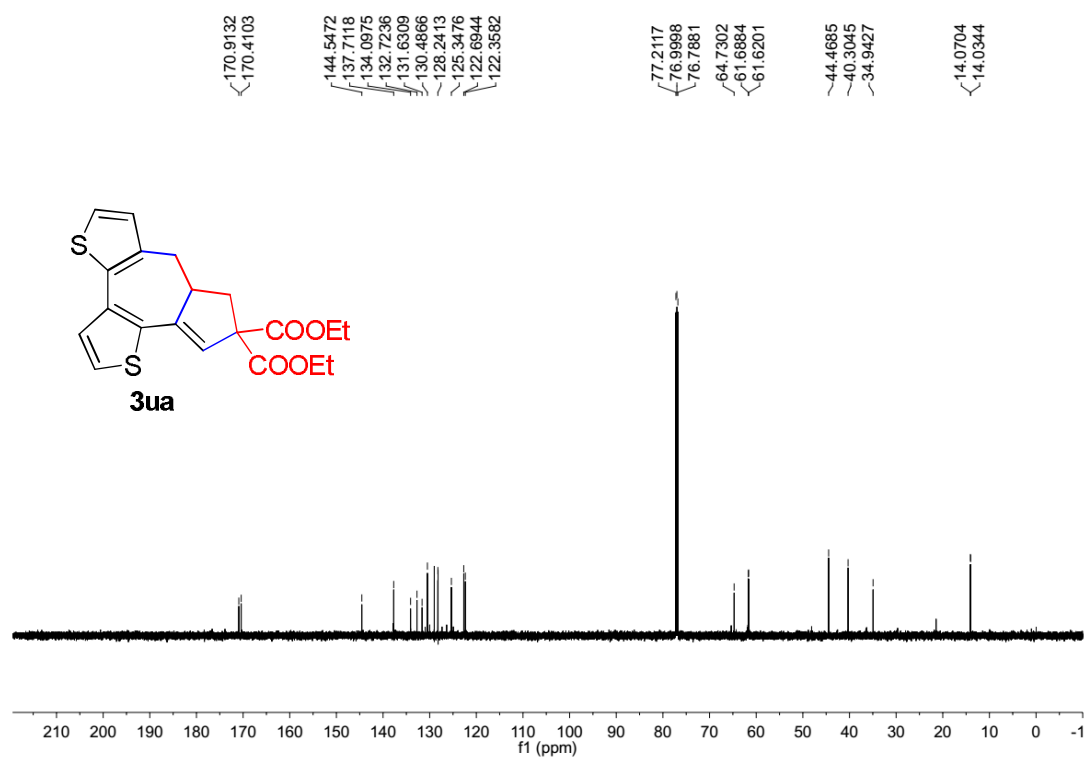
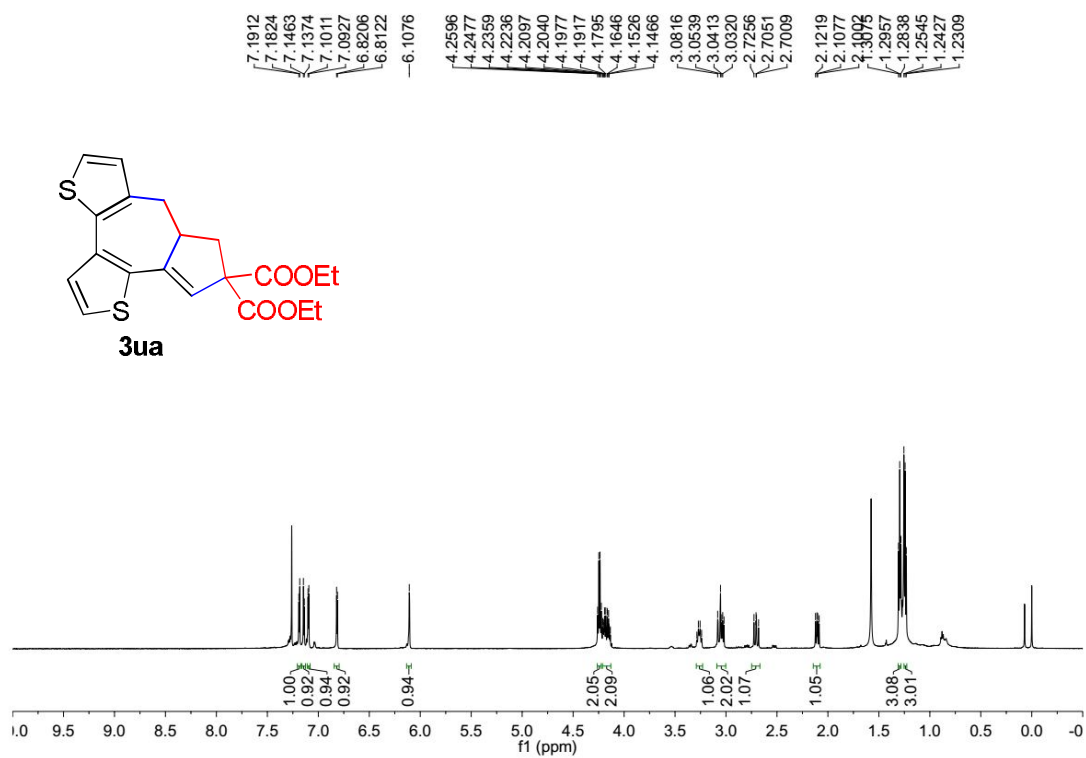


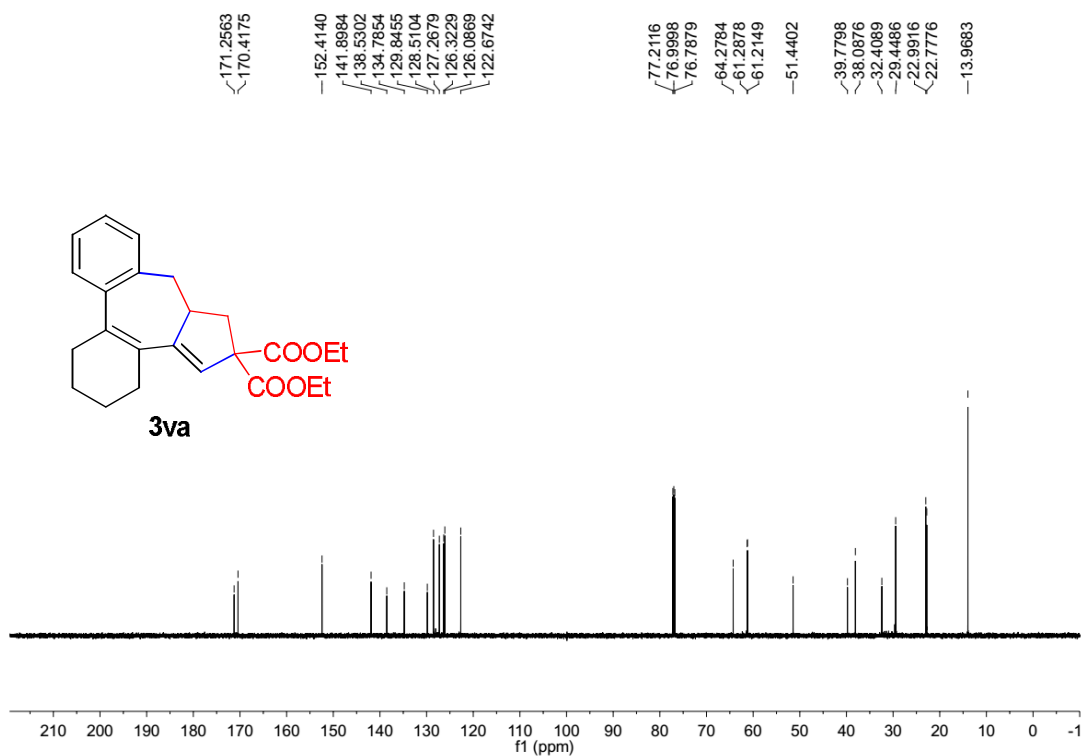
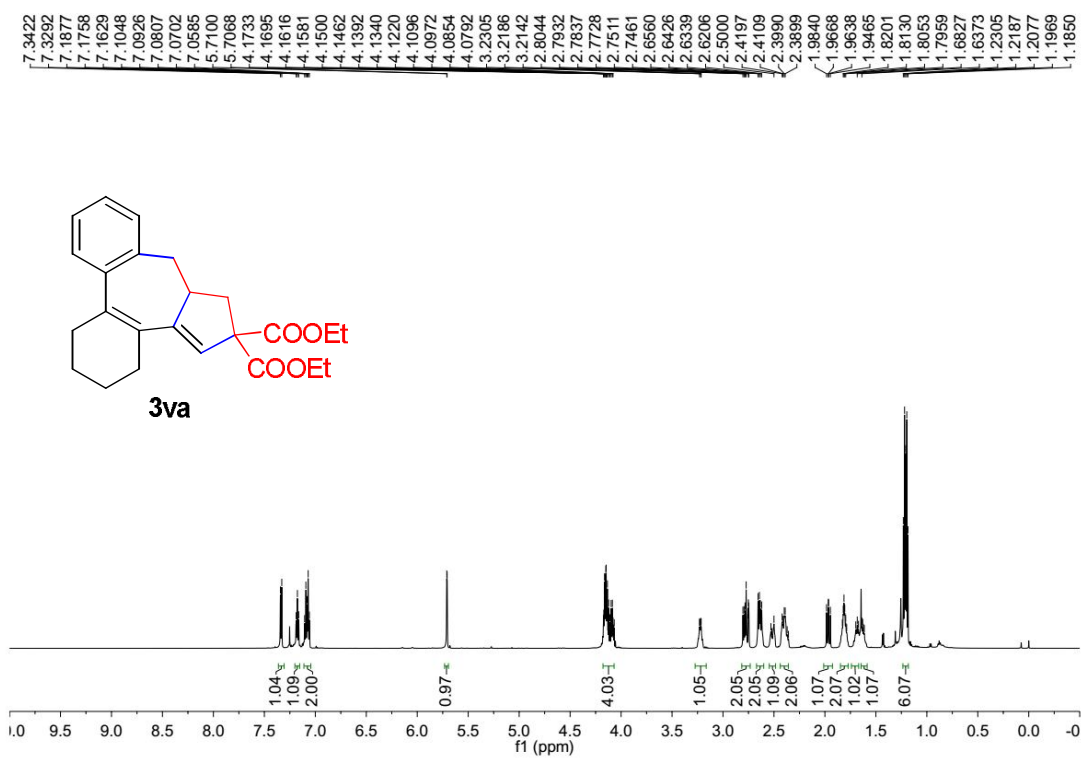


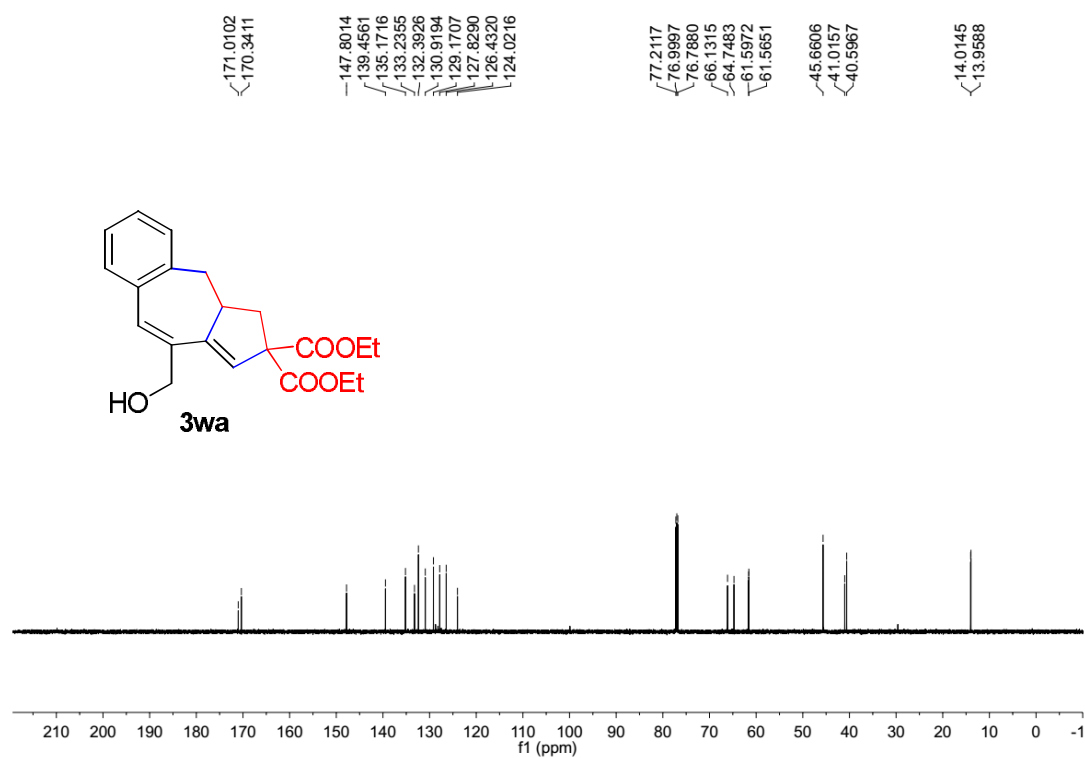
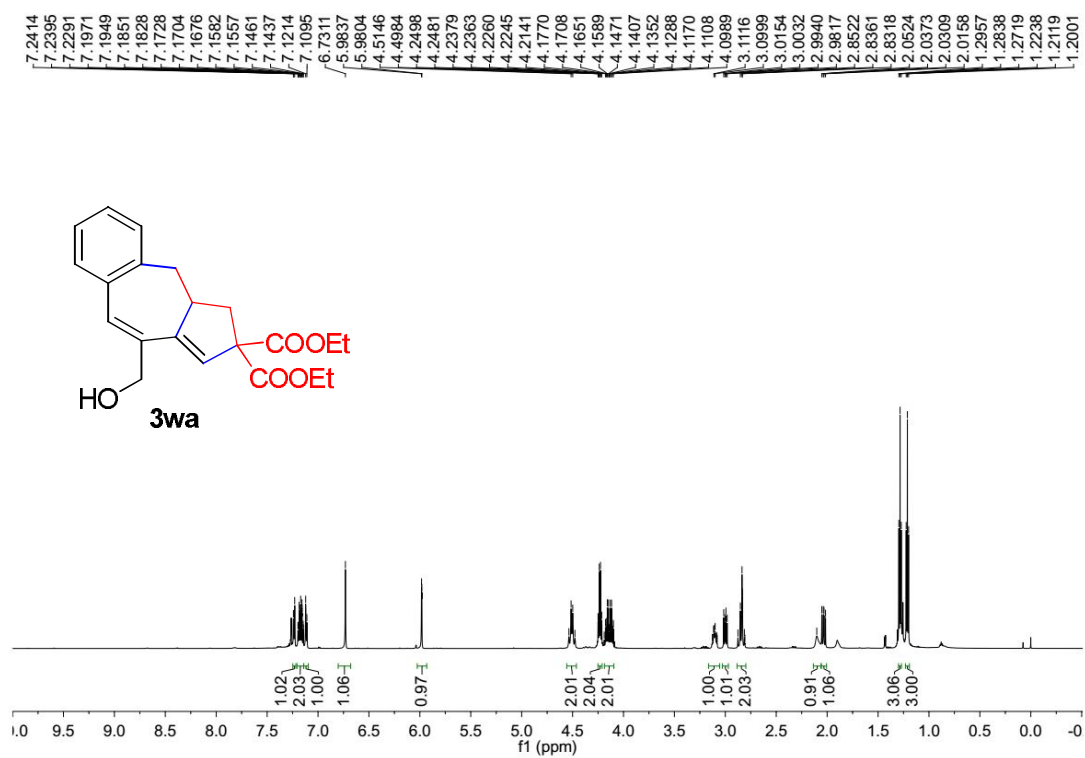


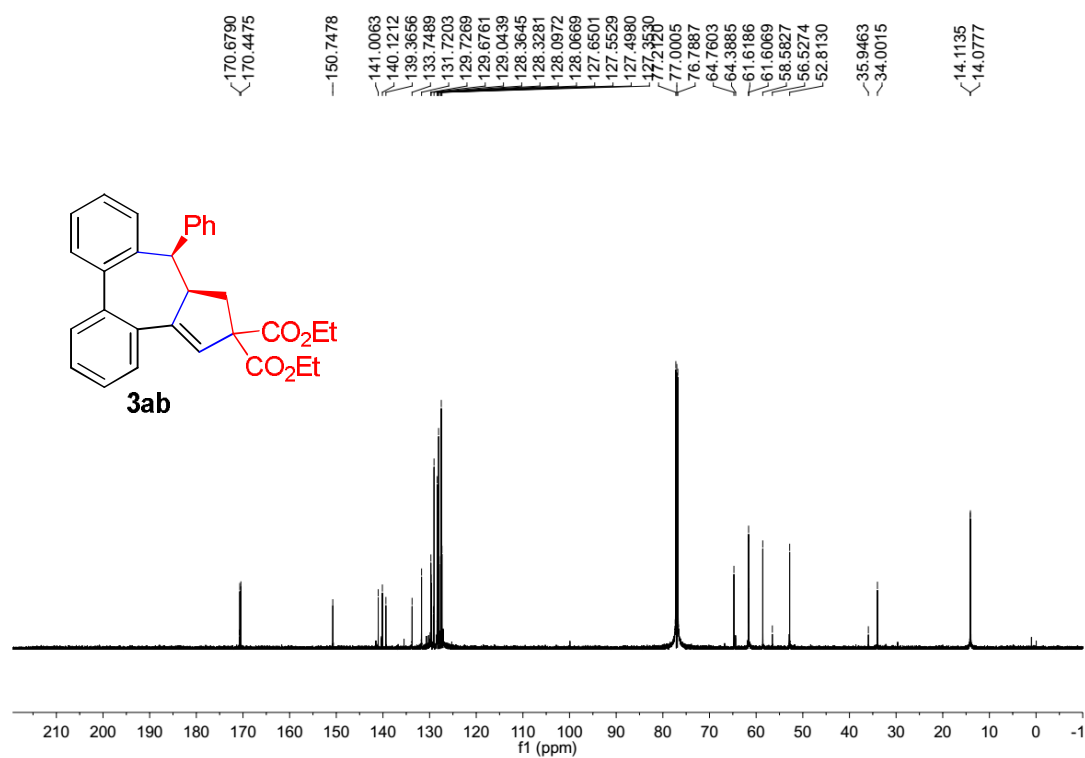
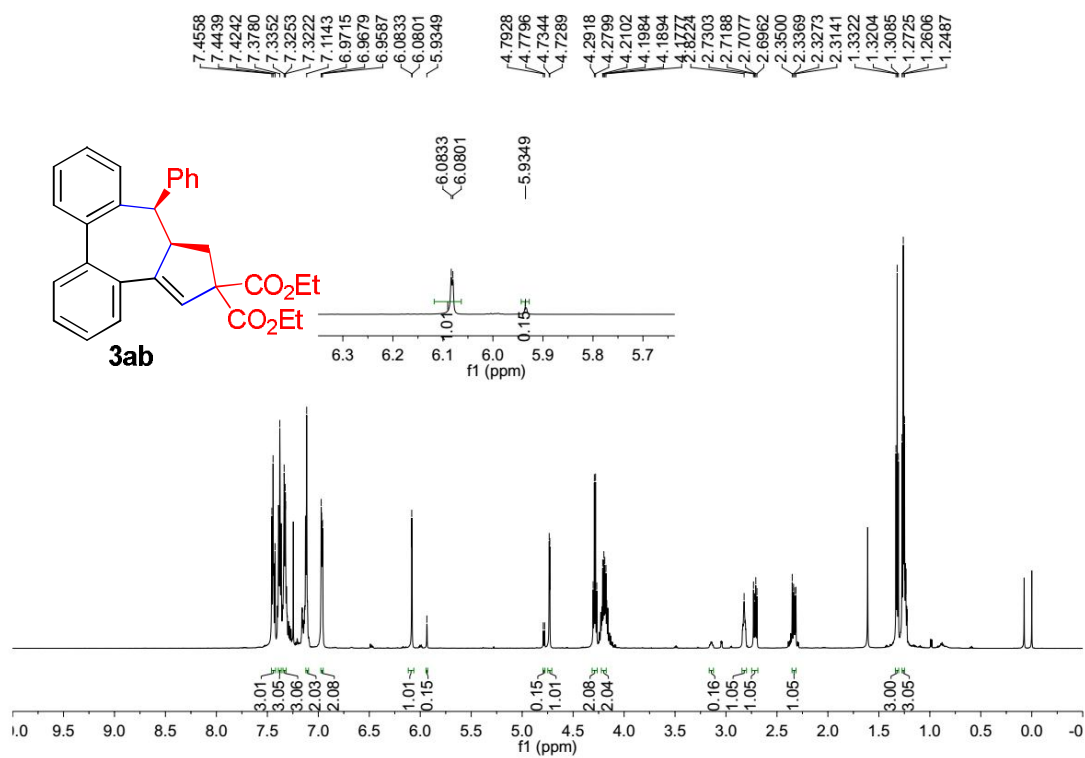


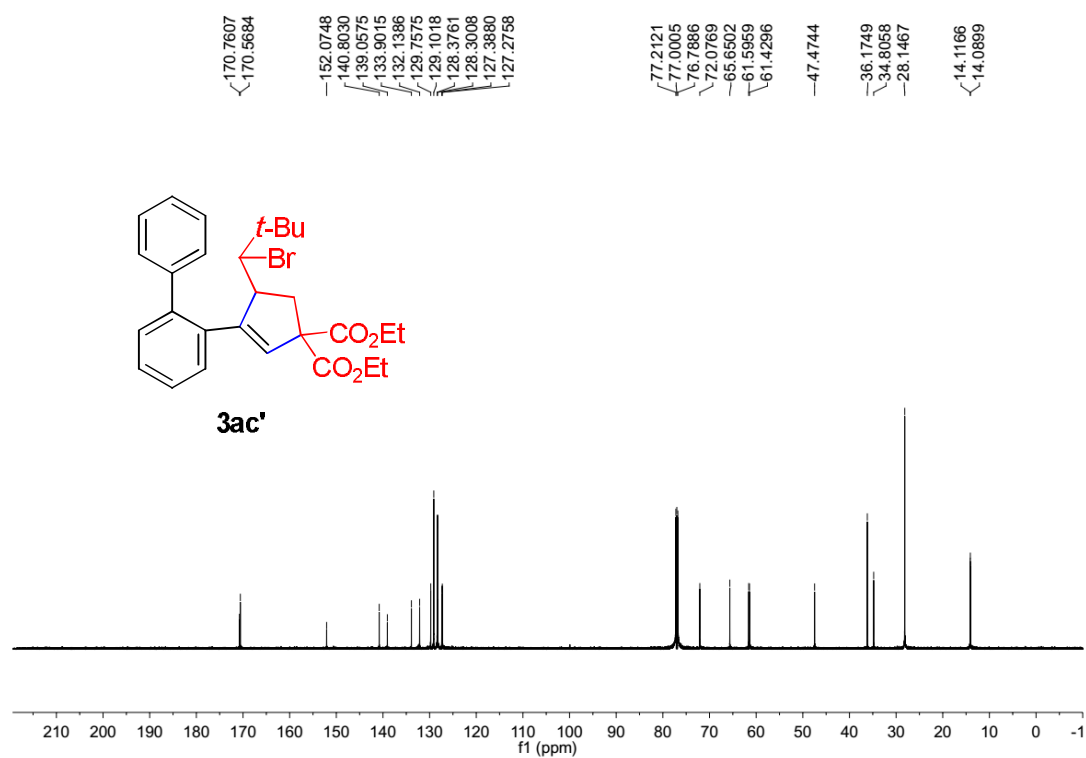
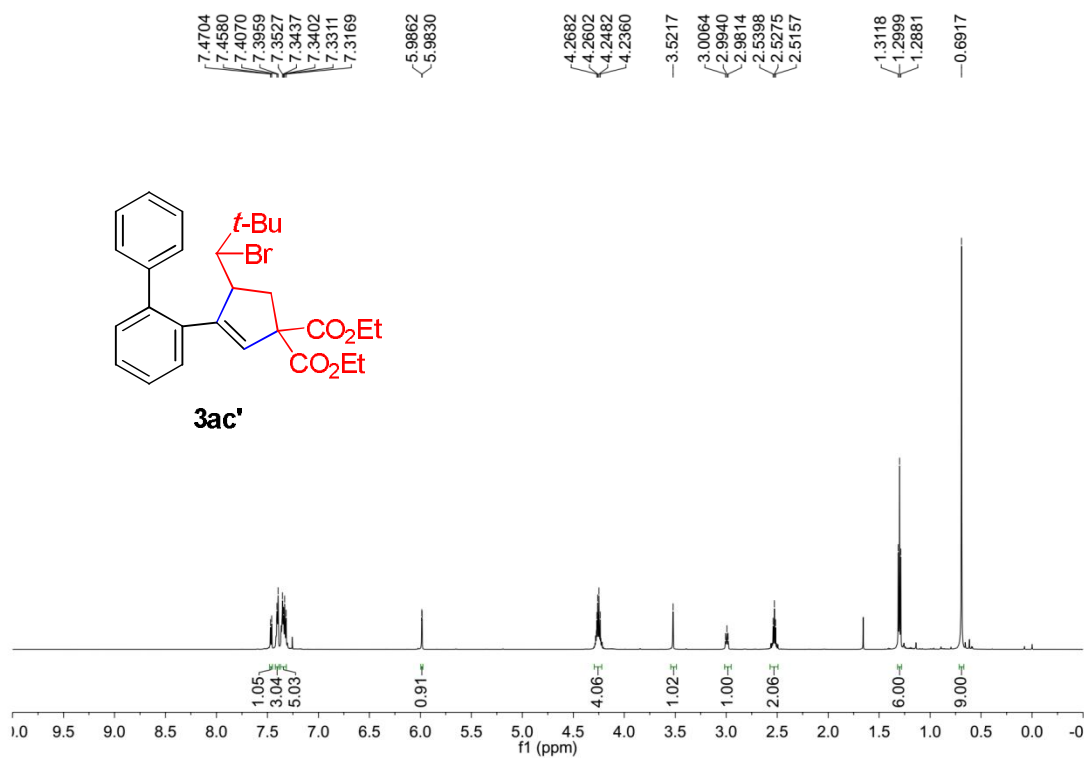


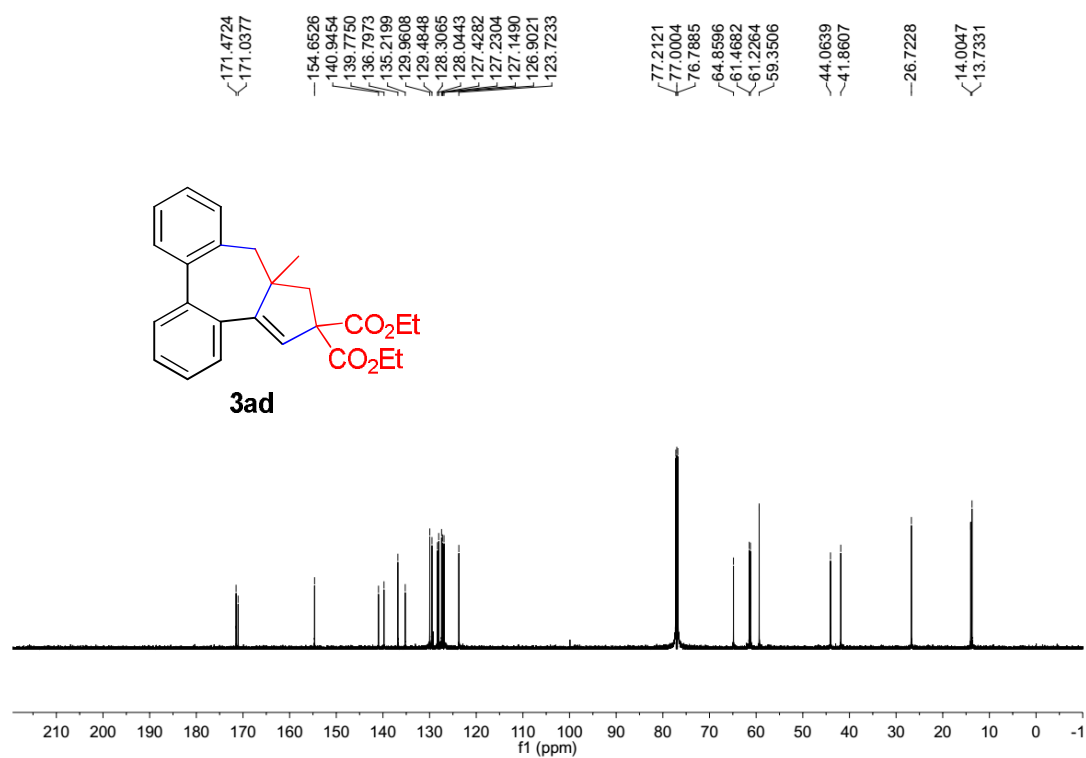
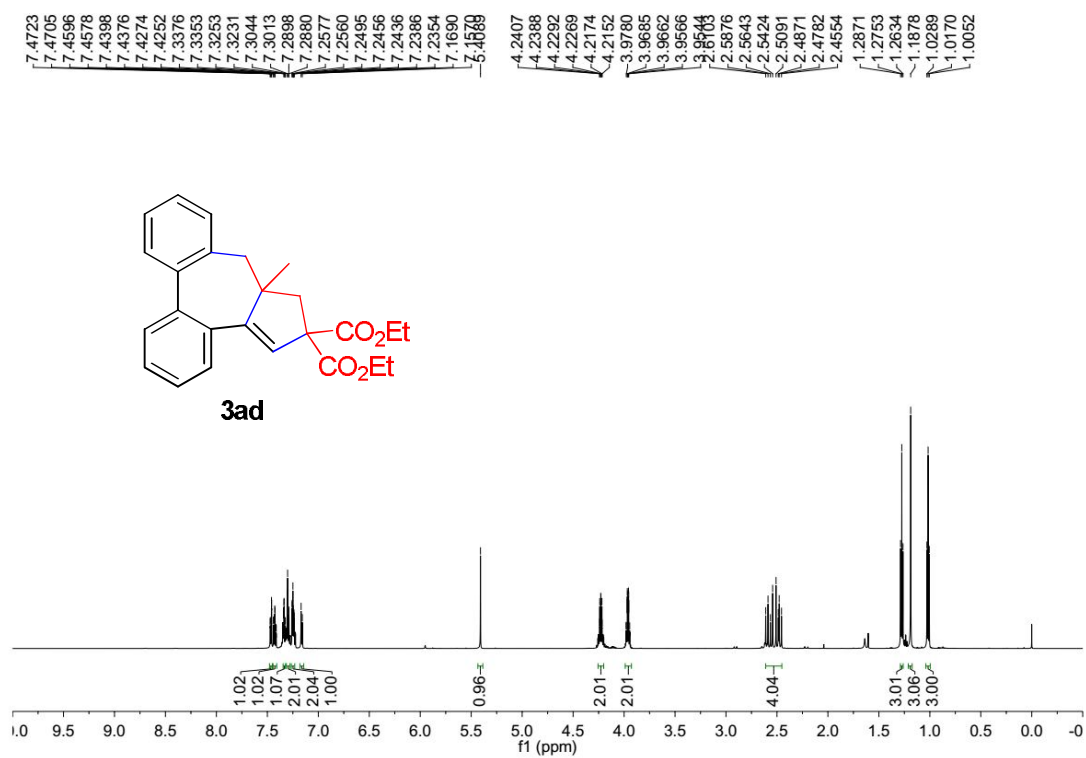


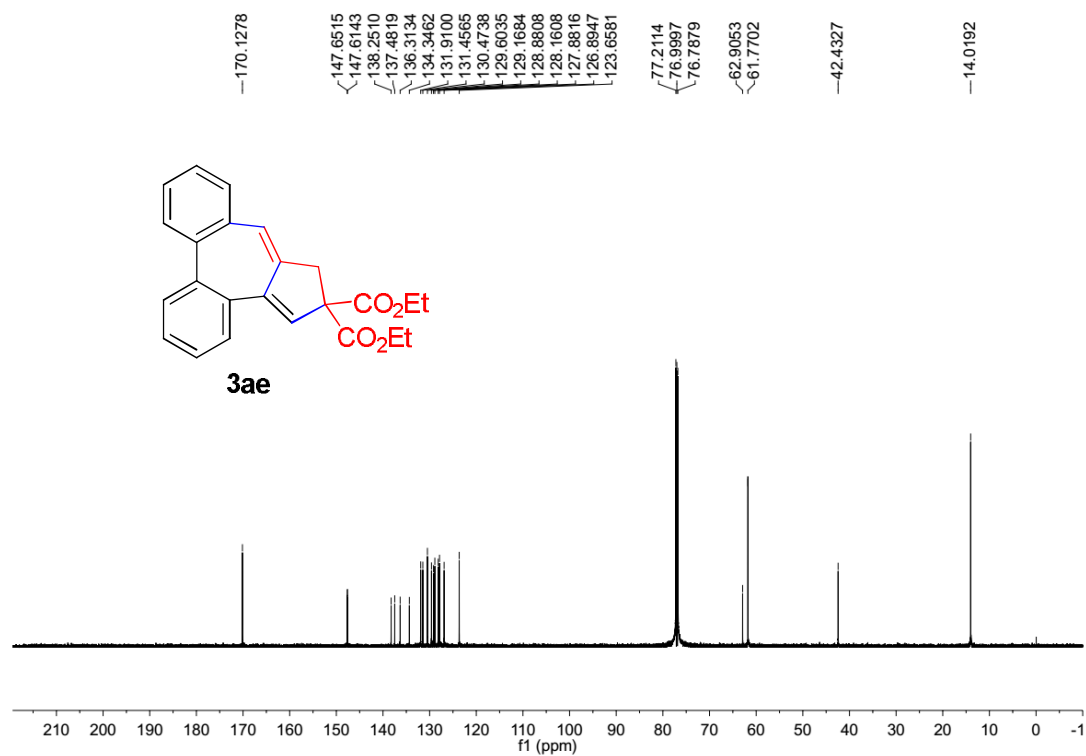
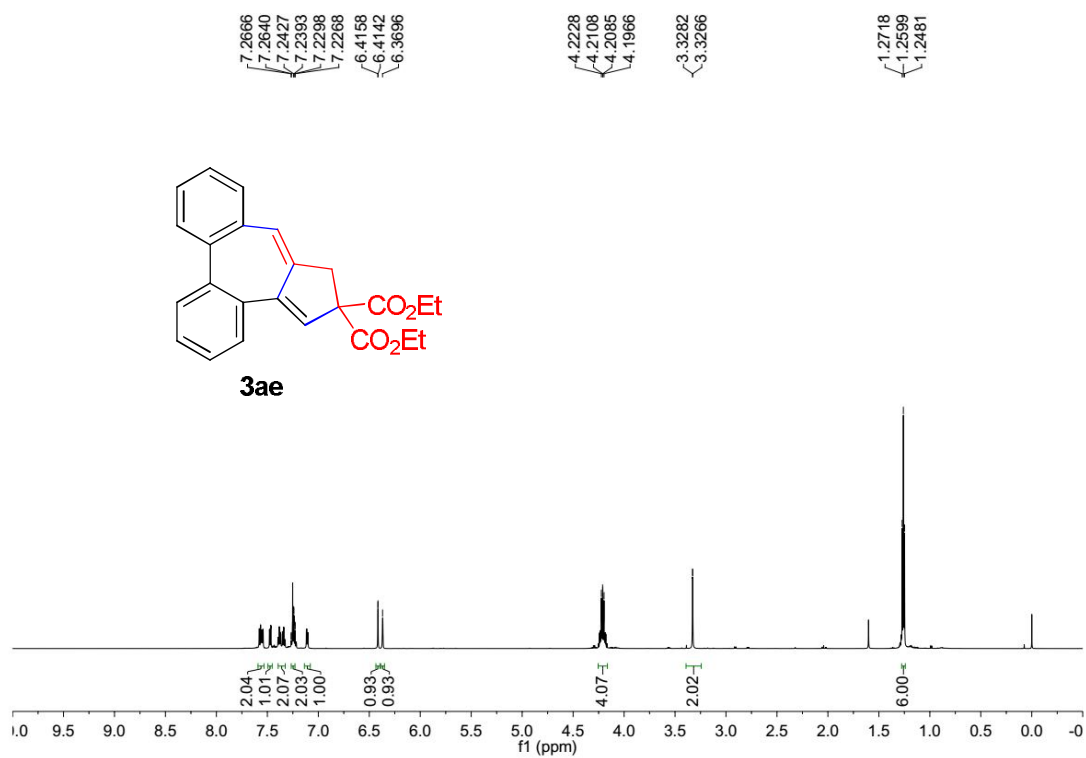


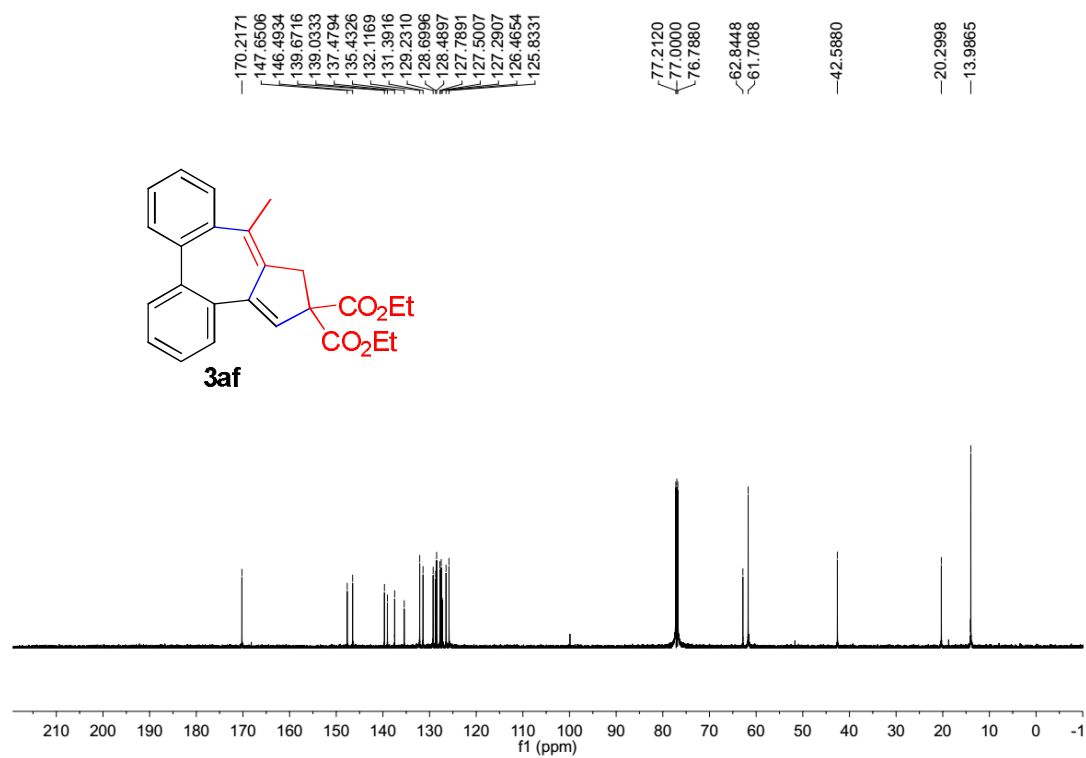
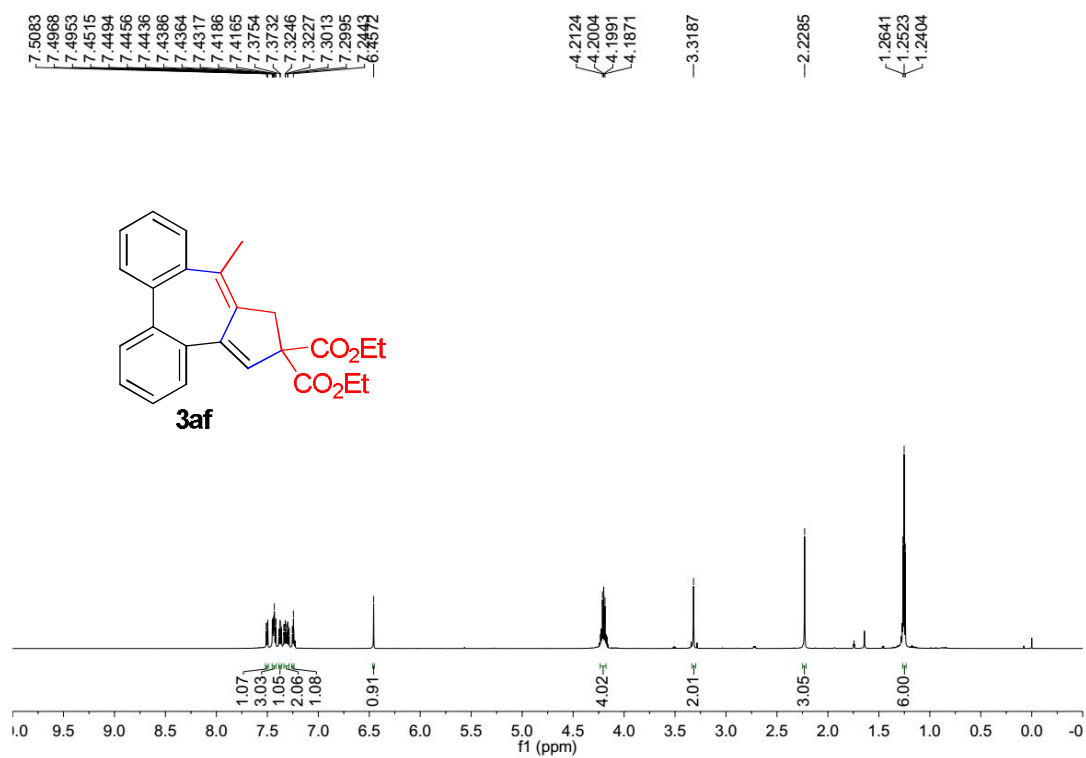


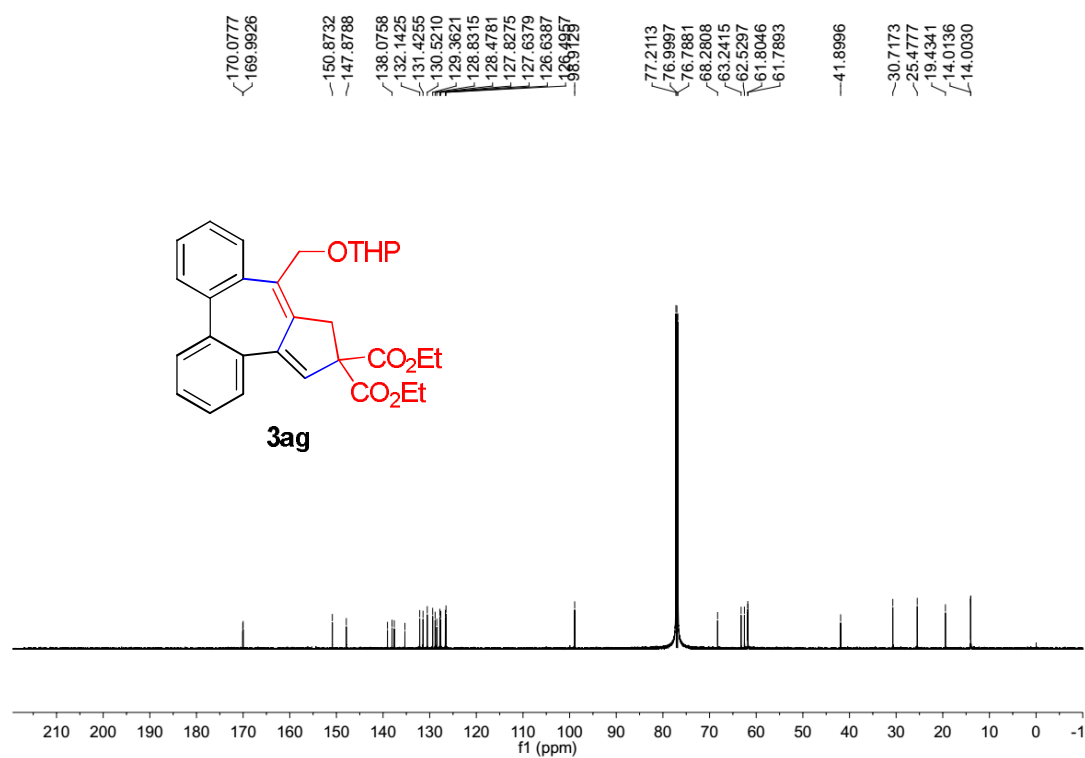
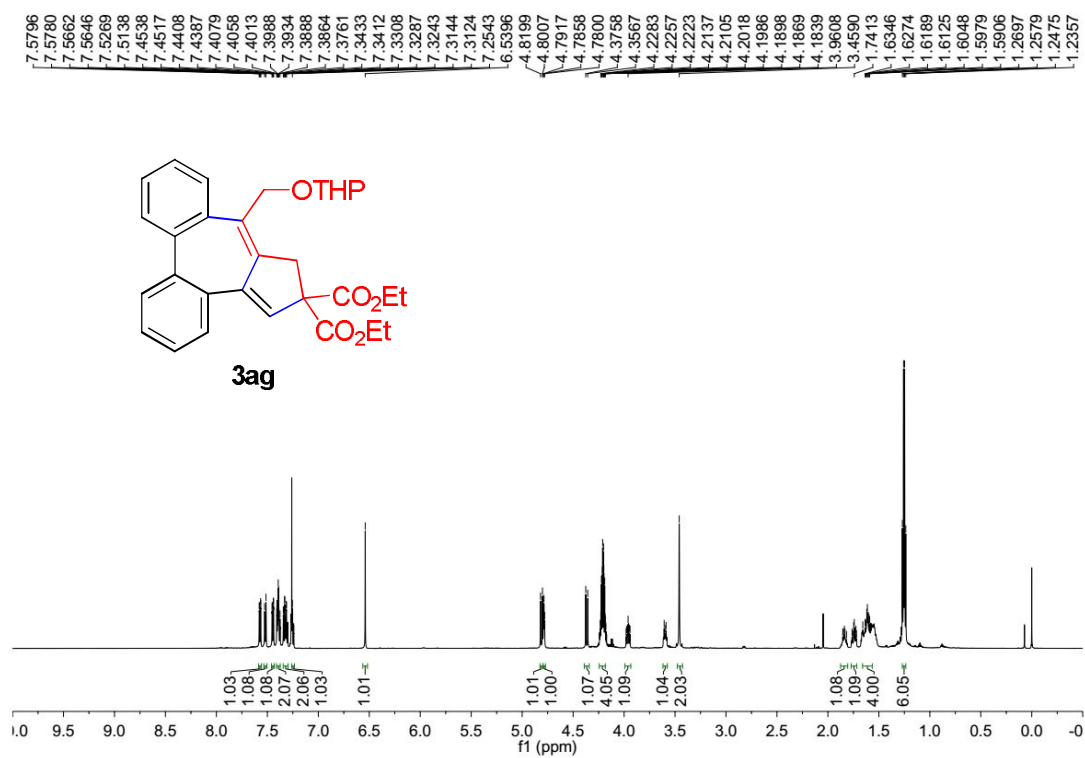


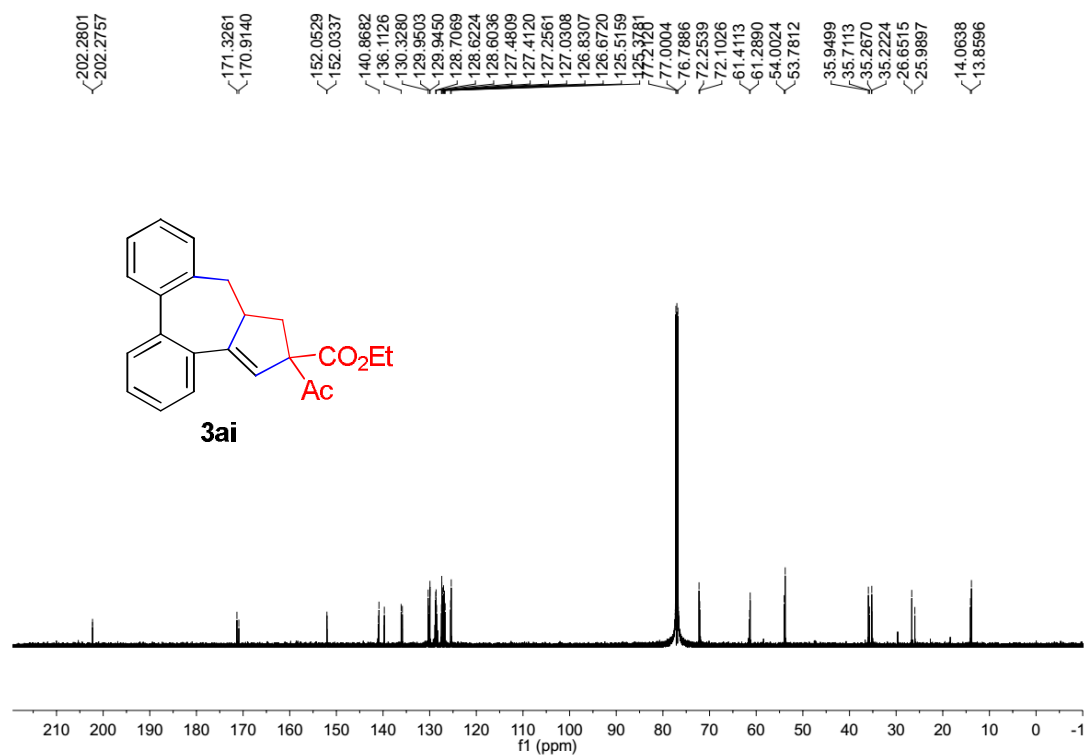
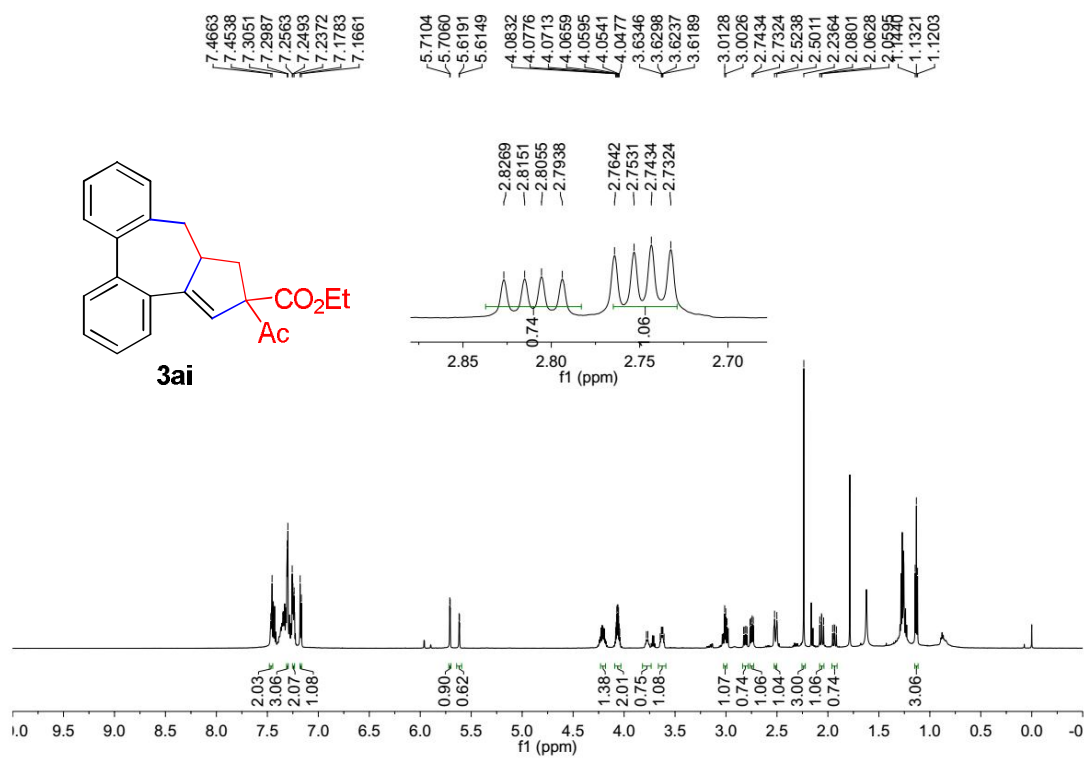


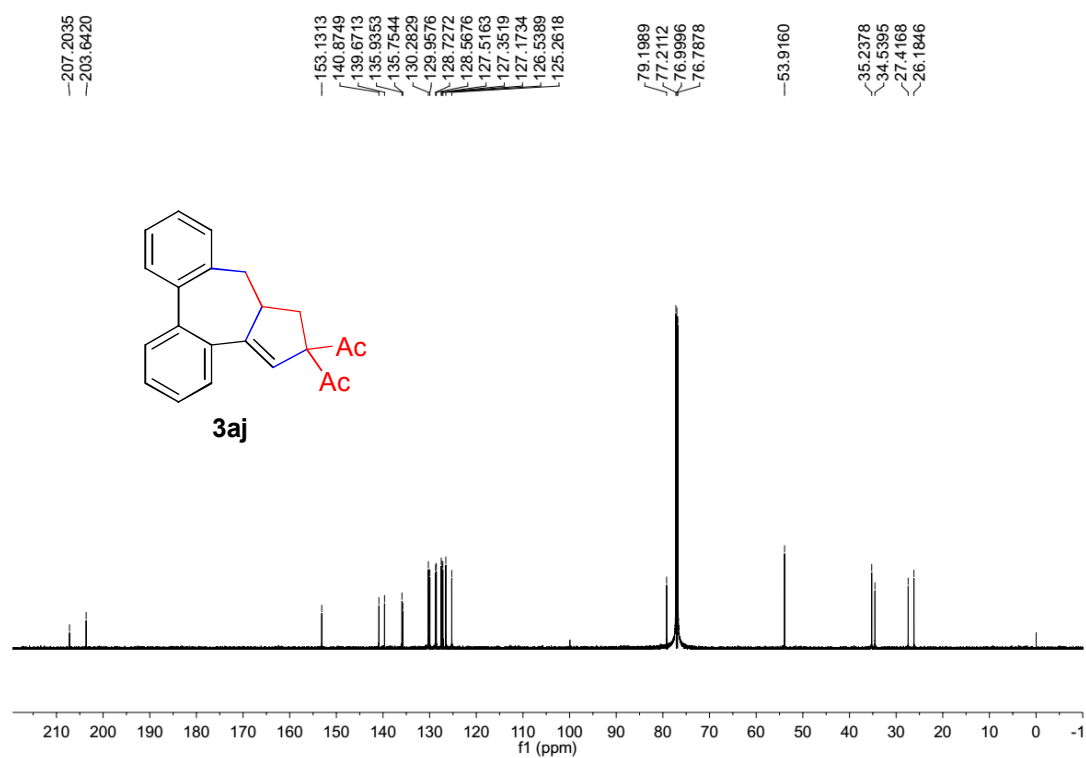
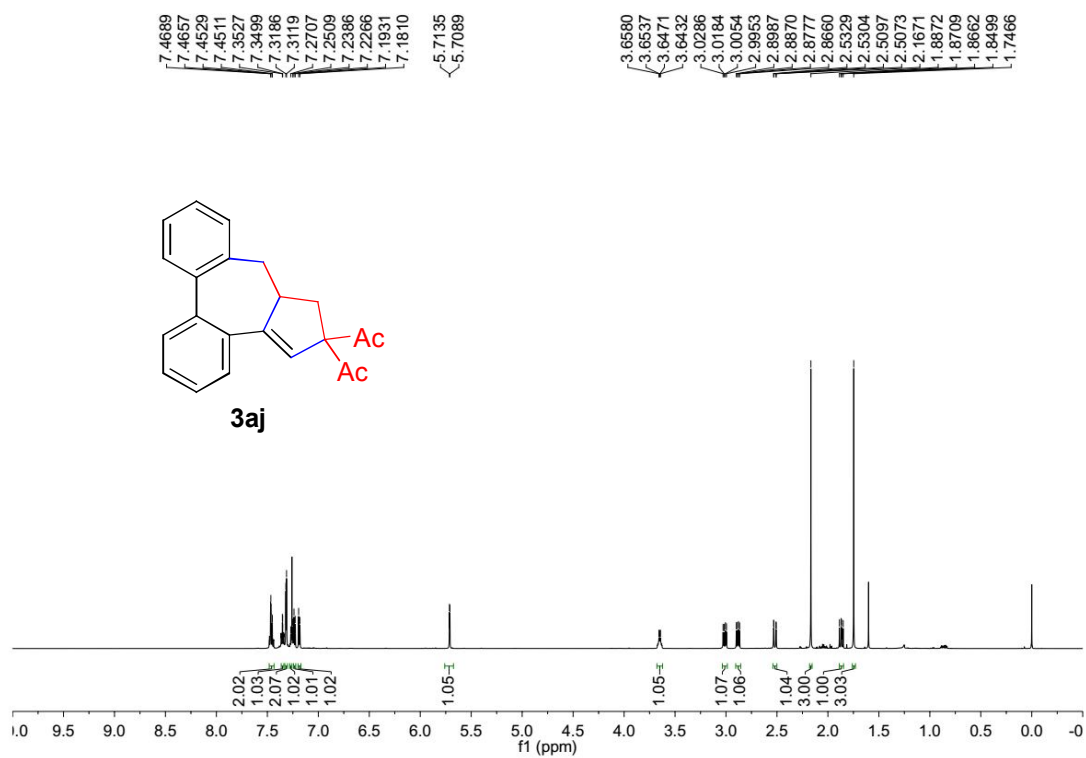


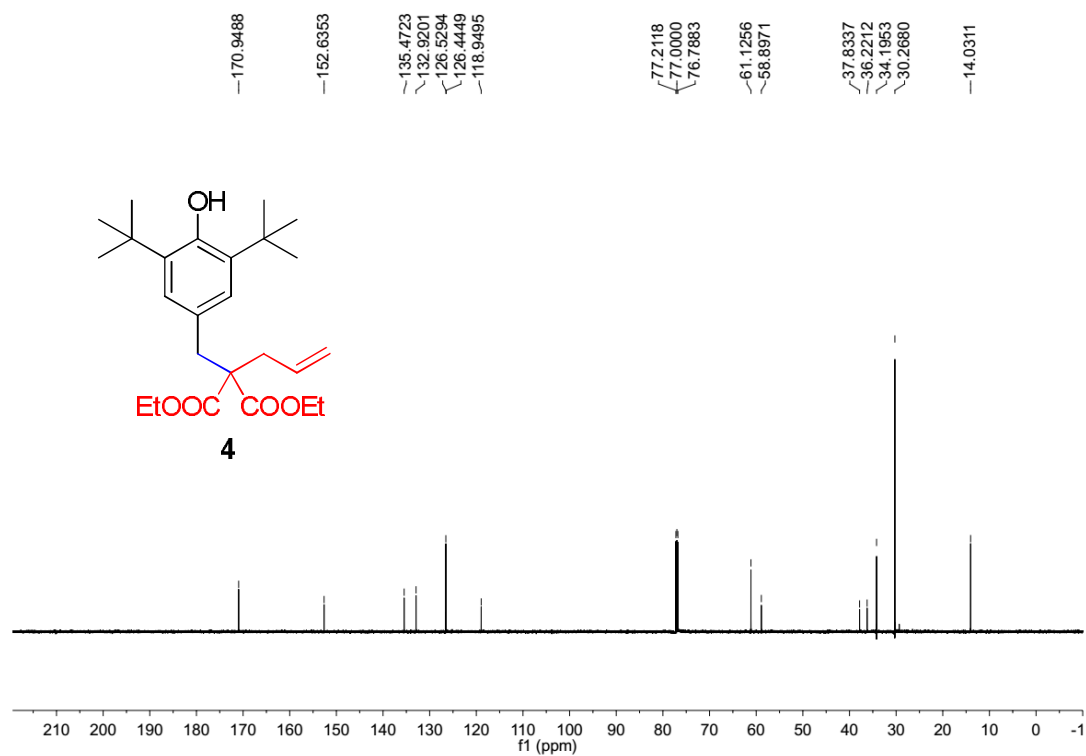
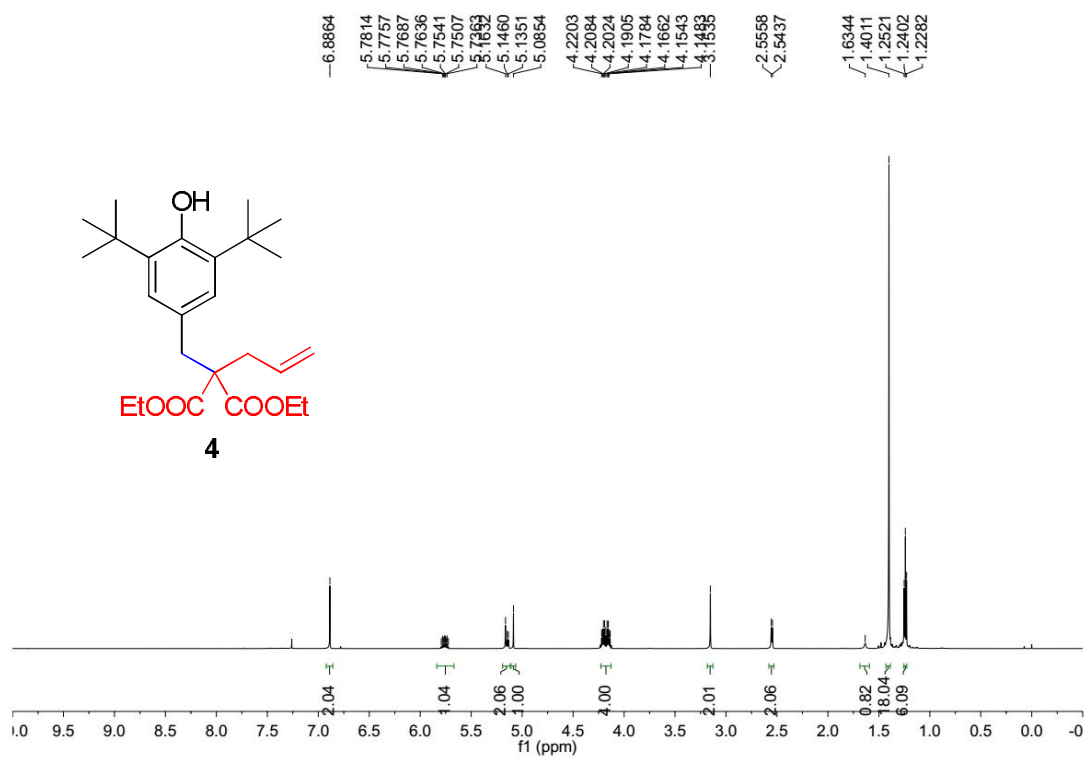




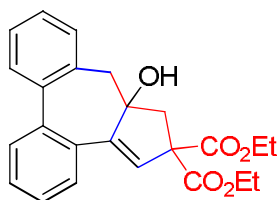




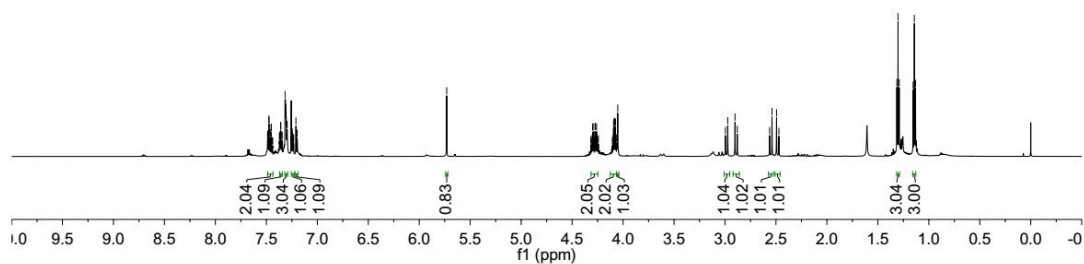




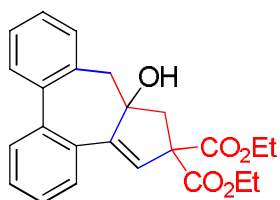
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