

Supporting Materials to

**Pd-catalyzed addition of boronic acids to ynol ethers: a highly regio-
and stereoselective synthesis of trisubstituted vinyl ethers**

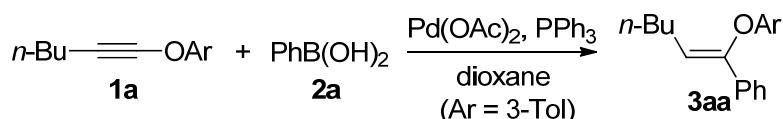
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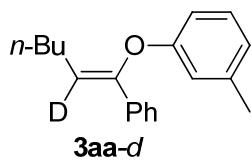
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General: Toluene, THF, and dioxane were distilled from sodium prior to use. Unless otherwise noted, all the reagents were obtained commercially and used without further purification. Column chromatography was performed using silica gel (300–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on 400 or 600 MHz NMR spectrometers. Chemical shifts were reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard. MS and microanalysis were performed in the state authorized analytical center of this university.

General procedure for the Pd-catalyzed addition of boronic acids to ynone ethers:

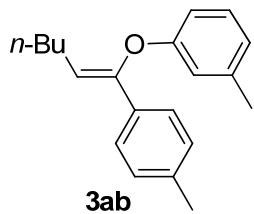


To a mixture of **2a** (79.3 mg, 0.65 mmol), Pd(OAc)_2 (5.6 mg, 0.025 mmol), PPh_3 (13.2 mg, 0.05 mmol) and Na_2CO_3 (80 mg, 0.75 mmol) in 2 mL of dioxane was added **1a** (94 mg, 0.5 mmol). After stirring at 60 °C for 4 h, the reaction mixture was concentrated and purified by column chromatography on silica (petroleum ether) to give 119 mg (yield: 90%) of **3aa** as a colorless oil. The stereochemistry was assigned by NOE measurements. ^1H NMR (600 MHz, CDCl_3): δ 7.48 (d, $J = 7.8$ Hz, 2H), 7.30–7.15 (m, 3H), 7.08 (t, $J = 7.9$ Hz, 1H), 6.79 (s, 1H), 6.73 (d, $J = 8.0$ Hz, 2H), 5.85 (t, $J = 7.4$ Hz, 1H), 2.27 (s, 3H), 2.20 (q, $J = 7.3$ Hz, 2H), 1.44–1.30 (m, 4H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.4, 148.6, 139.5, 135.6, 129.1, 128.4, 127.7, 125.1, 122.1, 118.2, 116.1, 112.3, 31.4, 25.6, 22.4, 21.5, 13.9; MS (EI, m/z): 266 (M^+ , 37), 158 (56), 143 (61), 117 (69), 115 (100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{22}\text{O}$ (M^+) 266.1671, found 266.1673.

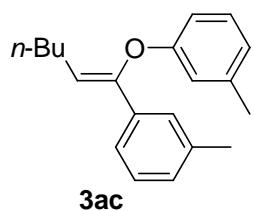


Compound **3aa-d**: it was obtained by replacing PhB(OH)_2 with 0.4 equiv of $(\text{PhBO})_3$ in the presence of 5 equiv of D_2O under the standard conditions, yield: 85%, colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.48 (d, $J = 7.8$ Hz, 2H), 7.28–7.15 (m, 3H), 7.08 (t, $J =$

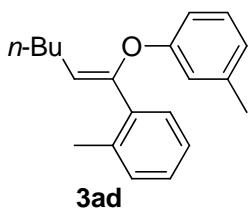
7.9 Hz, 1H), 6.79 (s, 1H), 6.73 (m, 2H), 5.85 (t, $J = 7.4$ Hz, 0.13H), 2.27 (s, 3H), 2.20 (q, $J = 7.3$ Hz, 2H), 1.44–1.30 (m, 4H), 0.87 (t, $J = 7.3$ Hz, 3H); MS (EI, m/z): 267 (M^+ , 38), 224 (43), 159 (86), 143 (68), 115 (100).



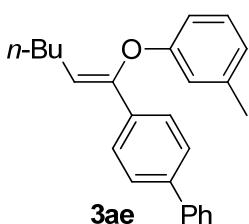
Compound **3ab**: yield: 85%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37 (d, $J = 8.2$ Hz, 2H), 7.10–7.05 (m, 3H), 6.79 (s, 1H), 6.72 (d, $J = 7.9$ Hz, 2H), 5.79 (t, $J = 7.4$ Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 2.18 (q, $J = 7.3$ Hz, 2H), 1.45–1.27 (m, 4H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.5, 148.7, 139.5, 137.5, 132.8, 129.1, 129.0, 125.1, 122.1, 117.3, 116.1, 112.3, 31.5, 25.5, 22.4, 21.5, 21.1, 13.9; MS (EI, m/z): 280 (M^+ , 41), 157 (60), 143 (41), 119 (80), 105 (100); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{24}\text{O}$ (M^+) 280.1827, found 280.1834.



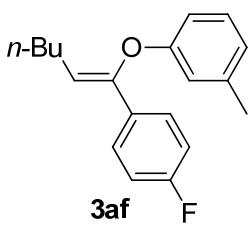
Compound **3ac**: yield: 86%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31–7.25 (m, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.79 (s, 1H), 6.73 (d, $J = 8.0$ Hz, 2H), 5.83 (t, $J = 7.4$ Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 2.18 (q, $J = 7.3$ Hz, 2H), 1.45–1.28 (m, 4H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 157.5, 148.7, 139.5, 137.9, 135.6, 129.1, 128.6, 128.3, 125.8, 122.4, 122.1, 118.1, 116.1, 112.3, 31.4, 25.6, 22.4, 21.5, 21.1, 13.9; MS (EI, m/z): 280 (M^+ , 57), 172 (62), 157 (87), 119 (88), 105 (100); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{24}\text{O}$ (M^+) 280.1827, found 280.1826.



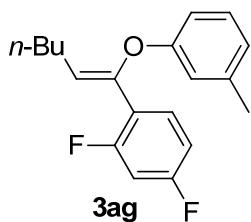
Compound **3ad**: yield: 82%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.42–7.33 (m, 1H), 7.14–6.99 (m, 4H), 6.74 (s, 1H), 6.72–6.65 (m, 2H), 5.33 (t, $J = 7.4$ Hz, 1H), 2.42 (s, 3H), 2.30–2.20 (m, 5H), 1.49–1.33 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 156.7, 149.8, 139.2, 136.1, 136.0, 130.6, 129.7, 128.9, 127.9, 125.5, 122.2, 120.9, 117.1, 113.1, 31.7, 25.4, 22.4, 21.4, 20.9, 13.9; MS (EI, m/z): 280 (M^+ , 41), 172 (83), 157 (79), 131 (84), 105 (100); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{24}\text{O}$ (M^+) 280.1827, found 280.1834.



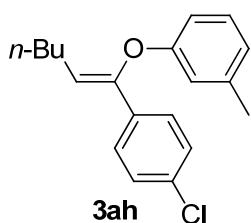
Compound **3ae**: yield: 65%, yellow solid, mp: 57–60 °C; ^1H NMR (600 MHz, CDCl_3): δ 7.60–7.48 (m, 6H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.3$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.82 (s, 1H), 6.79–6.73 (m, 2H), 5.91 (t, $J = 7.3$ Hz, 1H), 2.29 (s, 3H), 2.22 (q, $J = 7.3$ Hz, 2H), 1.47–1.30 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.5, 148.4, 140.6, 140.4, 139.6, 134.6, 129.2, 128.7, 127.3, 127.1, 126.9, 125.6, 122.2, 118.4, 116.1, 112.3, 31.4, 25.6, 22.4, 21.5, 13.9; MS (EI, m/z): 342 (M^+ , 32), 193 (48), 181 (68), 178 (74), 167 (100); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{26}\text{O}$ (M^+) 342.1984, found 342.1984.



Compound **3af**: yield: 93%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.46–7.42 (m, 2H), 7.09 (t, J = 7.8 Hz, 1H), 6.97–6.92 (m, 2H), 6.78–6.73 (m, 2H), 6.71 (dd, J = 8.2, 2.3 Hz, 1H), 5.76 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), 2.18 (q, J = 7.4 Hz, 2H), 1.43–1.28 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 162.4 (d, J = 247.3 Hz), 157.2, 147.8, 139.6, 131.8 (d, J = 3.3 Hz), 129.2, 126.9 (d, J = 8.1 Hz), 122.3, 117.9, 116.2, 115.3 (d, J = 21.8 Hz), 112.3, 31.4, 25.5, 22.4, 21.5, 13.9; MS (EI, m/z): 284 (M^+ , 64), 176 (74), 161 (83), 133 (100), 123 (90); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{21}\text{FO}$ (M^+) 284.1576, found 284.1577.

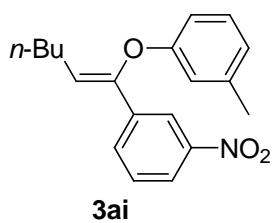


Compound **3ag**: yield: 86%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.38–7.34 (m, 1H), 7.09 (t, J = 7.8 Hz, 1H), 6.81–6.70 (m, 5H), 5.87 (t, J = 7.3 Hz, 1H), 2.28 (s, 3H), 2.22 (q, J = 7.3 Hz, 2H), 1.45–1.30 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 161.9 (dd, J = 254.1, 12.1 Hz), 160.2 (dd, J = 256.7, 11.7 Hz), 156.9, 142.1 (d, J = 4.6 Hz), 139.6, 129.5 (dd, J = 9.5, 4.3 Hz), 129.2, 123.5 (d, J = 9.7 Hz), 122.6, 120.0 (dd, J = 11.8, 3.9 Hz), 116.2, 112.3, 111.3 (dd, J = 21.2, 3.7 Hz), 104.4 (t, J = 25.8 Hz), 31.3, 25.7, 22.4, 21.4, 13.9; MS (EI, m/z): 302 (M^+ , 25), 153 (66), 151 (57), 127 (75), 108 (100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{20}\text{F}_2\text{O}$ (M^+) 302.1482, found 302.1480.

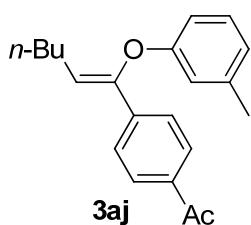


Compound **3ah**: yield: 90%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, J = 8.7 Hz, 2H), 7.26–7.18 (m, 2H), 7.09 (t, J = 7.9 Hz, 1H), 6.76–6.65 (m, 3H), 5.83 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), 2.19 (q, J = 7.3 Hz, 2H), 1.45–1.27 (m, 4H), 0.87 (t, J = 7.2

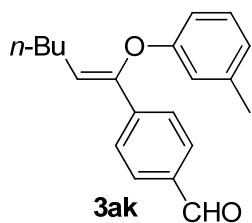
Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.2, 147.8, 139.6, 134.2, 133.4, 129.2, 128.6, 126.5, 122.4, 118.8, 116.1, 112.3, 31.3, 25.6, 22.4, 21.4, 13.9; MS (EI, m/z): 302 (11), 300 (M^+ , 39), 151 (81), 139 (86), 125 (100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{21}\text{ClO}$ (M^+) 300.1281, found 300.1275.



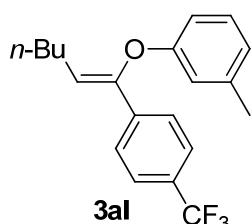
Compound **3ai**: yield 86%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.35 (s, 1H), 8.05 (d, $J = 7.6$ Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.10 (t, $J = 7.7$ Hz, 1H), 6.78–6.71 (m, 3H), 6.01 (t, $J = 7.3$ Hz, 1H), 2.29 (s, 3H), 2.32–2.22 (m, 2H), 1.46–1.32 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 156.7, 148.5, 146.8, 139.9, 137.6, 130.9, 129.4, 129.4, 122.8, 122.3, 121.2, 120.0, 116.1, 112.2, 31.1, 25.7, 22.4, 21.4, 13.8; MS (EI, m/z): 311 (M^+ , 19), 268 (34), 150 (45), 115 (36), 108 (100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ (M^+) 311.1521, found 311.1511.



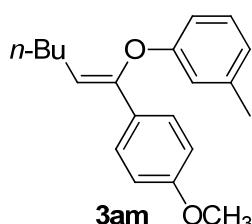
Compound **3aj**: yield: 68%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.77–6.67 (m, 3H), 6.01 (t, $J = 7.4$ Hz, 1H), 2.55 (s, 3H), 2.28 (s, 3H), 2.23 (q, $J = 7.4$ Hz, 2H), 1.46–1.27 (m, 4H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 197.5, 157.2, 147.9, 140.2, 139.7, 136.1, 129.3, 128.6, 125.2, 122.5, 121.1, 116.1, 112.2, 31.2, 26.5, 25.7, 22.4, 21.4, 13.9; MS (EI, m/z): 308 (M^+ , 33), 201 (60), 185 (49), 147 (58), 108 (100); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2$ (M^+) 308.1776, found 308.1781.



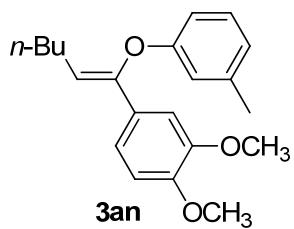
Compound **3ak**: yield: 72%, yellow oil; ¹H NMR (600 MHz, CDCl₃): δ 9.94 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.10 (t, J = 7.8 Hz, 1H), 6.80–6.68 (m, 3H), 6.06 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), 2.24 (q, J = 7.4 Hz, 2H), 1.44–1.26 (m, 4H), 0.89 (t, J = 7.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 191.6, 157.1, 147.8, 141.5, 139.8, 135.4, 129.9, 129.3, 125.5, 122.6, 121.9, 116.0, 112.1, 31.2, 25.8, 22.4, 21.4, 13.8; MS (EI, *m/z*): 294 (M⁺, 27), 186 (40), 133 (44), 115 (62), 108 (100); HRMS (EI) calcd for C₂₀H₂₂O₂ (M⁺) 294.1620, found 294.1616.



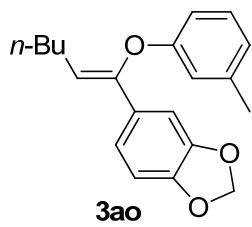
Compound **3al**: yield: 83%, yellow oil; ¹H NMR (600 MHz, CDCl₃): δ 7.58 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.10 (t, J = 8.0 Hz, 1H), 6.77–6.73 (m, 2H), 6.71 (d, J = 7.0 Hz, 1H), 5.96 (t, J = 7.4 Hz, 1H), 2.28 (s, 3H), 2.23 (q, J = 7.4 Hz, 2H), 1.45–1.30 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃): δ 157.1, 147.6, 139.8, 139.2 (q, J = 2.6 Hz, 1.4 Hz), 129.6 (q, J = 32.5 Hz), 129.3, 125.4 (q, J = 3.8 Hz), 125.3, 124.1 (q, J = 272.1 Hz), 122.6, 120.7, 116.1, 112.2, 31.2, 25.7, 22.4, 21.4, 13.9; MS (EI, *m/z*): 334 (M⁺, 19), 291 (26), 226 (25), 173 (42), 108 (100); HRMS (EI) calcd for C₂₀H₂₁F₃O (M⁺) 334.1544, found 334.1535.



Compound **3am**: yield: 82%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, $J = 8.8$ Hz, 2H), 7.08 (t, $J = 7.8$ Hz, 1H), 6.81–6.75 (m, 3H), 6.73 (d, $J = 8.0$ Hz, 2H), 5.71 (t, $J = 7.4$ Hz, 1H), 3.76 (s, 3H), 2.28 (s, 3H), 2.17 (q, $J = 7.1$ Hz, 2H), 1.44–1.28 (m, 4H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 159.2, 157.5, 148.3, 139.5, 129.1, 128.2, 126.5, 122.1, 116.3, 116.1, 113.8, 112.3, 55.2, 31.5, 25.5, 22.4, 21.5, 13.9; MS (EI, m/z): 296 (M^+ , 53), 189 (92), 147 (71), 135 (75), 121 (100); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2$ (M^+) 296.1776, found 296.1784.

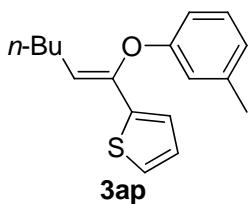


Compound **3an**: yield: 80%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.09 (t, $J = 7.8$ Hz, 1H), 7.04 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.00–6.97 (m, 1H), 6.78–6.73 (m, 4H), 5.71 (t, $J = 7.3$ Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.28 (s, 3H), 2.19 (q, $J = 7.3$ Hz, 2H), 1.42–1.30 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.5, 148.8, 148.7, 148.5, 139.5, 129.1, 128.6, 122.1, 118.0, 116.5, 116.1, 112.4, 111.0, 108.4, 55.8, 55.7, 31.5, 25.5, 22.4, 21.4, 13.9; MS (EI, m/z): 326 (M^+ , 63), 219 (91), 177 (63), 165 (92), 151 (100); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{26}\text{O}_3$ (M^+) 326.1882, found 326.1883.

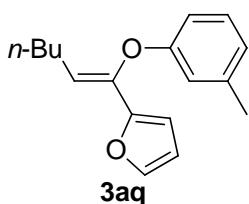


Compound **3ao**: yield: 76%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.09 (t, $J = 7.8$ Hz, 1H), 6.99–6.94 (m, 2H), 6.78–6.65 (m, 4H), 5.90 (s, 2H), 5.67 (t, $J = 7.3$ Hz, 1H), 2.28 (s, 3H), 2.16 (q, $J = 7.3$ Hz, 2H), 1.44–1.27 (m, 4H), 0.87 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.4, 148.3, 147.8, 147.3, 139.5, 130.1, 129.1, 122.2, 119.2, 116.9, 116.2, 112.3, 108.2, 105.8, 101.1, 31.5, 25.5, 22.4, 21.5, 13.9; MS (EI,

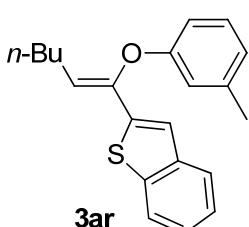
m/z): 310 (M^+ , 64), 203 (48), 149 (72), 135 (100), 131 (85); HRMS (EI) calcd for $C_{20}H_{22}O_3 (M^+)$ 310.1569, found 310.1567.



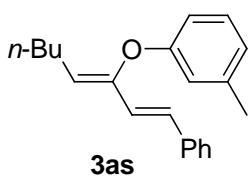
Compound **3ap**: yield: 84%, yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.14–7.07 (m, 2H), 6.97 (dd, J = 3.6, 1.0 Hz, 1H), 6.88–6.85 (m, 1H), 6.82 (s, 1H), 6.80–6.75 (m, 2H), 5.75 (t, J = 7.4 Hz, 1H), 2.29 (s, 3H), 2.15 (q, J = 7.3 Hz, 2H), 1.44–1.27 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 144.1, 139.9, 139.6, 129.2, 127.3, 124.3, 123.9, 122.5, 117.7, 115.9, 112.1, 31.3, 25.4, 22.4, 21.5, 13.9; MS (EI, *m/z*): 272 (M^+ , 44), 165 (70), 164 (34), 123 (100), 121 (56); HRMS (EI) calcd for $C_{17}H_{20}OS (M^+)$ 272.1235, found 272.1235.



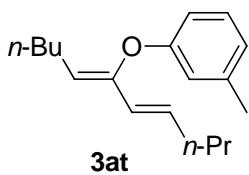
Compound **3aq**: yield: 78%, yellow oil; 1H NMR (600 MHz, $CDCl_3$): δ 7.32 (s, 1H), 7.13 (t, J = 7.8 Hz, 1H), 6.83–6.74 (m, 3H), 6.30 (dd, J = 3.3, 1.8 Hz, 1H), 6.12 (d, J = 3.3 Hz, 1H), 5.87 (t, J = 7.6 Hz, 1H), 2.30 (s, 3H), 2.15 (q, J = 7.4 Hz, 2H), 1.43–1.30 (m, 4H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 157.7, 150.0, 142.0, 141.0, 139.6, 129.2, 122.5, 116.9, 115.8, 112.0, 111.2, 106.7, 31.4, 24.9, 22.4, 21.5, 13.9; MS (EI, *m/z*): 256 (M^+ , 61), 213 (60), 149 (96), 148 (38), 107 (100); HRMS (EI) calcd for $C_{17}H_{20}O_2 (M^+)$ 256.1463, found 256.1468.



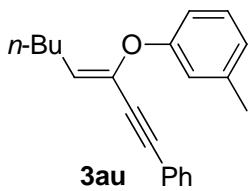
Compound **3ar**: yield: 75%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.81–7.74 (m, 1H), 7.65–7.63 (m, 1H), 7.33–7.29 (m, 2H), 7.23–7.15 (m, 2H), 6.94–6.80 (m, 3H), 5.92 (t, $J = 7.4$ Hz, 1H), 2.36 (s, 3H), 2.25 (q, $J = 7.4$ Hz, 2H), 1.50–1.35 (m, 4H), 0.93 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.4, 144.4, 140.0, 139.7, 139.4, 138.9, 129.3, 124.6, 124.4, 123.7, 122.6, 122.0, 120.8, 120.7, 115.8, 112.0, 31.1, 25.6, 22.4, 21.5, 13.8; MS (EI, m/z): 322 (M^+ , 76), 215 (75), 173 (100), 161 (77), 147 (76); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{22}\text{OS} (\text{M}^+)$ 322.1391, found 322.1383.



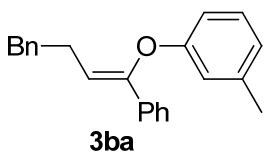
Compound **3as**: yield: 74%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36–7.30 (m, 2H), 7.28–7.23 (m, 2H), 7.21–7.10 (m, 2H), 6.83–6.75 (m, 3H), 6.67 (d, $J = 15.9$ Hz, 1H), 6.54 (d, $J = 15.9$ Hz, 1H), 5.46 (t, $J = 7.5$ Hz, 1H), 2.31 (s, 3H), 2.09 (q, $J = 7.3$ Hz, 2H), 1.38–1.25 (m, 4H), 0.85 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.7, 148.9, 139.6, 136.8, 129.2, 128.5, 128.2, 127.5, 126.5, 123.9, 123.5, 122.1, 115.6, 111.8, 31.2, 25.7, 22.3, 21.5, 13.9; MS (EI, m/z): 292 (M^+ , 57), 185 (65), 141 (99), 129 (100), 115 (85); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{24}\text{O} (\text{M}^+)$ 292.1827, found 292.1830.



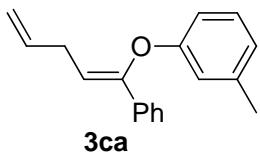
Compound **3at**: yield: 68%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.12 (t, $J = 8.1$ Hz, 1H), 6.76–6.71 (m, 3H), 5.91 (d, $J = 15.5$ Hz, 1H), 5.68–5.61 (m, 1H), 5.20 (t, $J = 7.4$ Hz, 1H), 2.31 (s, 3H), 2.05–1.97 (m, 4H), 1.37–1.23 (m, 6H), 0.85–0.81 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.7, 148.5, 139.4, 130.9, 129.0, 125.0, 121.8, 120.0, 115.6, 111.8, 34.4, 31.3, 25.3, 22.3, 21.5, 13.9, 13.6; MS (EI, m/z): 258 (M^+ , 43), 215 (100), 150 (50), 121 (37), 108 (75); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{26}\text{O} (\text{M}^+)$ 258.1984, found 258.1985.



Compound **3au**: yield: 86%, colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.31–7.24 (m, 5H), 7.19 (t, J = 7.8 Hz, 1H), 6.89–6.85 (m, 3H), 5.68 (t, J = 7.6 Hz, 1H), 2.35 (s, 3H), 2.24 (q, J = 7.4 Hz, 2H), 1.43–1.32 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 156.3, 139.3, 133.4, 131.5, 128.9, 128.4, 128.2, 126.8, 123.1, 122.4, 117.6, 113.8, 88.8, 84.7, 31.1, 25.5, 22.3, 21.4, 13.8; MS (EI, m/z): 290 (M^+ , 33), 247 (62), 141 (100), 139 (94), 115 (69); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{22}\text{O}$ (M^+) 290.1671, found 290.1665.

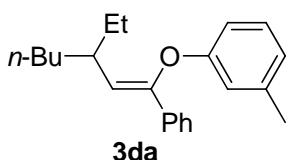


Compound **3ba**: yield: 92%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, J = 7.0 Hz, 2H), 7.27–7.14 (m, 8H), 7.05 (t, J = 7.8 Hz, 1H), 6.76–6.64 (m, 3H), 5.85 (t, J = 7.3 Hz, 1H), 2.73 (t, J = 7.7 Hz, 2H), 2.52 (q, J = 7.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.4, 149.3, 141.6, 139.5, 135.4, 129.2, 128.5, 128.4, 128.3, 127.9, 125.9, 125.3, 122.3, 116.8, 116.2, 112.3, 35.4, 27.6, 21.4; MS (EI, m/z): 314 (M^+ , 3), 223 (100), 224 (20), 145 (16), 115 (64); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{22}\text{O}$ (M^+) 314.1671, found 314.1670.

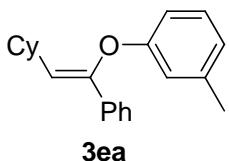


Compound **3ca**: yield: 85%, colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.50 (d, J = 7.3 Hz, 2H), 7.29–7.20 (m, 3H), 7.08 (t, J = 7.8 Hz, 1H), 6.79 (s, 1H), 6.77–6.71 (m, 2H), 5.89–5.80 (m, 2H), 5.09–5.05 (m, 1H), 5.01–4.99 (m, 1H), 2.99–2.91 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.3, 149.3, 139.6, 136.1, 135.3, 129.2, 128.4, 128.0, 125.3, 122.3, 116.2, 115.3, 115.0, 112.4, 30.2, 21.4; MS (EI, m/z): 250

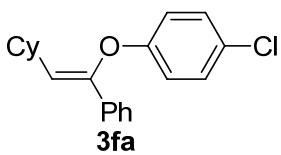
(M⁺, 23), 142 (61), 141 (81), 128 (100), 105 (83); HRMS (EI) calcd for C₁₈H₁₈O (M⁺) 250.1358, found 250.1358.



Compound **3da**: yield: 95%, colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.28–7.18 (m, 3H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 5.57 (d, *J* = 10.0 Hz, 1H), 2.50–2.42 (m, 1H), 2.26 (s, 3H), 1.51–1.37 (m, 2H), 1.37–1.15 (m, 6H), 0.89–0.82 (m, 6H); ¹³C NMR (151 MHz, CDCl₃): δ 157.6, 149.0, 139.3, 135.8, 129.0, 128.4, 127.6, 125.3, 123.2, 122.0, 116.4, 112.6, 37.5, 35.1, 29.7, 28.4, 22.9, 21.4, 14.1, 11.9; MS (EI, *m/z*): 308 (M⁺, 4), 279 (77), 251 (92), 128 (78), 105 (100); HRMS (EI) calcd for C₂₂H₂₈O (M⁺) 308.2140, found 308.2143.

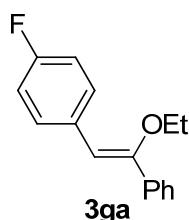


Compound **3ea**: yield: 96%, colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.26–7.15 (m, 3H), 7.06 (td, *J* = 7.9, 2.1 Hz, 1H), 6.80 (s, 1H), 6.73–6.71 (m, 2H), 5.67 (d, *J* = 9.4 Hz, 1H), 2.55–2.48 (m, 1H), 2.26 (s, 3H), 1.74–1.65 (m, 4H), 1.29–1.12 (m, 6H); ¹³C NMR (151 MHz, CDCl₃): δ 157.6, 147.3, 139.4, 135.7, 129.1, 128.3, 127.6, 125.4, 123.8, 122.2, 116.4, 112.4, 35.0, 32.9, 26.0, 25.7, 21.4; MS (EI, *m/z*): 292 (M⁺, 51), 172 (100), 141 (73), 128 (62), 105 (59); HRMS (EI) calcd for C₂₁H₂₄O (M⁺) 292.1827, found 292.1828.

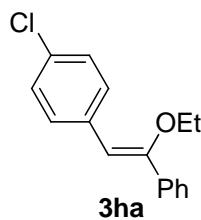


Compound **3fa**: yield: 91%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.43–7.41 (m, 2H), 7.27–7.13 (m, 5H), 6.89–6.85 (m, 2H), 5.69 (d, *J* = 9.4 Hz, 1H), 2.51–2.43 (m, 1H),

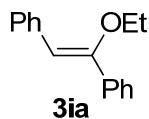
1.70–1.67 (m, 4H), 1.26–1.11 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 156.3, 147.2, 135.1, 129.4, 128.4, 127.9, 126.2, 125.3, 124.1, 116.8, 35.1, 32.9, 26.0, 25.7; MS (EI, m/z): 314 (11), 312 (M^+ , 40), 192 (84), 128 (100), 117 (97); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{21}\text{ClO} (\text{M}^+)$ 312.1281, found 312.1281.



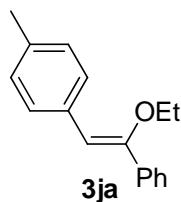
Compound **3ga**: yield: 75%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.72 (dd, $J = 8.8$ Hz, 5.6 Hz, 2H), 7.54 (d, $J = 7.1$ Hz, 2H), 7.31–7.41 (m, 3H), 7.02 (t, $J = 8.8$ Hz, 2H), 6.03 (s, 1H), 3.82 (q, $J = 7.0$ Hz, 2H), 1.33 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 161.3 (d, $J = 247.3$ Hz), 154.7, 136.7, 132.3 (d, $J = 3.3$ Hz), 130.1 (d, $J = 7.7$ Hz), 128.4, 128.3, 126.6, 115.1 (d, $J = 21.3$ Hz), 112.1, 65.8, 15.4; MS (EI, m/z): 242 (M^+ , 100), 183 (54), 165 (65), 136 (34), 105 (32); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{FO} (\text{M}^+)$ 242.1107, found 242.1100.



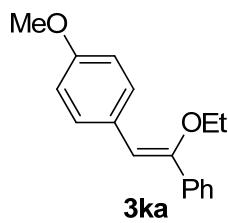
Compound **3ha**: yield: 72%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.68 (d, $J = 8.6$ Hz, 2H), 7.53 (dd, $J = 8.2$, 1.3 Hz, 2H), 7.40–7.33 (m, 3H), 7.29 (d, $J = 8.6$ Hz, 2H), 6.01 (s, 1H), 3.82 (q, $J = 7.0$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 155.7, 136.6, 134.6, 131.7, 129.7, 128.5, 128.4, 128.3, 126.6, 112.0, 65.9, 15.4; MS (EI, m/z): 260 (27), 258 (M^+ , 93), 166 (53), 165 (100), 152 (39); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{ClO} (\text{M}^+)$ 258.0811, found 258.0820.



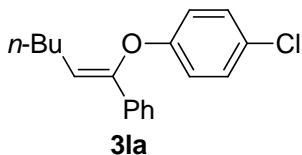
Compound **3ia**: yield: 78%, colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.74 (d, $J = 7.5$ Hz, 2H), 7.55 (d, $J = 7.4$ Hz, 2H), 7.40–7.29 (m, 5H), 7.19 (t, $J = 7.4$ Hz, 1H), 6.08 (s, 1H), 3.82 (q, $J = 7.0$ Hz, 2H), 1.33 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 155.1, 136.9, 136.1, 128.6, 128.4, 128.3, 128.2, 126.5, 126.4, 113.2, 65.8, 15.4; MS (EI, m/z): 224 (M^+ , 100), 167 (62), 165 (75), 152 (38), 105 (51); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}\text{O} (M^+)$ 224.1201, found 224.1210.



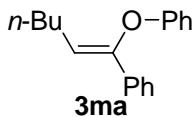
Compound **3ja**: yield: 70%, colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.65 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 7.2$ Hz, 2H), 7.39–7.31 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.09 (s, 1H), 3.82 (q, $J = 7.0$ Hz, 2H), 2.35 (s, 3H), 1.34 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 154.4, 137.0, 136.2, 133.2, 129.0, 128.5, 128.4, 128.0, 126.4, 113.3, 65.8, 21.2, 15.4; MS (EI, m/z): 238 (M^+ , 100), 209 (25), 181 (76), 165 (85), 105 (32); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{18}\text{O} (M^+)$ 238.1358, found 238.1356.



Compound **3ka**: yield: 66%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.70 (d, $J = 8.8$ Hz, 2H), 7.54 (d, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.08 (s, 1H), 3.85–3.80 (m, 5H), 1.35 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 158.2, 153.4, 137.0, 129.8, 128.9, 128.4, 127.9, 126.3, 113.7, 112.9, 65.7, 55.2, 15.4; MS (EI, m/z): 254 (M^+ , 85), 225 (51), 197 (100), 165 (55), 153 (27); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2 (M^+)$ 254.1307, found 254.1311.

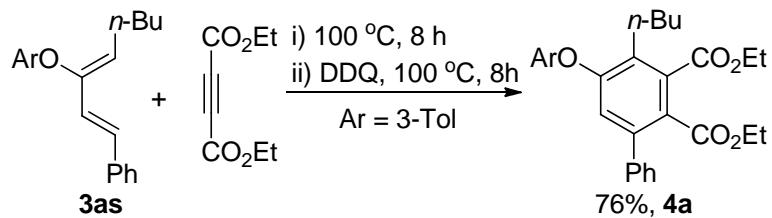


Compound **3la**: yield: 83%, yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 7.45–7.43 (m, 2H), 7.28–7.21 (m, 3H), 7.17–7.15 (m, 2H), 6.88–6.85 (m, 2H), 5.85 (t, $J = 7.4$ Hz, 1H), 2.18 (q, $J = 7.4$ Hz, 2H), 1.43–1.30 (m, 4H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 156.1, 148.6, 135.0, 129.4, 128.5, 127.9, 126.2, 125.2, 118.5, 116.7, 31.4, 25.5, 22.4, 13.9; MS (EI, m/z): 288 (8), 286 (M^+ , 27), 143 (63), 117 (93), 115 (100); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{19}\text{ClO} (M^+)$ 286.1124, found 286.1117.



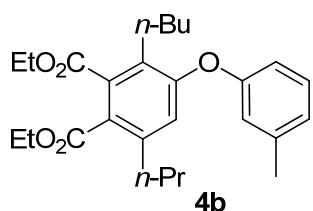
Compound **3ma**: yield: 81%, colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.48 (d, $J = 7.4$ Hz, 2H), 7.28–7.18 (m, 5H), 6.95–6.89 (m, 3H), 5.85 (t, $J = 7.4$ Hz, 1H), 2.20 (q, $J = 7.4$ Hz, 2H), 1.44–1.30 (m, 4H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3): δ 157.5, 148.7, 135.5, 129.4, 128.4, 127.7, 125.2, 121.3, 118.3, 115.4, 31.4, 25.6, 22.4, 13.9; MS (EI, m/z): 252 (M^+ , 35), 143 (55), 129 (48), 117 (68), 115 (100); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{O} (M^+)$ 252.1514, found 252.1513.

General procedure for the tandem Diels-Alder/aromatization reaction:

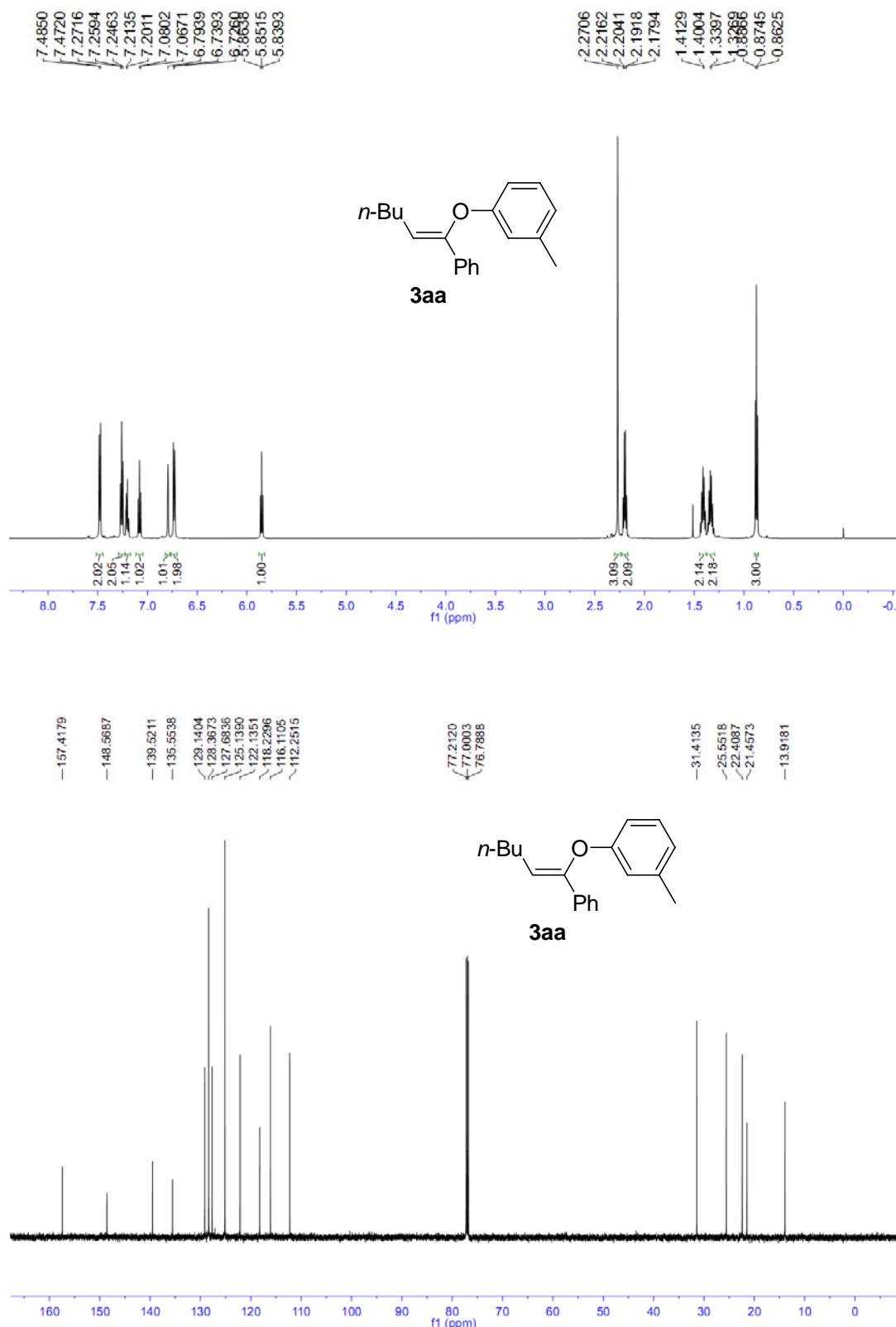


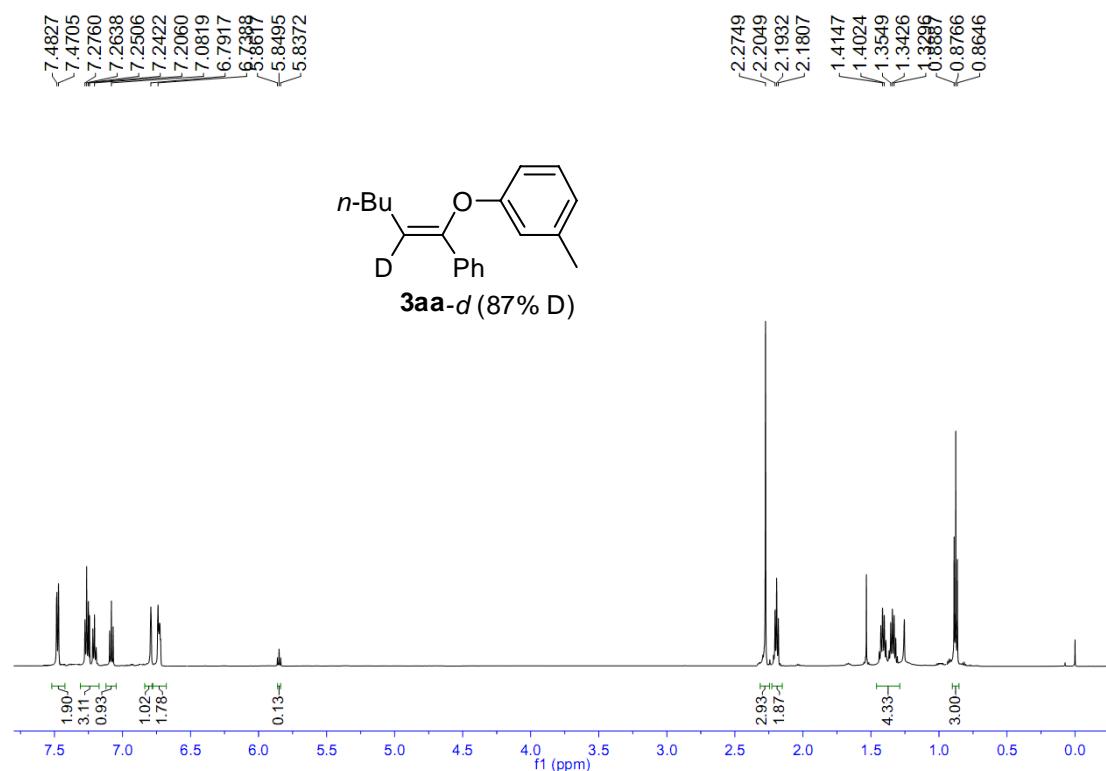
To a flask was charged with **3as** (73 mg, 0.25 mmol) and 0.25 mL of diethyl acetylenedicarboxylate. After stirring at 100 °C for 8 h, the reaction mixture was added 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (114 mg, 0.5 mmol). After stirring at 100 °C for another 8 h, the reaction was concentrated and purified by column chromatography on silica to give 87 mg (yield: 76%) of **4a** as a colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.32–7.28 (m, 3H), 7.24–7.21 (m, 3H), 6.92 (d, $J = 7.5$ Hz, 1H),

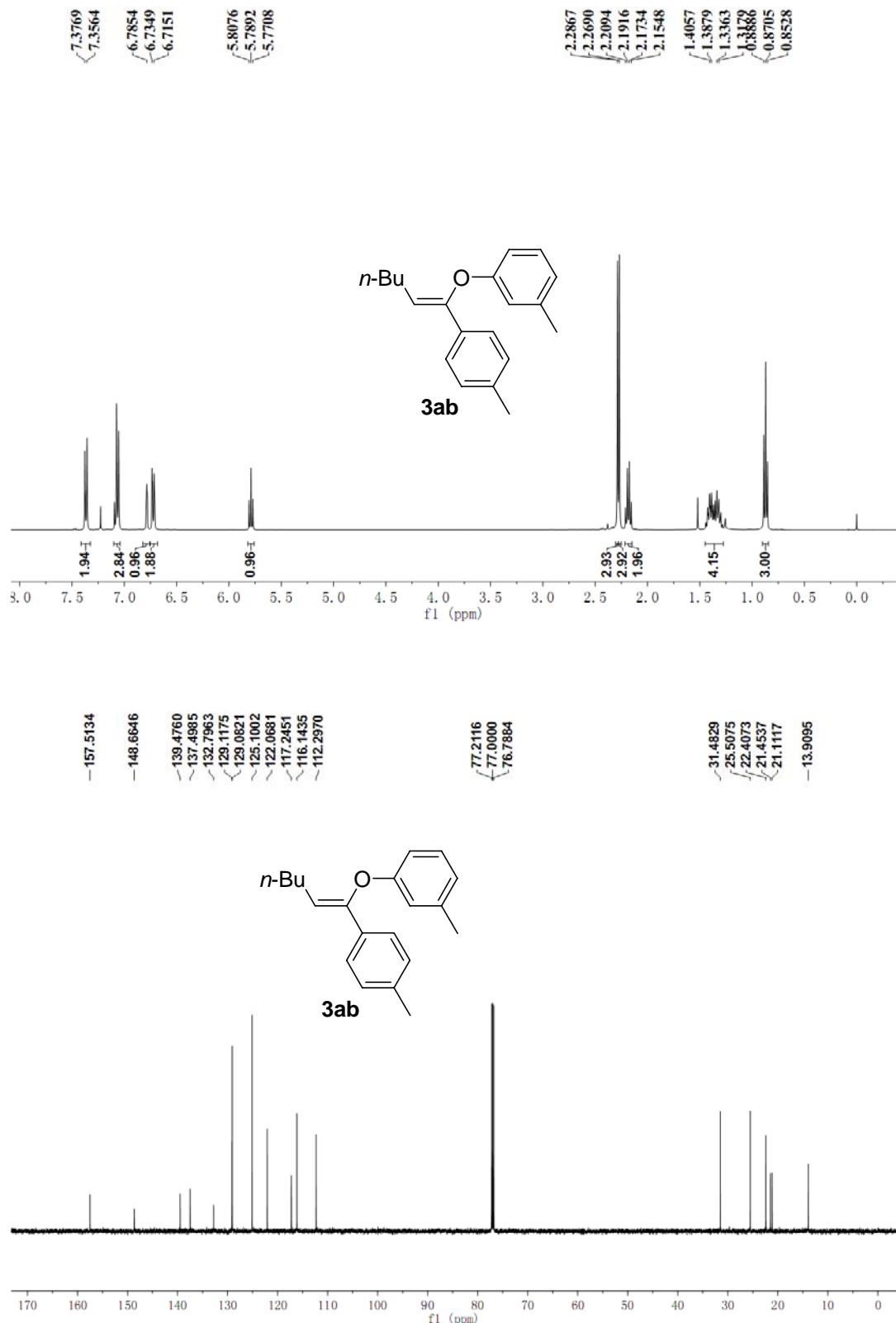
6.85 (s, 1H), 6.82–6.79 (m, 2H), 4.39 (q, $J = 7.1$ Hz, 2H), 4.00 (q, $J = 7.1$ Hz, 2H), 2.79–2.75 (m, 2H), 2.32 (s, 3H), 1.68–1.60 (m, 2H), 1.42–1.36 (m, 5H), 0.91 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.1, 168.0, 156.7, 156.5, 140.7, 140.2, 140.0, 135.2, 131.2, 129.6, 128.1, 128.0, 127.4, 126.1, 124.6, 120.4, 119.5, 115.8, 61.6, 61.2, 32.4, 27.2, 22.9, 21.3, 14.0, 13.8, 13.4; MS (EI, m/z): 460 (M^+ , 9), 414 (63), 385 (56), 367 (100), 343 (46); HRMS (EI) calcd for $\text{C}_{29}\text{H}_{32}\text{O}_5$ (M^+) 460.2250, found 460.2252.



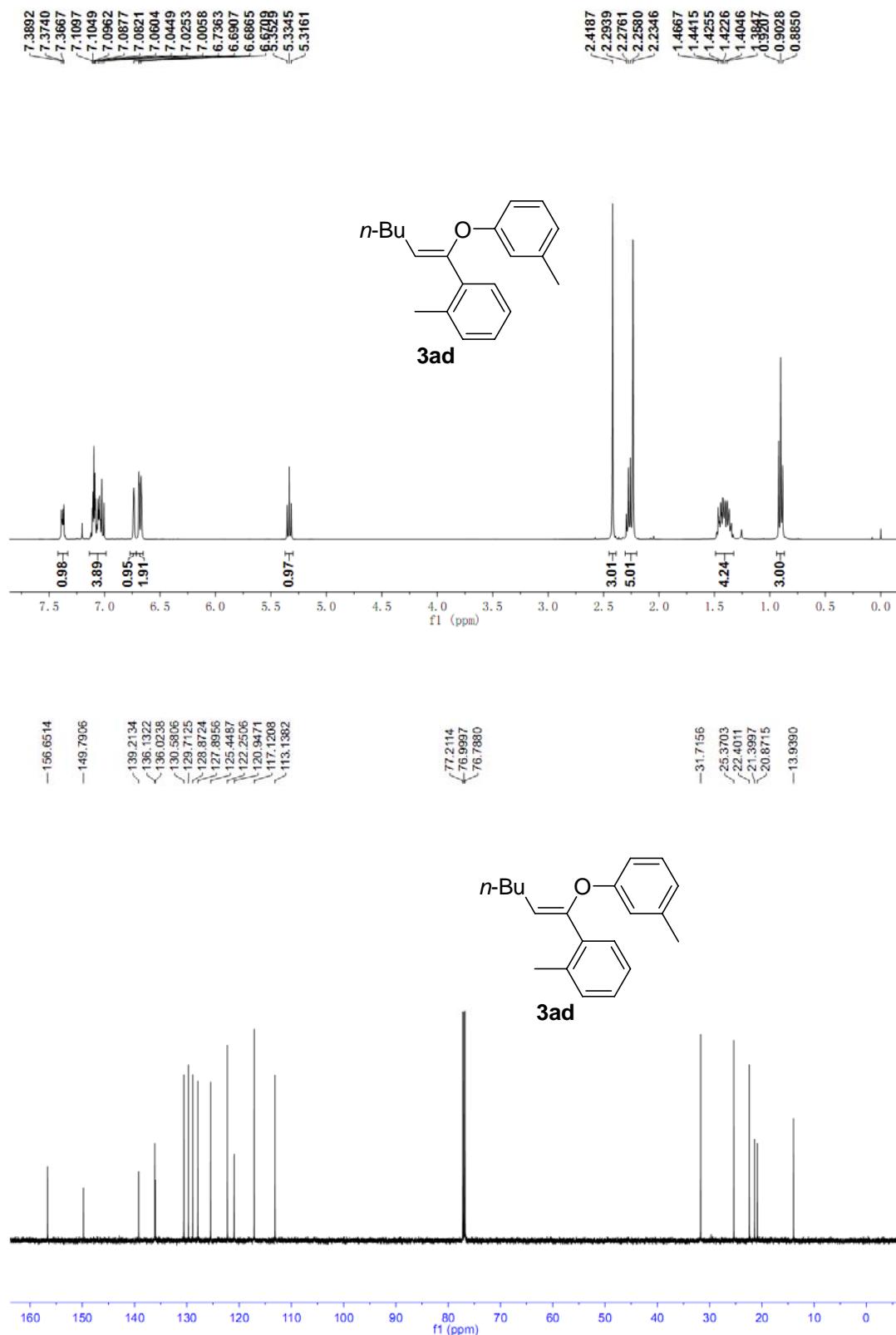
Compound **4b**: yield: 73%, colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 7.22 (t, $J = 7.8$ Hz, 1H), 6.93 (d, $J = 7.5$ Hz, 1H), 6.77–6.75 (m, 2H), 6.73 (s, 1H), 4.37–4.30 (m, 4H), 2.69–2.65 (m, 2H), 2.63–2.60 (m, 2H), 2.33 (s, 3H), 1.58–1.49 (m, 4H), 1.39–1.32 (m, 8H), 0.89–0.86 (m, 6H); ^{13}C NMR (151 MHz, CDCl_3): δ 168.4, 168.0, 156.9, 156.6, 141.3, 140.1, 135.1, 130.2, 129.5, 126.1, 124.2, 121.1, 119.1, 115.5, 61.4, 61.3, 35.7, 32.5, 27.1, 24.5, 22.9, 21.3, 14.1, 14.0, 13.9, 13.8; MS (EI, m/z): 426 (M^+ , 3), 380 (26), 281 (35), 208 (28), 207 (100); HRMS (EI) calcd for $\text{C}_{26}\text{H}_{34}\text{O}_5$ (M^+) 426.2406, found 426.2402.

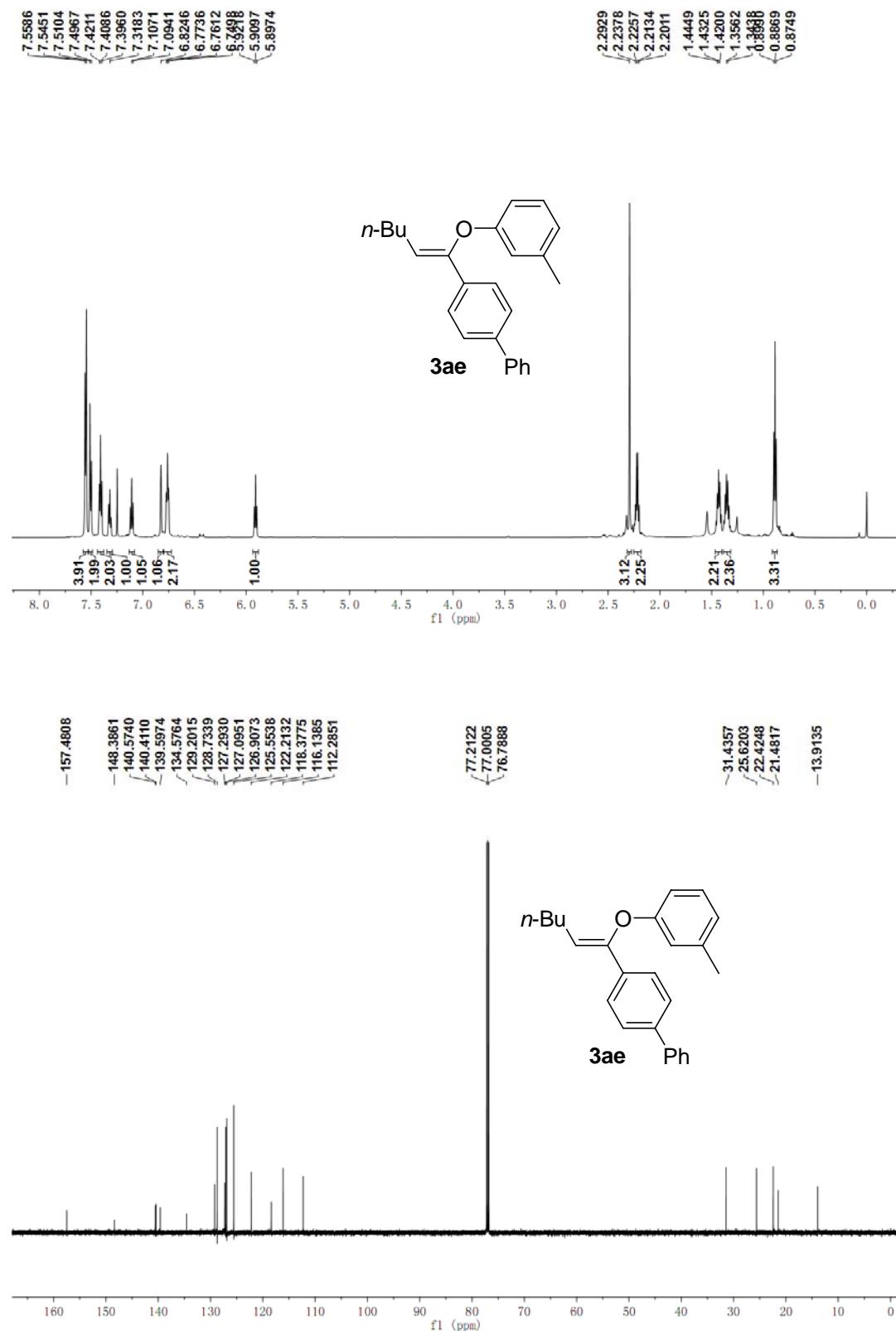


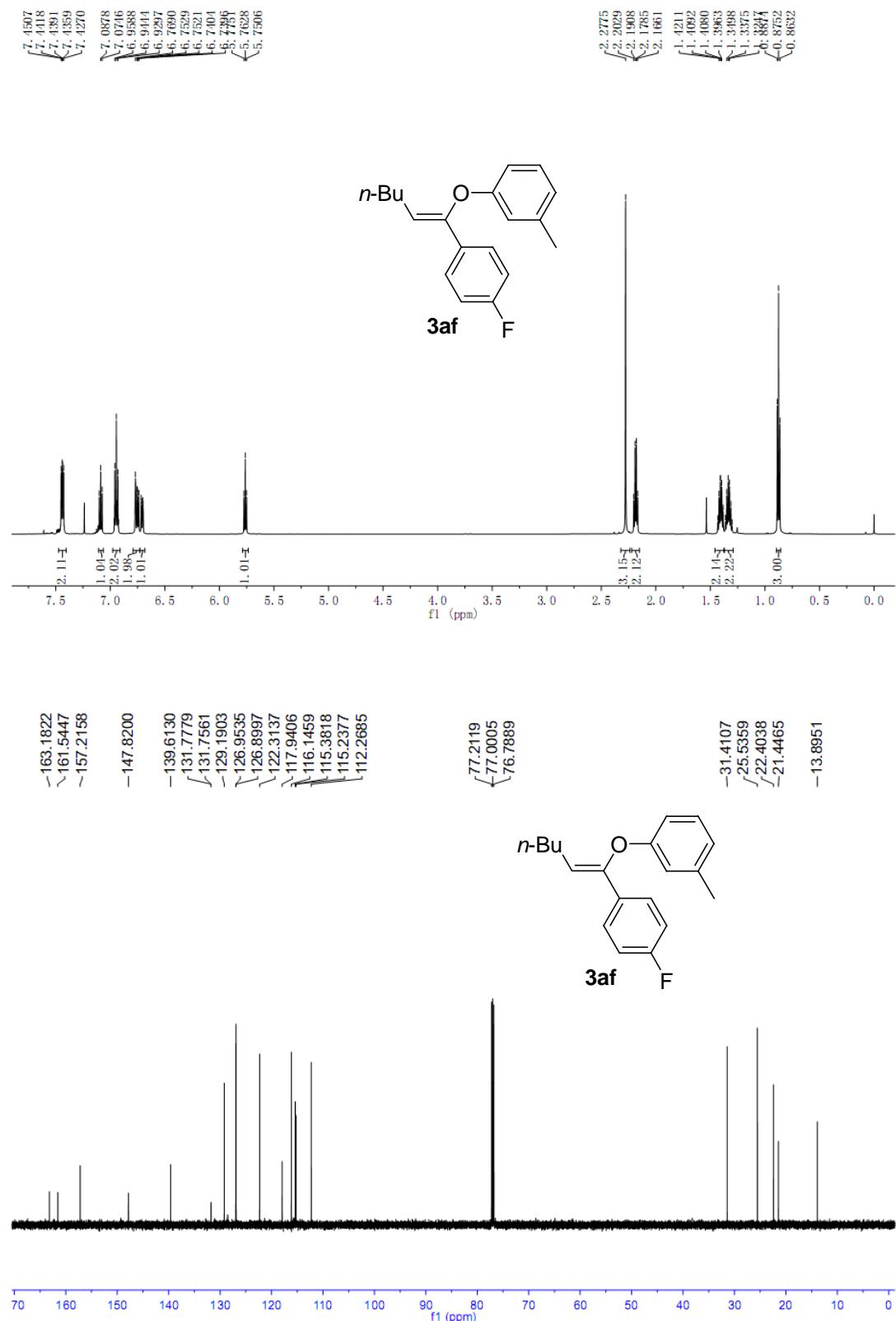


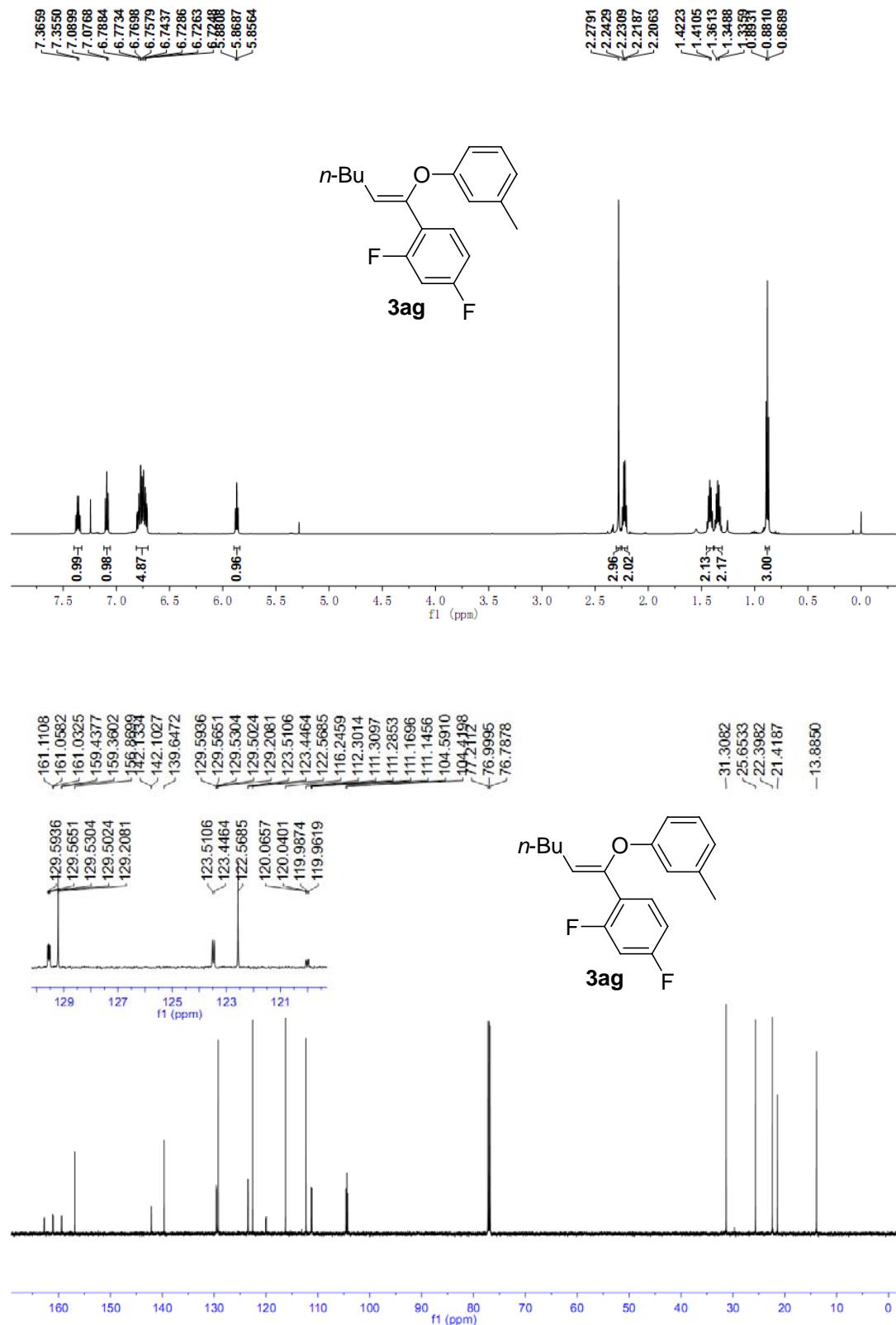




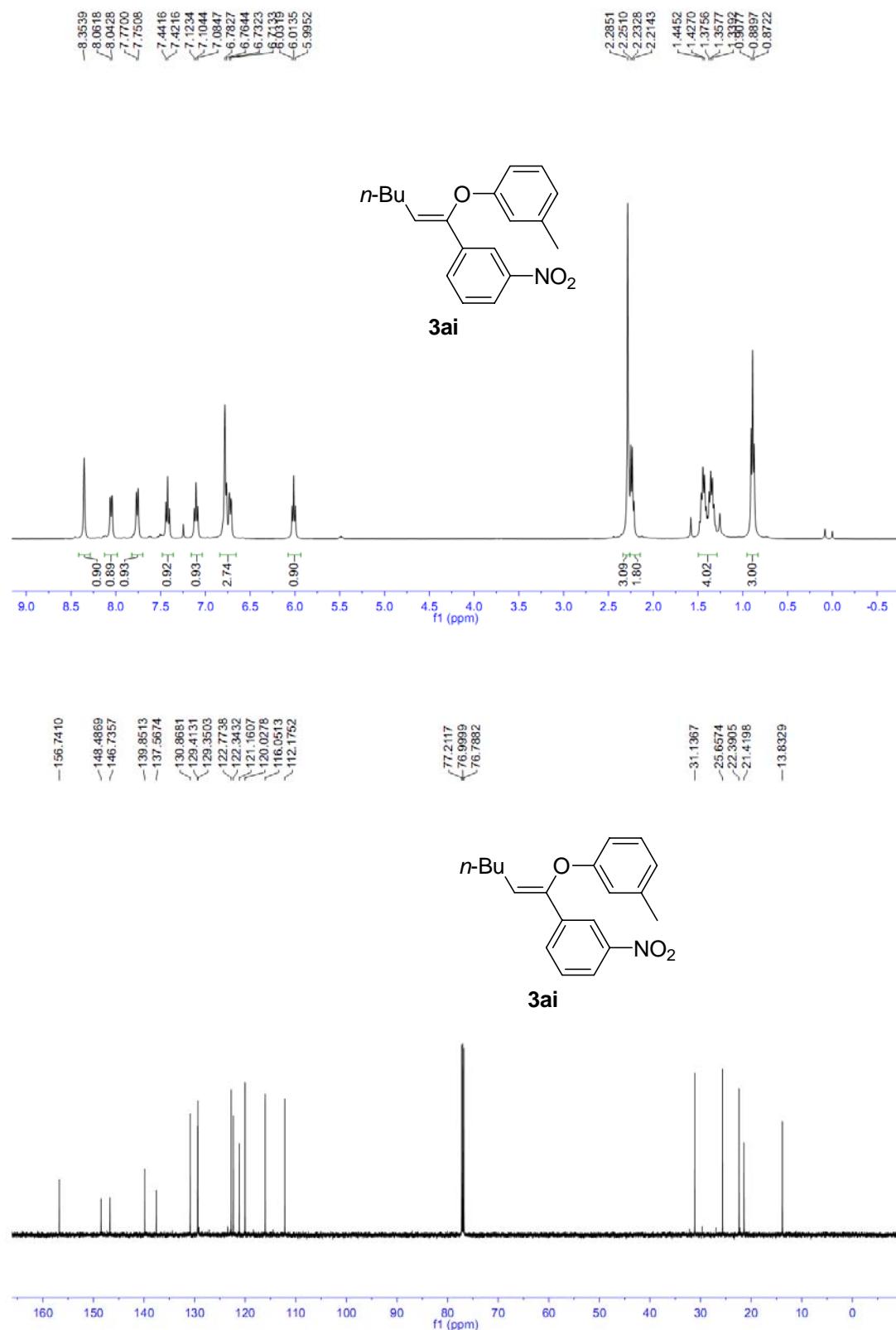


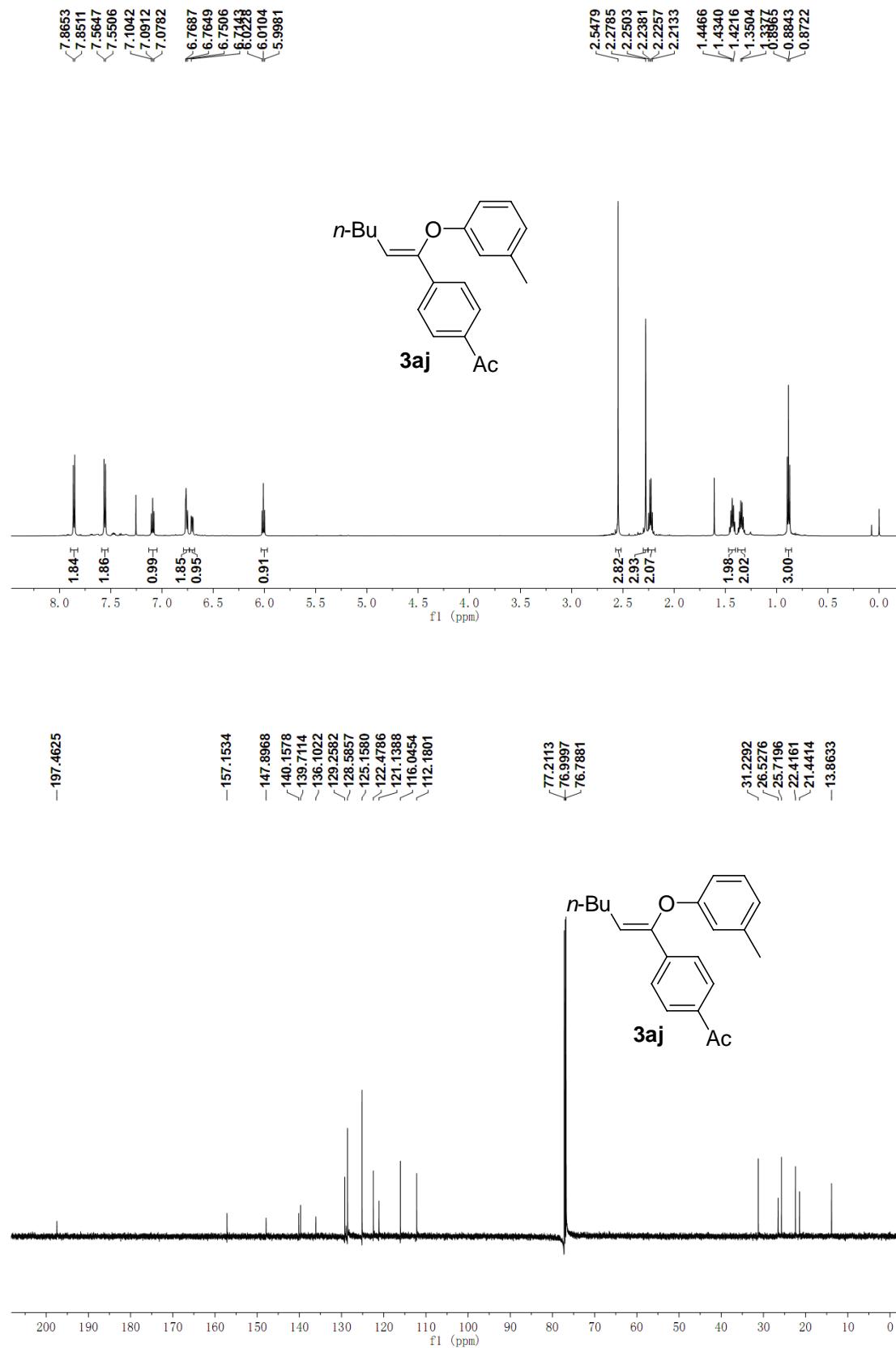


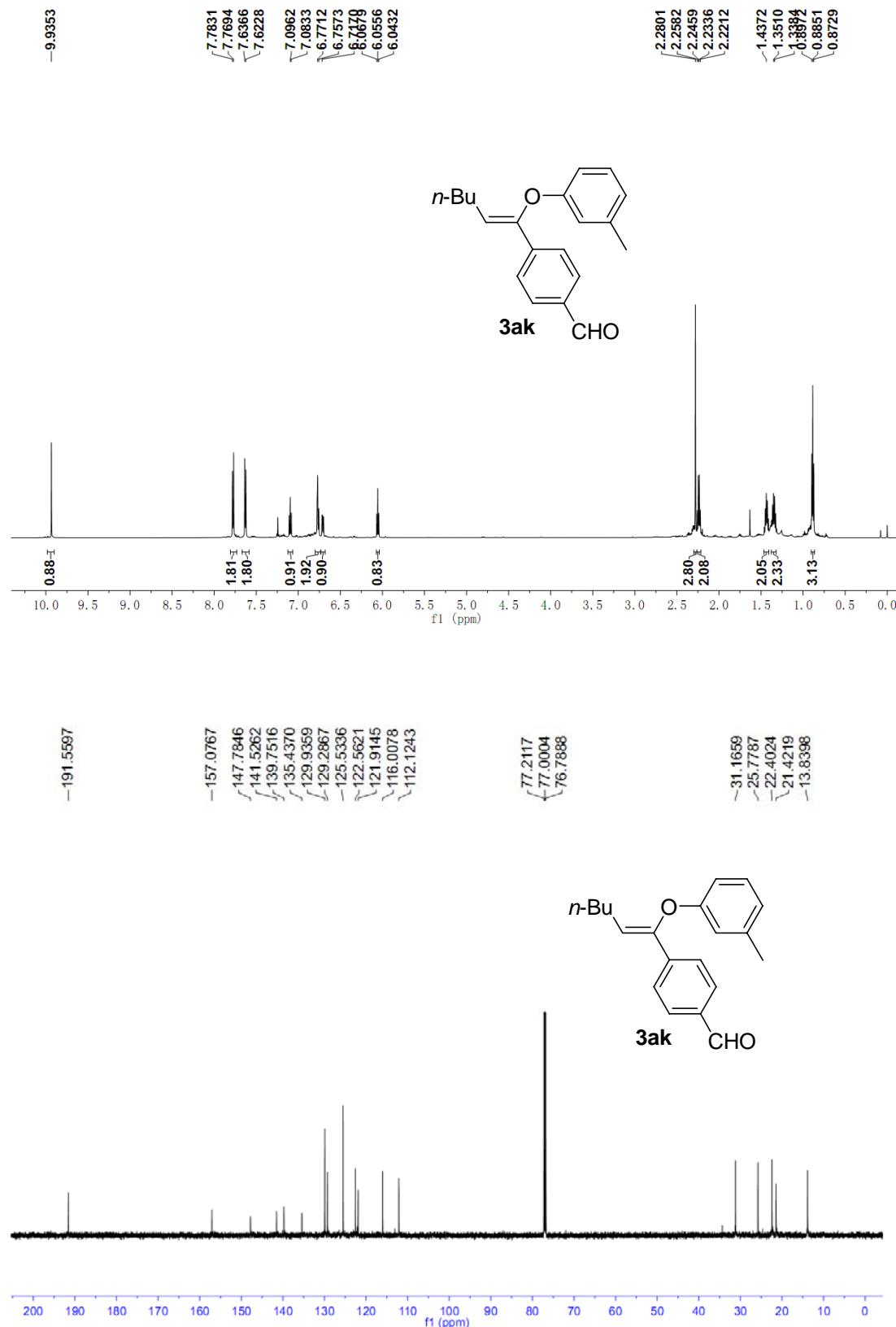


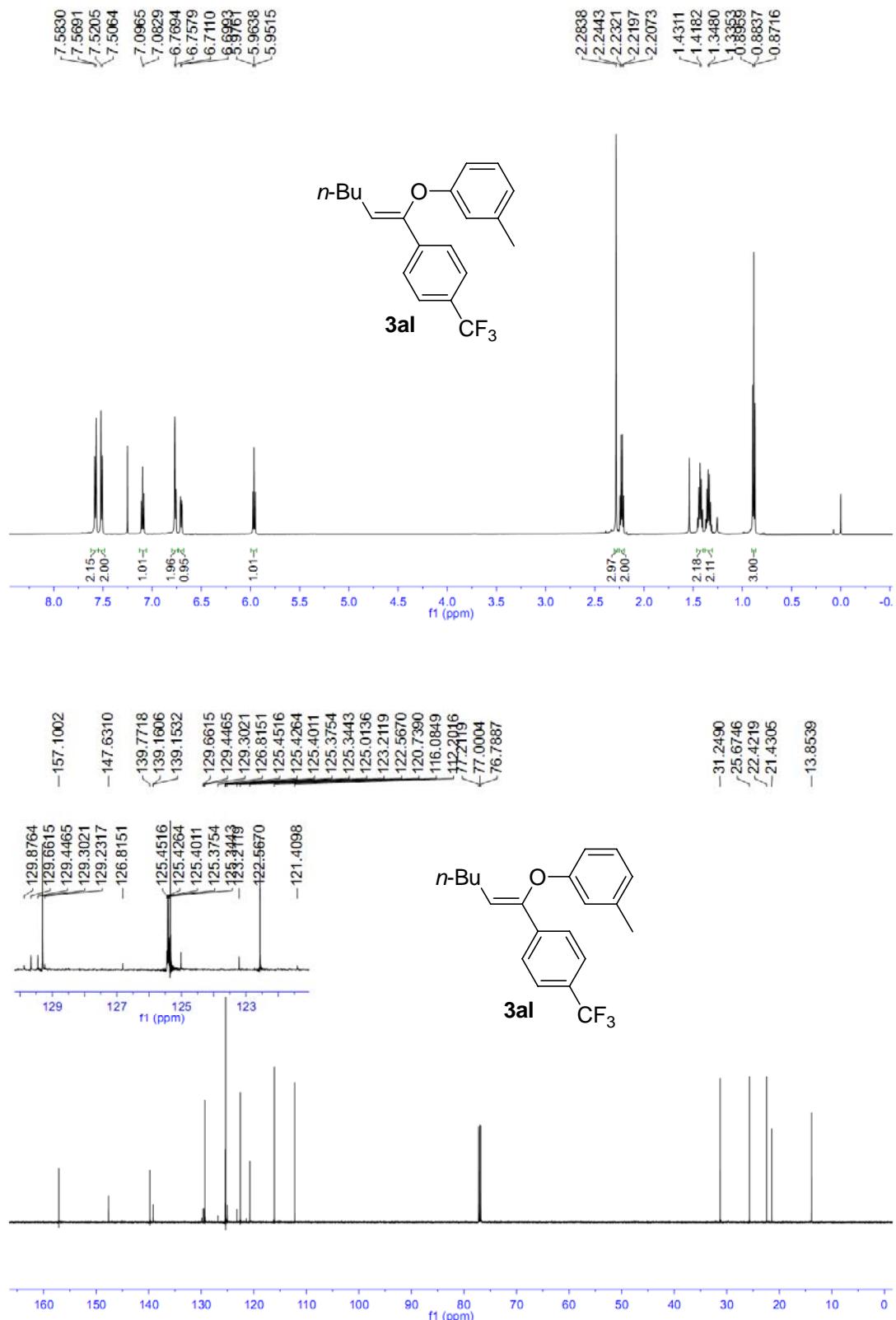


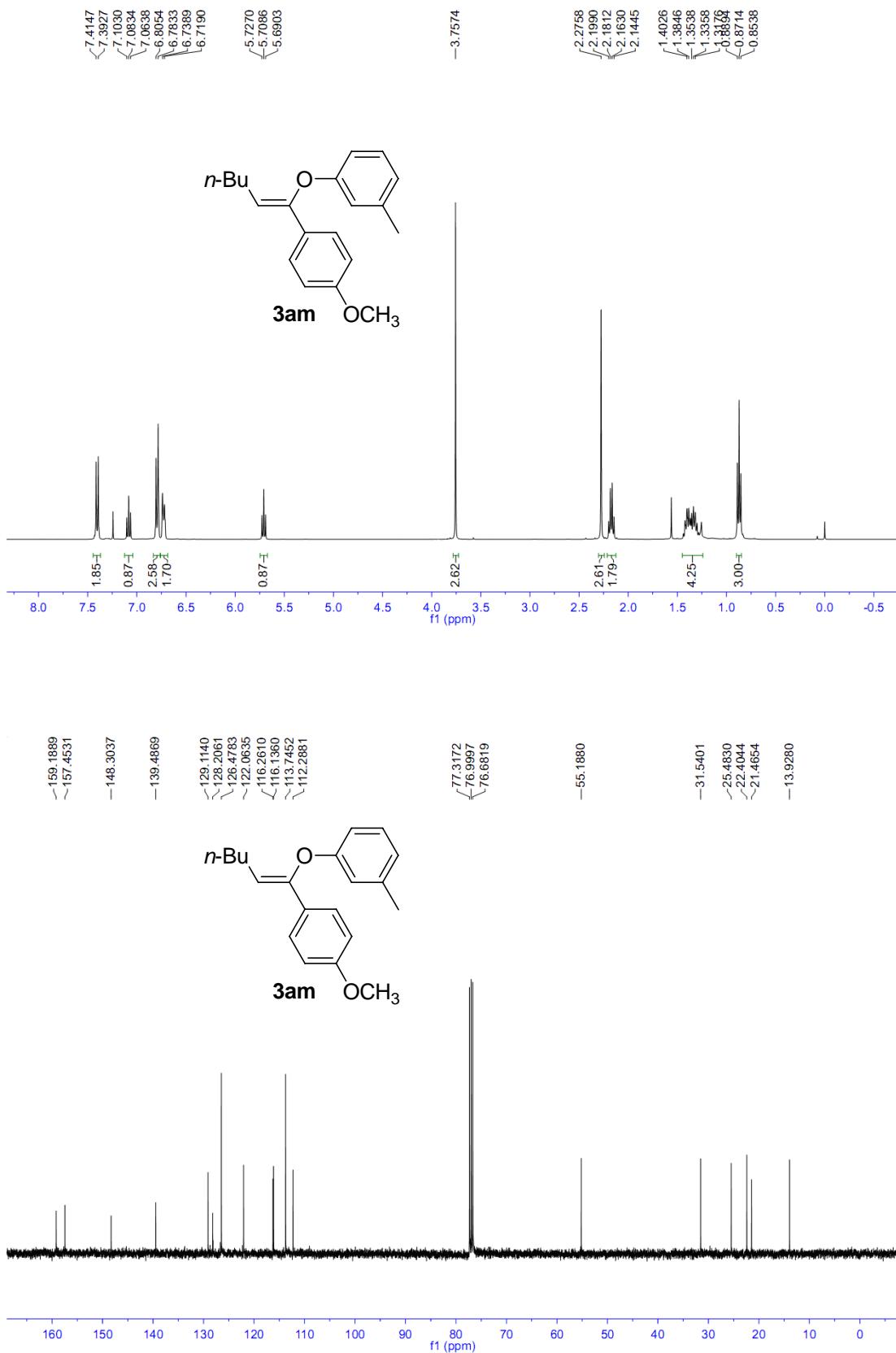


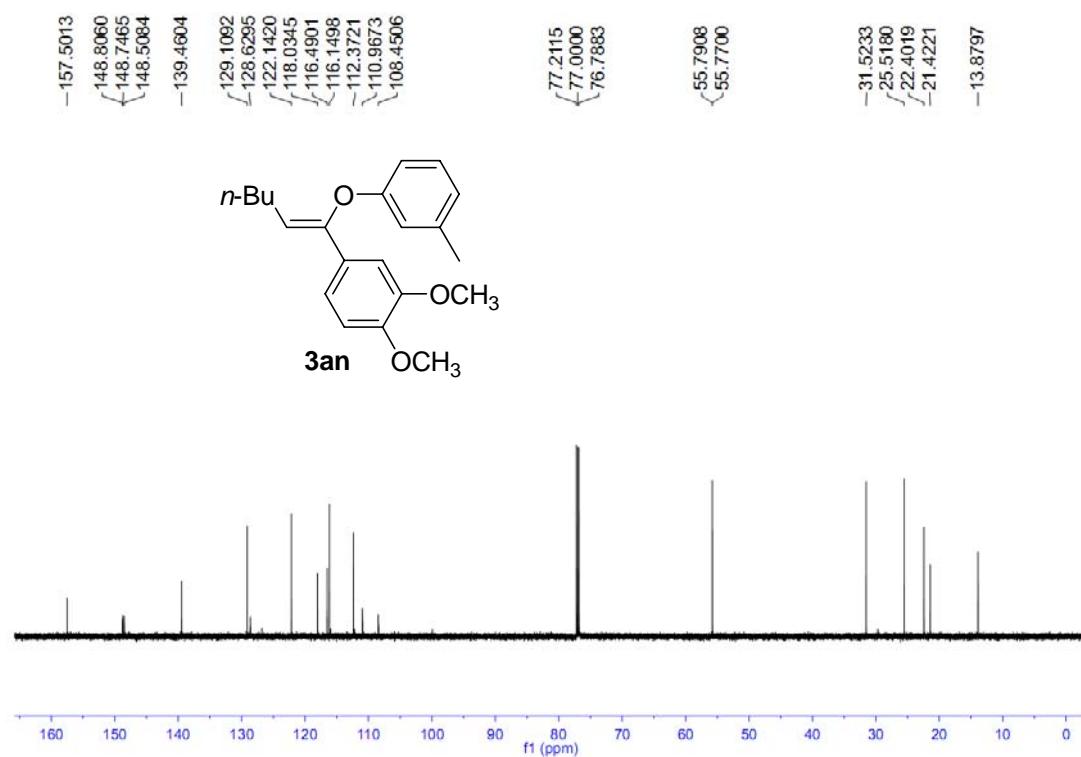
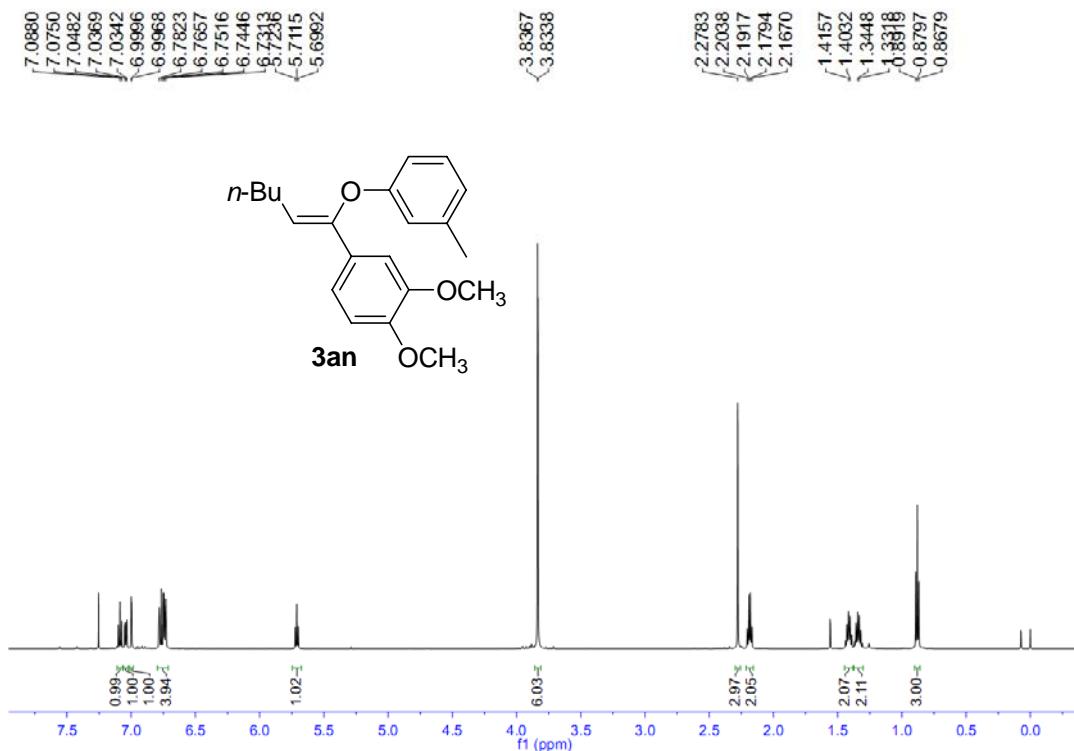


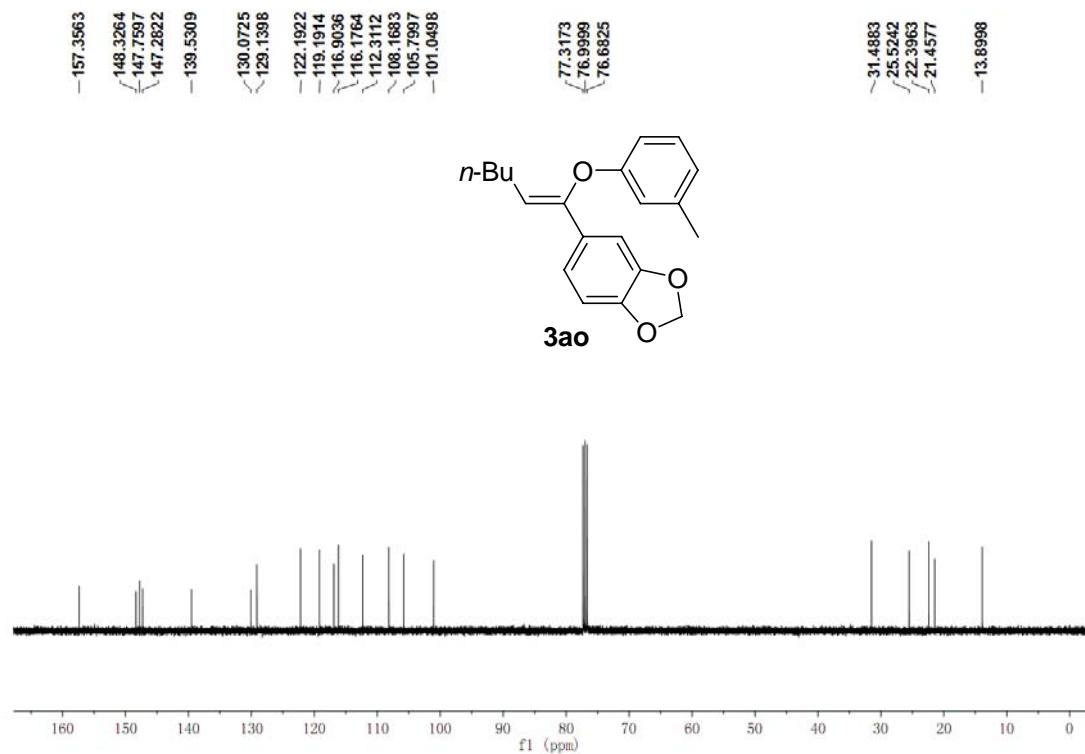
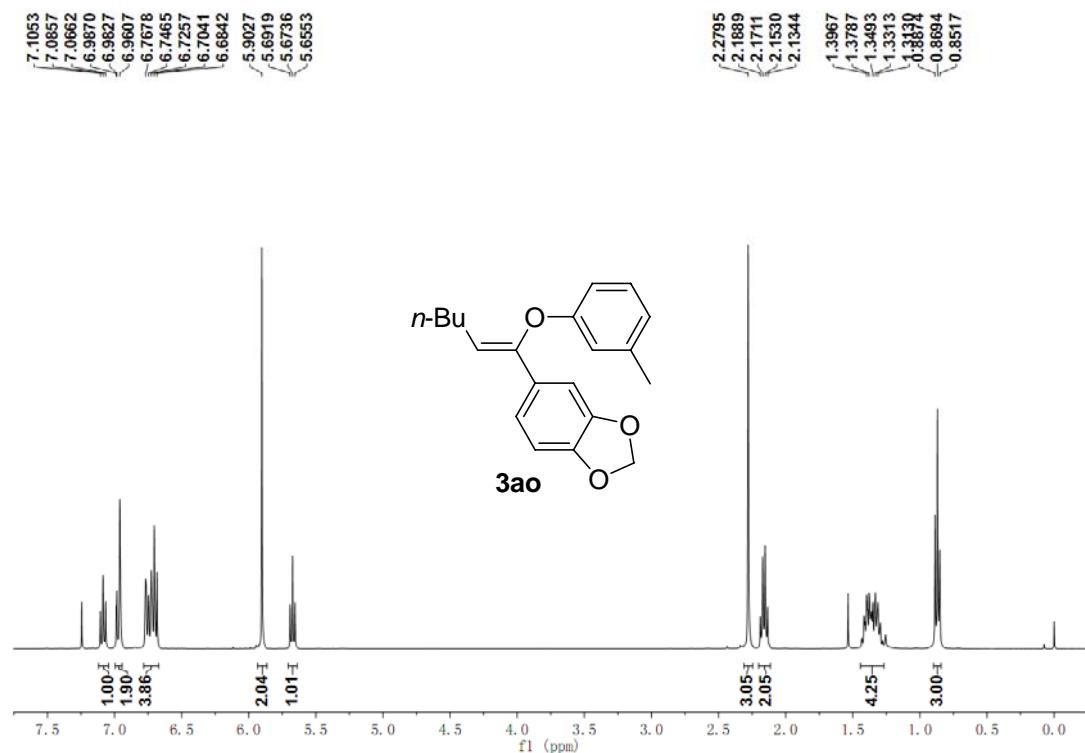


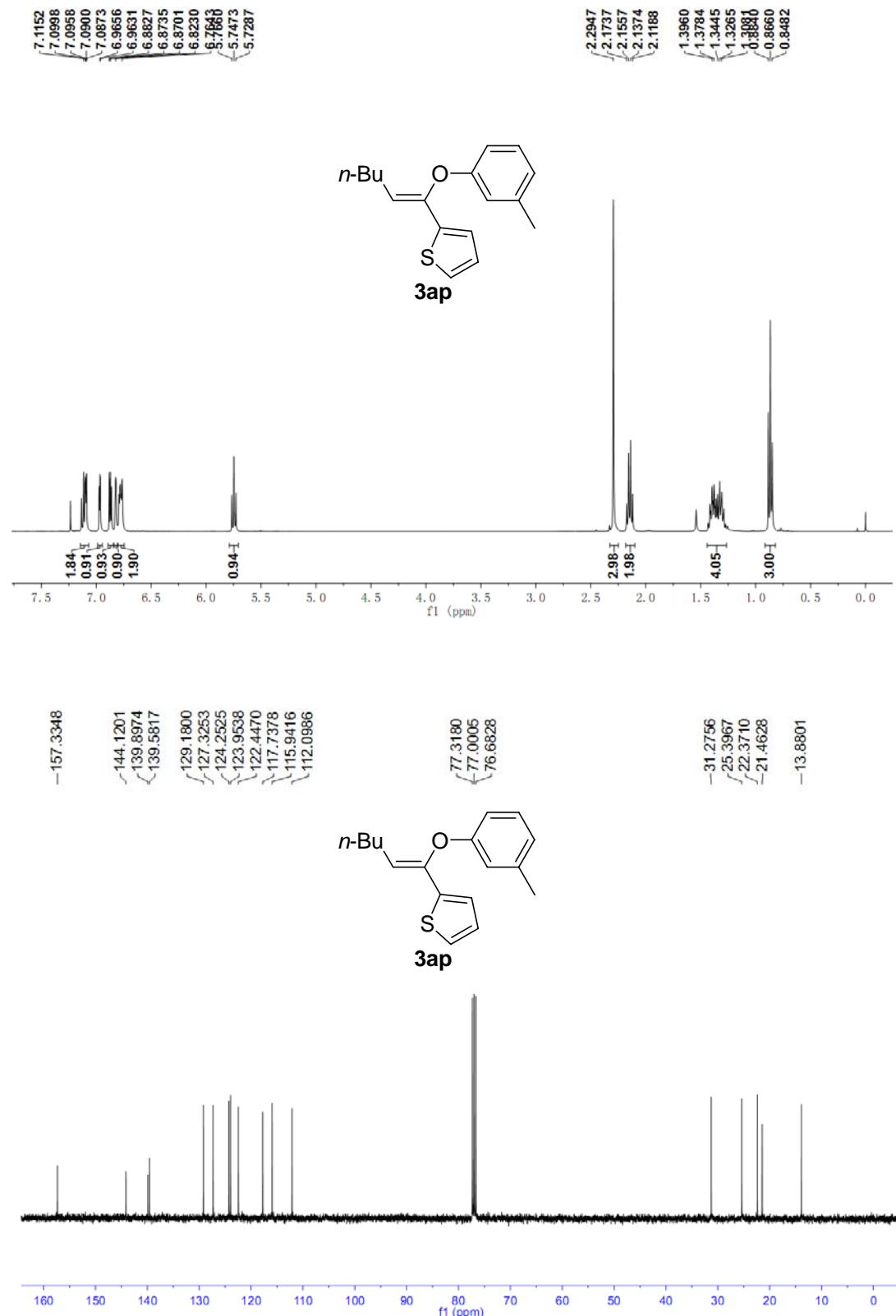


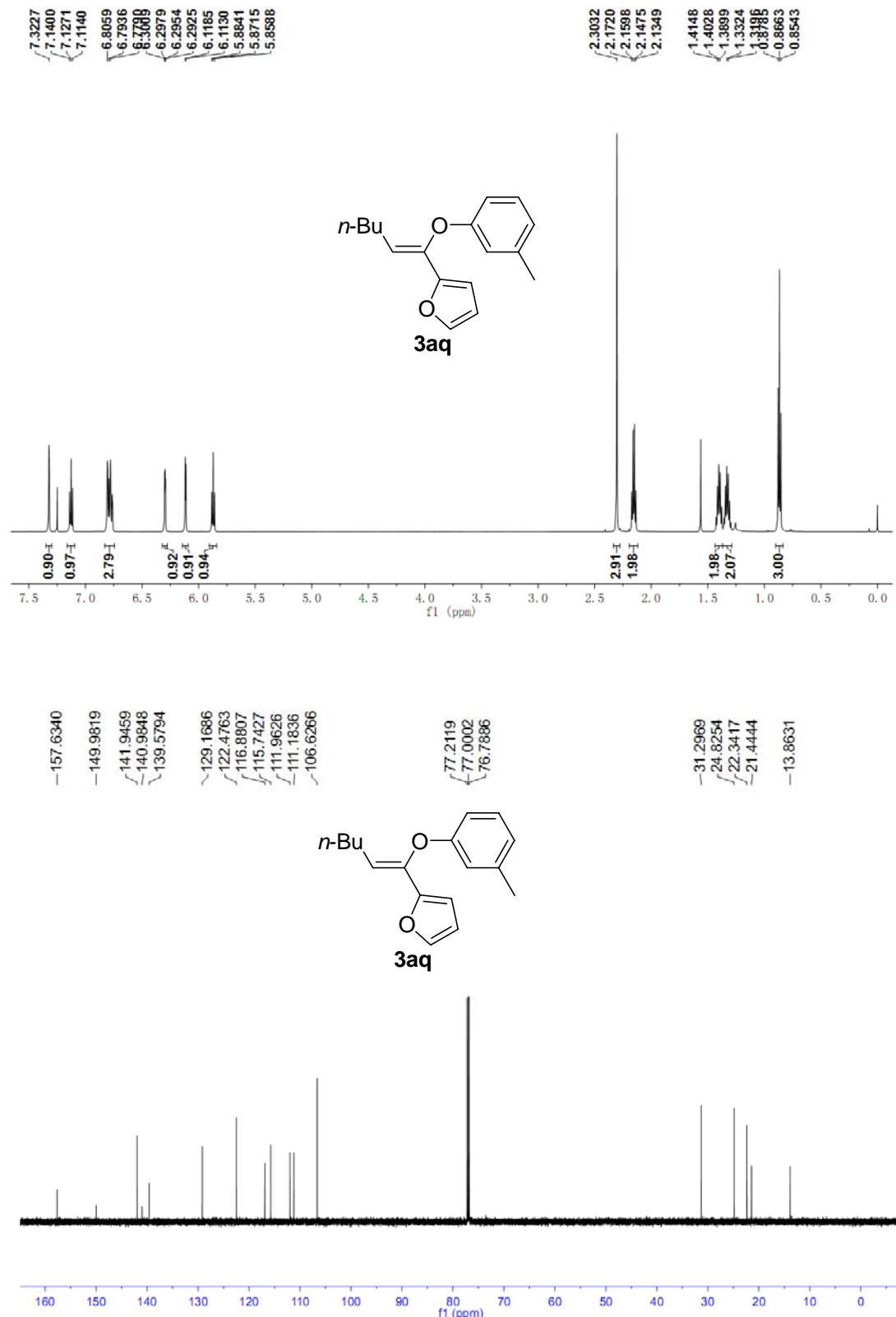


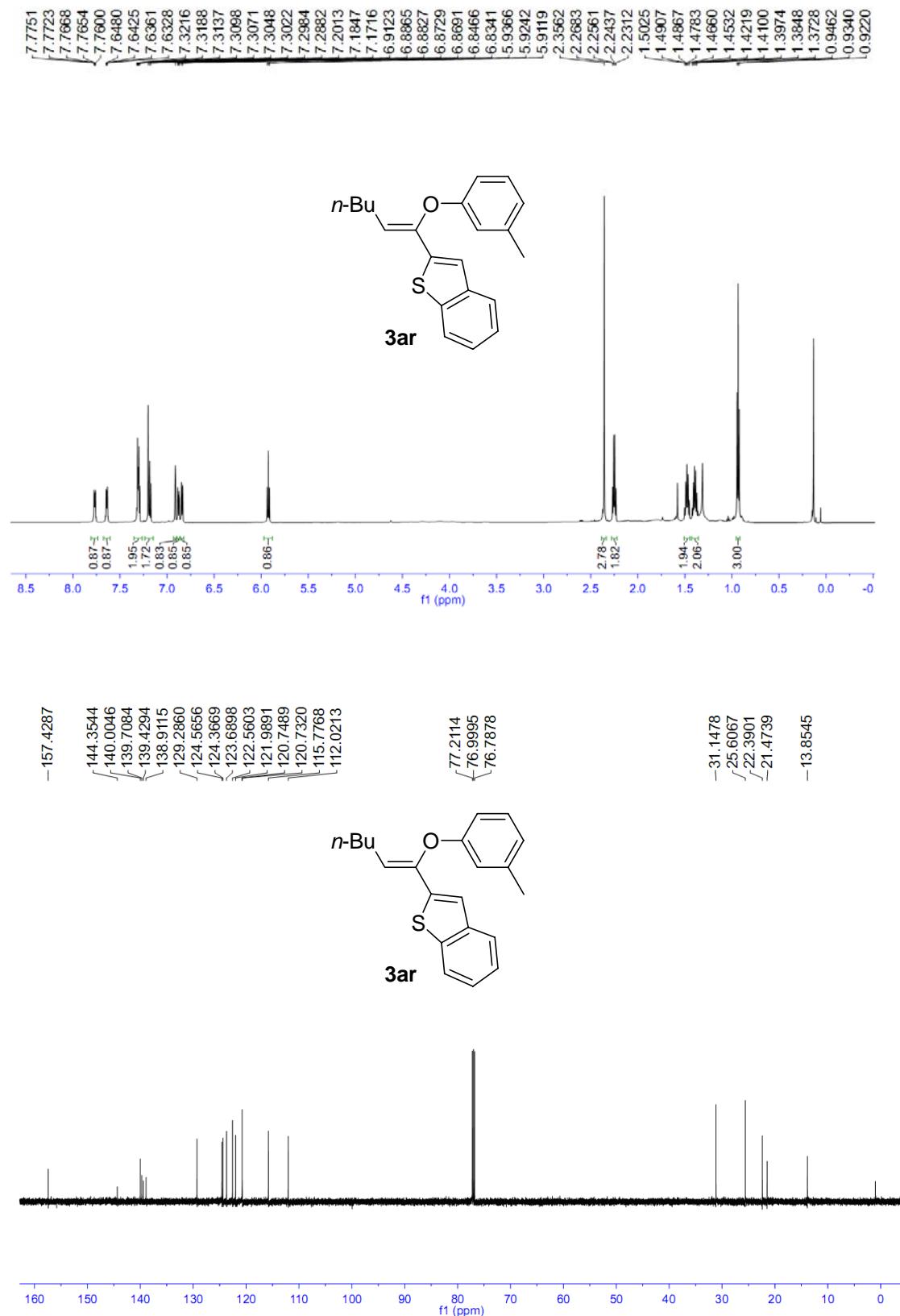


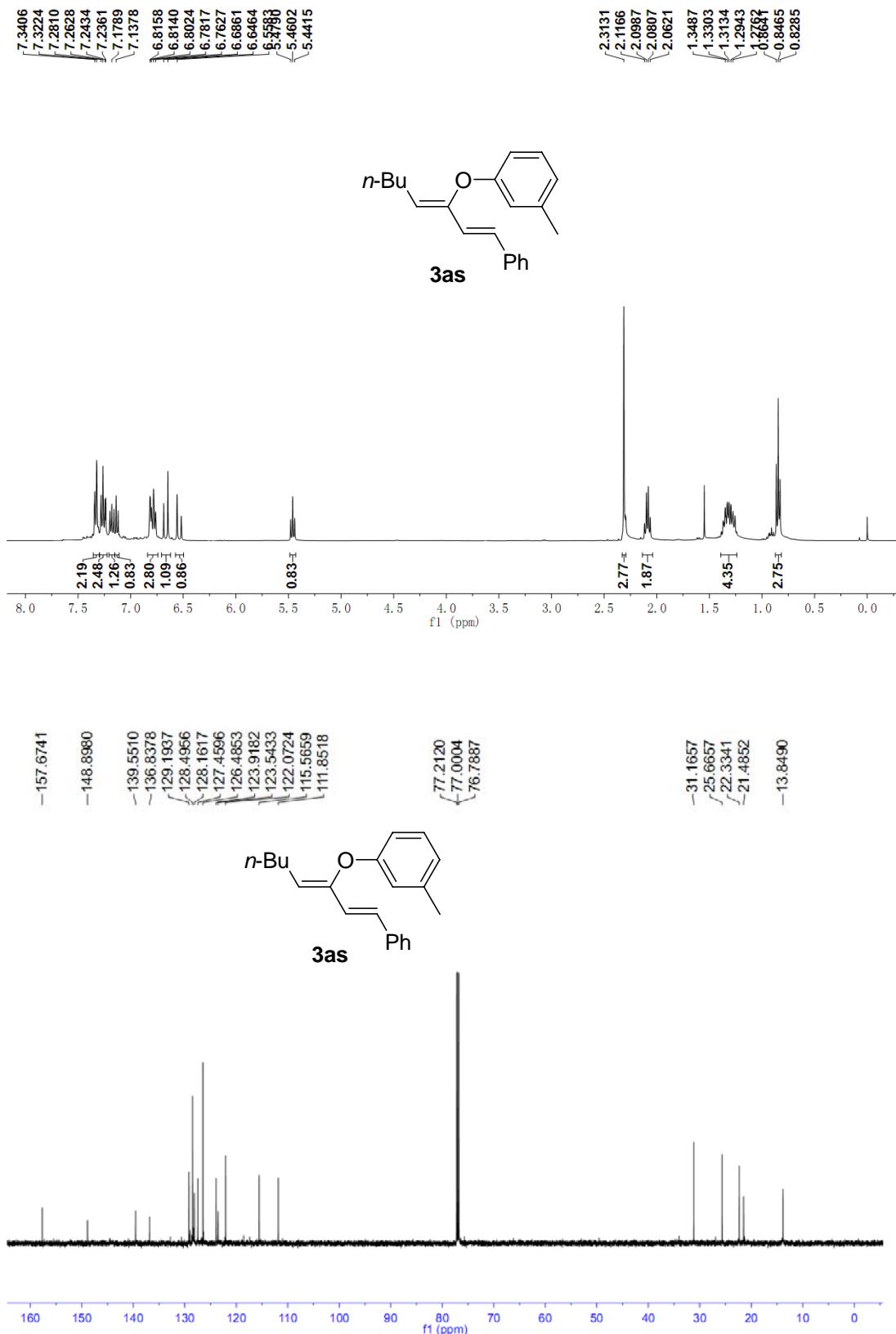


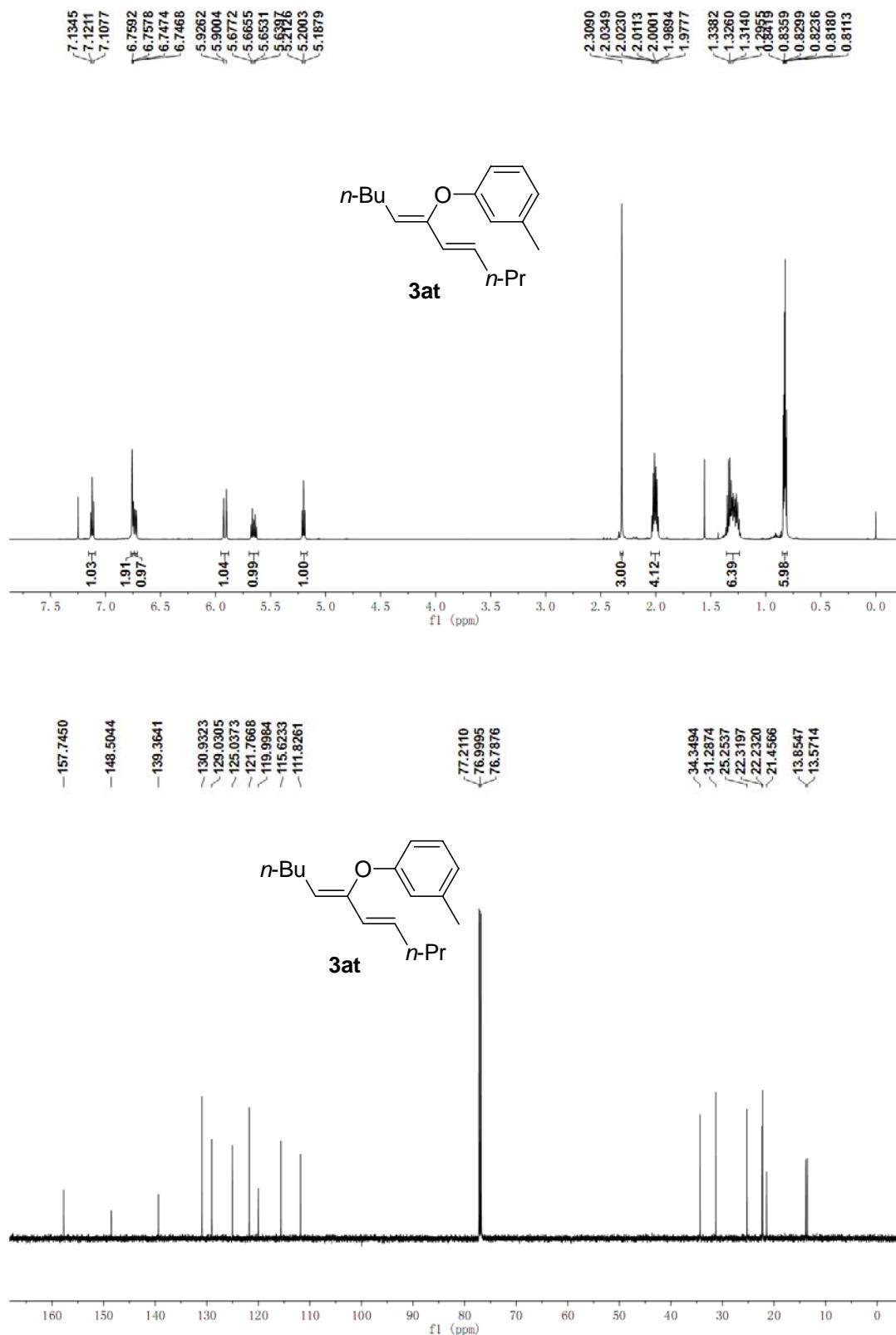


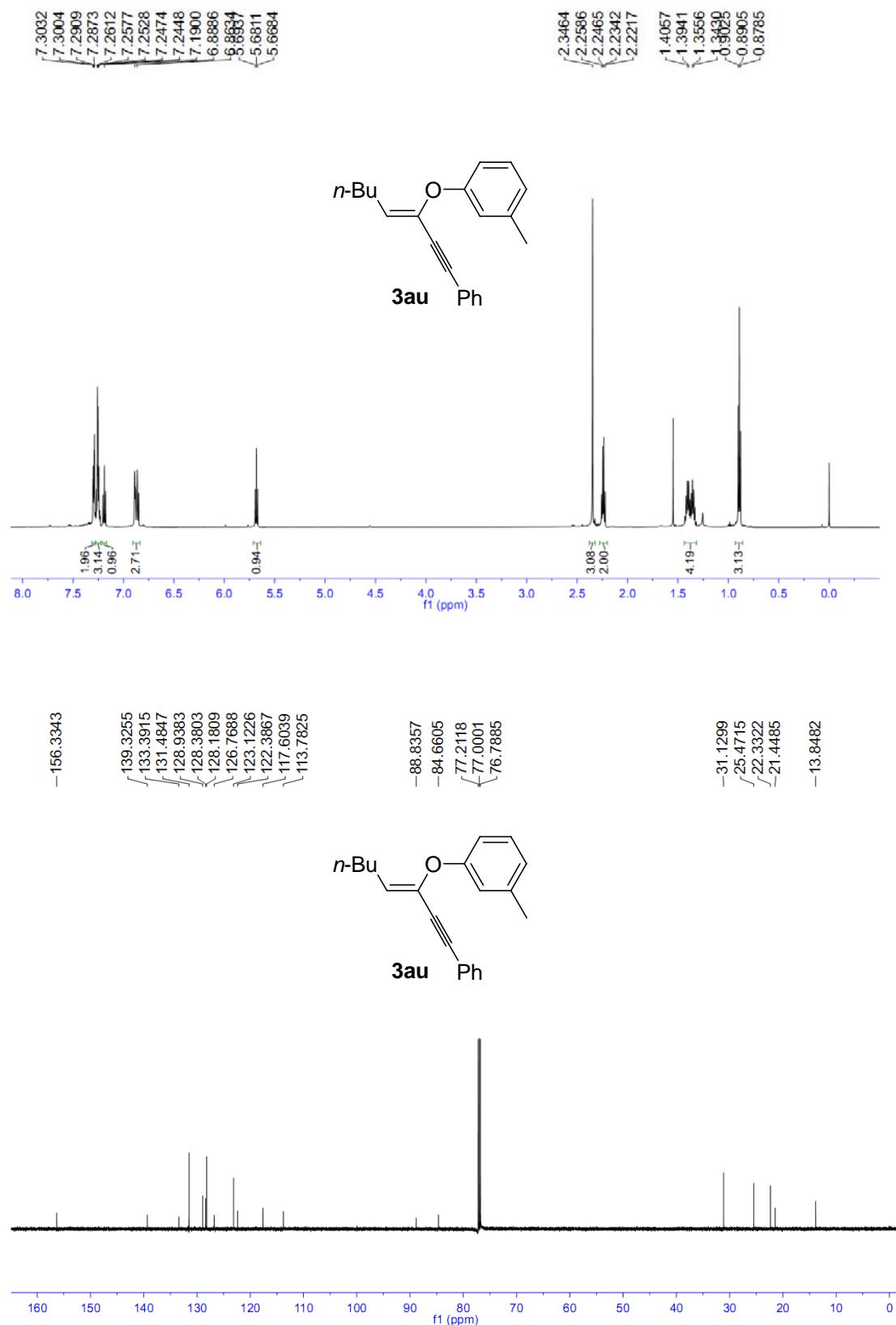


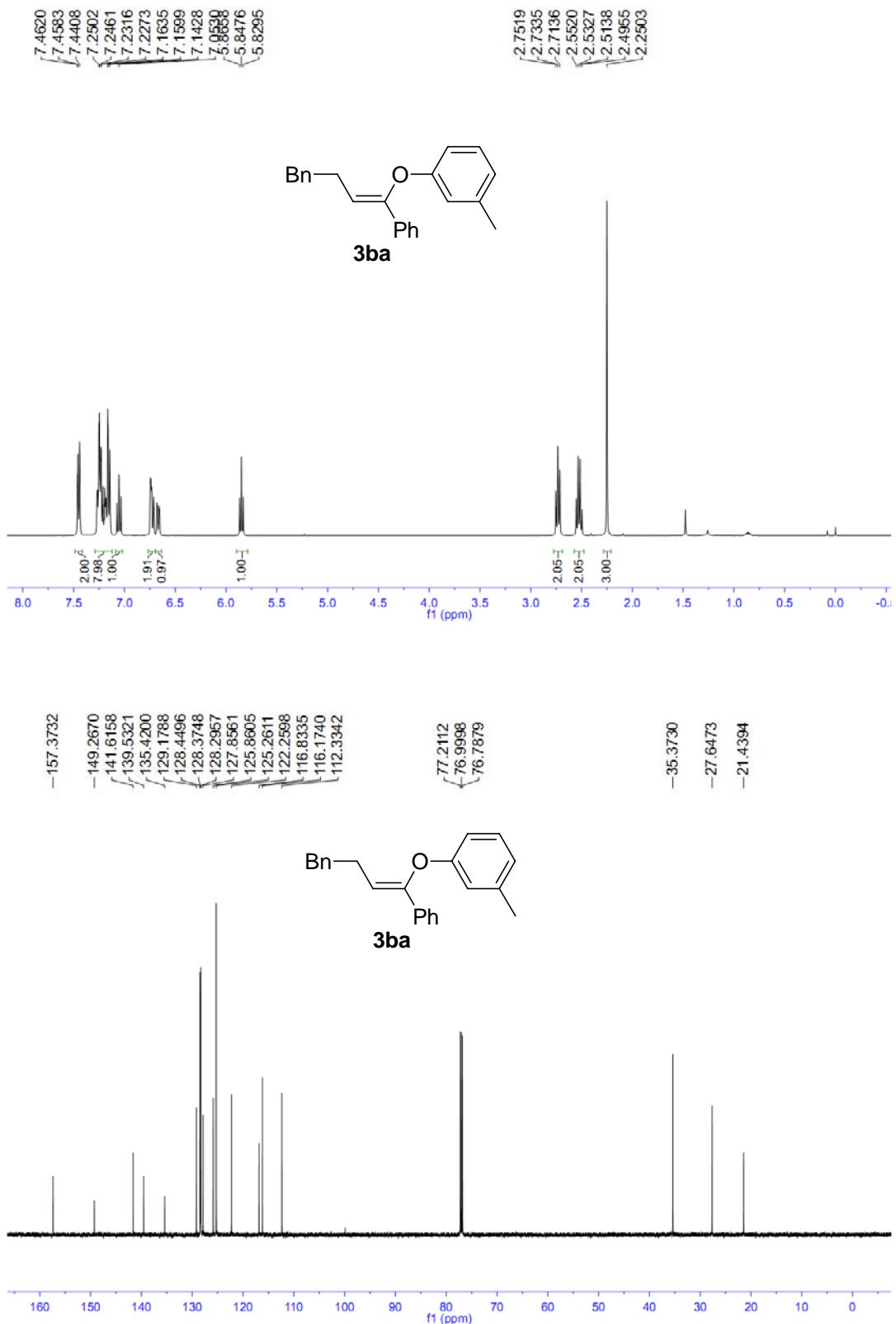


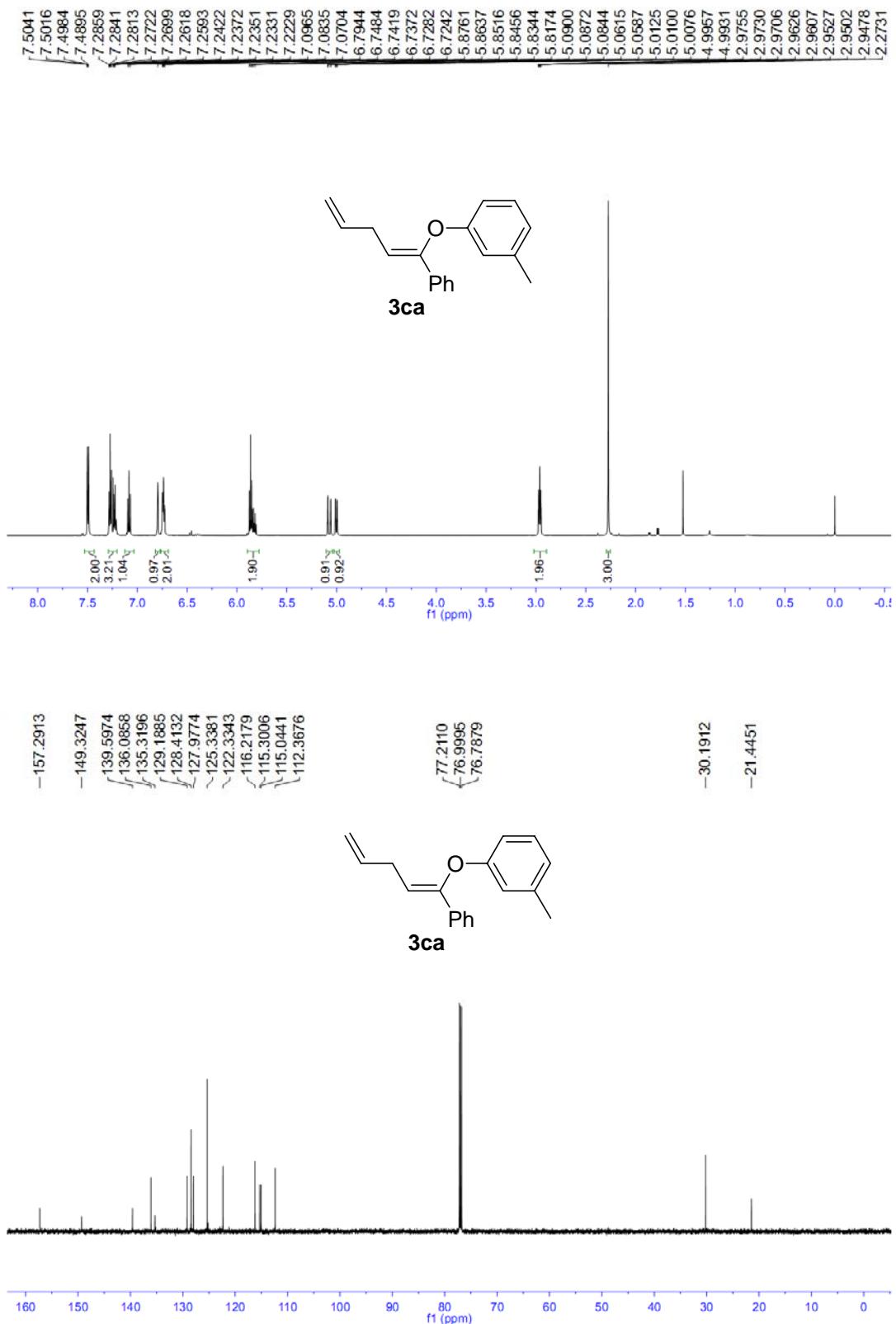


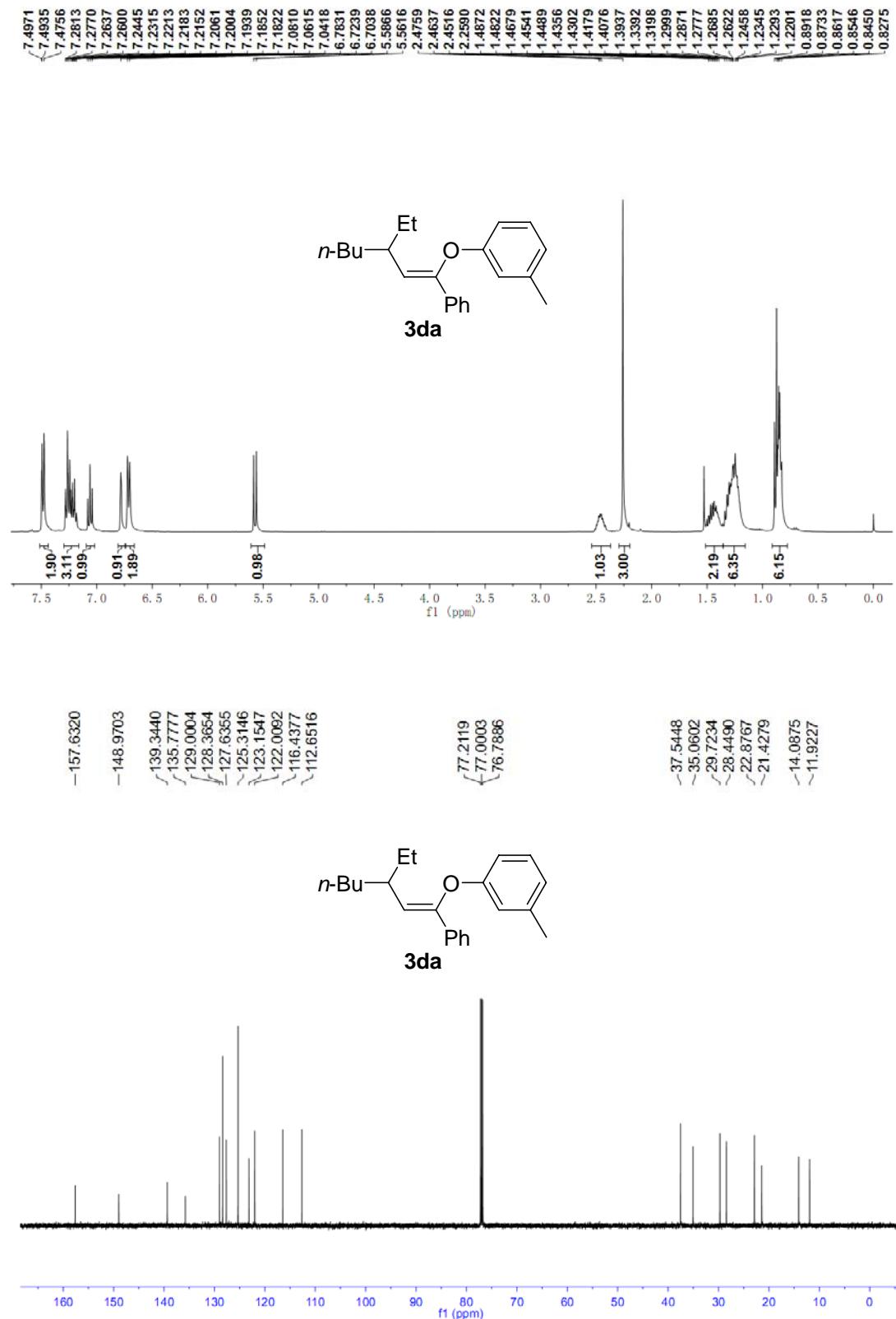


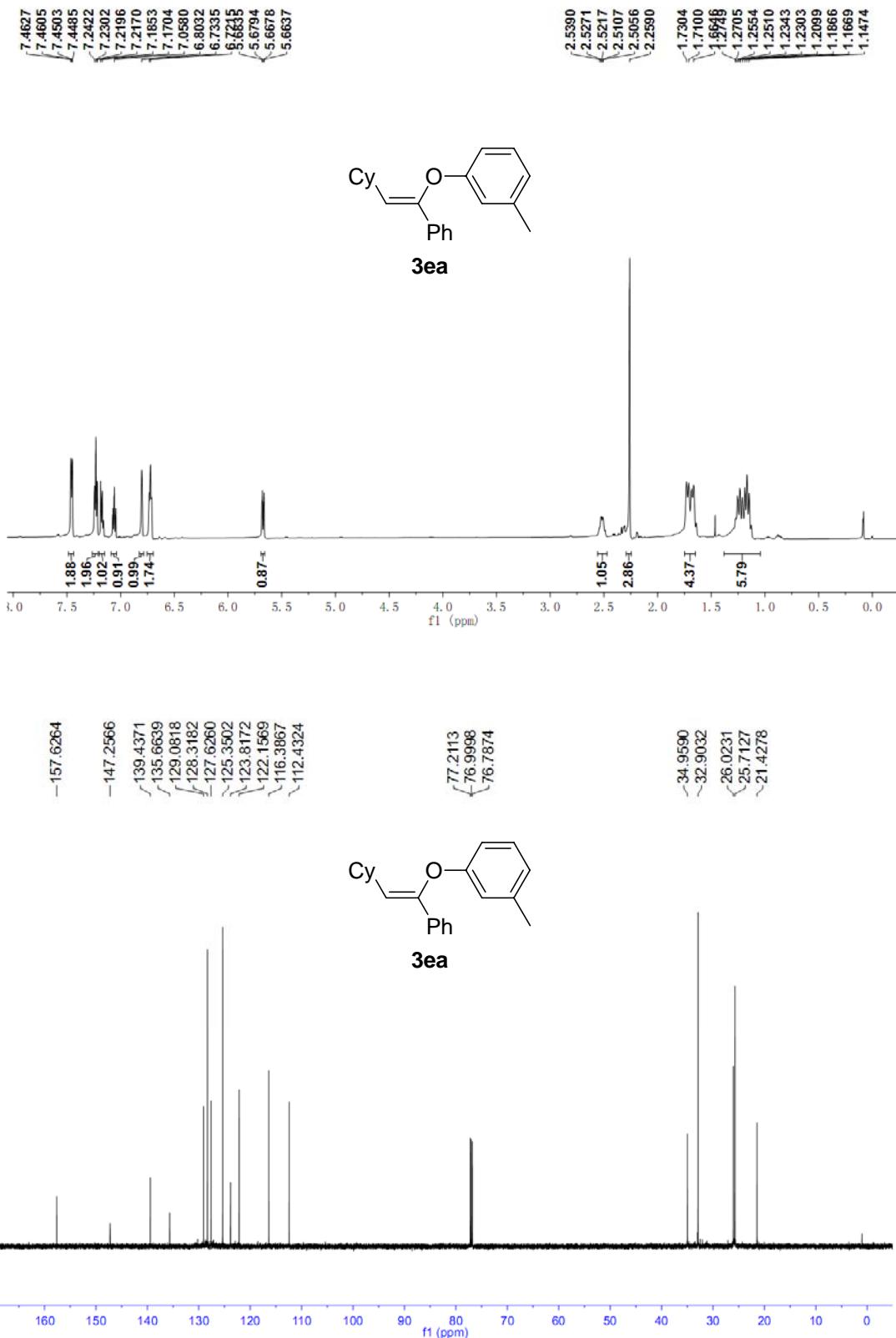


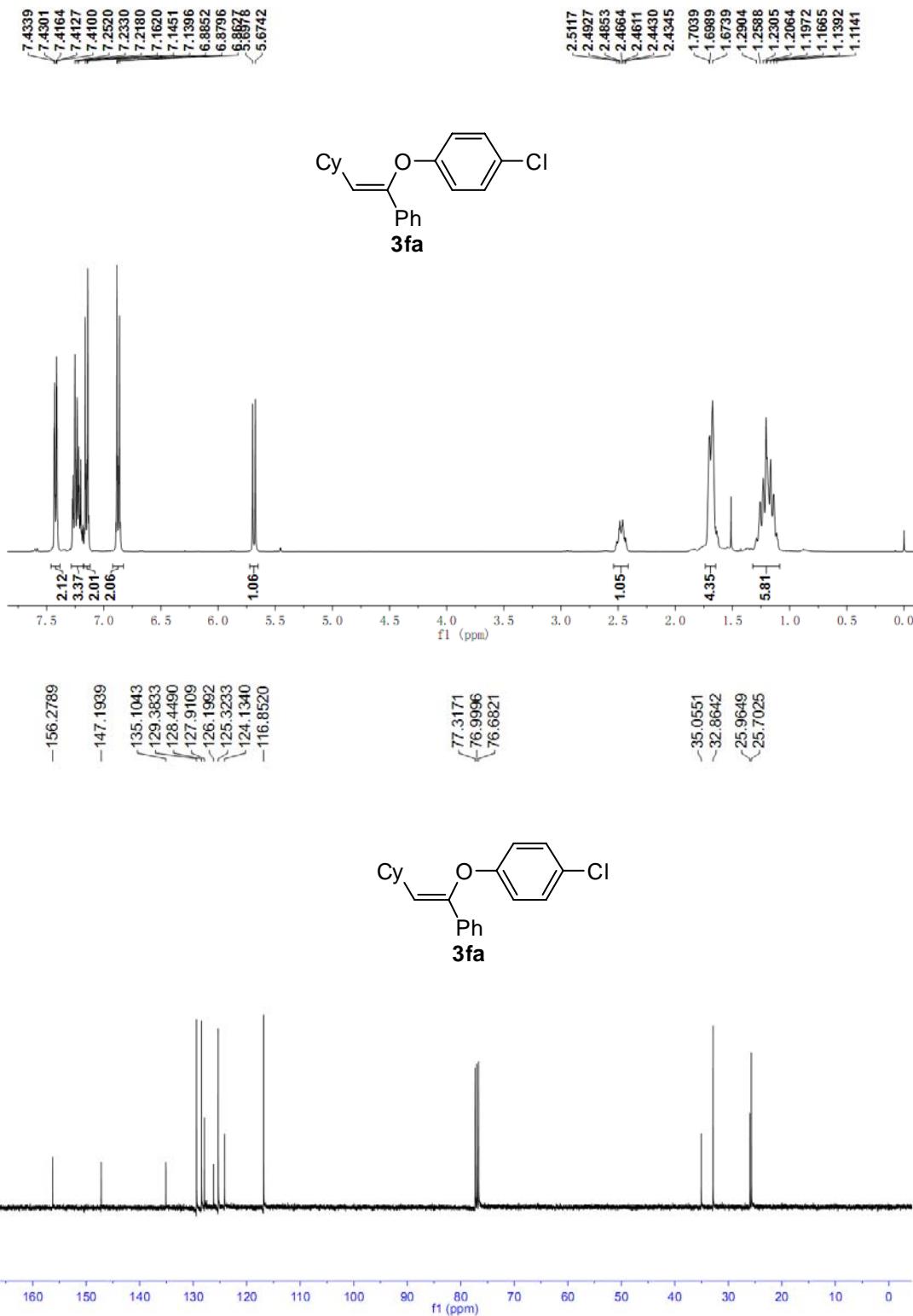


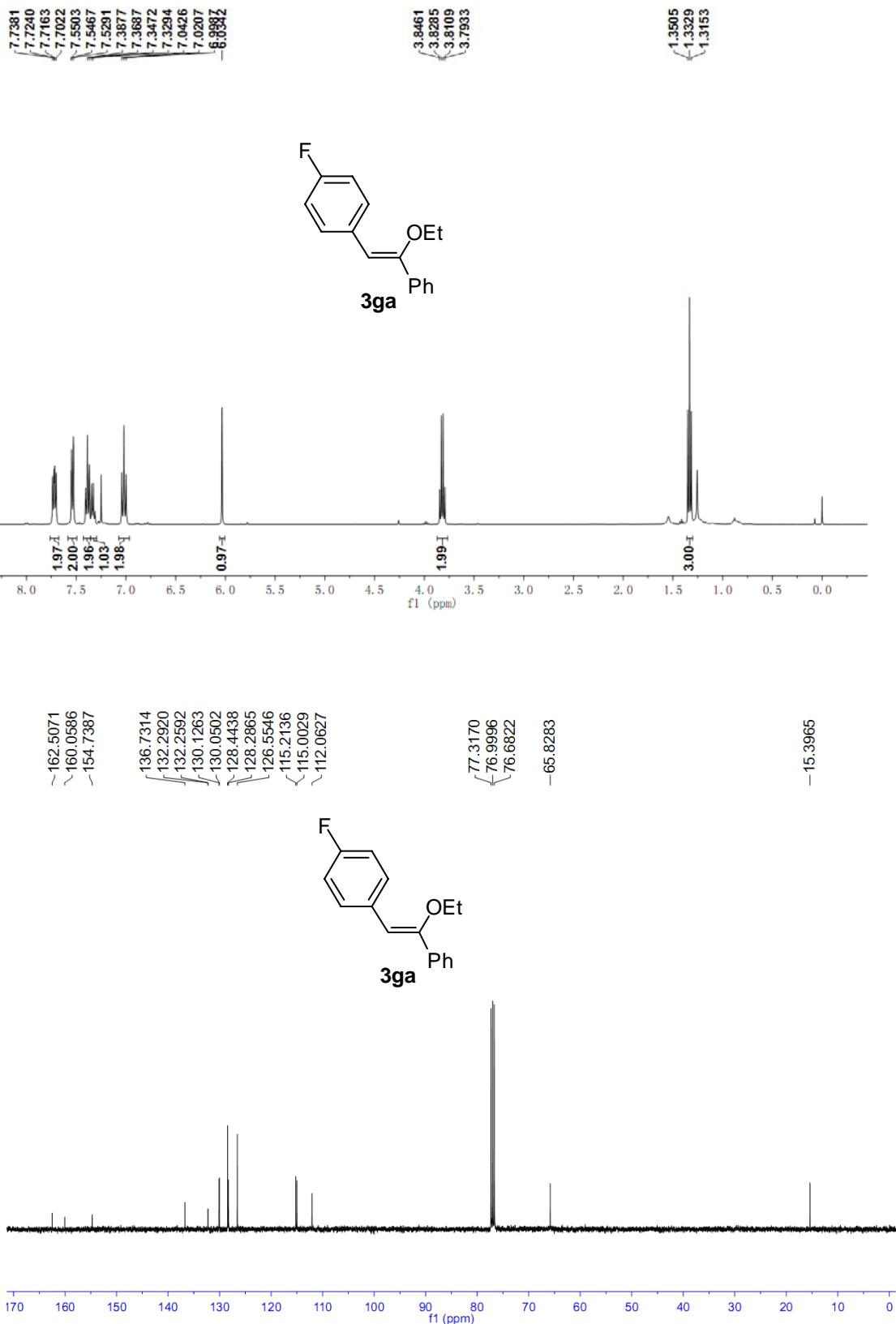


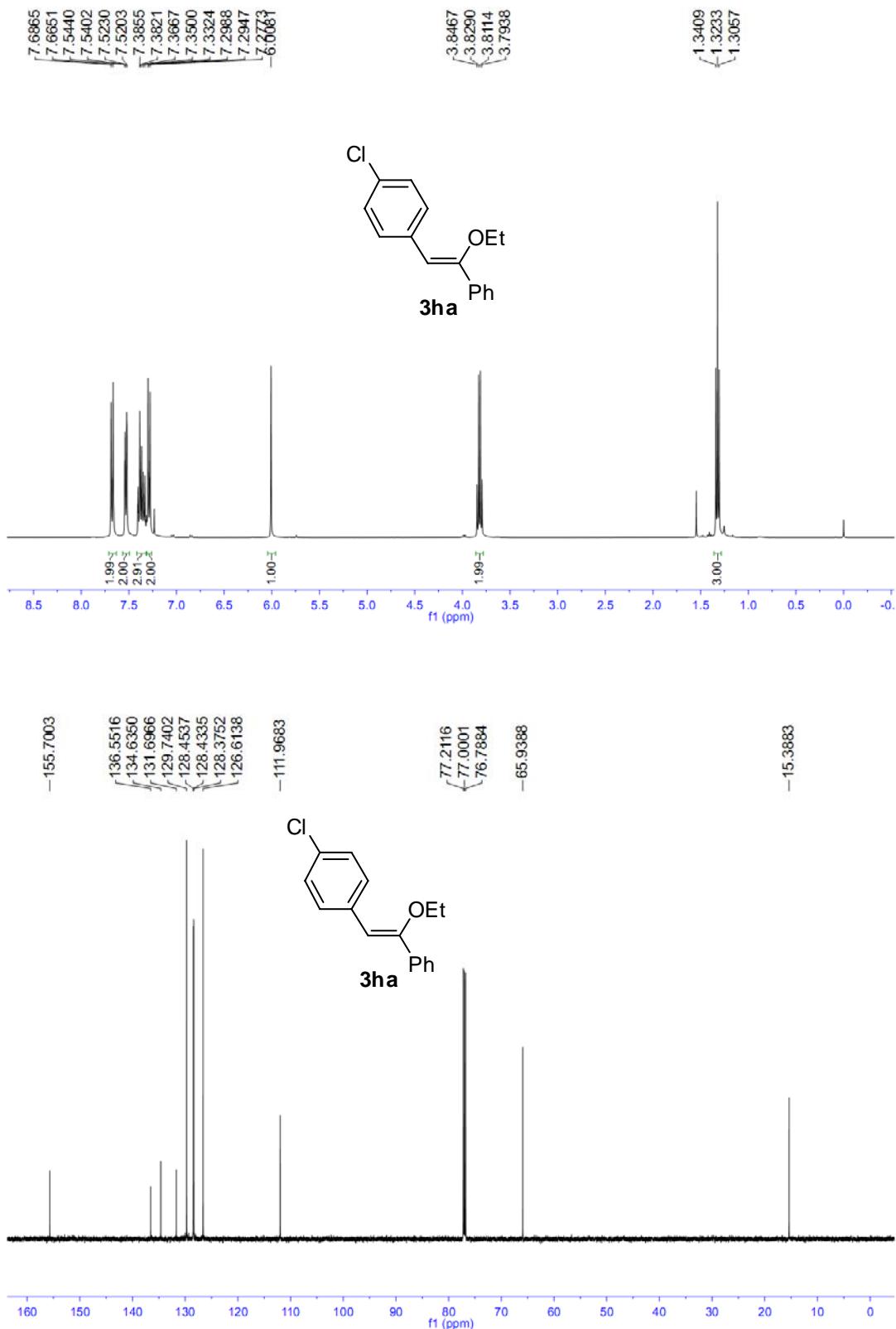


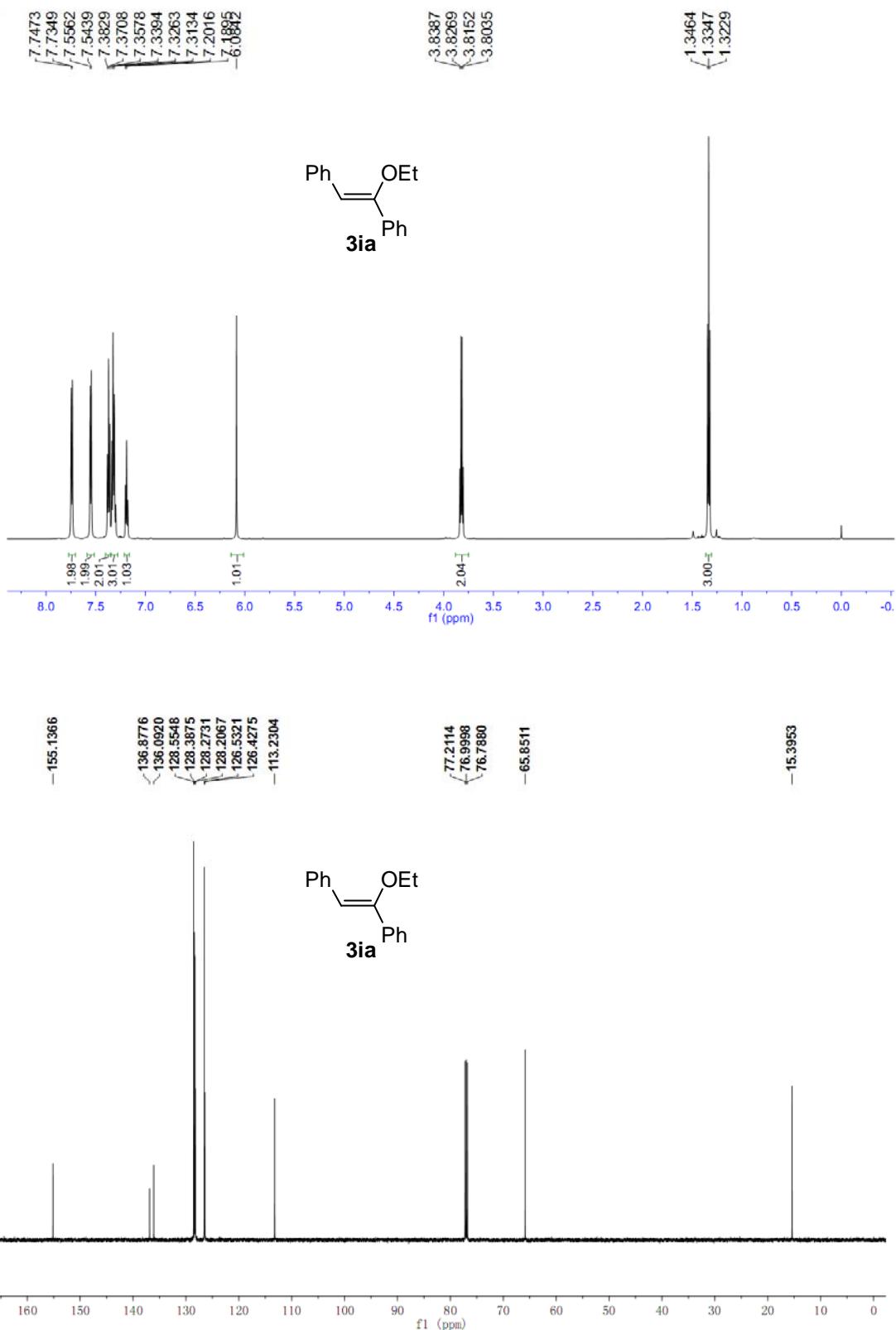


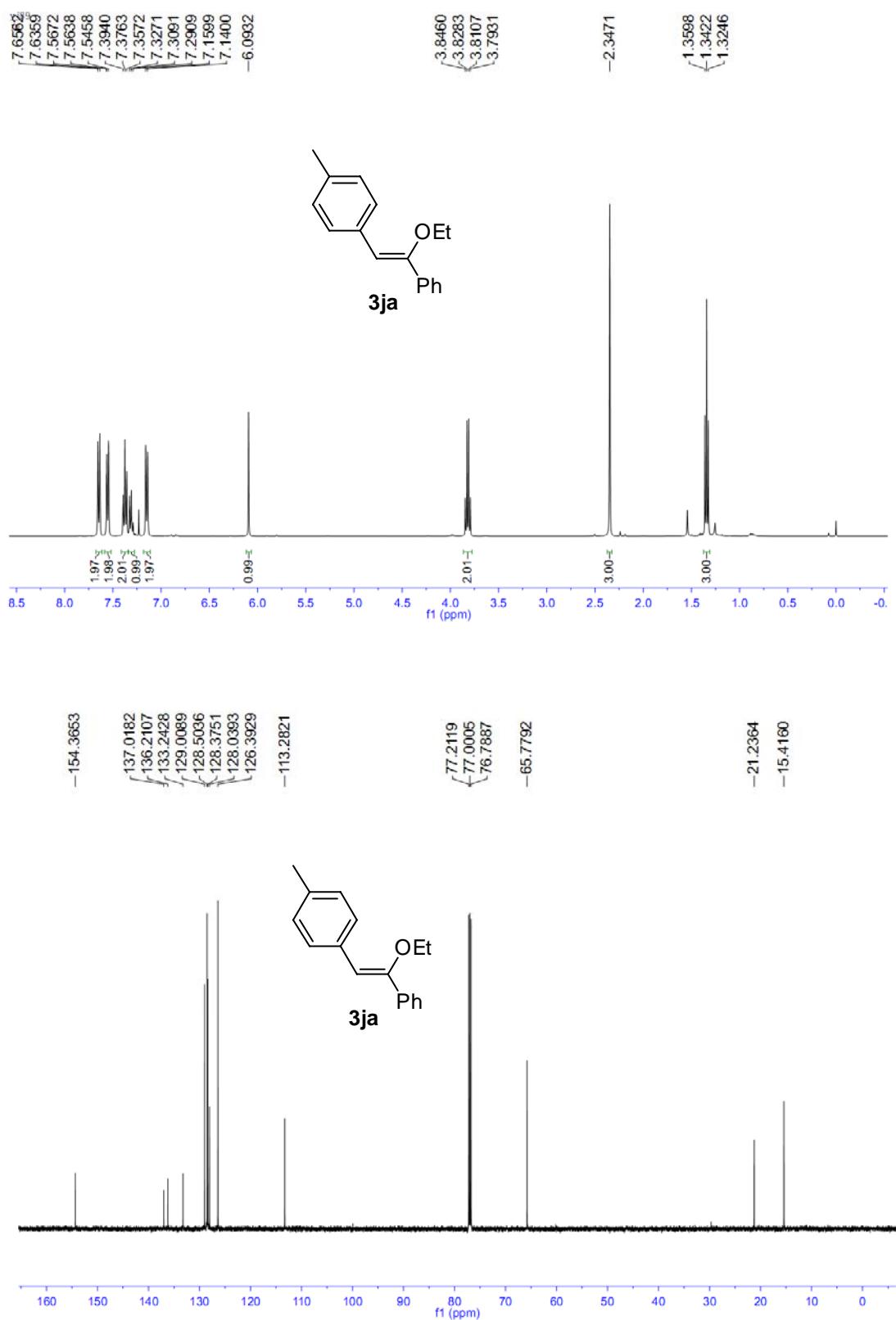


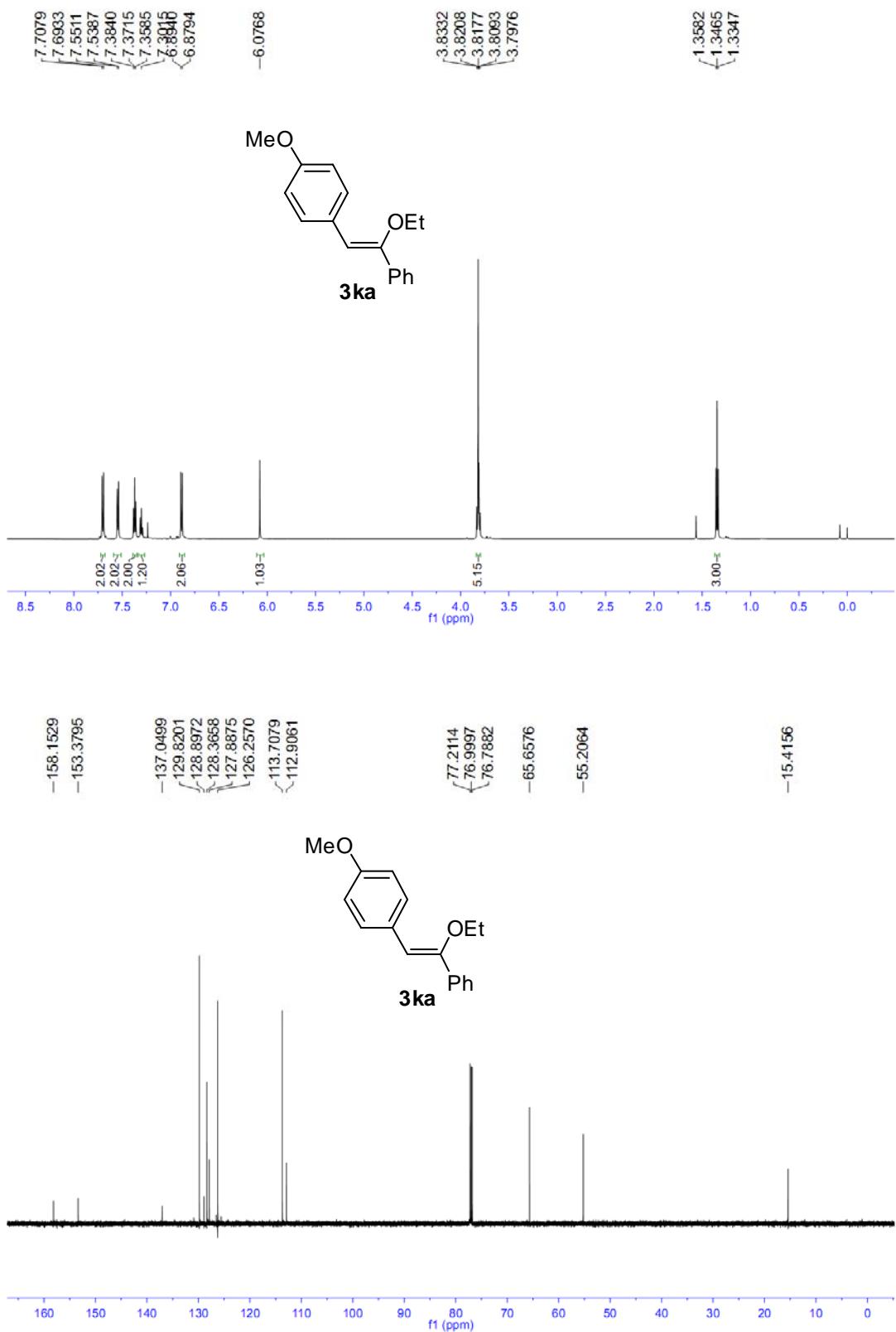


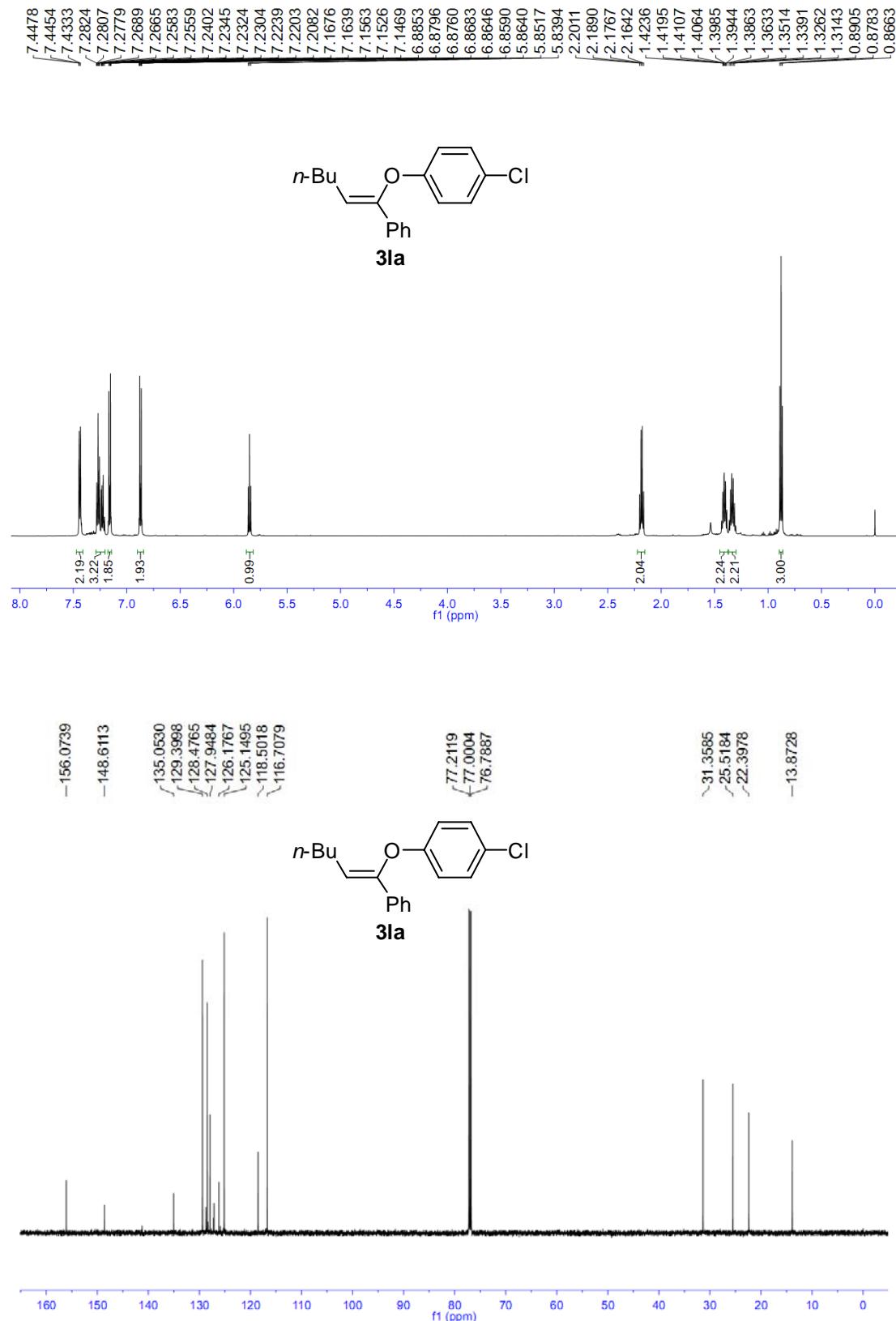


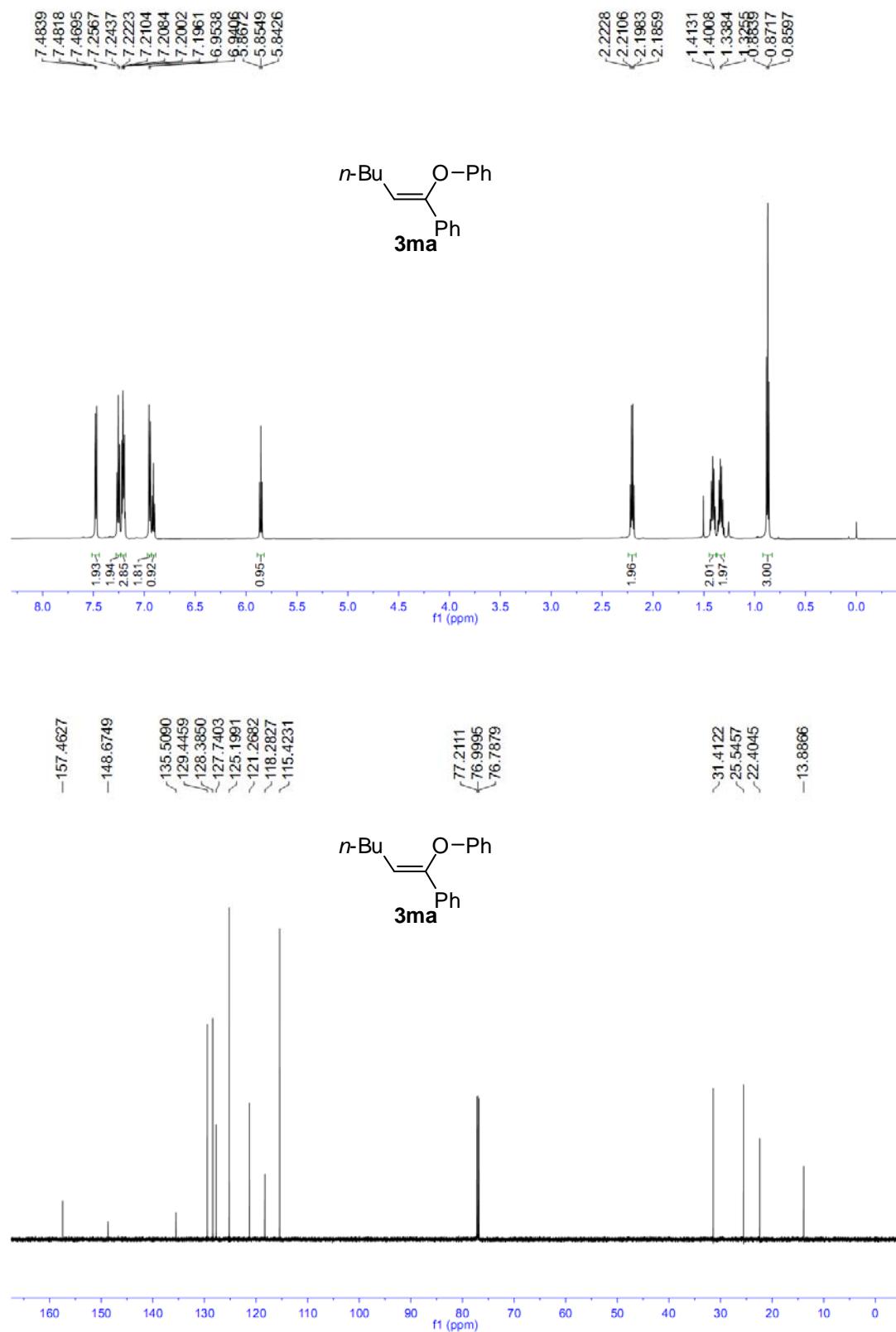


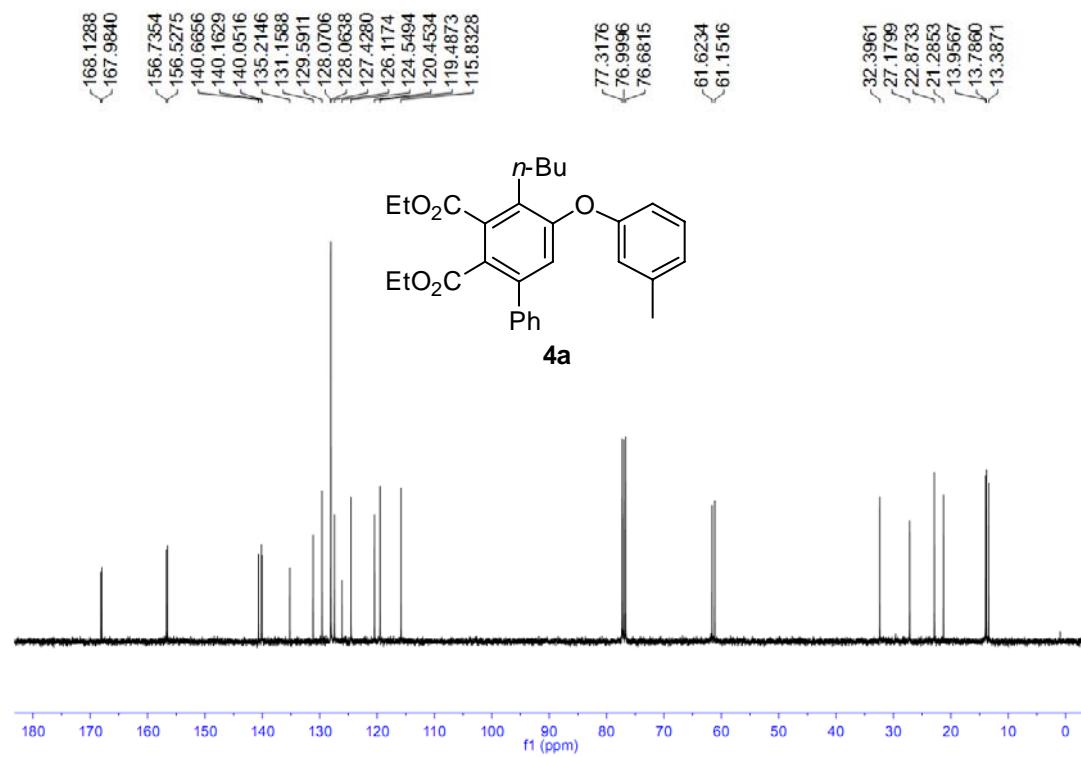
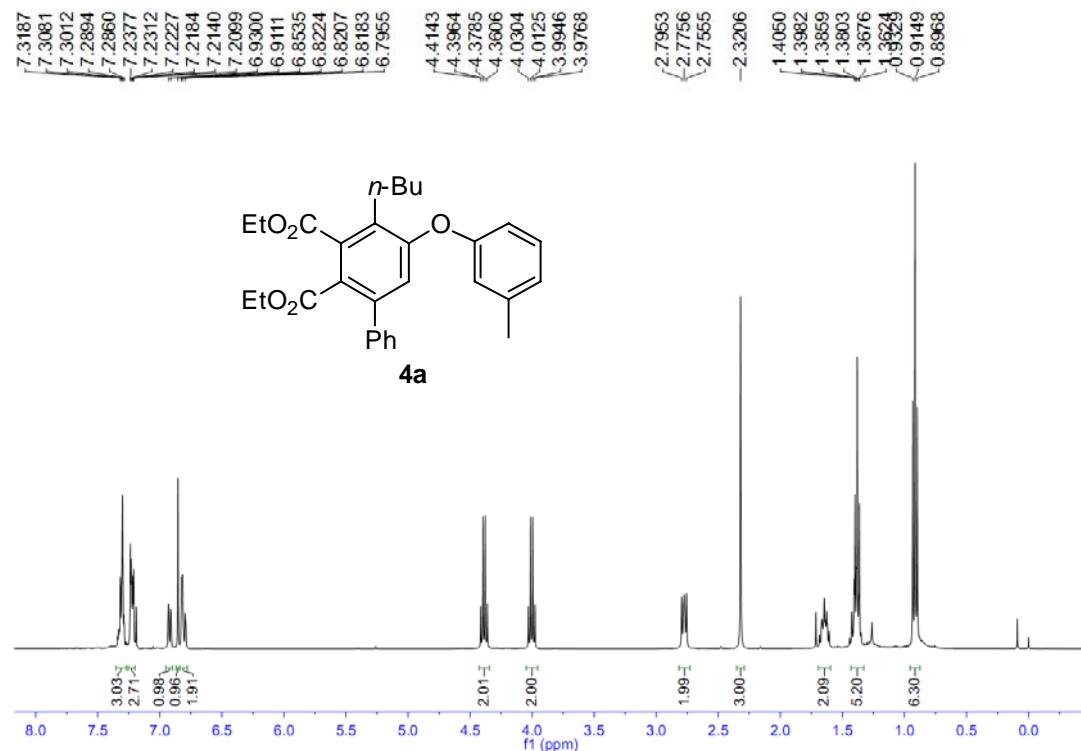


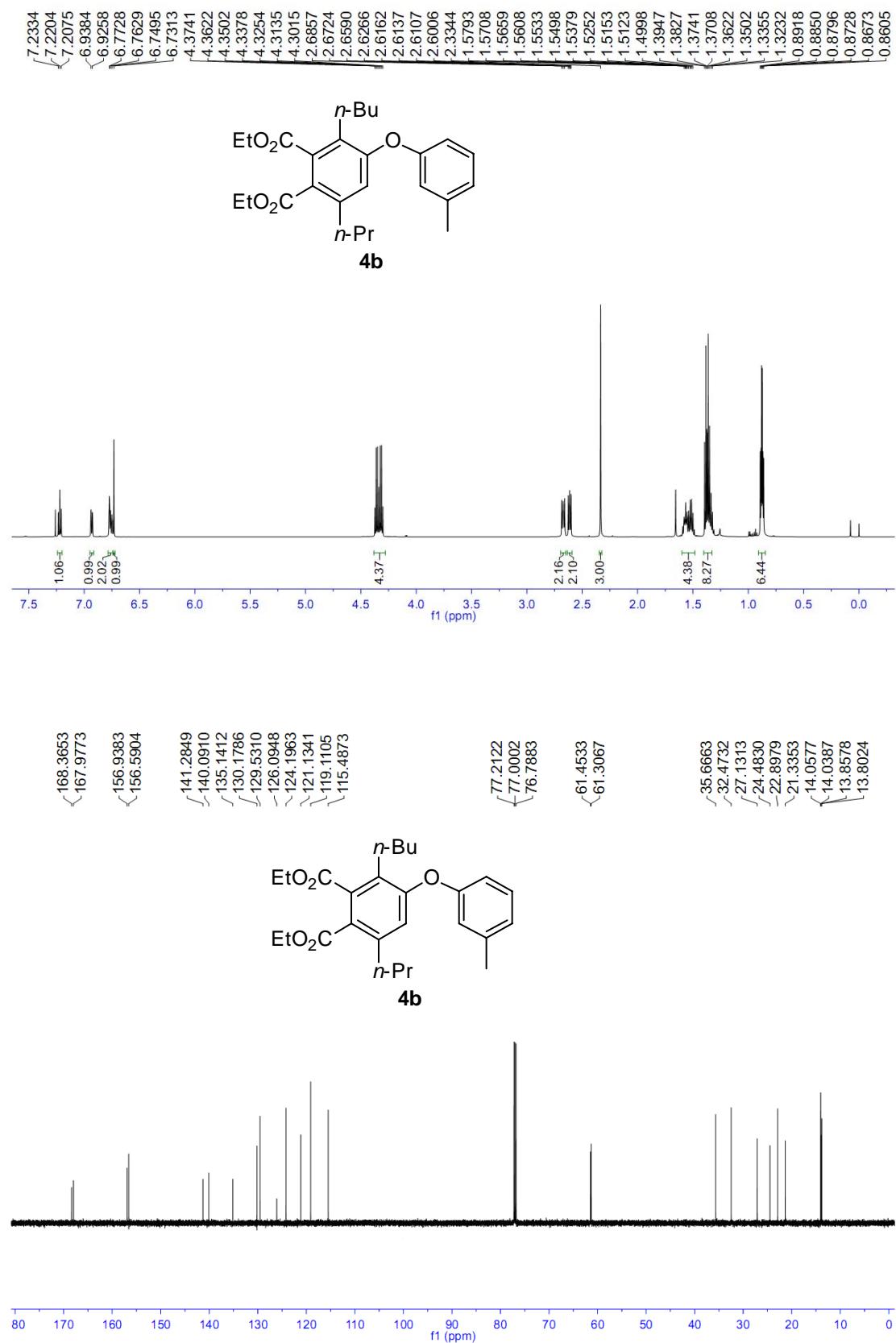












Selected NOE data

