

**Supporting Materials to**

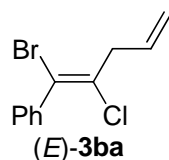
**Palladium-Catalyzed Highly Regio- and Stereoselective Synthesis of**  
**(1*E*)- or (1*Z*)-1,2-Dihalo-1,4-dienes via Haloallylation of Alkynyl**  
**Halides**

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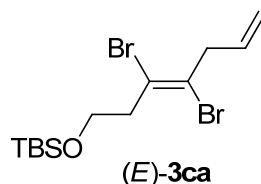
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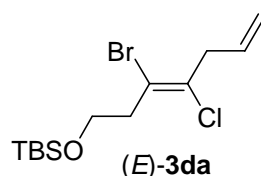




The title compound (*E*)-**3ba** was prepared using Representative Procedure A in 83% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.52 (d, *J* = 6.4 Hz, 2 H), 5.26 (dd, *J* = 10.8, 1.2 Hz, 1 H), 5.32 (dd, *J* = 0.9 Hz, 1 H), 5.88-5.98 (m, 1 H), 7.30-7.42 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 43.6, 117.4, 117.9, 128.2 (2 C), 128.7, 129.2, 129.3 (2 C), 131.7, 138.9; IR (neat, cm<sup>-1</sup>): 3092, 2908, 1636, 1490, 1443; MS (EI, *m/z*): 260 (4), 258 (18), 256 (M<sup>+</sup>, 14), 221 (3), 223 (3); Anal. Calcd. for C<sub>11</sub>H<sub>10</sub>BrCl, HRMS: Calcd. 255.9654, Found: 255.9659.

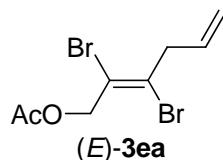


The title compound (*E*)-**3ca** was prepared using Representative Procedure A in 65% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.07 (s, 6 H), 0.90 (s, 9 H), 2.93 (t, *J* = 6.8 Hz, 2 H), 3.44 (d, *J* = 6.4 Hz, 2 H), 3.81 (t, *J* = 6.8 Hz, 2 H), 5.16 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.20 (dd, *J* = 16.0, 1.2 Hz, 1 H), 5.77-5.79 (m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ -5.3 (2 C), 18.2, 25.9 (3 C), 44.1, 45.4, 60.3, 117.5, 118.8, 120.2, 132.1; IR (neat, cm<sup>-1</sup>): 2929, 2858, 1648, 1478, 1432; MS (EI, *m/z*): 338 (20), 336 (28), 334 (12), 178 (33), 176 (100), 175 (33); Anal. Calcd. for C<sub>13</sub>H<sub>24</sub>Br<sub>2</sub>OSi: C: 40.64, H: 6.30, Br: 41.59, O: 4.16, Found C: 40.85, H: 6.57, Br: 41.93, O: 4.42.

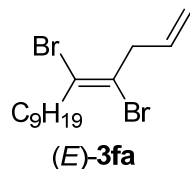


The title compound (*E*)-**3da** was prepared using Representative Procedure A in 84% yield as a colorless oil, *E/Z*: > 95:5. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.57 (s, 6 H), 0.89 (s, 9 H), 2.89 (t, *J* = 6.8 Hz, 2 H), 3.34 (d, *J* = 6.4 Hz, 2 H), 3.80 (t, *J* = 6.8 Hz, 2 H),

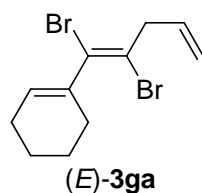
5.14 (dd,  $J = 10.0, 1.2$  Hz, 1 H), 5.19 (dd,  $J = 16.0, 1.2$  Hz, 1 H), 5.74-5.83 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  -5.4 (2 C), 18.2, 25.7 (3 C), 41.4, 43.0, 60.4, 117.5, 118.5, 129.4, 131.8; IR (neat,  $\text{cm}^{-1}$ ): 2957, 2859, 1658, 1471, 1422; MS (EI,  $m/z$ ): 285 (28), 283 (84), 281 ( $\text{M}^+ - \text{Bu}^t$ , 74), 169 (47), 167 (50); Anal. Calcd. for  $\text{C}_{13}\text{H}_{24}\text{BrClOSi}$ , HRMS: Cacl. 280.9764 ( $\text{M} - \text{Bu}^t$ ) $^+$ , Found: 280.9758.



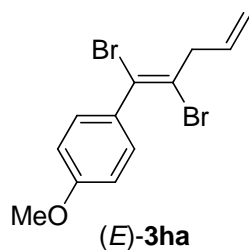
The title compound (*E*)-**3ea** was prepared using Representative Procedure A in 62% yield as a colorless oil, *E/Z*: > 98:2.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.25 (s, 3 H), 3.35 (d,  $J = 6.0$  Hz, 2 H), 4.12 (s, 2 H), 5.22 (dd,  $J = 10.4, 1.2$  Hz, 1H), 5.26 (d,  $J = 1.2$  Hz, 1 H), 5.79-5.89 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  20.6, 25.9, 40.0, 118.1, 119.1, 131.8, 142.8, 168.0; IR (neat,  $\text{cm}^{-1}$ ): 3084, 2926, 1765, 1659, 1447; MS (EI,  $m/z$ ): 258 (40), 256 (82), 254 ( $\text{M}^+ + \text{H} - \text{Ac}$ , 44), 219 (53), 217 (56); Anal. Calcd. for  $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_2$ , HRMS: Cacl. 253.8942 ( $\text{M} + \text{H} - \text{Ac}$ ) $^+$ , Found: 253.8950.



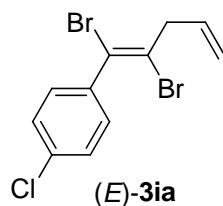
The title compound (*E*)-**3fa** was prepared using Representative Procedure A in 86% yield as a colorless oil, *E/Z*: > 98:2.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.88 (t,  $J = 6.4$  Hz, 3 H), 1.27-1.32 (m, 12 H), 1.53-1.60 (m, 2 H), 2.67 (t,  $J = 8.0$  Hz, 2 H), 3.44 (d,  $J = 6.4$  Hz, 2 H), 5.16 (dd,  $J = 5.6, 4.4$  Hz, 1 H), 5.20 (dd,  $J = 2.8, 1.2$  Hz, 1 H), 5.76-5.83 (m, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  14.1, 22.7, 27.4, 28.5, 29.3, 29.4, 29.5, 31.9, 40.7, 45.3, 117.3, 118.1, 123.1, 132.4; IR (neat,  $\text{cm}^{-1}$ ): 2927, 2856, 1725, 1640, 1468; MS (EI,  $m/z$ ): 354 (36), 352 (83), 350 ( $\text{M}^+$ , 40), 273 (2), 271 (3); Anal. Calcd. For  $\text{C}_{14}\text{H}_{24}\text{Br}_2$ , HRMS: Cacl. 350.0245, Found: 350.0241.



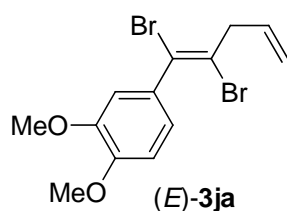
The title compound (*E*)-**3ga** was prepared using Representative Procedure A in 66% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.59-1.62 (m, 2 H), 1.69-1.72 (m, 2 H), 2.09-2.15 (m, 4 H), 3.47 (dd, *J* = 6.4, 1.2 Hz, 2 H), 5.19 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.23 (dd, *J* = 15.6, 1.6 Hz, 1 H), 5.79-5.86 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 21.6, 22.3, 25.1, 26.3, 117.1, 117.3, 117.4, 121.3, 130.3, 132.3, 137.9; IR (neat, cm<sup>-1</sup>): 2934, 2860, 1713, 1647, 1435; MS (EI, *m/z*): 308 (9), 306 (19), 304 (M<sup>+</sup>, 10), 227 (58), 225 (63); Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>Br<sub>2</sub>, HRMS: Cacl. 303.9462, Found: 303.9465.



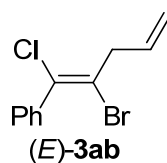
The title compound (*E*)-**3ha** was prepared using Representative Procedure A in 78% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.60 (d, *J* = 6.4 Hz, 2 H), 3.83 (s, 3 H), 5.24 (dd, *J* = 10.0, 0.8 Hz, 1 H), 5.30 (dd, *J* = 16.8, 1.2 Hz, 1 H), 5.88-5.95 (m, 1 H), 6.90 (d, *J* = 4.8 Hz, 2 H), 7.40 (d, *J* = 4.4 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 43.2, 55.2, 113.4 (2 C), 117.6, 119.2, 127.9, 130.6 (2 C), 131.0, 132.3, 159.7; IR (neat, cm<sup>-1</sup>): 2962, 2927, 1721, 1605, 1508; MS (EI, *m/z*): 334 (25), 332 (45), 330 (M<sup>+</sup>, 24), 253 (36), 251 (34); Anal. Calcd. for C<sub>12</sub>H<sub>12</sub>Br<sub>2</sub>O, HRMS: Cacl. 329.9255, Found: 329.9262.



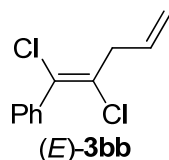
The title compound (*E*)-**3ia** was prepared using Representative Procedure A in 76% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.63 (dd, *J* = 6.4, 2.8 Hz, 2 H), 5.26 (dd, *J* = 8.8, 1.2 Hz, 1 H), 5.29 (dd, *J* = 15.2, 2.8 Hz, 1 H), 5.88-5.95 (m, 1 H), 7.32-7.38(m, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 45.6, 116.1, 118.0, 120.9, 128.5 (2C), 130.5 (2 C), 131.8, 134.6, 139.0; IR (neat, cm<sup>-1</sup>): 3096, 2954, 1639, 1590, 1487; MS (EI, *m/z*): 338 (17), 336 (28), 334 (M<sup>+</sup>, 13), 259 (3), 257 (8); Anal. Calcd. for C<sub>11</sub>H<sub>9</sub>Br<sub>2</sub>Cl, HRMS: Cacl. 333.8760, Found: 333.8768.



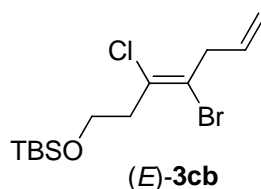
The title compound (*E*)-**3ja** was prepared using Representative Procedure A in 91% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) : δ 3.62 (dd, *J* = 6.4, 1.2 Hz, 2 H), 3.89 (s, 6 H), 5.25 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.29 (dd, *J* = 15.2, 1.6 Hz, 1 H), 5.88-5.97 (m, 1 H), 6.84-6.99 (m, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 45.8, 55.8, 55.9, 110.5, 112.3, 117.7, 117.8, 119.8, 122.1, 132.1, 133.0, 148.4, 149.2; IR (neat, cm<sup>-1</sup>): 3080, 2931, 1641, 1599, 1408; MS (EI, *m/z*): 364 (6), 362 (17), 360 (M<sup>+</sup>, 8), 203 (20), 202 (100), 201 (34); Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>Br<sub>2</sub>O<sub>2</sub>, HRMS: Cacl. 359.9361, Found: 359.9367.



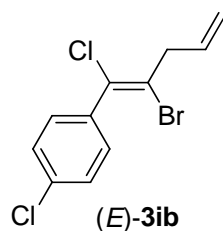
The title compound (*E*)-**3ab** was prepared using Representative Procedure A in 85% yield as a colorless oil, *E/Z*: >98/2, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.63 (d, *J* = 6.4 Hz, 2 H), 5.28 (dd, *J* = 10.0, 5.4 Hz, 1 H), 5.34 (d, *J* = 1.2 Hz, 1 H), 5.89-5.99 (m, 1 H), 7.37-7.49 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 43.1, 117.8, 119.8, 127.9, 128.2 (2 C), 128.9, 129.2 (2 C), 132.3, 138.8; IR(neat, cm<sup>-1</sup>): 3083, 2924, 1641, 1489, 1444; MS (EI, *m/z*): 260 (4), 258 (17), 256 (M<sup>+</sup>, 15), 223 (3), 221(3); Anal. Calcd. for C<sub>11</sub>H<sub>10</sub>BrCl, HRMS: Cacl. 255.9654, Found: 255.9660.



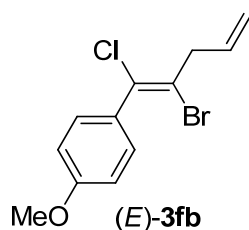
The title compound (*E*)-**3bb** was prepared using Representative Procedure A in 89% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.53 (dd, *J* = 6.4, 1.2 Hz, 2 H), 5.26 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.32 (dd, *J* = 16.8, 1.2 Hz, 1 H), 5.93-5.99 (m, 1 H), 7.37-7.44 (m, 3 H), 7.50-7.53 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 41.2, 117.8, 128.1 (2 C), 128.6, 128.8, 129.1 (2 C), 129.2, 131.8, 137.1; IR (neat, cm<sup>-1</sup>): 3080, 2920, 1642, 1486, 1442; MS (EI, *m/z*): 214 (10), 213 (2), 212 (M<sup>+</sup>, 15), 179 (19), 177 (57); Anal. Calcd. for C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>, HRMS: Cacl. 212.0160, Found: 212.0153.



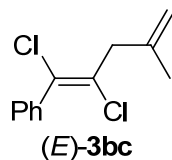
The title compound (*E*)-**3cb** was prepared using Representative Procedure A in 81% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.06 (s, 6 H), 1.65 (s, 9 H), 2.83 (t, *J* = 8.0 Hz, 2 H), 3.41 (d, *J* = 8.0 Hz, 2 H), 3.82 (t, *J* = 6.8 Hz, 2 H), 5.15 (dd, *J* = 8.8, 1.2 Hz, 1 H), 5.20 (d, *J* = 1.6 Hz, 1 H), 5.74-5.78 (m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ -5.4 (2 C), 18.3, 25.9 (3 C), 41.9, 42.5, 59.9, 117.4, 120.0, 128.1, 132.1; IR(neat, cm<sup>-1</sup>): 2927, 2858, 1636, 1471, 1423; MS (EI, *m/z*): 285 (25), 283 (82), 281 (M<sup>+</sup>-Bu<sup>t</sup>, 73), 169 (55), 167 (34); Anal. Calcd. for C<sub>13</sub>H<sub>24</sub>BrClOSi, HRMS: Cacl. 280.9764, Found: 280.9769.



The title compound (*E*)-**3ib** was prepared using Representative Procedure A in 90% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.61 (td, *J* = 6.4, 1.2 Hz, 2 H), 5.27 (dd, *J* = 12.0, 1.2 Hz, 1 H), 5.32 (dd, *J* = 4.4, 1.6 Hz, 1 H), 5.88-5.95 (m, 1 H), 7.36-7.41 (m, 4 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 43.1, 117.9, 120.5, 126.7, 128.5 (2 C), 130.6 (2 C), 132.0, 134.8, 137.1; IR (neat, cm<sup>-1</sup>): 3069, 2924, 1641, 1592, 1484; MS (EI, *m/z*): 294 (19), 292 (40), 290 (M<sup>+</sup>, 27), 257 (8), 255 (6); Anal. Calcd. for C<sub>11</sub>H<sub>9</sub>BrCl<sub>2</sub>, HRMS: Calcd. 289.9265, Found: 289.9261.



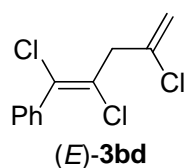
The title compound (*E*)-**3fb** was prepared using Representative Procedure A in 81% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.60 (d, *J* = 6.4 Hz, 2 H), 3.83 (s, 3 H), 5.24 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.30 (dd, *J* = 8.8, 1.2 Hz, 1 H), 5.89-5.95 (m, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 7.40 (d, *J* = 8.8 Hz, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 43.2, 55.3, 113.5, 117.7 (2 C), 119.7, 130.6 (2 C), 132.1, 131.0, 132.3, 159.7; IR (neat, cm<sup>-1</sup>): 2947, 2930, 1638, 1471, 1259; MS (EI, *m/z*): 290 (24), 288 (62), 286 (M<sup>+</sup>, 67), 253 (7), 251 (7); Anal. Calcd. For C<sub>12</sub>H<sub>12</sub>BrClO, HRMS: Calcd. 285.9760, Found: 285.9763.



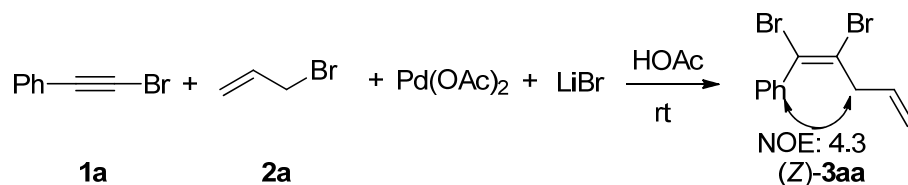
The title compound (*E*)-**3bc** was prepared using Representative Procedure A in 83% yield as a colorless oil, *E/Z*: > 98:2. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.87 (s, 3 H), 3.48 (s, 2 H), 4.97 (dd, *J* = 10.6, 0.6 Hz, 2 H), 7.37-7.41 (m, 3 H), 7.49-7.51 (m, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 21.8, 44.9, 113.3, 128.1 (2 C), 128.2, 128.7, 128.8, 129.1 (2 C), 137.3, 140.0; IR (neat, cm<sup>-1</sup>): 3081, 2924, 1655, 1444, 1376; MS (EI, *m/z*): 228



(21), 227 (3), 226 ( $M^+$ , 25), 213 (45), 211 (74); Anal. Calcd. for  $C_{12}H_{12}Cl_2$ , HRMS: Cacl. 226.0316, Found: 226.0322.

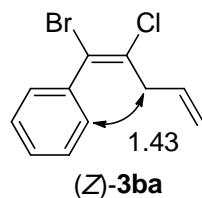


The title compound (*E*)-**3bd** was prepared using Representative Procedure A in 39% yield as a colorless oil, *E/Z*: > 98:2.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  3.77 (s, 2 H), 5.39 (dd,  $J = 8.0, 1.2$  Hz, 2 H), 7.37-7.43 (m, 3 H), 7.48-7.51 (m, 2 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  45.9, 115.0, 125.7, 128.2 (2 C), 129.0 (2 C), 129.1, 130.3, 136.5, 136.8; IR (neat,  $cm^{-1}$ ): 2926, 2867, 1725, 1636, 1489; MS (EI,  $m/z$ ): 250 (7), 248 (25), 246 ( $M^+$ , 23), 213 (16), 211 (28); Anal. Calcd. for  $C_{11}H_9Cl_3$ , HRMS: Cacl. 245.9770, Found: 245.9777.

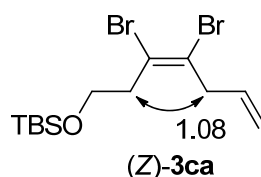


**Representative Procedure B:** To a mixture of **2a** (65  $\mu$  L, 0.75 mmol),  $LiBr$  (87 mg, 1.0 mmol) and  $Pd(OAc)_2$  (6.5 mg, 0.025 mmol) in 2 mL of  $HOAc$ , was added **1a** (73 mg, 0.5 mmol) at rt. After stirring for 2 h, the reaction mixture was quenched with water, extracted with  $CH_2Cl_2$ , washed with saturated  $NaHCO_3$  and brine, dried over  $MgSO_4$ , then concentrated and purified by column chromatography on silica (petroleum ether) to give 120 mg (yield: 80%) of (*Z*)-**3aa** as a colorless oil. *E/Z*: < 3/97, the stereochemistry was assigned by NOE measurements and related literature analysis.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  3.18 (d,  $J = 6.0$  Hz, 2 H), 5.10 (dd,  $J = 17.2, 1.2$  Hz, 1 H), 5.14 (dd,  $J = 10.0, 1.2$  Hz, 1 H), 5.77-5.86 (m, 1 H), 7.33-7.39 (m, 5 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  42.9, 117.6, 123.7, 127.1, 128.4 (2 C), 128.5 (2 C), 128.9, 133.6, 139.1; IR (neat,  $cm^{-1}$ ): 3085, 2927, 1645, 1617, 1488; MS (EI,  $m/z$ ): 304

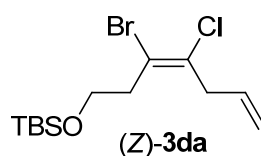
(4), 302 (14), 300 ( $M^+$ , 7), 223 (6), 221 (6); Anal. Calcd. for  $C_{11}H_{10}Br_2$ , HRMS: Cacl. 299.9149, Found: 299.9156.



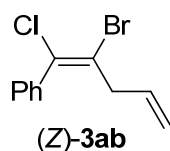
The title compound (Z)-3ba was prepared using Representative Procedure B in 81% yield as a colorless oil, *E/Z*: < 2:98.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  3.09 (d,  $J$  = 6.4 Hz, 2 H), 5.12 (dd,  $J$  = 17.2, 1.2 Hz, 1 H), 5.17 (dd,  $J$  = 9.2, 0.8 Hz, 1 H), 5.79-5.89 (m, 1 H), 7.33-7.40 (m, 5 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  40.8, 117.7, 120.4, 128.4 (2 C), 128.8 (2 C), 128.9, 133.0, 133.9, 138.7; IR (neat,  $cm^{-1}$ ): 3081, 2925, 1641, 1618, 1443; MS (EI,  $m/z$ ): 260 (4), 258 (16), 256 ( $M^+$ , 14), 223 (3), 221 (3); Anal. Calcd. for  $C_{11}H_{10}BrCl$ , HRMS: Cacl. 255.9654, Found: 255.9661.



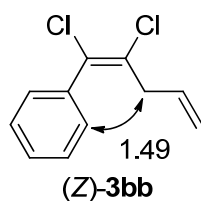
The title compound (Z)-3ca was prepared using Representative Procedure B in 62% yield as a colorless oil, *E/Z*: < 2:98.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.06 (s, 3 H), 0.88 (s, 9 H), 2.77 (t,  $J$  = 6.4 Hz, 2 H), 3.37 (d,  $J$  = 6.0 Hz, 2 H), 3.80 (t,  $J$  = 6.0 Hz, 2 H), 5.14 (dd,  $J$  = 8.8, 1.0 Hz, 1 H), 5.17 (dd,  $J$  = 9.6, 1.2 Hz, 1 H), 5.77-5.84 (m, 1 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  -5.4 (2 C), 18.3, 25.9 (2 C), 41.3, 42.3, 60.8, 117.2, 124.5, 125.4, 133.2; IR (neat,  $cm^{-1}$ ): 2762, 2855, 1641, 1617, 1471; MS (EI,  $m/z$ ): 290 (17), 288 (74), 286 (58), 253 (5), 251 (8); Anal. Calcd. for  $C_{13}H_{24}Br_2OSi$ : C: 40.64, H: 6.30, Br: 41.59, O: 4.16, Si: 7.31 Found C: 40.87, H: 6.05, Br: 41.72, O: 4.50.



The title compound (*Z*)-**3da** was prepared using Representative Procedure B in 68% yield as a colorless oil, *E/Z*: < 2:98. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 0.06 (s, 6 H), 0.89 (s, 9 H), 2.76 (t, *J* = 6.0 Hz, 2 H), 3.25 (d, *J* = 6.4 Hz, 2 H), 3.79 (t, *J* = 6.0 Hz, 2 H), 5.13 (dd, *J* = 6.4, 1.2 Hz, 1 H), 5.15 (dd, *J* = 13.2, 1.2 Hz, 1 H), 5.77-5.84 (m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ -5.4 (2 C), 18.3, 25.9 (2 C), 40.1, 41.0, 60.9, 117.3, 121.2, 132.7 (2 C); IR (neat, cm<sup>-1</sup>): 2955, 2859, 1642, 1471, 1105; MS (EI, *m/z*): 285 (23), 283 (100), 281 (M<sup>+</sup>-Bu<sup>t</sup>, 78), 169 (58), 167 (50); Anal. Calcd. for C<sub>13</sub>H<sub>24</sub>BrClOSi, HRMS: Cacl. 280.9764, Found: 280.9759.

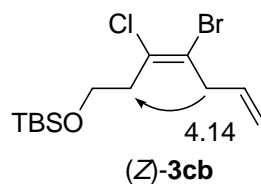


The title compound (*Z*)-**3ab** was prepared using Representative Procedure B in 80% yield as a mixture of two isomers, *E/Z*: 11/89. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.25 (dd, *J* = 7.2, 1.2 Hz, 2 H), 5.16 (dd, *J* = 16.8, 1.2 Hz, 1 H), 5.20 (dd, *J* = 10.0, 1.2 Hz, 1 H), 5.86-5.87 (m, 1 H), 7.38 (m, 5 H); IR (neat, cm<sup>-1</sup>): 3076, 2920, 1631, 1618, 1447; MS (EI, *m/z*): 260 (3), 258 (16), 256 (M<sup>+</sup>, 12), 223 (2), 221 (2); Anal. Calcd. for C<sub>11</sub>H<sub>10</sub>BrCl: C: 51.30, H: 3.91, Br: 31.02, Cl: 13.77 Found C: 51.57, H: 4.08, Br: 31.22, Cl: 14.03.

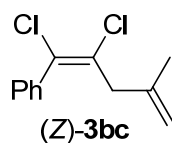


The title compound (*Z*)-**3bb** was prepared using Representative Procedure B in 89% yield as a colorless oil, *E/Z*: < 2:98, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.13 (d, *J* = 6.0 Hz, 2 H), 5.15 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.18 (dd, *J* = 11.2, 0.8 Hz, 1 H), 5.82-5.89 (m, 1 H), 7.33-7.42 (m, 5 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 40.6, 117.7, 128.5, 128.7 (2 C), 129.1 (2 C), 129.4, 131.2, 133.1, 136.9; IR(neat, cm<sup>-1</sup>): 3083, 2925, 1641, 1486, 1442; MS (EI, *m/z*): 214 (11), 213 (2), 212 (M<sup>+</sup>, 17), 179 (19), 177 (66);

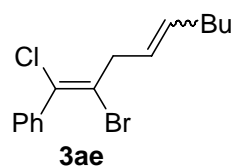
Anal. Calcd. for  $C_{12}H_{12}Cl_2$ , HRMS: Cacl. 212.0160, Found: 212.0168.



The title compound (*Z*)-**3cb** was prepared using Representative Procedure B in 72% yield as a colorless oil, *E/Z*: < 2:98.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.05 (s, 6 H), 0.88 (s, 9 H), 2.67 (t,  $J = 6.0$  Hz, 2 H), 3.35 (d,  $J = 6.4$  Hz, 2 H), 3.80 (t,  $J = 6.0$  Hz, 2 H), 5.15 (dd,  $J = 10.0, 1.2$  Hz, 1 H), 5.17 (dd,  $J = 2.8, 1.6$  Hz, 1 H), 5.77-5.83 (m, 1 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  -5.4 (2 C), 18.3, 25.9 (2 C), 39.1, 41.9, 60.2, 117.2, 122.2, 131.5, 133.3; IR (neat,  $cm^{-1}$ ): 2955, 2859, 1642, 1471, 1105; MS (EI,  $m/z$ ): 285 (23), 283 (81), 281 ( $M^+$ -Bu<sup>t</sup>, 63), 169 (41), 167 (27); Anal. Calcd. for  $C_{13}H_{24}BrClOSi$ , HRMS: Cacl. 280.9764, Found: 280.9771.



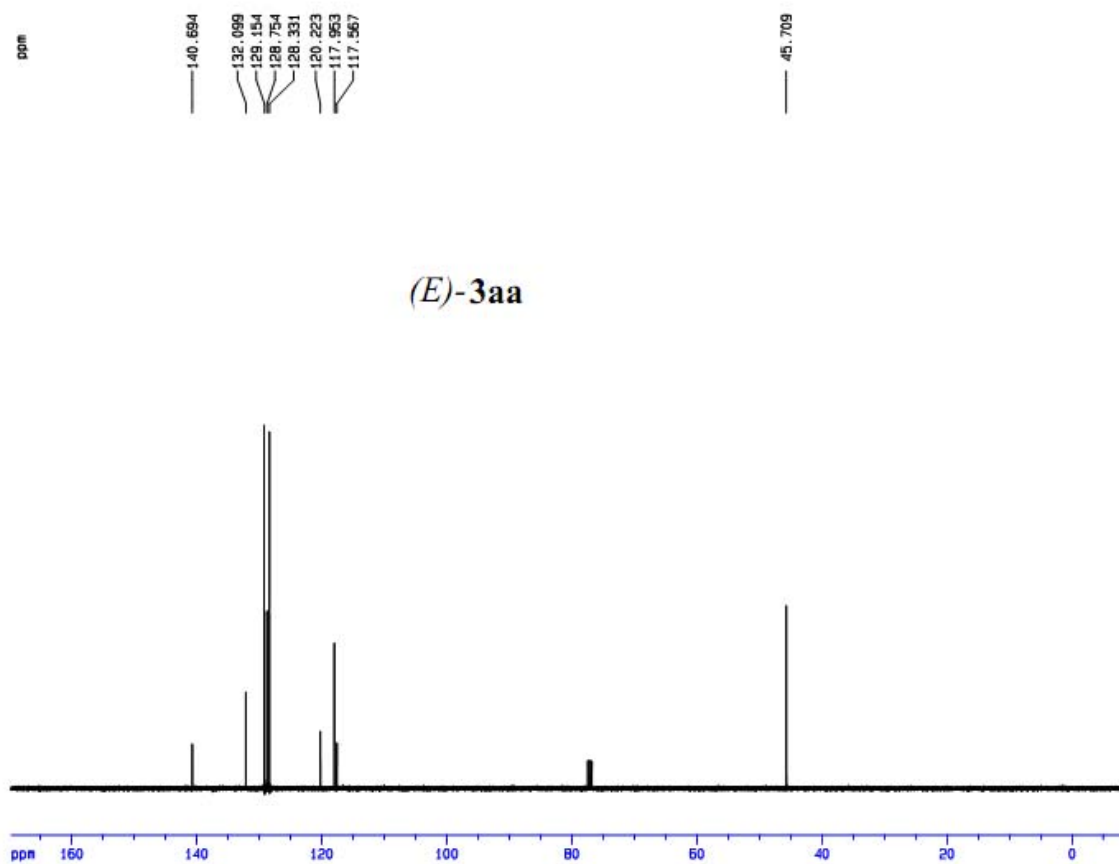
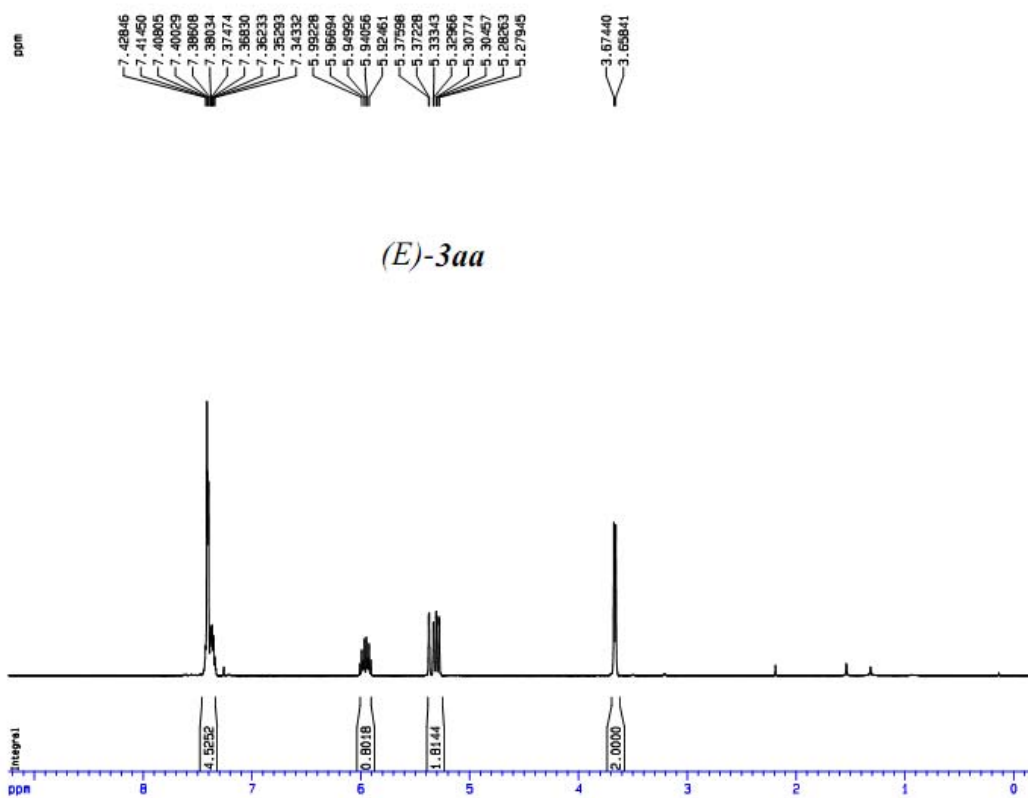
The title compound (*Z*)-**3bc** was prepared using Representative Procedure B in 72% yield as a colorless oil, *E/Z*: < 2:98.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.68 (s, 3 H), 3.08 (s, 2 H), 4.85 (d,  $J = 0.8$  Hz, 1 H), 4.93 (s, 1 H), 7.33-7.42 (m, 5 H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  22.0, 44.2, 113.2, 128.5, 128.6 (2 C), 129.0 (2 C), 130.0, 131.0, 137.0, 140.0; IR (neat,  $cm^{-1}$ ): 3082, 2925, 1740, 1655, 1445; MS (EI,  $m/z$ ): 228 (15), 227 (3), 226 ( $M^+$ , 25), 213 (45), 211 (74); Anal. Calcd. for  $C_{12}H_{12}Cl_2$ , HRMS: Cacl. 226.0316, Found: 226.0322.

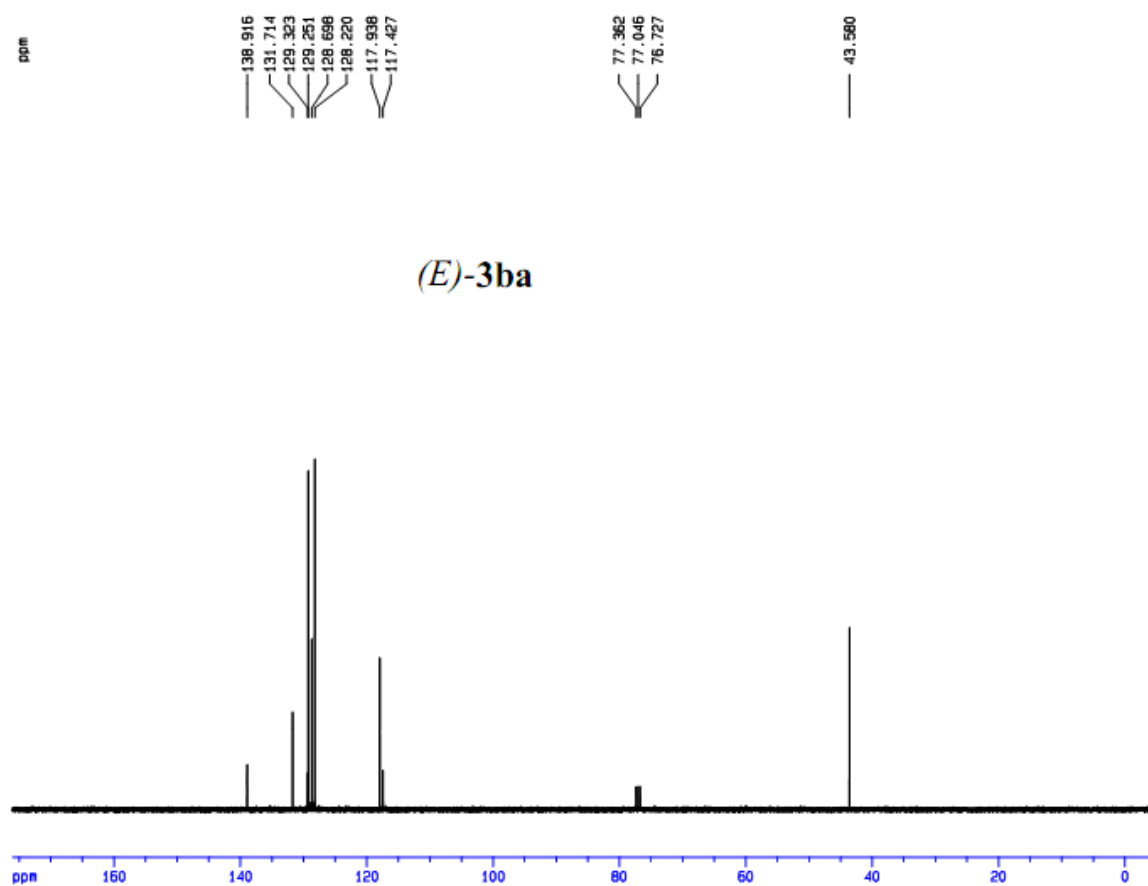
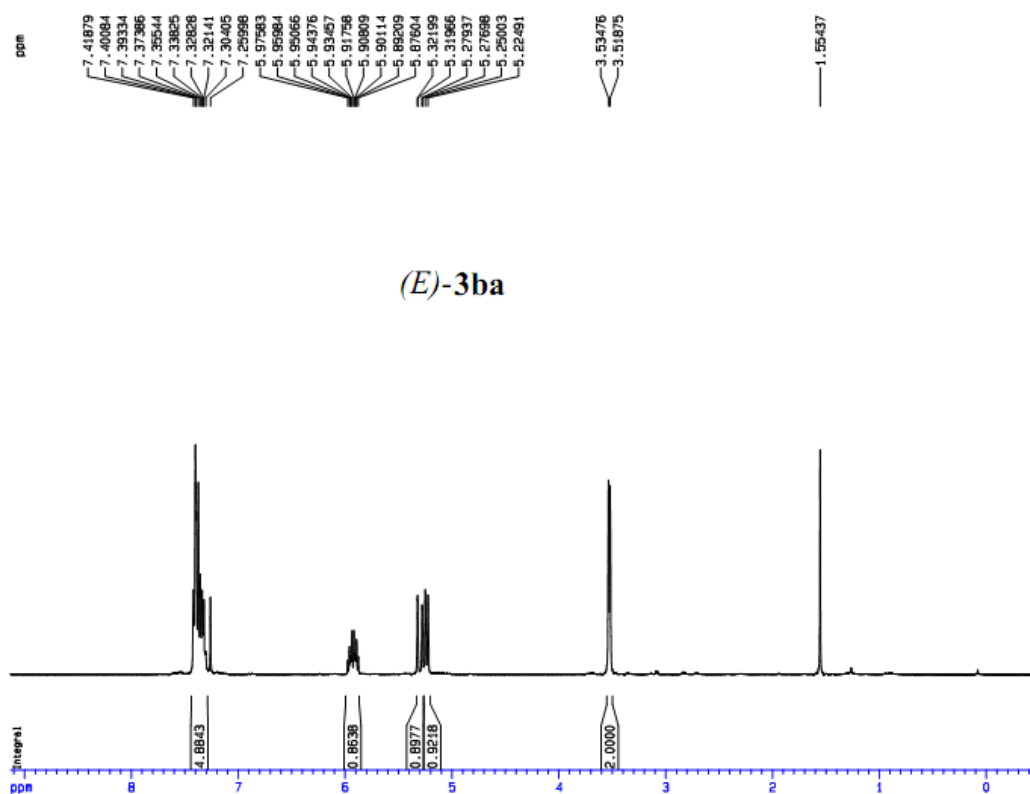


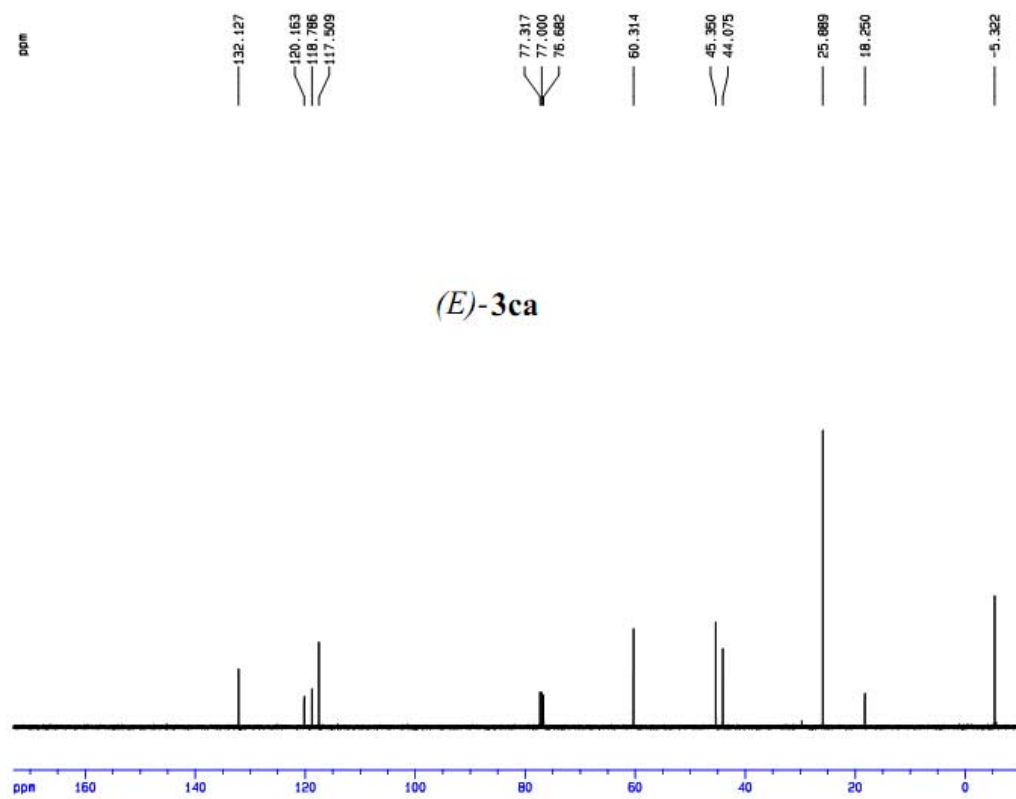
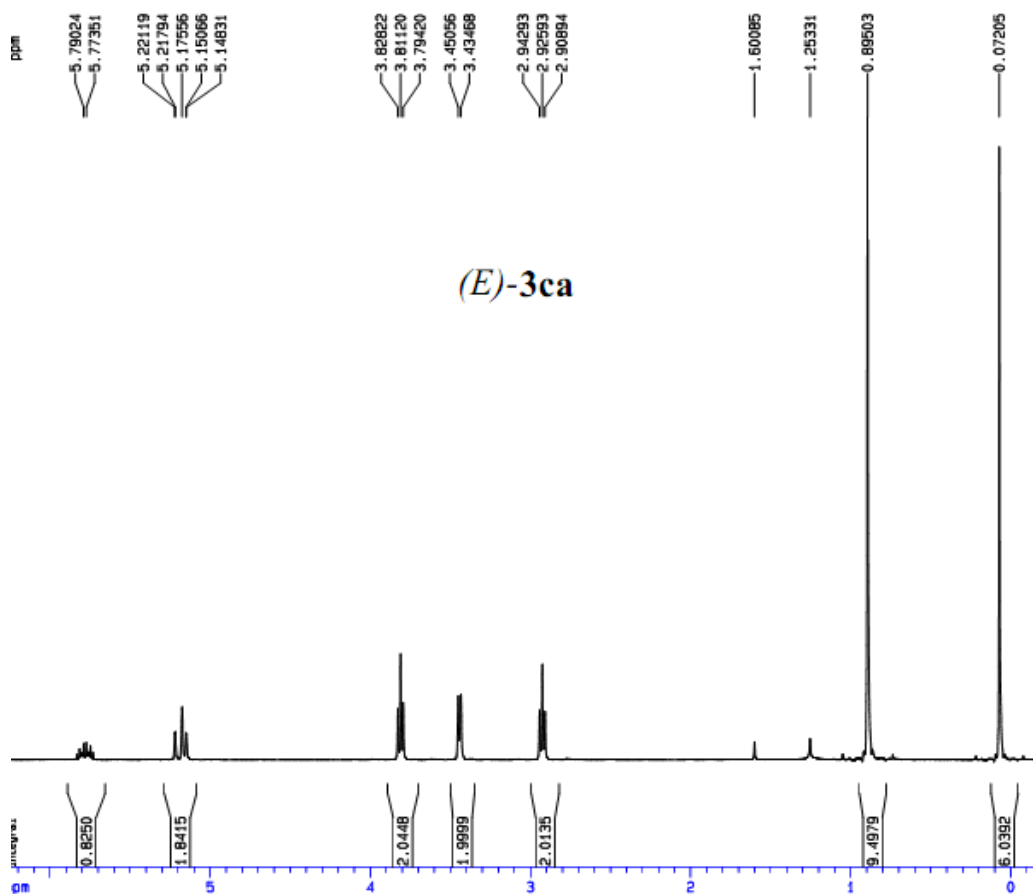
The title compound **3ae** was prepared using Representative Procedure A in 67% yield as two isomers, *4E/4Z* = 1:1. MS (EI, m/z): 316 (13), 314 (54), 312 (41), 279 (6), 277 (8); Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>BrCl: C: 57.44, H: 5.78, Br: 25.47, Cl: 11.30 Found C: 57.63, H: 6.02, Br: 25.19, Cl: 11.04.

References:

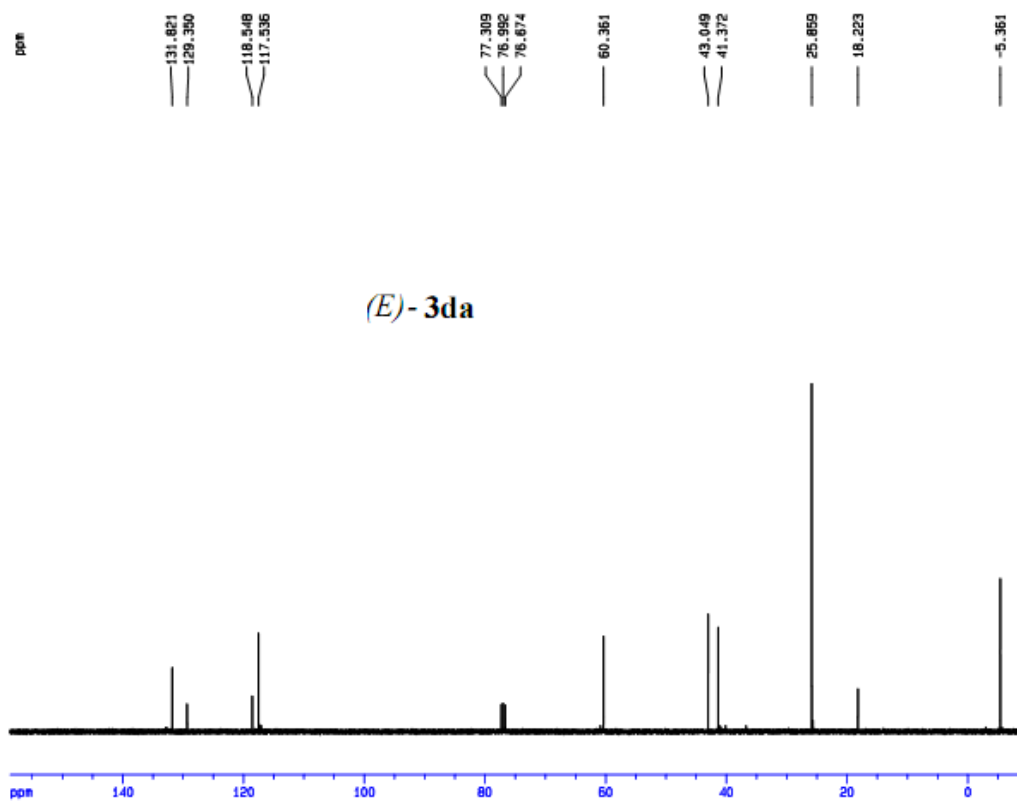
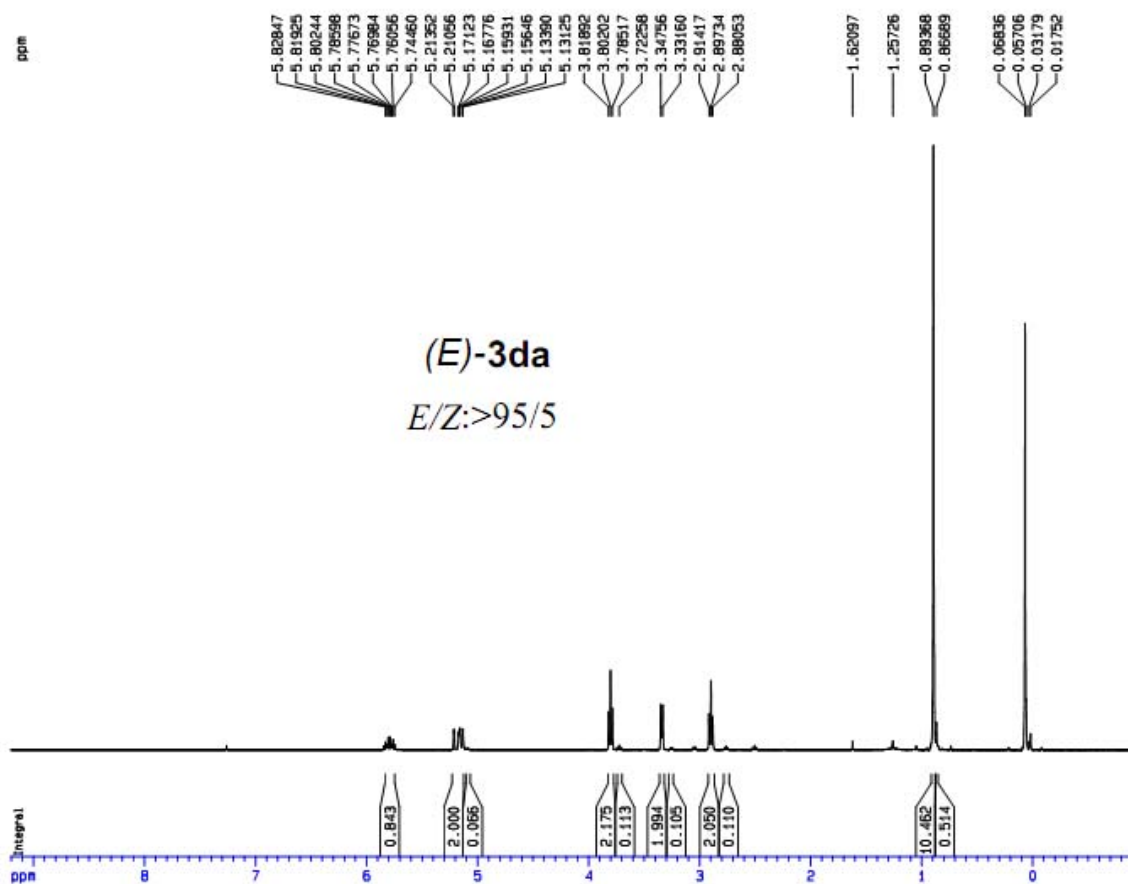
1. Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.
2. Bianchini, R.; Chiappe, C.; Lo Moro, G.; Lenoir, D.; Lemmen, P.; Goldberg, N. *Chem. Eur. J.* **1999**, *5*, 1570.

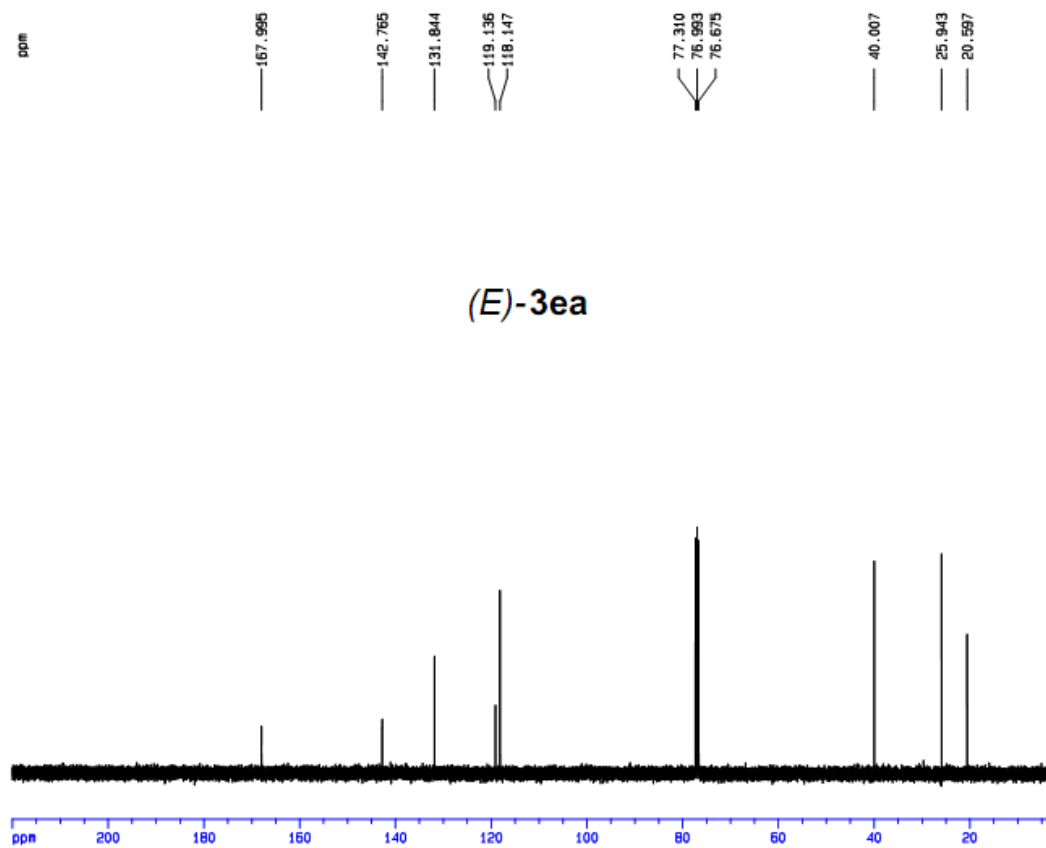
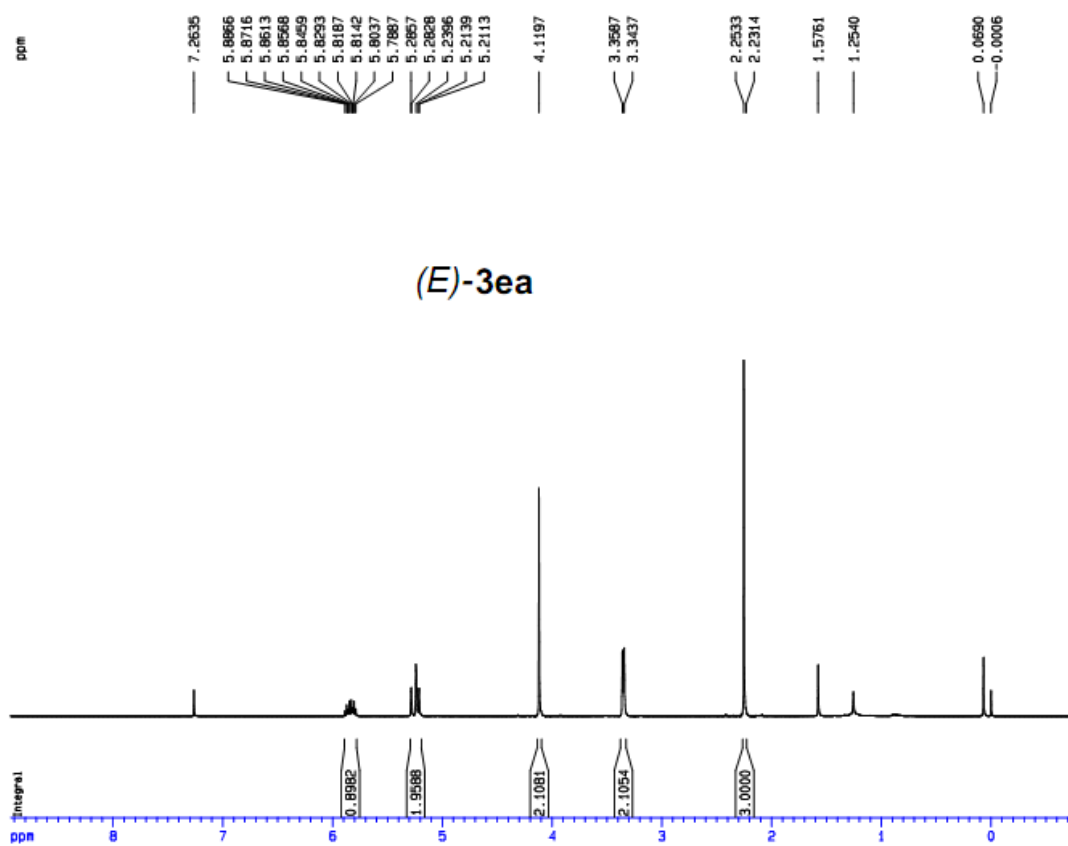






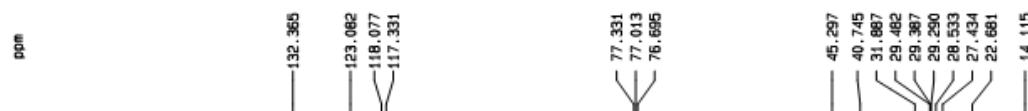
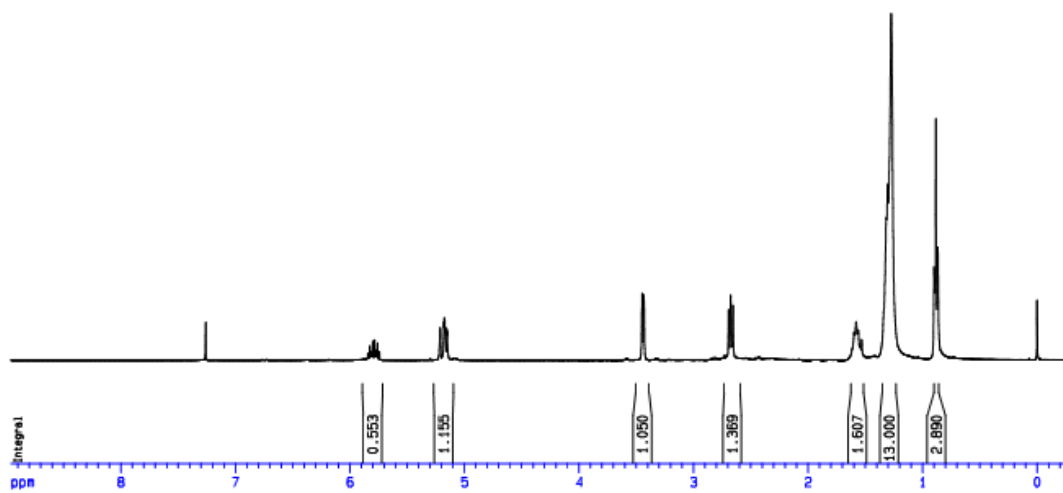




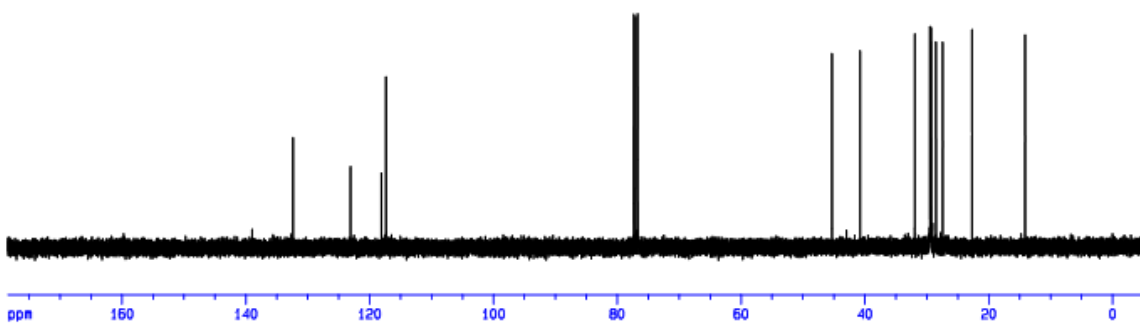


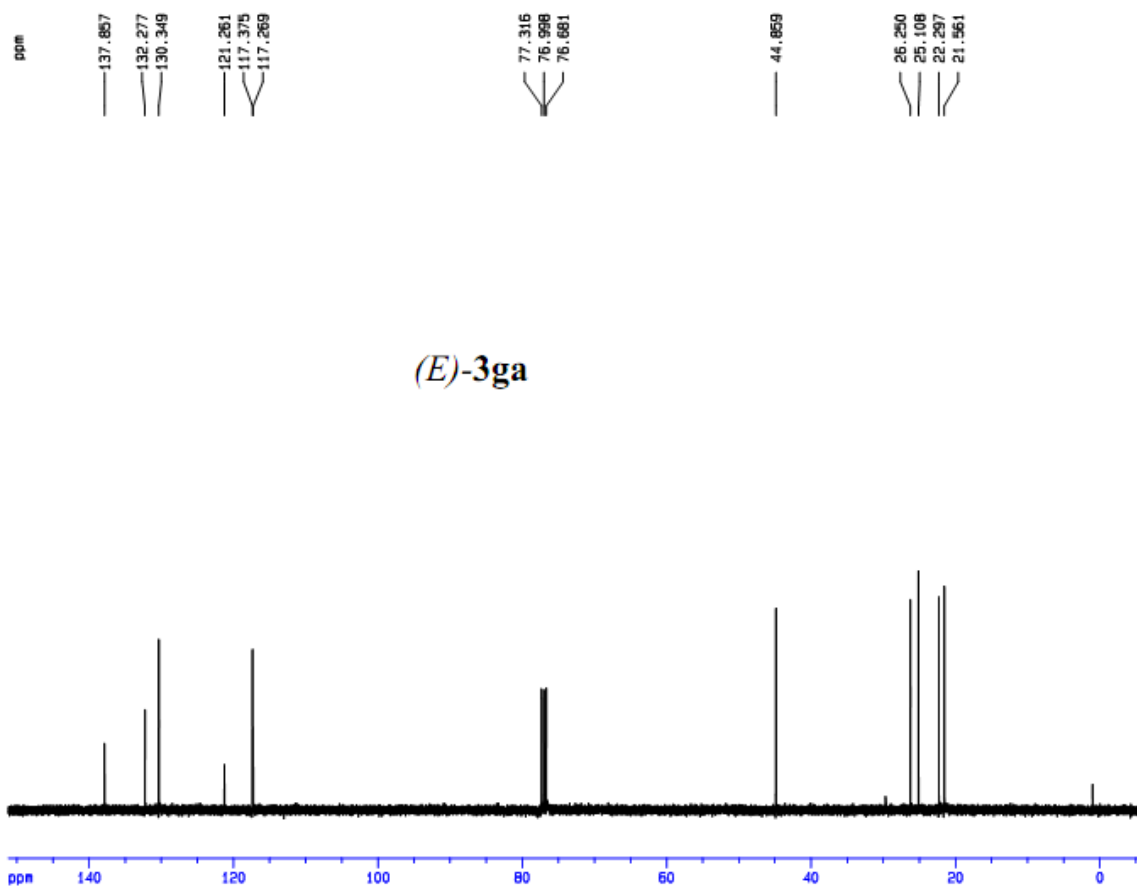
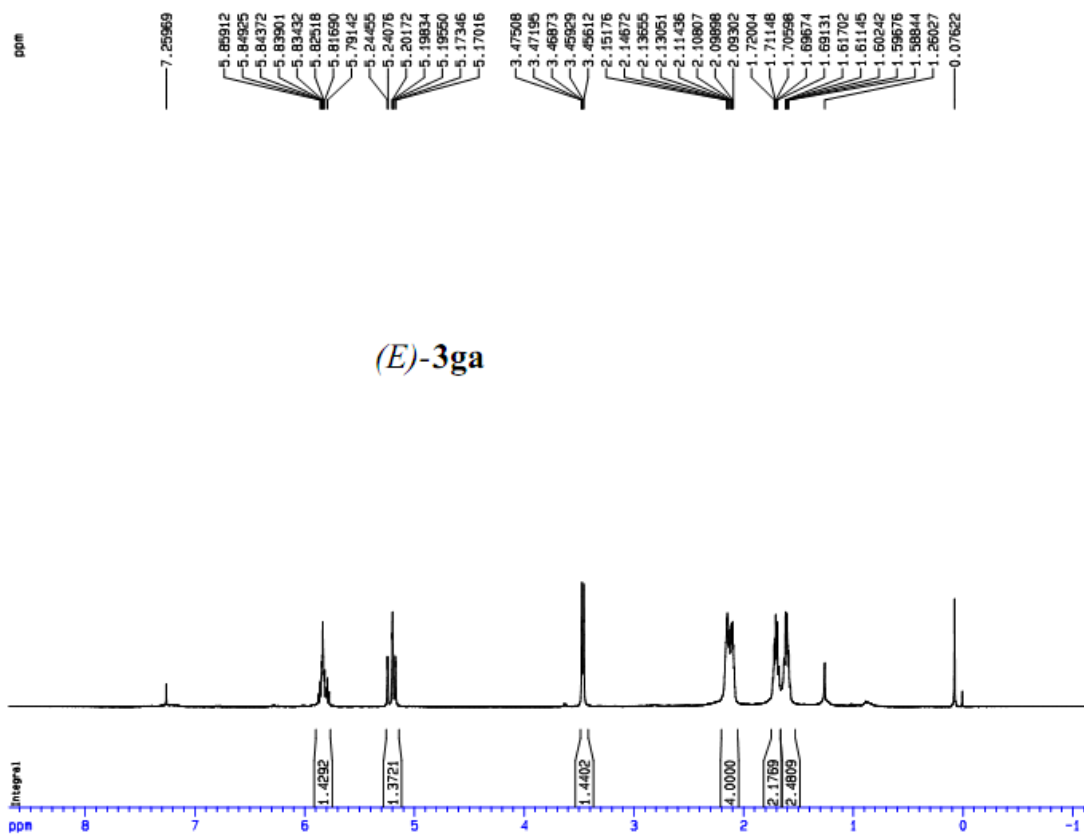


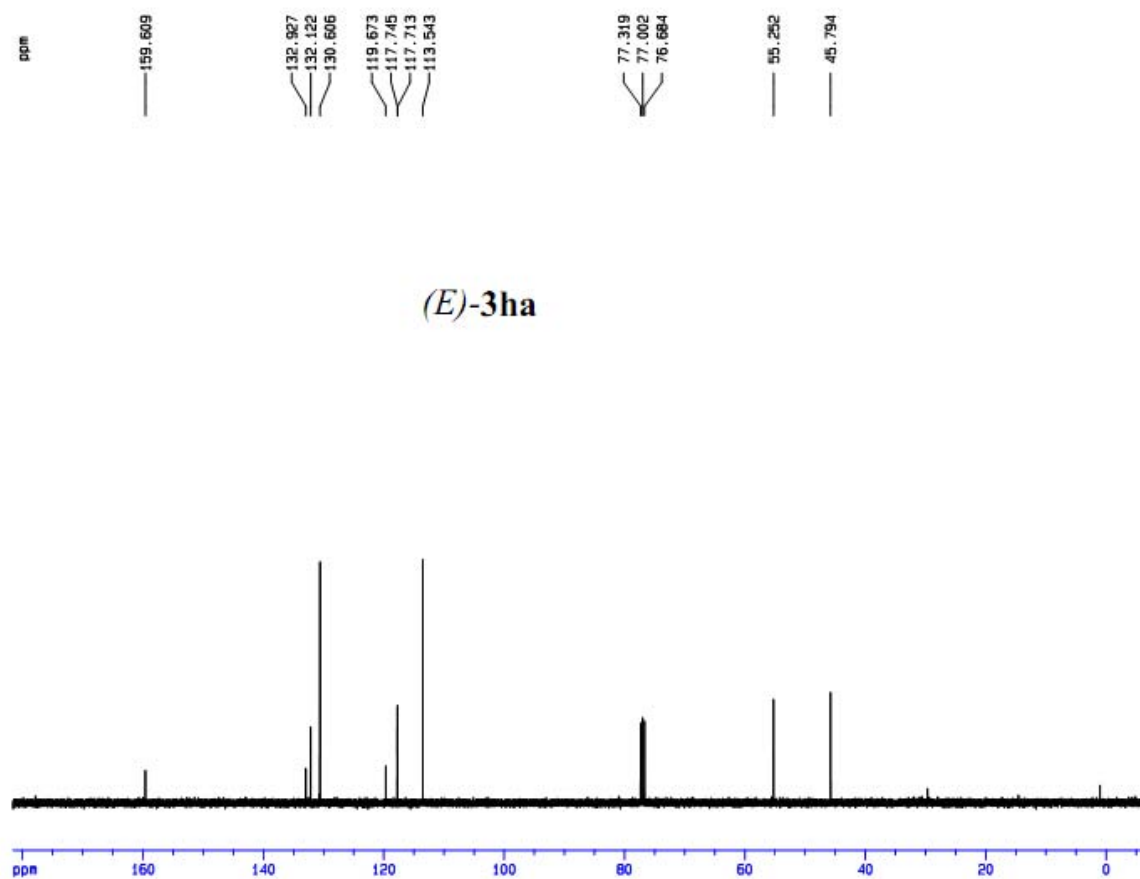
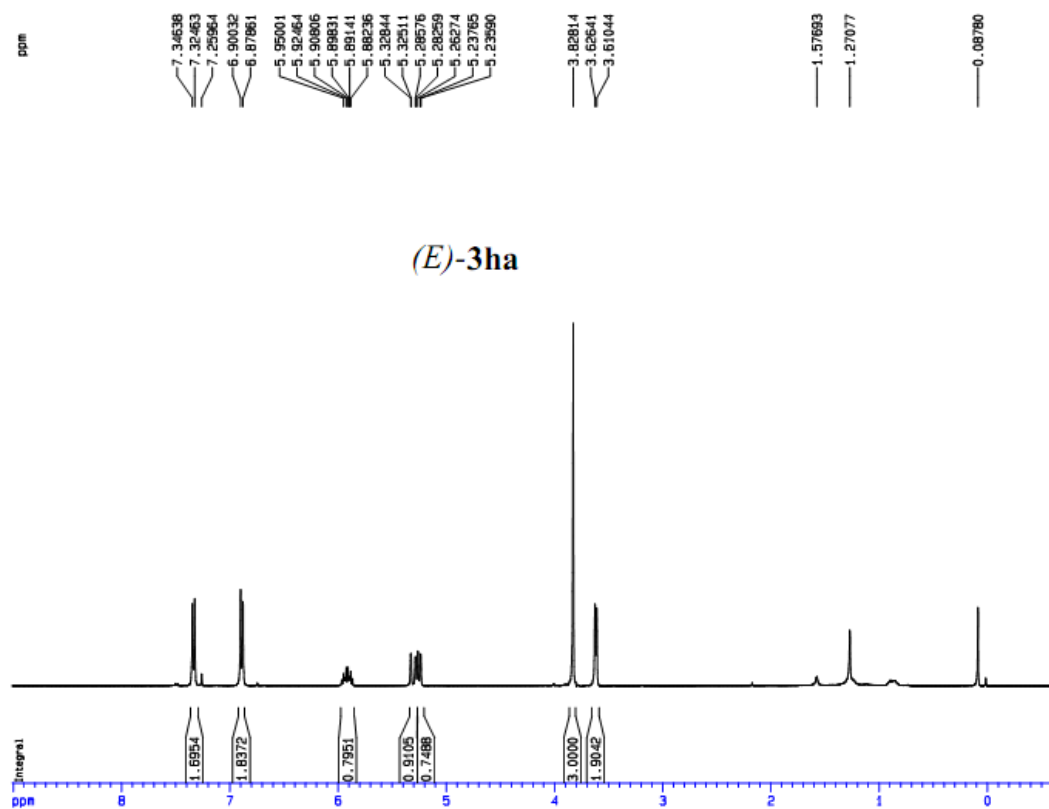
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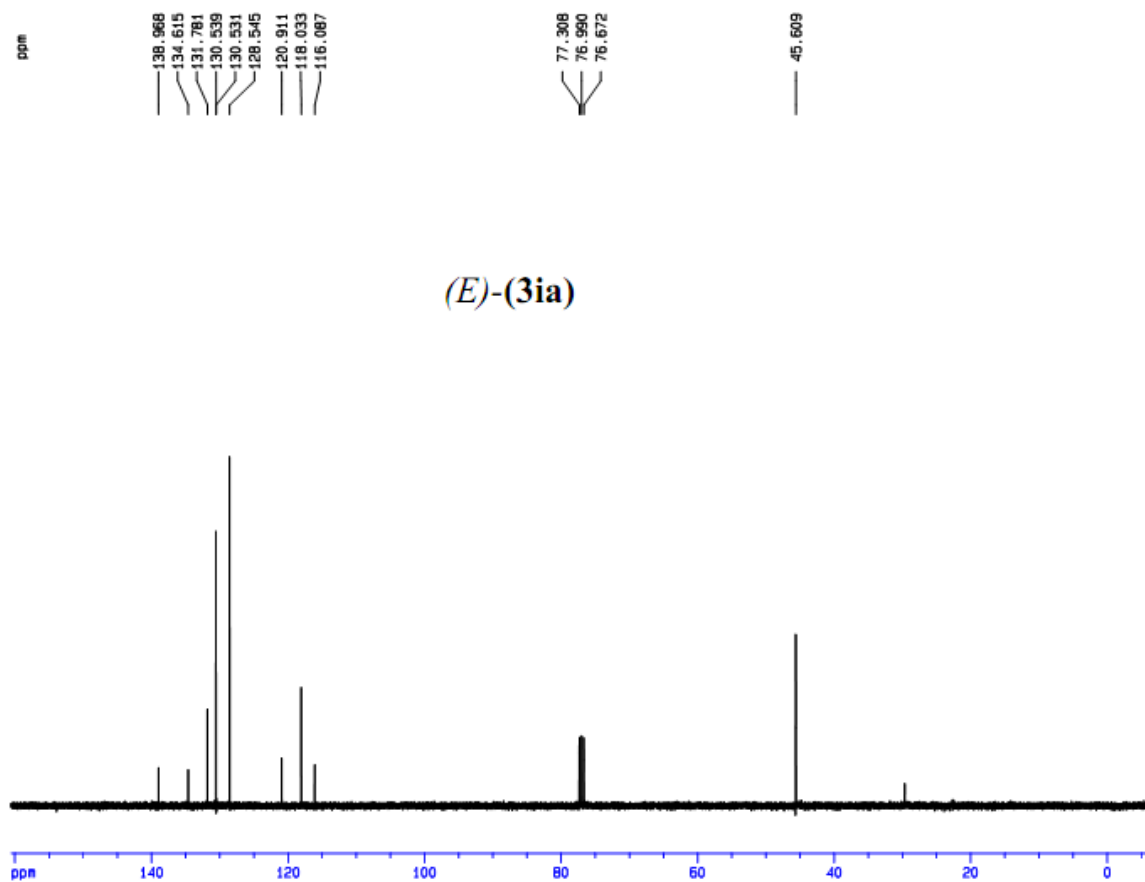
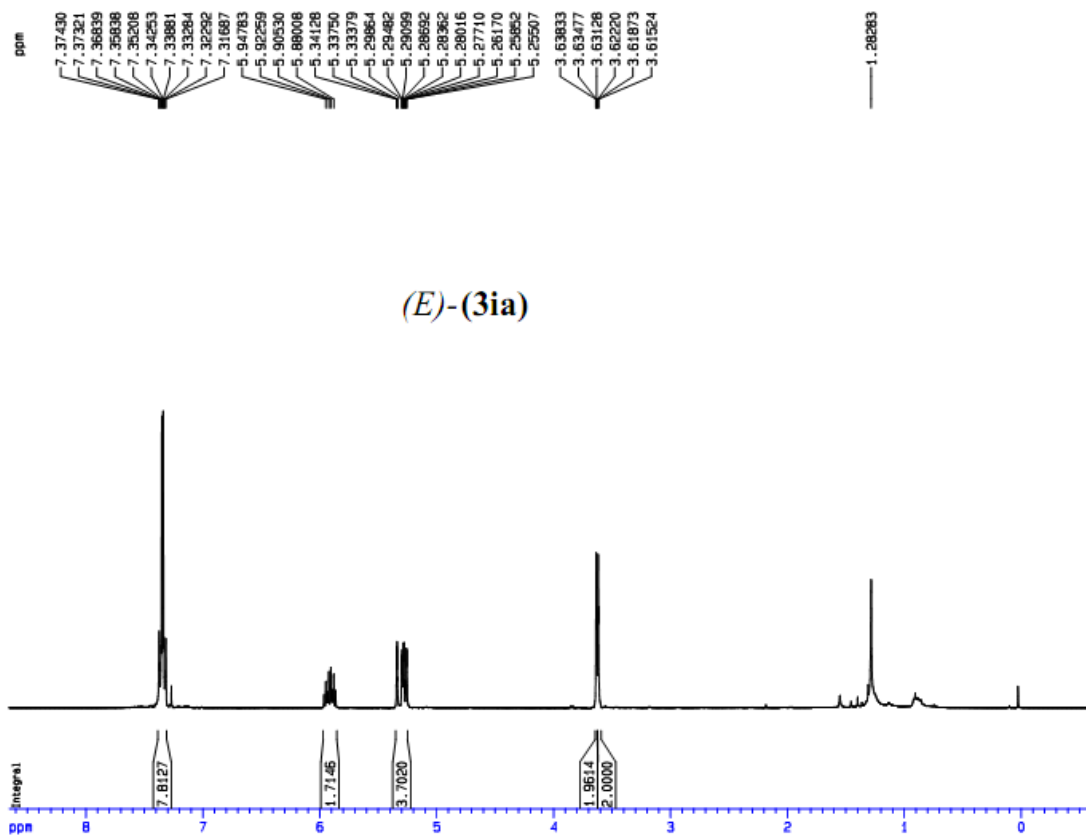


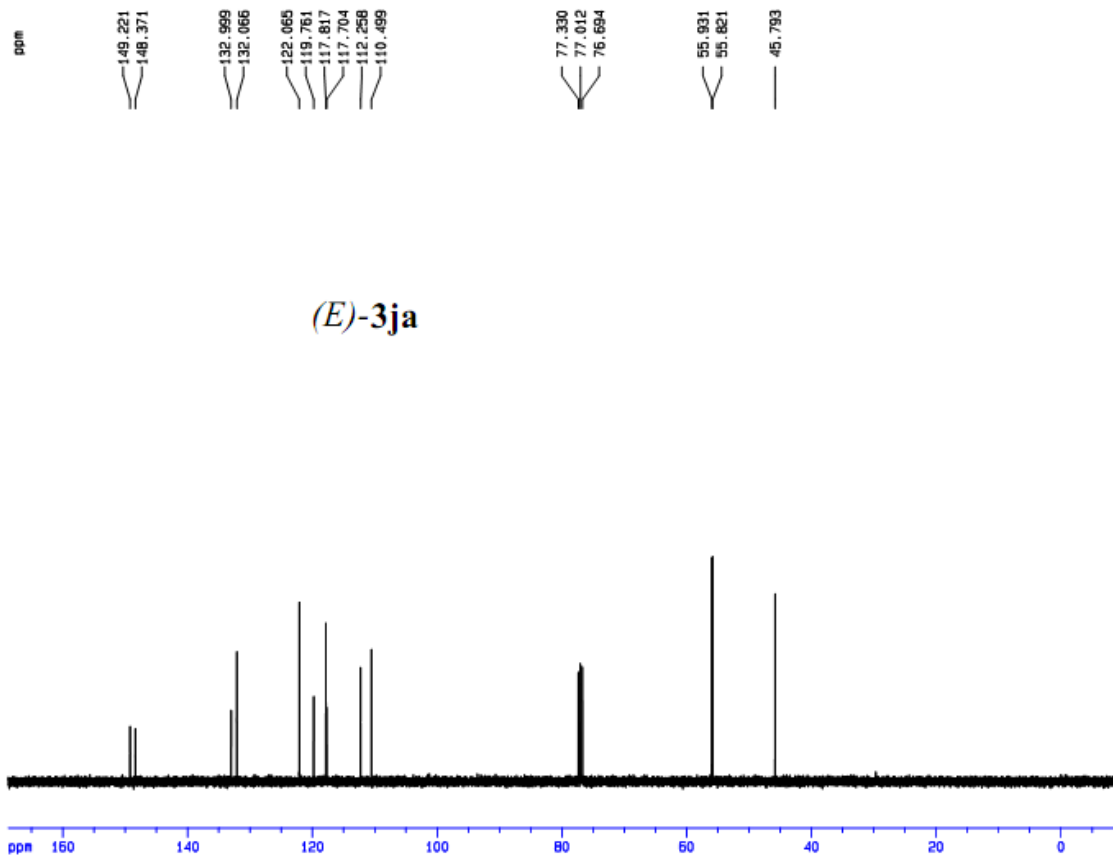
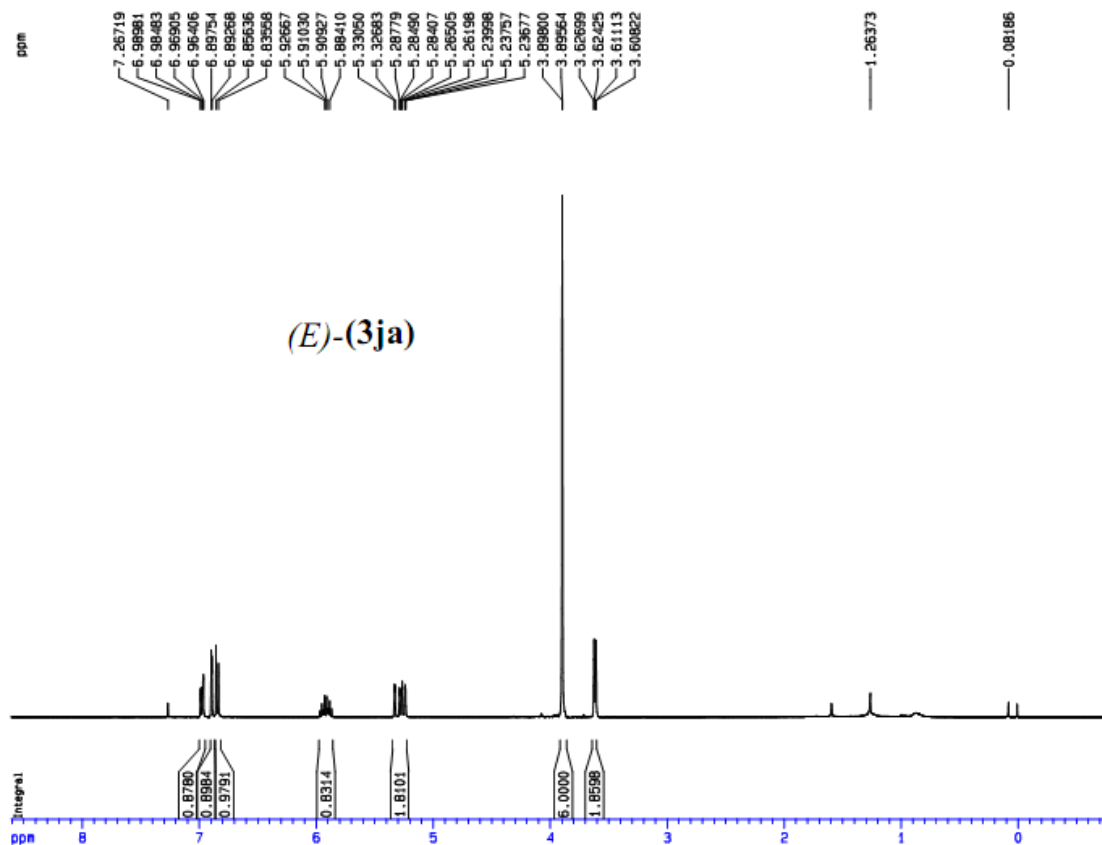
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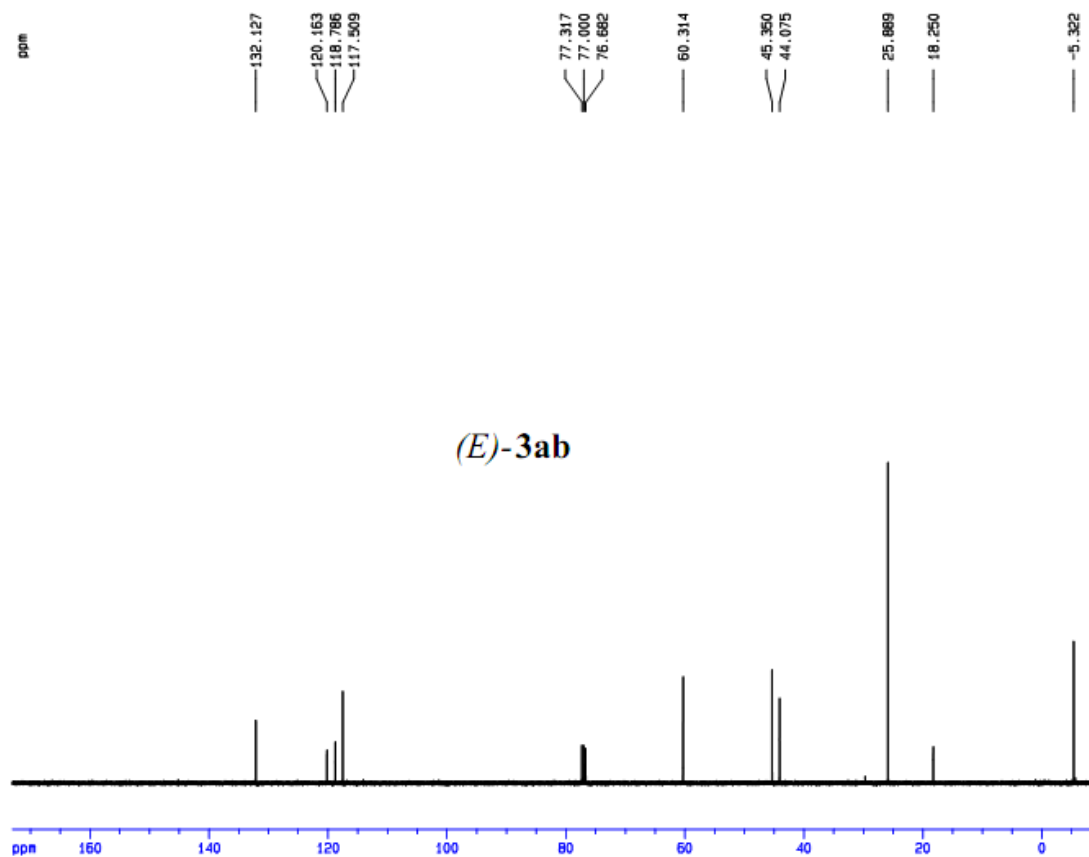
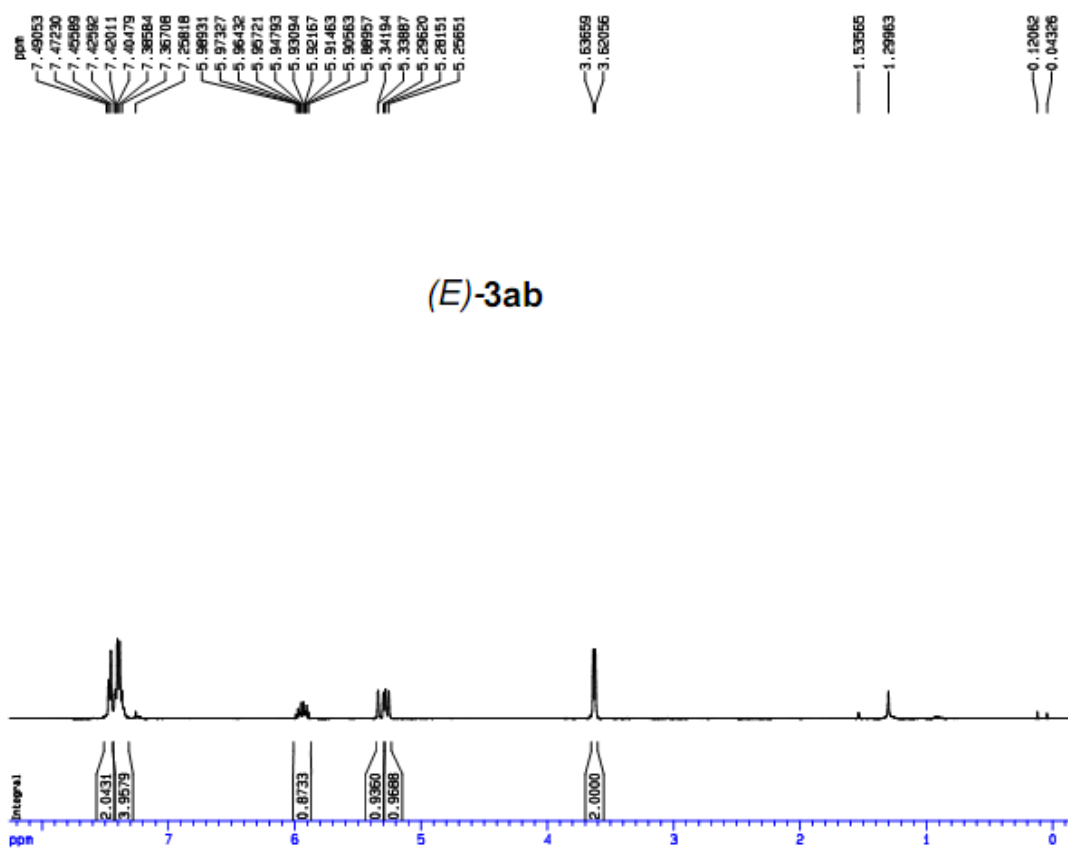




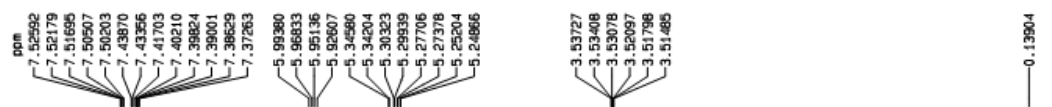




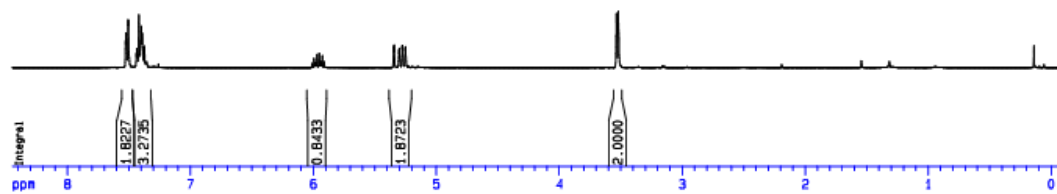




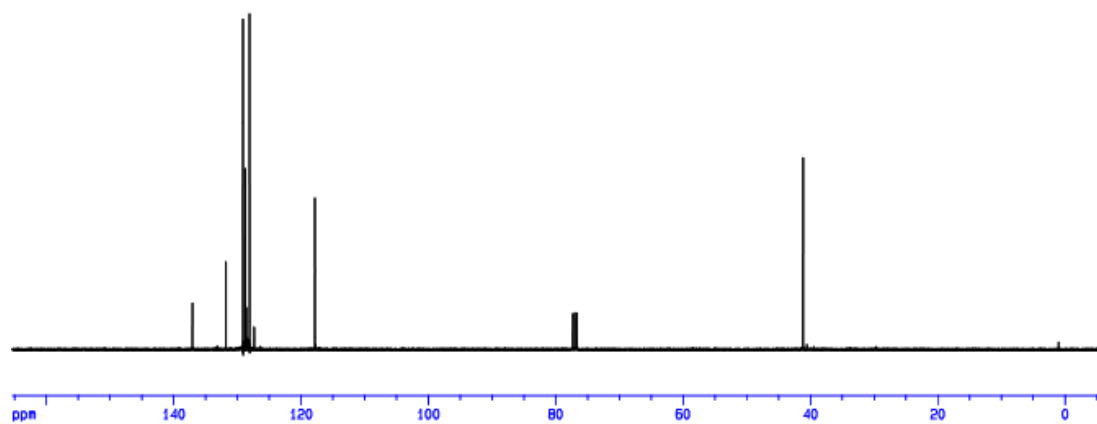


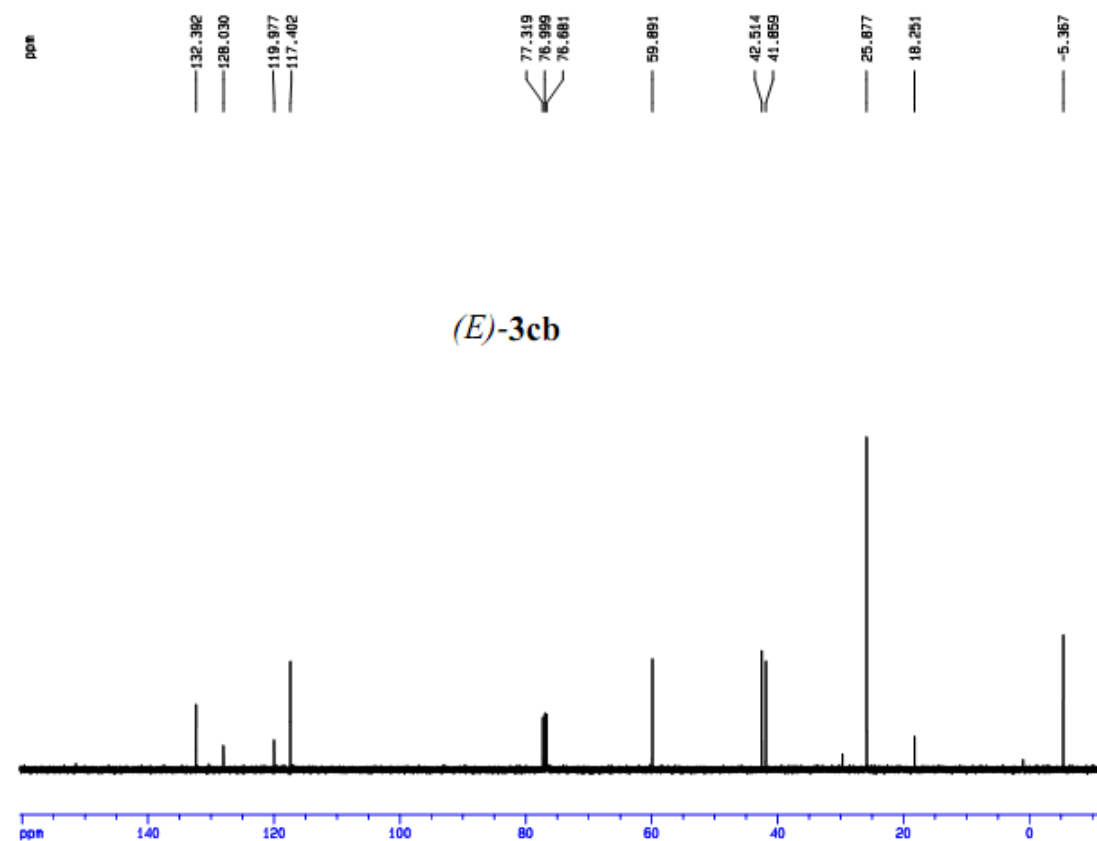
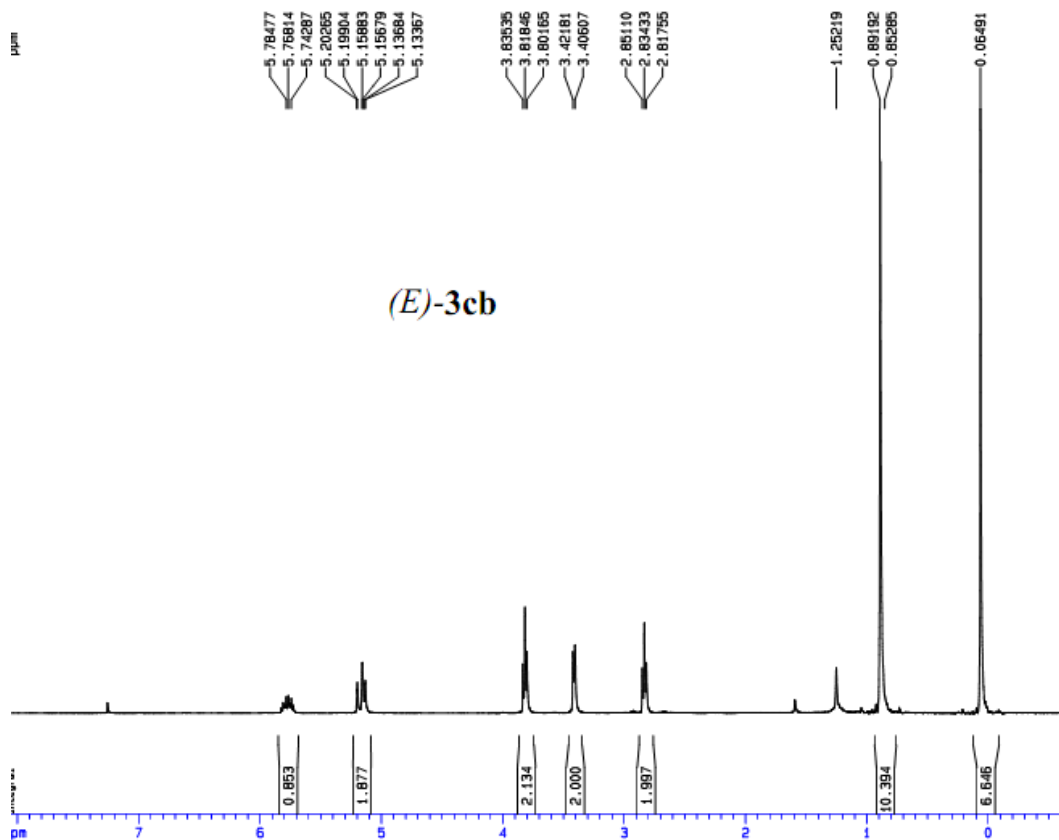


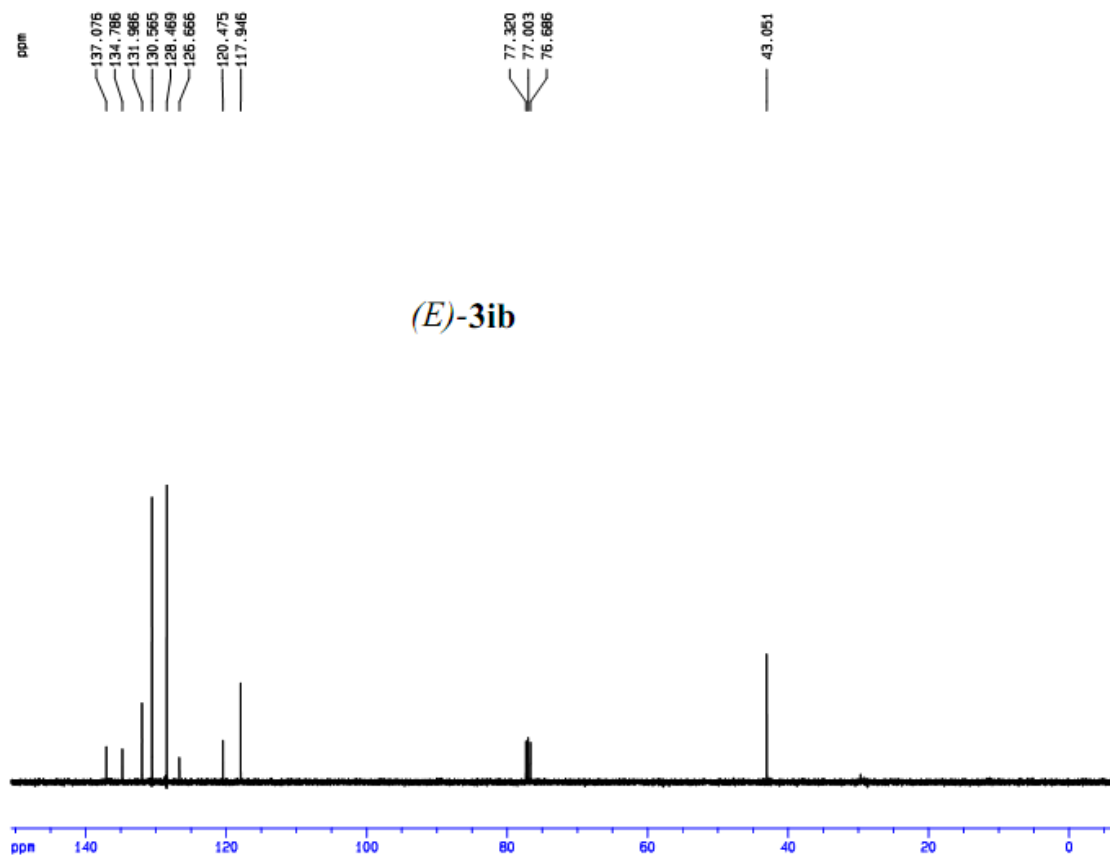
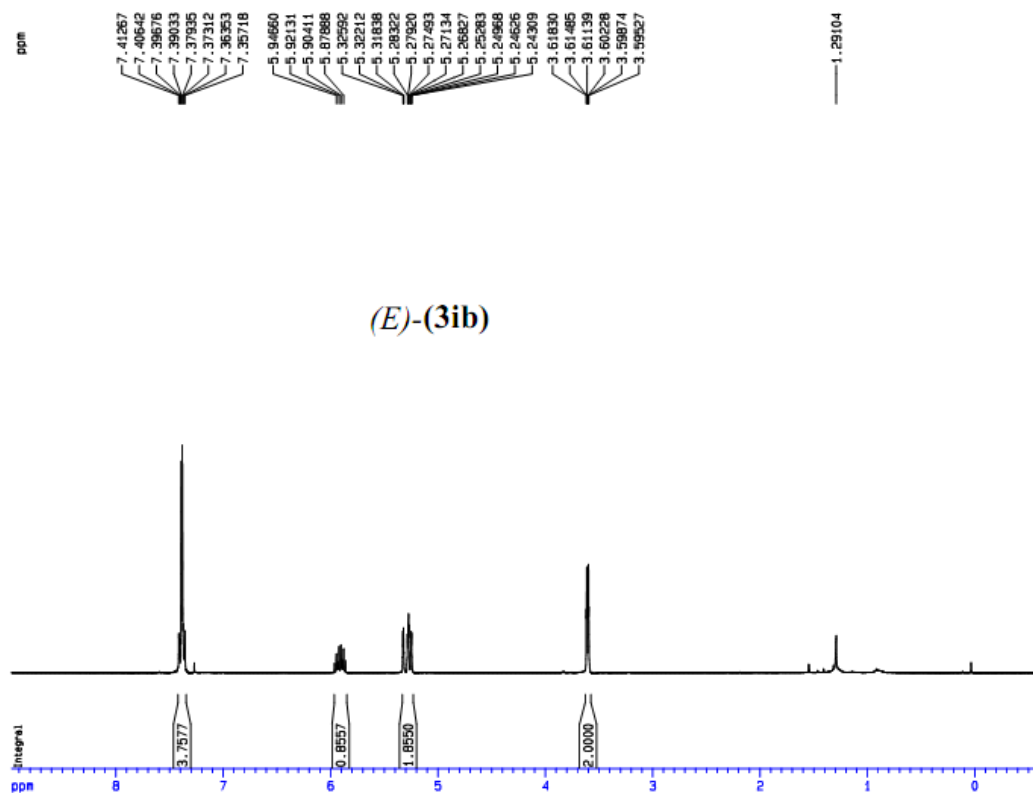
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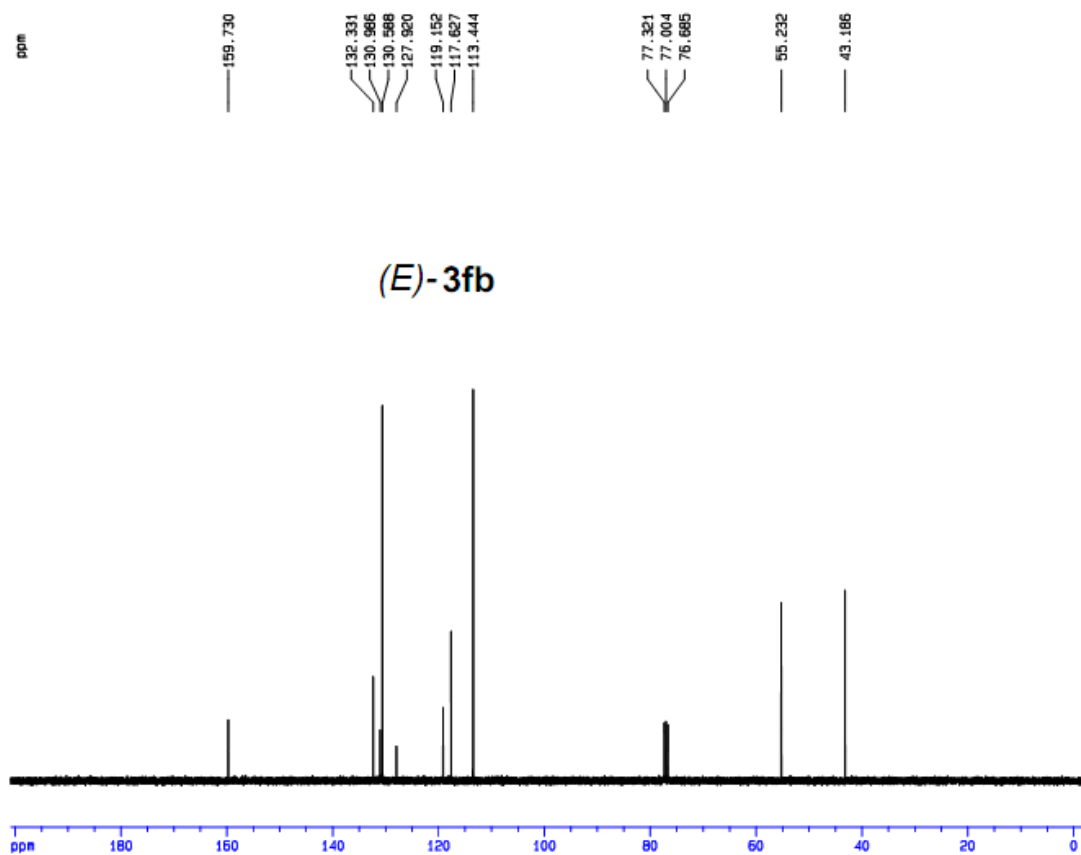
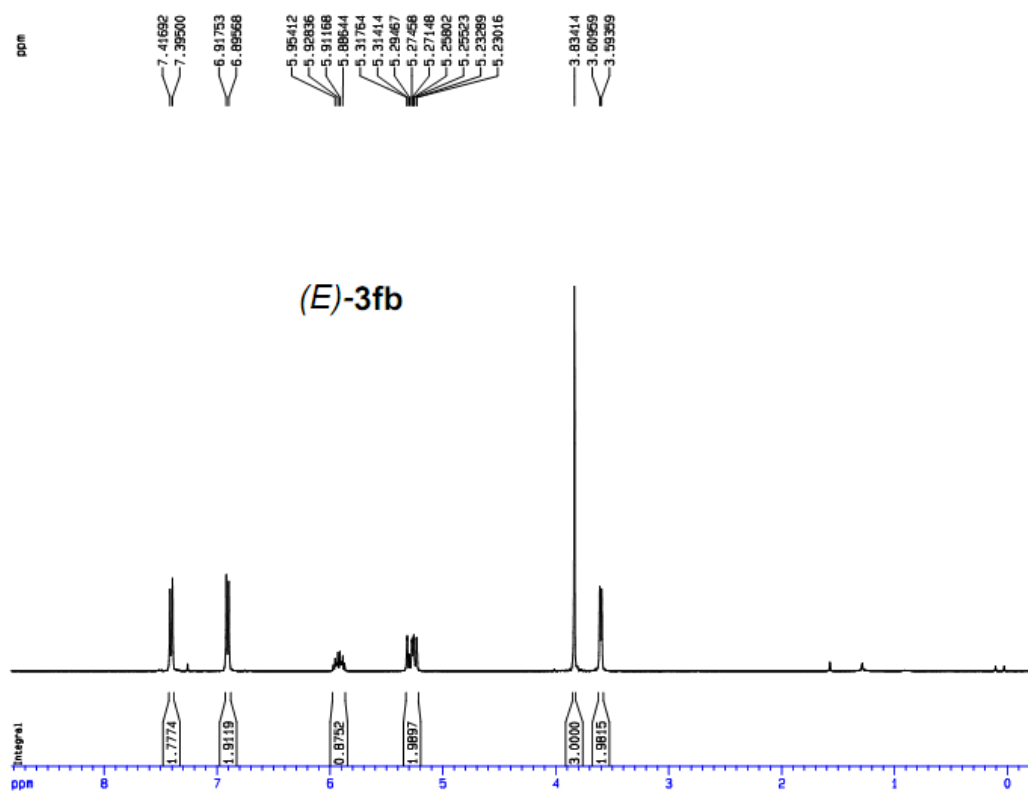


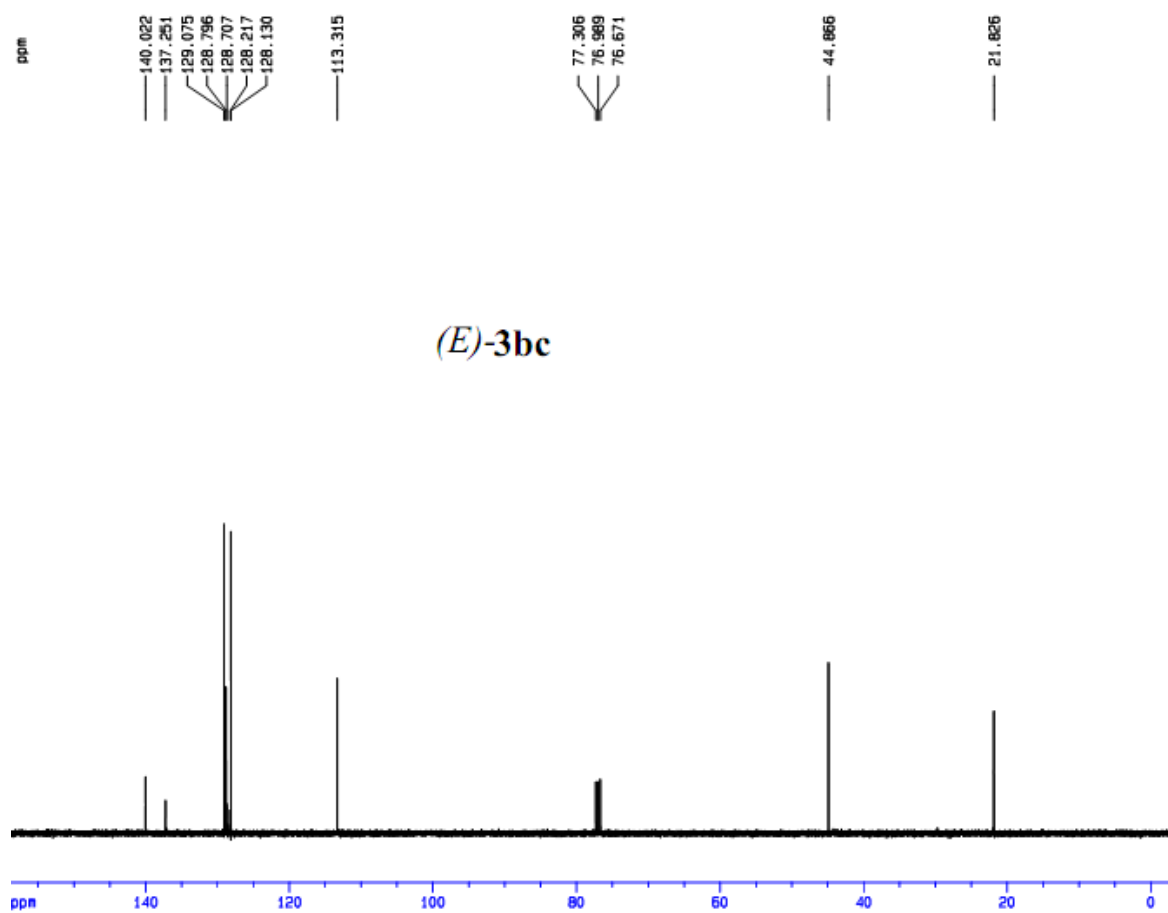
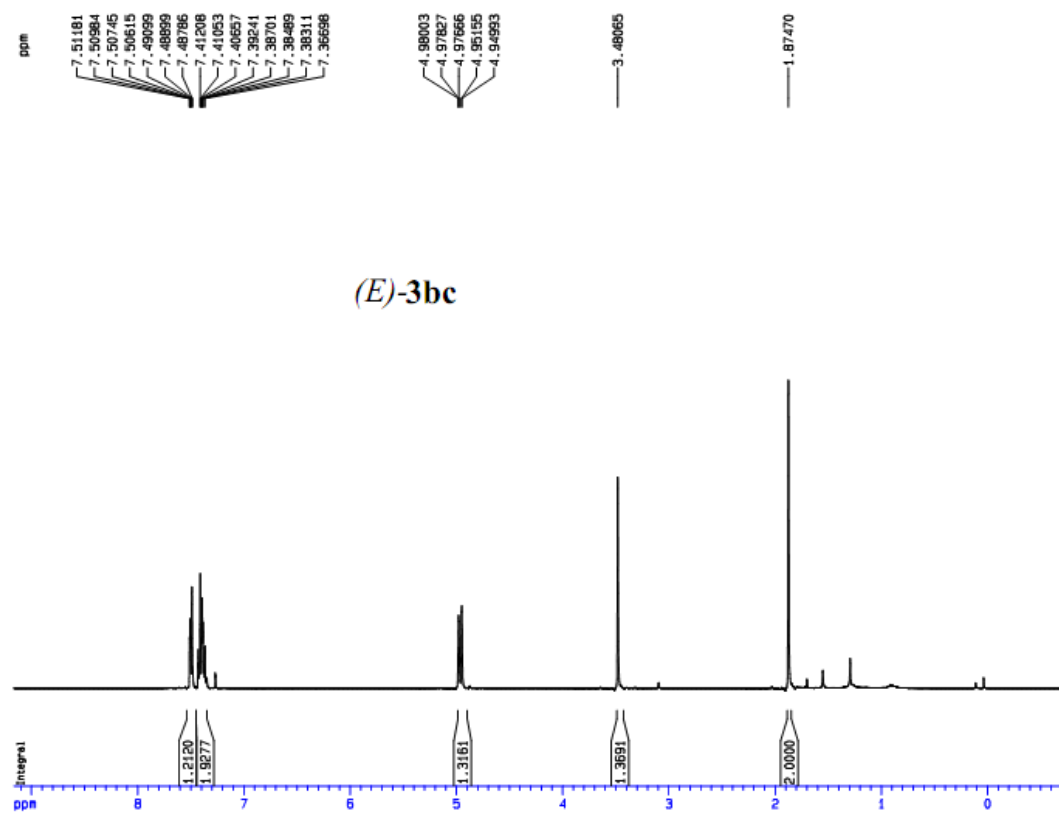
(E)-3bb

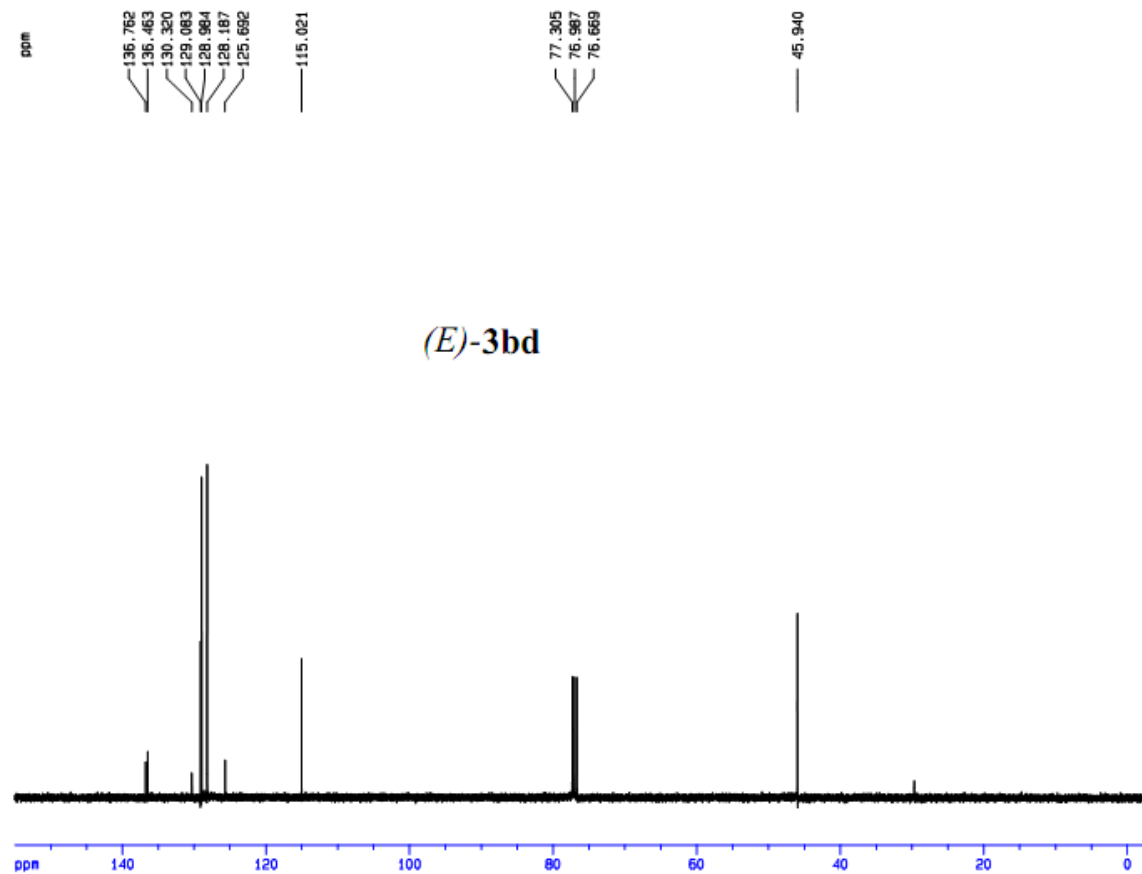
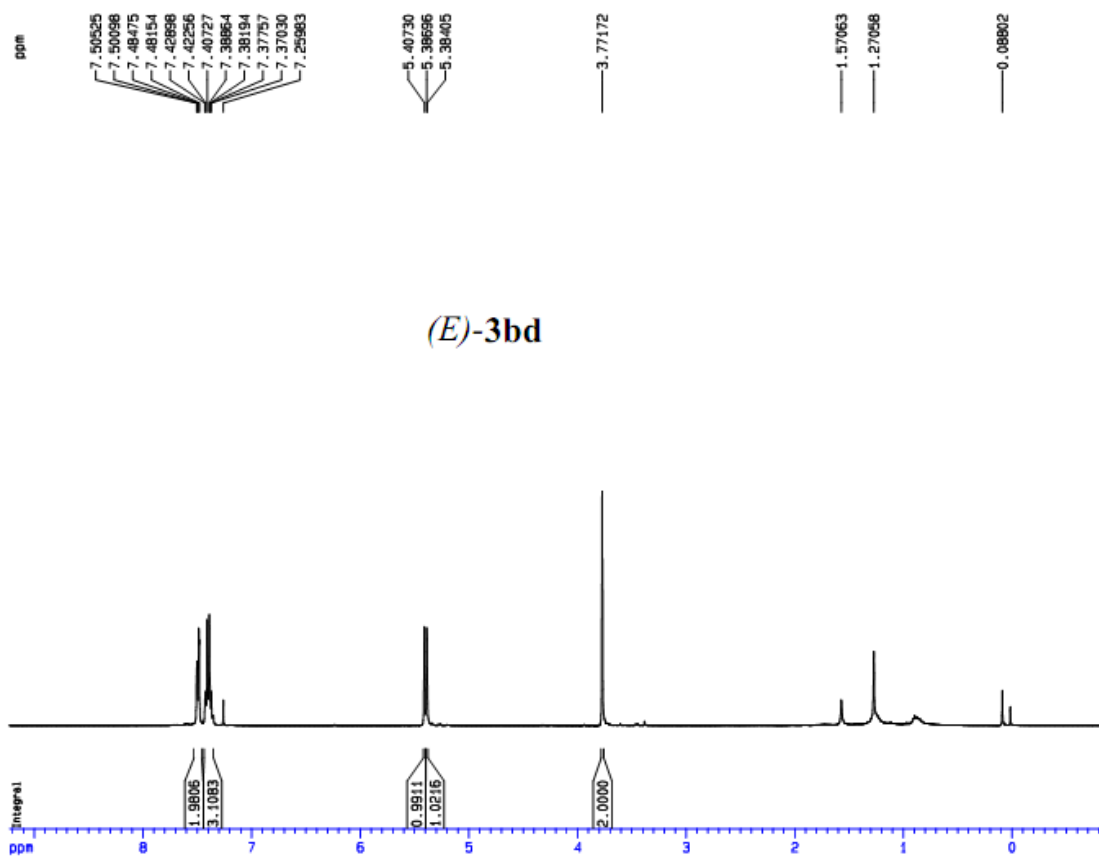


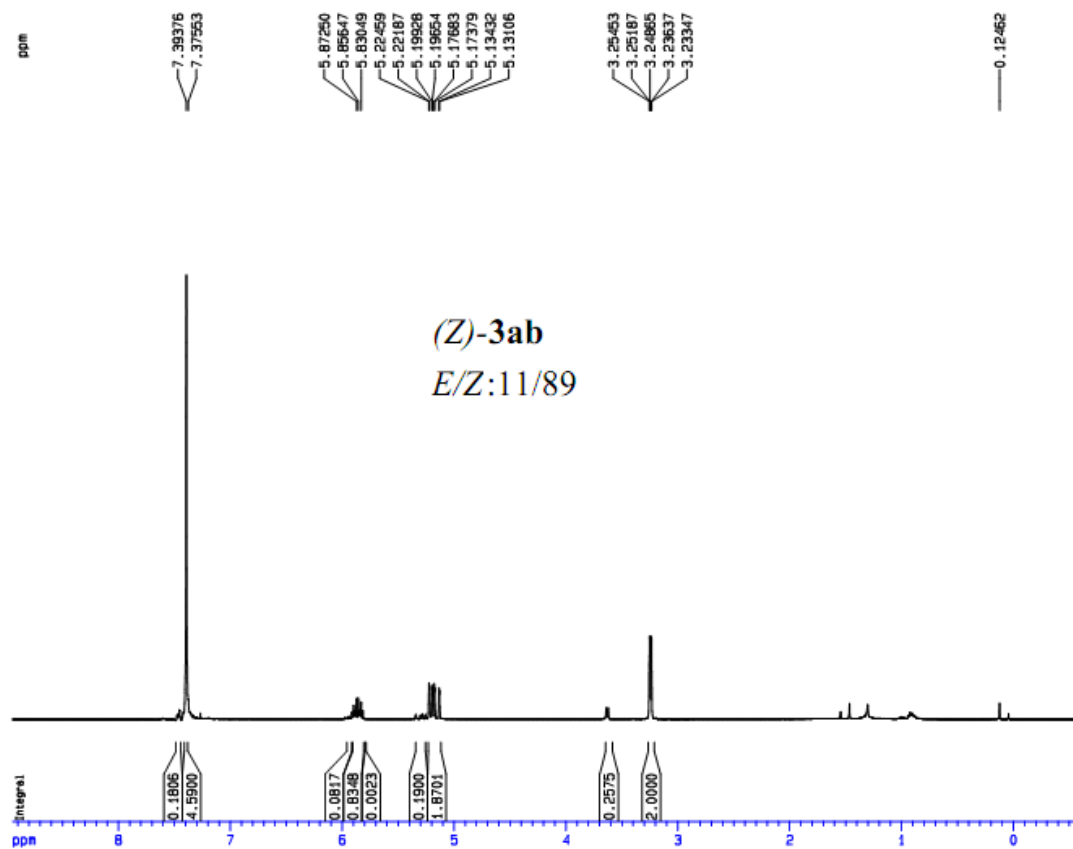


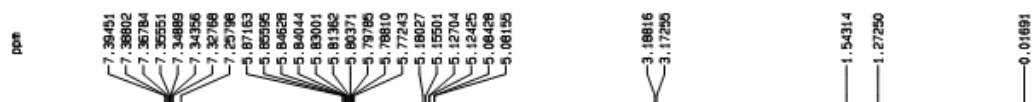




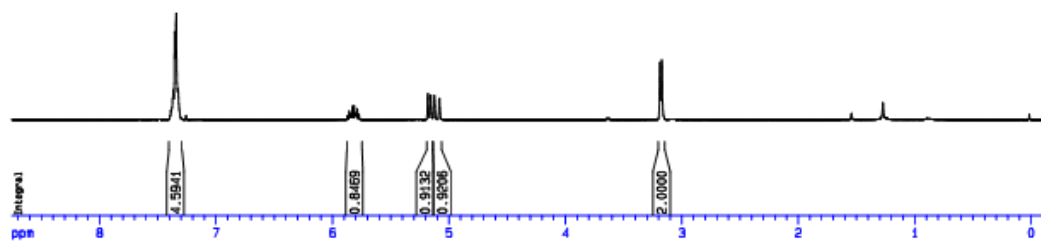








(Z)-3aa



(Z)-3aa

