

## SUPPORTING INFORMATION

Title: **Generation of *ortho*-Quinone Methides by *p*-TsOH on Silica and Their Hetero-Diels—Alder Reactions with Styrenes**

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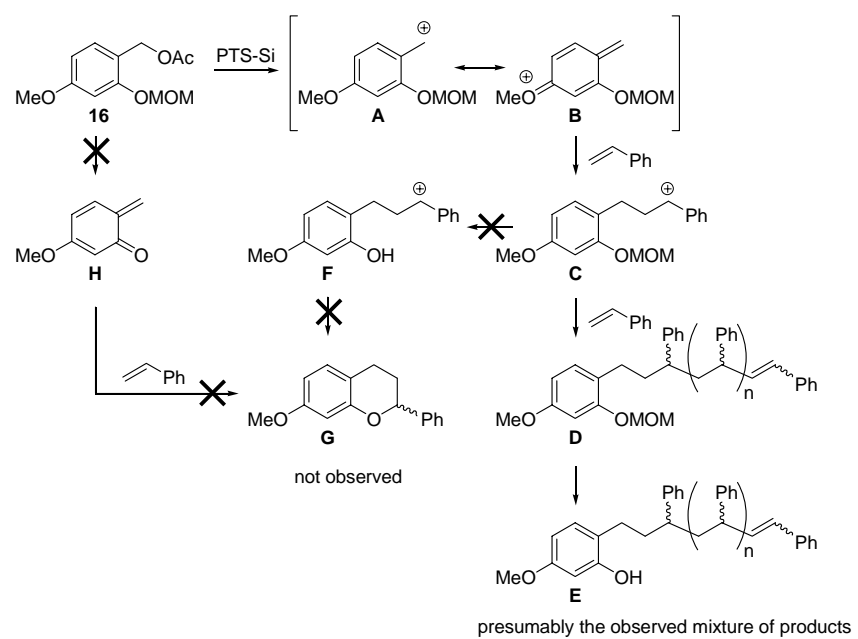
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## Supporting Information

### General Experimental Methods

Unless otherwise noted: Reactions were run in oven-dried round-bottomed flasks. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl while dichloromethane (DCM) from calcium hydride prior to use. All other compounds were used as received from the suppliers. PTS-Si (*p*-TsOH immobilized on silica) used in these experiments was purchased from Silicycle with the surface area of 500 m<sup>2</sup>/g as indicated by the supplier. The crude reaction mixtures were concentrated under reduced pressure by removing organic solvents on rotary evaporator. Column chromatography was performed using silica gel 60 (particle size 0.06-0.2 mm; 70-230 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F<sub>254</sub> aluminum sheets. Chemical shifts for <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), doublet of doublet (dd), and AB quartet (AB<sub>q</sub>). Resonances for infrared (IR) spectra were reported in wavenumbers (cm<sup>-1</sup>). Low resolution (LRMS) mass spectra were obtained either using electron ionization (EI) or time-of-flight (TOF) while high resolution (HRMS) mass spectra were obtained using time-of-flight (TOF). Melting points were uncorrected.

Proposed Mechanism(s) of the Reaction of Compound **16**

## Experimental Section

**A. General Procedure for the Preparation of Benzyl Acetates 14-16.** To a solution of aldehyde (**11-13**; 1.0 equiv) in DMF (10 mL/mmol of aldehyde) was added NaH (1.3 equiv, 55% dispersion) and the reaction was stirred at 0 °C for 1 h. At that time, chloromethyl methyl ether (MOMCl; 1.3 equiv) was added neat via syringe. The resulting mixture was warmed up and stirred at room temperature until complete consumption of the starting material phenol as indicated by tlc (normally 2-3 h). Water and EtOAc were added and the two phases were separated. The aqueous layer was extracted twice with EtOAc and the combined organic phases were washed with water (4 times), once with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product of the MOM-protected aryl ether which was used in the next step without further purification.

To a solution of the crude MOM-protected aryl ether product (1.0 equiv) in EtOH (10 mL/mmol of the crude product) was added NaBH<sub>4</sub> (1.3 equiv) at 0 °C and the reaction was warmed up and stirred at room temperature until complete consumption of the starting material aldehyde as indicated by tlc (normally 0.5-1 h). The resulting mixture was concentrated. Water and EtOAc were added and the two phases were separated. The aqueous layer was extracted twice with EtOAc and the combined organic phases were washed once with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product of the corresponding benzyl alcohol which was used in the next step without further purification.

To a solution of the crude benzyl alcohol product (1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL/mmol of the crude product) was added DMAP (0.6 equiv) and Et<sub>3</sub>N (1.2 equiv). The reaction mixture was subsequently cooled in an ice bath for 10 min. Acetyl chloride (1.2 equiv) was then added slowly by syringe and then the resulting mixture was warmed to room temperature and stirred until complete consumption of the starting material benzyl alcohol as indicated by tlc

(normally 3-4 h). Water and  $\text{CH}_2\text{Cl}_2$  were added and the two phases were separated. The aqueous layer was extracted twice with  $\text{CH}_2\text{Cl}_2$  and the combined organic phases were washed once with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure to give the crude benzyl acetate product which was further purified by column chromatography on silica (20% EtOAc/hexanes) to furnish the desired product (**14-16**).

**2-Methoxymethoxybenzyl acetate (14).** IR (neat):  $\nu_{\text{max}}$  2928, 1736, 1493, 1458, 1380, 1230, 1154, 1080  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.11 (s, 3H), 3.48 (s, 3H), 5.19 (s, 2H), 5.23 (s, 2H), 6.97-7.13 (m, 2H), 7.25-7.37 (m, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.9, 56.0, 61.7, 94.4, 114.1, 121.7, 125.1, 129.5, 129.8, 155.2, 170.8. LRMS (EI)  $m/z$  (rel intensity) 211 ( $\text{M} + \text{H}^+$ , 9), 210 ( $\text{M}^+$ , 100), 151 (32). TOF-HRMS calcd for  $\text{C}_{11}\text{H}_{14}\text{NaO}_4$  ( $\text{M} + \text{Na}^+$ ) 233.0784, found 233.0787.

**5-Bromo-2-methoxymethoxybenzyl acetate (15).** IR (neat):  $\nu_{\text{max}}$  2928, 1739, 1487, 1377, 1223, 1156, 1078  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.13 (s, 3H), 3.46 (s, 3H), 5.14 (s, 2H), 5.19 (s, 2H), 7.00 (d,  $J = 8.8$  Hz, 1H), 7.36 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.46 (d, 2.2 Hz, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.7, 55.9, 60.6, 94.0, 113.6, 115.4, 127.0, 131.6, 131.7, 153.6, 170.4. LRMS (EI)  $m/z$  (rel intensity) 290 ( $\text{M}^+ + 2$ , 100), 288 ( $\text{M}^+$ , 96), 230 (7), 228 (11). TOF-HRMS calcd for  $\text{C}_{11}\text{H}_{13}\text{BrNaO}_4$  ( $\text{M} + \text{Na}^+$ ) 310.9895, found 310.9890.

**4-Methoxy-2-methoxymethoxybenzyl acetate (16).** IR (neat):  $\nu_{\text{max}}$  2926, 1736, 1614, 1509, 1227, 1155, 1000  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.07 (s, 3H), 3.48 (s, 3H), 3.80 (s, 3H), 5.10 (s, 2H), 5.20 (s, 2H), 6.54 (dd,  $J = 8.0, 2.2$  Hz, 1H), 6.71 (d,  $J = 2.2$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.0, 55.4, 56.0, 61.7, 94.4, 101.4, 106.2, 117.3, 131.3, 156.5, 161.1, 171.0. LRMS (EI)  $m/z$  (rel intensity) 241 ( $\text{M} + \text{H}^+$ , 12), 240 ( $\text{M}^+$ , 100), 210 (59), 181 (24), (151) 26, 150 (32), 137 (17), 136 (46). TOF-HRMS calcd for  $\text{C}_{12}\text{H}_{16}\text{NaO}_5$  ( $\text{M} + \text{Na}^+$ ) 263.0890, found 263.0888.

**5-Bromo-2-hydroxy-4-methoxybenzaldehyde (17).** To a solution of 2-hydroxy-4-methoxybenzaldehyde (10.0 g, 65.7 mmol) in glacial acetic acid (1.85 mL/mmol of aldehydes) was added a solution of Br<sub>2</sub> (3.72 mL, 72.3 mmol) in glacial acetic acid (5 mL) at 0 °C and the reaction mixture was warmed up and stirred at room temperature for 1 h. Water (100 mL) was added and the precipitate was collected by filtration. Water (100 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL) were added to the white solid and the two phases were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 50 mL) and the combined organic layers were washed with brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product which was further recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to furnish the desired product **17** as a white solid (9.07 g, 39.4 mmol, 60 %). mp (CH<sub>2</sub>Cl<sub>2</sub>) 121–122 °C. IR (neat):  $\nu_{\max}$  2953, 2923, 2878, 2167, 1641, 1621, 1491, 1442, 1367, 1333, 1274, 1210, 1173, 1045 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  3.93 (s, 3H), 6.45 (s, 1H), 7.65 (s, 1H), 9.66 (s, 1H), 11.4 (s, 1H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  54.7, 98.2, 99.8, 113.6, 135.1, 160.4, 161.5, 191.6. LRMS (EI) *m/z* (rel intensity) 232 (M<sup>+</sup> + 2, 72), 231 (M<sup>+</sup> + 1, 65), 230 (M<sup>+</sup>, 100), 229 (M - H<sup>+</sup>, 49). TOF-HRMS calcd for C<sub>8</sub>H<sub>8</sub>BrO<sub>3</sub> (M + H<sup>+</sup>) 230.9651, found 230.9650.

**B. General Procedure for the Preparation of Benzyl Acetates 18-19.** To a solution of the aldehyde **17** (1.0 equiv) in DMF (1.5 mL/mmol of aldehyde) was added NaH (1.5 equiv, 55% dispersion) at 0 °C and the reaction mixture was stirred for 1 h. At that time, chloromethyl methyl ether (MOMCl) or *i*-PrBr (1.3 equiv), for **18** and **19** respectively, was added via syringe. The resulting mixture was warmed up and stirred at room temperature for 2 h. Water (5 mL) and EtOAc (5 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL) and the combined organic phases were washed with water (3 x 15 mL), brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated

under reduced pressure to give a crude product of the MOM-protected aryl ether which was used in the next step without further purification.

To a solution of the crude MOM-protected aryl ether product (1.0 equiv) in EtOH (7.5 mL/mmol of the crude product) was added NaBH<sub>4</sub> (2.5 equiv) at 0 °C and the reaction mixture was warmed up and stirred at room temperature for 2 h. The resulting mixture was concentrated. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product of the corresponding benzyl alcohol which was used in the next step without further purification.

To a solution of the crude benzyl alcohol product (1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL/mmol of the crude product) was added DMAP (1.5 equiv) and Et<sub>3</sub>N (1.5 equiv). The reaction mixture was subsequently cooled in an ice bath for 10 min. Acetyl chloride (1.5 equiv) was added slowly via syringe and then the resulting mixture was warmed to room temperature and stirred for 2 h. Water (5 mL) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were added and the two phases were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 10 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product which was further purified by column chromatography on silica (20% EtOAc/hexanes) to furnish the desired product.

**5-Bromo-4-methoxy-2-methoxymethoxybenzyl acetate (18).** IR (neat):  $\nu_{\max}$  2926, 1734, 1604, 1497, 1444, 1374, 1293, 1218, 1144, 1080, 1050 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  2.08 (s, 3H), 3.48 (s, 3H), 3.87 (s, 3H), 5.06 (s, 2H), 5.20 (s, 2H), 6.74 (s, 1H), 7.48 (s, 1H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  21.0, 56.1, 56.3, 60.8, 94.6, 99.4, 103.0, 118.4, 133.9, 155.7, 156.6, 170.9. LRMS (EI) m/z (rel intensity) 321 (M<sup>+</sup> + 2, 6), 320 (M + H<sup>+</sup>, 73),

319 ( $M^+$ , 100), 318 (9), 317 (16). TOF-HRMS calcd for  $C_{12}H_{15}BrNaO_5$  ( $M + Na^+$ ) 340.9995 found 340.9992.

**5-Bromo-2-isopropoxy-4-methoxybenzyl acetate (19).** IR (neat):  $\nu_{max}$  2977, 1734, 1601, 1500, 1444, 1374, 1296, 1222, 1159, 1110, 1054  $cm^{-1}$ .  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  1.35 (d,  $J = 6.0$  Hz, 6H), 2.09 (s, 3H), 3.89 (s, 3H), 4.55 (sept,  $J = 6.0$  Hz, 1H), 5.05 (s, 2H), 6.49 (s, 1H), 7.46 (s, 1H).  $^{13}C$  NMR (50 MHz,  $CDCl_3$ ):  $\delta$  21.02, 21.99, 56.3, 61.0, 71.3, 98.8, 101.6, 119.2, 133.9, 156.3, 156.5, 170.9. LRMS (EI)  $m/z$  (rel intensity) 319 ( $M^+ + 2$ , 9), 318 ( $M + H^+$ , 100), 316 (94), 259 (9), 257 (10), 217 (7), 216 (39), 215 (16), 214 (22), 188 (10), 186 (8). TOF-HRMS calcd for  $C_{13}H_{17}BrNaO_4$  ( $M + Na^+$ ) 339.0202, found 339.0203.

**2-(Benzyloxy)-5-bromo-4-methoxybenzyl acetate (20).** To a stirred suspension of aldehyde **17** (0.50 g, 2.16 mmol) in acetone (14 mL) was added  $K_2CO_3$  (0.60 g, 4.33 mmol) and benzyl bromide (0.27 mL, 2.27 mmol) at room temperature. The mixture was refluxed until all aldehyde **17** was consumed as indicated by tlc (typically 4-5 h). After cooling, the reaction mixture was concentrated under reduced pressure. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 10 mL) and the combined organic phases were washed with water (15 mL), brine (15 mL), dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure to give a crude product of the corresponding benzyl ether which was used in the next step without further purification.

To a solution of the crude benzyl ether product (0.71 g) in EtOH (15 mL) was added  $NaBH_4$  (0.21 g, 5.54 mmol) at 0 °C and the reaction mixture was warmed up and stirred at room temperature for 2 h. The resulting mixture was concentrated. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (15 mL), dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure to give a

crude product of the corresponding benzyl alcohol which was used in the next step without further purification.

To a solution of the crude benzyl alcohol product (0.71 g) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added DMAP (0.62 g, 5.10 mmol) and Et<sub>3</sub>N (0.85 mL, 6.12 mmol). The reaction mixture was subsequently cooled in an ice bath for 10 min. Acetyl chloride (0.44 mL, 6.12 mmol) was added slowly via syringe and then the resulting mixture was warmed to room temperature and stirred for 2 h. Water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added and the two phases were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 10 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (20% EtOAc/hexanes) to furnish the desired product (0.49 g, 1.34 mmol, 62 %). IR (neat):  $\nu_{\max}$  3033, 2940, 2853, 1971, 1735, 1604, 1504, 1443, 1376, 1295, 1224, 1161, 1055, 1022 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.08 (s, 3H), 3.85 (s, 3H), 5.11 (s, 1H), 5.13 (s, 1H), 6.52 (s, 1H), 7.31-7.43 (m, 5H), 7.49 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  21.0, 56.3, 60.9, 70.6, 98.0, 102.0, 118.3, 127.1, 128.1, 128.7, 134.1, 136.3, 156.7, 157.0, 170.9. LRMS (EI) *m/z* (rel intensity) 366 (M<sup>+</sup> + 2, 14), 364 (M<sup>+</sup>, 14), 305 (11), 304 (11), 216 (100), 214 (98), 91 (49). TOF-HRMS calcd for C<sub>17</sub>H<sub>15</sub>BrNaO<sub>4</sub> (M + Na<sup>+</sup>) 387.0202, found 387.0204.

**1-Bromo-2-methoxy-4-(methoxymethoxy)-5-(methoxymethyl)benzene (21).** To a solution of aldehyde **17** (0.18 g, 0.78 mmol) in DMF (5 mL) was added NaH (0.05 g, 1.18 mmol, 55% dispersion) and the reaction mixture was stirred for 1 h at 0 °C. At that time, MOMCl (0.08 mL, 1.02 mmol) was added via syringe. The resulting mixture was warmed up and stirred at room temperature for 2 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with water (2 x 10 mL), brine (10 mL),

dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product of the corresponding MOM-protected aryl ether which was used in the next step without further purification.

To a solution of the crude MOM-protected aryl ether product (0.21 g, 0.76 mmol) in EtOH (15 mL) was added NaBH<sub>4</sub> (0.07 g, 1.90 mmol) at 0 °C and the reaction mixture was warmed up and stirred at room temperature for 2 h. The resulting mixture was concentrated under reduced pressure. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude benzyl alcohol product which was used in the next step without further purification.

To a solution of the crude benzyl alcohol product (0.20 g, 0.72 mmol) in DMF (2 mL) was added NaH (0.07 g, 1.44 mmol, 55% dispersion) at 0 °C and the reaction mixture was stirred for 1 h. At that time, dimethylsulfate (0.08 mL, 0.79 mmol) was added via syringe and the resulting mixture was warmed to room temperature and stirred for 4 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (20% EtOAc/hexanes) to furnish the product (0.21 g, 0.72 mmol, 92 %). IR (neat):  $\nu_{\max}$  2931, 2827, 1603, 1578, 1496, 1446, 1387, 1291, 1217, 1189, 1144, 1081, 1051, 1003 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  3.39 (s, 3H), 3.49 (s, 3H), 3.88 (s, 3H), 4.42 (s, 2H), 5.21 (s, 2H), 6.75 (s, 1H), 7.50 (s, 1H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  56.0, 56.2, 58.0, 68.5, 94.7, 99.5, 103.1, 120.8, 133.2, 155.2, 155.9. LRMS (EI) *m/z* (rel intensity) 292 (M<sup>+</sup> + 2, 20), 290 (M<sup>+</sup>,

24), 231 (11), 229 (12), 216 (100), 178 (11). TOF-HRMS calcd for  $C_{11}H_{14}BrO_4$  ( $M - H^+$ ) 289.0081, found 289.0070.

**2-Benzyloxy-1-methoxy-4-vinylbenzene (25).** To a stirred suspension of methyltriphenylphosphonium bromide (3.83 g, 10.7 mmol) in THF (60 mL) was added *n*-BuLi (1.4 M in THF, 4.47 mL, 11.6 mmol) and the reaction mixture was stirred for 0.5 h at -78 °C, slowly warmed up to rt at which the reaction was stirred for 3 h. At that time, a precooled solution of 3-benzyloxy-4-methoxybenzaldehyde (2.00 g, 8.25 mmol) in THF (20 mL) was added via syringe. The resulting mixture was warmed up and stirred at room temperature for 16 h. Water (40 mL) and EtOAc (40 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 40 mL) and the combined organic phases were washed with brine (50 mL), dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure to give a crude product which was further purified by column chromatography on silica (5% EtOAc/hexanes) to furnish the desired product as solid (1.96 g, 8.16 mmol, 99%). mp (MeOH/hexanes) 68–69 °C.<sup>1</sup> IR (neat):  $\nu_{max}$  2926, 1599, 1576, 1513, 1262, 1234, 1158, 1138, 1010  $cm^{-1}$ . <sup>1</sup>H NMR (200 MHz,  $CDCl_3$ ):  $\delta$  3.88 (s, 3H), 5.10 (d,  $J = 11.6$  Hz, 1H), 5.16 (s, 2H), 5.53 (d,  $J = 17.6$  Hz, 1H), 6.60 (dd,  $J = 17.6, 11.6$  Hz, 1H), 6.84 (d,  $J = 8.2$  Hz, 1H), 6.93 (d,  $J = 2.2$  Hz, 1H), 6.99 (m, 1H), 7.29–7.49 (m, 5H). <sup>13</sup>C NMR (50 MHz,  $CDCl_3$ ):  $\delta$  55.9, 71.0, 111.2, 111.4, 111.8, 119.9, 127.3, 127.8, 128.5, 130.5, 136.3, 137.0, 148.1, 149.5. LRMS (EI)  $m/z$  (rel intensity) 241( $M + H^+$ , 9), 240 ( $M^+$ , 50), 149 (1), 91(100). TOF-HRMS calcd for  $C_{16}H_{17}O_2$  ( $M + H^+$ ) 241.1223, found 241.1221.

**C. Procedure for the Preparation of Styrene Derivatives 27-28.** To a stirred solution of benzaldehyde (1.0 equiv) in THF (1.0 mL/mmol of benzaldehyde) was added a solution of alkyl Grignard (1.5 equiv, 2M in THF, *n*-BuMgBr or *i*-BuMgBr for **27** and **28**, respectively) at 0 °C. The resulting mixture was warmed up and stirred at room temperature for 2 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The

aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude benzyl alcohol product which was passed through a plug of silica (15% EtOAc/hexanes). The eluted crude mixture was concentrated under reduced pressure and the trace amount of solvent was removed under vacuum to give the desired benzyl alcohol which was used in the next step without further purification.

A mixture of the alcohol (1.0 equiv) and *p*-toluenesulfonic acid (0.13 equiv) in benzene (20 mL/mmol of alcohol) was heated to reflux with a Dean-Stark apparatus until all starting material was consumed as indicated by tlc (approximately 2 h). The reaction was cooled to rt and the resulting mixture was quenched with Et<sub>3</sub>N (a few drops). The mixture was then diluted with water (10 mL) and EtOAc (10 mL). The two phases were separated and the aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with water (15 mL) and brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product which was further purified by column chromatography on silica (10% EtOAc/hexanes).

**(*E*)-1-Phenyl-1-pentene (27).**<sup>2</sup> IR (neat):  $\nu_{\max}$  3061, 3026, 2957, 2928, 2870, 1600, 1493, 1452, 1378, 1073, 1030 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.95 (t, *J* = 7.5 Hz, 3H), 1.51 (sext, *J* = 7.3 Hz, 2H), 2.19 (q, *J* = 7.1 Hz, 2H), 6.22 (dt, *J* = 15.6, 6.5 Hz, 1H), 6.38 (d, *J* = 16.2, 1H) 7.14-7.37 (m, 5H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  13.7, 22.5, 35.1, 125.9, 126.7, 128.4, 130.0, 131.0, 138.0. LRMS (EI) *m/z* (rel intensity) 293(2M + H<sup>+</sup>, 18), 292 (2M<sup>+</sup>, 100), 236 (25), 235 (87), 146 (M<sup>+</sup>, 1), 91(15). TOF-HRMS calcd for C<sub>11</sub>H<sub>15</sub> (M + H<sup>+</sup>) 147.1168, found 147.1166.

**(*E*)-4-Methyl-1-phenyl-1-pentene (28).**<sup>3</sup> IR (neat):  $\nu_{\max}$  2956, 2924, 2854, 1659, 1465, 1379 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.08 (d, *J* = 6.0 Hz, 6H), 2.44 (apparent sept, *J* = 6.7 Hz, 1H), 6.17 (dd, *J* = 16.2, 6.2 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 7.08-7.36 (m, 5H).

$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  22.4, 31.5, 125.9, 126.7, 126.8, 128.4, 137.9. LRMS (EI)  $m/z$  (rel intensity) 293( $2\text{M} + \text{H}^+$ , 14), 292 ( $2\text{M}^+$ , 100), 236 (22), 235 (100), 146 ( $\text{M}^+$ , 6), 145 ( $\text{M} - \text{H}^+$ , 19), 91(8). TOF-HRMS calcd for  $\text{C}_{11}\text{H}_{15}$  ( $\text{M} + \text{H}^+$ ) 147.1168, found 147.1166.

**D. Procedure for the Preparation of Benzyl Acetates 32-35.** To a solution of aldehyde **17** (1.00 g, 4.33 mmol) in DMF (6.50 mL) was added NaH (0.31 g, 6.49 mmol, 55% dispersion) and the reaction mixture was stirred for 1 h at 0 °C. At that time, chloromethyl methyl ether (MOMCl; 0.43 mL, 5.63 mmol) was added via syringe. The resulting mixture was warmed up and stirred at room temperature for 2 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with water (3 x 10 mL), brine (10 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure to give the crude MOM-protected aryl ether product as a colorless oil (1.18 g, 4.31 mmol, 99%). The material was spectroscopically pure as determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and was used in the next step(s) without further purification. IR (neat):  $\nu_{\text{max}}$  2925, 2860, 1670, 1596, 1484, 1441, 1386, 1317, 1268, 1142, 1081, 1044  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.54 (s, 3H), 3.96 (s, 3H), 5.32 (s, 2H), 6.77 (s, 1H), 8.01 (s, 1H), 10.3 (s, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  56.6, 95.1, 99.0, 105.0, 120.1, 132.6, 160.9, 161.5, 186.9. LRMS (EI)  $m/z$  (rel intensity) 276 ( $\text{M} + 2$ , 56), 275 ( $\text{M}+1$ , 66), 274 ( $\text{M}^+$ , 52), 259 (7), 245 (62), 243 (63). TOF-HRMS calcd for  $\text{C}_{10}\text{H}_{12}\text{BrO}_4$  ( $\text{M} + \text{H}^+$ ) 274.9913, found 274.9909.

**1-(5-Bromo-4-methoxy-2-(methoxymethoxy)phenyl)ethyl acetate (32).** To a solution of the crude MOM-protected aryl ether product (0.28 g, 1.00 mmol) in THF (5 mL) was added a solution of MeLi (1.4 M in  $\text{Et}_2\text{O}$ , 1.07 mL, 1.50 mmol) at -78 °C. The resulting mixture was stirred until all starting material was consumed as indicated by tlc (typically 2-3 h) at -78 °C. At that time, water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined

organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude benzyl alcohol product which was used in the next step without further purification.

To a solution of the crude benzyl alcohol product in CH<sub>2</sub>Cl<sub>2</sub> (2.50 mL) was added DMAP (0.29 g, 2.35 mmol) and Et<sub>3</sub>N (0.39 mL, 2.82 mmol). The reaction mixture was subsequently cooled in an ice bath for 10 min. Acetyl chloride (0.20 mL, 2.82 mmol) was added slowly via syringe and then the resulting mixture was warmed to room temperature and stirred for 2 h. Water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added and the two phases were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 15 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product which was further purified by column chromatography on silica (20% EtOAc/hexanes) to furnish the desired product (0.22 g, 0.66 mmol, 66%) as a white solid. mp (EtOAc) 53–54 °C. IR (neat):  $\nu_{\max}$  2927, 1733, 1603, 1495, 1446, 1369, 1294, 1236, 1147, 1066 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.46 (d, *J* = 6.2 Hz, 3H), 2.08 (s, 3H), 3.50 (s, 3H), 3.87 (s, 3H), 5.21 (s, 2H), 6.17 (q, *J* = 6.5 Hz, 1H), 6.74 (s, 1H), 7.50 (s, 1H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  21.0, 56.0, 56.2, 66.2, 94.5, 99.3, 103.3, 124.4, 130.0, 153.9, 155.7, 170.0. LRMS (EI) *m/z* (rel intensity) 335 (*M* + 2, 7), 333 (*M*<sup>+</sup>, 85), 332 (*M* - H<sup>+</sup>, 100), 320 (36), 318 (41), 275 (30), 243 (16), 230 (59), 228 (62). TOF-HRMS calcd for C<sub>13</sub>H<sub>17</sub>BrNaO<sub>5</sub> (*M* + Na<sup>+</sup>) 355.0157, found 355.0152.

**(5-Bromo-4-methoxy-2-(methoxymethoxy)phenyl)(phenyl)methyl acetate (33).** To a solution of the crude MOM-protected aryl ether product (0.16 g, 0.60 mmol) in THF (10 mL) was added a solution of PhLi (1.8 M in cyclohexane/ether, 0.50 mL, 0.90 mmol) at -78 °C. The resulting mixture was warmed up to room temperature and stirred until all starting material was consumed as indicated by tlc (typically 2-3 h). At that time, the reaction mixture was cooled in an ice bath for 10 min. Acetyl chloride (0.11 mL, 1.50 mmol) was

added slowly via syringe and then the resulting mixture was warmed to room temperature and stirred for 2 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product which was further purified by column chromatography on silica (20% EtOAc/hexanes) to furnish the desired product (0.16 g, 0.41 mmol, 68%) as a colorless oil. IR (neat):  $\nu_{\text{max}}$  2937, 1736, 1602, 1493, 1448, 1370, 1293, 1226, 1136, 1079 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  2.16 (s, 3H), 3.36 (s, 3H), 3.87 (s, 3H), 5.17 (ABq,  $J = 7.2$  Hz,  $\nu_{\text{A-B}} = 9.6$  Hz, 2H), 6.72 (s, 1H), 7.14 (s, 1H), 7.26-7.35 (m, 5H), 7.50 (s, 1H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  21.2, 56.0, 56.2, 70.8, 94.3, 99.3, 103.3, 123.0, 126.9, 127.7, 128.3, 131.0, 139.8, 154.1, 156.0, 169.7. LRMS (EI)  $m/z$  (rel intensity) 395 (M + 2, 5), 393 (M<sup>+</sup>, 3), 337 (7), 335 (9), 292 (52), 291 (93), 289 (50). TOF-HRMS calcd for C<sub>18</sub>H<sub>19</sub>BrNaO<sub>5</sub> (M + Na<sup>+</sup>) 417.0308, found 417.0309.

**(5-Bromo-4-methoxy-2-(methoxymethoxy)phenyl)(4-methoxyphenyl)methyl acetate (34).** To a solution of *p*-bromoanisole (0.15 mL, 1.20 mmol) in THF (16 mL) was added *t*-BuLi (1.7 M in pentane, 1.40 mL, 2.40 mmol) via syringe and the reaction mixture was stirred for 1 h at -78 °C. At that time, a solution of the crude MOM-protected aryl ether product (0.39 g, 1.20 mmol) in THF (5 mL) was added via syringe. The resulting mixture was warmed up and stirred at room temperature for 2 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the crude benzyl alcohol product which was used in the next step without further purification.

To a solution of the crude benzyl alcohol product in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) was added DMAP (0.22 g, 1.80 mmol) and Et<sub>3</sub>N (0.25 mL, 1.80 mmol). The reaction mixture was subsequently

cooled in an ice bath for 10 min. Acetyl chloride (0.13 mL, 1.80 mmol) was added slowly via syringe and then the resulting mixture was warmed to room temperature and stirred for 2 h. Water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added and the two phases were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 15 mL) and the combined organic phases were washed with brine (15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give a crude product which was further purified by preparative tlc (30% EtOAc/hexanes) to furnish the desired product (0.35 g, 0.82 mmol, 68%) as a colorless oil. IR (neat):  $\nu_{\max}$  2971, 1608, 1569, 1488, 1442, 1395, 1305, 1271, 1200, 1154, 1053 cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  2.14 (s, 3H), 3.35 (s, 3H), 3.78 (s, 3H), 3.87 (s, 3H), 5.07-5.21 (m, 2H), 6.71 (s, 1H), 6.85 (d,  $J$  = 8.8 Hz, 2H), 7.09 (s, 1H), 7.26 (d,  $J$  = 8.8 Hz, 2H), 7.52 (s, 1H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  21.2, 55.2, 56.0, 56.4, 70.7, 94.5, 99.6, 103.5, 113.7, 123.5, 128.5, 130.9, 132.0, 154.2, 156.1, 159.2, 169.8. LRMS (EI)  $m/z$  (rel intensity) 425 (M<sup>+</sup>, 11), 423 (13), 367(18), 365 (21), 322 (18), 321 (23), 320 (26), 319 (24), 291 (100), 289 (92), 151 (36). TOF-HRMS calcd for C<sub>19</sub>H<sub>21</sub>BrNaO<sub>6</sub> (M + Na<sup>+</sup>) 447.0413, found 447.0414.

**(5-Bromo-4-methoxy-2-(methoxymethoxy)phenyl)(4-(trifluoromethoxy)phenyl) methyl acetate (35).** To a solution of 1-bromo-4-(trifluoromethoxy)benzene (0.14 mL, 0.91 mmol) in THF (8 mL) was added *t*-BuLi (1.7 M in pentane, 1.07 mL, 1.83 mmol) via syringe and the reaction mixture was stirred for 1 h at -78 °C. At that time, a solution of the crude MOM-protected aryl ether product (0.25 g, 0.91 mmol) in THF (2 mL) was added via syringe. The resulting mixture was warmed up and stirred at room temperature for 2 h. At that time, the reaction mixture was cooled in an ice bath for 10 min. Acetyl chloride (0.13 mL, 1.83 mmol) was added slowly via syringe and then the resulting mixture was warmed to room temperature and stirred for 2 h. Water (10 mL) and EtOAc (10 mL) were added and the two phases were separated. The aqueous layer was extracted with EtOAc (2 x 15 mL) and the combined organic phases were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered,

and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (15% EtOAc/hexanes) to furnish the desired product (0.34 g, 0.71 mmol, 78%) as a colorless oil. IR (neat):  $\nu_{\max}$  2957, 2853, 1742, 1603, 1496, 1372, 1219, 1156, 1002  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.17 (s, 3H), 3.33 (s, 3H), 3.87 (s, 3H), 5.17 (ABq,  $J = 7.1$  Hz,  $\nu_{A-B} = 10.5$  Hz, 2H), 6.72 (s, 1H), 7.11 (s, 1H), 7.16 (d,  $J = 8.0$  Hz, 2H), 7.38 (d,  $J = 8.8$  Hz, 2H), 7.52 (s, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.2, 56.1, 56.4, 70.3, 94.6, 99.6, 103.7, 120.5 (q,  $J_{C-F} = 255.7$  Hz), 120.8, 122.7, 128.5, 131.0, 138.8, 148.7, 154.2, 156.5, 169.6. LRMS (EI)  $m/z$  (rel intensity) 479 ( $\text{M}^+$ , 2), 477 (3), 421 (4), 419 (5), 376 (48), 375 (100), 374 (49), 373 (85), 291 (47), 289 (41). TOF-HRMS calcd for  $\text{C}_{19}\text{H}_{18}\text{BrF}_3\text{NaO}_6$  ( $\text{M} + \text{Na}^+$ ) 501.0131, found 501.0138.

#### E. 2-Arylchroman Products **22**, **23**, **26**, **29**, **30**, **36-47**.

**2-Phenylchroman (22)**. IR (neat):  $\nu_{\max}$  3026, 2925, 2852, 1601, 1582, 1489, 1454, 1234, 1110, 1068  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.01-2.32 (m, 2H), 2.75-2.89 (m, 1H), 2.95-3.12 (m, 1H), 5.09 (dd,  $J = 9.4, 3.0$  Hz, 1H), 6.87-6.96 (m, 2H), 7.10-7.21 (m, 2H), 7.34-7.48 (m, 5H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  25.1, 29.9, 77.7, 116.9, 120.3, 121.8, 126.0, 127.3, 127.8, 128.5, 129.5, 141.7, 155.1. LRMS (EI)  $m/z$  (rel intensity) 211 ( $\text{M} + \text{H}^+$ , 18), 210 ( $\text{M}^+$ , 100), 209 ( $\text{M} - \text{H}^+$ , 33), 208 (19), 195 (14), 193 (19), 115 (6), 91 (8). TOF-HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{O}$  ( $\text{M} + \text{H}^+$ ) 211.1117, found 211.1114.

**6-Bromo-2-phenylchroman (23)**. IR (neat):  $\nu_{\max}$  2926, 1573, 1477, 1235, 1184, 1121, 1064, 1040  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.94-2.24 (m, 2H), 2.67-2.80 (m, 1H), 2.86-3.03 (m, 1H), 5.02 (dd,  $J = 9.6, 2.8$  Hz, 1H), 6.78 (d,  $J = 9.6$  Hz, 1H), 7.20 (m, 2H), 7.27-7.38 (m, 5H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.8, 29.4, 77.8, 112.3, 118.7, 124.0, 125.9, 127.9, 128.5, 130.1, 131.9, 141.1, 154.2. LRMS (EI)  $m/z$  (rel intensity) 290 ( $\text{M}^+ + 2$ , 100), 288 ( $\text{M}^+$ , 95), 209 (14), 208 (9). TOF-HRMS calcd for  $\text{C}_{15}\text{H}_{12}\text{BrO}$  ( $\text{M} - \text{H}^+$ ) 287.0063, found 287.0077.

**2-(3-Benzyloxy-4-methoxy)phenyl-6-bromo-7-methoxychroman (26).** IR (neat):  $\nu_{\max}$  2931, 1610, 1573, 1515, 1496, 1443, 1259, 1154  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.92-2.21 (m, 2H), 2.64-2.76 (m, 1H), 2.82-3.04 (m, 1H), 3.86 (s, 3H), 3.93 (s, 3H), 4.96 (dd,  $J = 9.4, 2.2$  Hz, 1H), 5.20 (s, 2H), 6.50 (s, 1H), 6.92-7.03 (m, 3H), 7.29-7.50 (m, 6H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  24.0, 29.4, 56.1, 56.2, 71.2, 77.8, 101.1, 101.9, 111.9, 112.4, 115.2, 119.1, 127.4, 127.8, 128.5, 133.0, 133.7, 137.0, 148.3, 149.6, 154.9, 155.1. LRMS (EI)  $m/z$  (rel intensity) 456 ( $\text{M}^+ + 2$ , 100), 455 ( $\text{M}^+$ , 95), 375 (14), 365 (36), 363 (33), 91 (81). TOF-HRMS calcd for  $\text{C}_{24}\text{H}_{24}\text{BrO}_4$  ( $\text{M} + \text{H}^+$ ) 455.0852, found 455.0866.

**8-Bromo-7-methoxy-4b,10,10a,11-tetrahydroindeno[1,2-*b*]chromene (29).** IR (neat):  $\nu_{\max}$  2037, 2847, 1609, 1576, 1493, 1443, 1402, 1196, 1155, 1052  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.46-2.58 (m, 1H), 2.73-3.13 (m, 4H), 3.79 (s, 3H), 5.48 (d,  $J = 5.8$  Hz, 1H), 6.45 (s, 1H), 7.19 (s, 1H), 7.23-7.30 (m, 3H), 7.48-7.52 (m, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.7, 36.6, 37.5, 56.1, 81.5, 101.5, 101.7, 116.0, 125.1, 125.2, 126.9, 128.9, 132.5, 142.2, 142.6, 154.7, 155.2. LRMS (EI)  $m/z$  (rel intensity) 332 ( $\text{M}^+ + 2$ , 100), 330 ( $\text{M}^+$ , 96), 318 (7), 217 (30), 215 (36), 116 (12). TOF-HRMS calcd for  $\text{C}_{17}\text{H}_{16}\text{BrO}_2$  ( $\text{M} + \text{H}^+$ ) 331.0328, found 331.0325.

**6-Bromo-7-methoxy-2-phenyl-3-propylchroman (30).** IR (neat):  $\nu_{\max}$  2957, 2930, 2871, 1610, 1575, 1495, 1433, 1310, 1282, 1200, 1156, 1057, 1011  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.75 (t,  $J = 7.1$  Hz, 3H, minor), 0.81 (t,  $J = 7.1$  Hz, 3H), 1.02-1.26 (m, 4H), 1.33-1.45 (m, 4H, minor), 2.04-2.13 (m, 1H), 2.17-2.20 (m, 1H, minor), 2.48 (dd,  $J = 16.1, 9.8$  Hz, 1H), 2.61 (dd,  $J = 16.1, 4.4$  Hz, 1H, minor), 2.81 (dd,  $J = 16.2, 5.0$  Hz, 1H), 2.98 (dd,  $J = 16.1, 5.4$  Hz, 1H, minor), 3.81 (s, 3H), 3.86 (s, 3H, minor), 4.71 (d,  $J = 8.6$  Hz, 1H), 5.22 (d,  $J = 2.6$  Hz, 1H, minor), 6.47 (s, 1H), 6.52 (s, 1H, minor), 7.23 (s, 1H), 7.24 (s, 1H, minor), 7.32-7.41 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 19.5, 20.5 (minor), 28.2 (minor), 28.4 (minor), 29.4, 33.8, 36.5 (minor), 37.1, 56.2, 80.2 (minor), 83.2, 100.7, 100.8 (minor),

101.8 (minor), 109.5 (minor), 115.2, 125.9, 127.0, 127.3 (minor), 128.1 (minor), 128.2, 128.5, 133.0, 133.5 (minor), 140.0, 154.8. LRMS (EI)  $m/z$  (rel intensity) 362 ( $M^+ + 2$ , 76), 360 ( $M^+$ , 79), 319 (4), 317 (5), 271 (72), 269 (81), 239 (8), 238 (22), 217 (14), 215 (15), 191 (20), 190 (100), 117 (50). TOF-HRMS calcd for  $C_{19}H_{22}BrO_2$  ( $M + H^+$ ) 361.0798, found 361.0801.

**6-Bromo-7-methoxy-4-methyl-2-phenylchroman (36).** IR (neat):  $\nu_{max}$  3031, 2960, 2872, 1609, 1568, 1488, 1442, 1399, 1378, 1302, 1264, 1200, 1155, 1060  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  1.32 (d,  $J = 6.8$  Hz, 3H), 1.37 (d,  $J = 7.1$  Hz, 3H, minor), 1.78 (ddd,  $J = 11.8, 11.8, 11.8$  Hz, 1H), 1.89 (apparent dt,  $J = 6.9, 2.8$  Hz, 1H, minor), 2.18 (ddd,  $J = 6.6, 3.3, 1.9$  Hz, 1H), 2.87-2.93 (m, 1H, minor), 3.06-3.15 (m, 1H), 3.81 (s, 3H), 3.82 (s, 3H, minor), 5.04 (dd,  $J = 5.8, 1.8$  Hz, 1H), 5.10 (dd,  $J = 5.2, 2.4$  Hz, 1H, minor), 6.48 (s, 1H), 6.50 (s, 1H, minor), 7.29-7.45 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  20.2, 23.6 (minor), 27.7 (minor), 29.5, 36.8 (minor), 39.6, 56.2, 74.0 (minor), 78.5, 101.1, 102.2, 102.7, 126.0 (minor), 126.1, 127.9 (minor), 128.1, 128.3 (minor), 128.6, 131.1, 132.8 (minor), 141.1, 141.2 (minor), 154.5 (minor), 154.9, 155.0. LRMS (EI)  $m/z$  (rel intensity) 319 (19), 317 (20), 253 (84), 238 (100), 230 (56), 228 (13), 162 (30), 91 (21), 78 (21). TOF-HRMS calcd for  $C_{17}H_{18}BrO_2$  ( $M + H^+$ ) 333.0485, found 333.0483.

**6-Bromo-7-methoxy-2,4-diphenylchroman (37).** IR (neat):  $\nu_{max}$  2922, 1608, 1568, 1487, 1442, 1311, 1263, 1195, 1150, 1054  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.22 (ddd,  $J = 13.8, 5.9, 1.9$  Hz, 1H), 2.38 (ddd,  $J = 13.8, 5.9, 1.9$  Hz, 1H), 3.84 (s, 3H), 3.88 (s, 3H, minor), 4.16 (dd,  $J = 5.4, 3.3$  Hz, 1H, minor), 4.27 (d,  $J = 12.0, 5.8$  Hz, 1H), 5.02 (dd,  $J = 10.5, 2.3$  Hz, 1H, minor), 5.18 (dd,  $J = 11.4, 1.6$  Hz, 1H), 6.54 (s, 1H), 6.60 (s, 1H, minor), 6.91 (s, 1H), 7.12-7.48 (m, 10H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  38.0 (minor), 39.4 (minor), 40.3, 42.7, 56.2, 73.6 (minor), 78.6, 101.9 (minor), 101.0, 102.4, 119.2 (minor), 124.0 (minor), 125.96 (minor), 126.01 (minor), 126.1, 126.6 (minor), 127.0, 128.0 (minor), 128.2,

128.3, 128.5, 128.6, 128.8, 133.0 (minor), 133.2, 134.2 (minor), 140.6, 143.8, 155.1, 155.6. LRMS (EI)  $m/z$  (rel intensity) 396 ( $M^+ + 2$ , 61), 395 ( $M + H^+$ , 13), 394 ( $M^+$ , 70), 317 (55), 315 (100), 292 (60), 289 (57), 288 (65), 191 (13). TOF-HRMS calcd for  $C_{17}H_{20}BrO_2$  ( $M + H^+$ ) 395.0641, found 395.0644.

**6-Bromo-7-methoxy-4-(4-methoxyphenyl)-2-phenylchroman (38).** IR (neat):  $\nu_{max}$  2953, 2923, 2853, 1608, 1568, 1510, 1486, 1442, 1397, 1311, 1287, 1249, 1196, 1175, 1149, 1057, 1038  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.20 (ddd,  $J = 11.8, 11.8, 11.6$  Hz, 1H), 2.39-2.43 (m, 1H, minor), 2.35 (ddd,  $J = 13.8, 5.9, 1.9$  Hz, 1H), 3.806 (s, 3H, minor), 3.811 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H, minor), 4.11 (dd,  $J = 10.0, 6.3$  Hz, 1H, minor), 4.22 (dd,  $J = 12.1, 5.8$  Hz, 1H), 5.01 (dd,  $J = 10.4, 2.3$  Hz, 1H, minor), 5.18 (dd,  $J = 11.4, 1.7$  Hz, 1H), 6.53 (s, 1H), 6.59 (s, 1H, minor), 6.87 (AA'BB',  $J = 8.7$  Hz, 2H), 6.91 (d,  $J = 1.0$ , 1H), 7.04 (AA'BB',  $J = 8.5$  Hz, 2H, minor), 7.12 (AA'BB',  $J = 8.7$  Hz, 2H), 7.28-7.45 (m, 5H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  38.2 (minor), 38.5 (minor), 40.4, 41.9, 55.3, 56.2, 73.6 (minor), 78.6, 100.9, 101.0, 102.4, 113.9 (minor), 114.2, 119.6, 125.99 (minor), 126.04, 127.9 (minor), 128.2, 128.5 (minor), 128.6, 129.3, 129.4 (minor), 133.3, 134.2 (minor), 135.8, 140.7, 155.1, 155.5, 158.5. LRMS (EI)  $m/z$  (rel intensity) 427 ( $M^+ + 2$ , 15), 426 ( $M + H^+$ , 100), 425 ( $M^+$ , 56), 424 ( $M - H^+$ , 50), 345 (58), 347 (14), 321 (21), 320 (38), 319 (35), 290 (20), 288 (21), 216 (13), 219 (11). TOF-HRMS calcd for  $C_{23}H_{22}BrO_3$  ( $M + H^+$ ) 425.0747, found 425.0745.

**6-Bromo-7-methoxy-2-phenyl-4-(4-(trifluoromethoxy)phenyl)chroman (39).** IR (neat):  $\nu_{max}$  2924, 2855, 1608, 1568, 1488, 1443, 1258, 1216, 1200, 1151, 1056  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.17 (ddd,  $J = 11.9, 11.8, 11.8$  Hz, 1H), 2.38 (ddd,  $J = 13.8, 5.9, 1.9$  Hz, 1H), 3.85 (s, 3H), 3.89 (s, 3H, minor), 4.17 (dd,  $J = 5.6, 3.5$  Hz, 1H, minor), 4.31 (dd,  $J = 12.0, 5.9$  Hz, 1H), 4.98 (dd,  $J = 10.5, 2.3$  Hz, 1H, minor), 5.17 (dd,  $J = 11.4, 1.6$  Hz, 1H), 6.54 (s, 1H), 6.60 (s, 1H, minor), 6.89 (d,  $J = 1.0$  Hz, 1H), 7.17-7.269 (m, 4H), 7.32-7.47 (m,

5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  40.5, 42.1, 56.2, 78.4, 101.1, 102.6, 113.6 (minor), 118.5, 121.0 (minor), 121.3, 126.0, 128.3, 128.57 (minor), 128.65, 129.6, 129.8 (minor), 133.1, 134.0 (minor), 140.3, 142.6, 148.1, 155.4, 155.7 LRMS (EI)  $m/z$  (rel intensity) 480 ( $\text{M}^+ + 2$ , 97), 479 ( $\text{M} + \text{H}^+$ , 32), 478 ( $\text{M}^+$ , 100), 399 (77), 375 (25), 373 (24), 291 (49), 289 (53), 276 (60), 224 (21). TOF-HRMS calcd for  $\text{C}_{23}\text{H}_{19}\text{BrF}_3\text{O}_3$  ( $\text{M} + \text{H}^+$ ) 479.0464, found 479.0473.

**2-(3-(Benzyloxy)-4-methoxyphenyl)-6-bromo-7-methoxy-4-methylchroman (40).** IR (neat):  $\nu_{\text{max}}$  2958, 1608, 1516, 1485, 1442, 1264, 1156, 1025  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.31 (d,  $J = 6.8$  Hz, 3H), 1.34 (d,  $J = 2.7$  Hz, 3H, minor), 1.73 (apparent q,  $J = 12.4$  Hz, 1H), 1.82 (apparent dt,  $J = 13.9, 7.2$  Hz, 1H, minor), 2.07-2.14 (m, 1H), 2.84-2.88 (m, 1H, minor), 3.07 (sept,  $J = 5.3$  Hz, 1H), 3.82 (s, 3H), 3.89 (s, 3H), 4.94 (dd,  $J = 11.5, 1.3$  Hz, 1H), 5.00 (dd,  $J = 10.4, 2.0$  Hz, 1H, minor), 5.16 (s, 2H), 6.45 (s, 1H), 6.46 (s, 1H, minor), 6.89-6.92 (m, 1H), 6.95-7.00 (m, 2H), 7.27-7.39 (m, 4H), 7.42-7.47 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.2, 23.6 (minor), 27.6 (minor), 29.5, 36.5 (minor), 39.3, 56.1, 56.2, 71.1, 73.7 (minor), 78.3, 101.1, 102.1, 111.7, 112.2, 119.1 (minor), 119.2, 120.7, 127.4 (minor), 127.5, 127.9, 128.5, 131.0, 132.8 (minor), 133.6, 137.0, 148.3, 149.6, 154.8, 155.5. LRMS (EI)  $m/z$  (rel. intensity) 470 ( $\text{M}^+ + 2$ , 100), 468 ( $\text{M}^+$ , 90), 379 (36), 377 (41), 298 (46), 240 (15), 137 (14), 91(85). TOF-HRMS calcd for  $\text{C}_{25}\text{H}_{26}\text{BrO}_4$  ( $\text{M} + \text{H}^+$ ) 469.1009, found 469.1008.

**2-(3-(Benzyloxy)-4-methoxyphenyl)-6-bromo-7-methoxy-4-phenylchroman (41).** IR (neat):  $\nu_{\text{max}}$  2928, 1607, 1516, 1488, 1442, 1261, 1199, 1150, 1024  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.17 (ddd,  $J = 12.1, 11.8, 11.8$  Hz, 1H), 2.31 (ddd,  $J = 13.7, 5.9, 1.9$  Hz, 1H), 3.84 (s, 3H), 3.87 (s, 3H, minor), 3.875 (s, 3H, minor), 3.884 (s, 3H), 4.11 (apparent t,  $J = 4.3$  Hz, 1H, minor), 4.23 (dd,  $J = 11.9, 5.7$  Hz, 1H), 4.92 (dd,  $J = 10.4, 2.2$  Hz, 1H, minor), 5.07 (dd,  $J = 11.3, 1.6$  Hz, 1H), 5.11 (s, 2H, minor), 5.16 (ABq,  $J = 12.0$  Hz,  $\nu_{A-B} = 8.6$  Hz,

2H), 6.50 (s, 1H), 6.55 (s, 1H, minor), 6.85 (d,  $J = 0.9$  Hz, 1H), 6.91 (apparent d,  $J = 7.2$  Hz, 2H), 7.02 (apparent d,  $J = 10.3$  Hz, 2H), 7.19 (apparent d,  $J = 7.6$  Hz, 2H), 7.25-7.47 (m, 7H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  37.8 (minor), 39.3 (minor), 40.1, 42.7, 56.1, 56.2, 71.1 (minor), 71.2, 73.4 (minor), 78.3, 100.9 (minor), 101.0, 102.4 (minor), 111.6 (minor), 111.7, 112.2 (minor), 112.3, 116.5 (minor), 119.1 (minor), 119.2 (minor), 119.3, 126.6 (minor), 127.0, 127.4 (minor), 127.5, 127.8, 128.3, 128.5, 128.8, 133.0, 133.3, 134.2, 136.9, 143.9, 145.5 (minor), 148.3, 149.7 (minor), 155.1, 155.7. LRMS (EI)  $m/z$  (rel. intensity) 532 ( $\text{M}^+ + 2$ , 30), 531 ( $\text{M} + \text{H}^+$ , 90), 530 ( $\text{M}^+$ , 33), 451 (17), 441 (40), 439 (43), 360 (28), 137 (12), 91(100). TOF-HRMS calcd for  $\text{C}_{30}\text{H}_{28}\text{BrO}_4$  ( $\text{M} + \text{H}^+$ ) 530.1084, found 530.1083.

**2-(3-(Benzyloxy)-4-methoxyphenyl)-6-bromo-7-methoxy-4-(4-methoxyphenyl)**

**chroman (42).** IR (neat):  $\nu_{\text{max}}$  2933, 1608, 1510, 1442, 1250, 1154, 1025  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.07 (ddd,  $J = 11.8, 11.8, 11.8$  Hz, 1H), 2.20 (ddd,  $J = 13.8, 5.8, 1.8$  Hz, 1H), 2.24-2.29 (m, 1H, minor), 3.73 (s, 3H, minor), 3.74 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H, minor), 3.80 (s, 3H, minor), 3.81 (s, 3H), 3.98 (apparent t,  $J = 4.5$  Hz, 1H, minor), 4.11 (dd,  $J = 12.0, 5.7$  Hz, 1H), 4.84 (dd,  $J = 10.3, 2.3$  Hz, 1H, minor), 4.99 (dd,  $J = 11.3, 1.6$  Hz, 1H), 5.04 (s, 2H, minor), 5.09 (ABq,  $J = 12.1$  Hz,  $\nu_{\text{A-B}} = 8.2$  Hz, 2H), 6.42 (s, 1H), 6.47 (s, 1H, minor), 6.77-6.84 (m, 5H), 6.92-6.97 (m, 2H), 7.04 (apparent dt,  $J = 8.7, 2.7$  Hz, 2H), 7.19-7.40 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  37.9 (minor), 38.5 (minor), 40.1, 40.9, 55.3, 56.1 (minor), 56.2, 71.1 (minor), 71.2, 73.4 (minor), 78.4, 100.8 (minor), 101.0, 102.3 (minor), 111.7 (minor), 111.8, 112.3, 113.8, 114.2, 116.9 (minor), 119.1 (minor), 119.3, 119.6 (minor), 127.4, 127.5, 127.8 (minor), 127.9, 128.5, 129.3, 129.4, 133.1 (minor), 133.3, 134.1, 135.8, 137.0, 148.2 (minor), 148.3, 149.7, 155.1, 155.6, 158.5. LRMS (EI)  $m/z$  (rel. intensity) 562 ( $\text{M} + \text{H}^+$ , 4), 561 ( $\text{M}^+$ , 6), 560 ( $\text{M} - \text{H}^+$ , 7), 471 (72), 469 (62), 390 (29), 321 (54), 268 (30), 267 (25), 165 (27), 91(100). TOF-HRMS calcd for  $\text{C}_{31}\text{H}_{30}\text{BrO}_5$  ( $\text{M} + \text{H}^+$ ) 561.1271, found 561.1249.

**2-(3-(Benzyloxy)-4-methoxyphenyl)-6-bromo-7-methoxy-4-(4-(trifluoromethoxy)phenyl)chroman (43).** IR (neat):  $\nu_{\max}$  2928, 2860, 1608, 1508, 1488, 1443, 1258, 1155, 1019  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.11 (apparent q,  $J = 12.4$  Hz, 1H), 2.30 (ddd,  $J = 13.8, 5.9, 1.7$  Hz, 1H), 3.85 (s, 3H), 3.89 (s, 3H), 4.27 (dd,  $J = 12.0, 5.9$  Hz, 1H), 5.06 (dd,  $J = 11.3, 1.4$  Hz, 1H), 5.17 (ABq,  $J = 12.0$  Hz,  $\nu_{A-B} = 9.0$  Hz, 2H), 6.51 (s, 1H), 6.88 (s, 1H), 6.91 (d,  $J = 8.0$  Hz, 2H), 7.00 (d,  $J = 1.9$  Hz, 2H), 7.02 (s, 1H), 7.17-7.23 (m, 3H), 7.28-7.38 (m, 2H), 7.45 (d,  $J = 7.0$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  40.2, 42.1, 56.1, 56.2, 71.2, 78.2, 101.1, 102.5, 111.7, 112.3, 118.4, 119.2, 121.3, 127.5, 127.9, 128.5, 129.6, 132.7, 133.1, 136.9, 142.7, 148.3, 149.8, 155.3, 155.7. LRMS (EI)  $m/z$  (rel intensity) 616 ( $\text{M}^+ + 2$ , 97), 614 ( $\text{M}^+$ , 100), 525 (42), 523 (37), 445 (15), 444 (11), 322 (7), 240 (11), 228 (12), 91 (67). TOF-HRMS calcd for  $\text{C}_{31}\text{H}_{27}\text{BrF}_3\text{O}_5$  ( $\text{M} + \text{H}^+$ ) 615.0988, found 615.0970.

**8-Bromo-7-methoxy-10-methyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (44).** IR (neat):  $\nu_{\max}$  2961, 2937, 1606, 1569, 1489, 1442, 1393, 1279, 1192, 1158, 1052  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.39 (d,  $J = 6.9$  Hz, 3H), 1.42 (d,  $J = 3.6$  Hz, 3H, minor), 2.59 (d,  $J = 16.0, 9.1$  Hz, 1H), 2.73 (d,  $J = 7.0, 4.5$  Hz, 1H, minor), 2.82 (dd,  $J = 16.0, 8.0$  Hz, 1H), 2.99-3.06 (m, 1H), 3.26 (pentet,  $J = 6.3$  Hz, 1H), 3.73 (s, 3H), 3.79 (s, 3H, minor), 5.48 (d,  $J = 6.2$  Hz, 1H, minor), 5.57 (d,  $J = 6.6$  Hz, 1H), 6.31 (s, 1H), 6.42 (s, 1H, minor), 7.16 (apparent t,  $J = 7.1$  Hz, 1H), 7.15-7.29 (m, 3H), 7.16 (apparent d,  $J = 7.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  16.1, 21.9 (minor), 29.1, 31.4 (minor), 32.1, 36.3 (minor), 44.7, 45.4 (minor), 56.1, 79.8 (minor), 83.0, 101.5 (minor), 101.7, 102.0, 120.9, 125.0, 125.1 (minor), 125.2 (minor), 125.5, 126.8, 129.1 (minor), 129.2, 130.1, 132.0 (minor), 142.0, 143.9, 154.6, 155.7. LRMS (EI)  $m/z$  (rel intensity) 346 ( $\text{M}^+ + 2$ , 49), 345 ( $\text{M} + \text{H}^+$ , 12), 344 ( $\text{M}^+$ , 49), 334 (26), 332 (32), 331 (17), 329 (15), 320 (13), 318 (14), 231(7), 239 (29), 116 (61), 115 (36). TOF-HRMS calcd for  $\text{C}_{18}\text{H}_{18}\text{BrO}_2$  ( $\text{M} + \text{H}^+$ ) 345.0485, found 345.0478.

**8-Bromo-7-methoxy-10-phenyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (45).**

IR (neat):  $\nu_{\max}$  3027, 2924, 2850, 2380, 2140, 1952, 1607, 1572, 1489, 1271, 1194, 1158, 1056  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.43 (dd,  $J = 14.4, 6.1$  Hz, 1H), 2.90-3.04 (m, 2H), 3.79 (s, 3H), 3.84 (s, 3H, minor), 4.60 (d,  $J = 5.7$  Hz, 1H), 4.75 (d,  $J = 4.9$  Hz, 1H, minor), 5.46 (d,  $J = 4.4$  Hz, 1H), 5.51 (d,  $J = 6.2$  Hz, 1H, minor), 6.42 (s, 1H), 6.54 (s, 1H, minor), 7.08 (d,  $J = 1.0$  Hz, 1H, minor), 7.10 (s, 1H), 7.16-7.41 (m, 8H), 7.25-7.54 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  33.1, 35.1 (minor), 35.9 (minor), 36.0 (minor), 42.2, 45.6, 45.8 (minor), 56.2, 66.9 (minor), 80.0 (minor), 81.3, 101.0, 101.9 (minor), 109.6 (minor), 116.5, 124.3 (minor), 124.9 (minor), 125.0, 125.2, 125.3 (minor), 126.8, 126.9 (minor), 127.0, 128.6 (minor), 128.64, 128.8 (minor), 129.0 (minor), 129.2, 129.3, 132.9, 133.2 (minor), 141.5, 142.0, 144.2, 154.9, 156.3. LRMS (EI)  $m/z$  (rel intensity) 408 ( $\text{M}^+ + 2$ , 92), 407 ( $\text{M} + \text{H}^+$ , 27), 406 ( $\text{M}^+$ , 100), 327 (33), 291 (88), 289 (57), 116 (43), 115 (40). TOF-HRMS calcd for  $\text{C}_{23}\text{H}_{20}\text{BrO}_2$  ( $\text{M} + \text{H}^+$ ) 407.0641, found 407.0644.

**8-Bromo-7-methoxy-10-(4-methoxyphenyl)-4b,10,10a,11-tetrahydroindeno[1,2-**

**b]chromene (46).** IR (neat):  $\nu_{\max}$  2937, 2909, 1607, 1570, 1510, 1488, 1394, 1249, 1194, 1158, 1055  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.46 (dd,  $J = 13.9, 5.6$  Hz, 1H), 2.82 (dd,  $J = 15.4, 5.5$  Hz, 1H, minor), 2.88-3.06 (m, 2H), 3.78 (s, 3H), 3.82 (s, 3H, minor), 3.83 (s, 3H, minor), 3.84 (s, 3H), 4.54 (dd,  $J = 5.3$  Hz, 1H), 5.45 (d,  $J = 4.4$  Hz, 1H), 5.52 (d,  $J = 6.2$  Hz, 1H, minor), 6.41 (s, 1H), 6.54 (s, 1H, minor), 6.92 (d,  $J = 8.6$  Hz, 2H), 7.07 (d,  $J = 1.0$  Hz, 1H), 7.07 (apparent dt,  $J = 8.7, 2.5$  Hz, 2H), 7.23-7.31 (m, 3H), 7.48-7.56 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  33.1, 35.9 (minor), 41.4, 42.2 (minor), 55.3, 56.1, 56.2 (minor), 80.2 (minor), 81.3, 101.0, 101.1 (minor), 101.9, 102.1 (minor), 113.6 (minor), 114.0, 114.1 (minor), 116.9 (minor), 124.9 (minor), 125.1, 125.2, 125.3 (minor), 126.8, 127.0 (minor), 127.4 (minor), 128.9, 129.3, 129.5, 129.6 (minor), 130.1, 132.8, 133.0 (minor), 133.4, 135.1 (minor), 142.0, 142.1 (minor), 144.3, 154.8, 155.1 (minor), 155.2 (minor), 156.2, 158.4

(minor), 158.5. LRMS (EI)  $m/z$  (rel intensity) 438 ( $M^+ + 2$ , 41), 436 ( $M^+$ , 45), 291 (48), 291 (88), 289 (59), 241 (43), 234 (73), 222 (78), 221 (37), 121 (30), 115 (14). TOF-HRMS calcd for  $C_{24}H_{22}BrO_3$  ( $M + H^+$ ) 437.0747, found 437.0743.

**8-Bromo-7-methoxy-9-(4-(trifluoromethoxy)phenyl)-4b,10,10a,11-tetrahydroindeno [1,2-b]chromene (47).** IR (neat):  $\nu_{max}$  2925, 2853, 1607, 1569, 1489, 1443, 1258, 1158, 1056  $cm^{-1}$ .  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  2.44 (dd,  $J = 14.9, 6.7$  Hz, 1H), 2.85-3.02 (m, 2H), 3.80 (s, 3H), 4.62 (d,  $J = 6.1$  Hz, 1H), 4.93 (d,  $J = 4.4$  Hz, 1H, minor), 5.47 (d,  $J = 4.6$  Hz, 1H), 6.44 (s, 1H), 7.04 (d,  $J = 0.7$  Hz, 1H), 7.16-7.30 (m, 7H), 7.52-7.54 (m, 1H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  33.0, 41.7, 45.3, 56.2, 81.1, 101.2, 102.1, 109.5, 115.9, 121.1, 125.0, 125.1, 126.9, 129.4, 130.4, 132.7, 140.2, 141.8, 143.8, 155.1, 156.2. LRMS (EI)  $m/z$  (rel intensity) 492 ( $M^+ + 2$ , 92), 491 ( $M + H^+$ , 29), 490 ( $M^+$ , 100), 411 (67), 377 (53), 375 (96), 373 (42), 291 (47), 289 (48), 116 (22), 116 (13). TOF-HRMS calcd for  $C_{24}H_{19}BrF_3O_3$  ( $M + H^+$ ) 491.0464, found 491.0461.

### References and Notes

1. (a) Krohn, K.; Loock, U.; Paavilainen, K.; Hausen, B. M.; Schmalle, H. W.; Kiesele, H. *Arkivoc* **2001**, 88-130. No melting point, <sup>13</sup>C NMR, LRMS and HRMS data were given in the reference. (b) The compound is also available from Aldrich which reports the mp to be 49-54 °C.
2. Kabalka, G. W.; Li, N.-S.; Tejedor, D.; Malladi, R. R.; Trotman, S. *J. Org. Chem.* **1999**, *64*, 3157-3161.
3. Jang, Y.-J.; Yan, M.-C.; Lin, Y.-F.; Yao, C.-F. *J. Org. Chem.* **2004**, *69*, 3961-3963.

**nOe Correlations and Data**

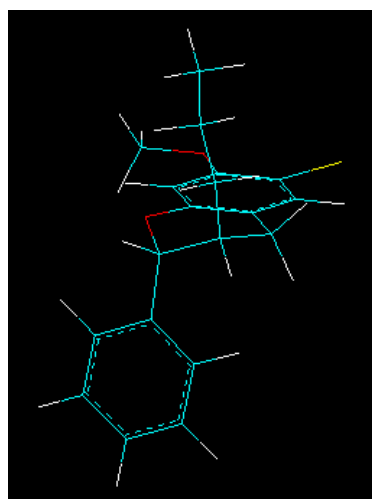
Energy-minimized structures were calculated by using the AM1 method in HyperChem 7.5.

**30, major**

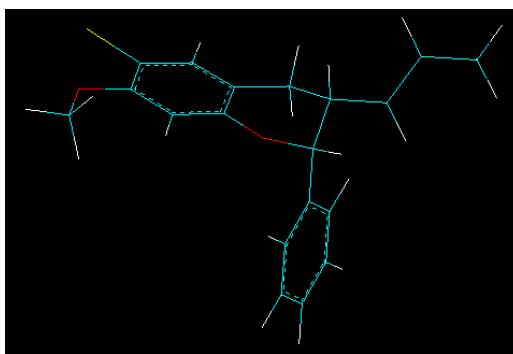
R = <i>n</i> -Pr	Irradiation	Position (% nOe)
	H-2	H-3 (2.7 %)
		H-4 $\alpha$ (3.1 %)
	H-3	H-2 (1.9 %)
		H-4 $\beta$ (3.3 %)
	H-4 $\alpha$	H-2 (3.8 %)
		H-4 $\beta$ (20.4 %)
	H-4 $\beta$	H-3 (6.0 %)
		H-4 $\alpha$ (23.4 %)

**30, minor**

R = <i>n</i> -Pr	Irradiation	Position (% nOe)
	H-2	H-3 (6.4 %)

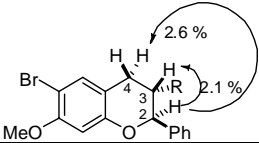
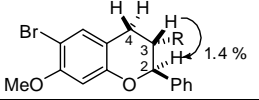
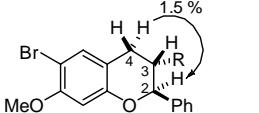


Major

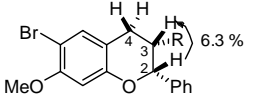


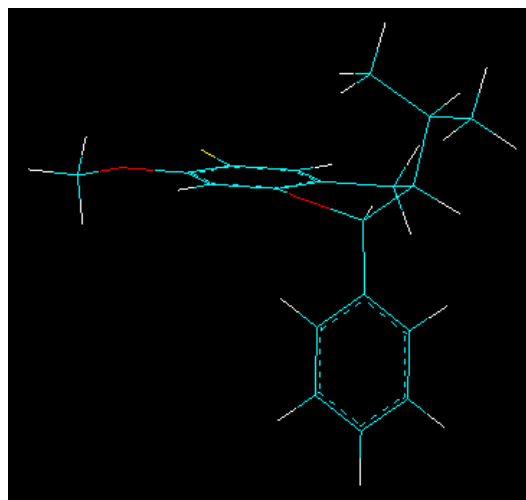
Minor

**31, major**

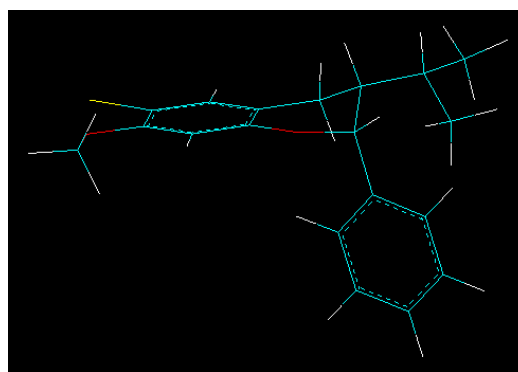
R = <i>i</i> -Pr	Irradiation	Position (% nOe)
	H-2	H-3 (2.1 %)
		H-4α (2.6 %)
	H-3	H-2 (1.4 %)
	H-4α	H-2 (1.5 %)

**31, minor**

R = <i>i</i> -Pr	Irradiation	Position (% nOe)
	H-2	H-3 (6.3 %)

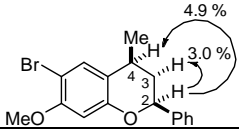
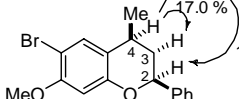


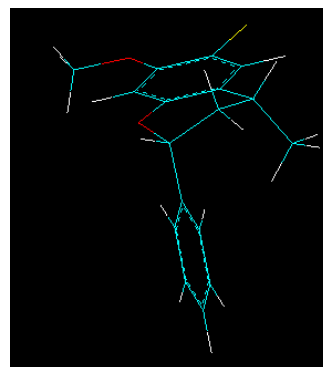
Major

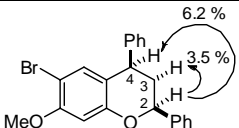
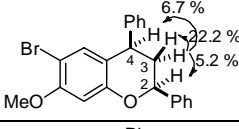
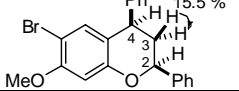
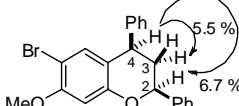


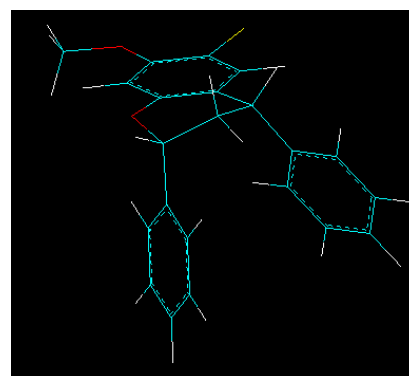
Minor

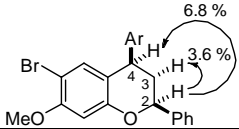
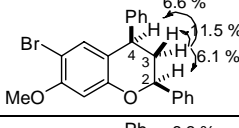
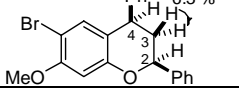
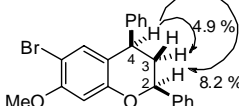
**36, Major**

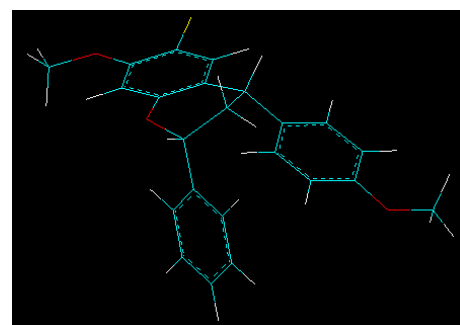
	Irradiation	Position (% nOe)
	H-2	H-3 (3.0 %)
		H-4 (4.9 %)
	H-4	H-2 (19.9 %)
		H-3 (17.0 %)

**37, Major**

	Irradiation	Position (% nOe)
	H-2	H-3α (3.5 %)
		H-4 (6.2 %)
	H-3α	H-2 (5.2%)
		H-3β (22.2 %)
		H-4 (6.7 %)
	H-3β	H-3α (15.5 %)
	H-4	H-2 (6.7 %)
		H-3α (5.5 %)

**38**

Ar = <i>p</i> -(OMe)Ph	Irradiation	Position (% nOe)
	H-2	H-3α (3.6 %)
		H-4 (6.8 %)
	H-3α	H-2 (6.1 %)
		H-3β (11.5 %)
		H-4 (6.6 %)
	H-3β	H-3α (6. %)
	H-4	H-2 (8.2 %)
		H-3α (4.9 %)

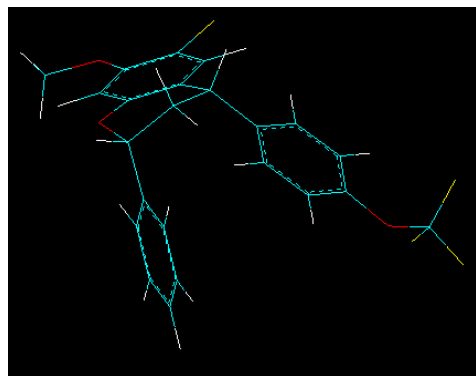


**39, Major**

Ar = <i>p</i> -(OCF <sub>3</sub> )Ph	Irradiation	Position (% nOe)
	H-2	H-3 $\alpha$ (3.8 %)
		H-4 (6.6 %)
	H-3 $\alpha$	H-2 (5.6%)
		H-3 $\beta$ (21.6 %)
		H-4 (6.3 %)
	H-3 $\beta$	H-3 $\alpha$ (20.4 %)
	H-4	H-2 (7.7 %)
		H-3 $\alpha$ (4.9 %)

**39, Minor**

Ar = <i>p</i> -(OCF <sub>3</sub> )Ph	Irradiation	Position (% nOe)
	H-2	H-3 $\beta$ (5.6 %)
	H-4	H-3 $\alpha$ (2.2 %)

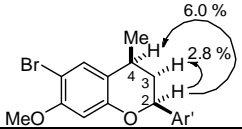
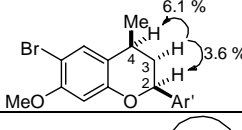
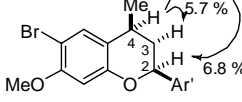


Major

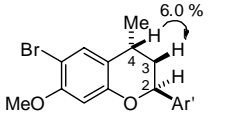


Minor

**40, Major**

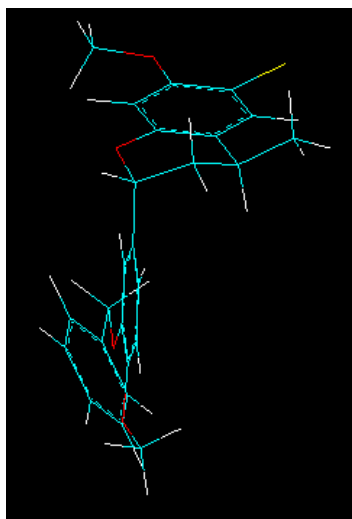
Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-2	H-3α (2.8 %)
		H-4 (6.0 %)
	H-3α	H-2 (3.6 %)
		H-4 (6.1 %)
	H-4	H-2 (6.8 %)
		H-3α (5.7 %)

**40, Minor**

Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-4	H-3 (6.0 %)

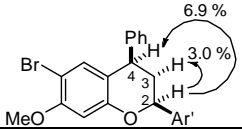
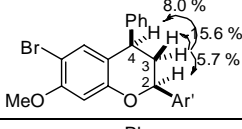
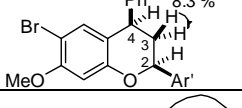
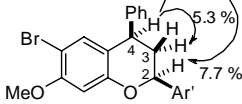


Major

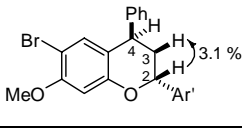
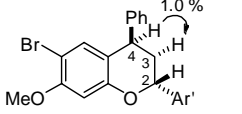


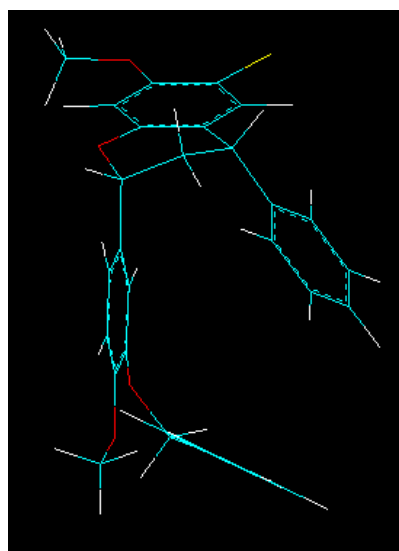
Minor

**41, Major**

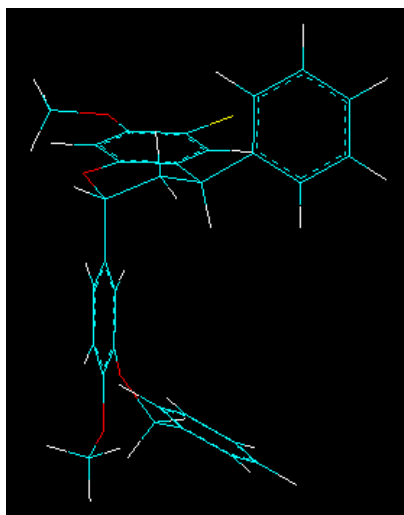
Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-2	H-3α (3.5 %)
		H-4 (6.2 %)
	H-3α	H-2 (5.7%)
		H-3β (15.6 %)
		H-4 (8.0 %)
	H-3β	H-3α (8.3 %)
	H-4	H-2 (7.7 %)
		H-3α (5.3 %)

**41, Minor**

Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-2	H-3β (3.1 %)
	H-4	H-3α (1.0 %)

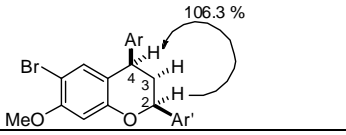
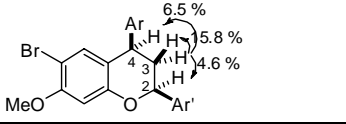
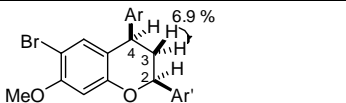


Major

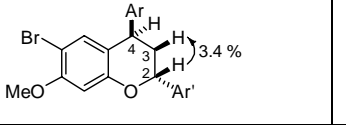
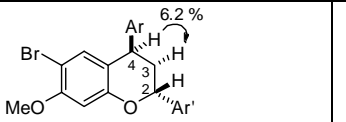


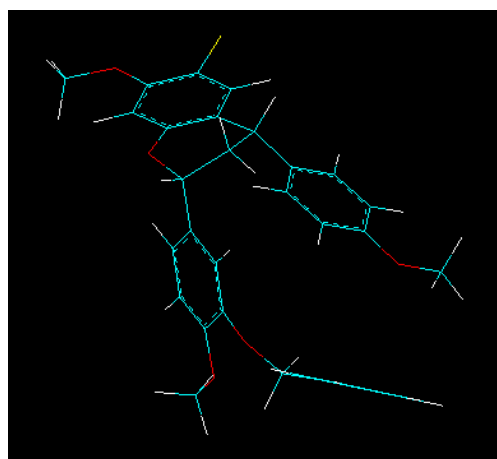
Minor

**42, Major**

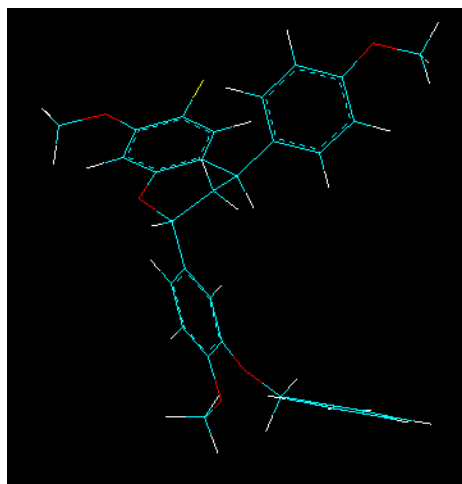
Ar = <i>p</i> -(OMe)Ph Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-2	H-4 (106.3 %)
	H-3α	H-2 (4.6 %)
		H-3β (15.8 %)
		H-4 (6.5 %)
	H-3β	H-3α (6.9 %)
		H-4

**42, Minor**

Ar = <i>p</i> -(OMe)Ph Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-2	H-3β (3.4 %)
	H-4	H-3α (6.2 %)



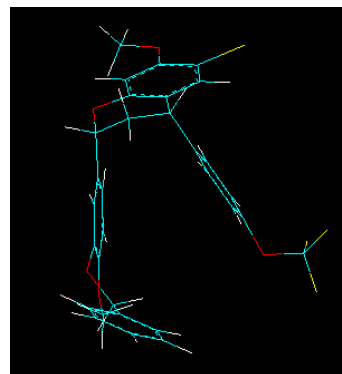
Major



Minor

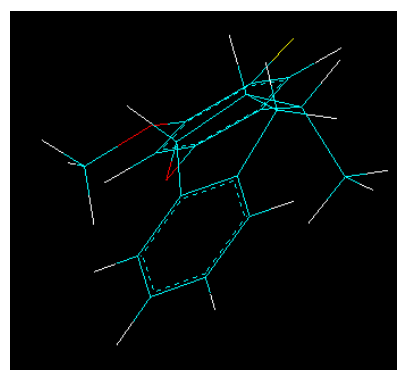
## 43

Ar = <i>p</i> -(OCF <sub>3</sub> )Ph Ar' = <i>p</i> -(OMe)- <i>m</i> -(OBn)Ph	Irradiation	Position (% nOe)
	H-2	H-3α (3.1 %)
		H-4 (6.9 %)
	H-3α	H-2 (5.7%)
		H-3β (22.5 %)
		H-4 (7.7 %)
	H-3β	H-3α (14.4 %)
	H-4	H-2 (7.8 %)
		H-3α (4.9 %)

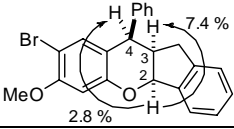
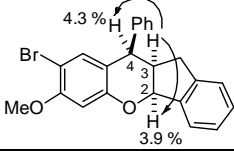
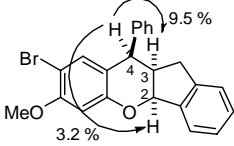


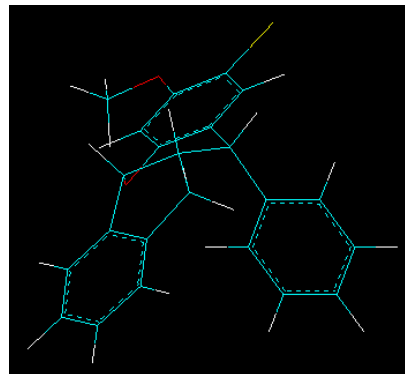
## 44, Major

	Irradiation	Position (% nOe)
	H-2	H-3 (1.9 %)
		H-4 (6.1 %)
	H-3	H-2 (7.4 %)
		H-4 (6.0 %)
	H-4	H-2 (6.8 %)
		H-3 (5.7 %)

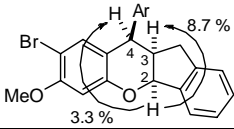
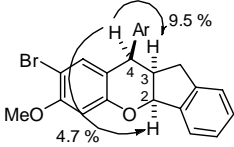


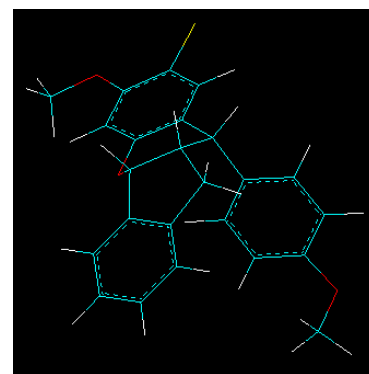
## 45, Major

	Irradiation	Position (% nOe)
	H-2	H-3 (7.4 %)
		H-4 (2.8 %)
	H-3	H-2 (3.9 %)
		H-4 (4.3 %)
	H-4	H-2 (3.2 %)
		H-3 (9.5 %)

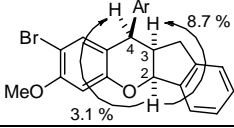
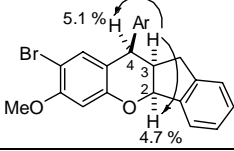
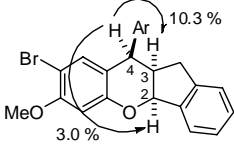


## 46, Major

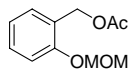
Ar = <i>p</i> -(OMe)Ph	Irradiation	Position (% nOe)
	H-2	H-3 (8.7 %)
		H-4 (3.3 %)
	H-4	H-2 (4.7 %)
		H-3 (9.5 %)



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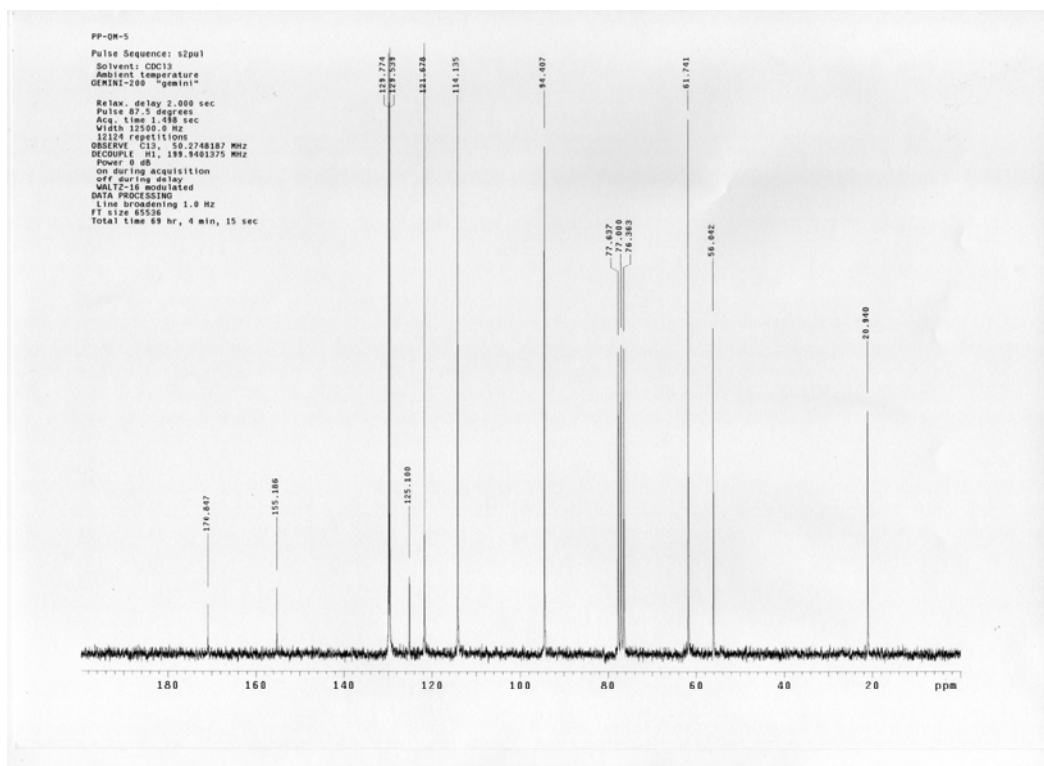
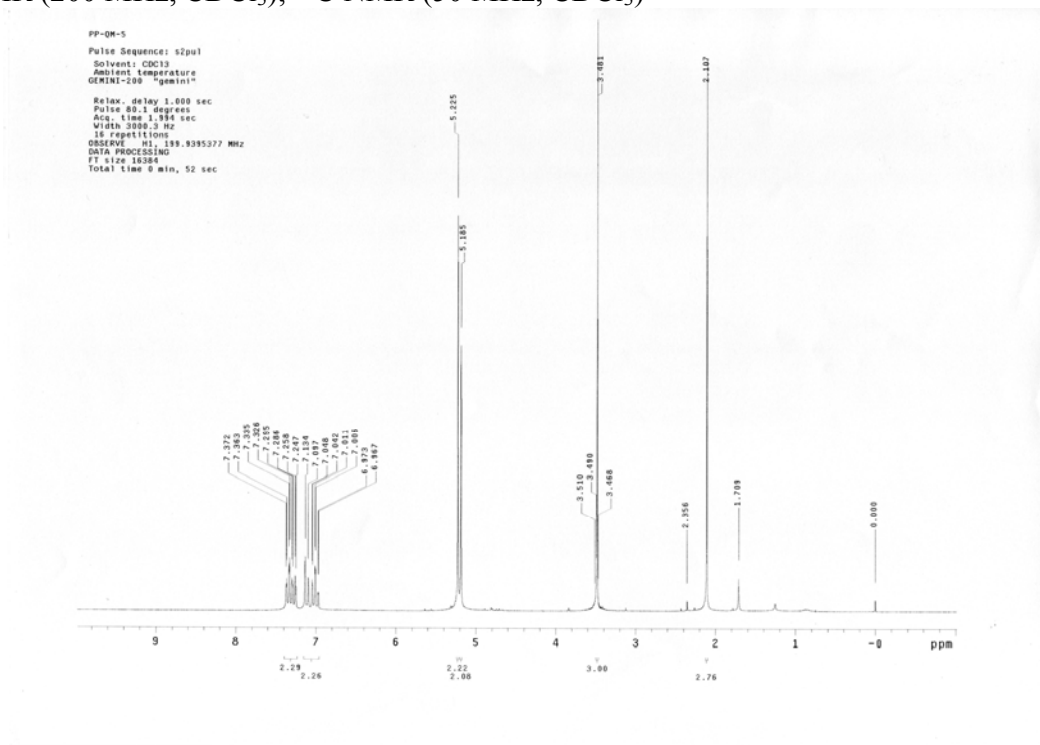
Ar = <i>p</i> -(OCF <sub>3</sub> )Ph	Irradiation	Position (% nOe)
	H-2	H-3 (8.7 %)
		H-4 (3.1 %)
	H-3	H-2 (4.7 %)
		H-4 (5.1 %)
	H-4	H-2 (3.2 %)
		H-3 (10.3 %)

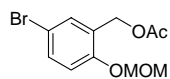




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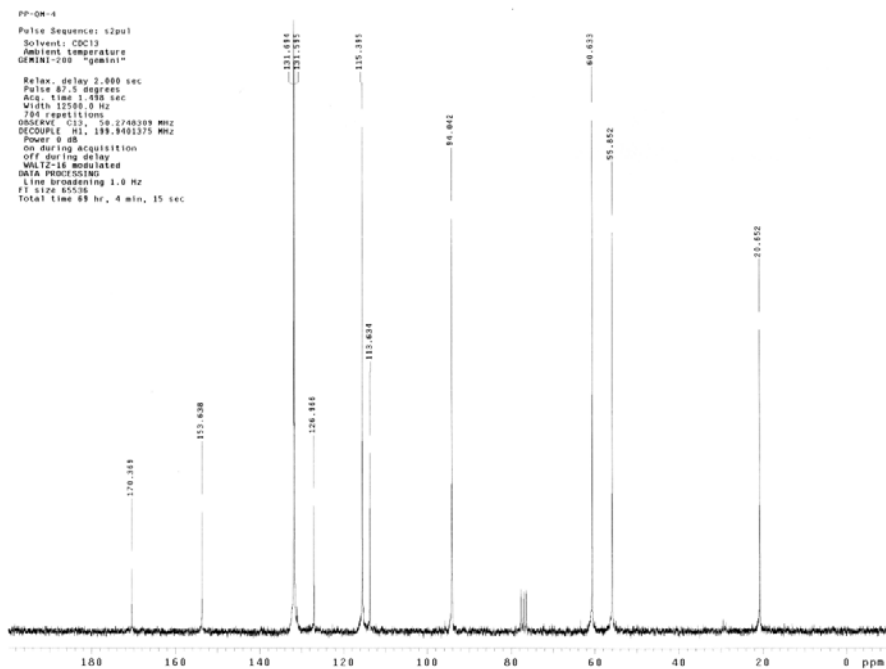
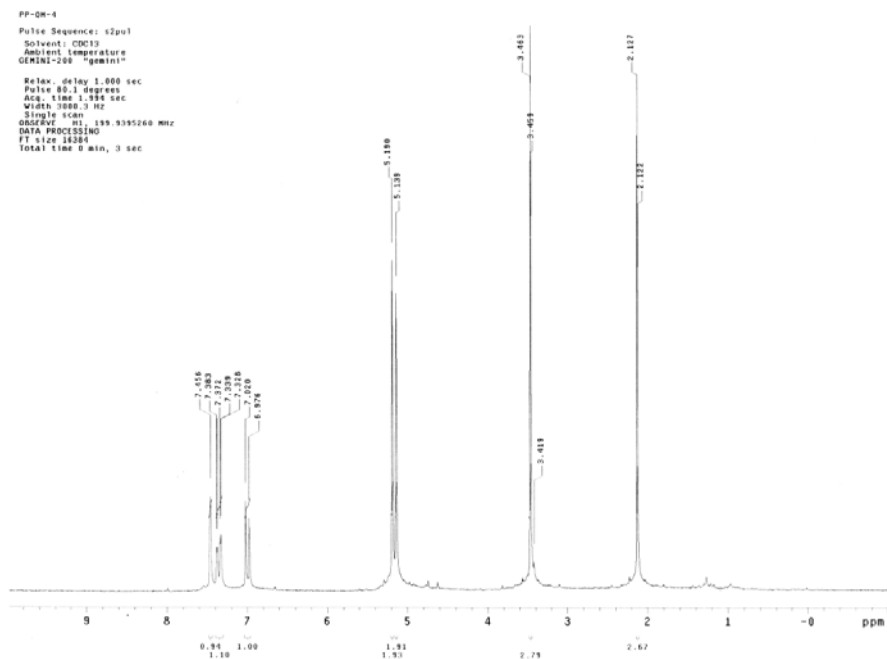
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )

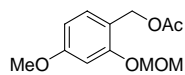




15

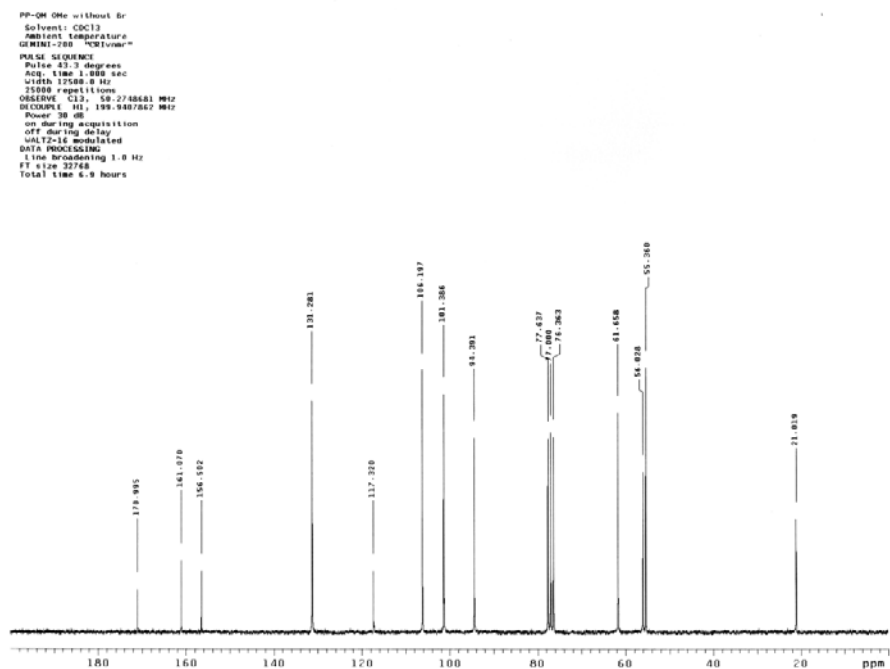
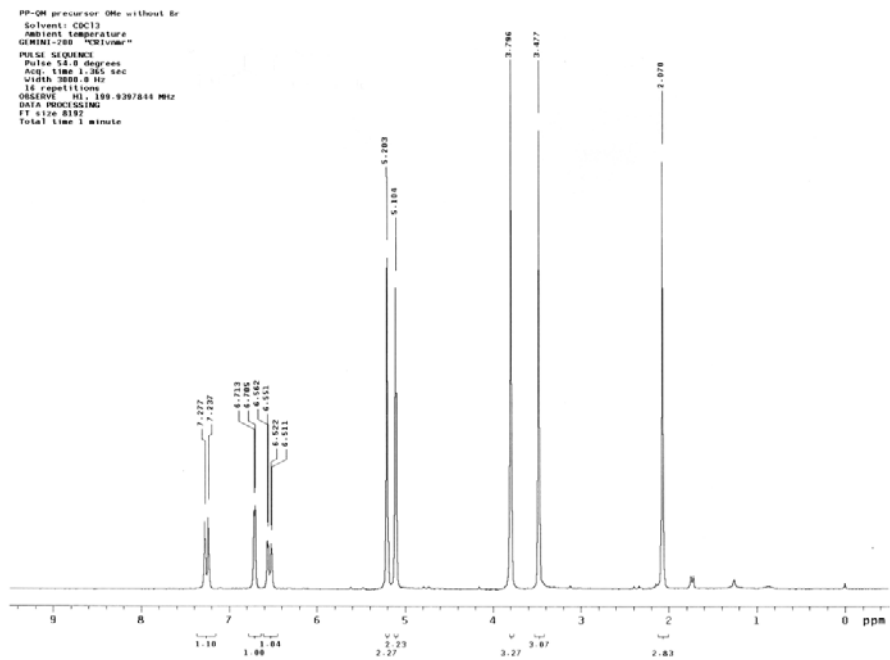
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )

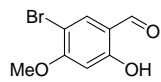




16

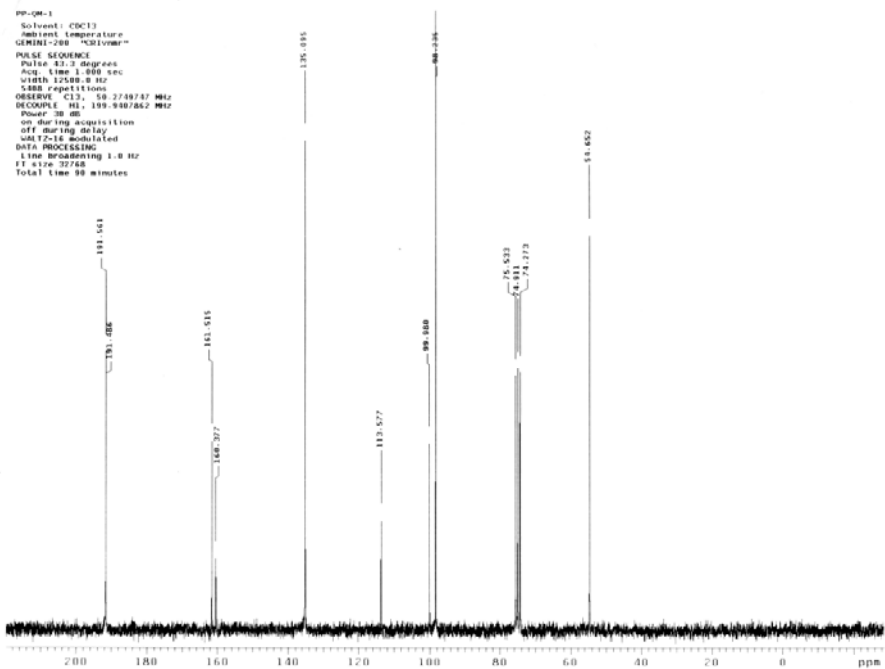
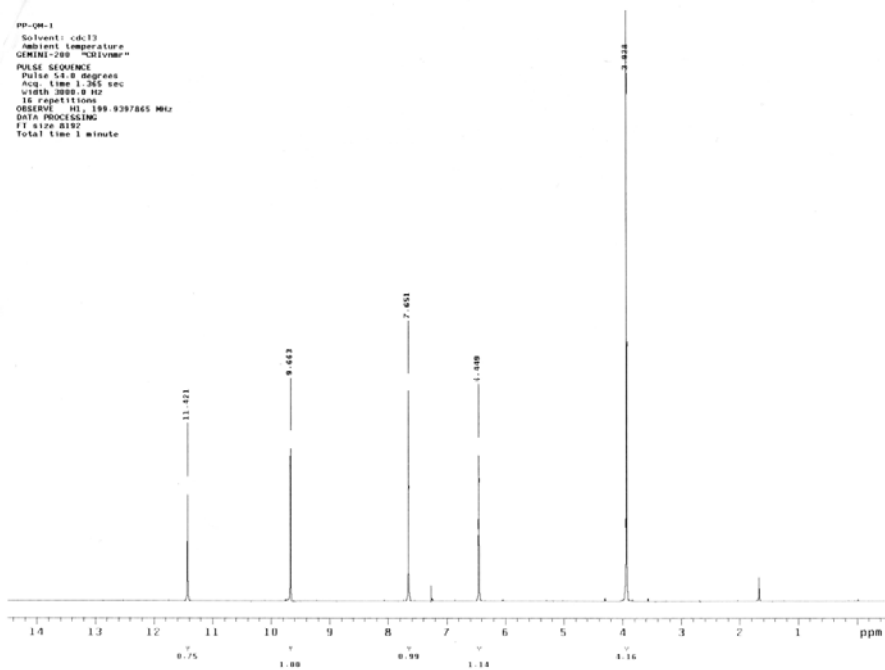
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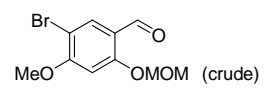




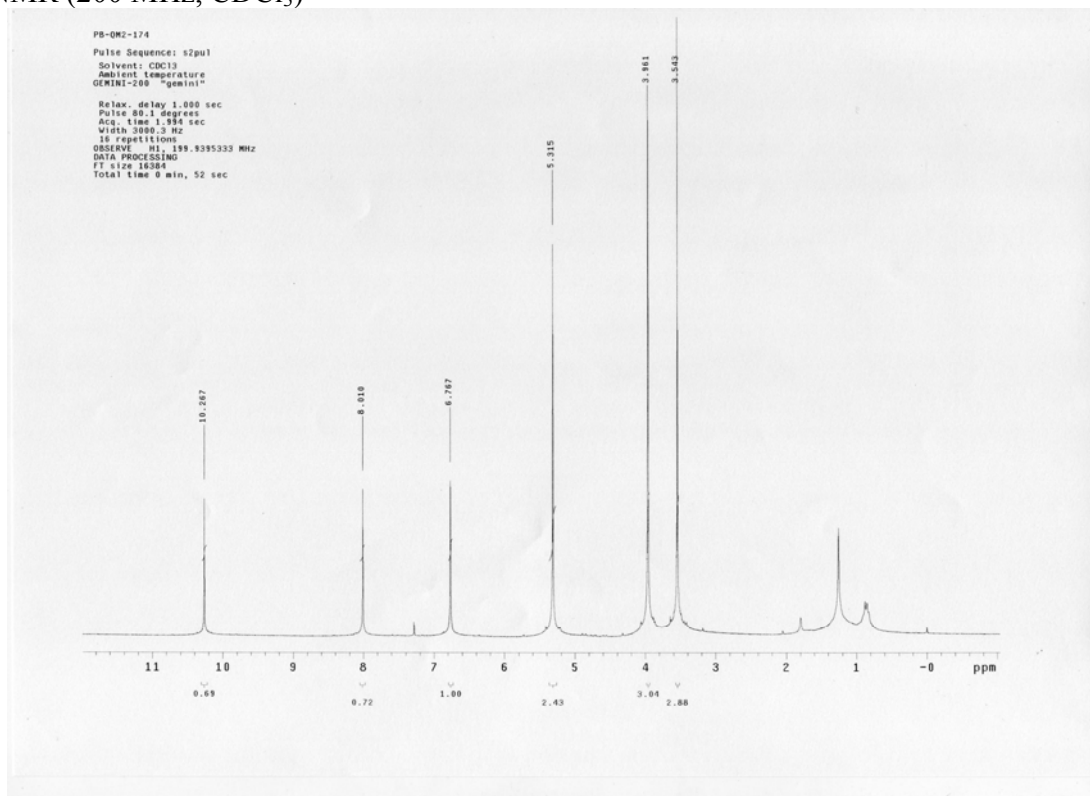
17

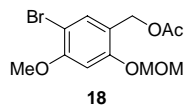
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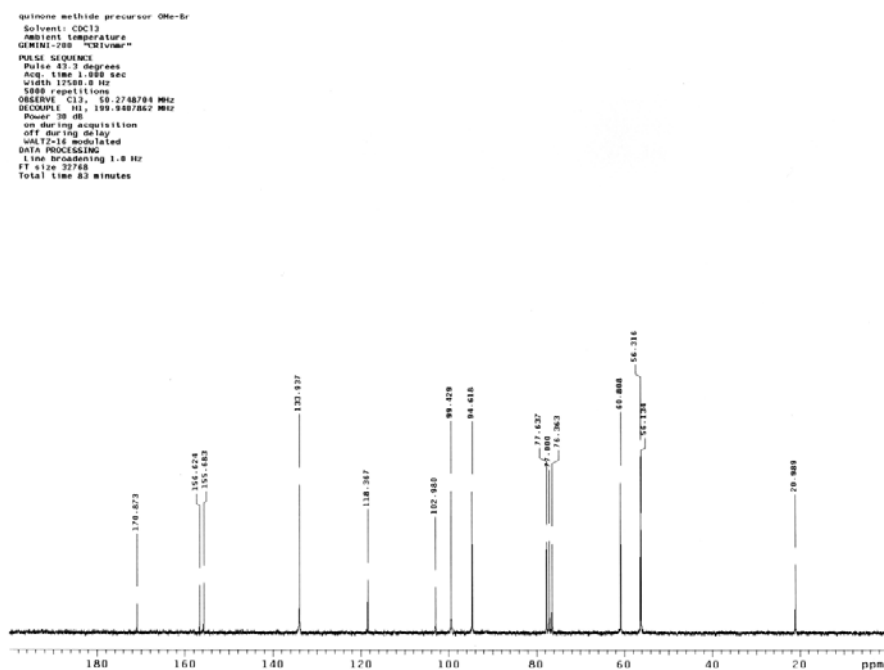
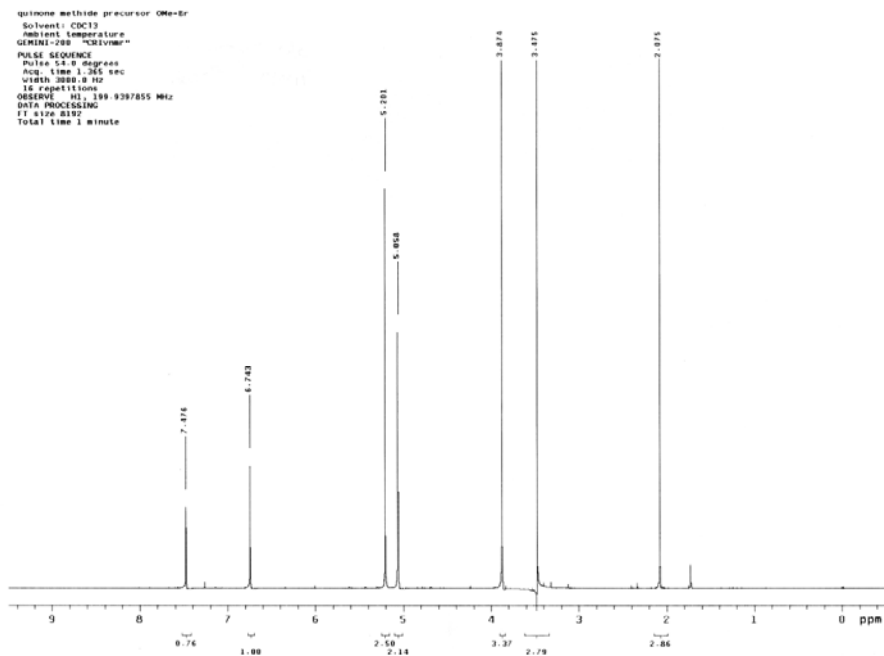


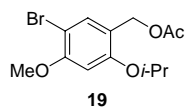
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)



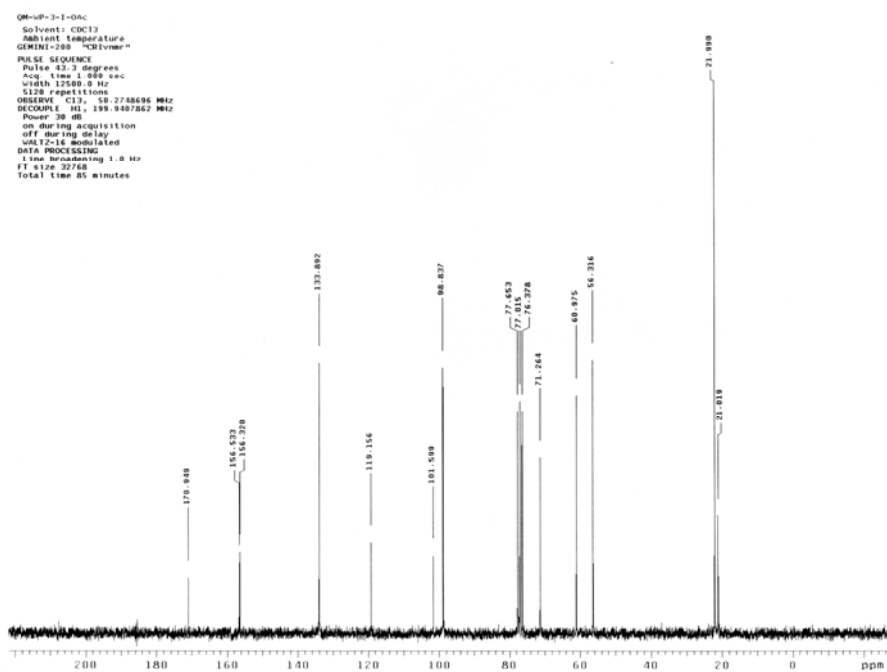
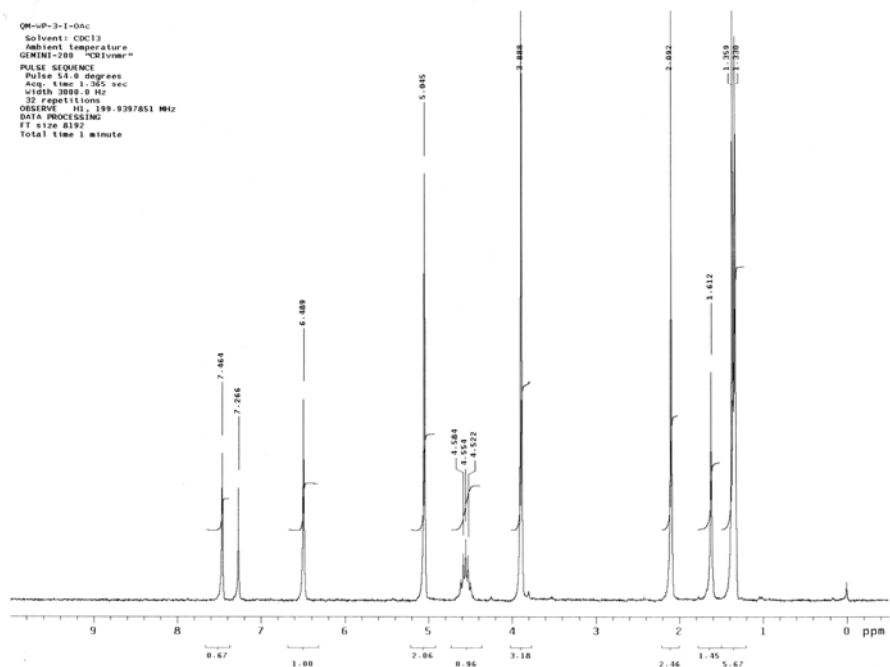


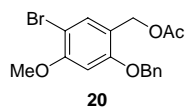
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )



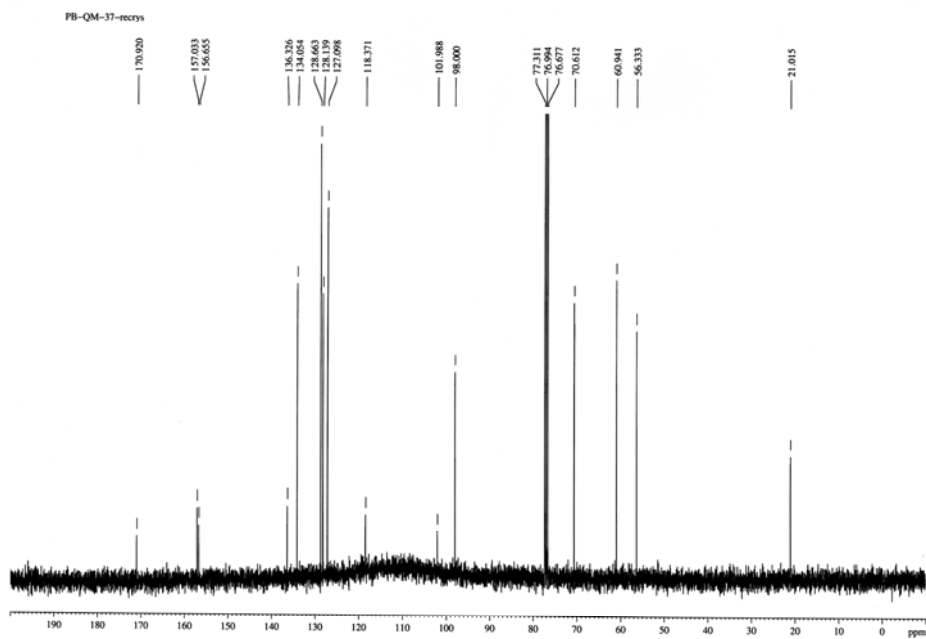
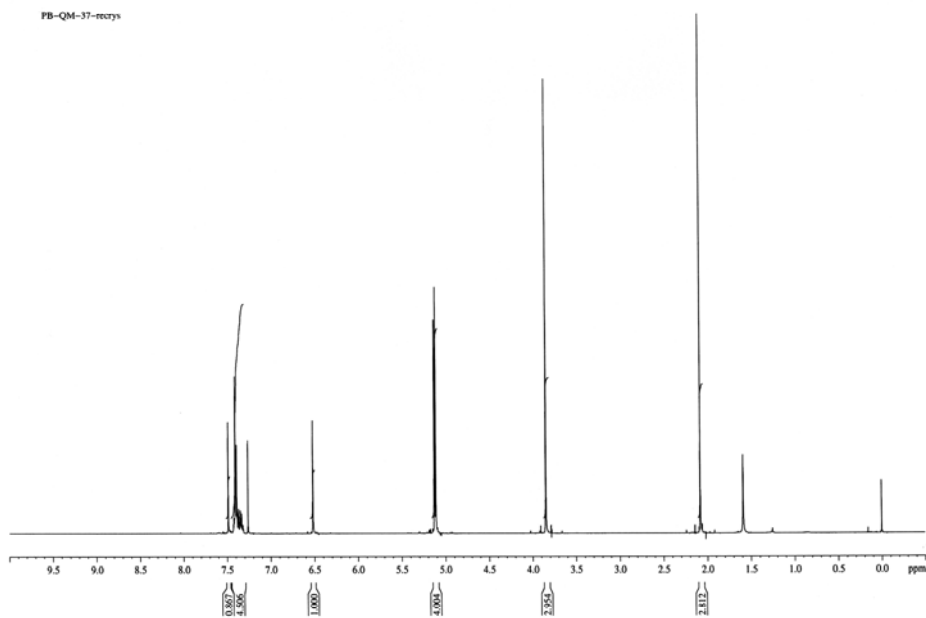


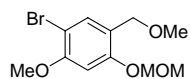
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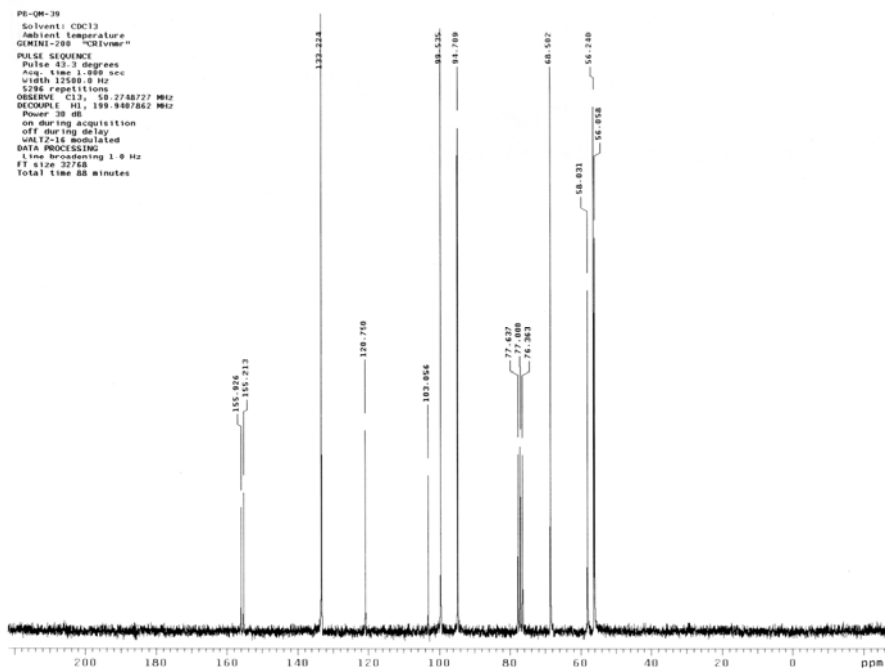
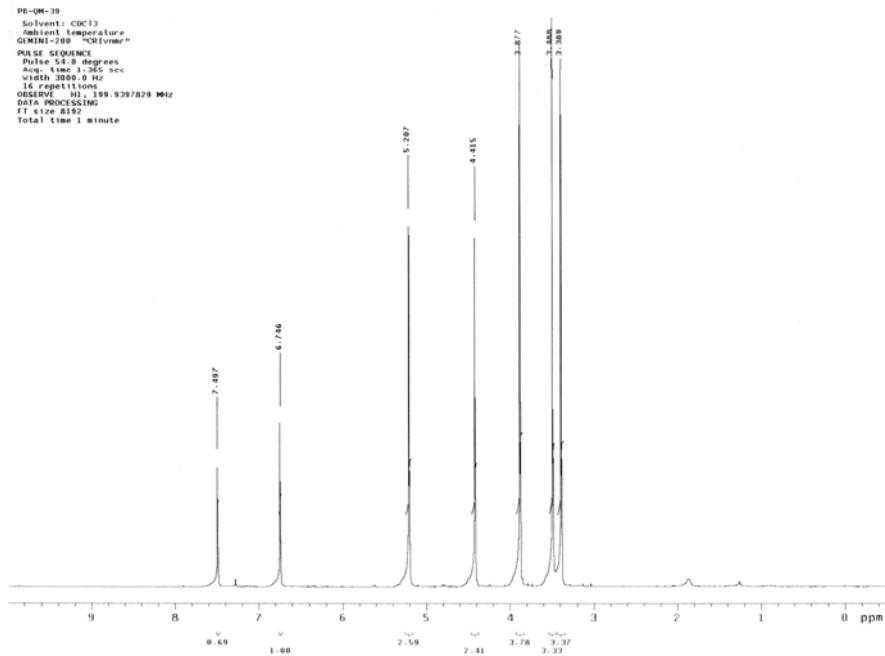
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

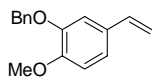




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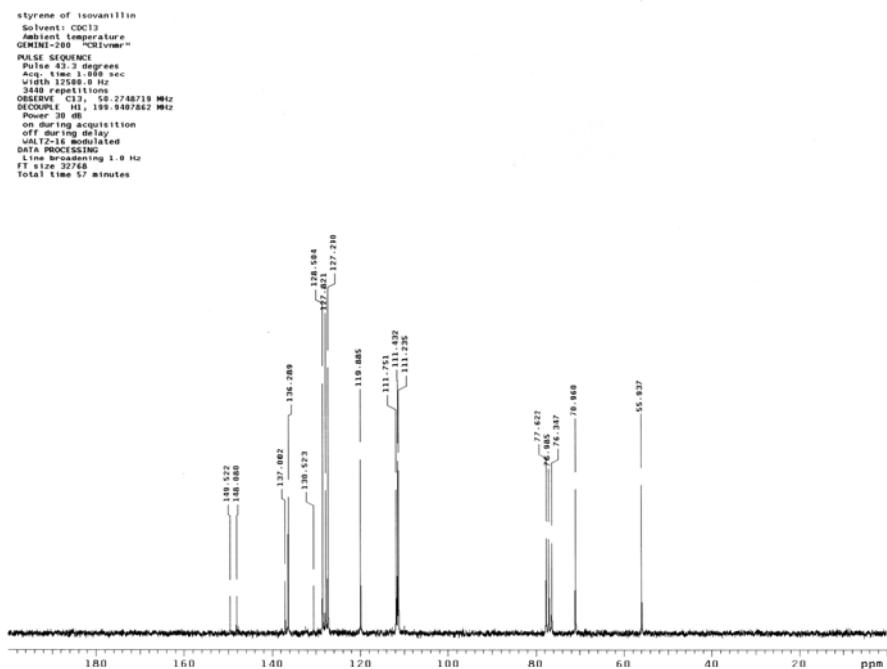
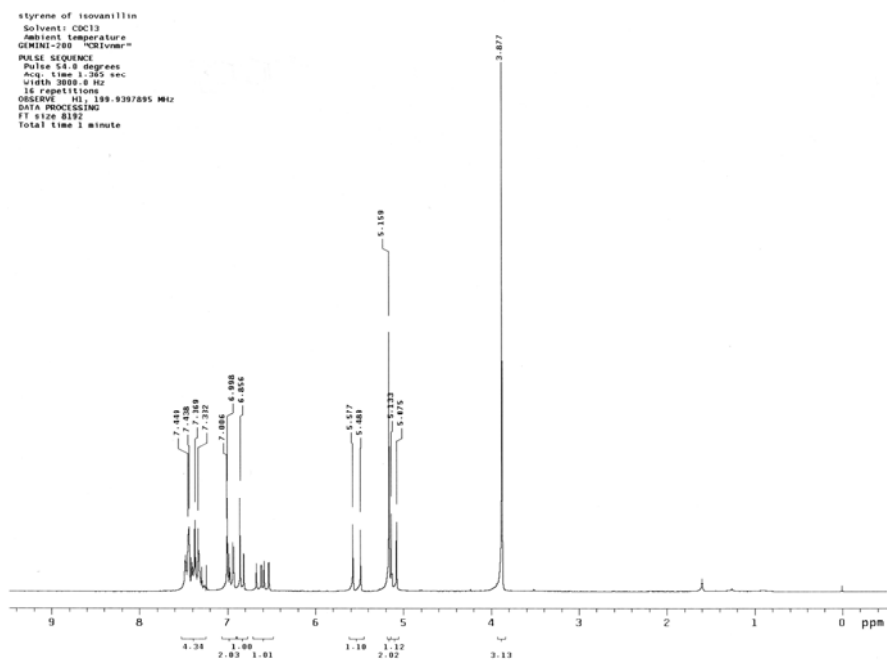
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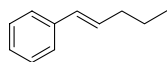




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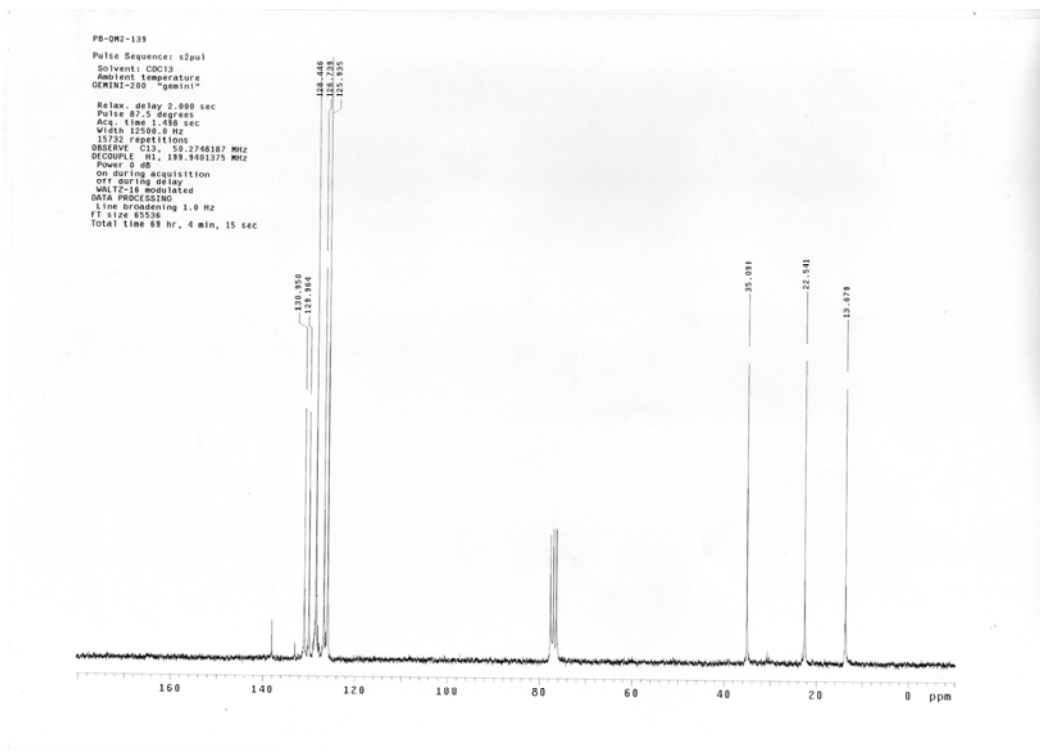
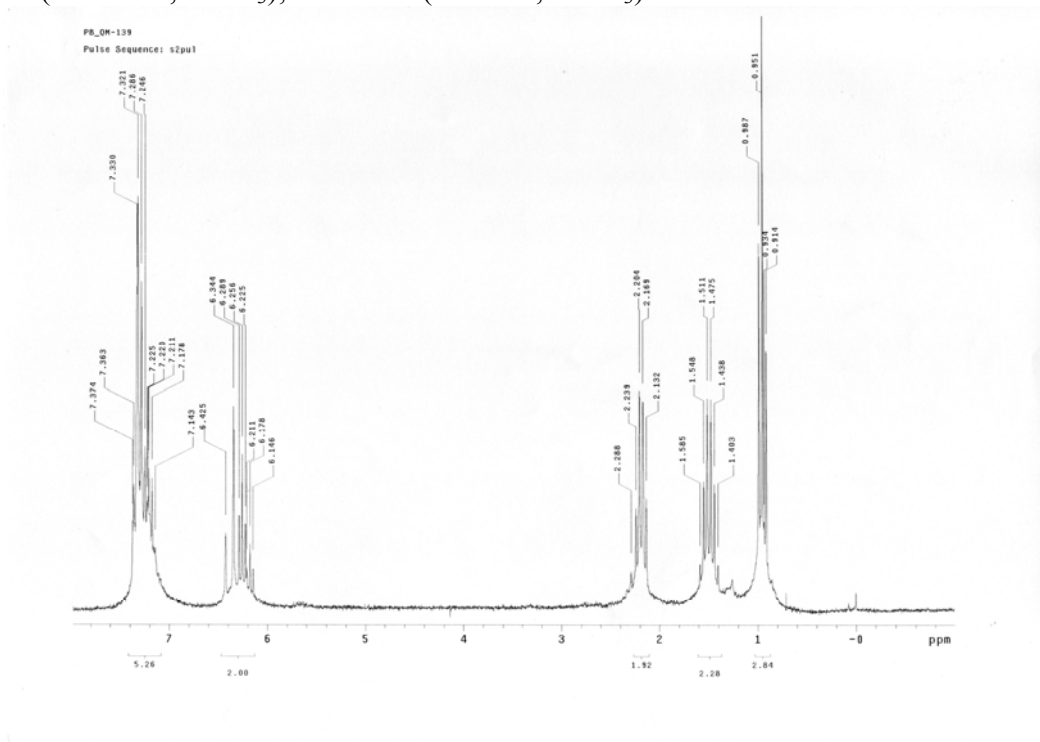
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )

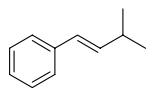




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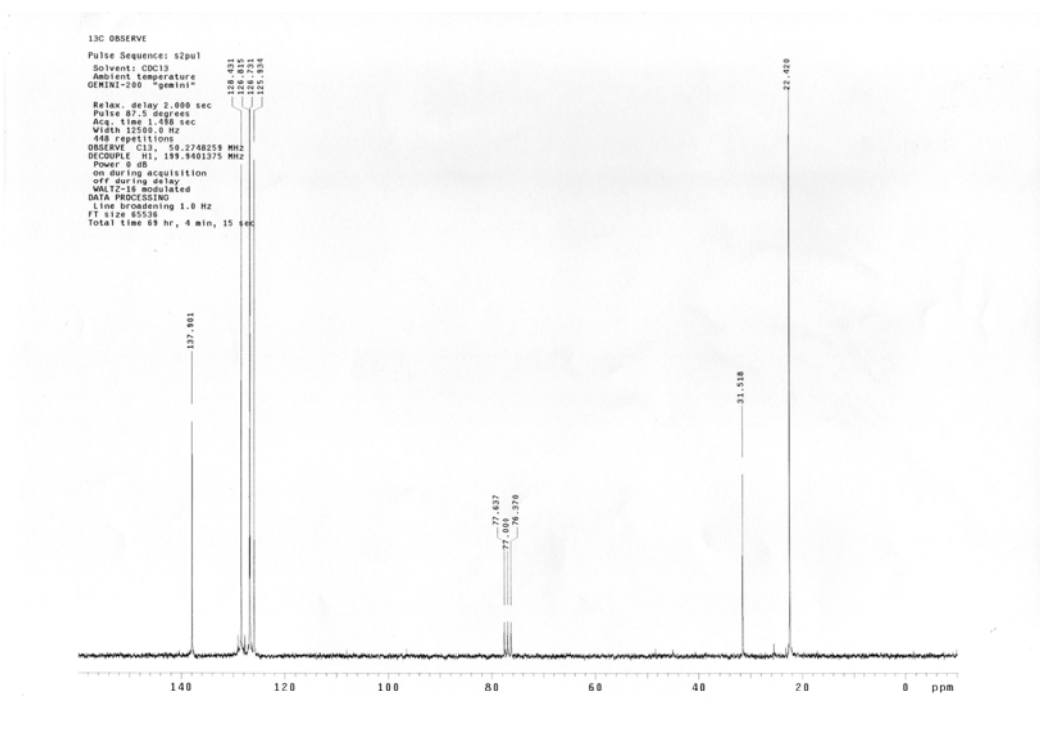
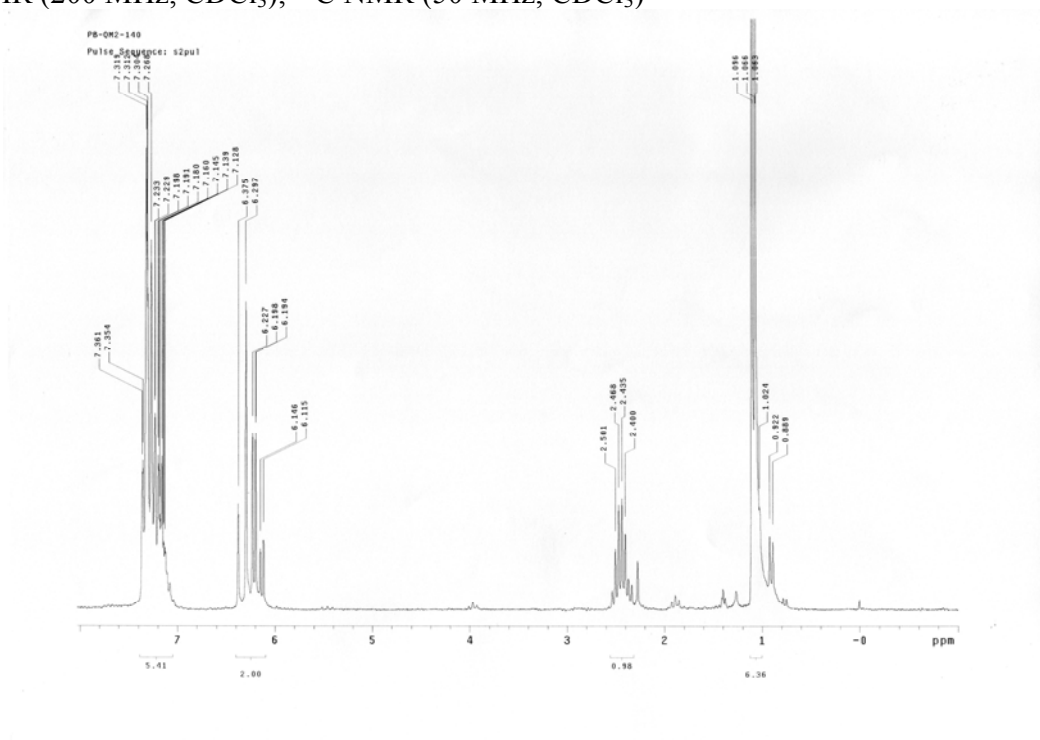
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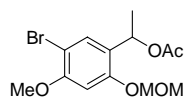




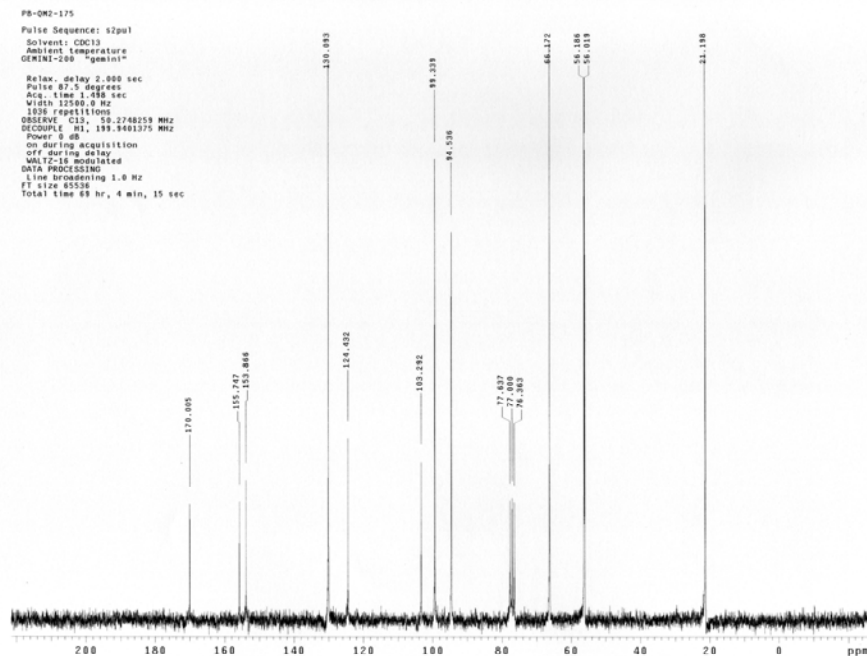
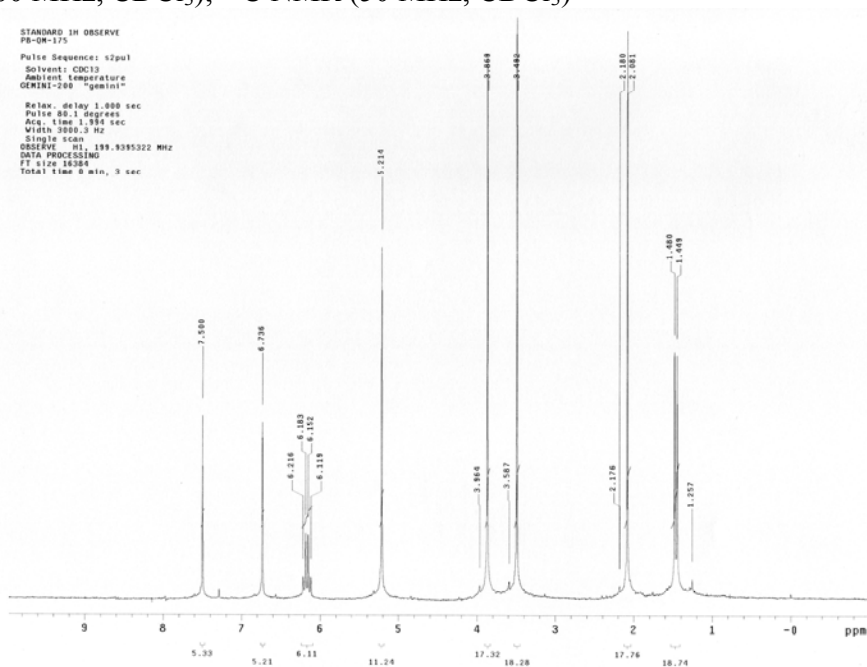
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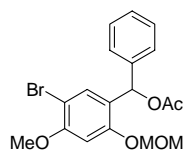
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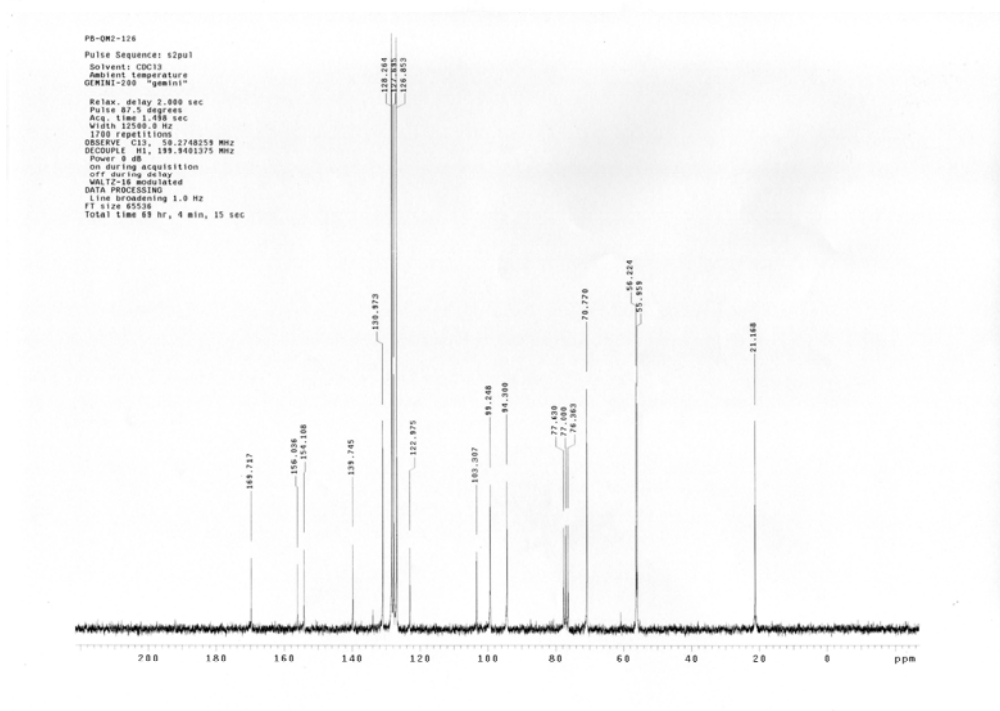
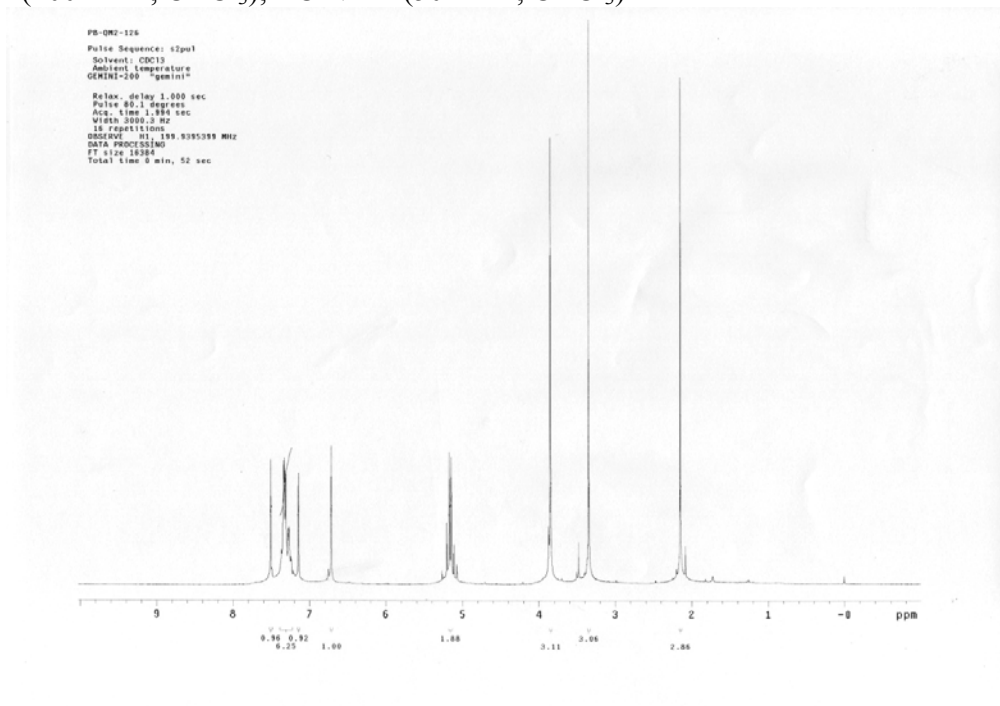
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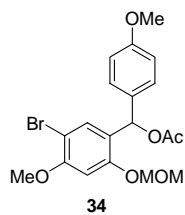




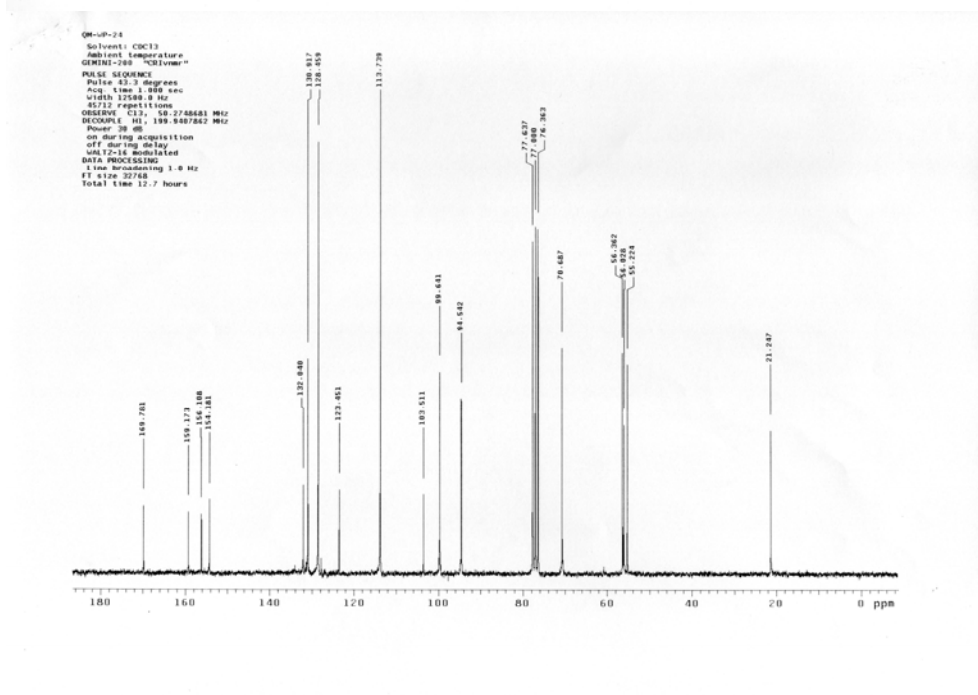
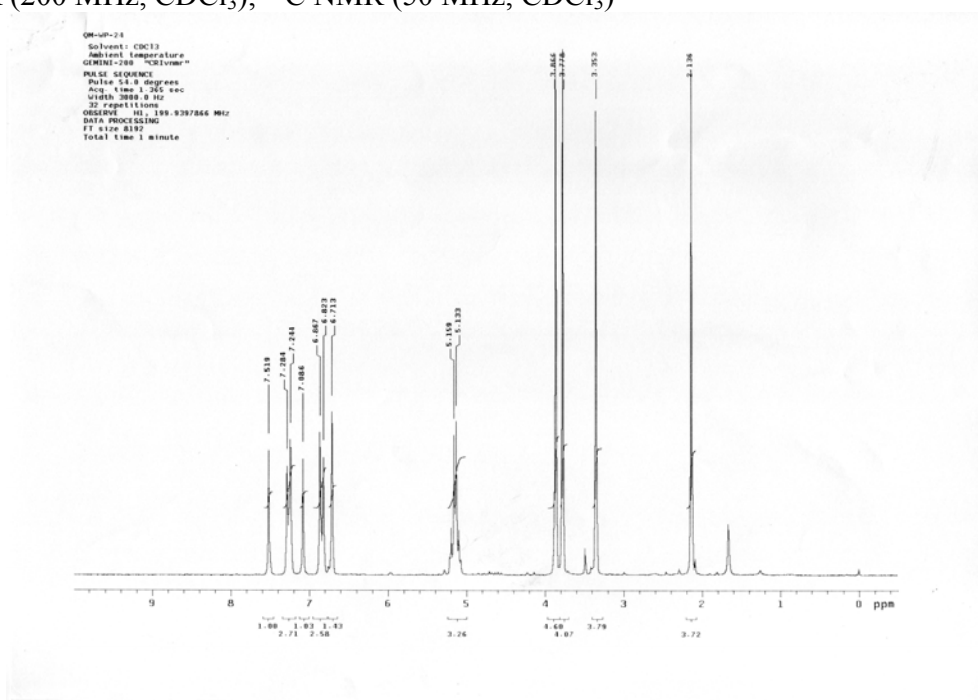
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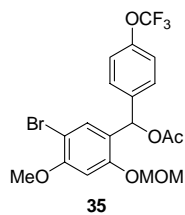
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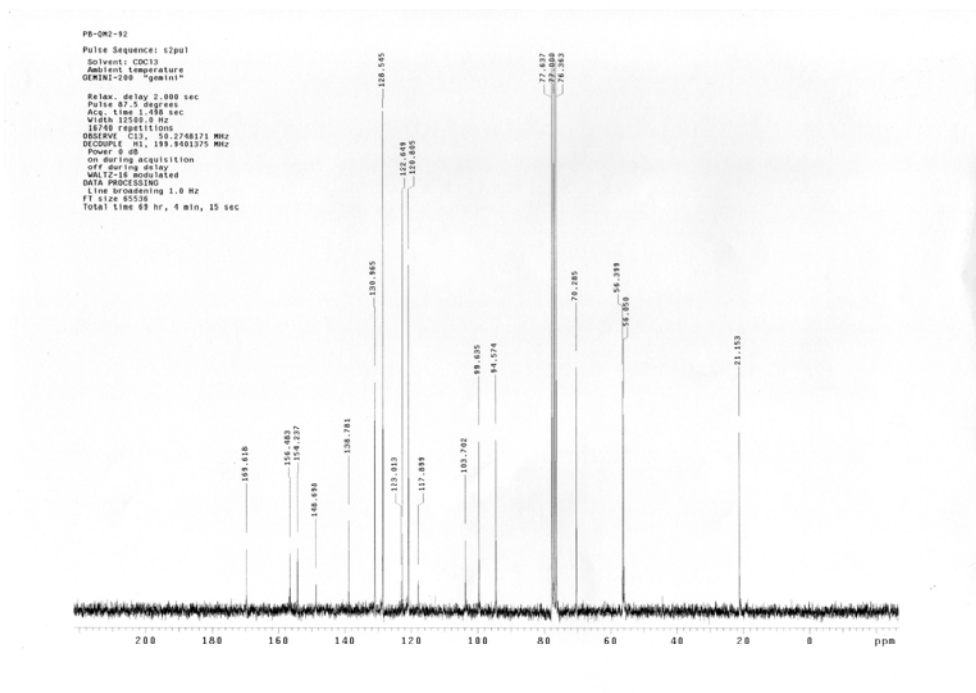
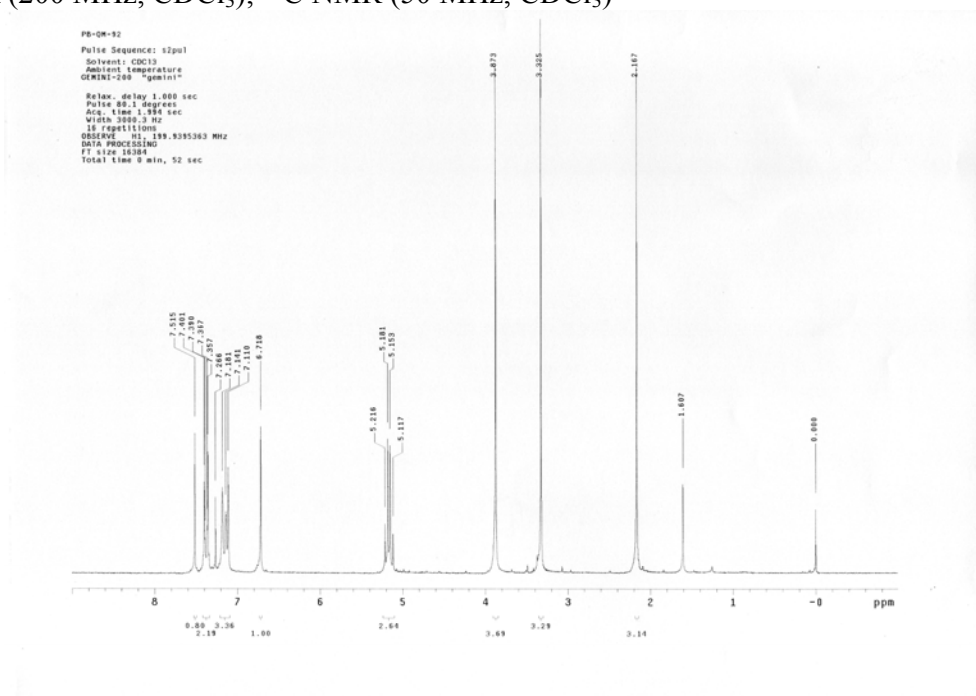


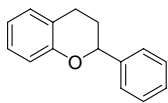
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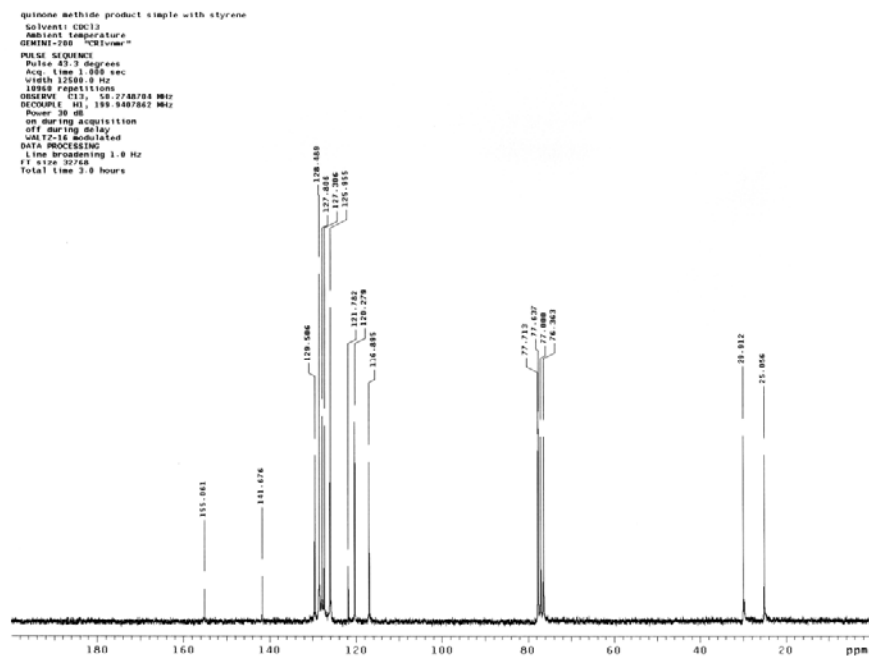
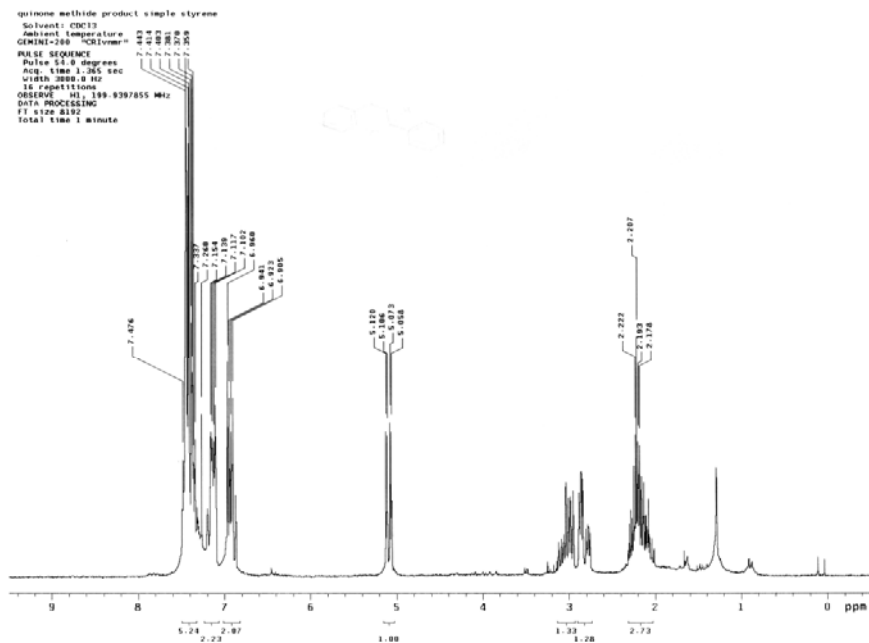
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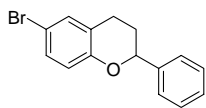




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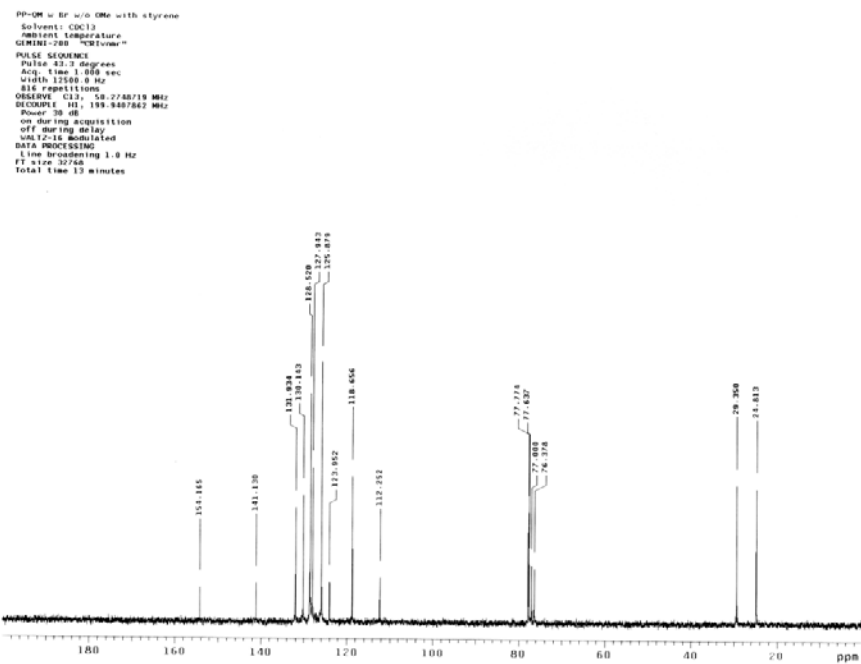
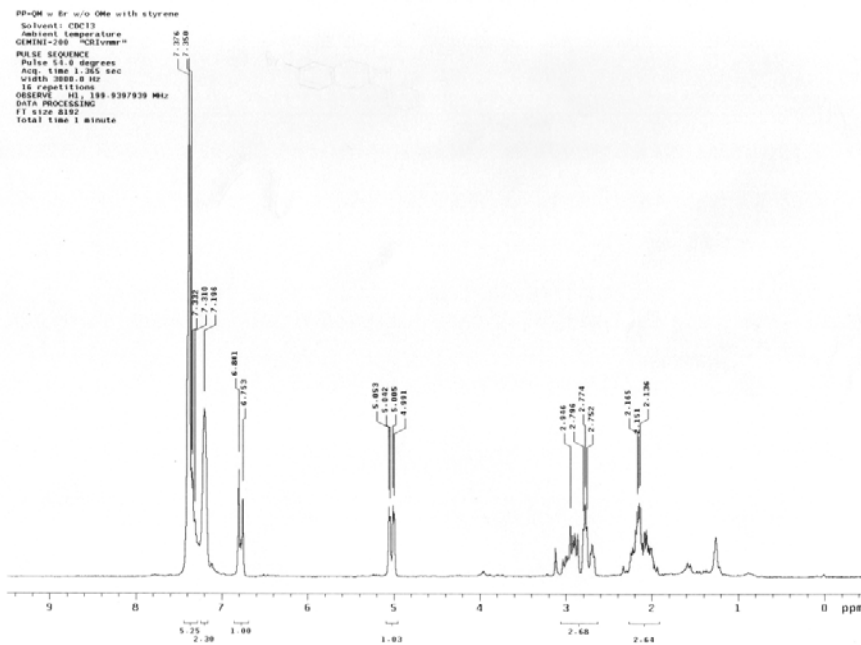
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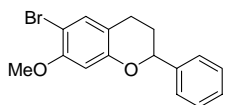




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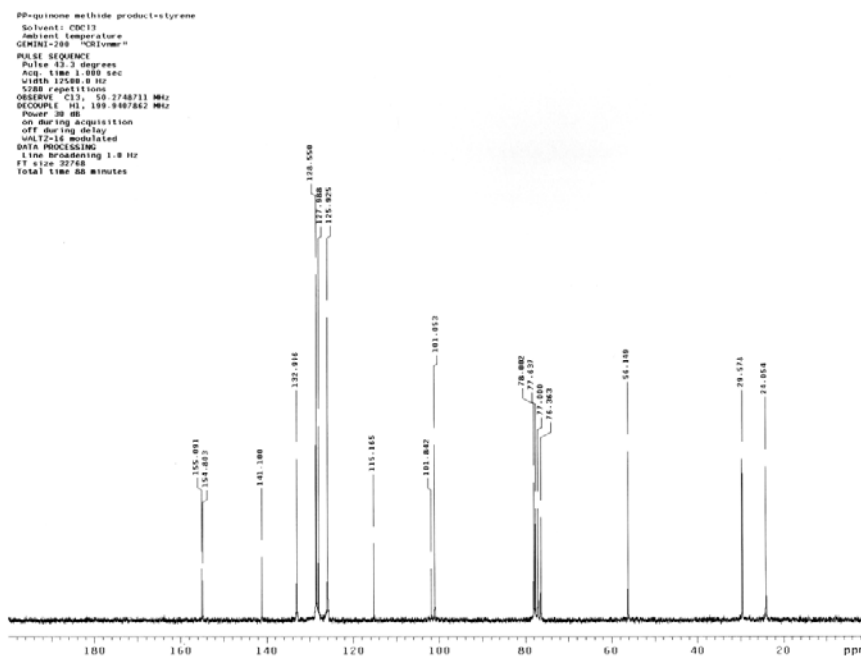
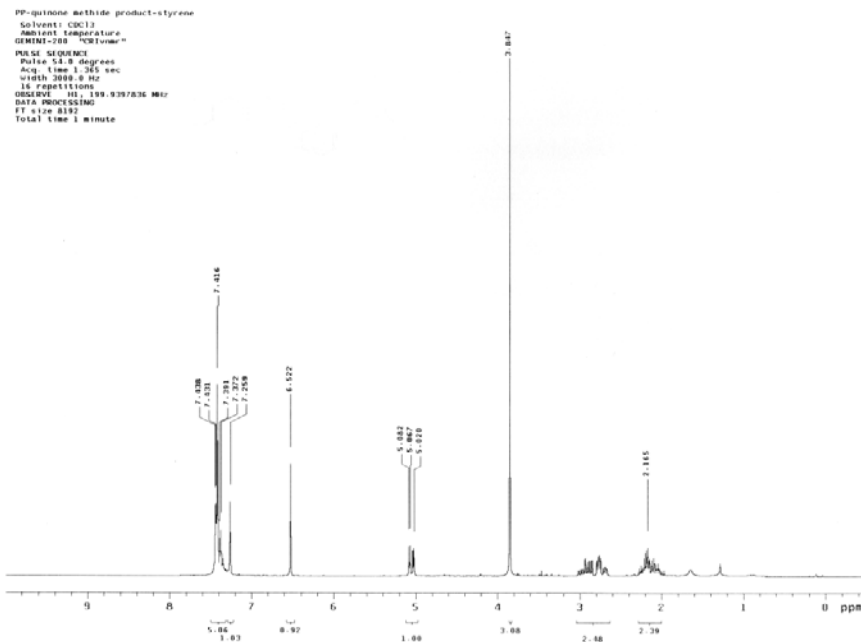
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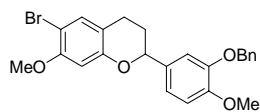




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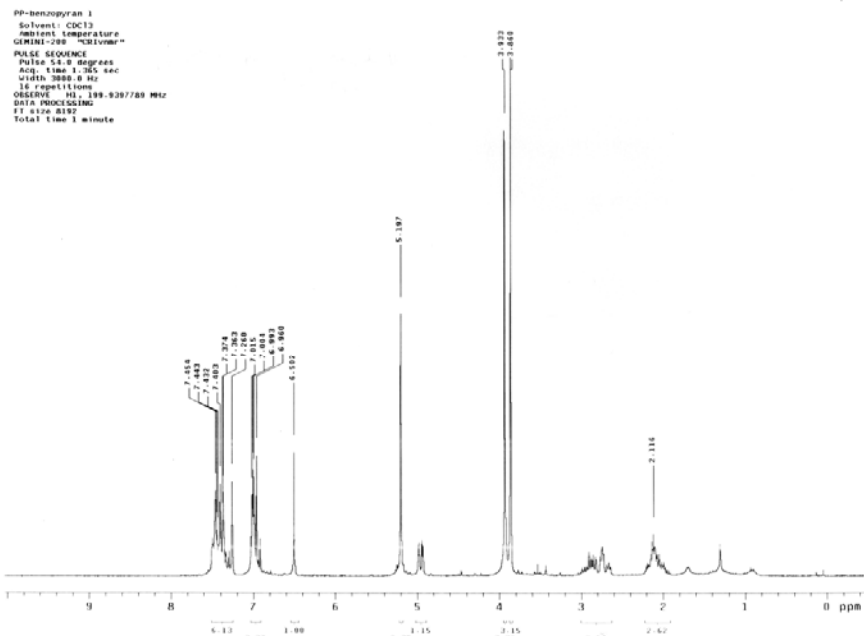
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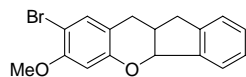




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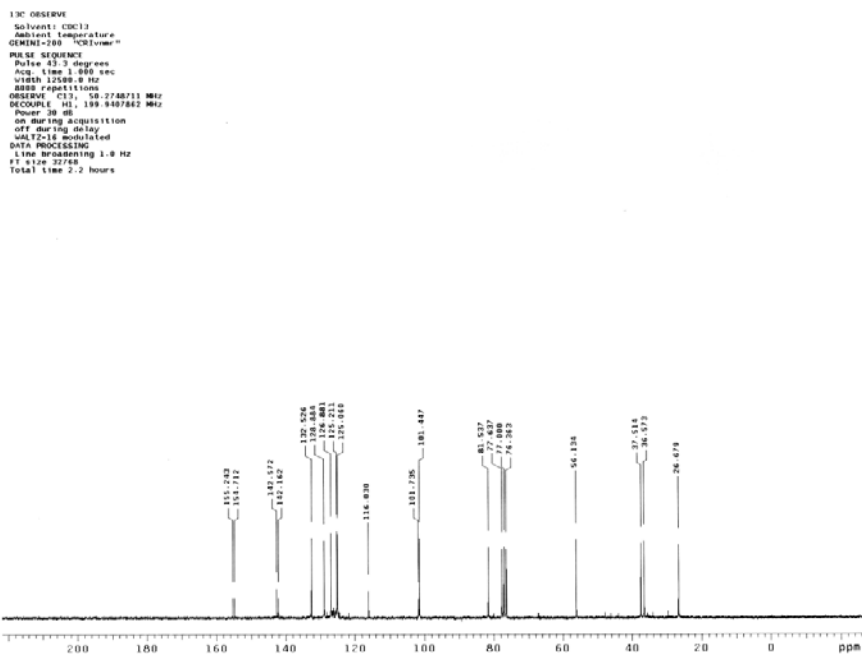
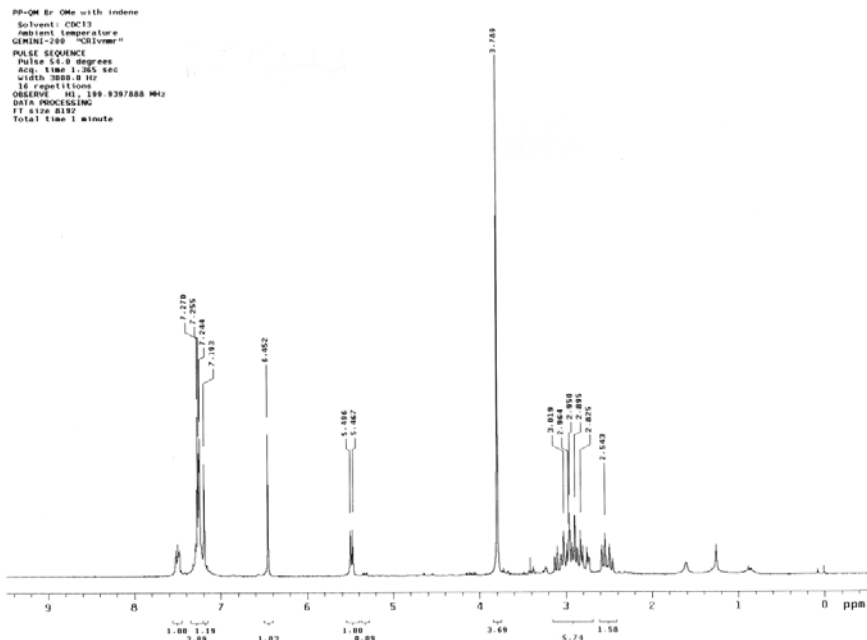
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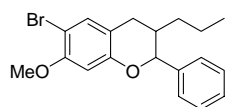




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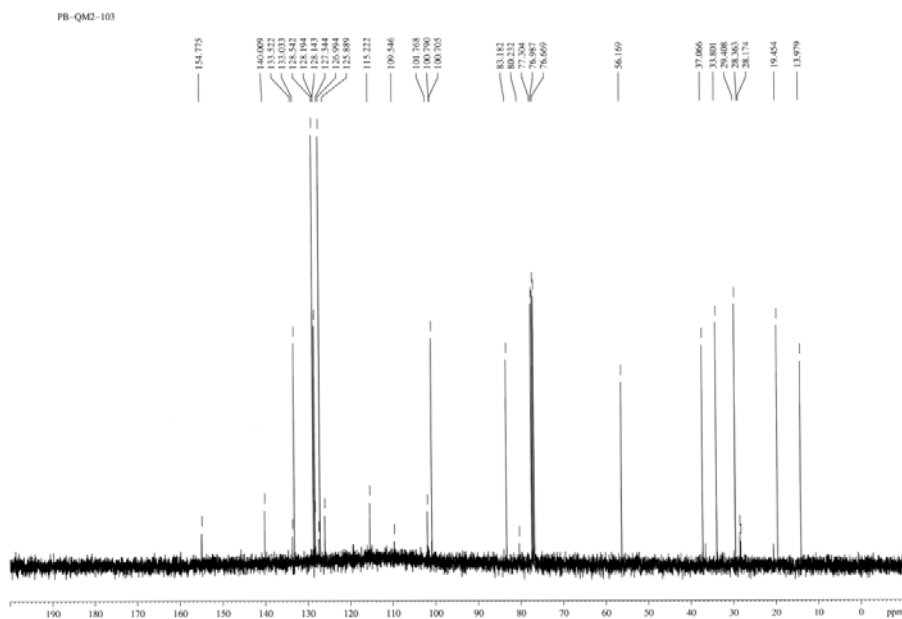
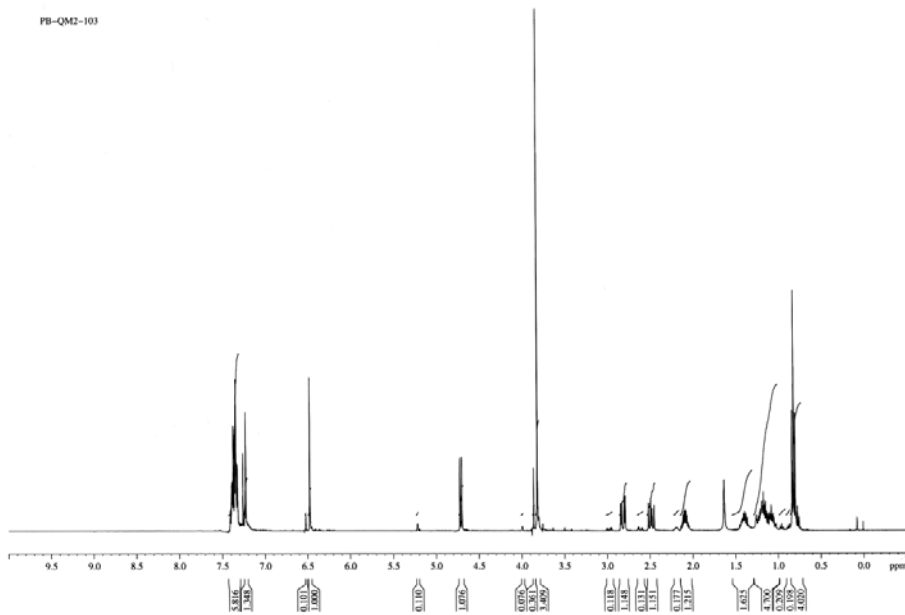
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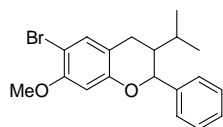




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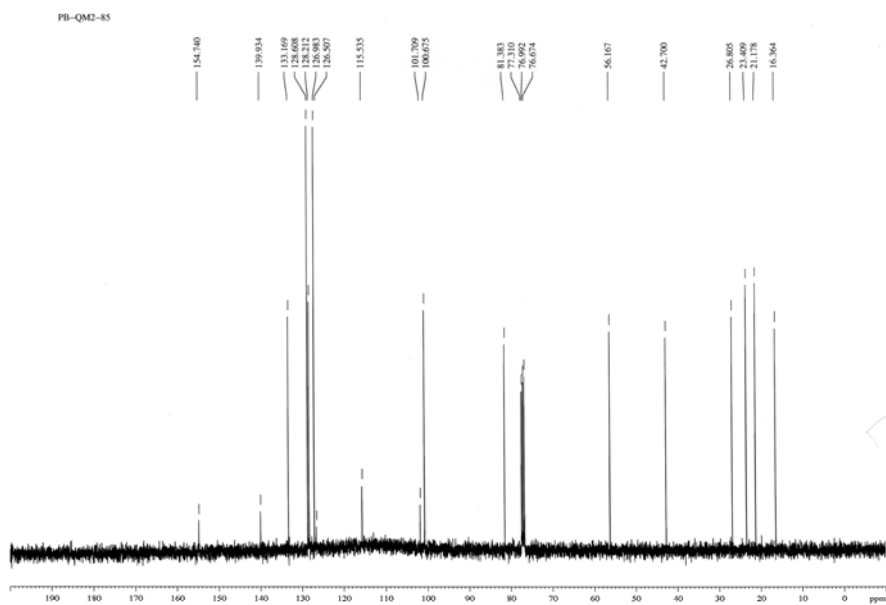
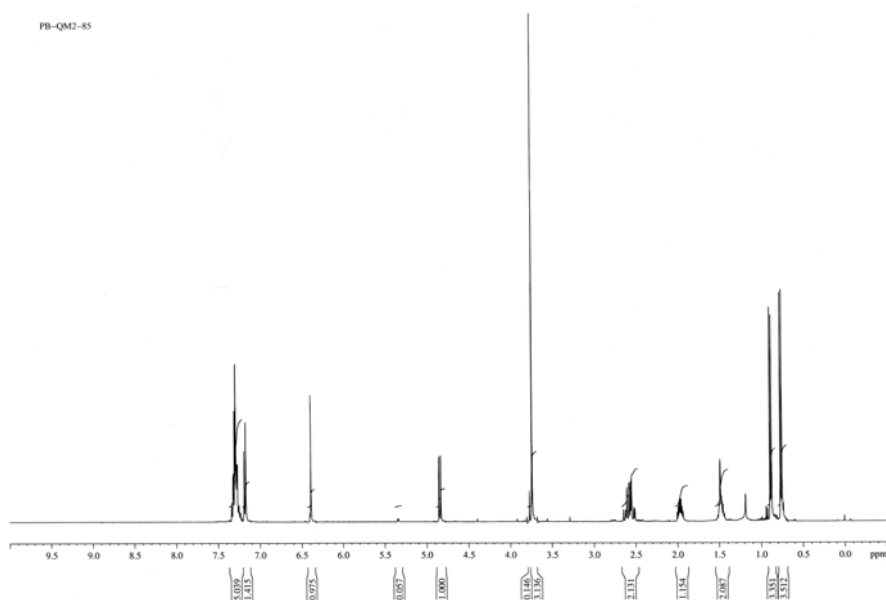
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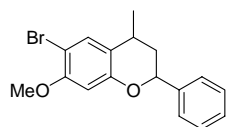




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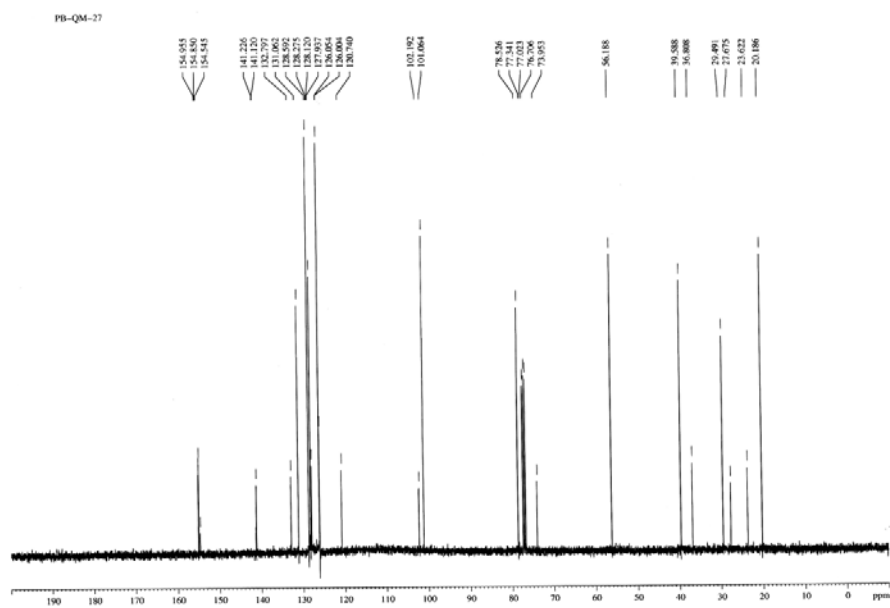
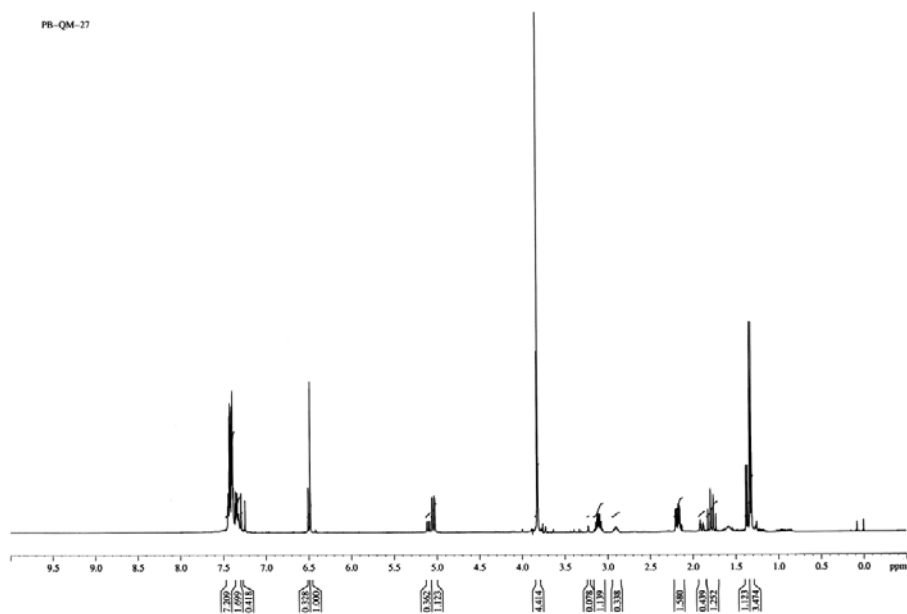
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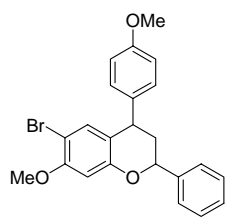


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$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

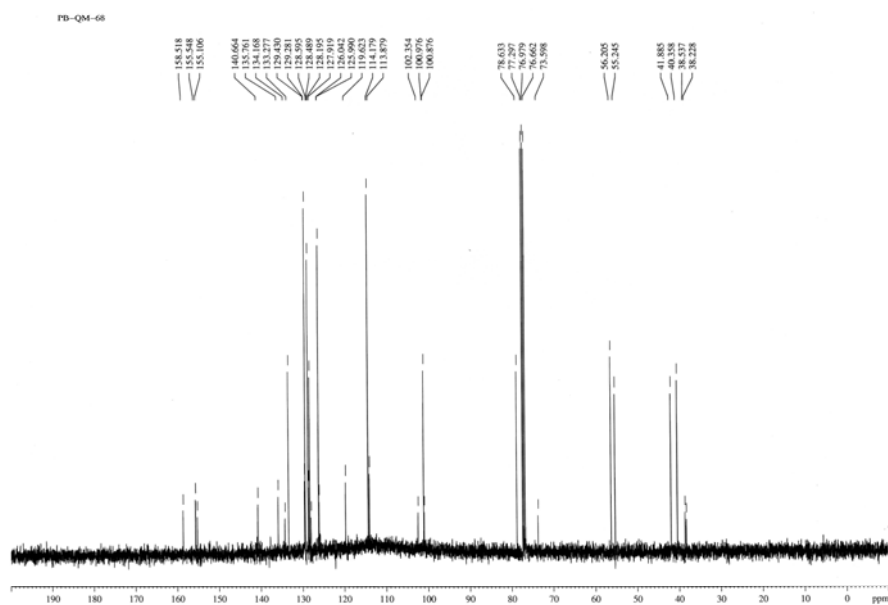
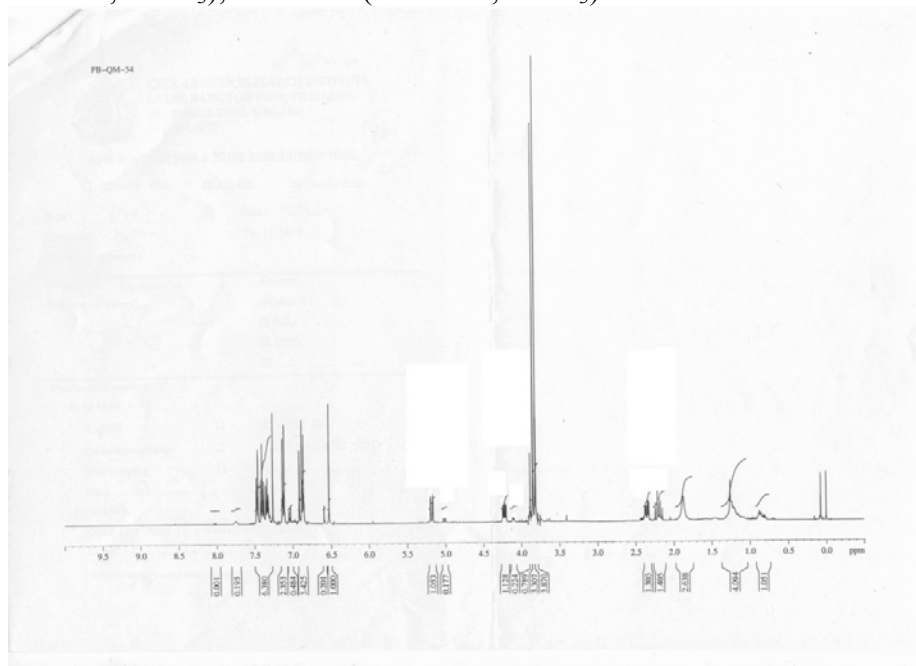


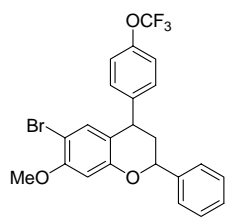




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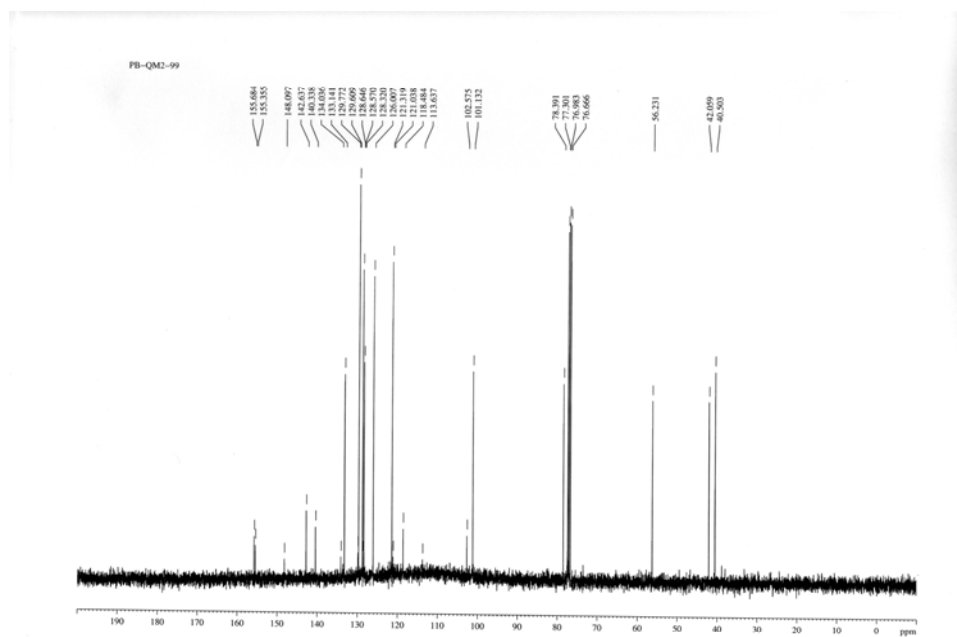
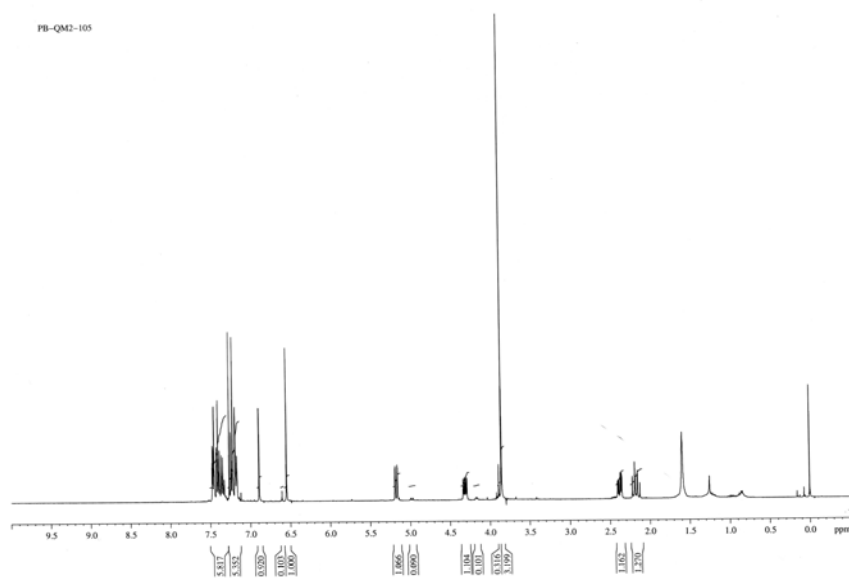
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

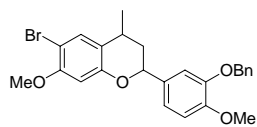




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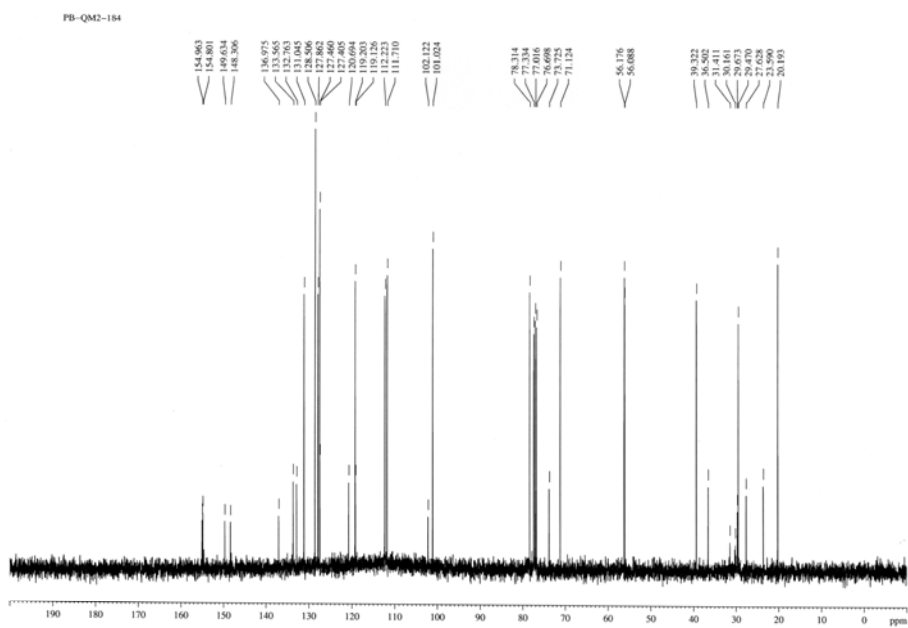
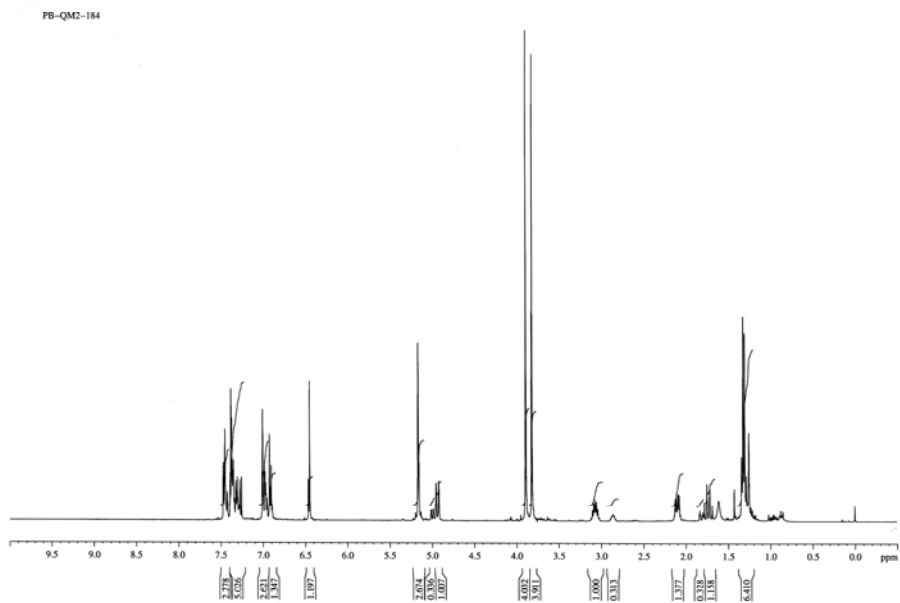
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

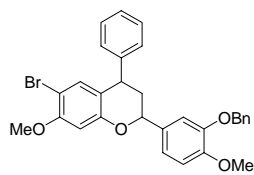




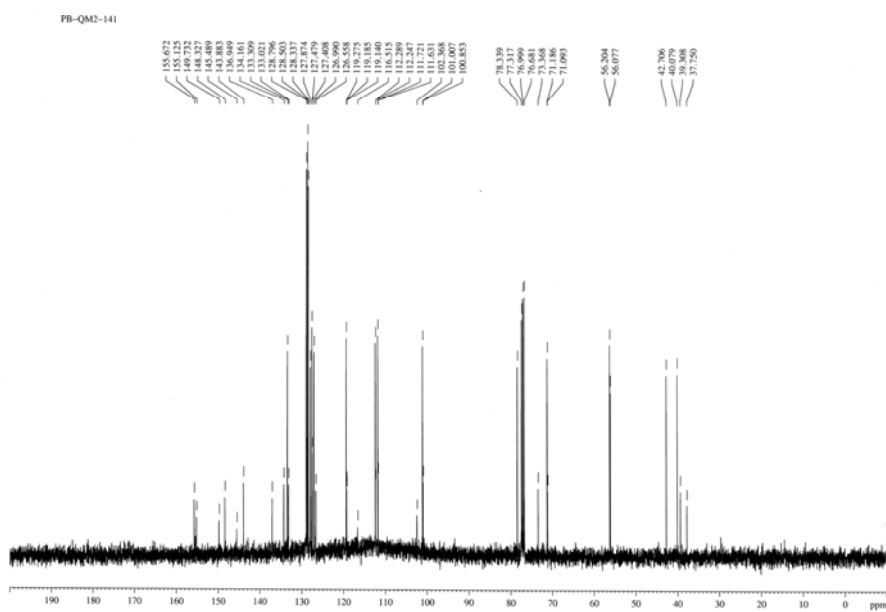
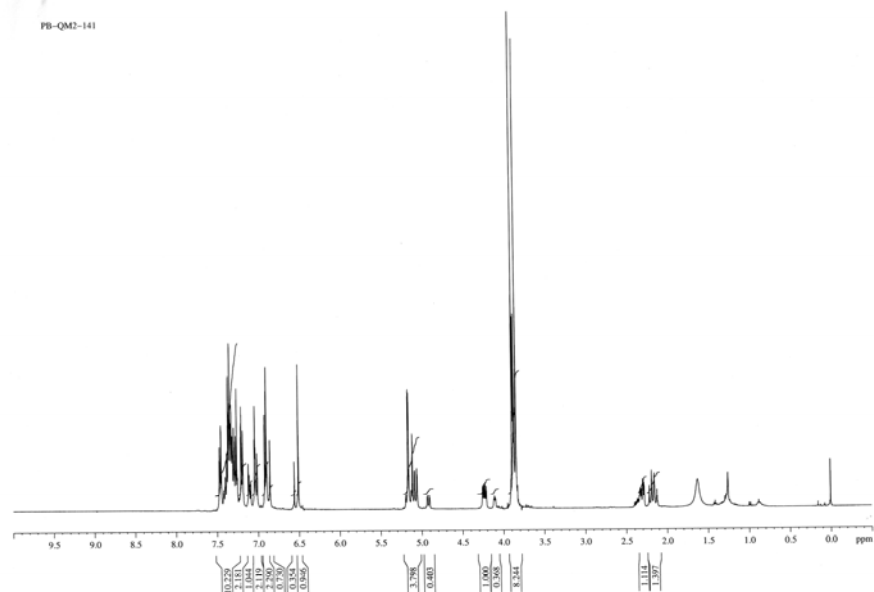
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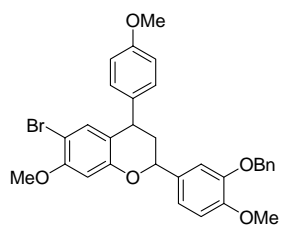
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





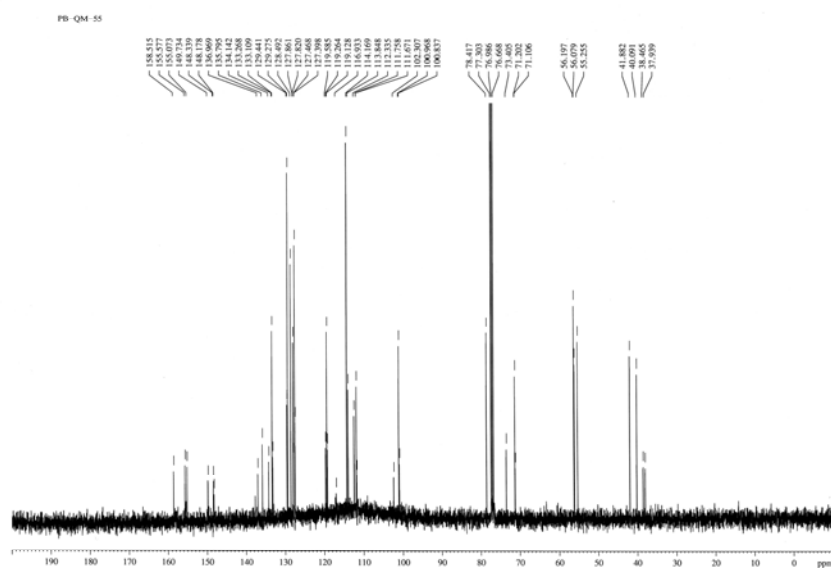
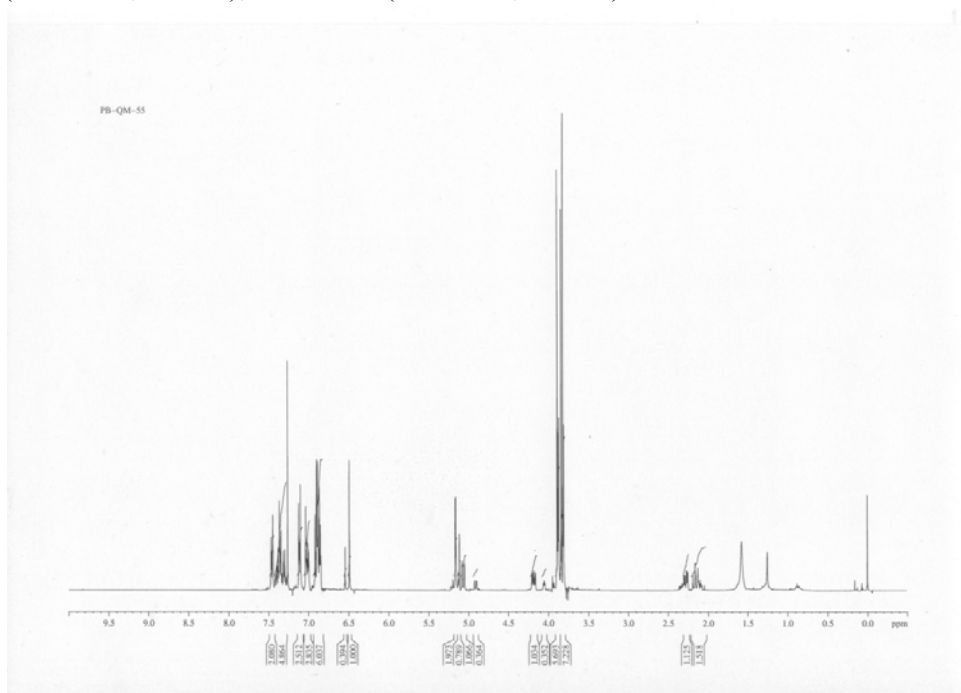
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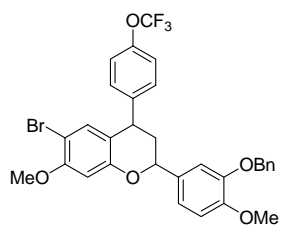




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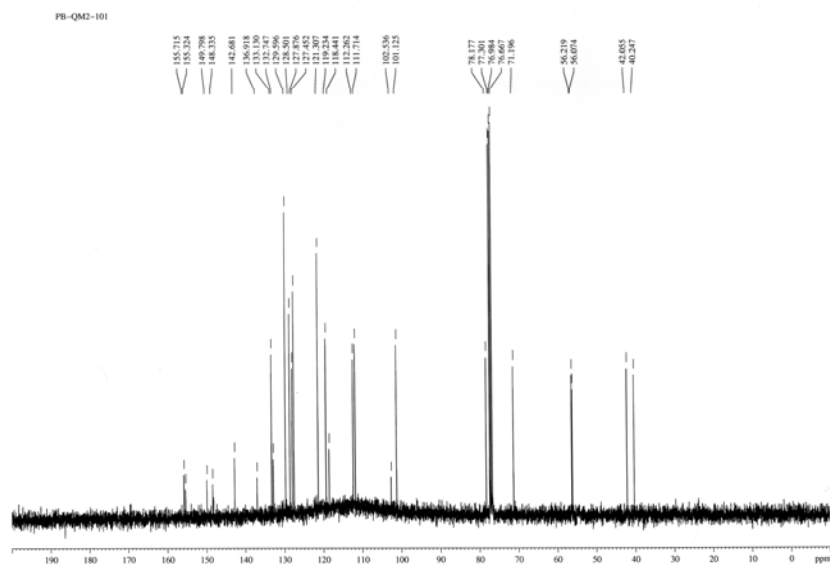
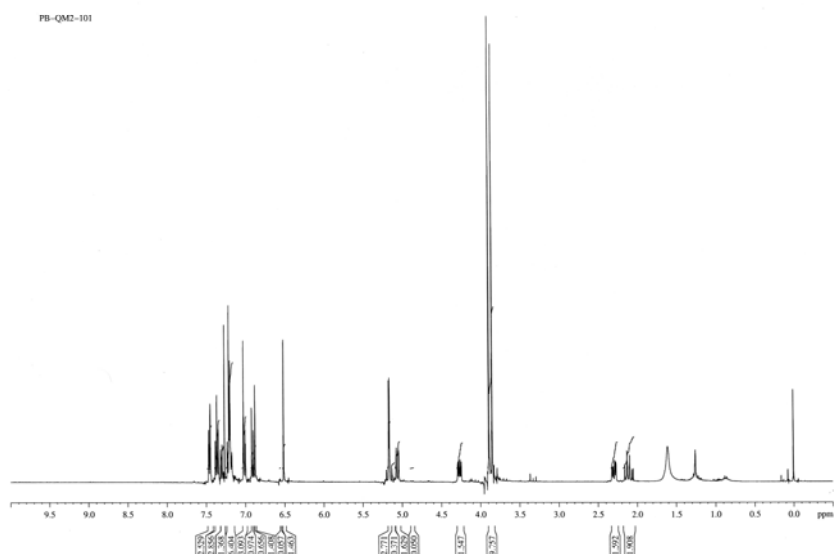
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

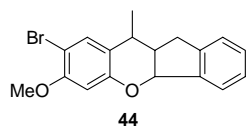




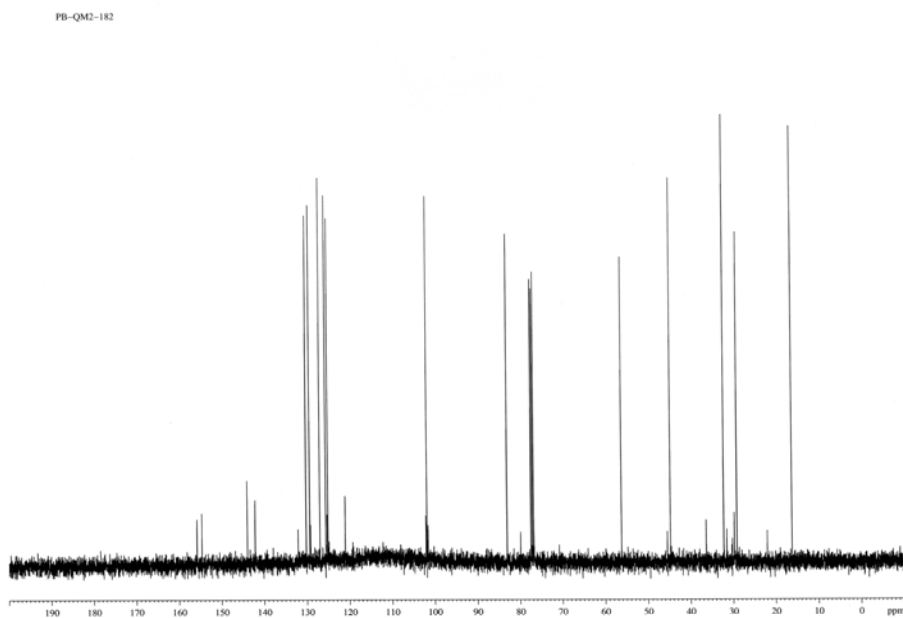
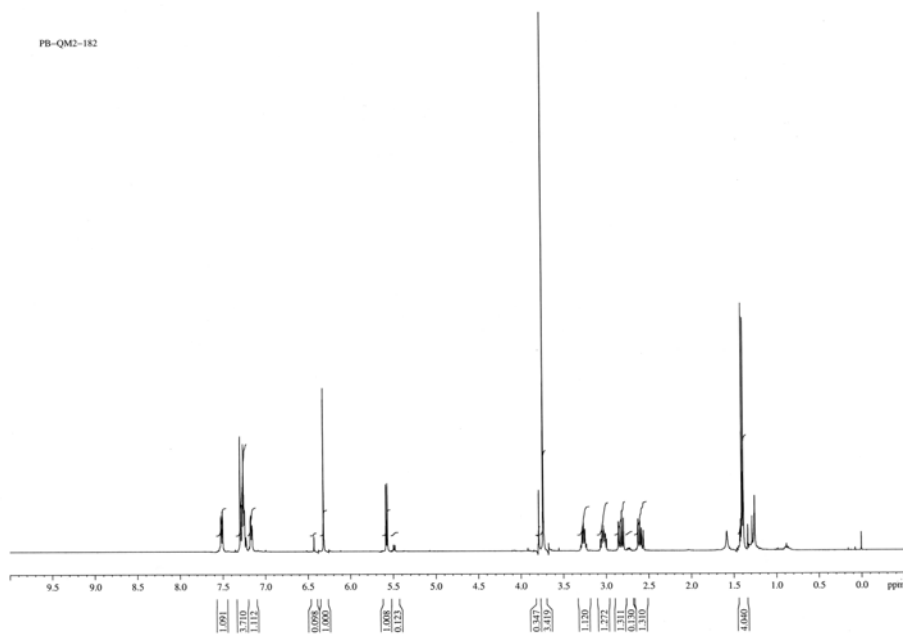
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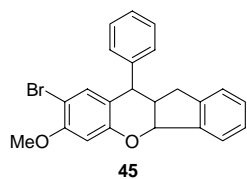
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



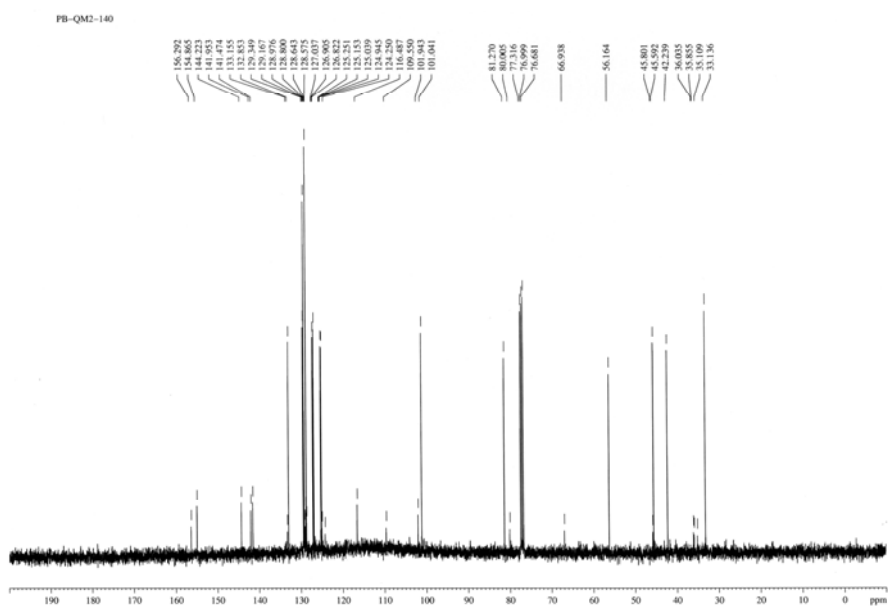
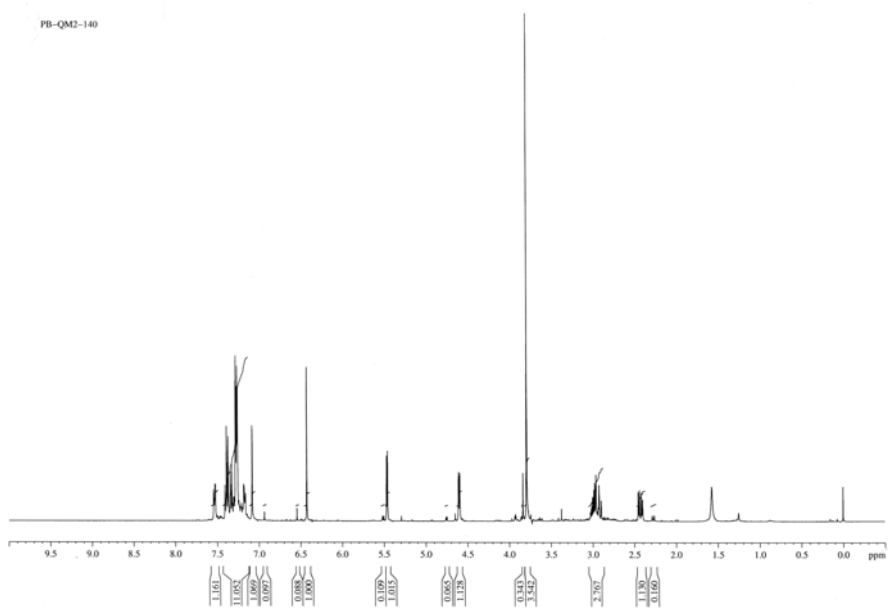


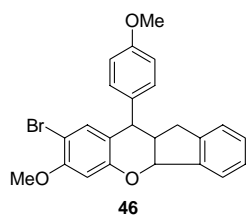
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



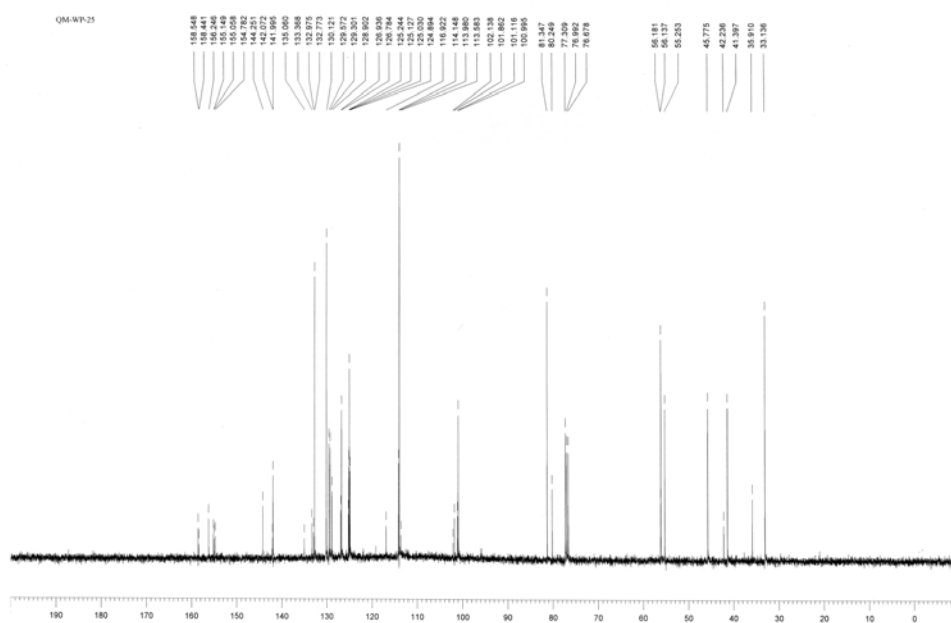
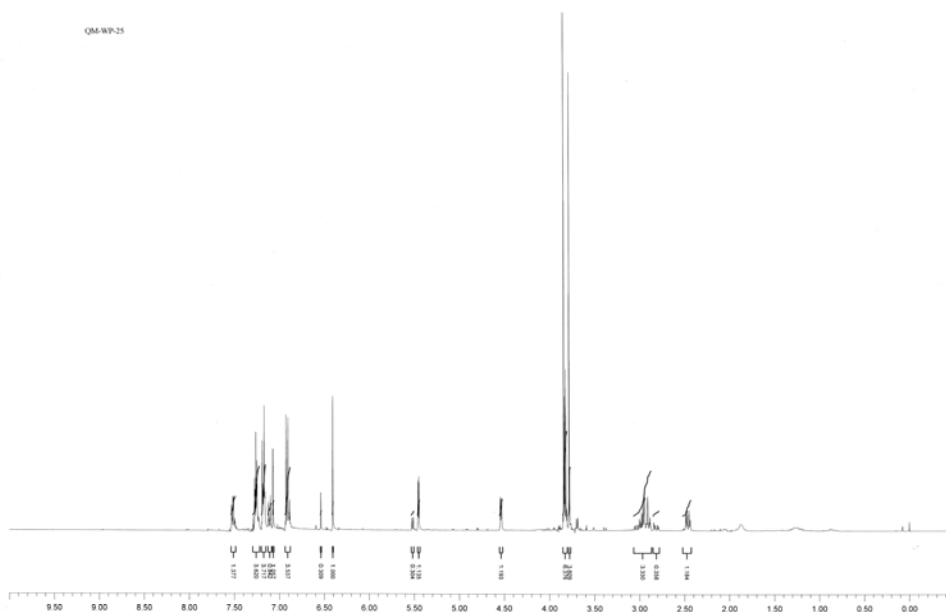


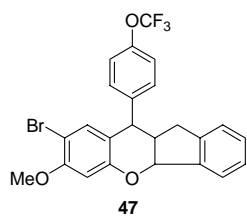
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

