

A New Synthetic Method for Non-symmetric Pillar[5]arenes with Simple Isolation and Improved Yield

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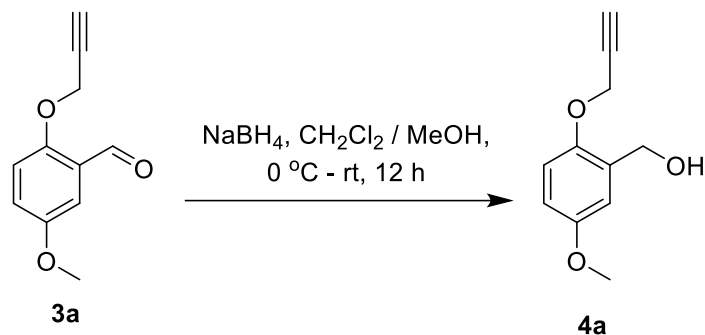
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Synthetic Procedures



To a 500 mL round bottom flask equipped with a magnetic stir bar was added compound **3a** (4.00 g, 21.0 mmol), CH_2Cl_2 (50 mL) and MeOH (50 mL). The solution was cooled to $0\text{ }^\circ\text{C}$ in ice water bath. NaBH_4 (800 mg, 21.2 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature and was stirred for another 12 h. The solvent was then removed under reduced pressure. Water (100 mL) was added, followed by extraction with ethyl acetate (20 mL \times 4). The organic layer was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. Column chromatography (silica, 300-400 mesh, dichloromethane/methanol, *v/v* 100:0-25:1) afforded compound **4a** as a white solid (4.00 g, 99%).

M.p. $38.6\text{--}40.2\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 6.96–6.90 (m, 2H), 6.79 (dd, $J_1 = 8.9\text{ Hz}$, $J_2 = 3.1\text{ Hz}$, 1H), 4.70 (d, $J = 2.4\text{ Hz}$, 2H), 4.68 (s, 2H), 3.78 (s, 3H), 2.51 (t, $J = 2.4\text{ Hz}$, 1H), 2.22 (brs, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.56, 131.35, 114.85, 113.69, 113.24, 78.84, 75.74, 61.82, 56.99, 55.85. FT-IR (KBr): ν_{max} (cm^{-1}) 3246, 2992, 2916, 2834, 1498, 1457, 1439, 1365, 1301, 1282, 1209, 1163, 1045, 793, 629. HR-MS: m/z calcd for $[\text{M} + \text{H}]^+$, $\text{C}_{11}\text{H}_{13}\text{O}_3$, 193.0865, found 193.0862 (error: 1.5 ppm).

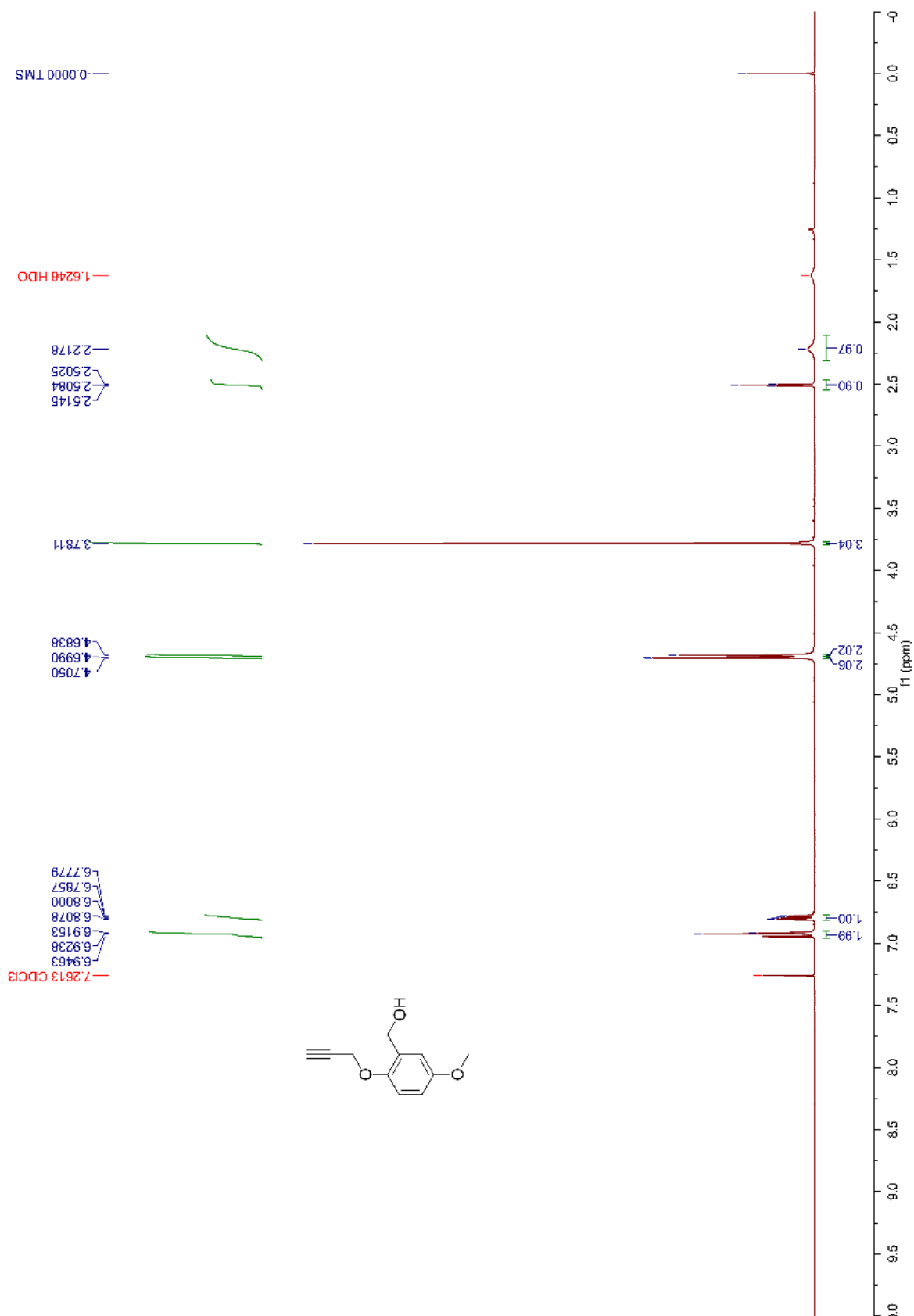


Fig. S1 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **4a**.

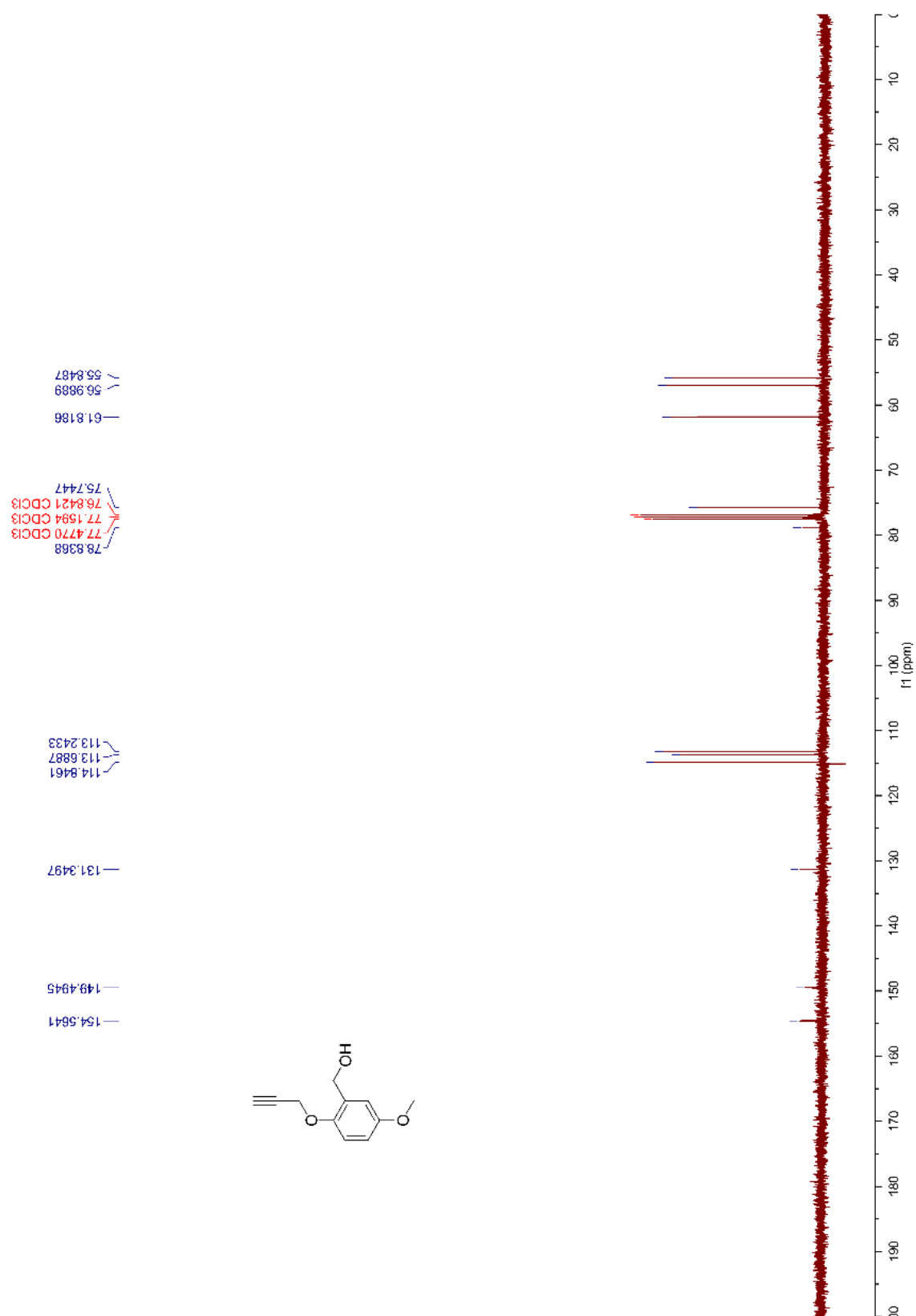
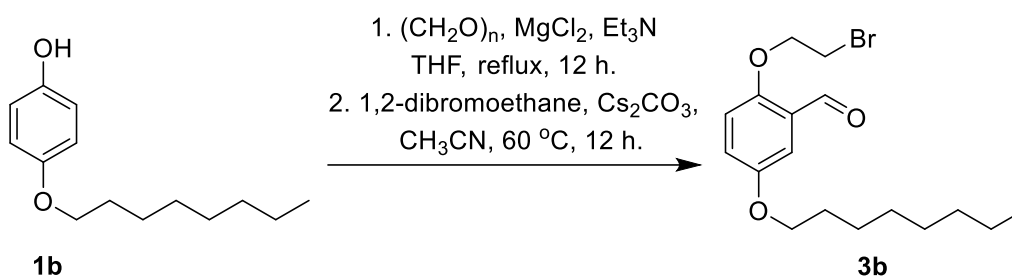


Fig. S2 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **4a**.



MgCl₂ (2.850 g, 30 mmol) and paraformaldehyde (1.500 g, 50 mmol) was added to a 500 mL three-necked round bottom flask fitted with a reflux condenser under an atmosphere of N₂. Anhydrous THF (100 mL) was added with a syringe followed by Et₃N (4.2 mL, 30 mmol). Compound **1b** (2.224 g, 10 mmol) was added under nitrogen atmosphere. The reaction mixture was then heated to reflux, during which period the solution turned yellow. The reaction was stirred for another 12 h, and quenched with 1 M aqueous HCl (100 mL). The aqueous phase was extracted with diethyl ether (50 mL × 3), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to afford crude product as a yellow oil. The crude product was directly used in the next step without further purification.

The crude product 5-(*n*-octyloxy)salicylaldehyde was dissolved in anhydrous MeCN (80 mL). Cs₂CO₃ (7.00 g, 21 mmol) was then added. The mixture was heated to 60 °C and stirred for 30 min. 1,2-dibromoethane (10.0 mL, 115 mmol) was added through a syringe and the reaction mixture was heated overnight. The mixture was cooled, filtered and concentrated under reduced pressure. The crude product was then dissolved in ethyl acetate (100 mL) and washed with brine (25 mL × 3). Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 9:1) afforded compound **3b** as a pale yellow solid (2.452 g, 69% for two steps).

M.p. 35.6-37.3 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.51 (s, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.12 (dd, *J*₁ = 8.5 Hz, *J*₂ = 2.4 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 4.38 (t, *J* = 5.8 Hz, 2H), 3.95 (t, *J* = 6.3 Hz, 2H), 3.68 (t, *J* = 5.8 Hz, 2H), 1.76 (m, 2H), 1.43 (m, 2H), 1.30 (m, 8H), 0.89 (t, *J* = 5.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 189.39, 154.92, 153.76, 125.62, 123.80, 114.84, 111.09, 69.08, 68.65, 31.77, 29.29, 29.20, 29.15, 29.02, 25.95, 22.62, 14.08. FT-IR (KBr) ν_{max} (cm⁻¹) 3065, 2955, 2917, 2869, 2852, 1682, 1613, 1590, 1495, 1469, 1427, 1406, 1392, 1379, 1314, 1277, 1256, 1217,

1172, 1071, 1046, 1034, 1020, 874, 865, 818, 788, 748, 719, 638, 602. HR-MS: m/z calcd for $[M + H]^+$, $C_{17}H_{25}BrO_3$, 357.1060, found 357.1062 (error: 0.6 ppm).

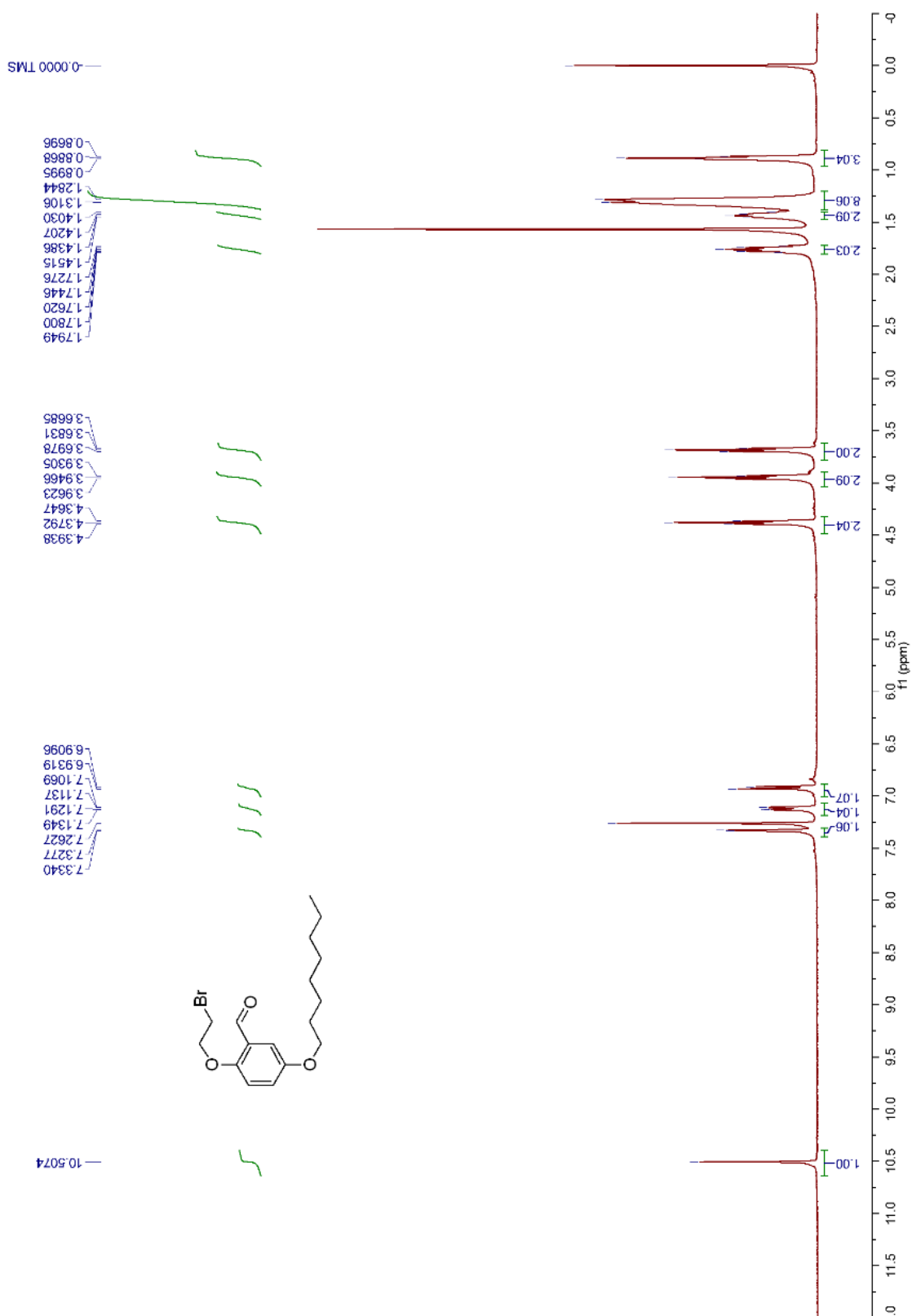


Fig. S3 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **3b**.

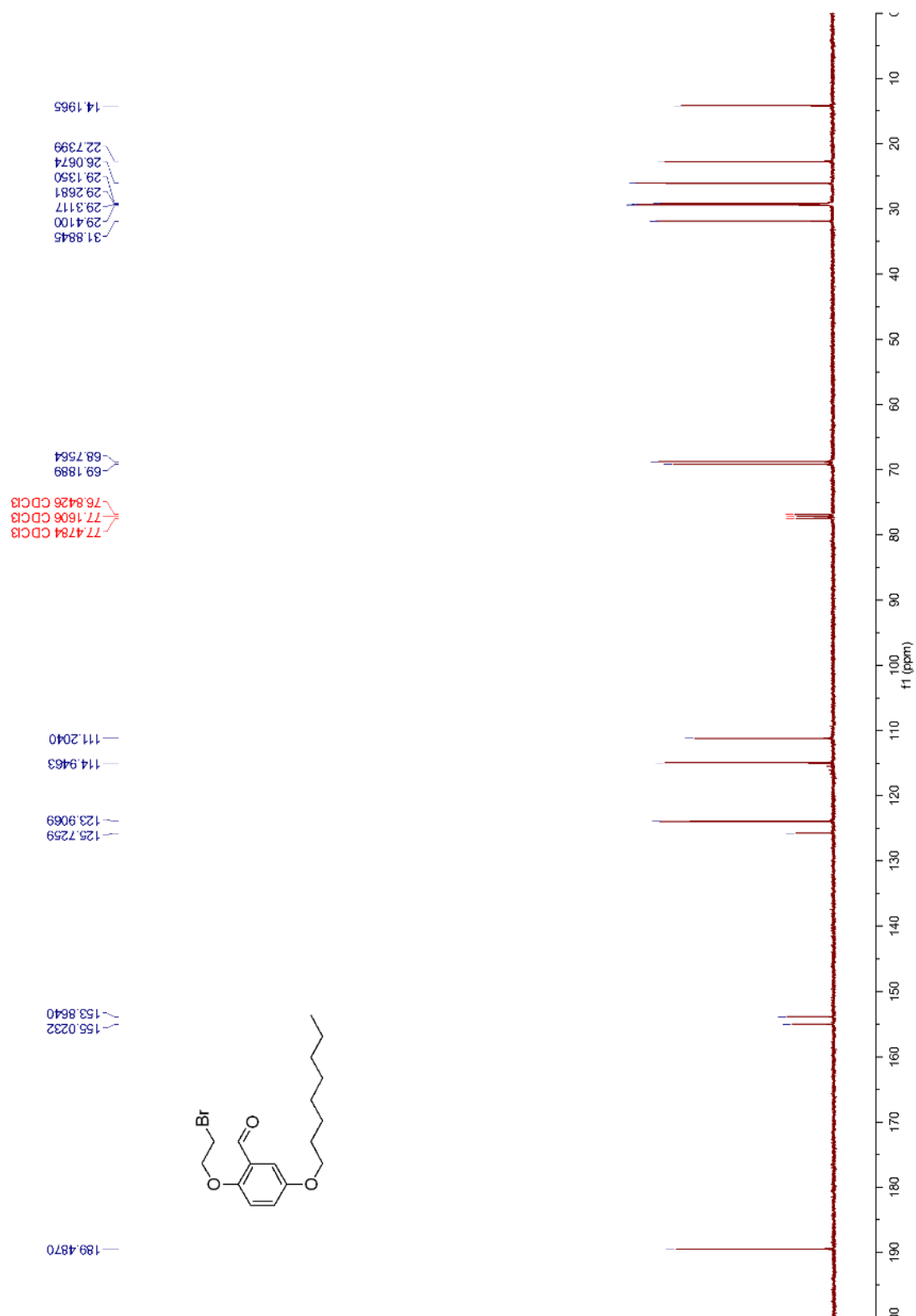
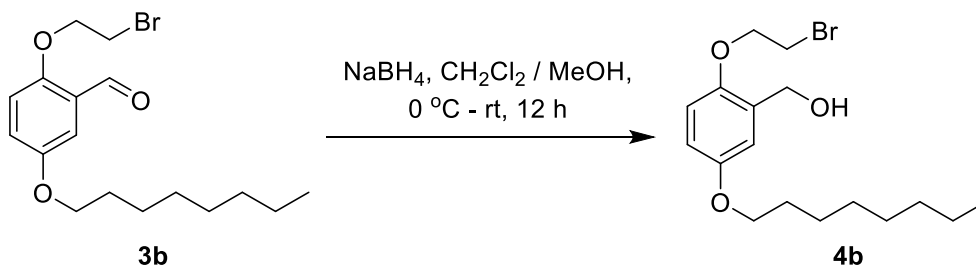


Fig. S4 ^{13}C NMR spectrum (100 MHz, CDCl_3 , 298 K) recorded for compound **3b**.



To a 250 mL round bottom flask equipped with a magnetic stir bar was added compound **3b** (2.390 g, 6.7 mmol), CH_2Cl_2 (50 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH_4 (370 mg, 9.8 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature, and was stirred for another 12 h. The solvent was then evaporated under reduced pressure. Water (50 mL) was added, followed by extraction with ethyl acetate (30 mL \times 5). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 3:1) afforded compound **4b** as a white solid (2.161 g, 90%).

M.p. 39.8-42.5 °C. ^1H NMR (400 MHz, CDCl_3): δ 6.89 (s, 1H), 6.77 (s, 2H), 4.68 (d, J = 5.0 Hz, 2H), 4.31 (t, J = 5.8 Hz, 2H), 3.91 (t, J = 5.8 Hz, 2H), 3.68 (t, J = 5.7 Hz, 2H), 2.45 (t, J = 6.7 Hz, 1H), 1.75 (m, 2H), 1.44 (m, 2H), 1.33 (m, 8H), 0.88 (t, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.75, 149.83, 130.81, 115.66, 113.87, 112.68, 68.59, 68.34, 62.00, 31.79, 29.99, 29.34, 29.31, 29.22, 26.01, 22.64, 14.09. FT-IR (KBr): ν_{max} (cm^{-1}) 3347, 2947, 2922, 2848, 1610, 1505, 1466, 1455, 1429, 1391, 1367, 1302, 1276, 1220, 1177, 1160, 1077, 1027, 870, 859, 815, 805, 765, 707, 583. HR-MS: m/z calcd for $[\text{M} + \text{NH}_4]^+$, $\text{C}_{17}\text{H}_{27}\text{BrO}_3$, 376.1482, found 376.1483 (error: 0.3 ppm).

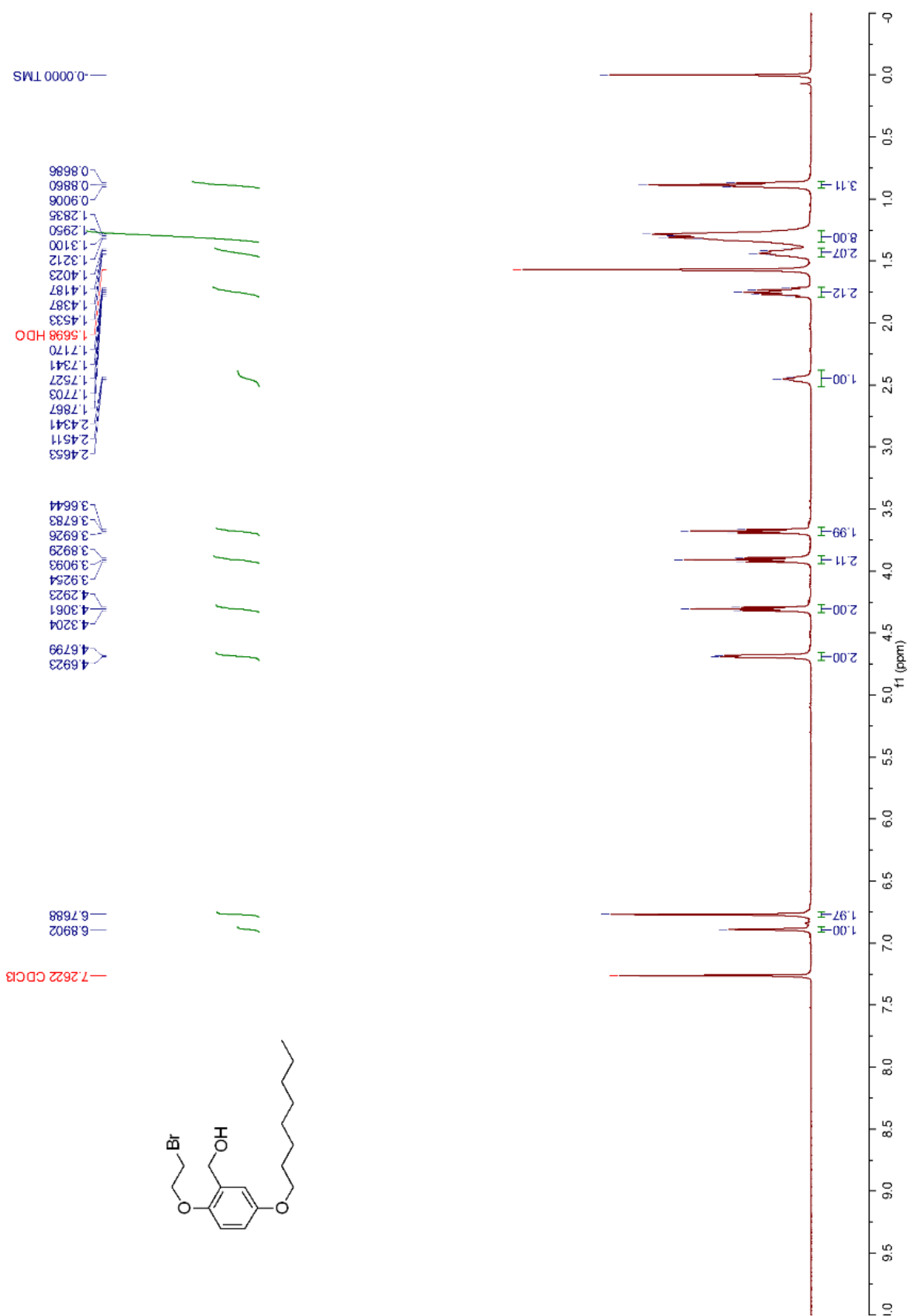


Fig. S5 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **4b**.

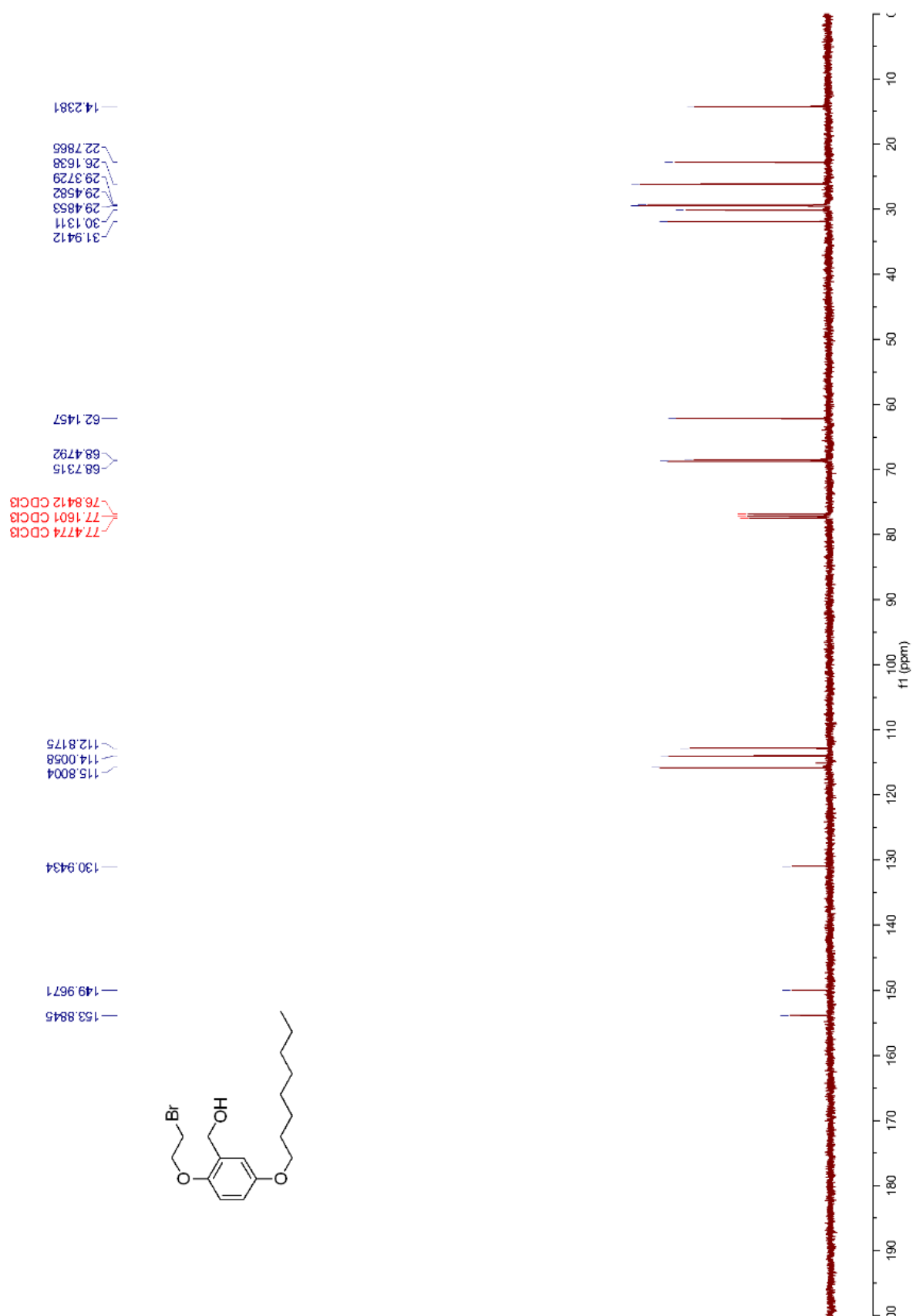
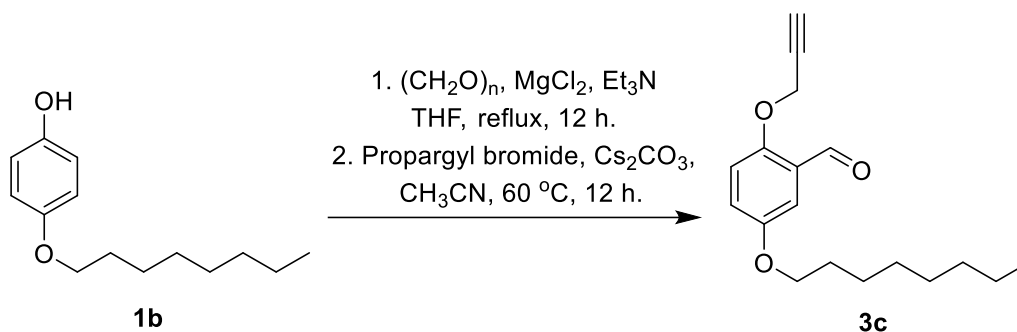


Fig. S6 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **4b**.



MgCl₂ (3.65 g, 38.3 mmol), paraformaldehyde (1.92 g, 60 mmol) was added to a 500 mL three-necked round bottom flask fitted with a reflux condenser under an atmosphere of N₂. Anhydrous THF (100 mL) was added with a syringe followed by Et₃N (5.4 mL, 38.6 mmol). Compound **1b** (2.85 g, 12.8 mmol) was added under nitrogen atmosphere. The reaction mixture was then heated to reflux, during which period the solution turned yellow. The reaction was stirred for another 12 h, and quenched with 1 M aqueous HCl (100 mL). The aqueous phase was extracted with diethyl ether (50 mL × 3), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to afford crude product as a yellow oil. The crude product was directly used in the next step without further purification.

The crude product 5-(*n*-octyloxy)salicylaldehyde was dissolved in anhydrous MeCN (100 mL). Cs₂CO₃ (11.70 g, 36 mmol) was then added. The mixture was heated to 60 °C and stirred for 30 min. Propargyl bromide (2.0 mL, 18 mmol) was added through a syringe and the reaction mixture was heated overnight. The mixture was cooled, filtered and concentrated under reduced pressure. The crude product was then dissolved in ethyl acetate (100 mL) and washed with brine (25 mL × 3). Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 9:1) afforded compound **3c** as a pale yellow solid (2.91 g, 79% for two steps).

M.p. 49.6-51.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.44 (s, 1H), 7.34 (d, *J* = 3.2 Hz, 1H), 7.14 (dd, *J*₁ = 9.0 Hz, *J*₂ = 3.2 Hz, 1H), 4.78 (d, *J* = 2.4 Hz, 2H), 3.95 (t, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H), 1.77 (m, 2H), 1.44 (m, 2H), 1.30 (m, 8H), 0.89 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 189.33, 154.28, 153.96, 126.07, 123.57, 116.01, 115.51, 115.23, 111.09, 77.94, 76.36, 68.59, 57.29, 31.76, 29.29, 29.19, 29.15, 25.95, 22.62, 14.06. FT-IR (KBr): ν_{max} (cm⁻¹) 3277, 2957, 2941, 2918, 2871, 2853, 2120,

1677, 1614, 1583, 1492, 1458, 1432, 1297, 1244, 1176, 1080, 1021, 946, 890, 814, 794, 760, 672, 657, 617, 525. HR-MS: m/z calcd for $[M + H]^+$, $C_{18}H_{24}O_3$, 289.1798, found 289.1797 (error: 0.3 ppm).

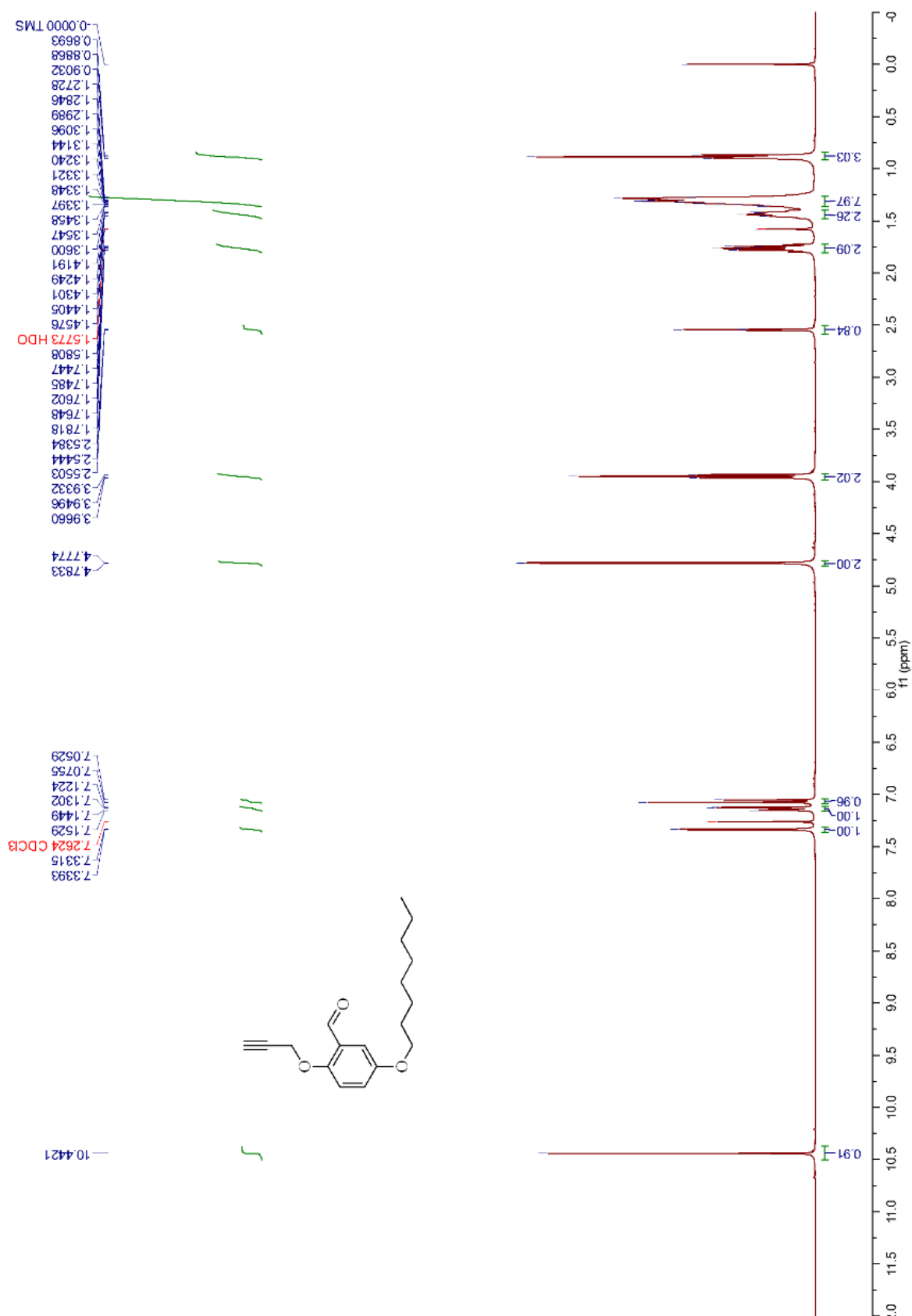


Fig. S7 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **3c**.

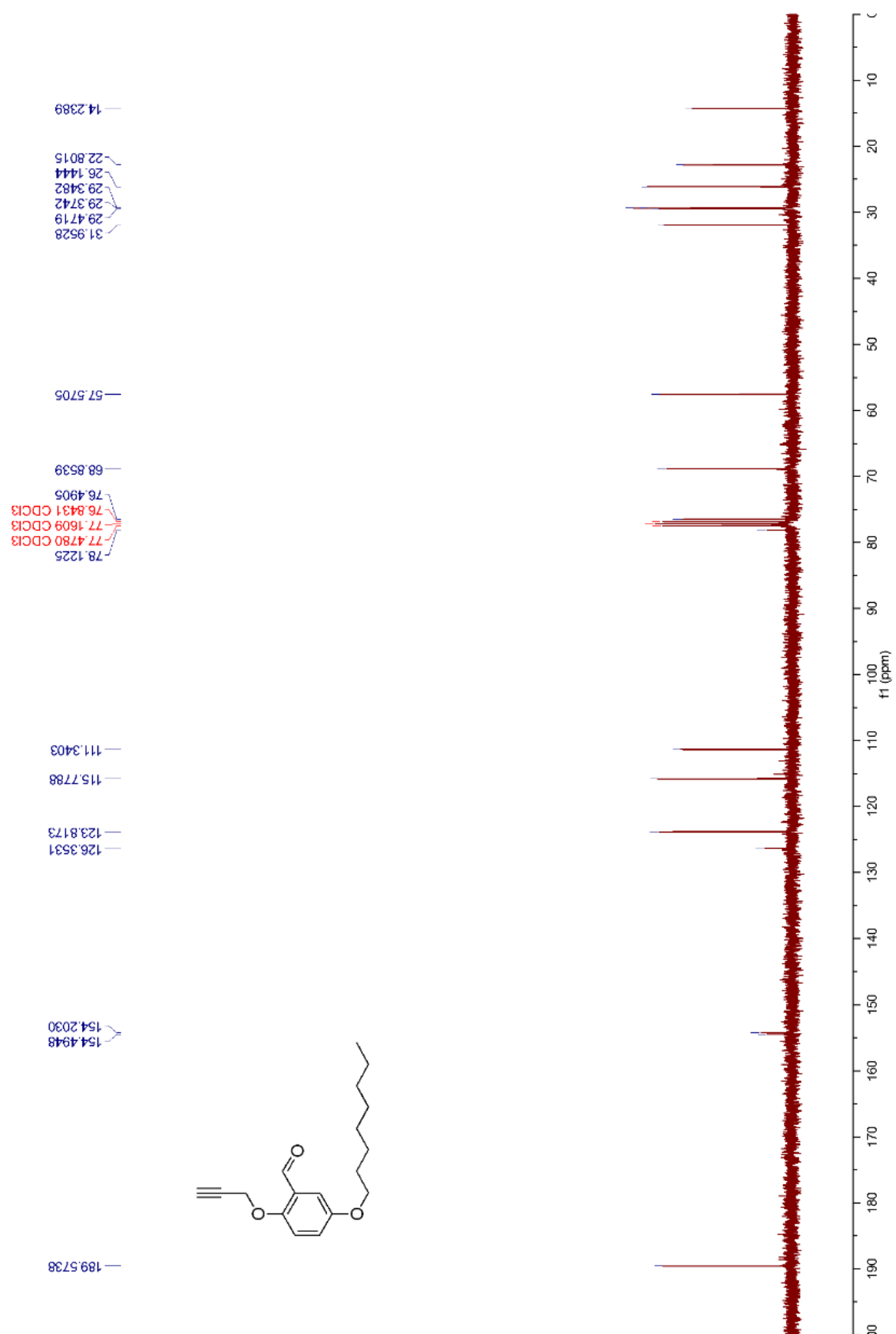


Fig. S8 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **3c**.

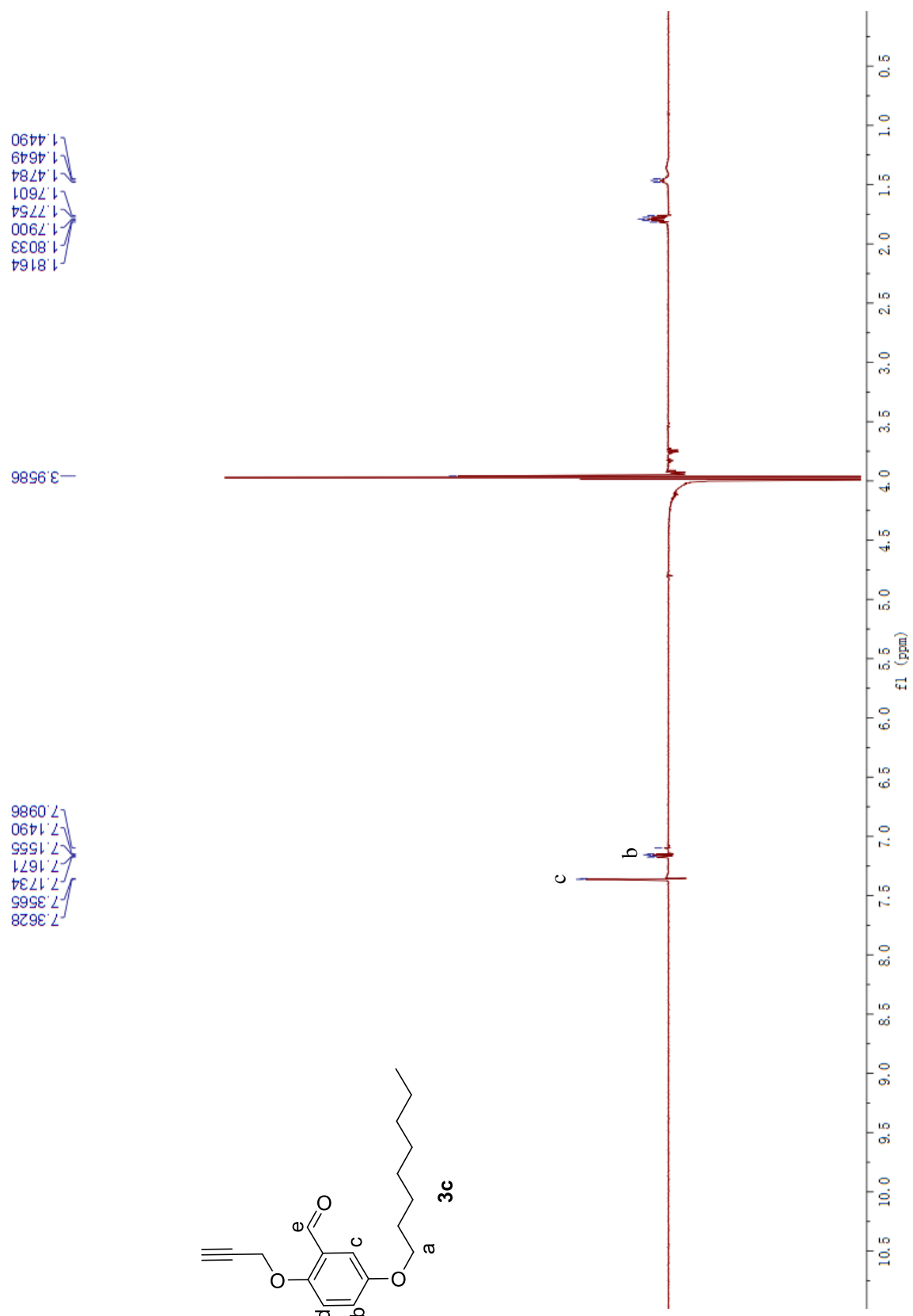
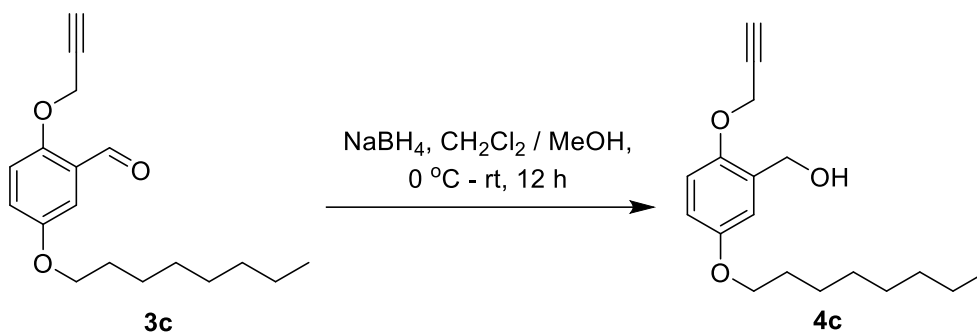


Fig. S9 NOE spectrum (400 MHz, CDCl₃) recorded for compound **3c**. H_a (3.95 ppm) was selectively excited. Strong coupling was observed for H_c and H_b, while weak or no coupling was observed for H_d and H_e.



To a 250 mL round bottom flask equipped with a magnetic stir bar was added compound **3c** (1.582 g, 5.0 mmol), CH_2Cl_2 (25 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH_4 (126 mg, 3.3 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature and was stirred for another 12 h. The solvent was then evaporated under reduced pressure. Water (50 mL) was added and followed by extraction with ethyl acetate (30 mL \times 5). The organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford compound **4c** as a white solid (1.512 g, 95%).

M.p. 54.6-57.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 6.92 (d, $J = 8.2$ Hz, 1H), 6.91 (s, 1H), 6.78 (dd, $J_1 = 8.8$ Hz, $J_2 = 3.0$ Hz, 1H), 4.70 (s, 2H), 4.68 (s, 2H), 3.91 (t, $J = 6.6$ Hz, 2H), 2.51 (s, 1H), 2.16 (brs, 1H), 1.75 (m, 2H), 1.44 (m, 2H), 1.28 (m, 8H), 0.89 (t, $J = 5.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.97, 149.20, 131.13, 115.34, 113.76, 113.49, 78.73, 75.54, 68.52, 61.62, 56.81, 31.79, 29.34, 29.31, 29.22, 26.02, 22.63, 14.09. FT-IR (KBr) ν_{max} (cm^{-1}) 3277, 2965, 2952, 2935, 2919, 2869, 2850, 2116, 1619, 1593, 1492, 1476, 1465, 1396, 1375, 1362, 1313, 1284, 1200, 1172, 1127, 1056, 1042, 1026, 1007, 922, 877, 789, 758, 739, 693, 672, 629. HR-MS: m/z calcd for $[\text{M} + \text{NH}_4]^+$, $\text{C}_{18}\text{H}_{26}\text{O}_3$, 308.2220, found 308.2227 (error: 2.3 ppm).

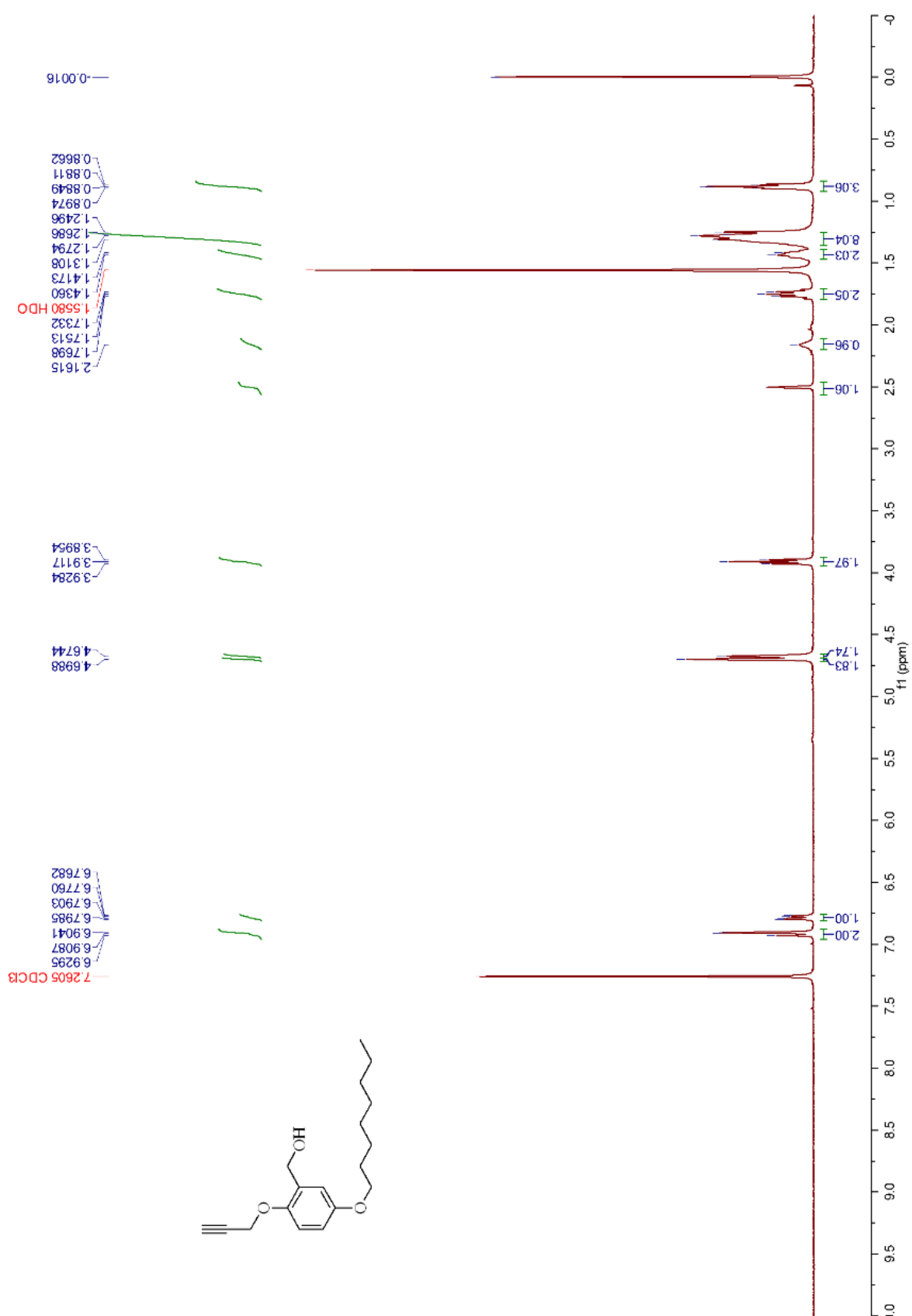


Fig. S10 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **4c**.

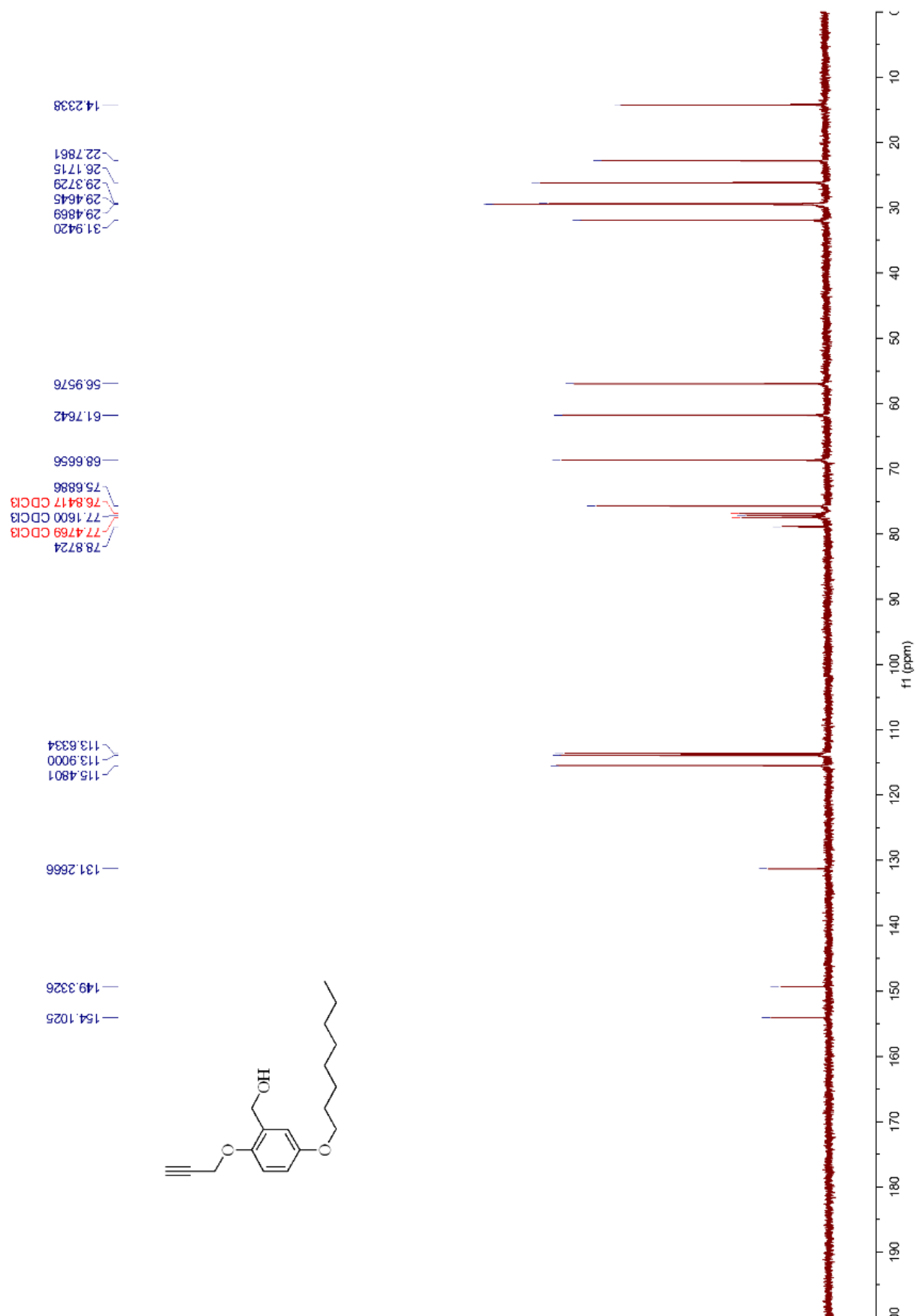
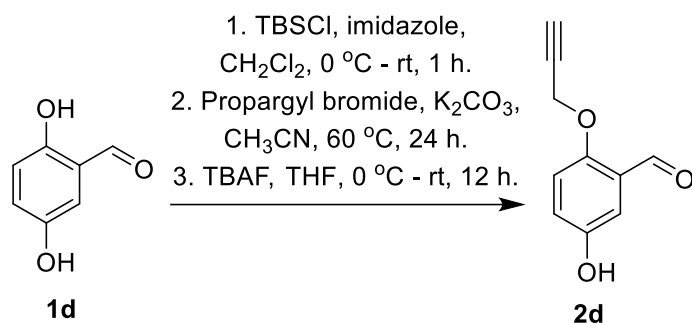


Fig. S11 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **4c**.



To a 500 mL round bottom flask equipped with a magnetic stir bar, compound **1d** (5.00 g, 36.2 mmol) and 1H-imidazole (3.70 g, 54.3 mmol) was dissolved in anhydrous CH_2Cl_2 (150 mL). The solution was cooled to 0 °C in ice water bath. *tert*-butyldimethylsilyl chloride (6.55 g, 43.4 mmol) was added portion wise into the solution. The reaction was warmed up to room temperature during a time period of 1 h. After the starting material was consumed, the reaction mixture was then filtered through a celite pad, dried over anhydrous Na_2SO_4 , and concentrated to afford a yellow oil. The crude 5-((*tert*-butyldimethylsilyl)oxy)salicylaldehyde was directly used in the next step without further purification.

The crude 5-((*tert*-butyldimethylsilyl)oxy)salicylaldehyde was dissolved in anhydrous MeCN (150 mL). K_2CO_3 (7.49 g, 54.3 mmol) was then added. The mixture was heated to 60 °C and stirred for 30 min. Propargyl bromide (ca. 9.2 mol/L solution in toluene) (5.9 mL, 54.3 mmol) was added through a syringe and the reaction mixture was heated overnight. After the starting material was consumed, the reaction mixture was cooled to room temperature, filtered and concentrated under reduced pressure. The crude product was then dissolved in ethyl acetate and washed with brine. Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, *v/v* 40:1) afforded the desired product as a yellow oil. The 5-((*tert*-butyldimethylsilyl)oxy)-2-(propargyloxy)benzaldehyde was directly subjected to deprotection without characterization.

To a 500 mL round bottom flask equipped with a magnetic stir bar, the crude 5-((*tert*-butyldimethylsilyl)oxy)-2-(propargyloxy)benzaldehyde was added and dissolved in THF (70 mL). The solution was cooled to 0 °C in ice water bath. Tetrabutylammonium fluoride (1 M solution in THF) (30 mL, 30 mmol) was added dropwise into the solution. The reaction mixture was warmed to room temperature and stirred for 12 h. The

reaction mixture was then concentrated under reduced pressure, diluted with ethyl acetate (100 mL), and washed with brine (50 mL x 3). Column chromatography (silica, 200-300 mesh, petroleum ether/ethyl acetate, v/v 3:1) afforded compound **2d** as a pale yellow solid (4.21 g, 66% for 3 steps).

M.p. 111.6-112.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 10.42 (s, 1H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.09 (d, *J* = 3.4 Hz, 1H), 7.06 (d, *J* = 4.8 Hz, 1H), 4.96 (s, 1H), 4.78 (s, 2H), 2.54 (t, *J* = 2.8 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 189.95, 152.98, 152.03, 125.86, 123.29, 116.79, 112.23, 78.98, 78.77, 57.42. FT-IR (KBr): ν_{max} (cm⁻¹) 3396, 3269, 3046, 2937, 2902, 2793, 2116, 1670, 1661, 1609, 1600, 1507, 1457, 1407, 1354, 1310, 1244, 1275, 1228, 1210, 1167, 1107, 1022, 1013, 976, 922, 881, 869, 816, 791, 661, 612, 594, 561, 531, 449. HR-MS: *m/z* calcd for [M + H]⁺, C₁₀H₈O₃, 177.0546, found 177.0551 (error: 2.8 ppm).

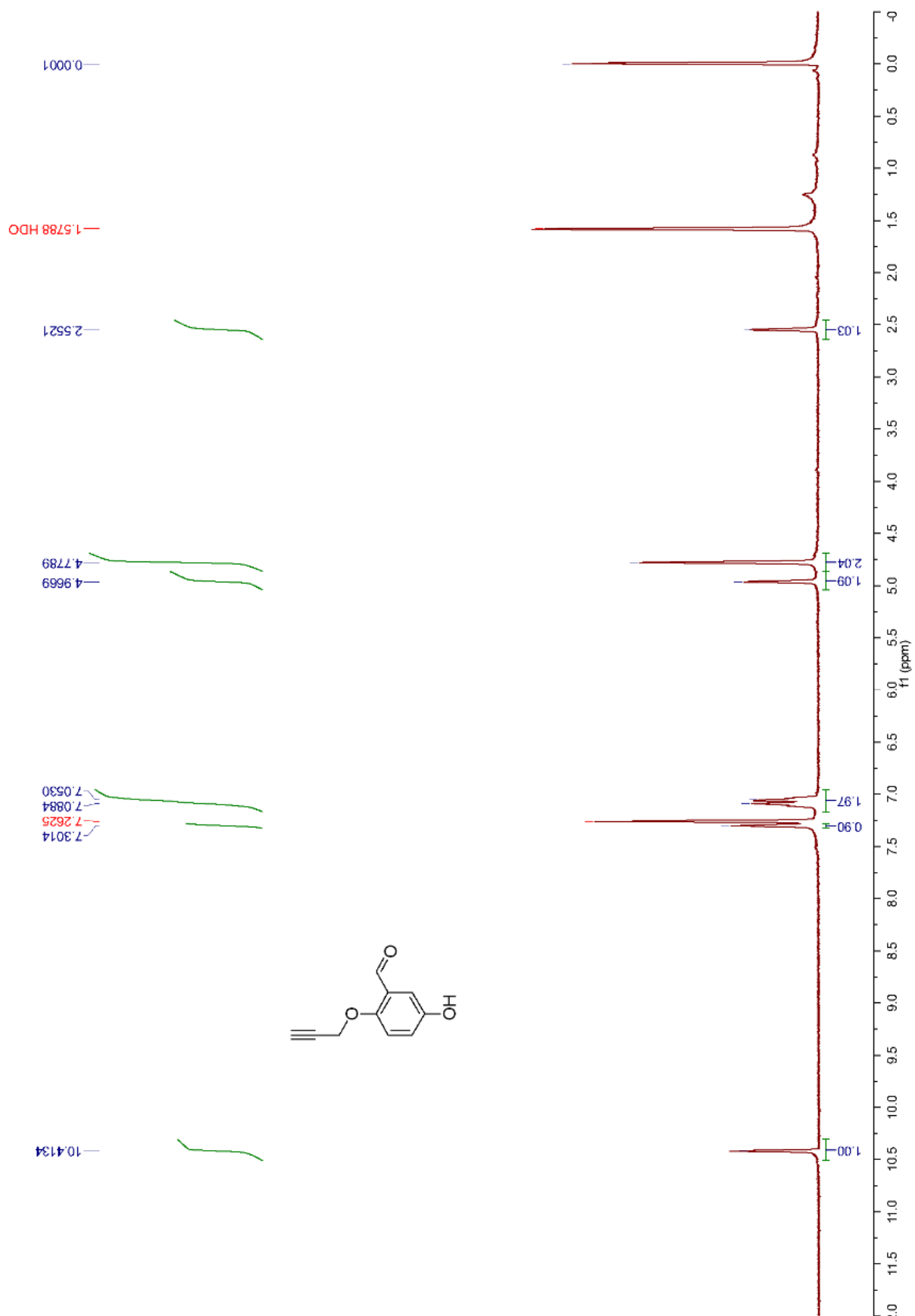


Fig. S12 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **2d**.

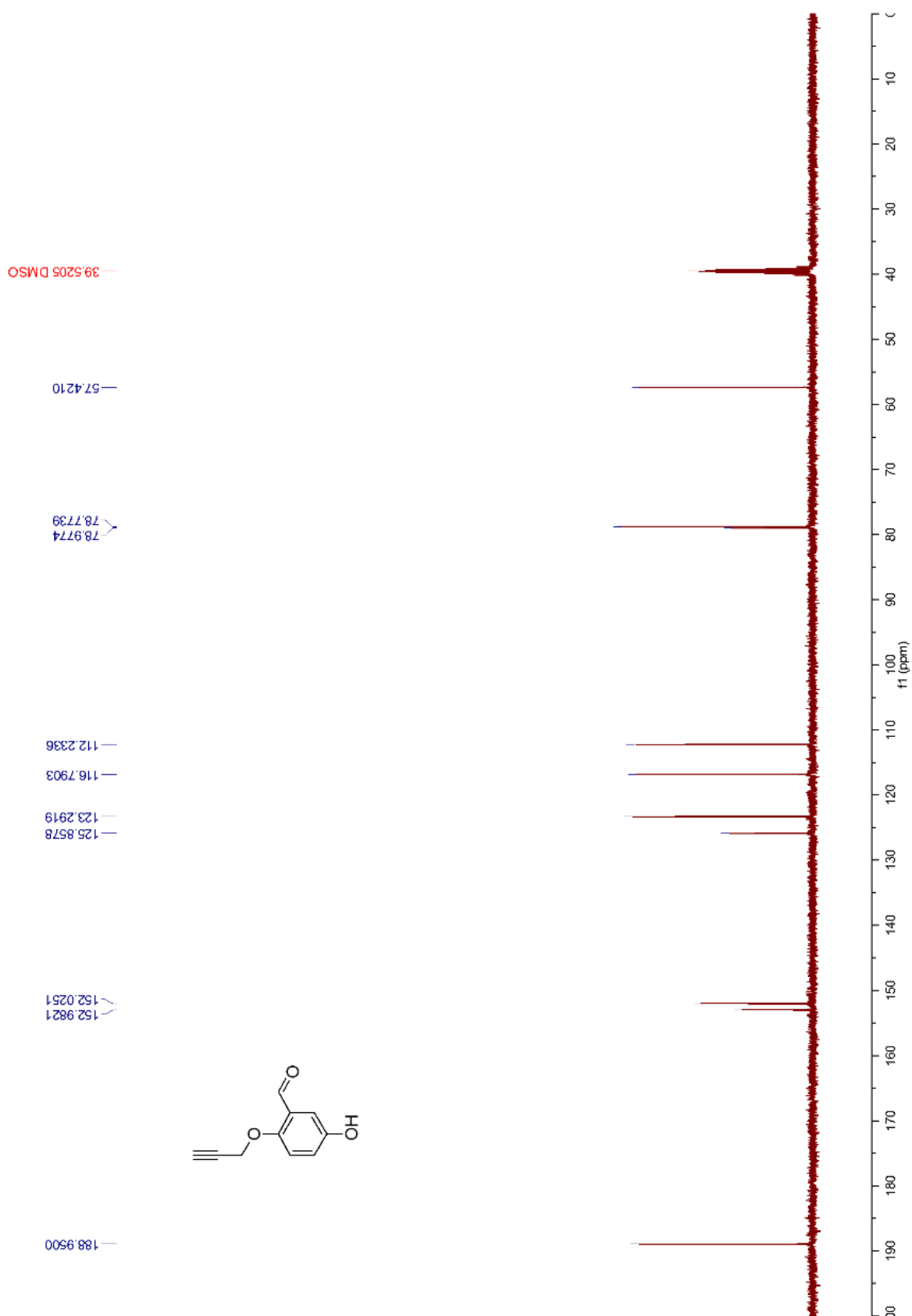
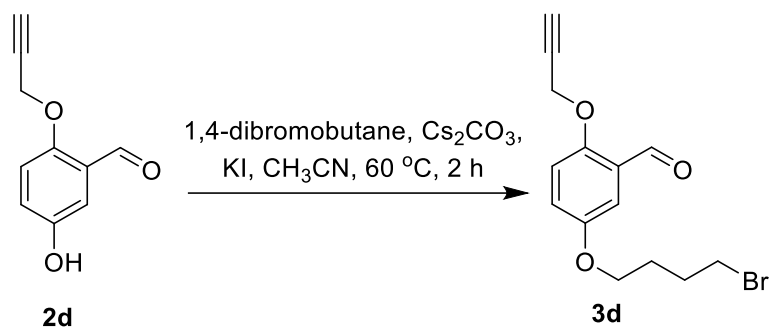


Fig. S13 ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) recorded for compound **2d**.



To a 250 mL round bottom flask equipped with a magnetic stir bar, compound **2d** (0.704 g, 4.0 mmol) was dissolved in MeCN (80 mL). Cs_2CO_3 (3.906 g, 12.0 mmol) and KI (125 mg) was then added. The mixture was heated to 60 °C and stirred for 30 min. 1,4-Dibromobutane (4.6 mL, 39 mmol) was then added and the mixture was stirred for another 2 h. After the starting material was consumed, the reaction mixture was cooled, filtered, and concentrated under reduced pressure. The crude product was diluted by ethyl acetate (50 mL) and washed with brine (25 mL). Column chromatography (silica, 200-300 mesh, petroleum ether/ethyl acetate, v/v 4:1) afforded compound **3d** as a pale yellow crystalline solid (1.146 g, 92%).

M.p. 79.8-81.1 °C. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 10.44 (s, 1H), 7.33 (d, $J = 3.1$ Hz, 1H), 7.13 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.2$ Hz, 1H), 7.07 (d, $J = 9.0$ Hz, 1H), 4.78 (d, $J = 2.4$ Hz, 2H), 4.00 (t, $J = 6.1$ Hz, 2H), 3.48 (t, $J = 6.5$ Hz, 2H), 2.54 (t, $J = 2.4$ Hz, 1H), 2.06 (m, 2H), 1.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ 189.33, 154.45, 153.66, 126.08, 123.55, 115.58, 111.12, 77.88, 76.41, 67.47, 57.31, 33.35, 29.37, 27.79. FT-IR (KBr): ν_{max} (cm^{-1}) 3279, 3100, 2970, 2950, 2915, 2877, 2773, 2120, 1675, 1615, 1584, 1493, 1474, 1456, 1432, 1407, 1393, 1282, 1242, 1210, 1178, 1043, 1020, 1007, 944, 891, 815, 794, 743, 701, 661, 616, 570, 516. HR-MS: m/z calcd for $[\text{M} + \text{H}]^+$, $\text{C}_{14}\text{H}_{15}\text{BrO}_3$, 311.0277, found 311.0279 (error: 0.6 ppm).

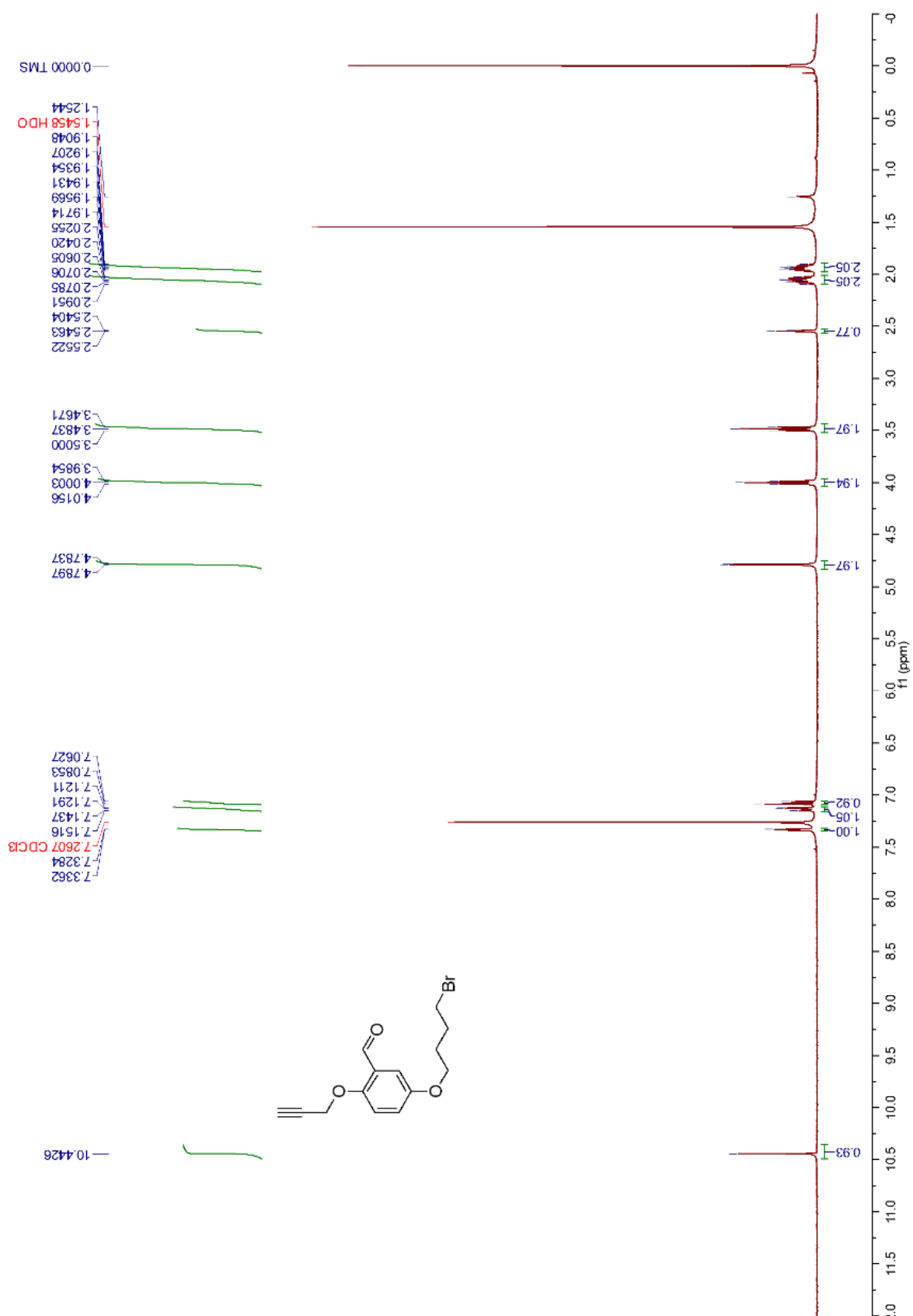


Fig. S14 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **3d**.

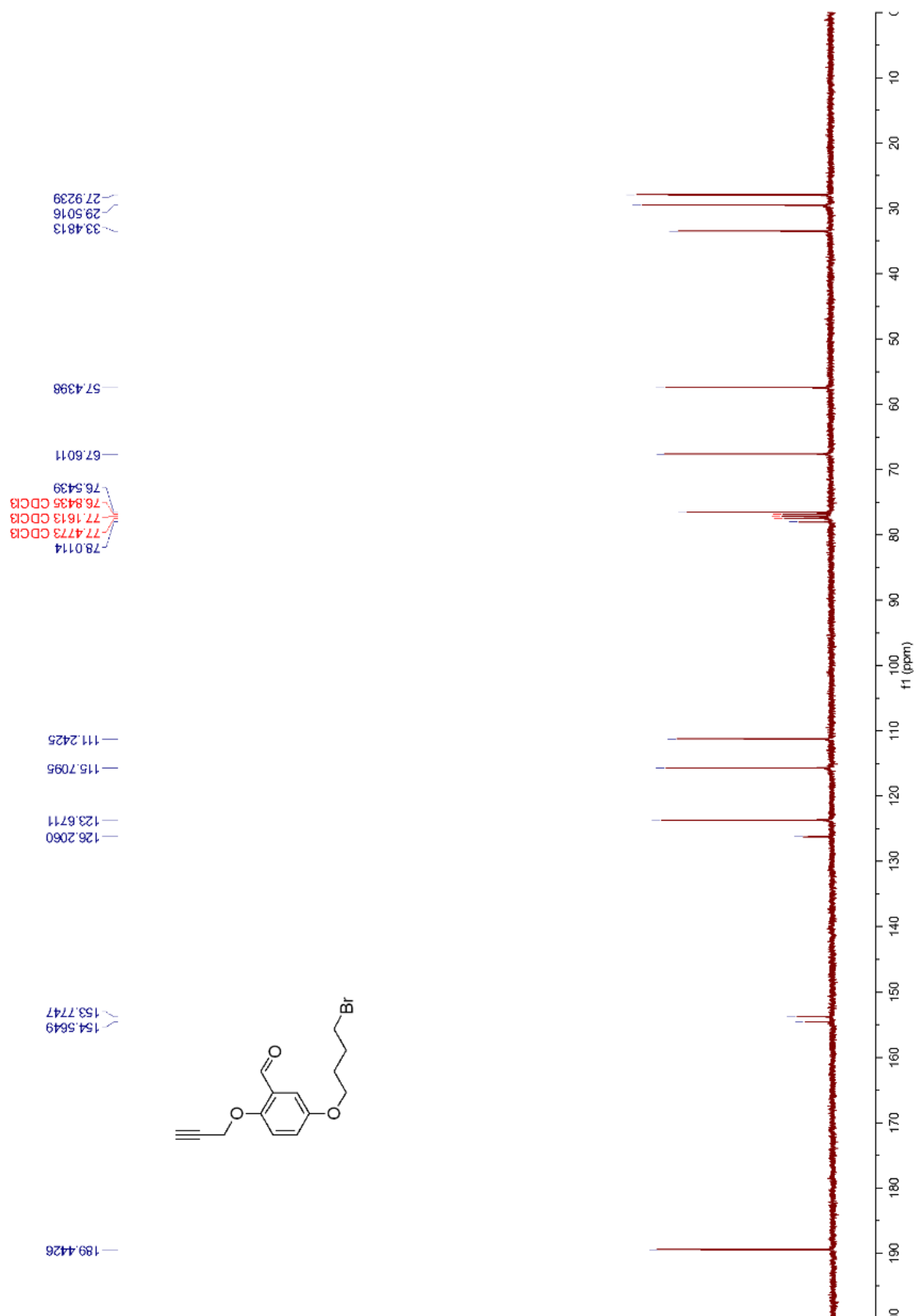


Fig. S15 ^{13}C NMR spectrum (100 MHz, CDCl_3) of compound **3d**.

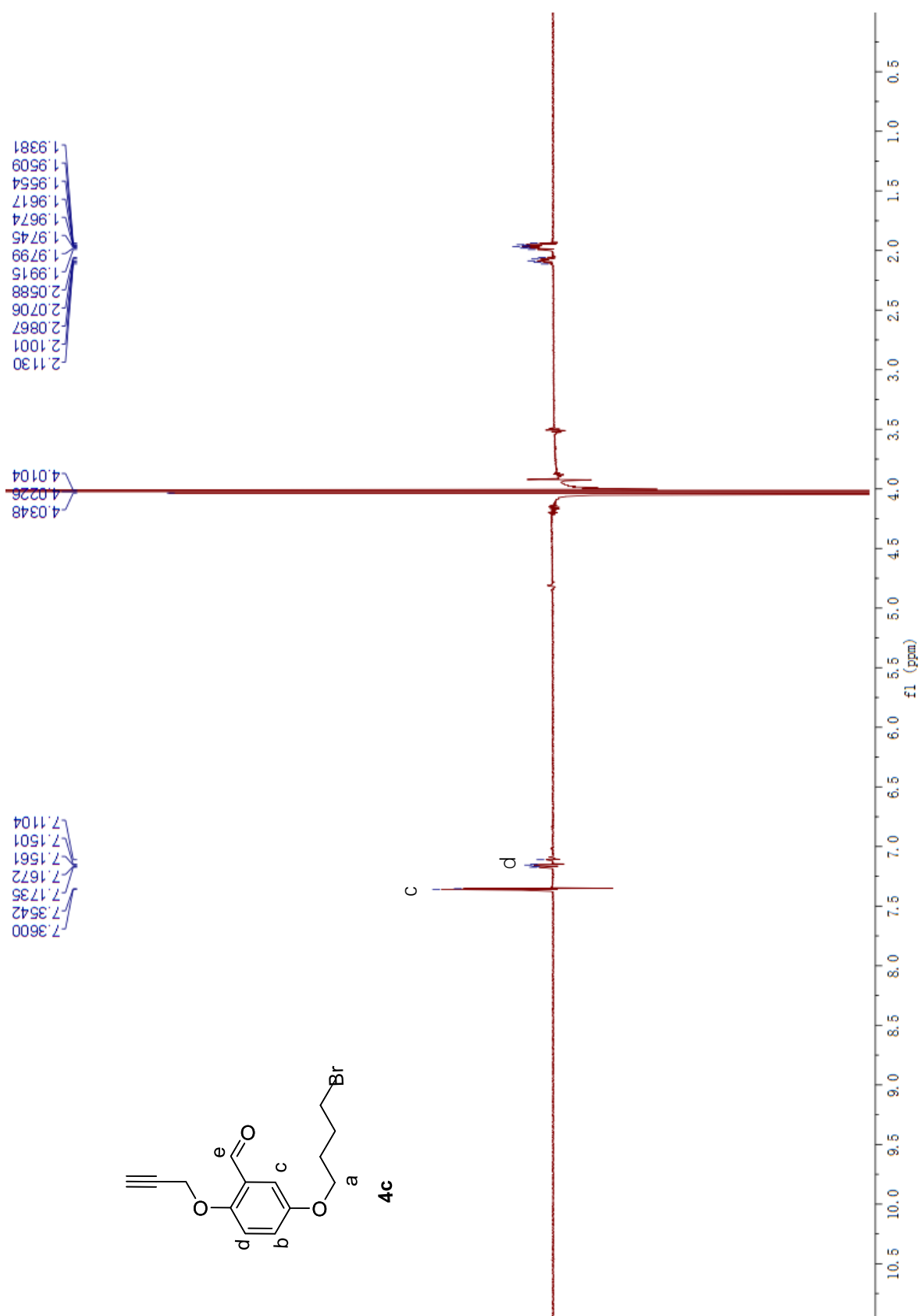
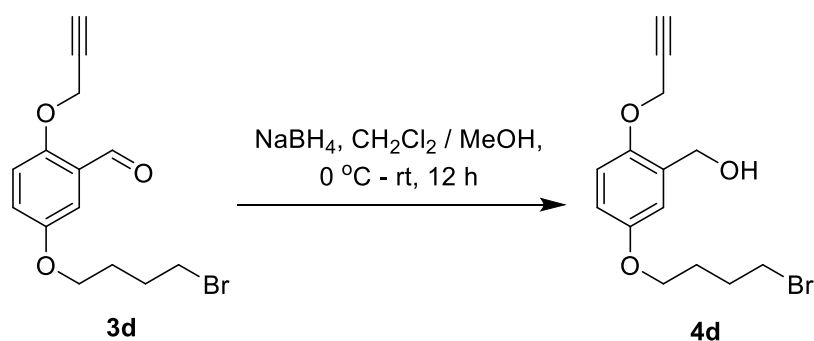


Fig. S16 NOE spectrum (400 MHz, CDCl₃) recorded for compound **3c**. H_a (4.00 ppm) was selectively excited. Strong coupling was observed for H_c and H_b, while weak or no coupling was observed for H_d and H_e.



To a 250 mL round bottom flask equipped with a magnetic stir bar was added compound **3d** (1.478 g, 4.75 mmol), CH_2Cl_2 (30 mL) and MeOH (50 mL). The solution was cooled to 0 °C in ice water bath. NaBH_4 (190 mg, 5.0 mmol) was then added in 3 portions. The reaction was allowed to warm up to room temperature and was stirred for another 12 hours. The solvent was then evaporated under reduced pressure. Water (20 mL) was added and followed by extraction with ethyl acetate (20 mL \times 4). The organic layer was dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. Column chromatography (silica, 300-400 mesh, petroleum ether/ethyl acetate, v/v 3:1) afforded compound **3d** as a white solid (1.447 g, 97%).

M.p. 40.1-42.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 6.92 (d, $J = 9.0$ Hz, 1H), 6.90 (d, $J = 3.3$ Hz, 1H), 6.77 (dd, $J_1 = 8.8$ Hz, $J_2 = 3.1$ Hz, 1H), 4.70 (s, 2H), 4.67 (d, $J = 5.5$ Hz, 2H), 3.96 (t, $J = 6.0$ Hz, 2H), 3.48 (t, $J = 6.6$ Hz, 2H), 2.50 (t, $J = 2.4$ Hz, 1H), 2.16 (t, $J = 6.2$ Hz, 1H), 2.05 (m, 2H), 1.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.62, 149.20, 131.31, 115.09, 113.62, 113.48, 78.81, 75.70, 67.34, 61.09, 56.80, 33.64, 29.44, 27.92. FT-IR (KBr): ν_{max} (cm^{-1}) 3347, 3276, 3069, 2941, 2930, 2912, 2896, 2861, 2118, 1595, 1500, 1476, 1451, 1440, 1392, 1379, 1347, 1290, 1277, 1259, 1209, 1135, 1056, 1043, 1023, 991, 969, 921, 877, 831, 797, 770, 747, 677, 645. HR-MS: m/z calcd for $[\text{M} + \text{Na}]^+$, $\text{C}_{14}\text{H}_{17}\text{BrO}_3$, 335.0253, found 335.0255 (error: 0.6 ppm).

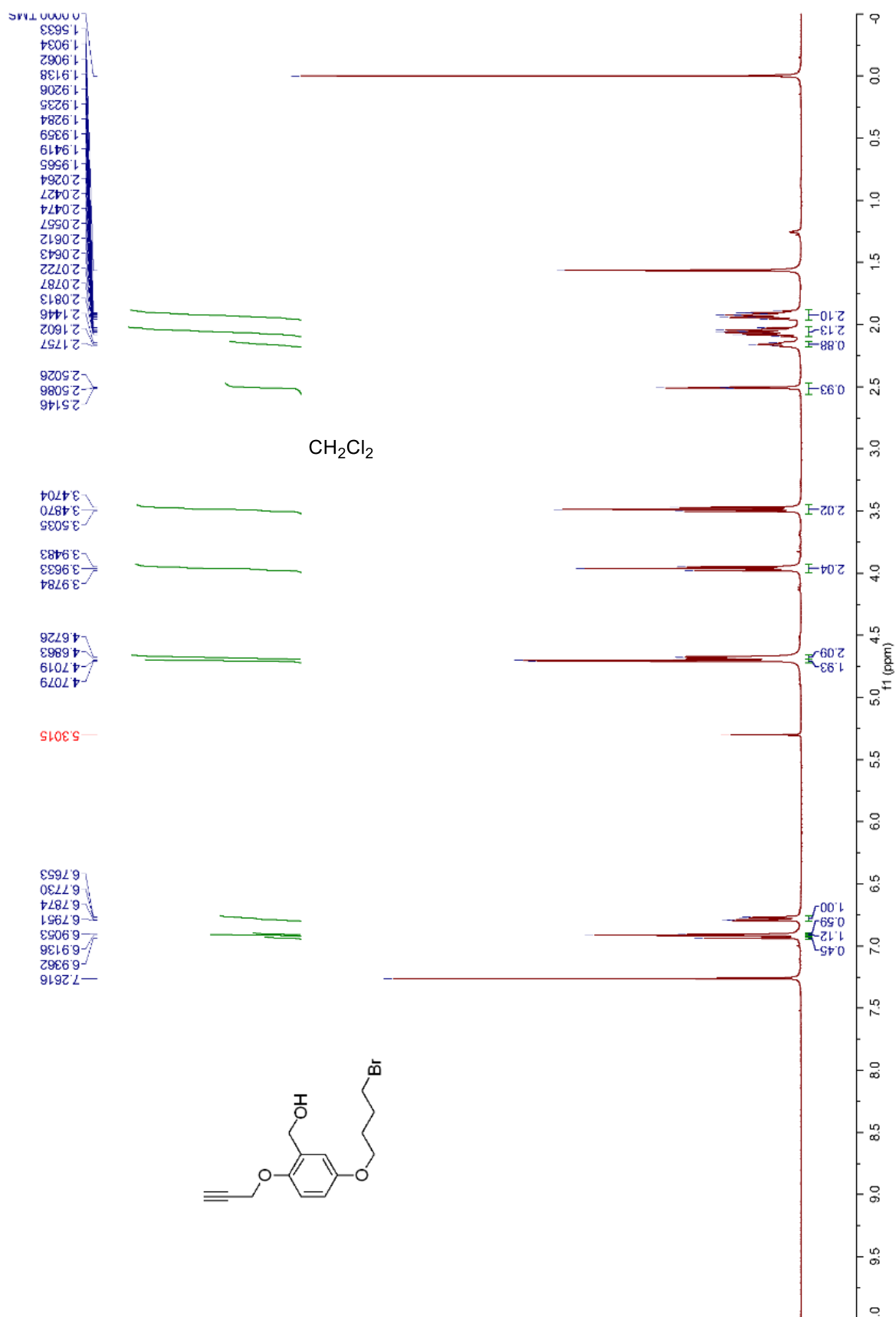


Fig. S17 ^1H NMR spectrum (400 MHz, CDCl_3) recorded for compound 4d.

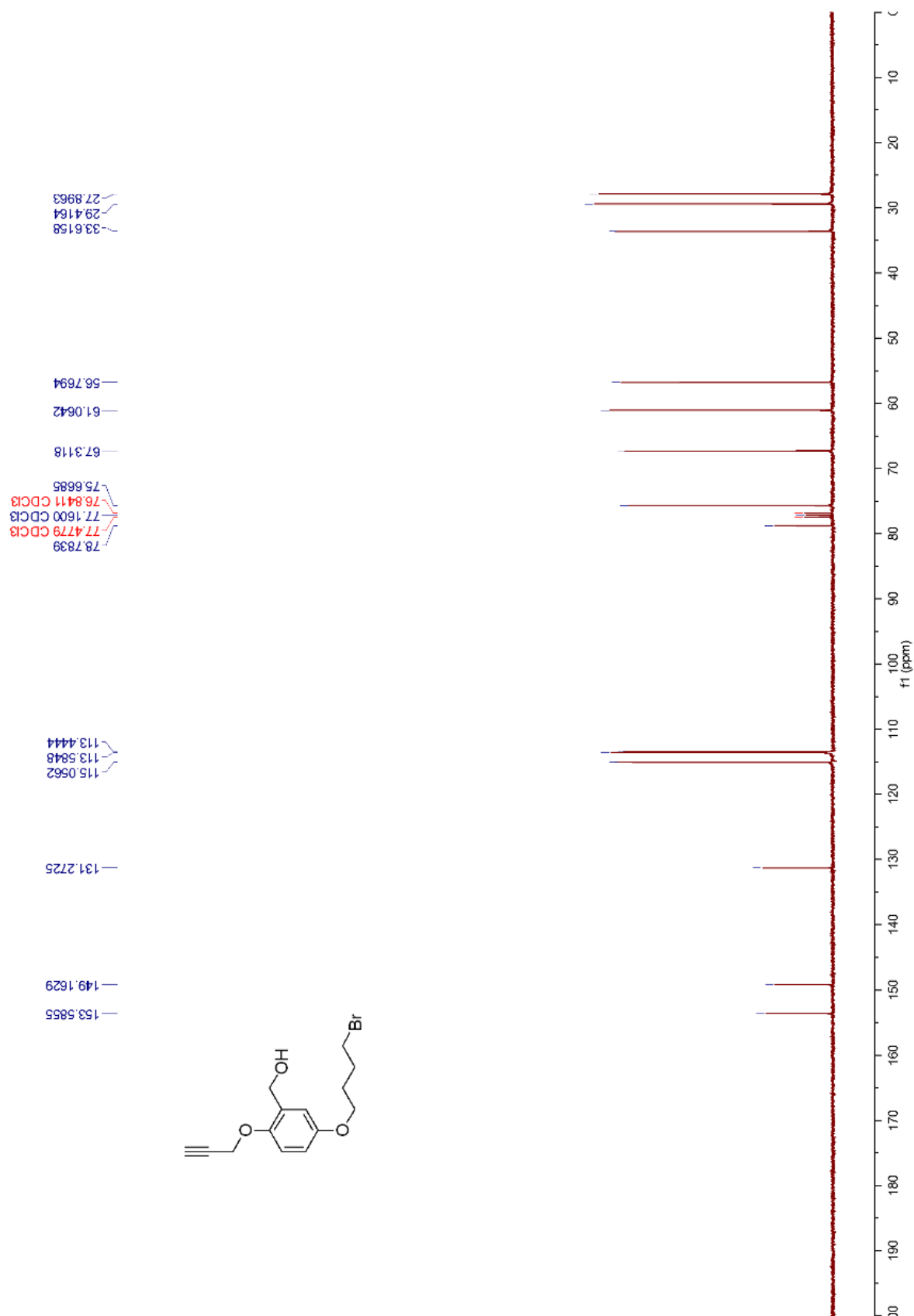
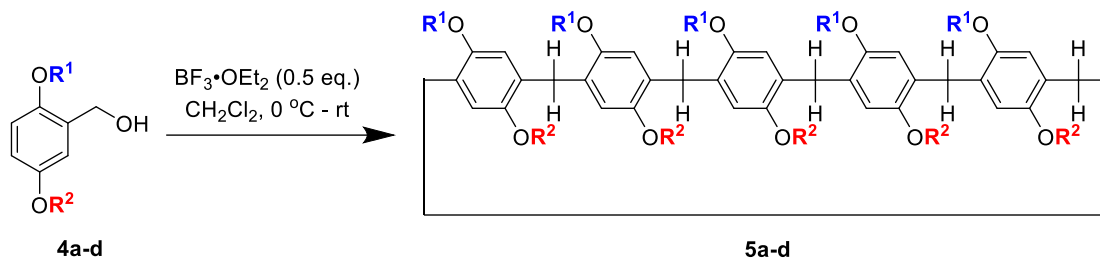


Fig. S18 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **4d**.

Syntheses of Non-symmetric PA[5]s **5a-d**.



Compound **5a**: 88.3 mg, yield = 16%, eluent: petroleum ether/dichloromethane, *v/v* 1:2, white solid. M.p. 110.1-114.5 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.91 (s, 5H), 6.87 (s, 5H), 4.56 (s, 10H), 3.79 (s, 10H), 3.75 (s, 15H), 2.46 (s, 5H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ 151.34, 148.97, 129.11, 128.33, 115.73, 114.16, 79.39, 74.85, 56.59, 56.02, 29.81. FT-IR (KBr) ν_{max} (cm⁻¹): 3454, 3282, 3942, 2859, 2829, 1637, 1500, 1467, 1402, 1375, 1266, 1210, 1042, 933, 881, 857, 779, 740, 708, 651. HR-MS: *m/z* calcd for [M+H]⁺ 871.3482, found 871.3440 (error: 4.8ppm).

Compound **5b**: 147.6 mg, yield = 14%, eluent: petroleum ether/dichloromethane, *v/v* 2:1, white solid. M.p. 72.6-74.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.92 (s, 5H), 6.80 (s, 5H), 4.17 (t, *J* = 6.0 Hz, 10H), 3.86 (t, *J* = 6.3 Hz, 10H), 3.79 (s, 10H), 3.58 (t, *J* = 5.6 Hz, 10H), 1.83 (m, 10H), 1.54 (m, 10H), 1.30 (m, 40H), 0.86 (t, *J* = 6.3 Hz, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 150.74, 149.07, 129.08, 128.53, 116.43, 114.80, 69.24, 68.49, 32.01, 30.91, 30.01, 29.76, 29.57, 29.47, 26.54, 22.81, 14.25. FT-IR (KBr) ν_{max} (cm⁻¹): 3455, 2929, 2855, 1637, 1499, 1475, 1406, 1278, 1208, 1101, 1069, 1029, 938, 880, 852, 779, 712, 655, 578, 478. HR-MS: calculated for [M+Na]⁺ 1724.5166, found 1724.5470 (error: 18 ppm).

Compound **5c**: 114.3 mg, yield = 15%, eluent: petroleum ether/dichloromethane, *v/v* 2:1, white solid. M.p. 87.6-88.7 °C. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 6.94 (s, 5H), 6.75 (s, 5H), 4.56 (s, 10H), 3.86 (t, *J* = 6.1 Hz, 10H), 3.78 (s, 10H), 2.31 (s, 5H), 1.79

(m, 10H), 1.53 (m, 10H), 1.25 (m, 40H), 0.82 (t, $J = 5.8$ Hz, 15H). ^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ 150.51, 148.69, 128.76, 128.16, 115.17, 114.69, 79.63, 74.84, 68.31, 56.49, 31.91, 29.92, 29.70, 29.41, 26.48, 22.75, 14.24. FT-IR (KBr) ν_{max} (cm^{-1}) 3294, 2929, 2856, 2129, 1610, 1500, 1477, 1467, 1458, 1406, 1375, 1307, 1212, 1048, 965, 937, 879, 853, 782, 744, 670, 632. HR-MS: m/z calcd for $[\text{M} + \text{NH}_4]^+$, $\text{C}_{90}\text{H}_{120}\text{O}_{10}$, 1378.9220, found 1378.9221 (error: 0.1 ppm).

Compound **5d**: 117.0 mg, yield = 13%, eluent: petroleum ether/dichloromethane, v/v 1:1, white solid. M.p. 139.2-142.4 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 6.93 (s, 5H), 6.71 (s, 5H), 4.56 (s, 10H), 3.92 (t, $J = 6.1$ Hz, 10H), 3.78 (s, 10H), 3.46 (t, $J = 6.5$ Hz, 10H), 2.26 (s, 5H), 2.08 (m, 10H), 1.93 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.33, 148.90, 128.83, 128.28, 115.47, 114.78, 79.47, 74.94, 67.59, 56.54, 33.92, 29.97, 29.75, 28.59. FT-IR (KBr) ν_{max} (cm^{-1}) 3287, 3047, 2963, 2866, 2127, 1611, 1499, 1474, 1454, 1439, 1407, 1246, 1208, 1044, 878, 852, 780, 736, 642, 560. HR-MS: m/z calcd for $[\text{M} + \text{NH}_4]^+$, $\text{C}_{70}\text{H}_{75}\text{O}_{10}\text{Br}_5$, 1494.1558, found 1494.1582 (error: 1.6 ppm).

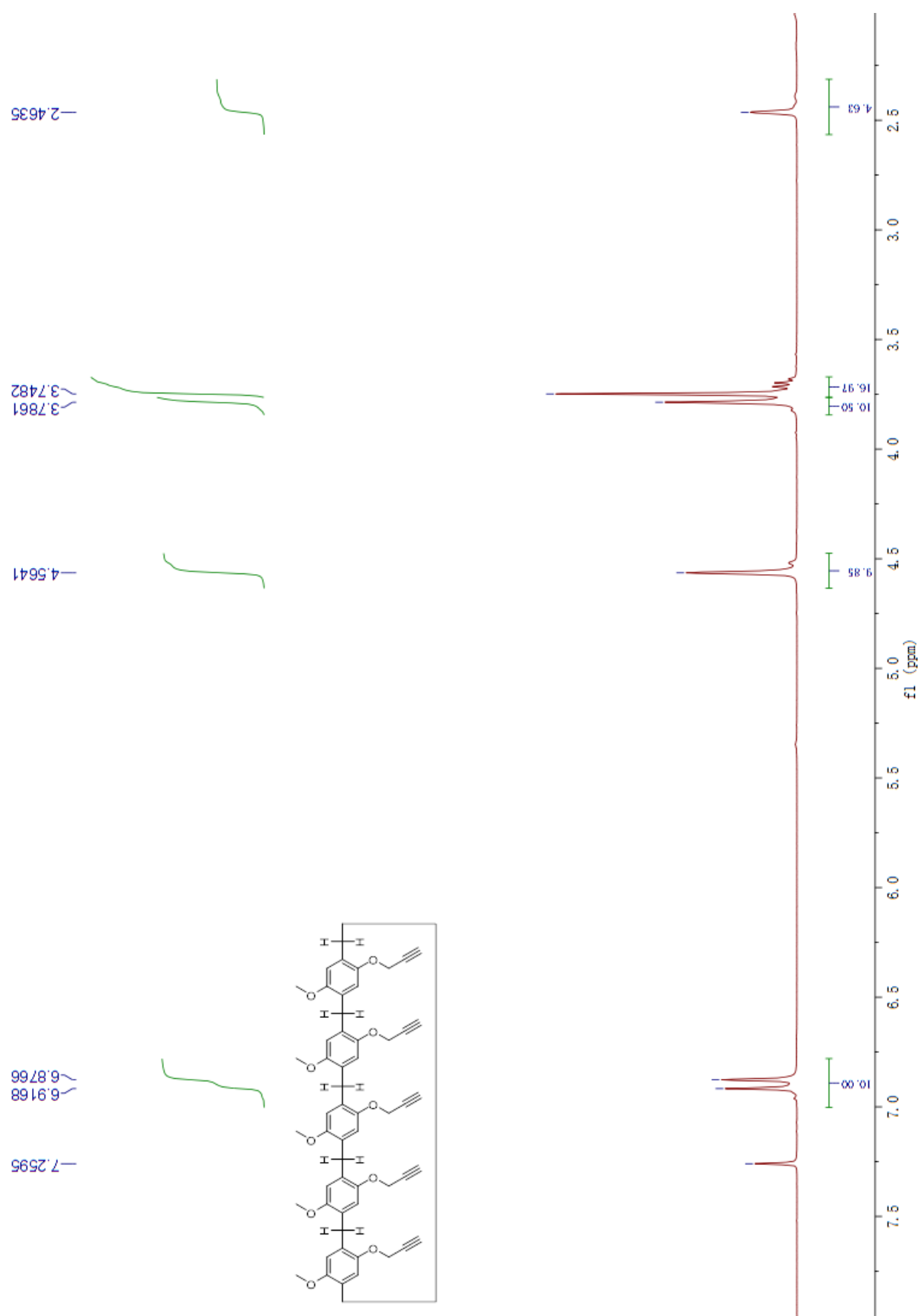


Fig. S19 ^1H NMR spectrum (400 MHz, CDCl_3) recorded for compound **5a**

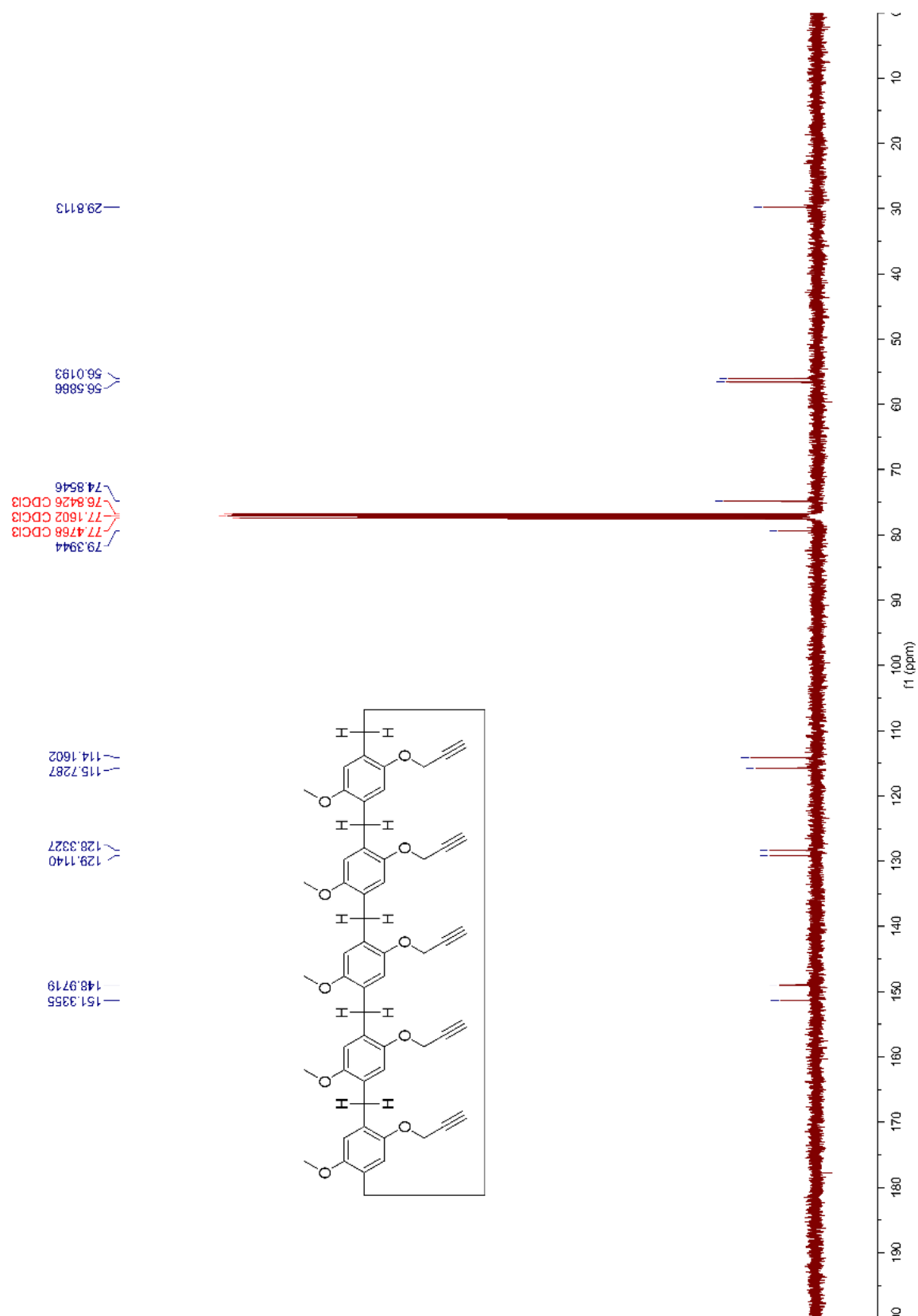


Fig. S20 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **5a**

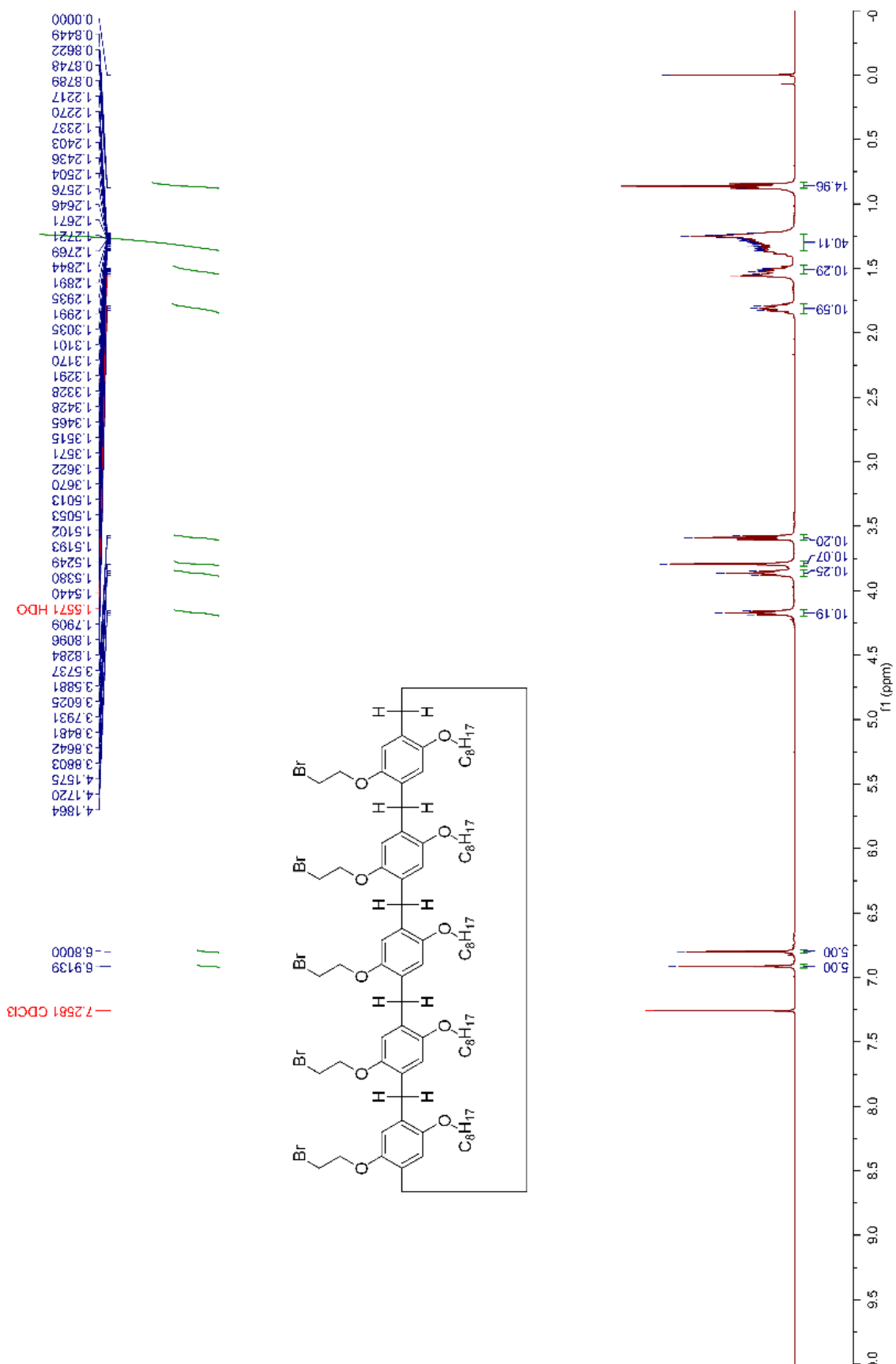


Fig. S21 1H NMR spectrum (400 MHz, $CDCl_3$) recorded for compound **5b**.

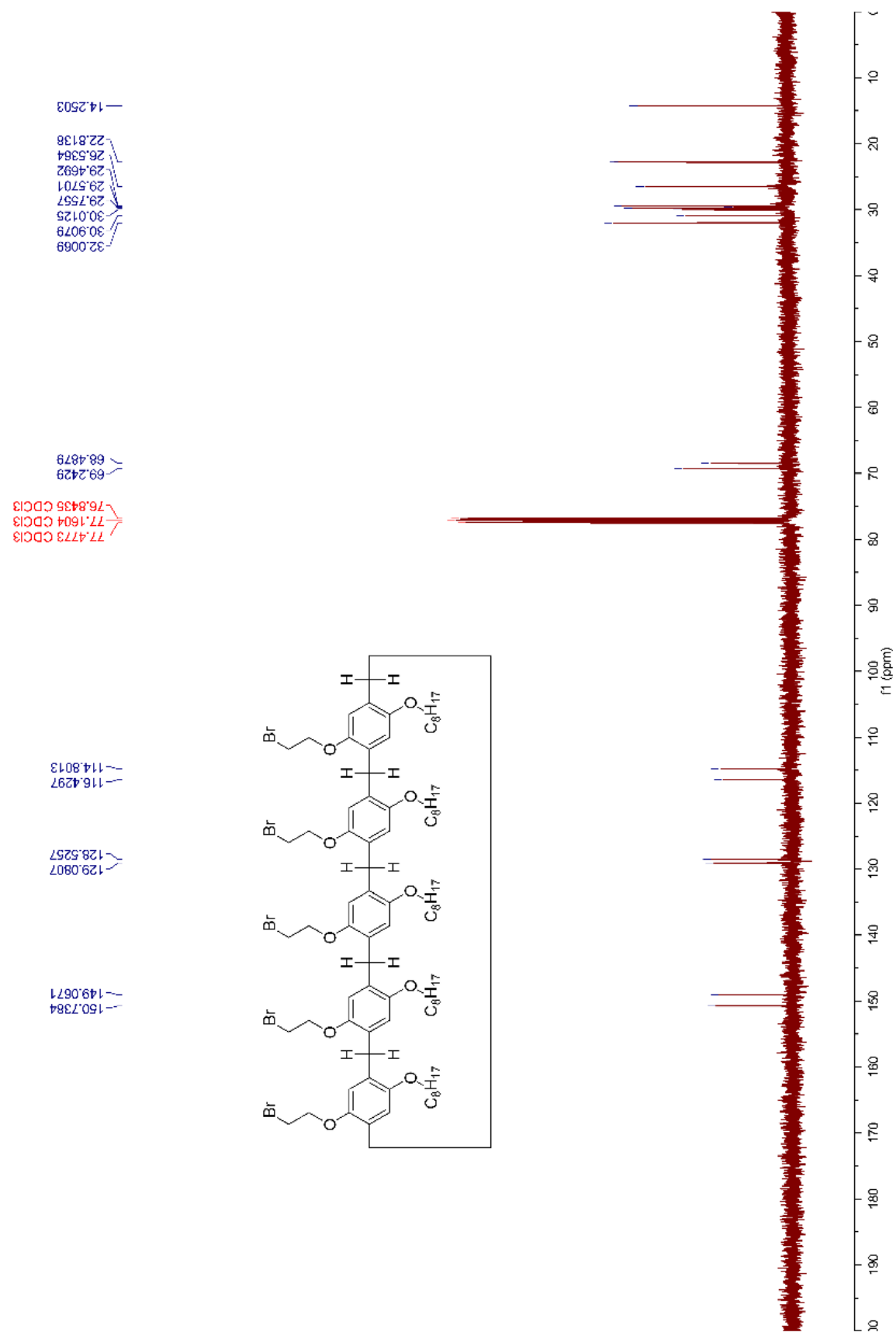


Fig. S22 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **5b**.

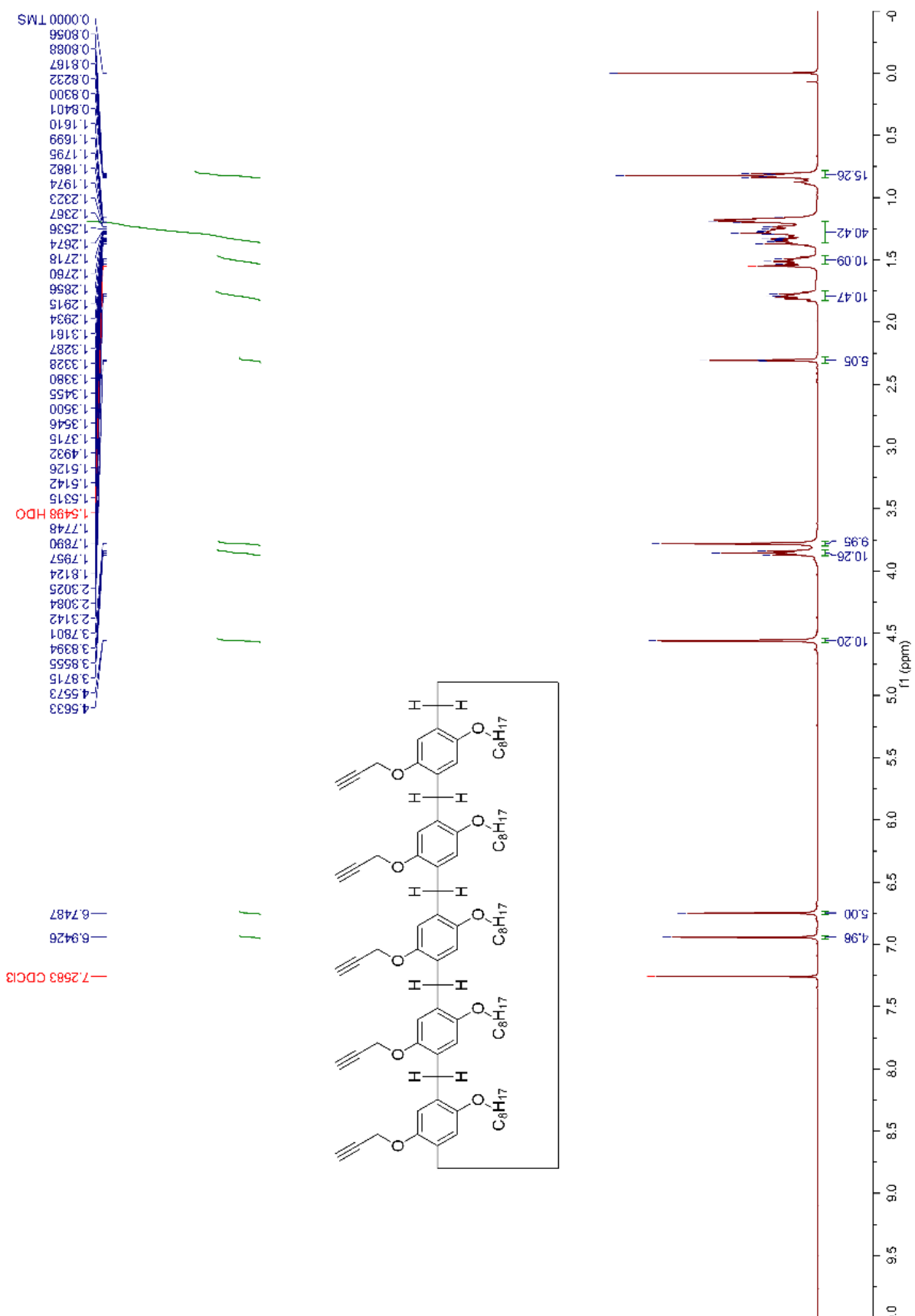


Fig. S23 ¹H NMR spectrum (400 MHz, CDCl₃) recorded for compound **5c**.

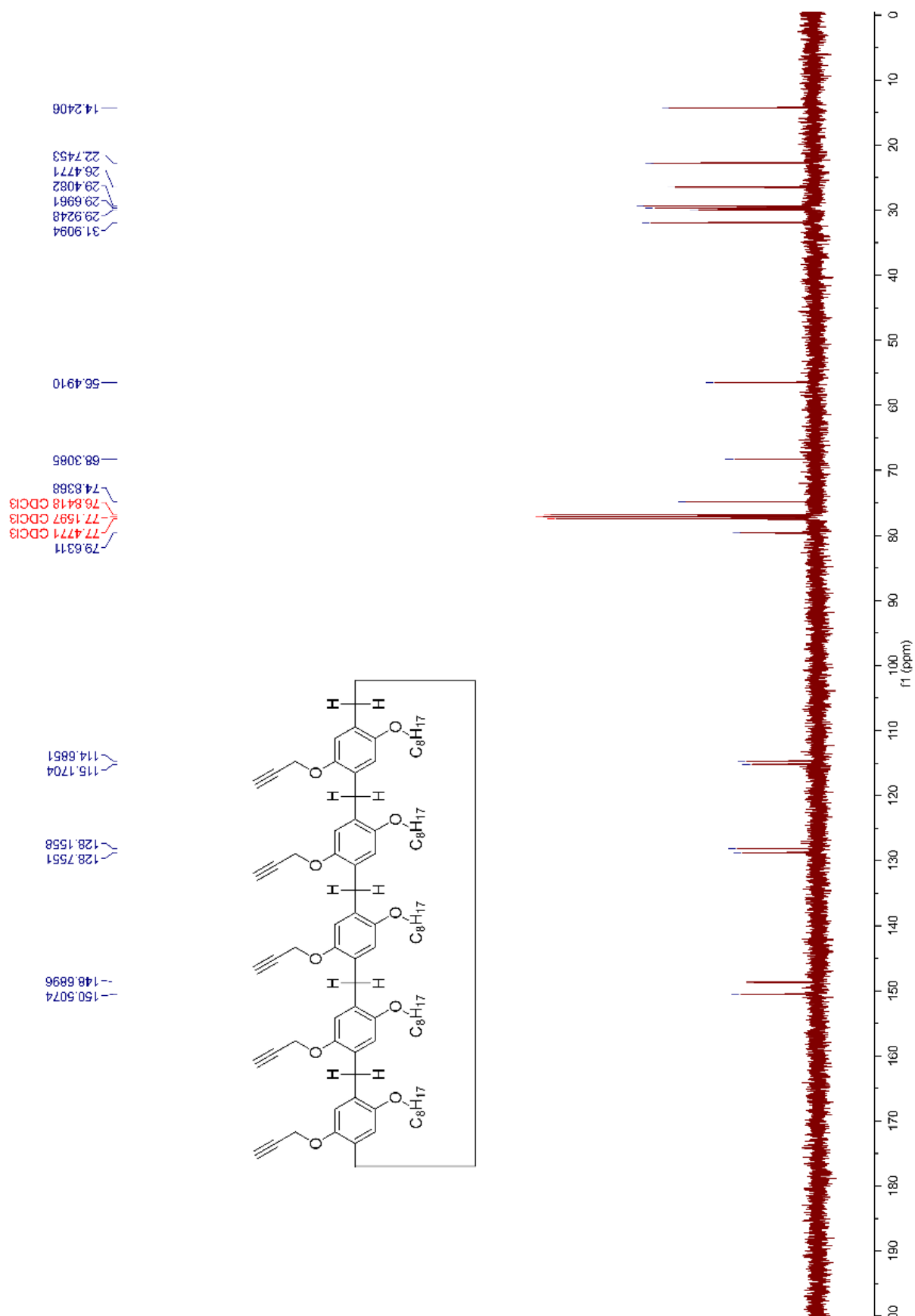


Fig. S24 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **5c**.

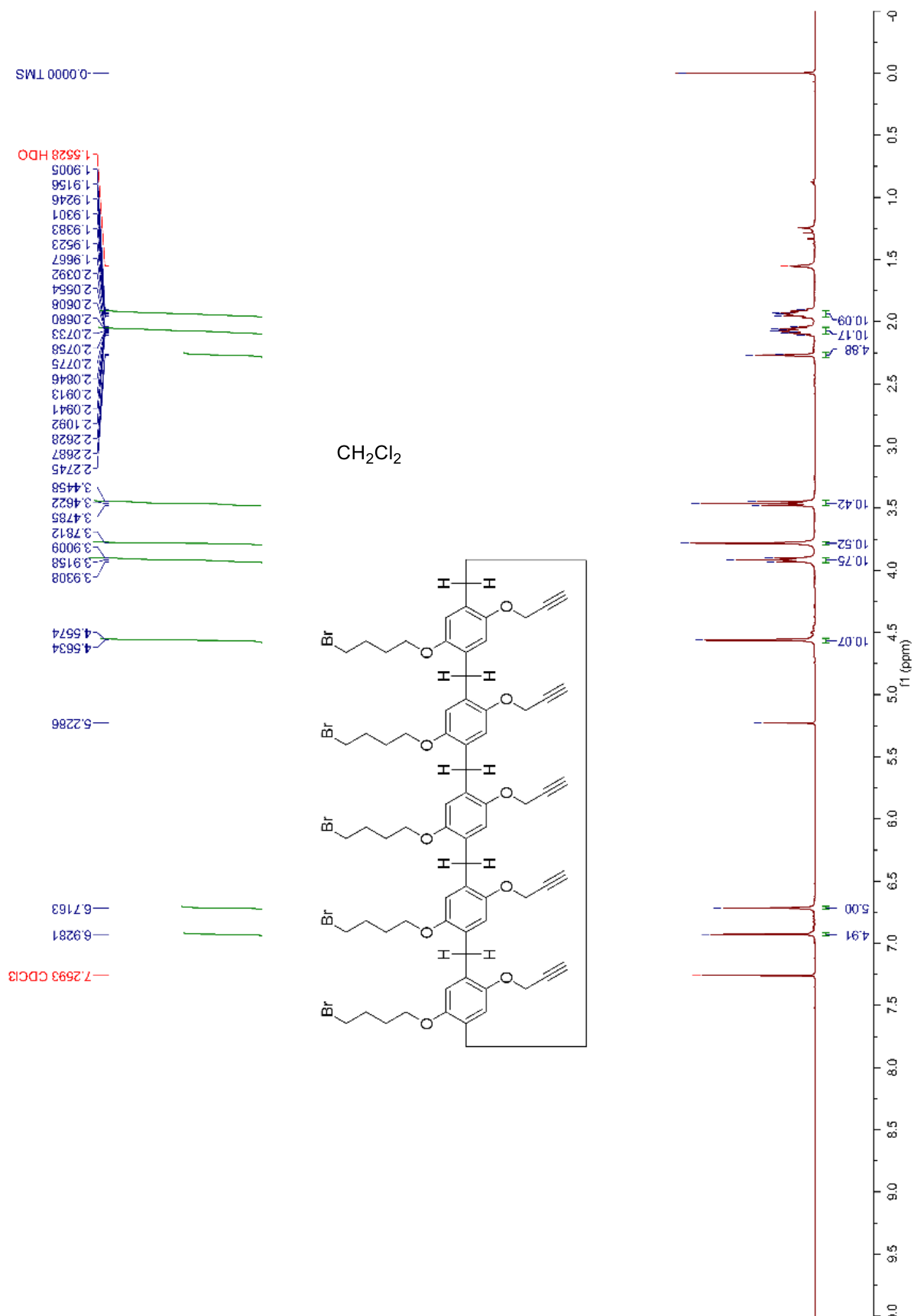


Fig. S25 ^1H NMR spectrum (400 MHz, CDCl_3) recorded for compound **5d**.

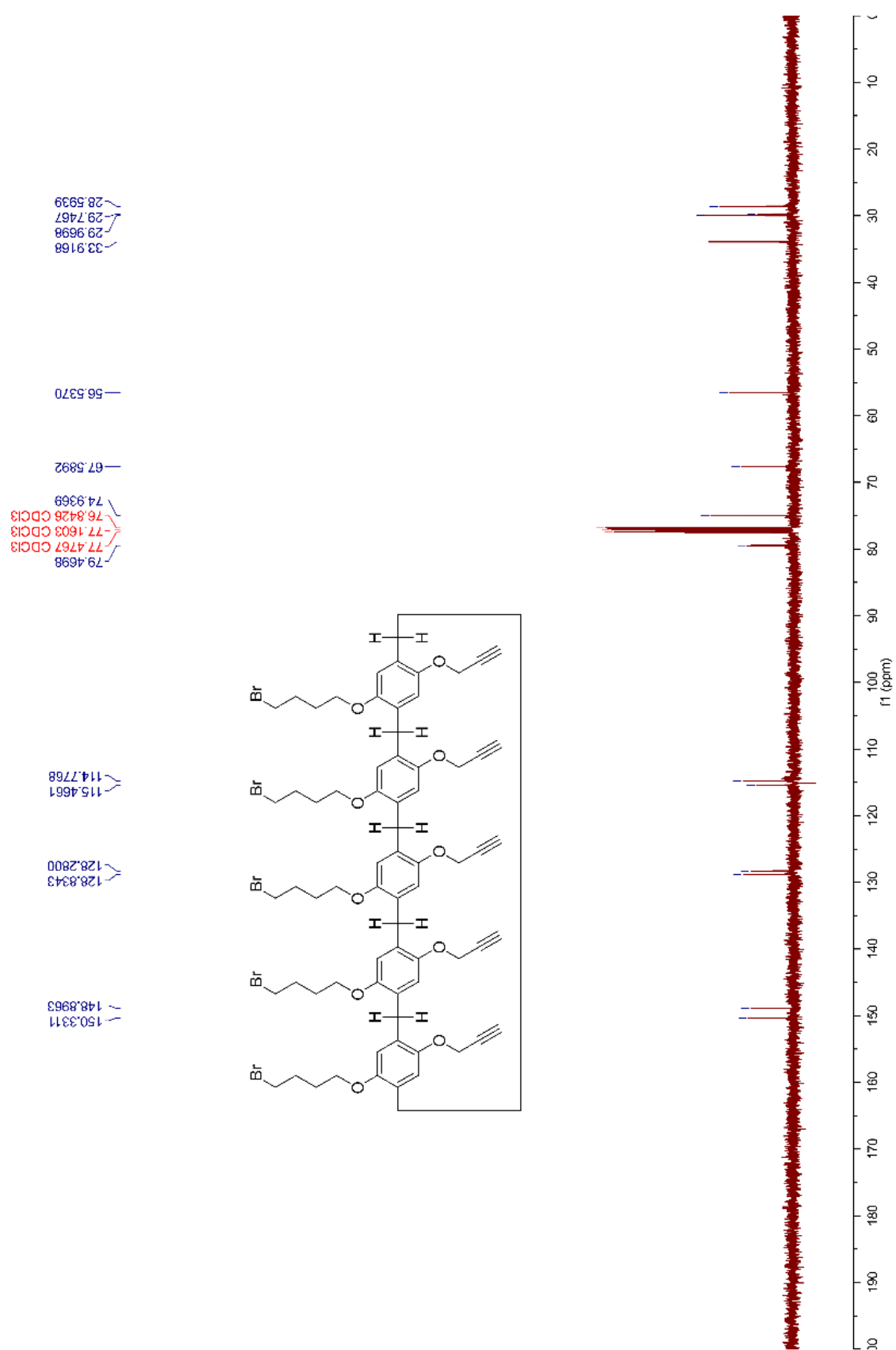


Fig. S26 ¹³C NMR spectrum (100 MHz, CDCl₃) recorded for compound **5d**.

Single crystal XRD data

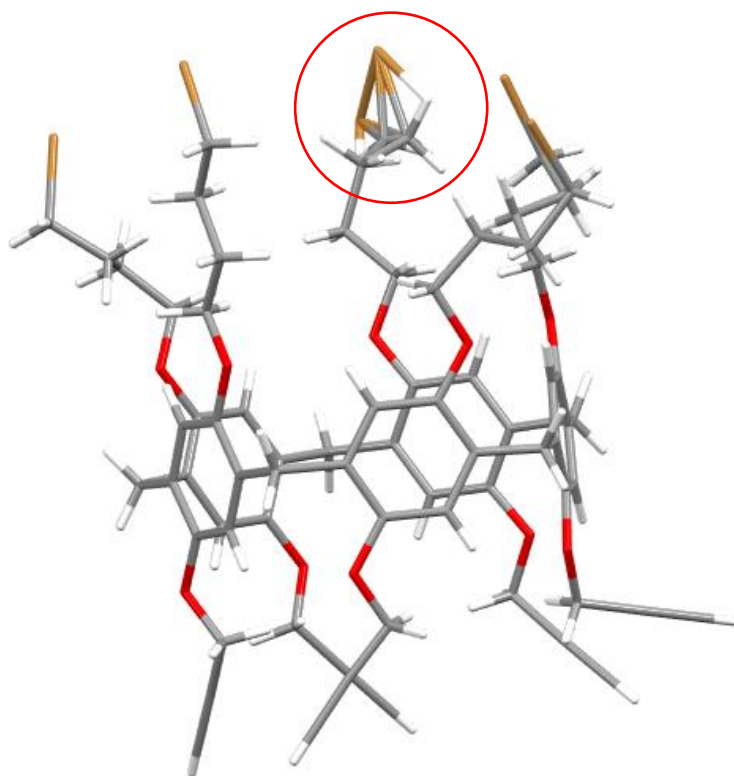


Fig. S27 Single crystal structure of compound **5d**. Color code: C, grey; H, white; O, red; Br, brown. The red circle indicates the two possible bromobutyl chain conformations.