Supporting Information

A One-pot Synthesis and Functionalization of Polyynes

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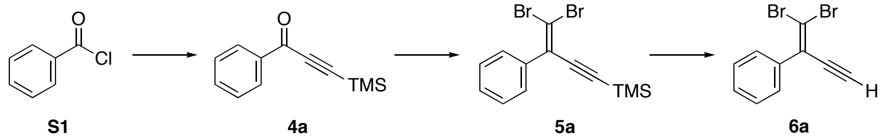
General. Reagents were purchased reagent grade from commercial suppliers and used without further purification. Et_2O, toluene, and THF were distilled from sodium/benzophenone ketyl, and hexanes and CH_2Cl_2 were distilled from CaH_2 immediately prior to use. Anh. $MgSO_4$ or Na_2SO_4 were used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at water-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of Ar or N_2. Column chromatography: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada*. Thin Layer Chromatography (TLC): aluminum sheets covered with *silica gel-60* F_{254} from *Macherey-Nagel*; visualization by UV light or $KMnO_4$ stain. Mp: *Gallenkamp* apparatus; uncorrected. IR spectra (cm^{-1}): *Nicolet Magna-IR 750* (neat) or *Nic-Plan IR Microscope* (solids). ^1H- and ^{13}C-NMR: *Varian Gemini-300*, *400* or *500* instruments, at rt in $CDCl_3$; solvent peaks (7.24 for ^1H and 77.0 for ^{13}C) as reference. EI MS (*m/z*): *Kratos MS50* instrument. Elemental analyses were conducted by Spectral Services at the University of Alberta.

For simplicity, the coupling constants for the aryl protons for *para*-substituted phenyl groups have been reported as pseudo first-order, even though they are second-order spin systems. For mass spectral analyses, low-resolution data are provided in cases when M^+ is not the base peak; otherwise, only high-resolution data are provided.

In cases where crude reaction mixtures were passed through a plug of silica gel and celite, the following procedure was employed: To a fritted funnel (35 mL), a mixture of silica gel and hexanes was added, which was then covered by celite. A sample solution was introduced and flushed with the solvent (as indicated below). Progress of separation was monitored by means of TLC.

All new compounds are characterized below; references are provided for known compounds. In cases where spectral data were not provided in these original reports, it is provided herein.

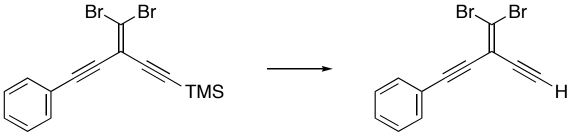
Synthesis and Characterization



Compound 5a. To benzoyl chloride **S1** (4.2 g, 30 mmol) in CH_2Cl_2 (80 mL) was added bis(trimethylsilyl)acetylene (5.2 g, 30 mmol), and the temperature was lowered to 0 °C. Powdered $AlCl_3$ (5.8 g, 44 mmol) was slowly added. The reaction was stirred and warmed to rt. After 22 h, the reaction mixture was carefully quenched by addition to HCl (conc, 15 mL) diluted with ice (85 mL). The organic phase was separated, washed with saturated aqueous NH_4Cl, and dried over $MgSO_4$. The crude mixture was plugged through a silica gel column, and the resulting solution reduced to afford the

intermediate ketone **4a**,[1,2,3] $R_f = 0.4$ (hexanes/CH_2Cl_2 1:1), that was carried onto the next step without further purification. CBr_4 (19 g, 55 mmol) and PPh_3 (29 g, 110 mmol) were added to CH_2Cl_2 (150 mL). The heterogeneous mixture was added to a solution of the crude ketone **4a** in CH_2Cl_2 (50 mL) at 0 °C and stirred overnight at rt. After the reaction mixture was reduced, hexanes (200 mL) was added. The mixture was filtered through a short silica gel column to afford **5a** (8.3 g, 77% based on **S1**) as a pale yellow oil. $R_f = 0.6$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$, cast) 2959, 2136 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.39–7.34 (m, 3H), 0.22 (9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 131.0, 128.6, 128.5, 128.3, 104.2, 103.4, 100.4, -0.30. HRMS calcd. for $C_{13}H_{14}{}^{79}Br^{81}BrSi$ 357.9211, found 357.9211. Anal. calcd. for $C_{13}H_{14}Br_2Si$: C, 43.60; H, 3.94. Found: C, 43.52; H, 4.03.

Compound 6a. Dibromoolefin **5a** (7.00 g, 19.5 mmol) was dissolved in THF (50 mL) and MeOH (50 mL), and pulverized K_2CO_3 (0.10 g, 0.75 mmol) was added at rt. TLC analysis was used to monitor the reaction until desilylation was completed. After 1 h, diluted sat. NH_4Cl (100 mL) and Et_2O (100 mL) were added. The organic layer was separated, washed with H_2O, and dried over $MgSO_4$. $MgSO_4$ was filtered off, and the solvent was reduced. The solution was passed through a short silica gel column to afford **6a** (5.21 g, 93%) as a white solid. Mp 39–42 ˚C. $R_f = 0.6$ (hexanes/CH_2Cl_2 3:1). IR ($CHCl_3$, cast) 3290 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.39–7.34 (m, 3H), 3.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 130.1, 128.7, 128.5, 128.4, 100.8, 85.8, 82.7. EIMS *m/z* 285.9 (M^+, 49), 126.0 ($[C_{10}H_6]^+$, 100); HRMS calcd. for $C_{10}H_6Br_2$ 285.8816, found 285.8816. Anal. calcd. for $C_{10}H_6Br_2$: C, 42.00; H, 2.11. Found: C, 41.80; H, 1.95.



5b **6b**

Compound 6b. Dibromoolefin **5b**[4] (1.9 g, 5.0 mmol) was dissolved in THF (40 mL) and MeOH (40 mL), and pulverized K_2CO_3 (0.10 g, 0.75 mmol) was added at rt. TLC analysis was used to monitor the reaction until desilylation was completed. After 1 h, sat. NH_4Cl (200 mL) and Et_2O (200 mL) were added. The organic layer was separated, washed with H_2O, and dried over $MgSO_4$. $MgSO_4$ was filtered off, and the solvent was reduced. The solution was passed through a short silica gel column to afford **6b** (1.2 g, 77%) as a pale yellow oil. As the neat oil **6b** slowly discolored, **6b** is best stored in a solution of hexanes, under refrigeration, unless used immediately. $R_f = 0.5$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$,

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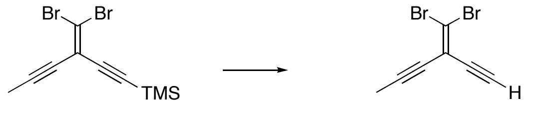
[1] Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E.; Arimoto, M.; Yamaguchi, H. *Tetrahedron Lett.* **1985**, *26*, 4501–4504.

[2] Maurette, L.; Tedeschi, C.; Sermot, E.; Soleilhavoup, M.; Hussain, F.; Donnadieu, B.; Chauvin, R. *Tetrahedron* **2004**, *60*, 10077–10098.

[3] Walton, D. R. M.; Waugh, F. *J. Organomet. Chem.* **1972**, *37*, 45–56.

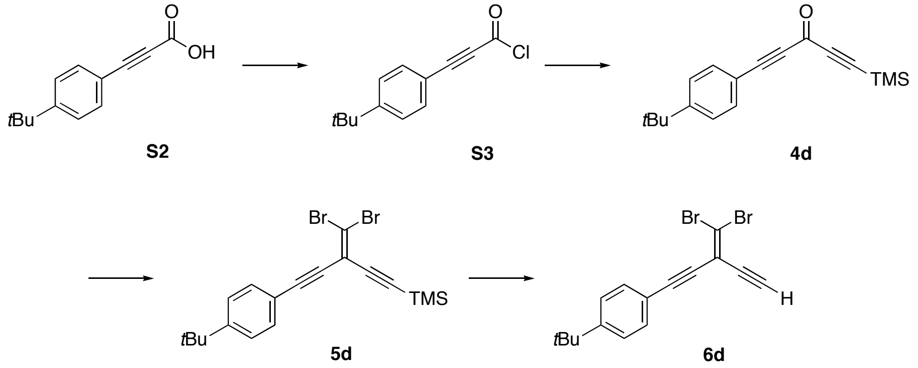
[4] Eisler, S.; Chahal, N.; McDonald, R.; Tykwinski, R. R. *Chem. Eur. J.* **2003**, *9*, 2542–2550.

cast) 3293, 2226, 2189, 2108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 2H), 7.34–7.30 (m, 3H), 3.50 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 131.6, 129.3, 128.4, 121.9, 113.4, 109.5, 96.2, 85.8, 83.9, 79.7. EIMS *m/z* 309.9 (M^{+}, 95), 150.0 ($[C_{12}H_6]^+$, 100); HRMS calcd. for $C_{12}H_6{}^{79}Br^{81}Br$ 309.8816, found 309.8809. Anal. calcd. for $C_{12}H_6Br_2$: C 46.50; H 1.95. Found: C 46.74, H 1.97.



5c **6c**

Compound 6c. Dibromoolefin **5c**[5] (861 mg, 2.69 mmol) was dissolved in THF (10 mL) and MeOH (10 mL), and pulverized K_2CO_3 (0.10 g, 0.75 mmol) was added at rt. TLC analysis was used to monitor the reaction until desilylation was completed. After 1 h, sat. NH_4Cl (10 mL) and Et_2O (10 mL) were added. The organic layer was separated, washed with H_2O, and dried over $MgSO_4$. $MgSO_4$ was filtered off, and the solvent was reduced. The solution was passed through a short silica gel column to afford **6c** (516 mg, 77%) as a pale yellow oil. As the neat oil **6c** slowly discolored, **6c** is best stored in a solution of hexanes under refrigeration, unless used immediately. R_f = 0.5 (hexanes). IR ($CHCl_3$, cast) 3291, 2915, 2284, 2225, 2103 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (s, 1H), 1.98 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 113.6, 108.2, 94.3, 83.2, 80.2, 76.6, 4.8. HRMS calcd. for $C_7H_4{}^{79}Br^{81}Br$ 247.8659, found 247.8665.



S2 **S3** **4d**

5d **6d**

Compound 5d. To **S2**[6] (1.0 g, 5.0 mmol) was added thionyl chloride (4.08 g, 34.3 mmol) and the reaction was stirred at rt overnight, protected from moisture by a drying tube filled with $CaSO_4$. The excess thionyl chloride was removed in vacuo. To the acid chloride **S3** in CH_2Cl_2 (35 mL) was added bis(trimethylsilyl)acetylene (0.87 g, 5.1 mmol), and the temperature was lowered to –30 °C. Powdered $AlCl_3$ (0.87 g, 6.5 mmol) was slowly added. The reaction was stirred and warmed to rt. After 2 h, the reaction mixture was carefully quenched by pouring into HCl (conc, 15 mL) diluted with ice (85 mL). The organic phase was separated, washed with saturated aq. NH_4Cl, and dried over $MgSO_4$. The crude mixture was plugged through a silica gel column, and the resulting solution reduced to afford the

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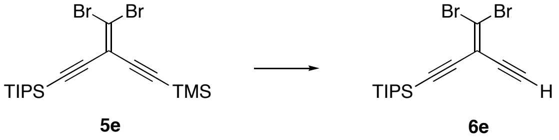
5. Mukai, C.; Miyakoshi, N.; Hanaoka, M. *J. Org. Chem.* **2001**, *66*, 5875-5880.
6. Schottelius, M. J.; Chen, P. *Helv. Chim. Acta* **1998**, *81*, 2341–2347.

intermediate ketone **4d**, $R_f = 0.4$ (hexanes/CH_2Cl_2 1:1), that was carried on without further purification. CBr_4 (2.5 g, 7.5 mmol) and PPh_3 (4.0 g, 15 mmol) were added to CH_2Cl_2 (150 mL). The mixture was added to a solution of the crude ketone **4d** in CH_2Cl_2 (10 mL) at rt and stirred for 30 min. The reaction mixture was reduced, and CH_2Cl_2 (5 mL) and hexanes (50 mL) were added. The heterogeneous mixture was filtered through a short silica gel column to afford **5d** (0.76 g, 35% based on **S2**) as a pale yellow solid. Mp 74–75 °C. $R_f = 0.6$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$, cast) 2963, 2204, 2155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 9H), 1.34 (s, 9H), 7.38 (d, $J = 8.0$ H, 2H), 7.49 (d, $J = 8.0$, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -0.4, 31.1, 34.8, 85.4, 96.2, 100.3, 102.3, 108.7, 114.4, 119.1, 125.4, 131.4, 152.5. EIMS *m/z* 438.0 (M^+, 71), 423.0 ($[M - CH_3]^+$, 100); HRMS calcd. for $C_{19}H_{22}{}^{79}Br^{81}BrSi$ 437.9837, found 437.9825. Anal. calcd. for $C_{19}H_{22}Br_2Si$: C, 52.07; H, 5.06. Found: C, 51.94; H, 5.07.

Compound 6d. Dibromoolefin **5d** (0.65 g, 1.5 mmol) was dissolved in THF (15 mL) and MeOH (15 mL), and pulverized K_2CO_3 (0.073 g, 0.52 mmol) was added at rt. TLC analysis was used to monitor the reaction until the desilylation was completed. After 30 min, HCl (2N, 15 mL) and Et_2O (50 mL) were added. The organic layer was separated, washed with H_2O, and dried over $MgSO_4$. $MgSO_4$ was filtered off, and the solvent was reduced. The solution was passed through a short silica gel column to afford **6d** (0.51 g, 93%) as a pale yellow solid. Mp 82–83 °C. $R_f = 0.6$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$, cast) 3294, 2228, 2193, 2108 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 3.50 (s, 1H), 7.35 (d, $J = 8.0$ H, 2H), 7.44 (d, $J = 8.0$, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 31.1, 34.9, 79.8, 83.8, 85.3, 96.6, 109.1, 113.5, 118.9, 125.5, 131.4, 152.8. EIMS *m/z* 365.9 (M^+, 44), 350.9 ($[M - CH_3]^+$, 100); HRMS calcd. for $C_{16}H_{14}{}^{79}Br^{81}Br$ 365.9442, found 365.9439. Anal. calcd. for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85. Found: C, 52.39; H, 3.95.



Compound 6e. Dibromoolefin **5e**[7] (183 mg, 0.398 mmol) was dissolved in THF (10 mL) and MeOH (10 mL), and pulverized K_2CO_3 (0.10 g, 0.75 mmol) was added at rt. TLC analysis was used to monitor the reaction until desilylation was completed. After 1 h, sat. NH_4Cl (10 mL) and Et_2O (10 mL) were added. The organic layer was separated, washed with H_2O, and dried over $MgSO_4$. $MgSO_4$ was filtered off, and the solvent was reduced. The solution was passed through a short silica gel column to afford **6e** (112 mg, 72%) as a pale yellow oil. As the neat oil **6e** slowly discolored, **6e** is best stored in a solution of hexanes, under refrigeration, unless used immediately. $R_f = 0.5$ (hexanes). IR ($CHCl_3$, cast) 3302, 2943, 2890, 2180, 2135 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.44 (s, 1H), 1.09 (s, 21H); ^{13}C NMR (125

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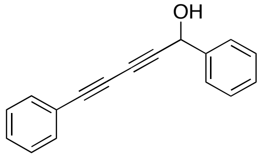
[7] Anthony, J.; Boldi, A. M.; Rubin, Y.; Hobi, M.; Gramlich, V.; Knobler, C. B.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 13-45.

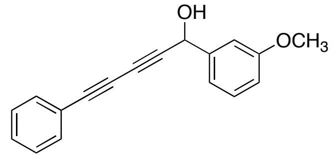
MHz, $CDCl_3$) δ 113.8, 110.4, 101.7, 100.3, 83.7, 79.8, 18.6, 11.1. EIMS *m/z* 390.0 (M^+, 20), 346.9 ($[M - iPr]^+$, 100); HRMS calcd. for $C_{15}H_{22}Si^{79}Br^{81}Br$ 389.9837, found 389.9826.

General procedure for the synthesis of functionalized polyynes by trapping with electrophiles. A solution of dibromoolefin **6a,b,c** (0.5–1.0 nmol) was dissolved in toluene (2 mL) and this mixture was then diluted with hexanes (10 mL) and cooled to –20 ˚C under an Ar atmosphere. To this solution with stirring, BuLi (2.2 equiv, 1.6 or 2.5 M in hexanes) was added via syringe over a period of ca. 1 min. The reaction mixture was allowed to slowly warm to 0 ºC. The reaction was then cooled to –20 ºC again, and Et_2O (10 mL) was added, followed by the addition of the electrophile (dissolved in 2 mL of Et_2O) via a canula. The reaction mixture was allowed to slowly warm to rt overnight. Sat. aq. NH_4Cl (10 mL) and Et_2O (10 mL) were added, the organic phase was separated, washed with sat. aq. NaCl (2 x 10 mL), and dried over $MgSO_4$. Solvent removal and purification by column chromatography (silica gel, solvent systems indicated below) gave the desired product. Additional steps, as required, are also indicated below.



8a

Compound 8a.[8] Dibromoolefin **6a** (167 mg, 0.586 mmol), BuLi (2.5 M in hexanes, 0.52 mL, 1.3 mmol), and benzaldehyde (73 mg, 0.69 mmol) were used as per the general procedure and yielded **8a** (94.7 mg, 70%) as an orange solid. $R_f = 0.5$ (CH_2Cl_2/hexanes 2:1). Mp 75–78 ˚C. IR ($CHCl_3$, cast) 3332, 3032, 2242 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.8 Hz, 2H), 7.49 (dt, *J* = 6.8, 2.0 Hz, 2H), 7.42-7.29 (m, 6H), 5.58 (d, *J* = 6.0 Hz, 1H), 2.35 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 132.6, 129.4, 128.8, 128.7, 128.4, 126.7, 121.3, 81.6, 79.4, 73.2, 71.3, 65.2. HRMS calcd. for $C_{17}H_{12}O$ 232.0888, found 232.0888.



8b

Compound 8b. Dibromoolefin **6a** (175 mg, 0.611 mmol), BuLi (2.5 M in hexanes, 0.54 mL, 1.4 mmol), and *m*-methoxylbenzaldehyde (92 mg, 0.67 mmol) were used as per the general procedure and yielded **8b** (116 mg, 72%) as a yellow solid. Mp 28-31 °C. $R_f = 0.6$ (CH_2Cl_2). IR ($CHCl_3$, cast) 3375,

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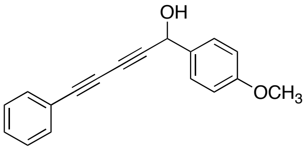
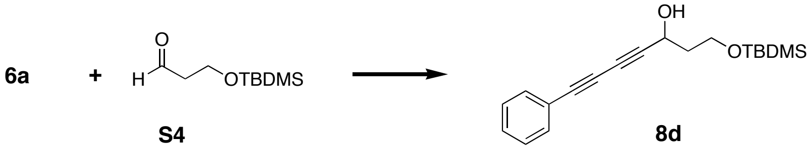
[8] Alami, M.; Crousse, B.; Linstrumelle, G. *Tetrahedron Lett.* **1995**, *36*, 3687–3690.

2241, 2210, 1262 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2H), 7.41–7.29 (m, 4H), 7.15–7.10 (m, 2H), 6.90 (dd, J = 2.7, 0.9 Hz, 1H), 5.57 (d, J = 6.5 Hz, 1H), 3.82 (s, 3H), 2.51 (d, J = 6.5, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 141.2, 132.6, 129.8, 129.4, 128.4, 121.4, 118.9, 114.4, 112.1, 81.6, 79.4, 73.2, 71.3, 65.1, 55.4. HRMS calcd. for $C_{18}H_{14}O_2$ 262.0994, found 262.0996. Anal. calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.33; H, 5.29.

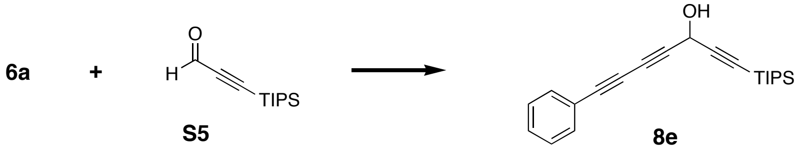


8c

Compound 8c. Dibromoolefin **6a** (172 mg, 0.600 mmol), BuLi (2.5 M in hexanes, 0.52 mL, 1.3 mmol), and *p*-methoxybenzaldehyde (90 mg, 0.7 mmol) were used as per the general procedure and yielded **8c** (114 mg, 72%) as a yellow solid. Mp 67–69 ˚C. R_f = 0.4 (CH_2Cl_2). IR ($CHCl_3$, cast) 3395, 2241, 2211, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.35 (m, J = 6.8 Hz, 4H), 7.37-7.28 (m, 3H), 6.91 (dt, J = 8.8, 2.5 Hz, 2H), 5.53 (d, J = 6.0 Hz, 1H), 3.80 (s, 3H), 2.16 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 132.6, 132.1, 129.4, 128.4, 128.2, 121.4, 114.1, 81.9, 79.4, 73.2, 71.1, 64.8, 55.4. HRMS calcd. for $C_{18}H_{14}O_2$ 262.0994, found 262.1004.



Compound 8d. Dibromoolefin **6a** (516 mg, 1.78 mmol), BuLi (1.6 M in hexanes, 2.4 mL, 3.8 mmol), and aldehyde **S4**[9] (324 mg, 1.73 mmol) were used as per the general procedure and yielded **8d** (307 mg, 57%) as a yellow oil. R_f = 0.5 (hexanes/EtOAc 4:1). IR ($CHCl_3$, cast) 3405, 3063, 2242 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.37–7.26 (m, 3H), 4.73 (dt, J = 6.3, 4.2, 1H), 4.05 (ddd, J = 9.9, 8.4, 3.9 Hz, 1H), 3.84 (ddd, J = 10.5, 5.4, 4.2 Hz, 1H), 3.59 (d, J = 6.3 Hz, 1H), 2.10–2.00 (m, 1H), 1.94–1.84 (m, 1H), 0.90 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.5, 129.2, 128.4, 121.6, 83.1, 78.3, 73.4, 69.6, 62.3, 60.9, 38.4, 25.9, 18.2, -5.5. EIMS *m/z* 257.1 ([M – tBu]$^+$, 24), 105.0 ([$C_3H_9O_2Si$]$^+$, 100); HRMS calcd. for $C_{15}H_{17}O_2Si$ 257.0998, found 257.0995. Anal. calcd. for $C_{19}H_{26}O_2Si$: C, 72.56; H, 8.33. Found: C, 72.20; H, 8.43.



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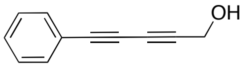
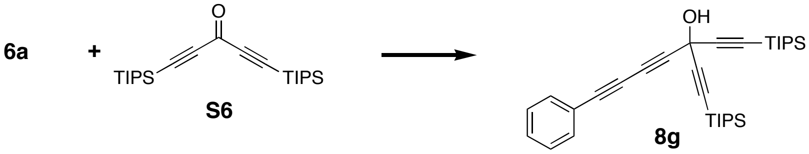
[9] Vijn, R. J.; Hiemstra, H.; Kok, J. J.; Knotter, M.; Speckamp, N. W. *Tetrahedron* **1987**, *43*, 5019-5030.

Compound 8e. Dibromoolefin **6a** (185 mg, 0.646 mmol), BuLi (2.5 M in hexanes, 0.57 mL, 1.4 mmol), and aldehyde **S5**[10] (140 mg, 0.665 mmol) were used as per the general procedure and yielded **8e** (159 mg, 75%) as a yellow oil. R_f = 0.3 (hexanes/CH_2Cl_2 4:3). IR ($CHCl_3$, cast) 3349, 2243, 2208, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 6.8, 1.6 Hz, 2H), 7.36–7.31 (m, 3H), 5.24 (d, 6.0 Hz, 1H), 2.29 (d, J = 6.8 Hz, 1H), 1.08 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 129.5, 128.4, 121.2, 102.6, 87.3, 79.5, 78.7, 73.0, 69.0, 53.2, 18.5, 11.1. EIMS m/z 336.2 (M^+, 36), 293.1 ($[M - iPr]^+$, 43). HRMS calcd. for $C_{22}H_{28}OSi$ 336.1910, found 336.1909.

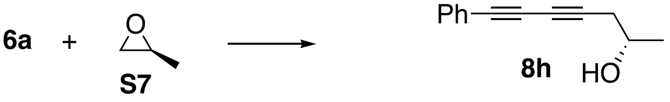


8f

Compound 8f.[11] Dibromoolefin **6a** (203 mg, 0.709 mmol), BuLi (2.5 M in hexanes, 0.62 mL, 1.6 mmol), and paraformaldehyde (641 mg, 2.13 mmol) were used as per the general procedure and yielded **8f** (64.1 mg, 58%) as a yellow oil. R_f = 0.2 (CH_2Cl_2). IR ($CHCl_3$, cast) 3324, 3061, 2914, 2243 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.38–7.27 (m, 3H), 4.40 (bd, J = 5.1, 2H), 1.52 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 129.3, 128.4, 121.4, 80.5, 78.6, 73.2, 70.4, 51.6. HRMS calcd. for $C_{11}H_8O$ 156.0575, found 156.0574.



Compound 8g. Dibromoolefin **6a** (181 mg, 0.636 mmol), BuLi (2.5 M in hexanes, 0.53 mL, 1.3 mmol), and ketone **S6**[12] (219 mg, 0.56 mmol) were used as per the general procedure and yielded **8g** (275 mg, 95%) as a yellow oil. R_f = 0.3 (hexanes/CH_2Cl_2 3:1). IR ($CHCl_3$, cast) 3447, 2892, 2232 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, J = 6.6, 3.3 Hz, 2H), 7.40–7.28 (m, 3H), 2.79 (s, 1H), 1.08 (s, 42H), (OH peak was not observed); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.7, 129.6, 128.4, 121.2, 103.0, 85.6, 80.4, 78.6, 73.0, 67.3, 54.9, 18.5, 11.1. EIMS m/z 473.3 ($[M - iPr]^+$, 23), 347.2 ($[C_{20}H_{35}OSi]^+$, 48); HRMS calcd. for $C_{33}H_{48}OSi_2$ 473.2696, found 473.2696.



Compound (–)-8h. Dibromoolefin **6a** (201 mg, 0.703 mmol), BuLi (2.5 M in hexanes, 0.62 mL, 1.6 mmol), and *S*-(–)-propylene oxide **S7** (Aldrich, 49 mg, 0.06 mL, 0.84 mmol) were used as per the

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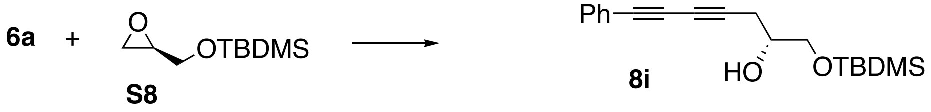
[10] Eisler, S.; Slepkov, A. D.; Elliott, E.; Luu, T.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 2666–2676. See supporting information.

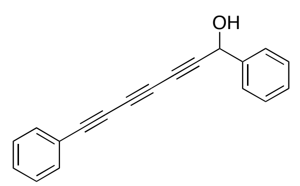
[11] Lee, H. J.; Shim, S. C. *J. Chem. Soc. Chem. Commun.* **1993**, 1420–1422.

[12] Lange, T.; van Loon, J.-D.; Tykwinski, R. R.; Schreiber, M.; Diederich, F. *Synthesis* **1996**, 537–550.

general procedure and yielded **(–)-8h** (45 mg, 35%) as a yellow oil. R_f = 0.2 (hexanes). $[\alpha]^{20}_D$ –9.3 (c 1.31, MeOH); IR ($CHCl_3$, cast) 3356, 3055, 2971, 2230 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 8.0, 1.3 Hz, 2H), 7.35–7.26 (m, 3H), 4.02 (bm, 1H), 2.55 (A part of ABX, J = 17.2, 5.6 Hz, 1H), 2.52 (B part of ABX, J = 17.2, 5.6 Hz, 1H), 1.87 (bd, J = 4 Hz, 1H), 1.29 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.5, 129.0, 128.4, 121.8, 80.7, 75.4, 74.0, 67.4, 66.4, 30.2, 22.6. EIMS m/z 184.1 (M^+, 32), 347.2 ($[C_{11}H_8]^+$, 100); HRMS calcd. for $C_{13}H_{12}O$ 184.0888, found 184.0887.[13]



Compound (–)-8i. A solution of dibromoolefin **6a** (213.3 mg, 0.7459 mmol) was dissolved in toluene (2 mL) and the mixture was diluted with hexanes (10 mL) and cooled to –20 ˚C under an Ar atmosphere. To this solution with stirring, BuLi (2.5 M in hexanes, 0.66 mL, 2.2 equiv) was added via syringe over a period of ca. 1 min, and the reaction allowed to slowly warm to 0 ºC. The reaction was then cooled to –20 ºC, Et_2O (10 mL) was added, followed by the *tert*-butyldimethylsilyl (*R*)-(+)-glycidyl ether **S8** (Aldrich, 0.13 g, 0.14 mL, 0.68 mmol, dissolved in 2 mL of Et_2O) and HMPA (0.3 mL). The reaction mixture was allowed to warm to rt overnight. Sat. aq. NH_4Cl (10 mL) and Et_2O (10 mL) were added, the organic phase was separated, washed with sat. aq. NaCl (2 x 10 mL), and dried over $MgSO_4$. Solvent removal and purification by column chromatography (silica gel, hexanes/CH_2Cl_2 1:1) yielded **(–)-8i** (47 mg, 22%) as a light brown oil. R_f = 0.25 (hexanes/CH_2Cl_2 1:1). $[\alpha]^{20}_D$ –7.3 (c 0.24, MeOH); IR ($CHCl_3$, cast) 3429, 3063, 2929, 2247 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.0, 1.3 Hz, 2H), 7.34–7.26 (m, 3H), 3.85 (m, 1H), 3.72 (dd, J = 10.0, 4.0 Hz, 1H), 3.63 (dd, J = 10.0, 5.6 Hz, 1H), 2.60 (A part of ABM, J = 17.6 Hz, 1H), 2.57 (B part of ABM, J = 17.6 Hz, 1H), 2.47 (d, J = 5.6 Hz, 1H), 0.90 (s, 9H), 0.087 (s, 3H), 0.085 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.5, 128.9, 128.3, 121.9, 80.3, 75.3, 74.1, 70.1, 66.0, 65.6, 25.8, 24.4, 18.2, -5.40, -5.42. EIMS m/z 314.2 (M^+, 1), 257.1 ($[M - tBu]^+$, 45), 141.1 ($[C_{11}H_9]^+$, 100); HRMS calcd. for $C_{19}H_{26}O_2Si$ 314.1702, found 314.1700. Anal. calcd. for $C_{19}H_{26}O_2Si$: C, 72.56; H, 8.33. Found: C, 72.06; H, 8.33.



9a

Compound 9a. Dibromoolefin **6b** (219 mg, 0.705 mmol), BuLi (2.5 M in hexanes, 0.62 mL, 1.5

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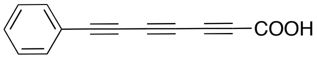
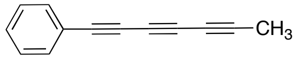
13. Spectral data consistent with that reported for the (+)-enantiomer, see: Chang, M.-H.; Wang, G.-J.; Kuo, Y.-H.; Lee, C.-K. *J. Chin. Chem. Soc.* **2000**, *47*, 1131-1136.

mmol), and benzaldehyde (82 mg, 0.77 mmol) were used as per the general procedure and yielded **9a** (98 mg, 54%) as a yellow oil. $R_f = 0.4$ (CH_2Cl_2). IR ($CHCl_3$, cast) 3362, 3063, 2957, 2191 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.52 (m, 4H), 7.44–7.32 (m, 6H), 5.57 (s, 1H), 2.28 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 133.0, 129.8, 128.85, 128.84, 128.5, 126.7, 120.7, 78.9, 77.7, 74.1, 71.7, 65.7, 65.2, 64.3. EIMS *m/z* 256.1 (M^+, 88), 226.1 ($[C_{18}H_{10}]^+$, 100); HRMS calcd. for $C_{19}H_{12}O$ 256.0888, found 256.0883.



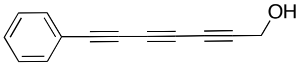
9b

Compound 9b.[14] Dibromoolefin **6b** (358 mg, 1.16 mmol), BuLi (2.5 M in hexanes, 1.0 mL, 2.5 mmol) were reacted as per the general procedure. CO_2, generated from dry ice, was passed through a drying tube filled with $CaCl_2$ and then was bubbled through the reaction mixture via syringe. After quenching the mixture with 10% aq. HCl, it was basicified by using a 10% aq. NaOH. The aqueous layer was separated and neutralized with 10% aq. HCl and Et_2O (5 mL). The mixture was reduced to dryness and yielded **9b** (146 mg, 65%) as a brown solid. DSC analysis showed an exothermic peak at 112 ˚C (decomposed). IR ($CHCl_3$, cast) 2927, 2206, 2182 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.43 (dt, *J* = 7.4, 1.6 Hz, 1H), 7.34 (dt, *J* = 7.2, 1.2 Hz, 2H), (*H*O not observed); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 133.4, 130.6, 128.7, 119.7, 80.7, 73.8, 73.4, 69.7, 67.3, 64.1. HRMS calcd. for $C_{13}H_6O_2$ 194.0368, found 194.0370.



9c

Compound 9c.[15] Dibromoolefin **6b** (479 mg, 1.54 mmol), BuLi (2.5 M in hexanes, 1.3 mL, 3.4 mmol), and methyliodide (331 mg, 2.31 mmol) were used as per the general procedure and yielded **9c** (164 mg, 65%) as a light brown crystalline solid. Spectral data were consistent with those reported.[15]



9d

Compound 9d.[16] Dibromoolefin **6b** (534 mg, 1.72 mmol), BuLi (1.6 M in hexanes, 2.4 mL, 3.8 mmol), and paraformaldehyde (101 mg, 3.33 mmol) were used as per the general procedure and yielded **9d** (224 mg, 72%) as a yellow oil. Spectral data were consistent with those reported.[16]

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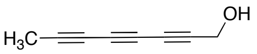
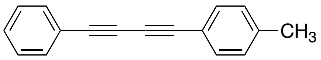
[14] Bohlmann, F.; Sucrow, W.; Queck, I. *Chem. Ber.* **1964**, *97*, 2586–2597.
[15] Shi Shun, A. L. K.; Tykwinski, *J. Org. Chem.* **2003**, *68*, 6810–6813.
[16] Luu, T.; Shi, W.; Lowary, T. L.; Tykwinski, R. R. *Synthesis* **2005**, 3167–3178.



10

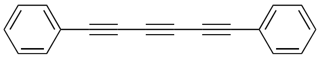
Compound 10.[16] Dibromoolefin **6c** (574 mg, 2.07 mmol), BuLi (2.5 M in hexanes, 1.8 mL, 4.5 mmol), and paraformaldehyde (187 mg, 6.22 mmol) were used as per the general procedure and yielded **10** (146 mg, 59%) as a magenta crystalline solid. Spectral data were consistent with those reported.[16]

Procedure for the FBW-Negishi method. Dibromoolefin **6a,b,d,e** (1.0 mmol) in toluene (10 mL) was cooled to –40 °C under N_2 atmosphere. To this solution with stirring, BuLi (2.5 M in hexanes, 0.90 mL, 2.2 mmol) was added by a syringe over a period of ca. 5 min. The reaction mixture was allowed to slowly warm to –20 °C. The reaction mixture was cooled to –40 °C again. To this mixture with stirring, $ZnCl_2$ (0.50 M in THF, 2.4 mL, 1.2 mmol) was added by a syringe over a period of ca. 5 min. The reaction mixture was allowed to slowly warm to 0 °C. Aryl halide (1.1 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) were added directly under a flow of N_2, and this mixture was heated up to 70 °C. After 20 h, the reaction mixture was filtered through a Celite column. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give the target compounds.



11

Compound 11.[17] Dibromoolefin **6a** (286 mg, 0.998 mmol), BuLi (2.5 M in hexanes, 0.90 mL, 2.3 mmol), $ZnCl_2$ (0.5 M in THF, 2.4 mL, 1.2 mmol), *p*-tolyl iodide (260 mg, 1.19 mmol), and $Pd(PPh_3)_4$ (57 mg, 0.049 mmol) were used as per the general procedure and yielded **11** (195 mg, 90%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.51 (m, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.36–7.30 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 132.5, 132.4, 129.2, 129.1, 128.4, 121.9, 118.7, 81.9, 81.2, 74.1, 73.3, 21.6.



12a

Compound 12a.[18] Dibromoolefin **6b** (150 mg, 0.484 mmol), BuLi (2.5 M in hexanes, 0.45 mL, 1.1 mmol), $ZnCl_2$ (0.5 M in THF, 1.2 mL, 0.60 mmol), phenyl iodide (121 mg, 0.593 mmol), and $Pd(PPh_3)_4$ (27.7 mg, 0.024 mmol) were used as per the general procedure and yielded **12a** (76.1 mg,

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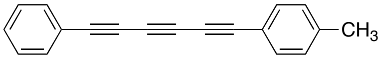
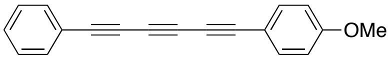
17. Fiandanese, V.; Bottalico, D.; Marchese, G.; Punzi, A. *Tetrahedron Lett.* **2003**, *44*, 9087–9090.
18. Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943–6949.

70%) as a white solid. Spectral data were consistent with those reported.[18]



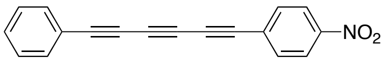
12b

Compound 12b. Dibromoolefin **6b** (312 mg, 1.01 mmol), BuLi (2.5 M in hexanes, 1.0 mL, 2.5 mmol), $ZnCl_2$ (0.5 M in THF, 2.5 mL, 1.3 mmol), *p*-iodotoluene (234 mg, 1.07 mmol), and $Pd(PPh_3)_4$ (58 mg, 0.051 mmol) were used as per the general procedure and yielded **12b** (195 mg, 81%) as a white solid. Mp 111–112 °C. R_f = 0.6 (hexanes/CH_2Cl_2 3:1). IR ($CHCl_3$, cast) 3081, 3018, 2247, 2195 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 7.12 (d, J = 8.0 Hz, 2H), 7.32–7.40 (m, 3H), 7.42 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 66.2, 66.7, 73.9, 74.5, 78.4, 79.0, 117.8, 121.1, 128.5, 129.3, 129.6, 132.9 (2x), 140.2. HRMS calcd. for $C_{19}H_{12}$ 240.0939, found 240.0934. Anal. calcd. for $C_{19}H_{12}$: C, 94.97; H, 5.05. Found: C, 95.05; H, 5.08.



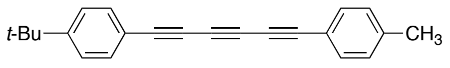
12c

Compound 12c. Dibromoolefin **6b** (309 mg, 0.996 mmol), BuLi (2.5 M in hexanes, 0.90 mL, 2.3 mmol), $ZnCl_2$ (0.5 M in THF, 2.4 mL, 1.2 mmol), *p*-iodoanisole (255 mg, 1.09 mmol), and $Pd(PPh_3)_4$ (56 mg, 0.049 mmol) were used as per the general procedure and yielded **12c** (203 mg, 80%) as an orange solid. Mp 120–121 °C. R_f = 0.6 (hexanes/CH_2Cl_2 3:2). IR ($CHCl_3$, cast) 2194, 2174 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.87 (d, J = 8.8 Hz, 2H), 7.34–7.40 (m, 3H), 7.50 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 66.0, 66.8, 73.4, 74.6, 78.3, 79.0, 112.8, 114.2, 121.1, 128.5, 129.6, 132.9, 134.7, 160.8. HRMS calcd. for $C_{19}H_{12}O$ 256.0888, found 256.0882. Anal. calcd. for $C_{19}H_{12}O$: C, 89.04; H, 4.72. Found: C, 89.05; H, 4.69.



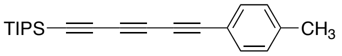
12d

Compound 12d. Dibromoolefin **6b** (233 mg, 0.752 mmol), BuLi (2.5 M in hexanes, 0.70 mL, 1.8 mmol), $ZnCl_2$ (0.5 M in THF, 1.7 mL, 0.85 mmol), *p*-iodonitrobenzene (222 mg, 0.891 mmol), and $Pd(PPh_3)_4$ (40 mg, 0.035 mmol) were used as per the general procedure and yielded **12d** (171 mg, 84%) as a yellow solid. Mp 205 °C (decomp). R_f = 0.3 (hexanes/CH_2Cl_2 7:3). IR ($CHCl_3$, cast) 3103, 3066, 2190, 2174 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.42 (m, 3H), 7.53 (t, J = 7.2 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.5, 69.2, 74.1, 75.9, 79.3, 80.2, 120.6, 123.8, 128.1, 128.6, 130.2, 133.1, 133.7, 147.8. HRMS calcd. for $C_{18}H_9NO_2$ 271.0633, found 271.0635.



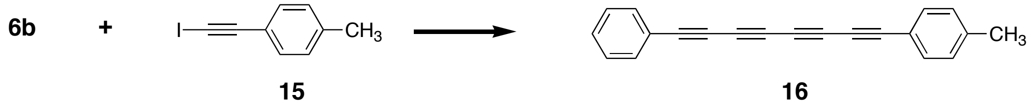
13

Compound 13. Dibromoolefin **6d** (250 mg, 0.683 mmol), BuLi (1.6 M in hexanes, 1.0 mL, 1.6 mmol), $ZnCl_2$ (0.5 M in THF, 1.5 mL, 0.75 mmol), iodotoluene (150 mg, 0.688 mmol), and $Pd(PPh_3)_4$ (41 mg, 0.035 mmol) were used as per the general procedure and yielded **13** (123 mg, 60%) as a pale yellow solid. Mp 175 °C (decomp). $R_f = 0.6$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$, cast) 3084, 3038, 2962, 2248, 2193 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.35 (s, 3H), 7.12 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 31.1, 35.0, 66.3, 66.4, 74.0 (2x), 78.8, 78.9, 117.9 (2x), 125.5, 129.3, 132.8, 132.9, 140.1, 153.2. EIMS m/z 296.2 (M^+, 86), 281.1 ($[M - CH_3]^+$, 100]); HRMS calcd. for $C_{23}H_{20}$ 296.1565, found 296.1553. Anal. calcd. for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 92.91; H, 6.91.



14

Compound 14. Dibromoolefin **6e** (390 mg, 1.00 mmol), BuLi (1.6 M in hexanes, 1.5 mL, 2.4 mmol), $ZnCl_2$ (0.5 M in THF, 2.5 mL, 1.3 mmol), p-iodotoluene (220 mg, 1.01 mmol), and $Pd(PPh_3)_4$ (57 mg, 0.049 mmol) were used as per the general procedure and yielded **14** (221 mg, 69%) as a white solid. Mp 69 °C. $R_f = 0.7$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$, cast) 2891, 2178, 2072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (m, 21H), 2.37 (s, 3H), 7.14 (d, J = 8.4 H, 2H), 7.41 (d, J = 8.4 H, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 18.5, 21.6, 60.8, 67.0, 73.8, 76.9, 86.4, 89.9, 117.7, 129.3, 133.0, 140.2. EIMS m/z 320.2 (M^+, 34), 277.1 ($[M - iPr]^+$, 100); HRMS calcd. for $C_{22}H_{28}Si$ 320.1960, found 320.1958. Anal. calcd. for $C_{22}H_{28}Si$: C, 82.43; H, 8.80. Found: C, 82.60; H, 8.83.



Compound 16. Dibromoolefin **6b** (310 mg, 1.00 mmol), BuLi (1.6 M in hexanes, 1.5 mL, 2.1 mmol), $ZnCl_2$ (0.5 M in THF, 2.5 mL, 1.3 mmol), iodoacetylene **15**[19] (251 mg, 1.15 mmol), and $Pd(PPh_3)_4$ (53.5 mg, 0.046 mmol) were used as per the general procedure and yielded **16** (90.0 mg, 34%) as a yellow solid. Mp 93–94 °C. $R_f = 0.6$ (hexanes/CH_2Cl_2 4:1). IR ($CHCl_3$, cast) 2200, 2130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 7.13 (d, J = 7.9 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz,

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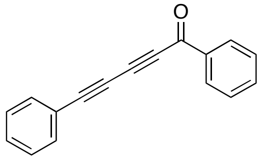
[19] Synthesized as reported by Luithle, J.E.A.; Pietruszka, J. *Eur. J. Org. Chem.* **2000**, 2557-2562, with spectroscopic data consistent with that reported by Lee, G. C. M.; Tobias, B.; Holmes, J.M.; Harcourt, D.A.; Garst, M.E. *J. Am. Chem. Soc.* **1990**, *112*, 9330-9336.

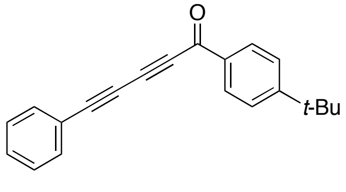
1H), 7.42 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 63.5, 63.9, 66.9, 67.3, 73.9, 74.5, 77.6, 78.1, 117.3, 120.6, 128.5, 129.4, 130.0, 133.2 (2x), 140.6. HRMS calcd. for $C_{21}H_{12}$ 264.0939, found 264.0936. Anal. calcd for $C_{21}H_{12}$: C, 95.42; H, 4.58. Found: C, 95.66; H, 4.62.

General procedure for the FBW-Stille method. A solution of **6a, b** (0.70 mmol) in toluene (3.0 mL) was cooled to –40 °C under N_2 atmosphere. To this solution with stirring, BuLi (2.5 M in hexanes, 0.65 mL, 1.6 mmol) was added by a syringe over a period of ca. 5 min. The reaction mixture was allowed to slowly warm to –20 °C. The reaction mixture was cooled to –40 °C again. To this mixture with stirring, Bu_3SnCl (0.45 mL, ρ = 1.2, 0.54 g, ca 1.2 mmol) was added by a syringe over a period of 5 min. The reaction mixture was allowed to slowly warm to rt and stirred for 2 h. Acid chloride (0.70 mmol) and $PdCl_2(PPh_3)_2$ (25 mg, 0.035 mmol) in CH_2Cl_2 (15 mL) were added, and this mixture was refluxed overnight. The reaction mixture was cooled to rt. Aqueous KF solution (30 mL) and ether (30 mL) were added and stirred vigorously for 15 minutes. This solution was filtered by using a Celite column. The organic phase was separated, washed with water, and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give the target compound **18a-e**.



18a

Compound 18a.[20,21] Dibromoolefin **6a** (143 mg, 0.501 mmol), BuLi (1.6 M in hexanes, 0.70 mL, 1.1 mmol), Bu_3SnCl (0.30 mL, 0.36 mg, 0.80 mmol), benzoyl chloride (73.2 mg, 0.521 mmol), and $PdCl_2(PPh_3)_2$ (18 mg, 0.025 mmol) were used as per the general procedure and yielded **18a** (86.8 mg, 75%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.15 (m, 2H), 7.66–7.57 (m, 3H), 7.53–7.43 (m, 3H), 7.40–7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 136.5, 134.4, 133.0, 130.5, 129.6, 128.6 (2x), 120.1, 86.3, 77.8, 77.4, 72.4.



18b

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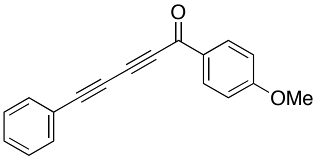
[20] Müller, E.; Segnitz, A. *Synth. Commun.* **1970**, 147-149.

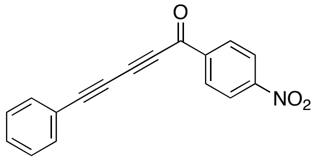
[21] Nash, B. W.; Thomas, D. A.; Warburton, W. K.; Williams, T. D. *J. Chem. Soc.* **1965**, 2983-2988.

Compound 18b. Dibromoolefin **6a** (199 mg, 0.696 mmol), BuLi (1.6 M in hexanes, 1.0 mL, 1.6 mmol), Bu_3SnCl (0.42 mL, 0.50 g, 1.1 mmol), *p-tert*-butylbenzoyl chloride (142 mg, 0.723 mmol), and $PdCl_2(PPh_3)_2$ (26 mg, 0.036 mmol) were used as per the general procedure and yielded **18b** (142 mg, 71%) as a pale yellow solid. Mp 94 °C. R_f = 0.5 (hexanes/CH_2Cl_2 1:1). IR (microscope) 3066, 2965, 2211, 2139, 1639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 7.35 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 35.2, 72.5, 76.9, 78.0, 86.0, 120.1, 125.6, 128.5, 129.5, 130.4, 132.9, 134.1, 158.4, 176.4. EIMS m/z 286.1 (M^+, 81), 271.1 ($[M - CH_3]^+$, 100); HRMS calcd. for $C_{21}H_{18}O$ 286.1358, found 286.1354. Anal. calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.90; H, 6.37.



18c

Compound 18c.[22] Dibromoolefin **6a** (193 mg, 0.676 mmol), BuLi (2.5 M in hexanes, 0.65 mL, 1.6 mmol), Bu_3SnCl (0.45 mL, 0.54 g, 1.2 mmol), *p*-methoxybenzoyl chloride (120 mg, 0.703 mmol), and $PdCl_2(PPh_3)_2$ (25 mg, 0.035 mmol) were used as per the general procedure and yielded **18c** (125 mg, 71%) as a pale yellow solid. Mp 96–97 °C. R_f = 0.2 (hexanes/CH_2Cl_2 1:1). IR ($CHCl_3$, cast) 3064, 3037, 3020, 2213, 2139, 1607 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.97 (d, J = 6.8 Hz, 2H), 7.38 (t, J = 6.8 Hz, 2H), 7.43 (t, J = 6.8 Hz, 1H), 7.57 (d, J = 7.0 Hz, 2H), 8.12 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 72.6, 76.6, 77.9, 85.8, 113.9, 120.3, 128.6, 130.0, 130.4, 132.0, 133.0, 164.8, 175.4. HRMS calcd. for $C_{18}H_{12}O_2$ 260.0837, found 260.0834. Anal. calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.12; H, 4.66.



18d

Compound 18d. Dibromoolefin **6a** (193 mg, 0.676 mmol), BuLi (2.5 M in hexanes, 0.65 mL, 1.6 mmol), Bu_3SnCl (0.42 mL, 0.50 g, 1.1 mmol), *p*-nitrobenzoyl chloride (130 mg, 0.716 mmol), and $PdCl_2(PPh_3)_2$ (26 mg, 0.037 mmol) were used as per the general procedure and yielded **18d** (103 mg, 56%) as a pale yellow solid. Mp 127 °C (decomp). R_f = 0.3 (hexanes/CH_2Cl_2 1:1). IR ($CHCl_3$, cast)

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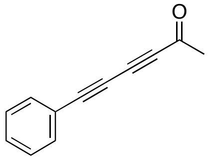
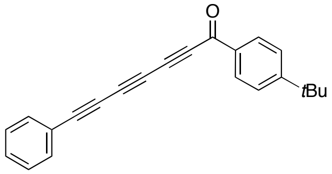
[22] Fukumaru, T.; Awata, H.; Hamma, N.; Komatsu, T. *Agr. Biol. Chem.* **1975**, *39*, 519–527.

3102, 2212, 2138, 1638 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (t, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 8.30 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 72.1, 77.1, 79.6, 88.1, 119.7, 123.8, 128.7, 130.4, 130.9, 133.1, 140.6, 151.0, 174.8. EIMS *m/z* 275.1 (M$^+$, 24), 150.1 ([$C_7H_4NO_3$]$^+$, 74); HRMS calcd. for $C_{17}H_9NO_3$ 275.0583, found 275.0583. Anal. calcd. for $C_{17}H_9NO_3$: C, 74.18; H, 3.30; N 5.09. Found: C, 74.49; H, 3.31; N, 5.11.



18e

Compound 18e.[20,21] Dibromoolefin **6a** (196 mg, 0.685 mmol), BuLi (1.6 M in hexanes, 1.0 mL, 1.6 mmol), Bu$_3$SnCl (0.42 mL, 0.50 g, 1.1 mmol), acetyl chloride (61.1 mg, 0.778 mmol), and PdCl$_2$(PPh$_3$)$_2$ (27 mg, 0.039 mmol) were used as per the general procedure and yielded **18e** (38 mg, 33%) as an unstable orange oil (previously reported as a low temperature melting solid, 38-39 °C), see ref. 20). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55–7.53 (m, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.4 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 183.3, 133.0, 130.5, 128.6, 120.1, 86.5, 78.7, 75.0, 72.1, 32.6.



19

Compound 19. Dibromoolefin **6b** (210 mg, 0.648 mmol), BuLi (2.5 M in hexanes, 0.65 mL, 1.6 mmol), Bu$_3$SnCl (0.45 mL, 0.54 g, 1.7 mmol), 4-*tert*-butylbenoyl chloride (0.141 g, 0.717 mmol), and PdCl$_2$(PPh$_3$)$_2$ (24 mg, 0.035 mmol) were used as per the general procedure. While the reaction progressed as for **18b**, with **19** seemingly formed based on TLC analysis, decomposition during workup, isolation, and purification was observed, and compound **19** could not be purified or characterized.

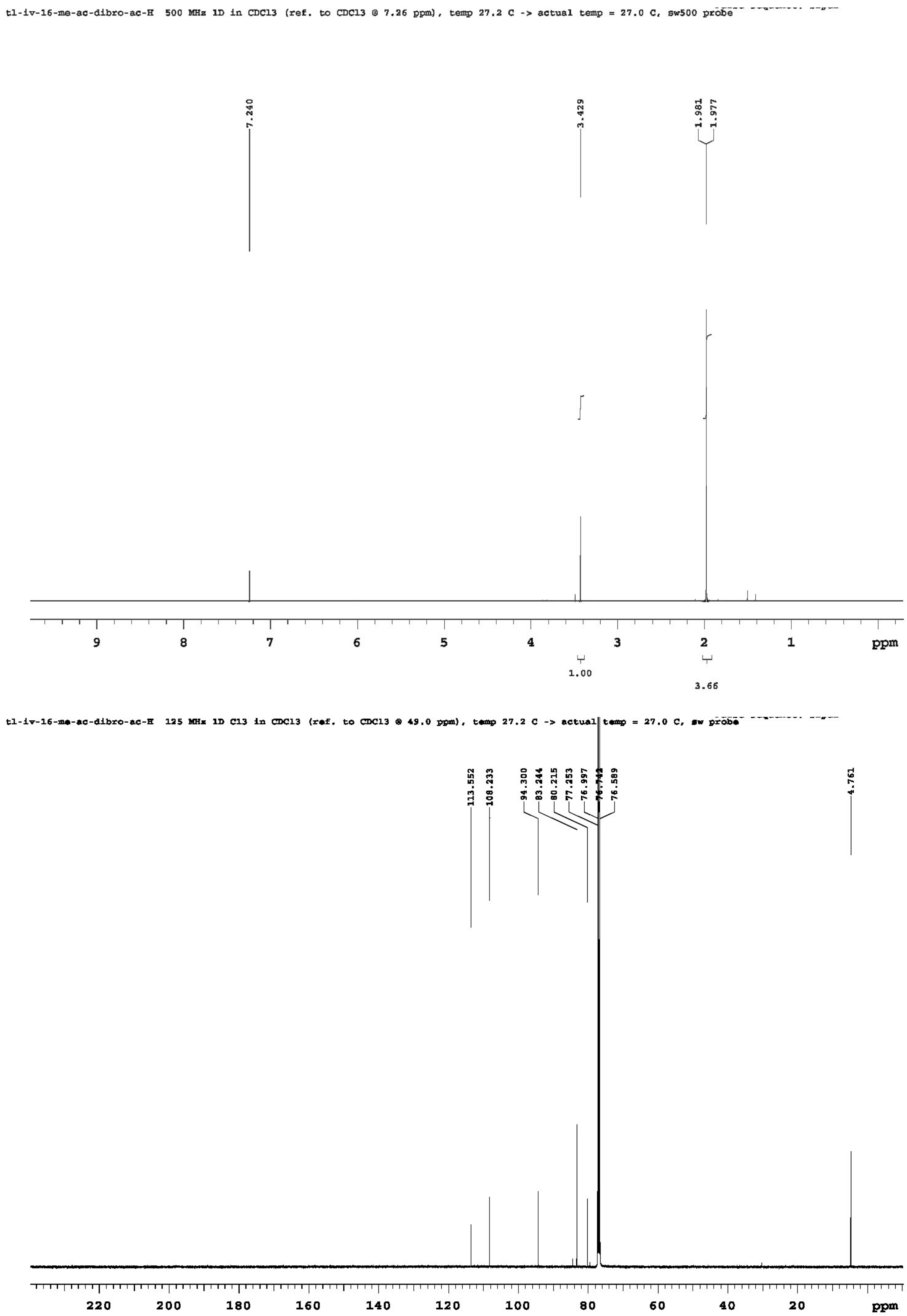


Figure S1-$^{1}H/^{13}C$ NMR spectra of **6c**

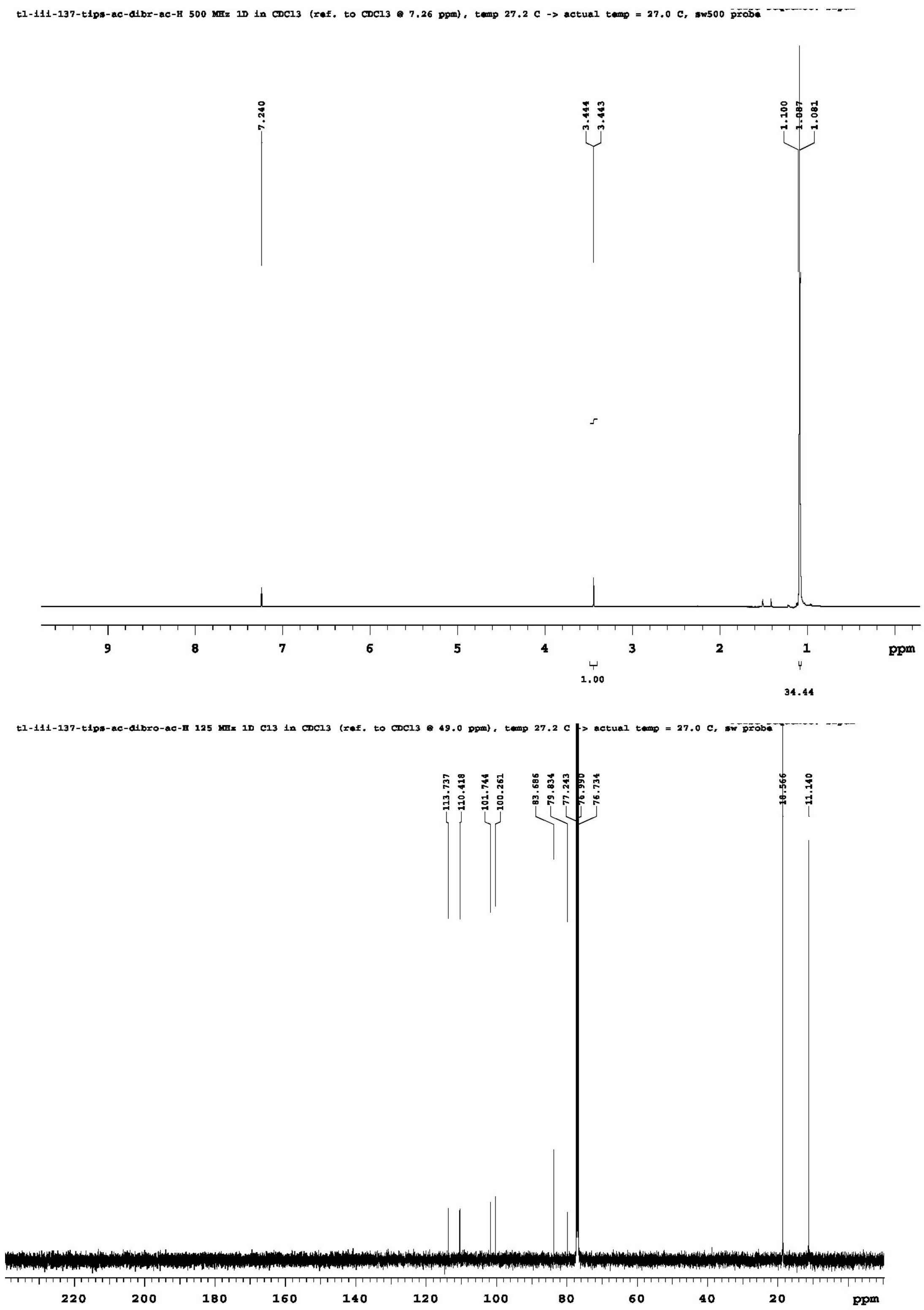
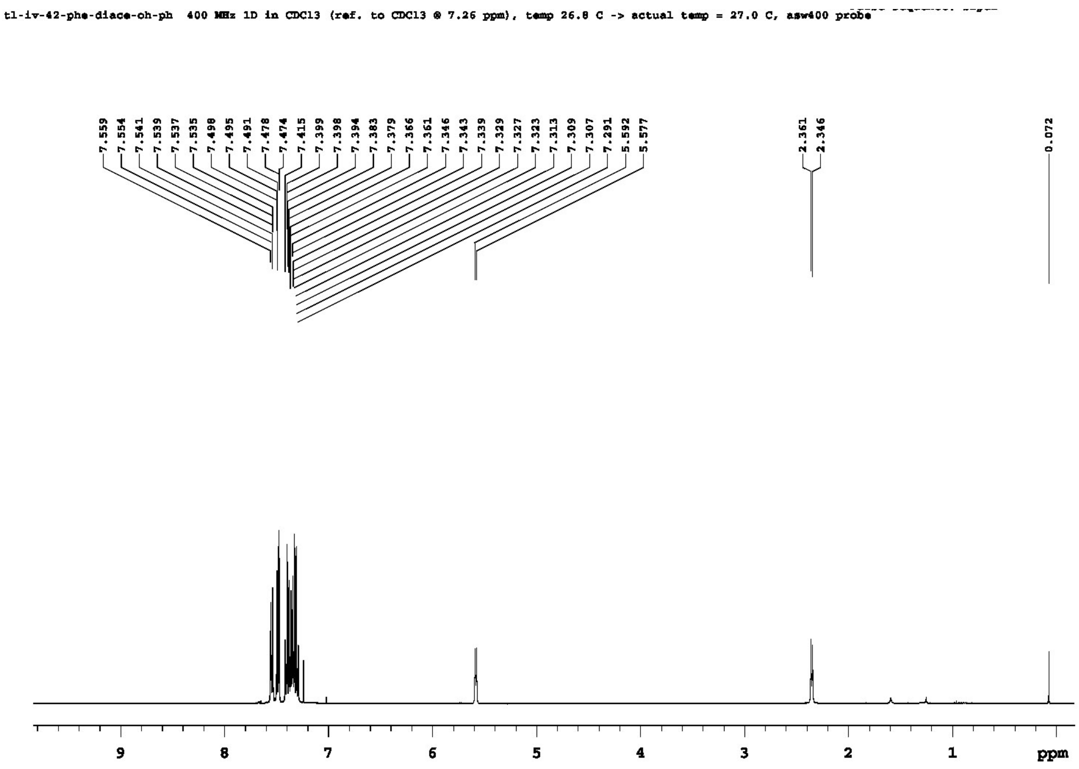


Figure S2-$^{1}H/^{13}C$ NMR spectra of **6e**



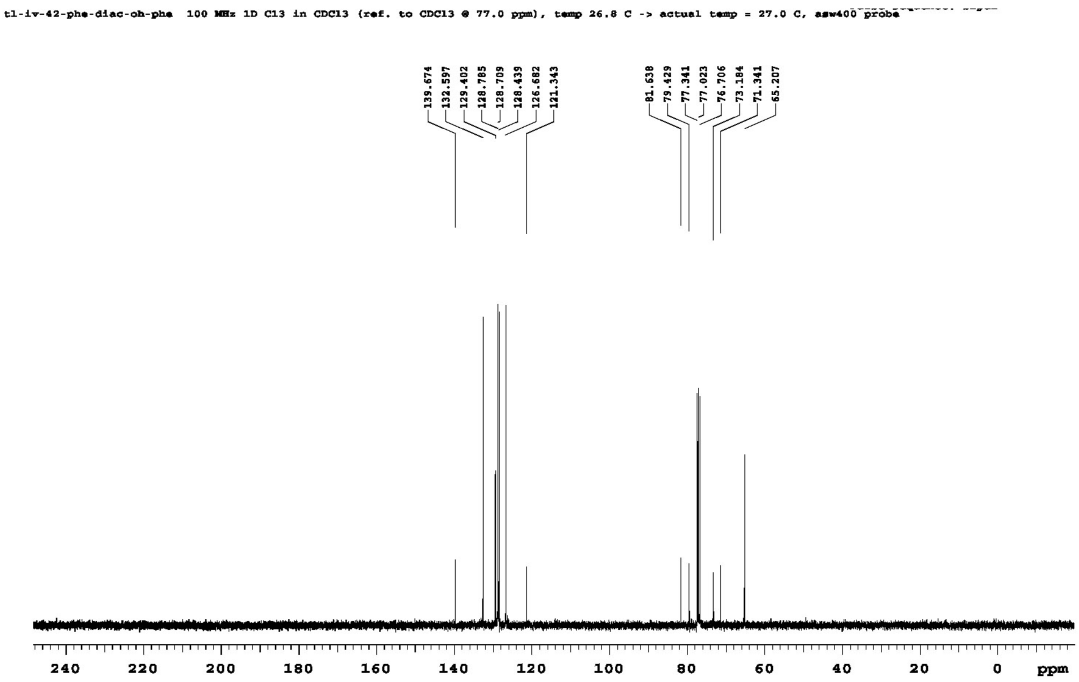


Figure S3-$^{1}H/^{13}C$ NMR spectra of **8a**

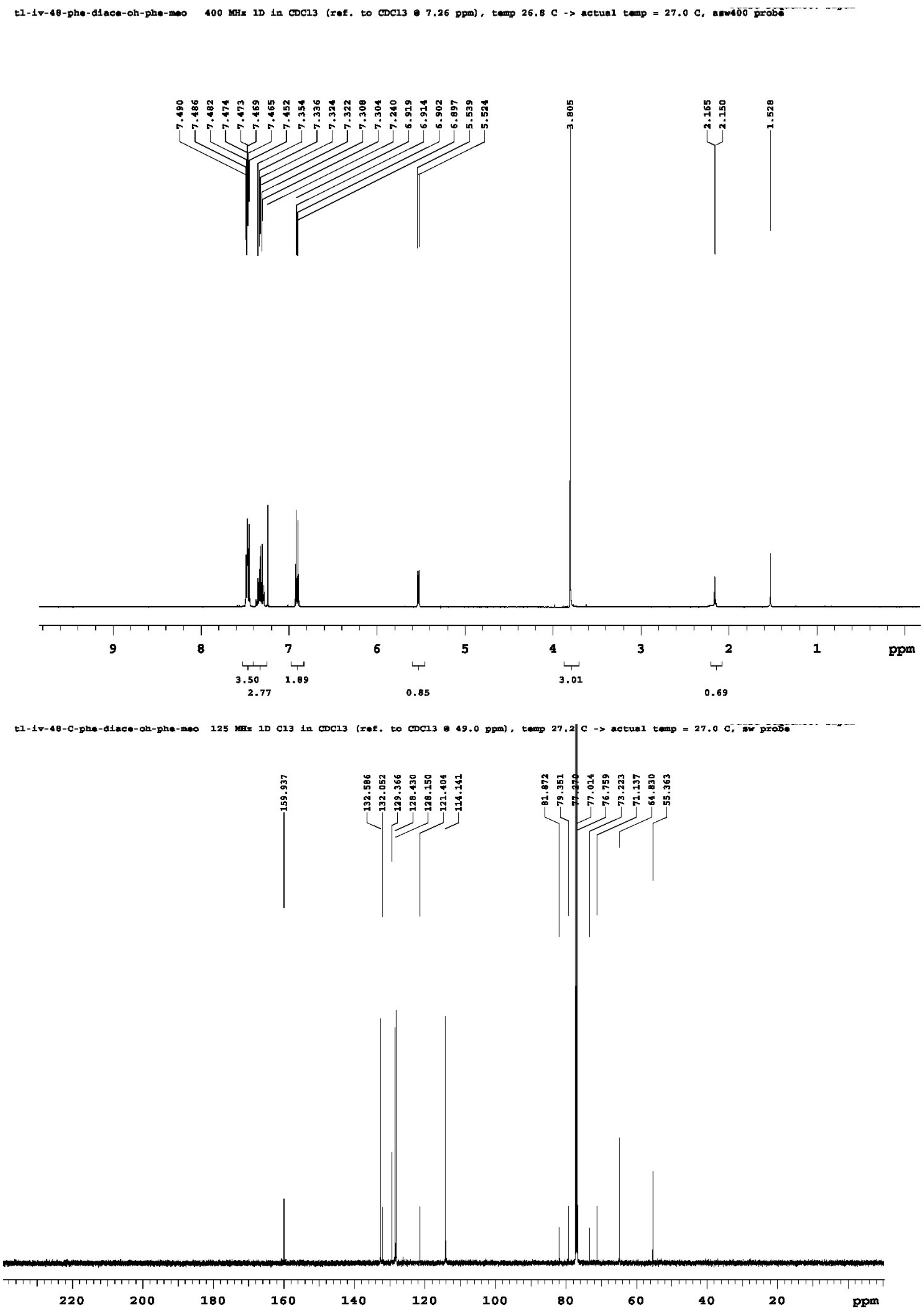


Figure S4-$^{1}H/^{13}C$ NMR spectra of **8c**

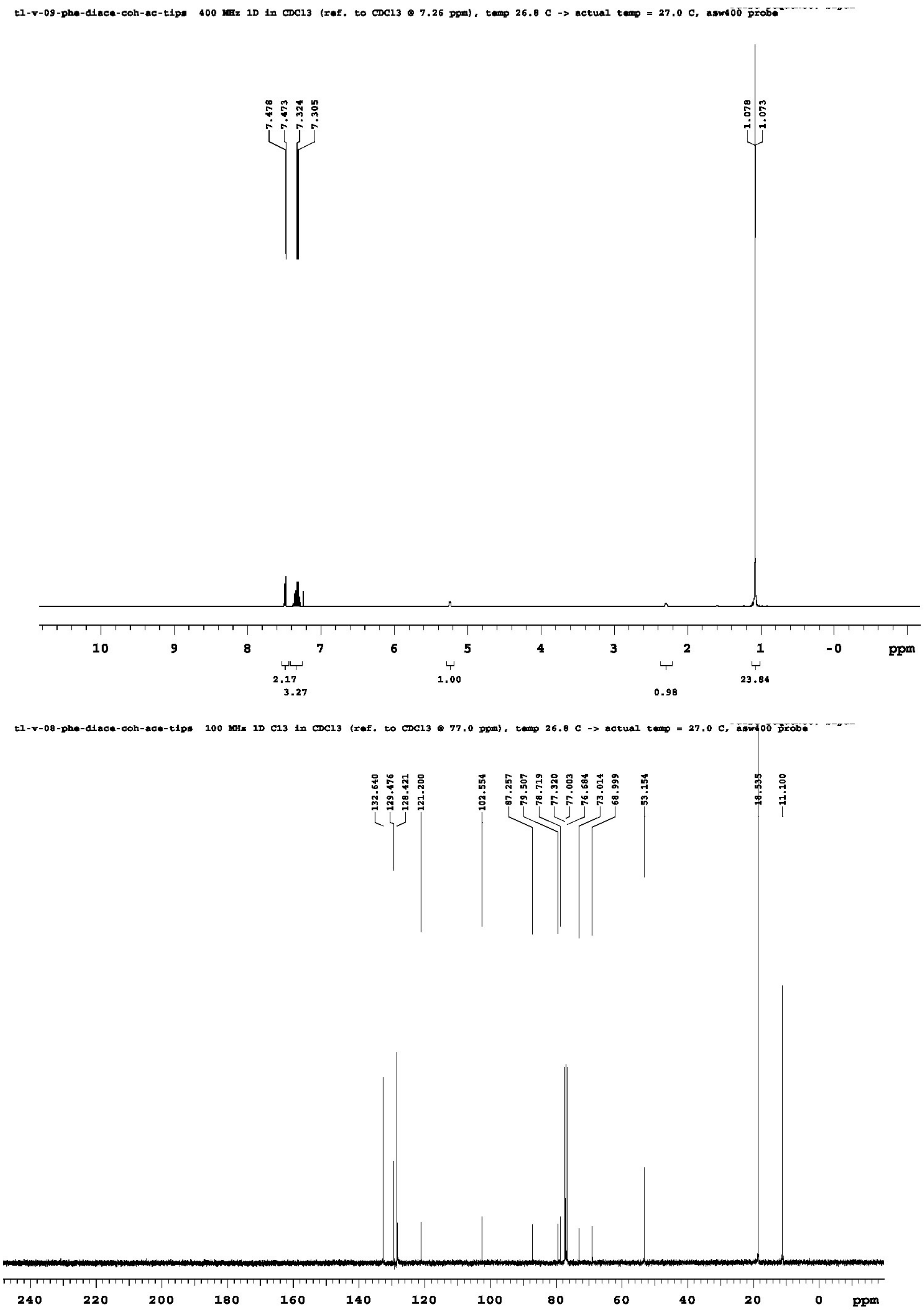


Figure S5-$^{1}H/^{13}C$ NMR spectra of **8e**

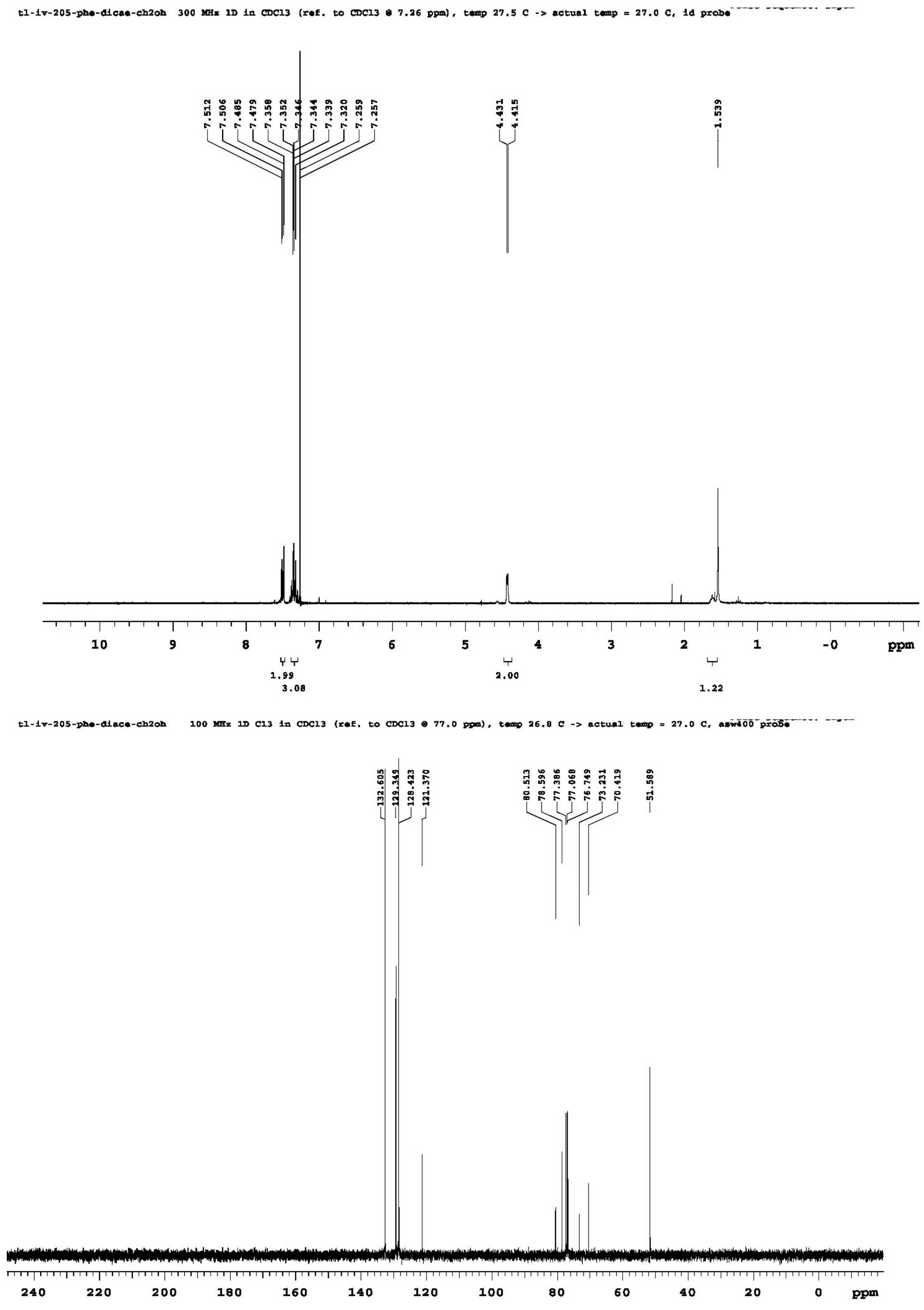


Figure S6-$^{1}H/^{13}C$ NMR spectra of **8f**

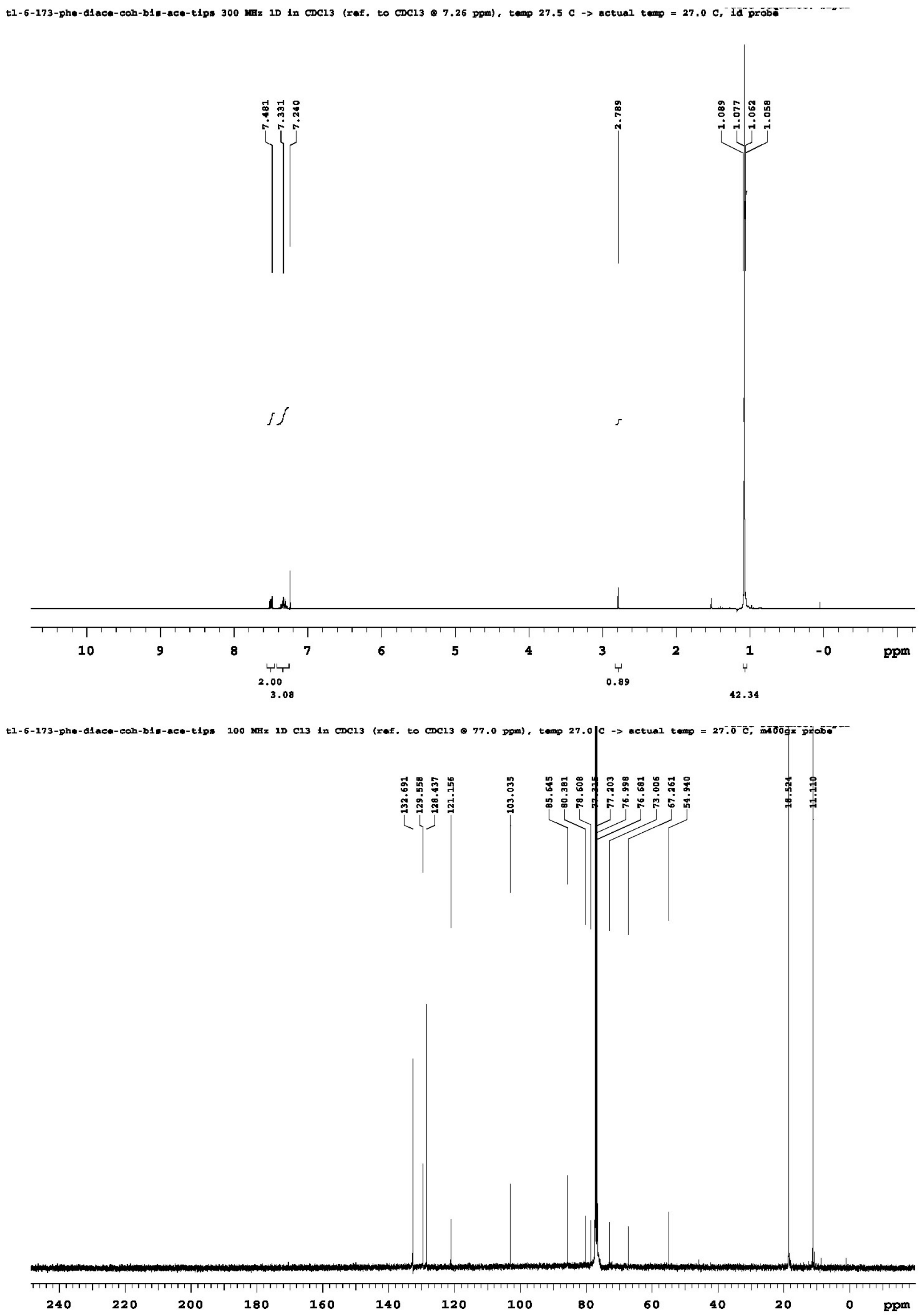


Figure S7-$^{1}H/^{13}C$ NMR spectra of **8g**

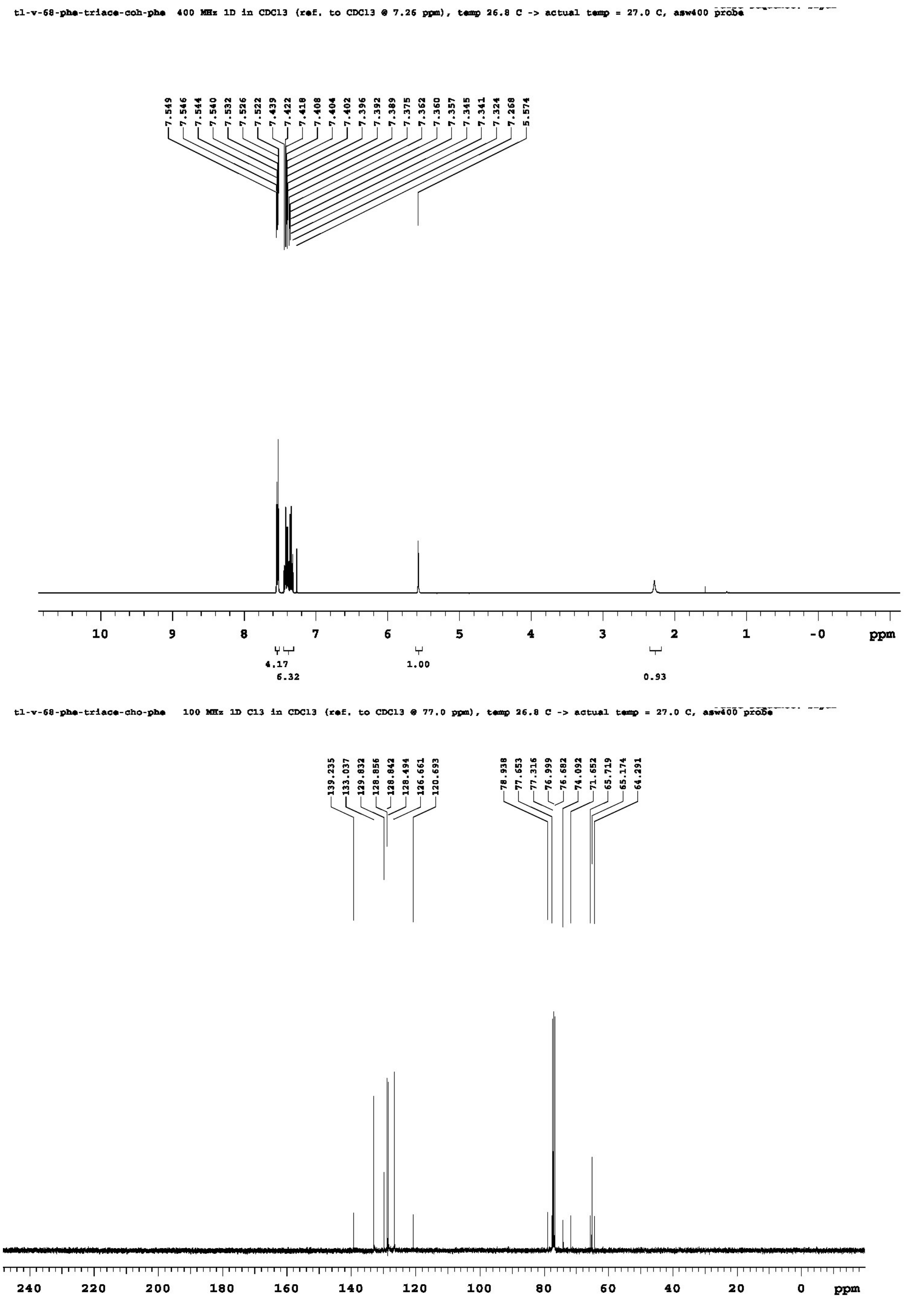


Figure S8-^{1}H/^{13}C NMR spectra of **9a**

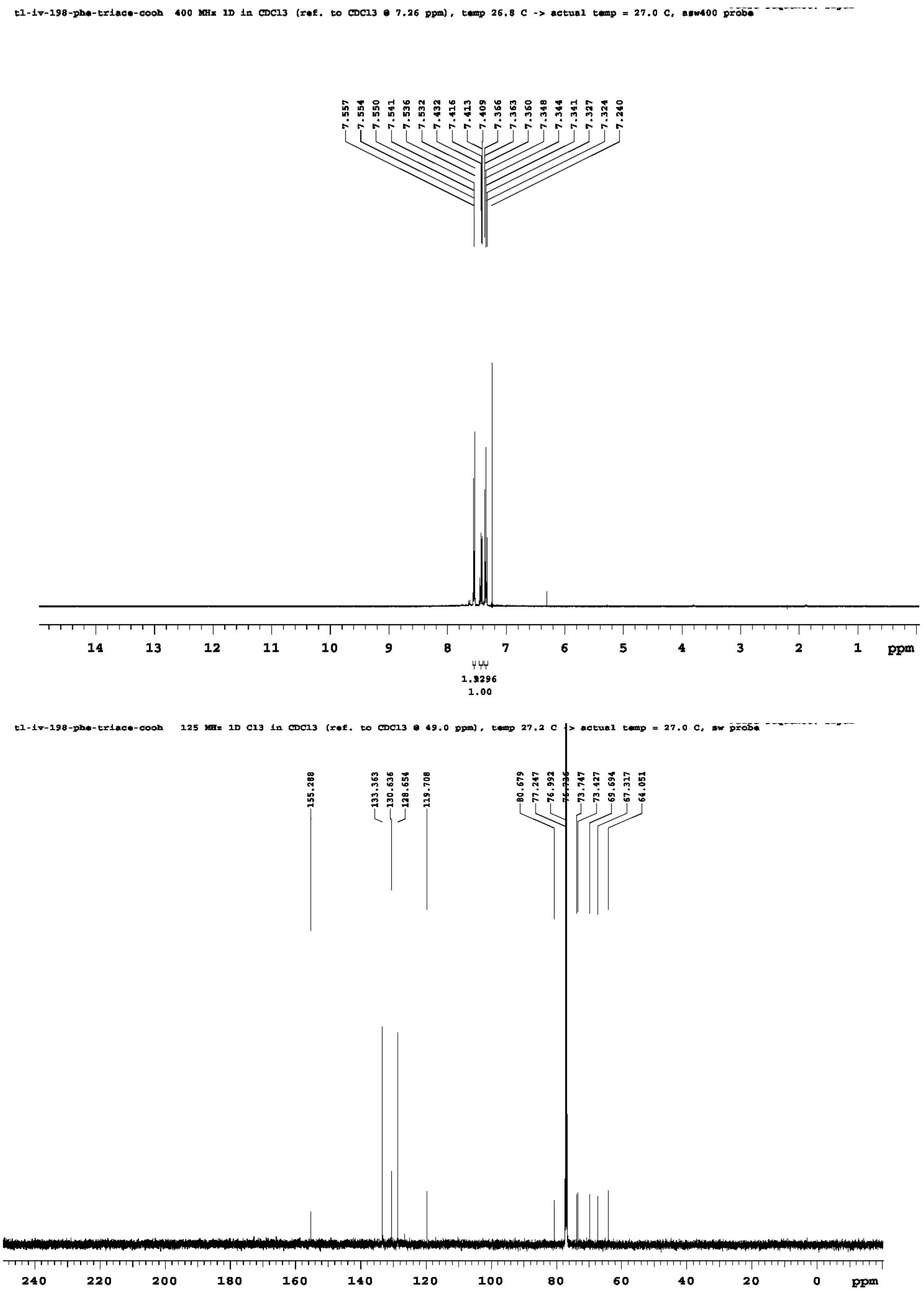


Figure S9-$^{1}H/^{13}C$ NMR spectra of **9b**

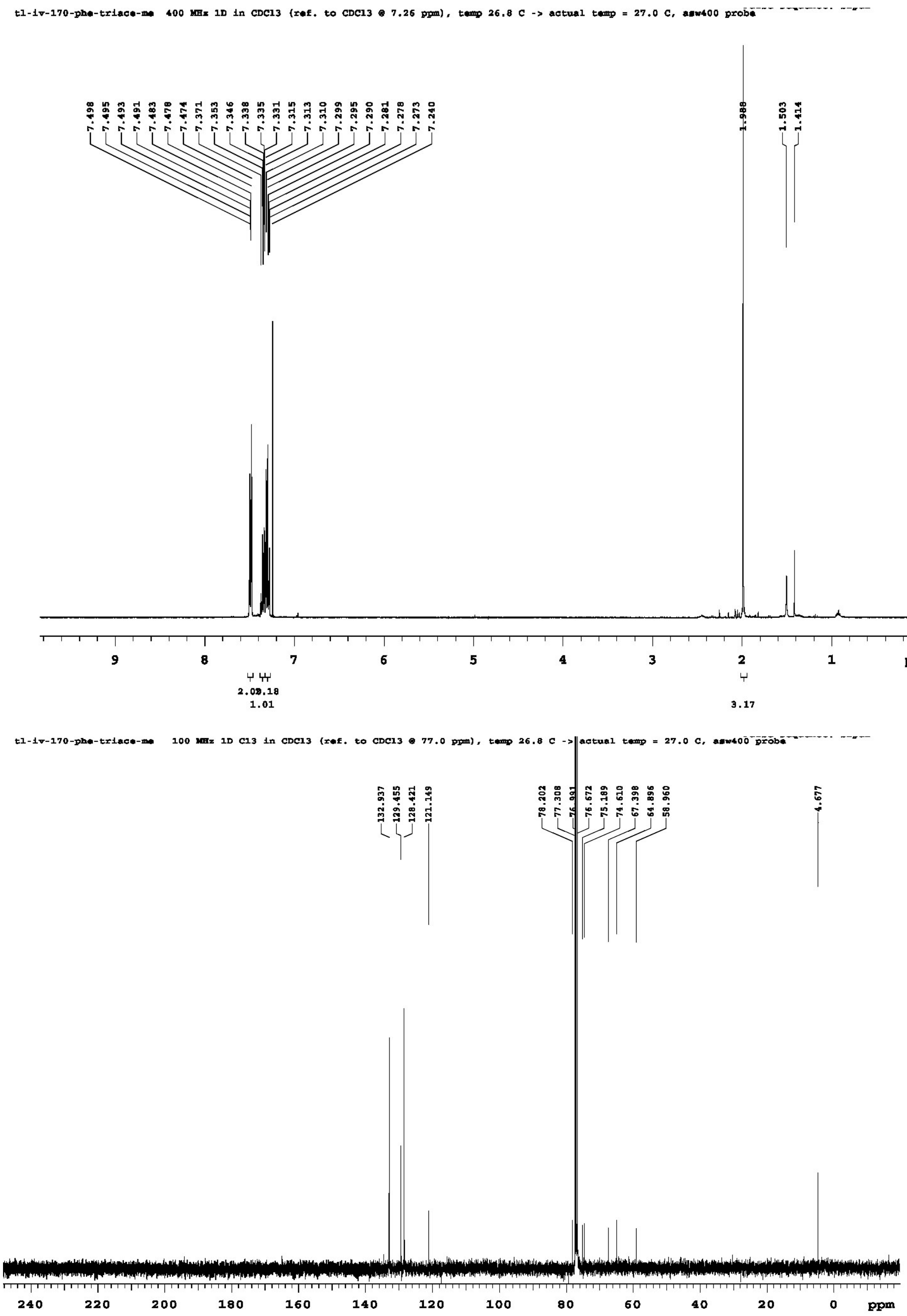
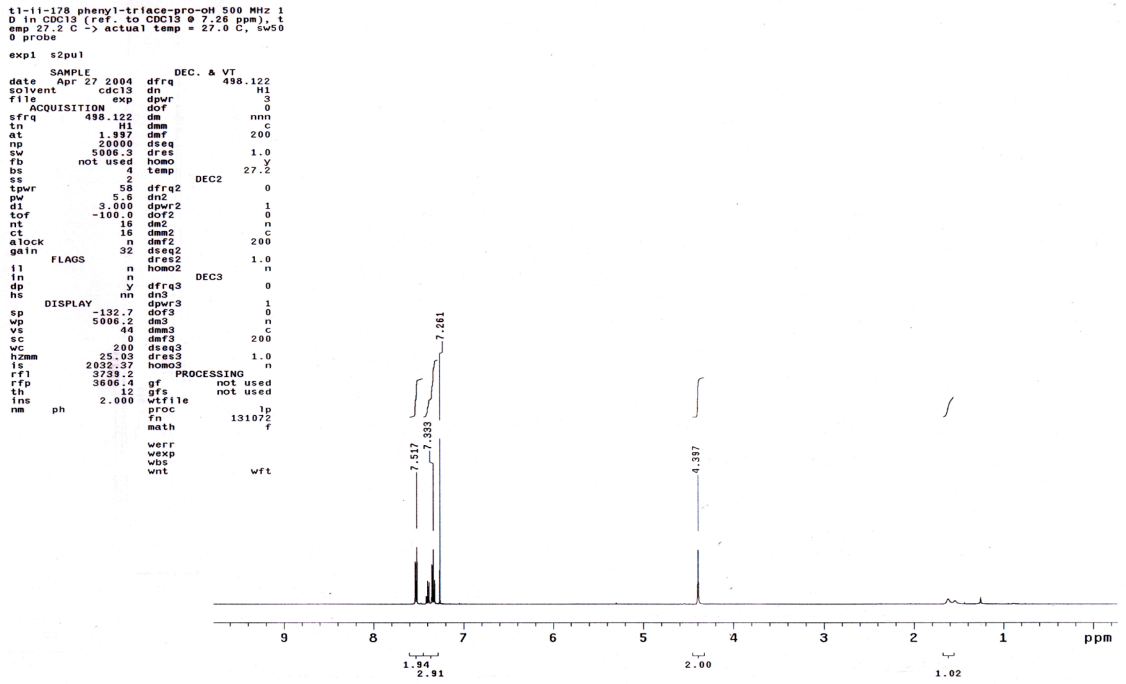


Figure S10-$^{1}H/^{13}C$ NMR spectra of **9c**



```
tl-ii-178 phenyl-triace-pro-oH 500 MHz 1
D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), t
emp 27.2 C -> actual temp = 27.0 C, sw50
0 probe

exp1  s2pul

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solvent       cdcl3   dn               H1
file            exp   dpwr              3
   ACQUISITION        dof               0
sfrq        498.122   dm              nnn
tn               H1   dmm               c
at            1.997   dmf             200
np            20000   dseq
sw           5006.3   dres            1.0
fb         not used   homo              y
bs                4   temp           27.2
ss                2          DEC2
tpwr             58   dfrq2             0
pw              5.6   dn2
d1            3.000   dpwr2             1
tof          -100.0   dof2              0
nt               16   dm2               n
ct               16   dmm2              c
alock             n   dmf2            200
gain             32   dseq2
      FLAGS           dres2           1.0
il                n   homo2             n
in                n          DEC3
dp                y   dfrq3             0
hs               nn   dn3
     DISPLAY          dpwr3             1
sp           -132.7   dof3              0
wp           5006.2   dm3               n
vs               44   dmm3              c
sc                0   dmf3            200
wc              200   dseq3
hzmm          25.03   dres3           1.0
is          2032.37   homo3             n
rfl          3739.2       PROCESSING
rfp          3606.4   gf         not used
th               12   gfs        not used
ins           2.000   wtfile
nm    ph              proc             lp
                      fn           131072
                      math              f

                      werr
                      wexp
                      wbs
                      wnt             wft
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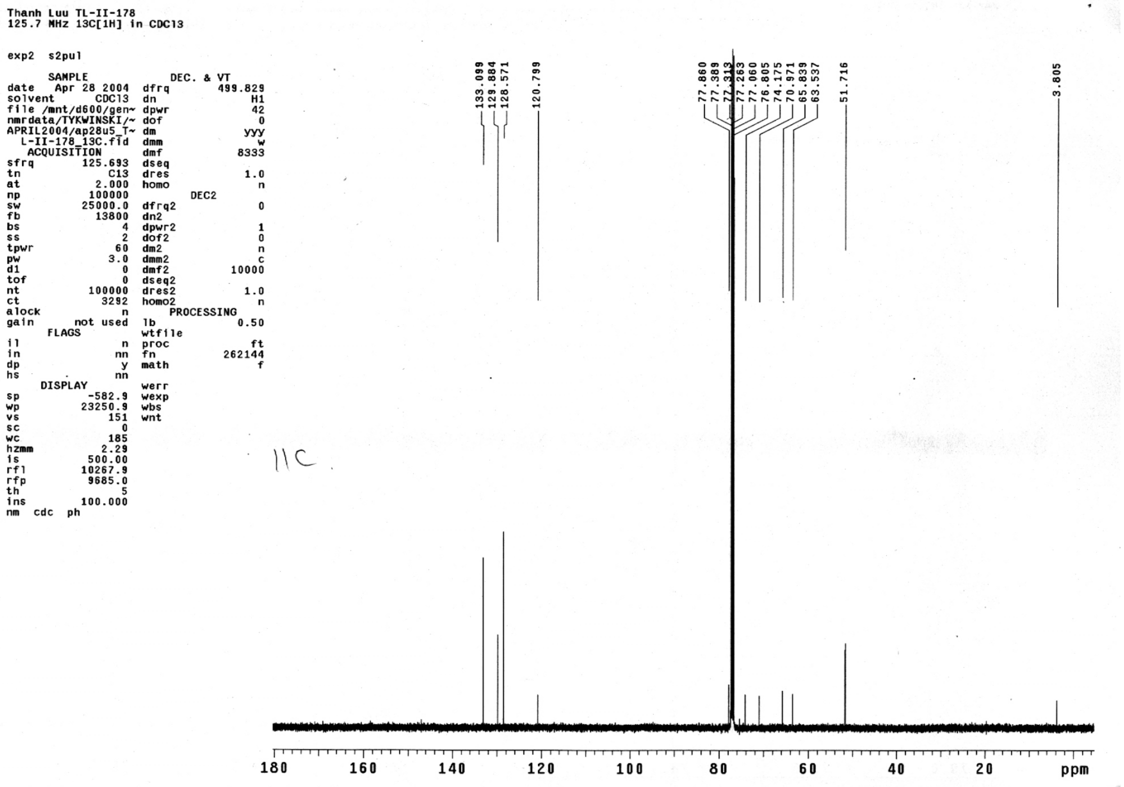

```
Thanh Luu TL-II-178
125.7 MHz 13C[1H] in CDCl3

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solvent       CDCl3   dn               H1
file /mnt/d600/gen~   dpwr             42
nmrdata/TYKWINSKI/~   dof               0
APRIL2004/ap28u5_T~   dm              yyy
  L-II-178_13C.fid    dmm               w
   ACQUISITION        dmf            8333
sfrq        125.693   dseq
tn              C13   dres            1.0
at            2.000   homo              n
np           100000          DEC2
sw          25000.0   dfrq2             0
fb            13800   dn2
bs                4   dpwr2             1
ss                2   dof2              0
tpwr             60   dm2               n
pw              3.0   dmm2              c
d1                0   dmf2          10000
tof               0   dseq2
nt           100000   dres2           1.0
ct             3292   homo2             n
alock             n      PROCESSING
gain       not used   lb             0.50
      FLAGS           wtfile
il                n   proc             ft
in               nn   fn           262144
dp                y   math              f
hs               nn
     DISPLAY          werr
sp           -582.9   wexp
wp          23250.9   wbs
vs              151   wnt
sc                0
wc              185
hzmm           2.29
is           500.00
rfl         10267.9
rfp          9685.0
th                5
ins         100.000
nm  cdc  ph
```

Figure S11-^{1}H/^{13}C NMR spectra of **9d**

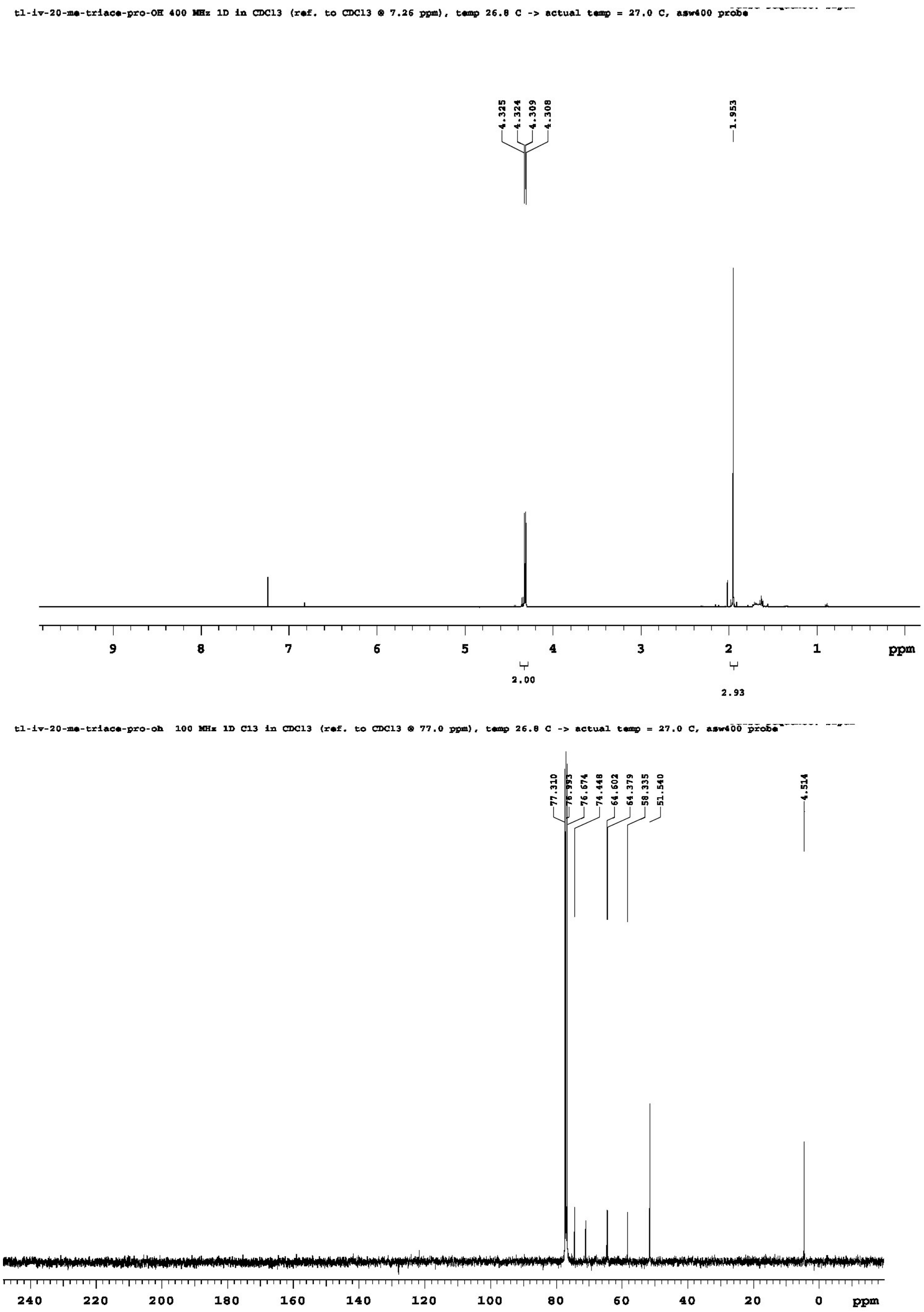
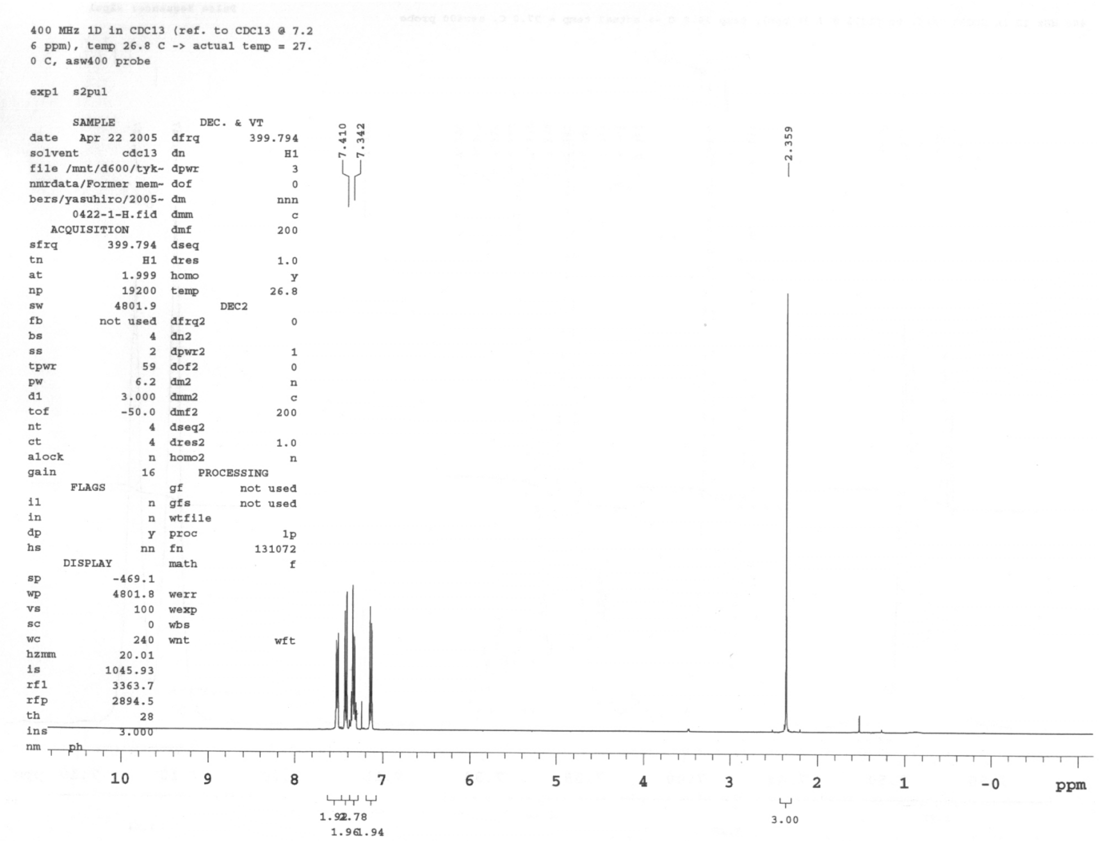


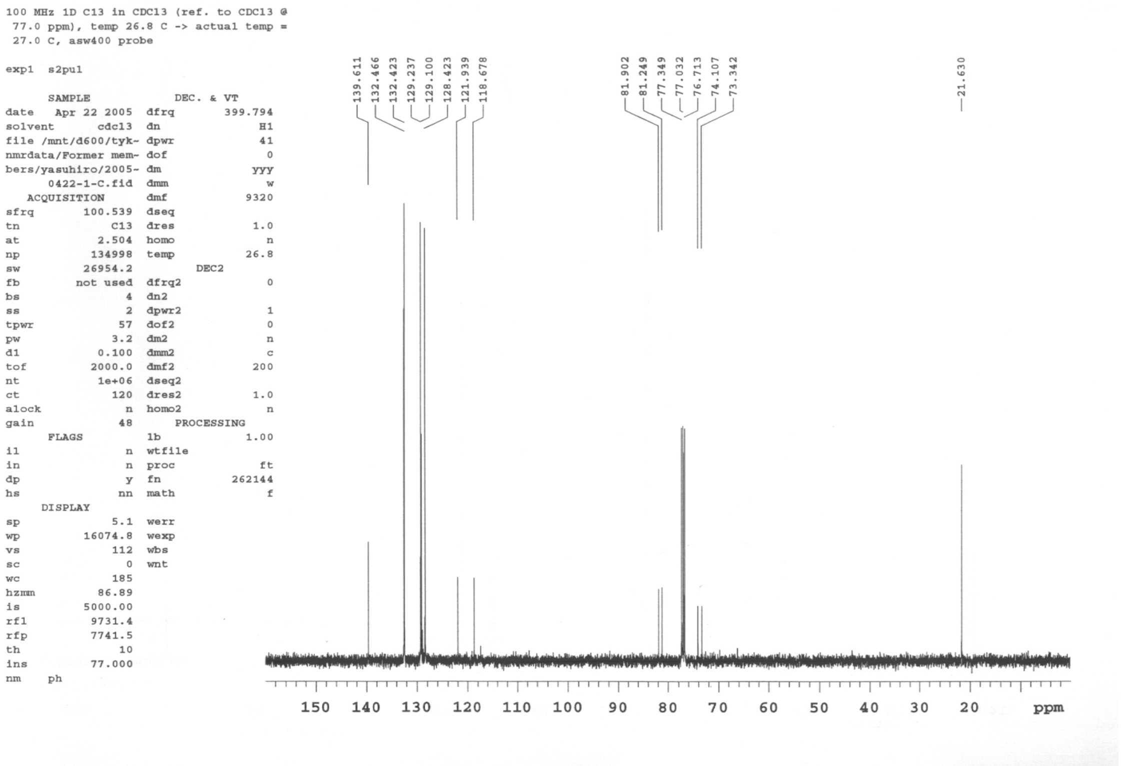
Figure S12-$^{1}H/^{13}C$ NMR spectra of **10**



```
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.2
6 ppm), temp 26.8 C -> actual temp = 27.
0 C, asw400 probe

exp1  s2pul

      SAMPLE              DEC. & VT
date   Apr 22 2005  dfrq        399.794
solvent       cdcl3  dn               H1
file /mnt/d600/tyk-  dpwr              3
nmrdata/Former mem-  dof               0
bers/yasuhiro/2005-  dm              nnn
      0422-1-H.fid  dmm                c
   ACQUISITION       dmf             200
sfrq        399.794  dseq
tn               H1  dres            1.0
at            1.999  homo              y
np            19200  temp           26.8
sw           4801.9        DEC2
fb         not used  dfrq2             0
bs                4  dn2
ss                2  dpwr2             1
tpwr             59  dof2              0
pw              6.2  dm2               n
d1            3.000  dmm2              c
tof           -50.0  dmf2            200
nt                4  dseq2
ct                4  dres2           1.0
alock             n  homo2             n
gain             16      PROCESSING
      FLAGS          gf         not used
il                n  gfs        not used
in                n  wtfile
dp                y  proc             lp
hs               nn  fn           131072
     DISPLAY         math              f
sp           -469.1
wp           4801.8  werr
vs              100  wexp
sc                0  wbs
wc              240  wnt             wft
hzmm          20.01
is          1045.93
rfl          3363.7
rfp          2894.5
th               28
ins           3.000
nm   ph
```



```
100 MHz 1D C13 in CDCl3 (ref. to CDCl3 @
 77.0 ppm), temp 26.8 C -> actual temp =
 27.0 C, asw400 probe

exp1  s2pul

      SAMPLE              DEC. & VT
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solvent       cdcl3  dn               H1
file /mnt/d600/tyk-  dpwr             41
nmrdata/Former mem-  dof               0
bers/yasuhiro/2005-  dm              yyy
      0422-1-C.fid  dmm                w
   ACQUISITION       dmf            9320
sfrq        100.539  dseq
tn              C13  dres            1.0
at            2.504  homo              n
np           134998  temp           26.8
sw          26954.2        DEC2
fb         not used  dfrq2             0
bs                4  dn2
ss                2  dpwr2             1
tpwr             57  dof2              0
pw              3.2  dm2               n
d1            0.100  dmm2              c
tof          2000.0  dmf2            200
nt            1e+06  dseq2
ct              120  dres2           1.0
alock             n  homo2             n
gain             48      PROCESSING
      FLAGS          lb             1.00
il                n  wtfile
in                n  proc             ft
dp                y  fn           262144
hs               nn  math              f
     DISPLAY
sp              5.1  werr
wp          16074.8  wexp
vs              112  wbs
sc                0  wnt
wc              185
hzmm          86.89
is          5000.00
rfl          9731.4
rfp          7741.5
th               10
ins          77.000
nm   ph
```

Figure S13-^{1}H/^{13}C NMR spectra of **11**

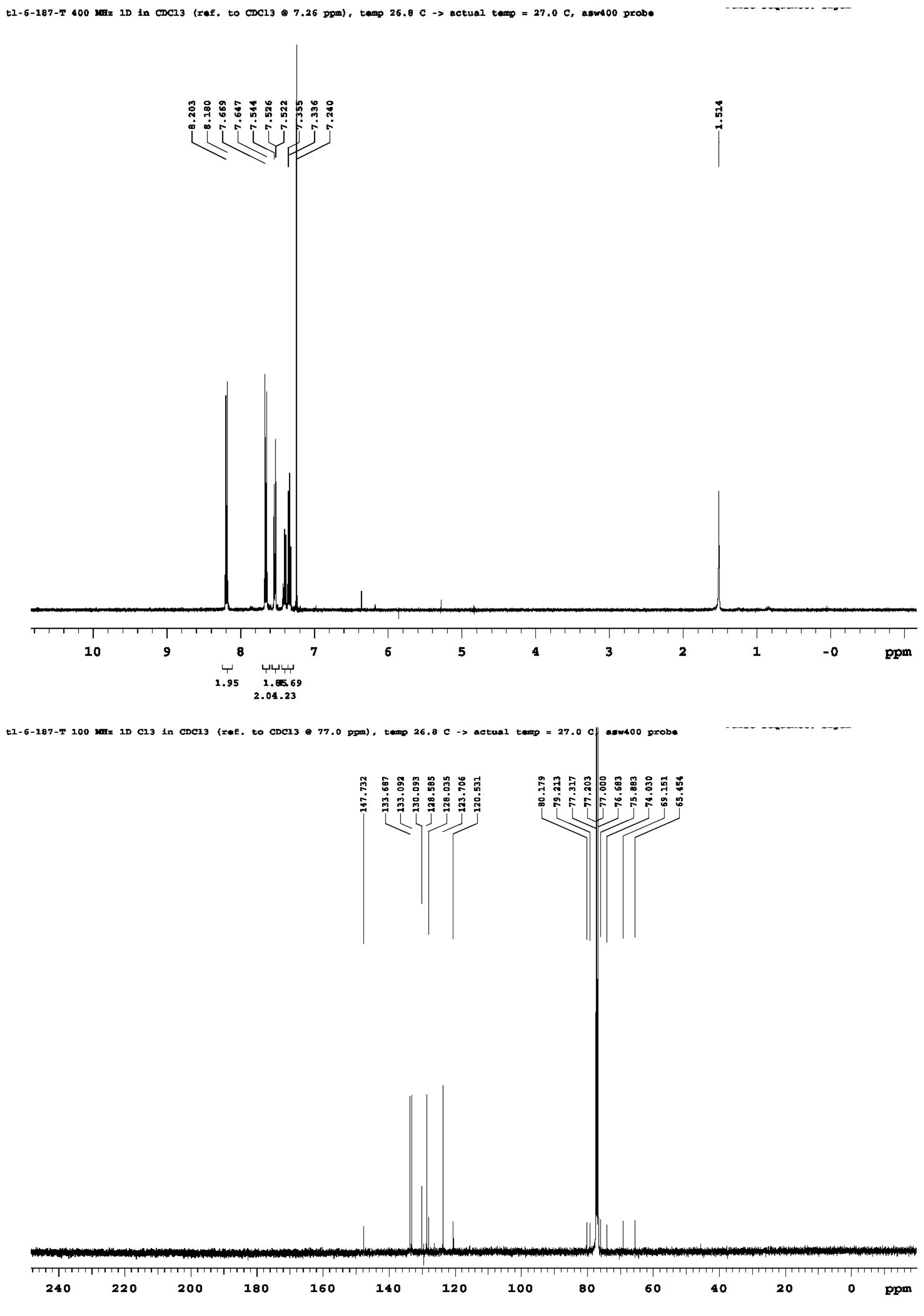


Figure S14-^{1}H/^{13}C NMR spectra of **12d**

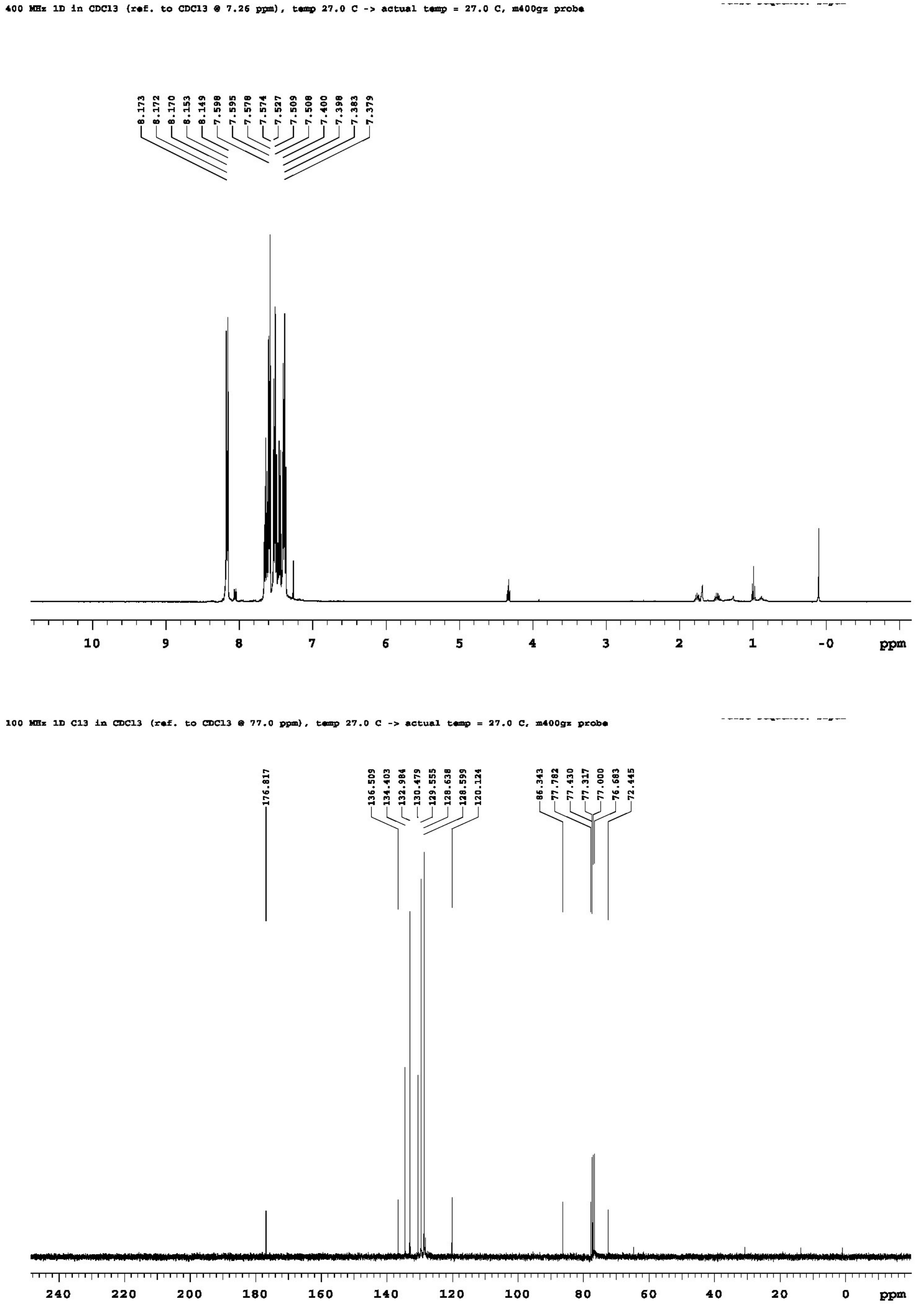
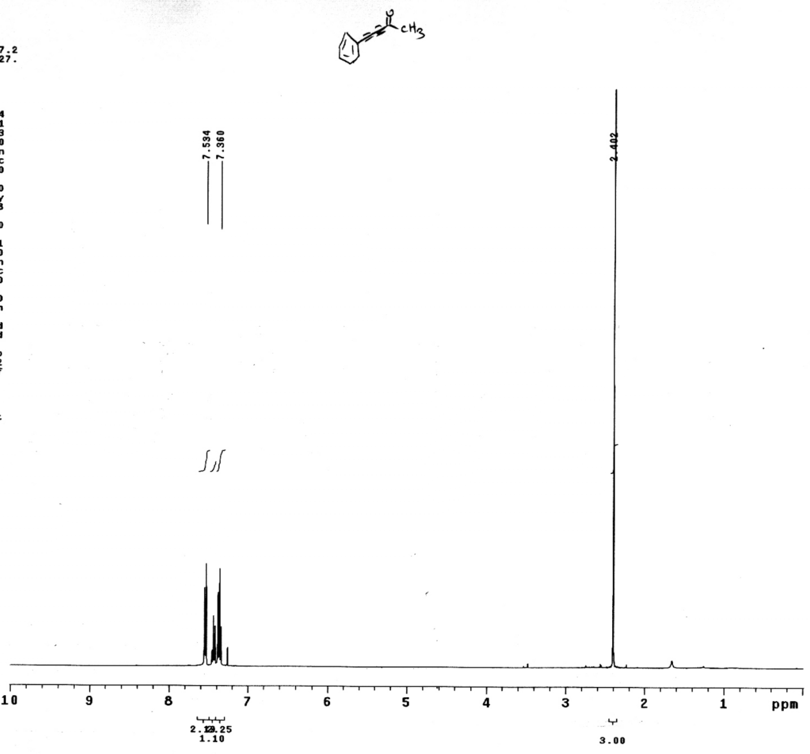


Figure S15-^{1}H/^{13}C NMR spectra of **18a**

```
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.2
6 ppm), temp 26.8 C -> actual temp = 27.
0 C, asw400 probe

exp2  s2pul

      SAMPLE                DEC. & VT
date    Jun  8 2005  dfrq       399.794
solvent       cdcl3  dn              H1
file /mnt/d600/tyk~  dpwr             3
nmrdata/Former mem~  dof              0
bers/yasuhiro/2005~  dm             nnn
       0608-H.fid    dmm              c
   ACQUISITION       dmf            200
sfrq        399.794  dseq
tn               H1  dres           1.0
at            1.999  homo             y
np            19200  temp          26.8
sw           4801.9          DEC2
fb         not used  dfrq2            0
bs                4  dn2
ss                2  dpwr2            1
tpwr             59  dof2             0
pw              6.2  dm2              n
d1            3.000  dmm2             c
tof           -50.0  dmf2           200
nt                4  dseq2
ct                4  dres2          1.0
alock             n  homo2            n
gain             16      PROCESSING
      FLAGS          gf        not used
il                n  gfs       not used
in                n  wtfile
dp                y  proc            lp
hs               nn  fn          131072
     DISPLAY         math             f
sp             -4.8
wp           4004.3  werr
vs              149  wexp
sc                0  wbs
wc              185  wnt            wft
hzmm          21.64
is          1286.41
rfl          3361.9
rfp          2902.5
th               22
ins           3.000
nm    ph
```



```
100 MHz 1D C13 in CDCl3 (ref. to CDCl3 @
 77.0 ppm), temp 26.8 C -> actual temp =
 27.0 C, asw400 probe

exp2  s2pul

      SAMPLE                DEC. & VT
date    Jun  8 2005  dfrq       399.794
solvent       cdcl3  dn              H1
file /mnt/d600/tyk~  dpwr            41
nmrdata/Former mem~  dof              0
bers/yasuhiro/2005~  dm             yyy
       0608-C.fid    dmm              w
   ACQUISITION       dmf           9320
sfrq        100.539  dseq
tn              C13  dres           1.0
at            2.504  homo             n
np           134998  temp          26.8
sw          26954.2          DEC2
fb         not used  dfrq2            0
bs                4  dn2
ss                2  dpwr2            1
tpwr             57  dof2             0
pw              3.2  dm2              n
d1            0.100  dmm2             c
tof          2000.0  dmf2           200
nt            1e+06  dseq2
ct              172  dres2          1.0
alock             n  homo2            n
gain             48      PROCESSING
      FLAGS          lb            1.00
il                n  wtfile
in                n  proc            ft
dp                y  fn          262144
hs               nn  math             f
     DISPLAY
sp             24.7  werr
wp          20111.0  wexp
vs              125  wbs
sc                0  wnt
wc              185
hzmm         108.71
is          5000.00
rfl          9734.2
rfp          7740.6
th               12
ins         100.000
nm    ph
```

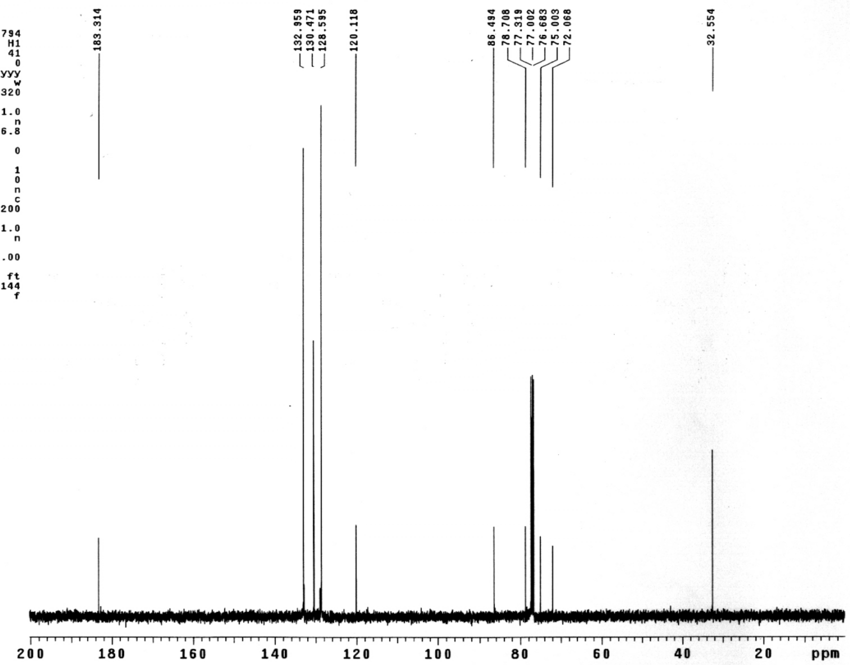


Figure S16-$^{1}H/^{13}C$ NMR spectra of **18e**