

Supporting information

Chemo- and regioselective reductive deoxygenation of 1-en-4-yn-ols into 1,4-enynes through FeF_3 and TfOH co-catalysis

Zonglian Yang,^a Rapolu Kiran Kumar^a Peiqiu Liao,^a Zhaohong Liu,^a Xingqi Li and Xihe Bi^{*ab}

^aDepartment of Chemistry, Northeast Normal University, Changchun 130024, China

^bState Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Email: bixh507@nenu.edu.cn

Table of Contents

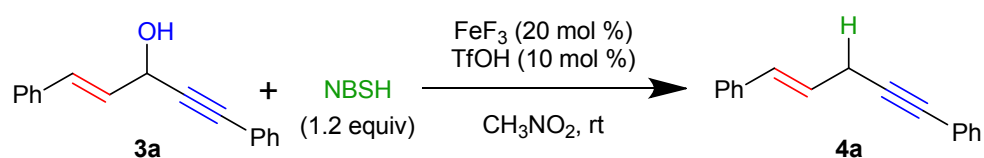
1. General information.....	2
2. Synthesis and analytical data of compounds 4a-l , 6a-f and 8	2-9
3. References	9-10
4. NMR spectral copies of 4a-l , 6a-f and 8	11-32

1. General information

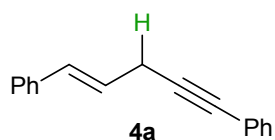
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H -NMR and ^{13}C -NMR spectra were recorded at 25 °C on a Varian 500 MHz and 125 MHz, or on a Varian 400 MHz and 100 MHz, respectively, and TMS was used as internal standard.

2. Synthesis and analytical data of compounds 4a-l, 6a-f and 8

The synthesis of compounds **4a-l**, **6a-f** and **8** is performed according to the below given procedure for the synthesis of compound **4a**.

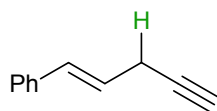


NBSH (130.2 mg, 0.60 mmol) was added at room temperature to a solution of **3a** (117.1 mg, 0.5 mmol) in CH_3NO_2 (3.0 mL). The resulting mixture was stirred until NBSH fully dissolved, then FeF_3 (11.2 mg, 20 mol %) was added, followed by adding TfOH (4.4 μL , 10 mol %). The reaction mixture was stirred at room temperature for 1.0 h under N_2 and the reaction was monitored by TLC. Upon completing the reaction, the mixture was quenched with saturated aqueous NaHCO_3 , extracted with diethyl ether (3 x 30 mL). The combined organic solvents were washed with brine, dried with MgSO_4 , filtered, and concentrated under reduced pressure at room temperature. The residue was finally purified by silica gel column chromatography to give product **4a** as a colorless oil (103.5 mg, 95%).



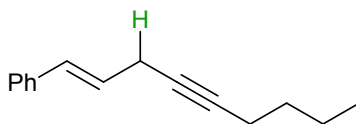
(E)-Pent-1-en-4-yne-1,5-diylidibenzene (4a):¹ Colorless liquid; Yield = 103.5 mg, 95%; ^1H -NMR (400 MHz, CDCl_3): δ = 3.35 (d, J = 5.6 Hz, 2H), 6.24 (dt, J = 5.6 Hz, J = 15.5 Hz, 1H), 6.70 (d, J = 15.5 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.25-7.35 (m, 5H), 7.38 (d, J = 7.6 Hz, 2H); 7.44-7.47 (m, 2H); ^{13}C -NMR (CDCl_3 , 100 MHz): δ = 23.0, 82.8, 86.7, 123.6, 124.2, 126.2, 127.3, 127.8, 128.2, 128.5, 131.4, 131.6, 137.1. FT-IR (neat): ν = 3080, 3057, 3028, 2968,

2878, 2810, 2231, 1948, 1879, 1802, 1750, 1653, 1598, 1574, 1490, 1444, 1414, 1341, 1310, 1269, 1206, 1177, 1156, 1070, 1027, 964, 913, 840, 795, 755, 731, 690, 554, 524, 493, 416 cm⁻¹.



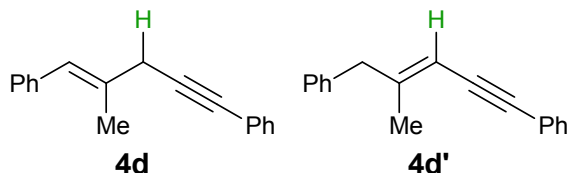
4b

(E)-pent-1-en-4-yn-1-ylbenzene (4b): Colorless liquid; Yield = 65.5 mg, 92%; ¹H-NMR (500 MHz, CDCl₃): δ = 2.17 (t, *J* = 5.0 Hz, 1H), 3.12-3.14 (m, 2H), 6.135 (dt, *J* = 5.6 Hz, *J* = 15.5 Hz, 1H), 6.66 (dt, *J* = 2.0 Hz, *J* = 15.5 Hz, 1H), 7.20-7.24 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 22.0, 70.6, 81.2, 123.5, 126.2, 127.4, 128.5, 131.5, 136.9. FT-IR (neat): ν = 3297, 3081, 3059, 3027, 2965, 2885, 2815, 2362, 2119, 1948, 1877, 1803, 1749, 1653, 1599, 1577, 1494, 1448, 1417, 1309, 1293, 1264, 1208, 1156, 1074, 1058, 1026, 965, 910, 841, 797, 732, 692, 641, 544, 493 cm⁻¹.

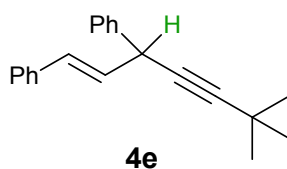


4c

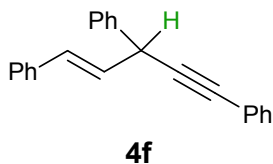
(E)-non-1-en-4-yn-1-ylbenzene (4c): Colorless liquid; Yield = 69.7 mg, 70%; ¹H-NMR (500 MHz, CDCl₃): δ = 0.92 (t, *J* = 7.0 Hz, 3H), 1.40-1.53 (m, 4H), 2.22 (t, *J* = 7.0 Hz, 2H), 3.06-3.12 (m, 2H), 6.17 (dt, *J* = 5.6 Hz, *J* = 15.5 Hz, 1H), 6.63 (d, *J* = 15.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 13.6, 18.5, 21.9, 22.4, 31.1, 76.6, 82.9, 125.2, 126.1, 127.1, 128.4, 130.7, 137.2. FT-IR (neat): ν = 3647, 3081, 3059, 3027, 2957, 2931, 2872, 1943, 1871, 1800, 1747, 1699, 1655, 1599, 1577, 1495, 1464, 1448, 1431, 1419, 1378, 1339, 1328, 1265, 1205, 1156, 1103, 1073, 1029, 964, 908, 795, 730, 691, 543, 494 cm⁻¹.



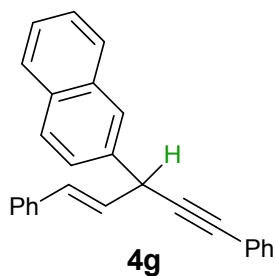
(E)-(2-Methylpent-1-en-4-yne-1,5-diyl)dibenzene (4d)² and **(E)-(4-methylpent-3-en-1-yne-1,5-diyl)dibenzene (4d')**: Colorless liquid; Yield = 106.8 mg, 92%; ¹H-NMR (500 MHz, CDCl₃): δ = 1.97 (d, *J* = 1.0 Hz, 3H, **4d**, 83%), 2.07 (d, *J* = 1.5 Hz, 3H, **4d'**, 17%), 3.28-3.31 (m, 2H), 6.40 (s, 1H, **4d'**, 17%), 6.64 (s, 1H, **4d**, 83%), 7.18-7.22 (m, 1H), 7.26-7.31 (m, 5H), 7.31-7.35 (m, 2H), 7.42-7.47 (m, 2H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 17.8, 23.5, 23.9, 30.3, 81.1, 83.3, 87.0, 87.7, 123.7, 123.8, 126.1, 126.2, 126.4, 126.8, 127.7, 127.8, 128.0, 128.18, 128.21, 128.24, 128.6, 128.8, 131.6, 133.5, 133.9, 137.6, 138.0.



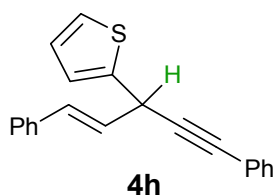
(E)-(6,6-dimethylhept-1-en-4-yne-1,3-diyl)dibenzene (4e): Colorless liquid; Yield = 115.0 mg, 85%; ¹H-NMR (500 MHz, CDCl₃): δ = 1.33 (s, 9H), 4.52 (d, *J* = 6.5 Hz, 1H), 6.27 (dd, *J* = 6.5 Hz, *J* = 15.5 Hz, 1H), 6.72 (d, *J* = 15.5 Hz, 1H), 7.22-7.28 (m, 2H), 7.28-7.41 (m, 7H), 7.46 (d, *J* = 7.5 Hz, 2H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 27.6, 31.3, 40.6, 77.5, 94.3, 126.4, 126.7, 127.3, 127.6, 128.46, 128.49, 129.6, 130.8, 137.1, 141.0.



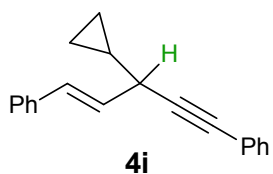
(E)-Pent-1-en-4-yne-1,3,5-triyltribenzene (4f)³: Colorless liquid; Yield = 130.8 mg, 89%; ¹H-NMR (500 MHz, CDCl₃): δ = 4.75 (d, *J* = 6.5 Hz, 1H), 6.33 (dd, *J* = 6.5 Hz, *J* = 15.5 Hz, 1H), 6.77 (d, *J* = 15.5 Hz, 1H), 7.19-7.22 (m, 1H), 7.25-7.32 (m, 6H), 7.34-7.39 (m, 4H), 7.48-7.50 (m, 4H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 41.2, 85.4, 88.8, 123.4, 126.5, 127.1, 127.5, 127.7, 128.0, 128.2, 128.5, 128.7, 129.6, 130.4, 131.7, 136.8, 140.2.



(E)-2-(1,5-diphenylpent-1-en-4-yn-3-yl)naphthalene (4g): Colorless liquid; Yield = 107.2 mg, 62%; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 4.89 (d, J = 6.5 Hz, 1H), 6.39 (dd, J = 6.5 Hz, J = 16.0 Hz, 1H), 6.82 (d, J = 16 Hz, 1H), 7.15-7.21 (m, 1H), 7.26-7.31 (m, 5H), 7.38 (d, J = 7.5 Hz, 2H), 7.41-7.46 (m, 2H), 7.50-7.52 (m, 2H), 7.57 (dd, J = 1.5 Hz, J = 8.5 Hz, 1H), 7.80 (t, J = 8.5 Hz, 3H), 7.92 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ = 41.3, 85.6, 88.8, 123.4, 125.8, 126.1, 126.2, 126.5, 127.5, 127.6, 127.8, 128.0, 128.2, 128.4, 128.5, 129.4, 130.7, 131.7, 132.6, 133.5, 136.7, 137.6.

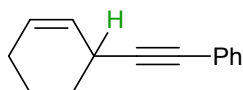


(E)-2-(1,5-diphenylpent-1-en-4-yn-3-yl)thiophene (4h):⁴ Colorless liquid; Yield = 86.0 mg, 57%; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 4.99 (d, J = 7.0 Hz, 1H), 6.39 (dd, J = 7.0 Hz, J = 15.5 Hz, 1H), 6.78 (d, J = 15.5 Hz, 1H), 6.98 (dd, J = 3.5 Hz, J = 5 Hz, 1H), 7.09-7.11 (m, 1H), 7.22-7.25 (m, 2H), 7.30-7.33 (m, 5H), 7.42 (d, J = 7.5 Hz, 2H), 7.48-7.51 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ = 36.5, 84.7, 88.1, 123.1, 124.7, 124.8, 126.6, 126.9, 127.7, 128.17, 128.24, 128.5, 128.7, 130.9, 131.7, 136.5, 144.2.



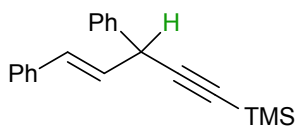
(E)-2-(3-cyclopropylpent-1-en-4-yn-1,5-diyl)dibenzene (4i): Colorless liquid; Yield = 96.8 mg, 75%; $^1\text{H-NMR}$ (500

MHz, CDCl₃): δ = 0.44-0.54 (m, 2H), 0.55-0.58 (m, 2H), 1.07-1.13 (m, 1H), 3.20 (t, J = 6.0 Hz, 1H), 6.30 (dd, J = 6.5 Hz, J = 16.0 Hz, 1H), 6.71(d, J = 16.0 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.28-7.33 (m, 5H), 7.41 (d, J = 7.0 Hz, 2H), 7.43-7.46 (m, 2H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 2.8, 3.5, 15.5, 38.8, 83.7, 88.7, 123.6, 126.4, 127.3, 127.8, 128.2, 128.5, 129.3, 130.1, 131.7, 137.2.



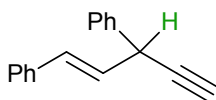
4j

3-(Phenylethynyl)cyclohexene (4j):^{1b,5} Colorless liquid; Yield = 77.7 mg, 85%; ¹H-NMR (500 MHz, CDCl₃): δ = 1.58-1.65 (m, 1H), 1.77-1.90 (m, 2H), 1.96-2.07 (m, 3H), 3.28-3.31 (m, 1H), 5.71-5.80 (m, 2H), 7.26-7.29 (m, 3H), 7.39-7.41 (m, 2H); ¹³C-NMR (CDCl₃, 100 MHz): δ = 20.6, 24.7, 28.0, 29.4, 80.3, 92.8, 123.8, 127.0, 127.5, 128.0, 128.1, 131.6.



4k

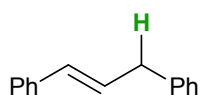
(E)-(3,5-Diphenylpent-4-en-1-ynyl)trimethylsilane (4k):^{3e} Colorless liquid; Yield = 126.6 mg, 87%; ¹H-NMR (400 MHz, CDCl₃): δ = 0.22 (s, 9H), 4.55 (d, J = 6.5 Hz, 1H), 6.24 (dd, J = 6.5 Hz, J = 16.0 Hz, 1H), 6.68 (d, J = 16.0 Hz, 1H), 7.19-7.37 (m, 8H), 7.42 (d, J = 7.2 Hz, 2H); ¹³C-NMR (CDCl₃, 125 MHz): δ = 0.1, 41.6, 89.7, 105.3, 126.5, 127.0, 127.5, 127.7, 128.5, 128.6, 129.5, 130.4, 136.8, 139.9.



4l

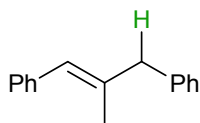
(E)-pent-1-en-4-yne-1,3-diylidibenzene (4l):^{3e,6} Colorless liquid; Yield = 103.5 mg, 95%; ¹H-NMR (500 MHz, CDCl₃): δ = 2.49 (d, J = 2.5 Hz, 1H), 4.53 (d, J = 6.5 Hz, 1H), 6.25 (dd, J = 6.5 Hz, J = 15.5 Hz, 1H), 6.74 (d, J = 15.5

Hz, 1H), 7.21(t, J = 7.5 Hz, 1H), 7.25-7.31 (m, 3H), 7.33-7.37 (m, 4H), 7.42 (d, J = 7.5 Hz, 2H); ^{13}C -NMR (CDCl_3 , 125 MHz): δ = 40.3, 73.3, 83.3, 126.5, 127.2, 127.56, 127.60, 128.5, 128.7, 128.9, 130.6, 136.6, 139.7.



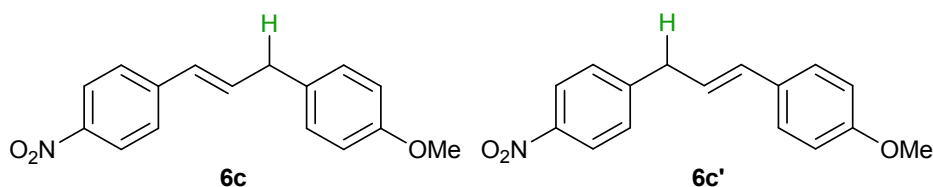
6a

(E)-1,3-Diphenylpropene (6a):⁷ Colorless liquid; Yield = 76.5 mg, 79%; ^1H -NMR (500 MHz, CDCl_3): δ = 3.54 (d, J = 6.5 Hz, 2H), 6.35 (dt, J = 6.5 Hz, J = 16.0 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 7.16-7.25 (m, 4H), 7.26-7.32 (m, 4H), 7.35 (d, J = 7.5 Hz, 2H); ^{13}C -NMR (CDCl_3 , 125 MHz): δ = 39.3, 126.1, 126.2, 127.1, 128.46, 128.47, 128.6, 129.2, 131.0, 137.4, 140.1.



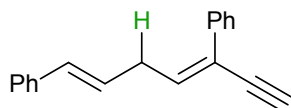
6b

(E)-(2-Methylprop-1-ene-1,3-diyl)dibenzene (6b):^{7c,8} Colorless liquid; Yield = 91.4 mg, 88%; ^1H -NMR (500 MHz, CDCl_3): δ = 1.79 (s, 3H), 3.46 (s, 2H), 6.37 (s, 1H), 7.16-7.22 (m, 2H), 7.23-7.25 (m, 4H), 7.28-7.31 (m, 4H); ^{13}C -NMR (CDCl_3 , 125 MHz): δ = 17.6, 47.1, 126.0, 126.1, 126.7, 128.0, 128.3, 128.8, 129.0, 138.0, 138.3, 139.8.



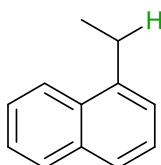
(E)-1-methoxy-4-(3-(4-nitrophenyl)allyl)benzene (6c)⁹ and **(E)-1-methoxy-4-(3-(4-nitrophenyl)prop-1-en-1-yl)benzene (6c')**^{9,10} Colorless liquid; Yield = 77.0 mg, 57%; ^1H -NMR (500 MHz, CDCl_3): δ = 3.53 (d, J = 6.3 Hz, 2H, **6c**), 3.61 (d, J = 7.0 Hz, 2H, **6c'**), 3.80 (s, 3H, **6c** + **6c'**), 6.12-6.20 (m, 1H, **6c'**), 6.40-6.48 (m, 1H, **6c** + **6c'**), 6.51-6.56 (m, 1H, **6c**), 6.82-6.89 (m, 2H, **6c** + **6c'**), 7.15 (d, J = 8.5 Hz, 2H, **6c**), 7.29 (d, J = 8.5 Hz, 2H, **6c'**), 7.39 (d, J =

8.5 Hz, 2H, **6c'**), 7.45 (d, $J = 8.5$ Hz, 2H, **6c**), 8.11-8.17 (m, 2H, **6c** + **6c'**); ^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 38.5$, 39.0, 55.3, 113.96, 114.01, 123.7, 123.9, 124.7, 126.5, 127.3, 127.6, 128.8, 129.4, 129.59, 129.64, 130.9, 131.9, 144.0, 146.5, 148.3, 158.2, 159.1.



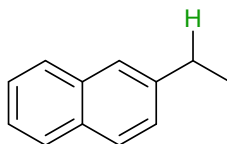
6d

(1E, 4Z)-hepta-1,4-dien-6-yne-1,5-diyl dibenzene (6d): Colorless liquid; Yield = 105.0 mg, 86%; ^1H -NMR (400 MHz, CDCl_3): $\delta = 3.37$ (s, 1H), 3.42 (t, $J = 7.2$ Hz, 2H), 6.22-6.30 (m, 1H), 6.47-6.54 (m, 2H), 7.19 (t, $J = 7.2$ Hz, 1H), 7.27-7.36 (m, 7H), 7.62 (d, $J = 7.6$ Hz, 2H); ^{13}C -NMR (CDCl_3 , 100 MHz): $\delta = 34.6$, 80.7, 83.6, 123.6, 126.0, 126.1, 127.0, 127.1, 127.8, 128.4, 128.5, 131.3, 136.8, 137.4.



6e

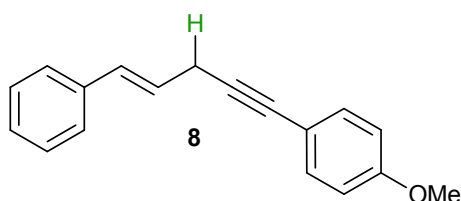
1-Ethynaphthalene (6e):¹¹ Colorless liquid; Yield = 40.8 mg, 52%; ^1H -NMR (500 MHz, CDCl_3): $\delta = 1.38$ (t, $J = 7.5$ Hz, 3H), 3.10 (q, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 7.0$ Hz, 1H), 7.38-7.41 (m, 1H), 7.44-7.51 (m, 2H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 8.05 (d, $J = 8.5$ Hz, 1H); ^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 15.0$, 25.9, 123.7, 124.8, 125.4, 125.6, 126.4, 128.7, 131.7, 133.8, 140.2.



6f

2-Ethynaphthalene (6f):¹² Colorless liquid; Yield = 36.0 mg, 46%; ^1H -NMR (500 MHz, CDCl_3): $\delta = 1.30$ (t, $J = 7.5$

Hz, 3H), 2.77 (q, $J = 7.5$ Hz, 2H), 7.31 (d, $J = 7.5$ Hz, 1H), 7.36-7.42 (m, 2H), 7.59 (s, 1H), 7.72-7.77 (m, 3H); ^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 15.5, 29.0, 125.0, 125.5, 125.8, 127.0, 127.4, 127.6, 127.8, 131.9, 133.7, 141.7$.



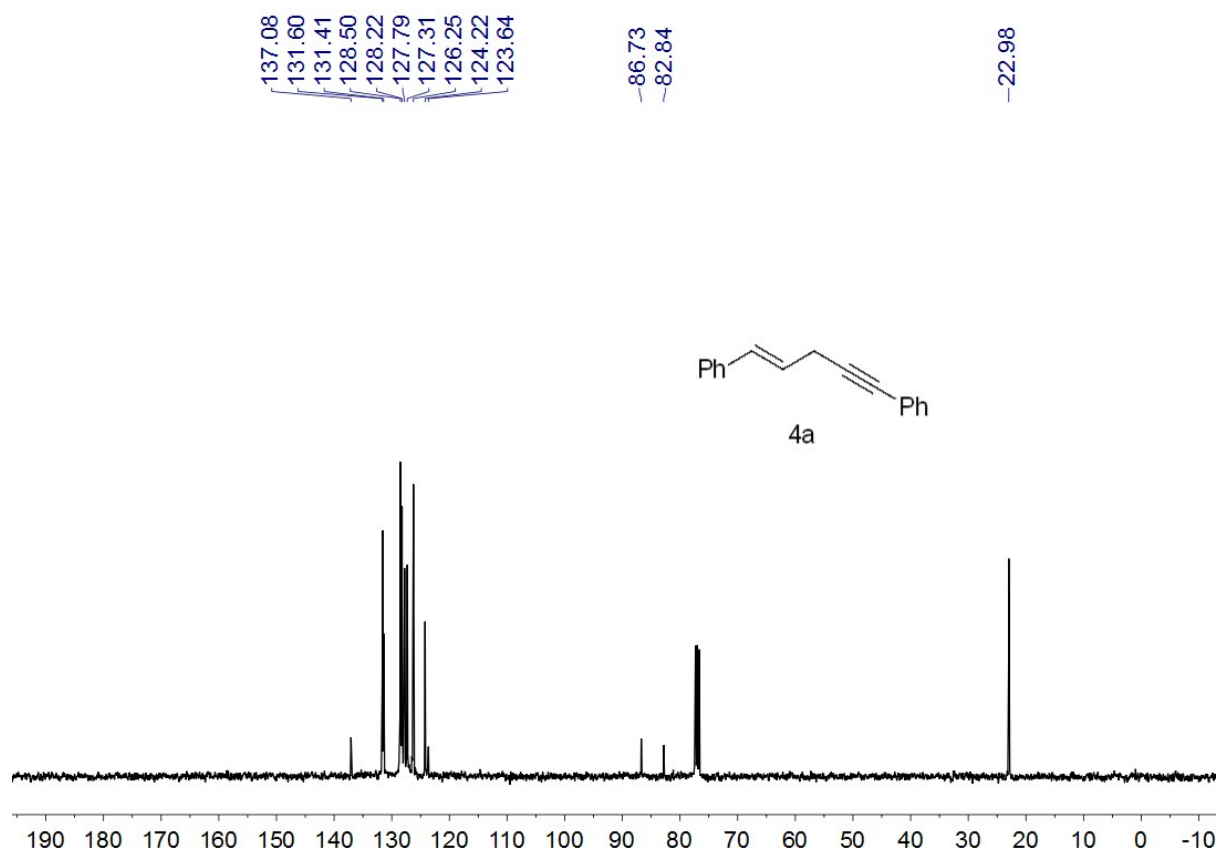
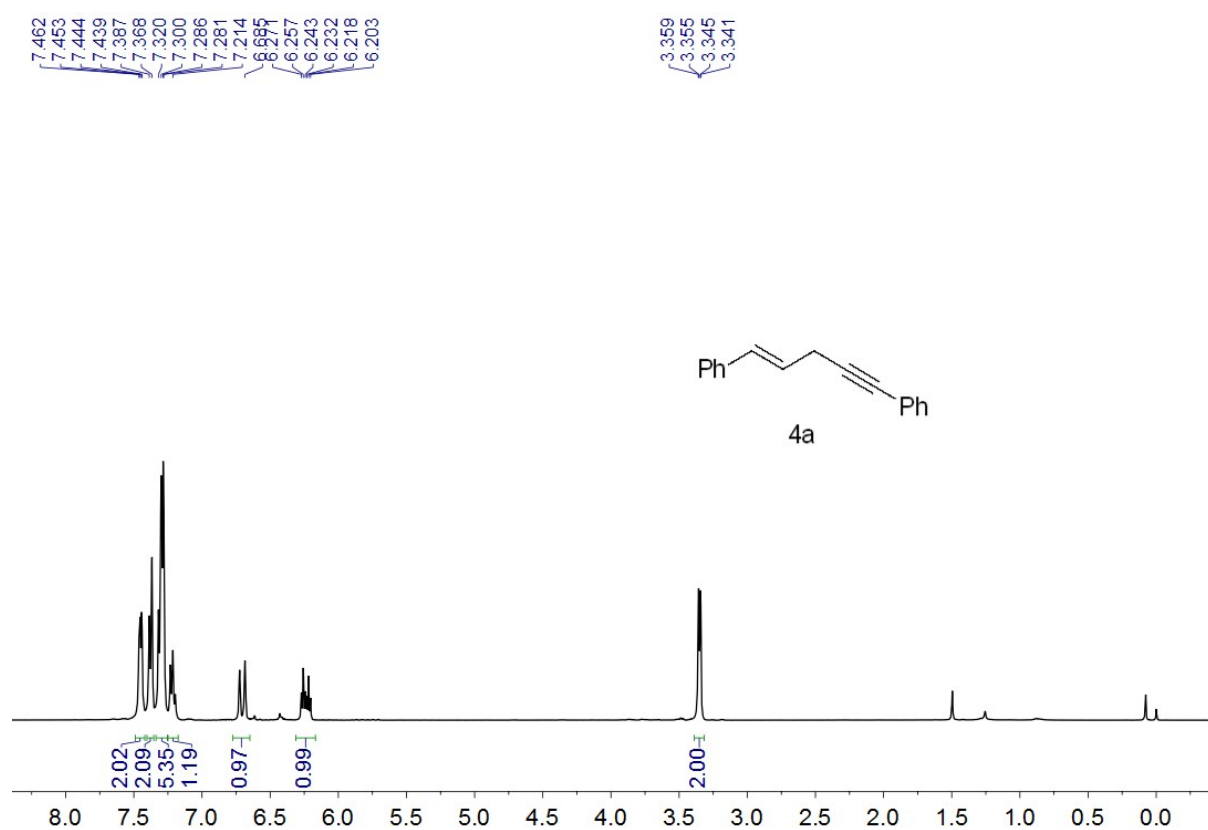
(E)-1-methoxy-4-(5-phenylpent-4-en-1-yn-1-yl)benzene (8):^{1a} Colorless liquid; Yield = 109.6 mg, 88%; ^1H -NMR (400 MHz, CDCl_3): $\delta = 3.39$ (dd, $J = 1.5$ Hz, $J = 5.5$ Hz, 2H), 3.83 (s, 3H), 6.29 (dd, $J = 5.5$ Hz, $J = 16.0$ Hz, 1H), 6.75 (d, $J = 16.0$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.26 (t, $J = 7.0$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.41-7.46 (m, 4H); ^{13}C -NMR (CDCl_3 , 100 MHz): $\delta = 23.0, 55.2, 82.6, 85.1, 113.8, 115.7, 124.5, 126.2, 127.3, 128.5, 131.2, 132.9, 137.1, 159.2$.

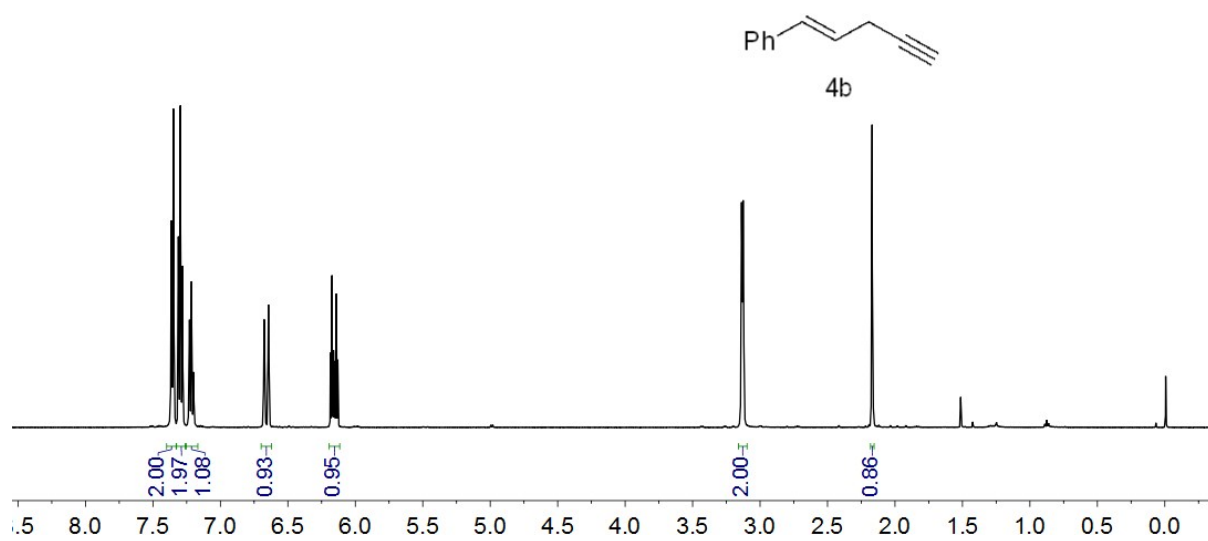
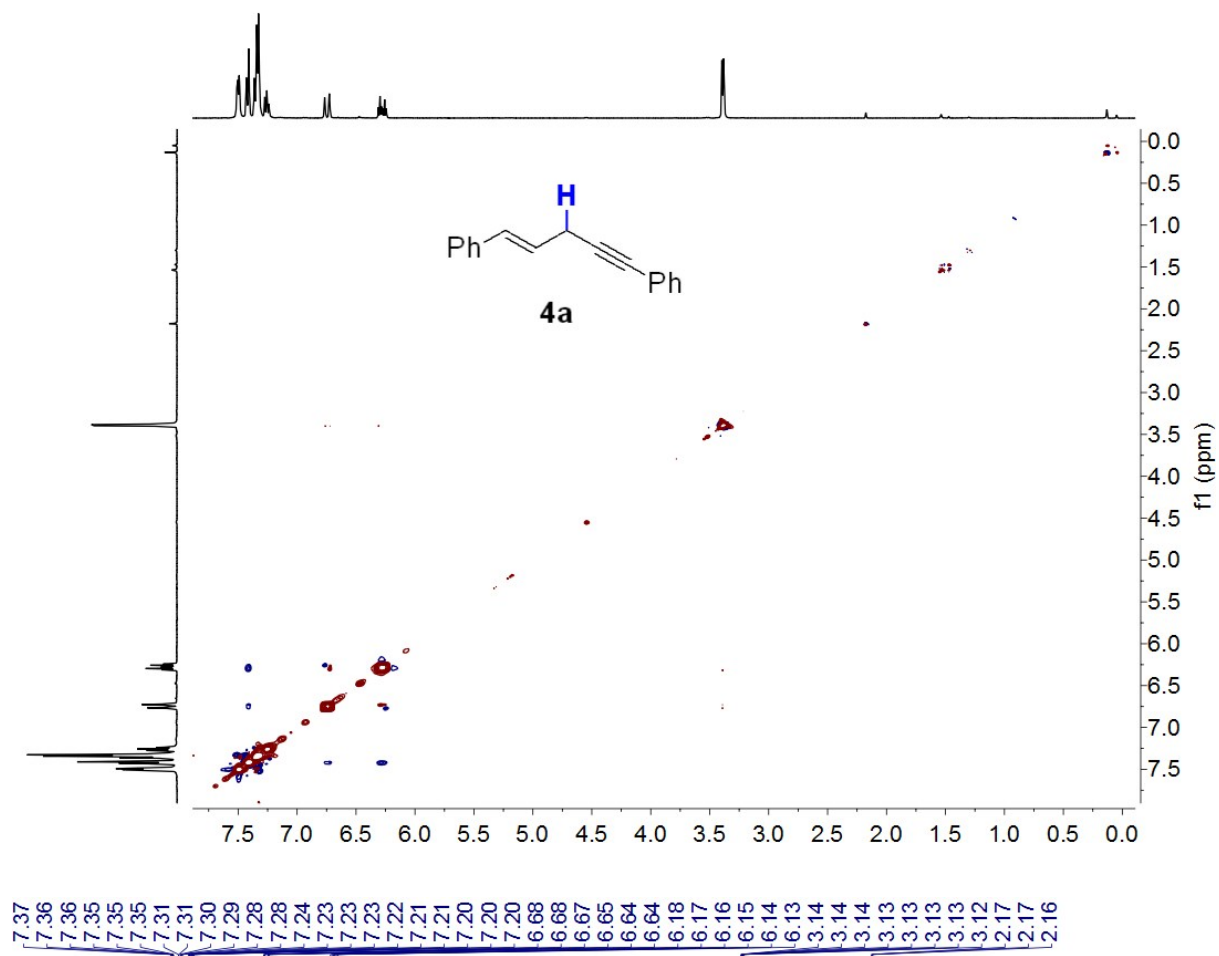
3. References

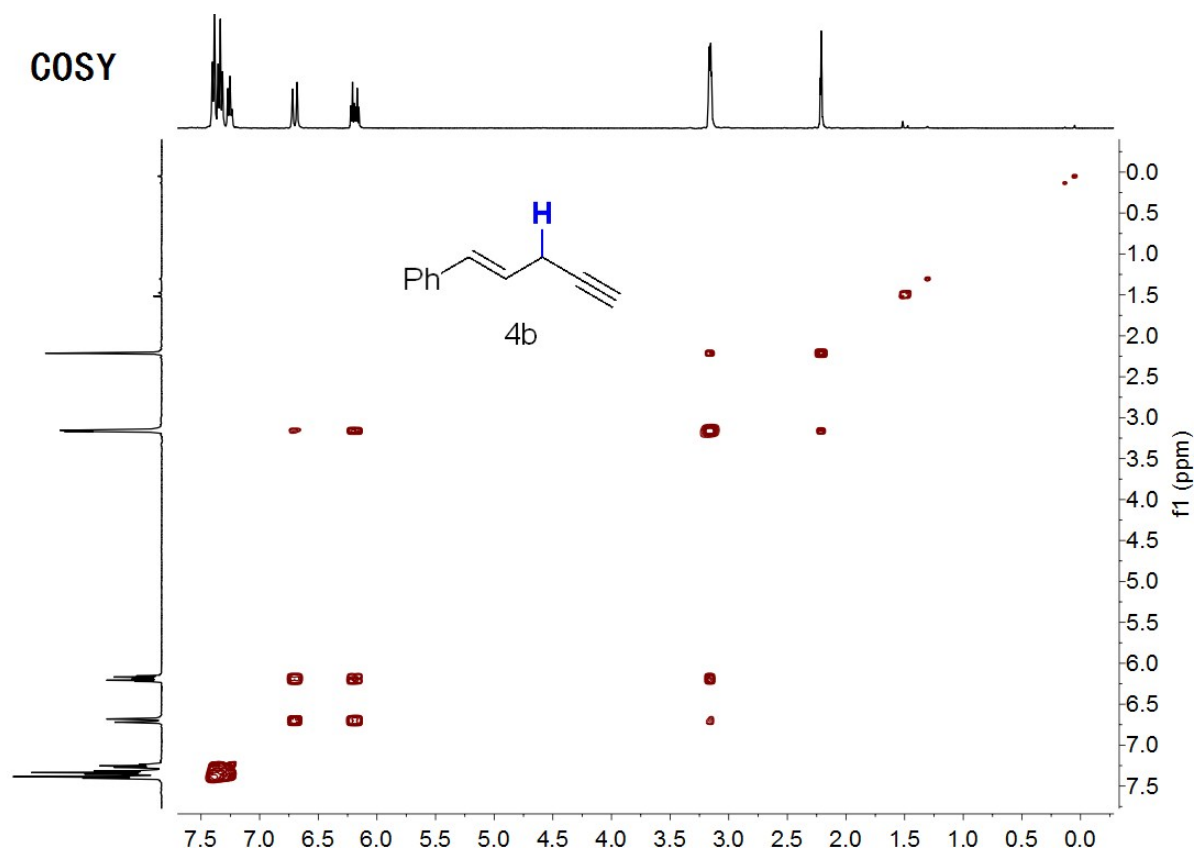
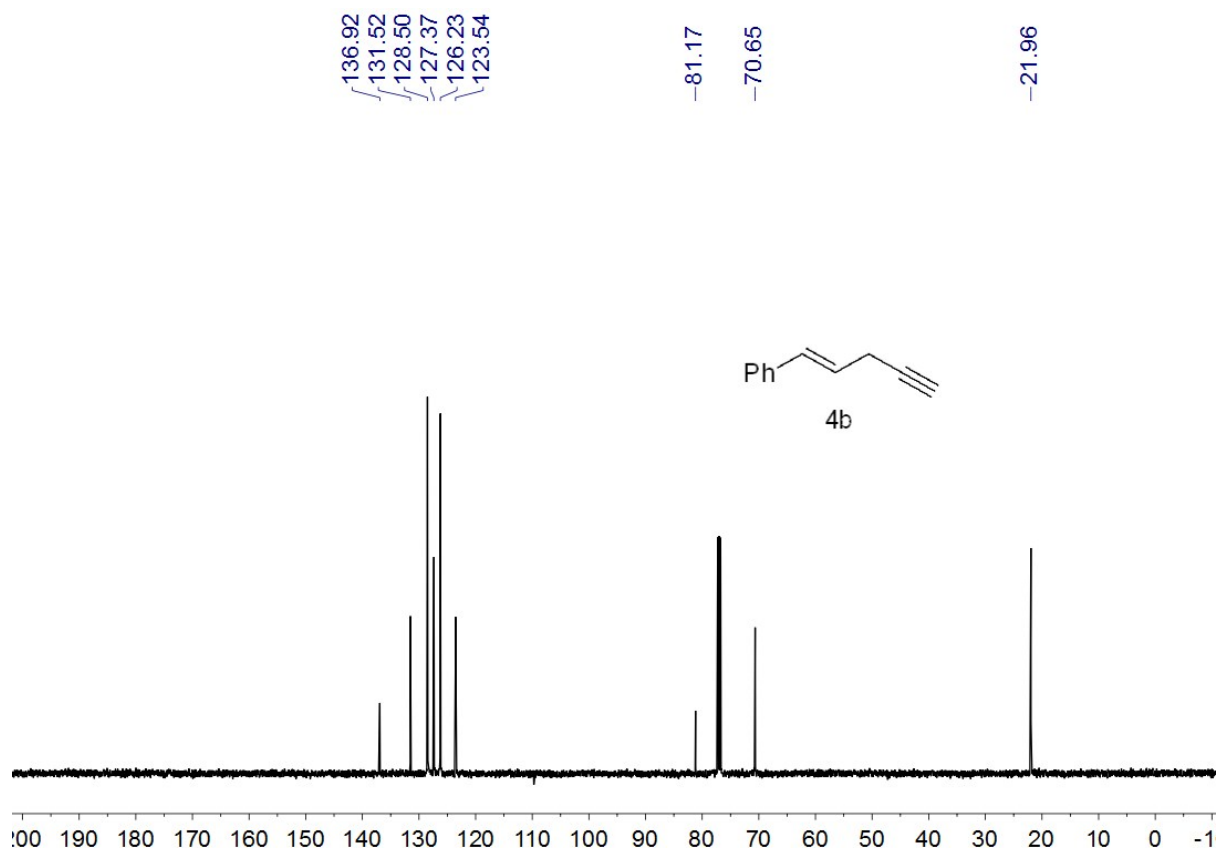
- (a) Y.-X. Li, Q.-Q. Xuan, L. Liu, D. Wang, Y.-J. Chen and C.-J. Li, *J. Am. Chem. Soc.*, 2013, **135**, 12536; (b) D. K. Rayabarapu and J. A. Tunge, *J. Am. Chem. Soc.*, 2005, **127**, 13510.
- L. Villarino, F. López, L. Castedo and J. L. Mascareñas, *Chem. Eur. J.*, 2009, **15**, 13308.
- (a) Q. Yang, Y. Zhou, J. Chen, X. He, J. Xu, F. Y. Kwong and B. Fan, *Eur. J. Org. Chem.*, 2015, 5330; (b) G. G. K. S. N. Kumar and K. K. Laali, *Org. Biomol. Chem.*, 2012, **10**, 7347; (c) G. W. Kabalka, M.-L. Yao and S. Borella, *Org. Lett.*, 2006, **8**, 879; (d) G.-B. Huang, X. Wang, Y.-M. Pan, H.-S. Wang, G.-Y. Yao and Y. Zhang, *J. Org. Chem.*, 2013, **78**, 2742; (e) P. Trillo, A. Baeza and C. Nájera, *J. Org. Chem.*, 2012, **77**, 7344; (f) V. J. Meyer and M. Niggemann, *Eur. J. Org. Chem.*, 2011, 3671; (g) K. Ren, P. Li, L. Wang and X. Zhang, *Tetrahedron*, 2011, **67**, 2753; (h) F. Han, L. Yang, Z. Li, Y. Zhao and C. Xia, *Adv. Synth. Catal.* 2014, **356**, 2506; (i) C. A. Correia and C.-J. Li, *Adv. Synth. Catal.* 2010, **352**, 1446.
- D. Leboeuf, M. Presset, B. Michelet, C. Bour, S. Bezzenine-Lafollée and V. Gandon, *Chem. Eur. J.*, 2015, **21**, 11001.
- (a) D.-M. Cui, N. Hashimoto, S.-i. Ikeda and Y. Sato, *J. Org. Chem.*, 1995, **60**, 5752; (b) H. Chen and M. Z. Deng, *J. Organomet. Chem.*, 2000, **603**, 189.

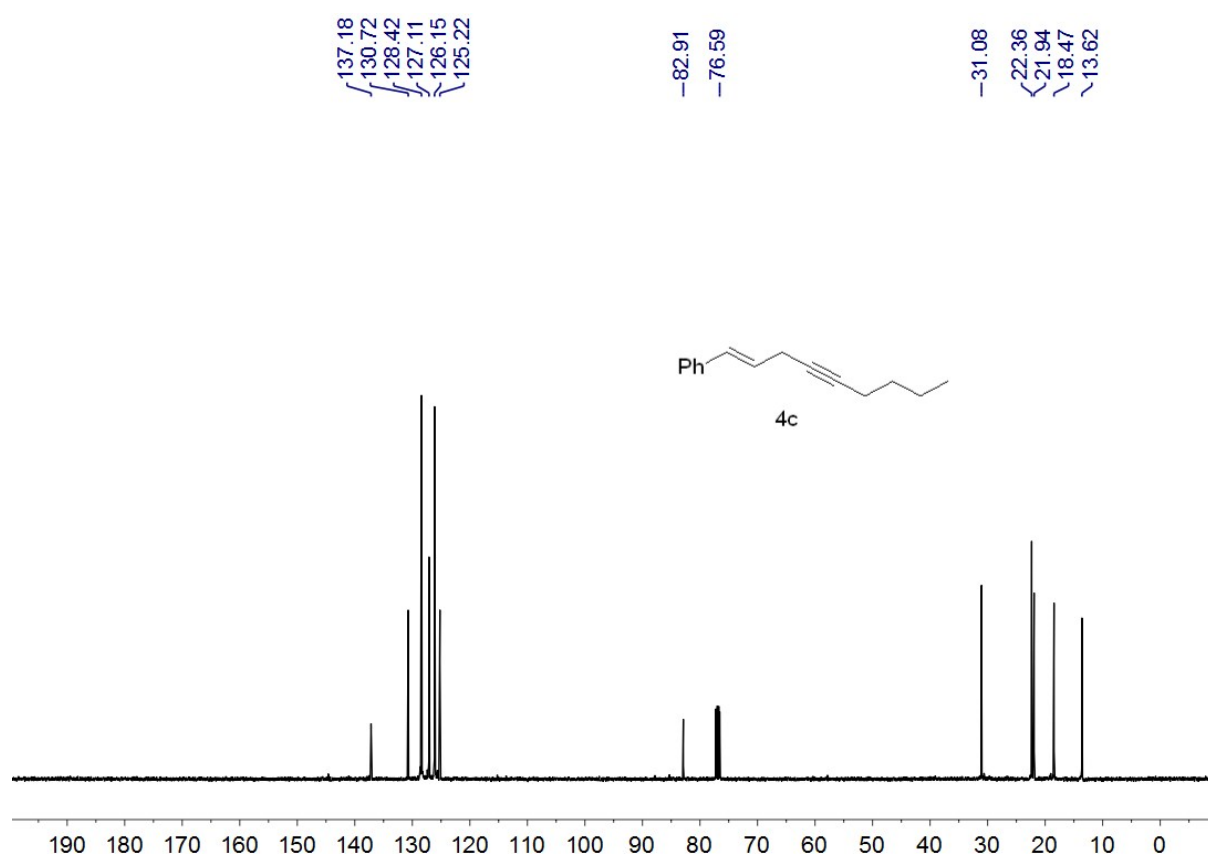
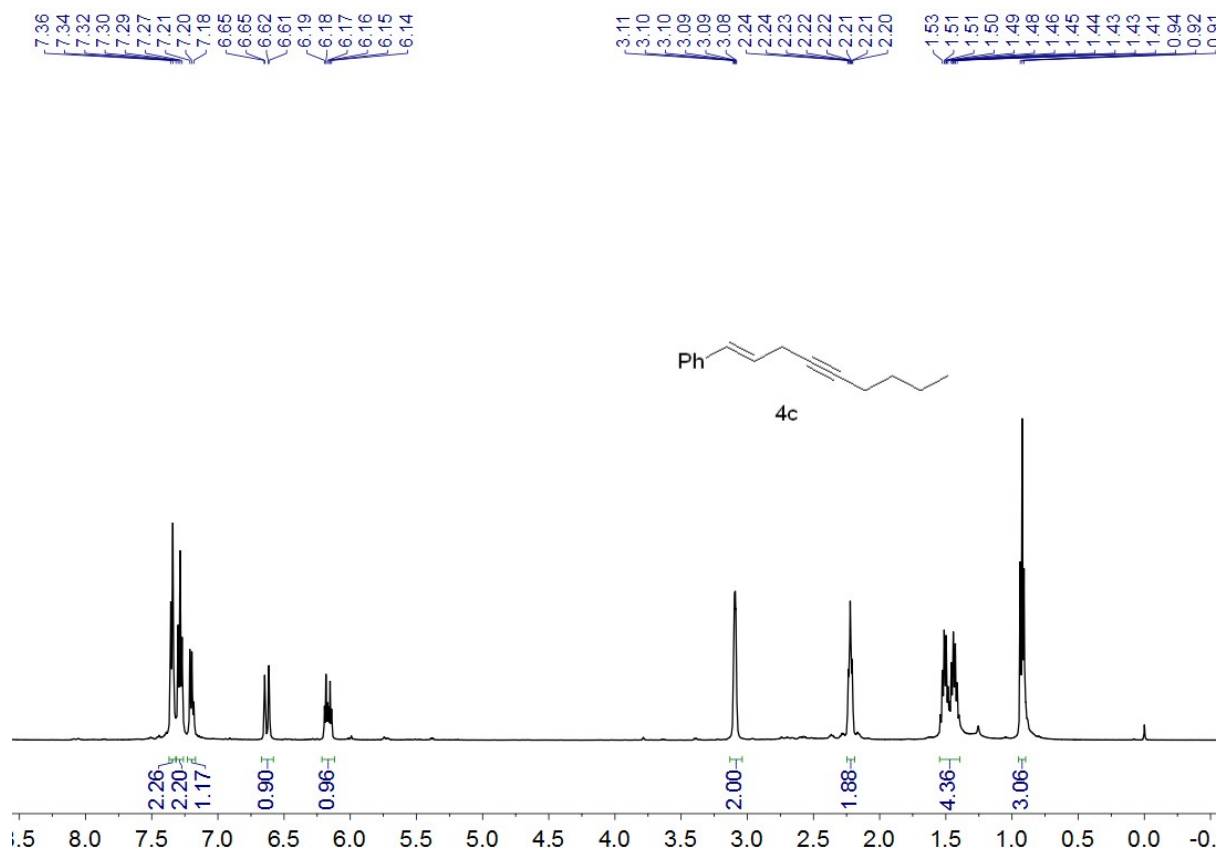
- 6 H.-L. Yue, W. Wei, M.-M. Li, Y.-R. Yang and J.-X. Ji, *Adv. Synth. Catal.* 2011, **353**, 3139.
- 7 (a) Q. Yuan, K. Yao, D. Liu and W. Zhang, *Chem. Commun.*, 2015, **51**, 11834. (b) E. Alacid and C. Nájera, *Org. Lett.*, 2008, **10**, 5011; (c) G. Hamasaka, F. Sakurai and Y. Uozumi, *Chem. Commun.*, 2015, **51**, 3886; (d) M.-B. Li, Y. Wang and S.-K. Tian, *Angew. Chem. Int. Ed.*, 2012, **51**, 2968.
- 8 B. Bhayana, B. P. Fors, S. L. Buchwald, *Org. Lett.* 2009, **11**, 3954.
- 9 (a) J. Wang, W. Huang, Z. Zhang, X. Xiang, R. Liu and X. Zhou, *J. Org. Chem.*, 2009, **74**, 3299; (b) M. Ueda, K. Nishimura, R. Kashima and I. Ryu, *Synlett*, 2012, 1085.
- 10 Q. Liu, H. Yi, J. Liu, Y. Yang, X. Zhang, Z. Zeng and A. Lei, *Chem. Eur. J.*, 2013, **19**, 5120.
- 11 B.-T. Guan, S.-K. Xiang, B.-Q. Wang, Z.-P. Sun, Y. Wang, K.-Q. Zhao and Z.-J. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 3268.
- 12 (a) J. W. Grissom, D. Klingberg, S. Meyenburg, B. L. Stallman, *J. Org. Chem.*, 1994, **59**, 7876; (b) D.-G. Yu, X. Wang, R.-Y. Zhu, S. Luo, X.-B. Zhang, B.-Q. Wang, L. Wang, and Z.-J. Shi, *J. Am. Chem. Soc.*, 2012, **134**, 14638.

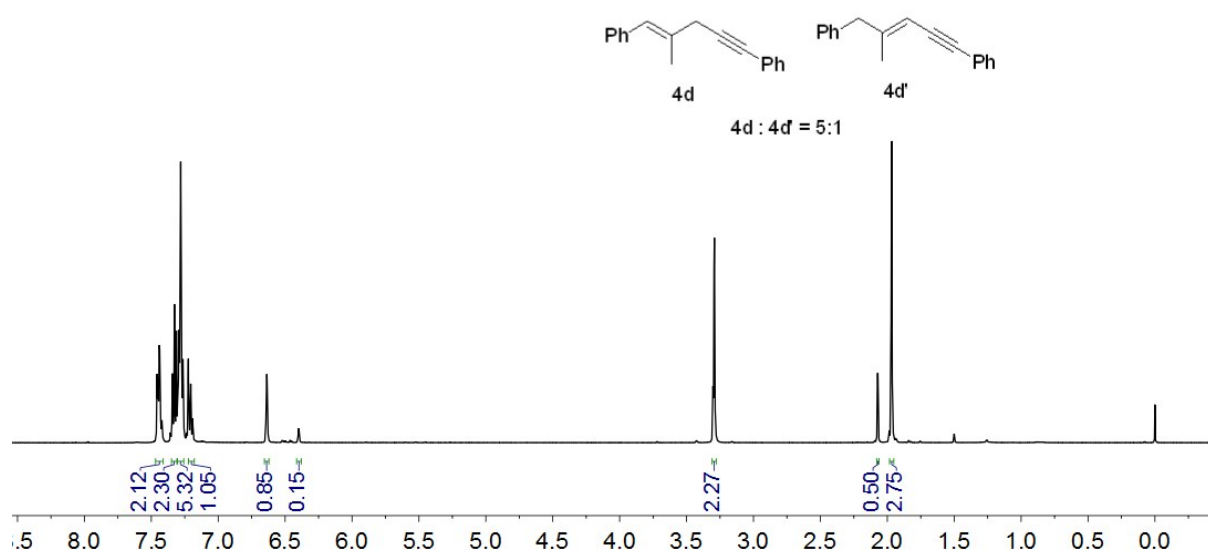
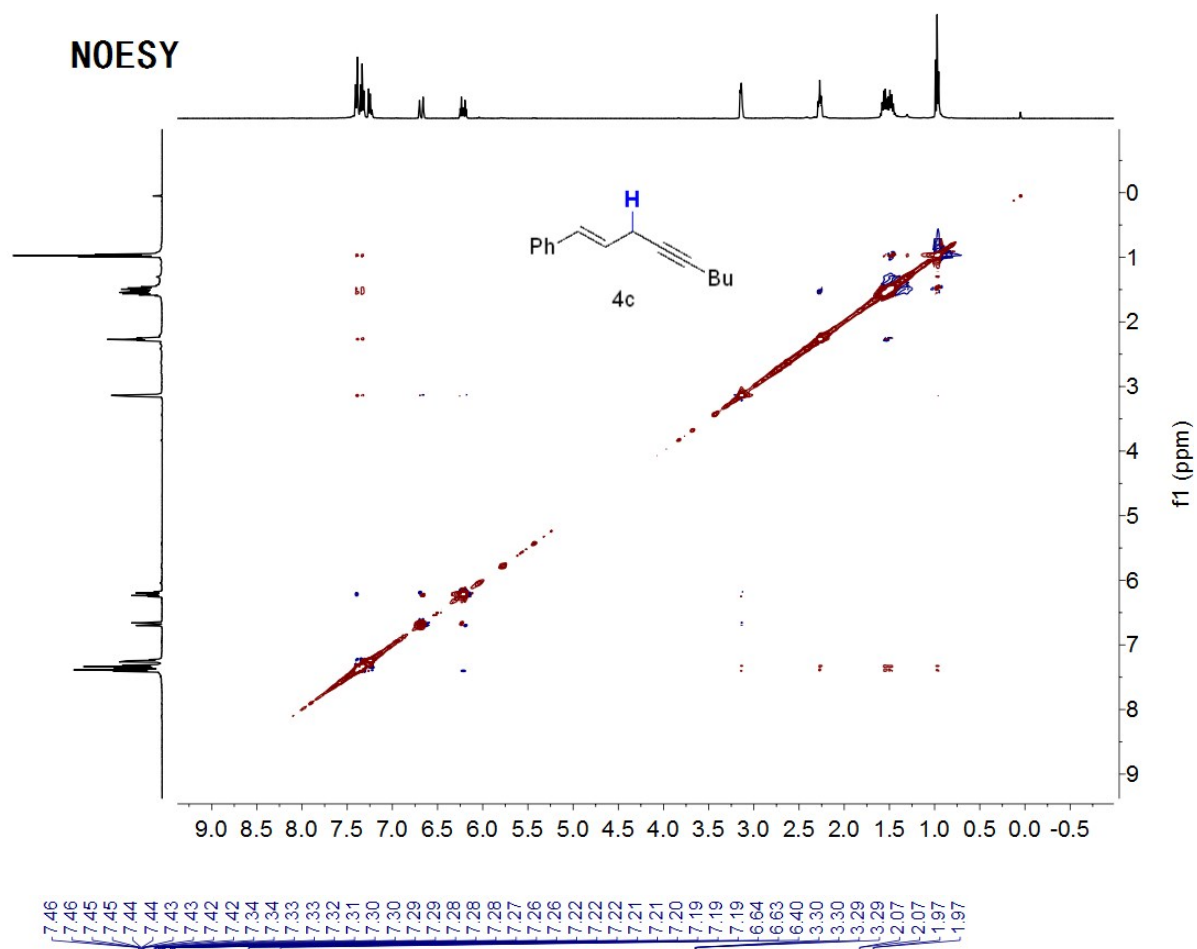
4. NMR spectral copies of 4a-l, 6a-f and 8

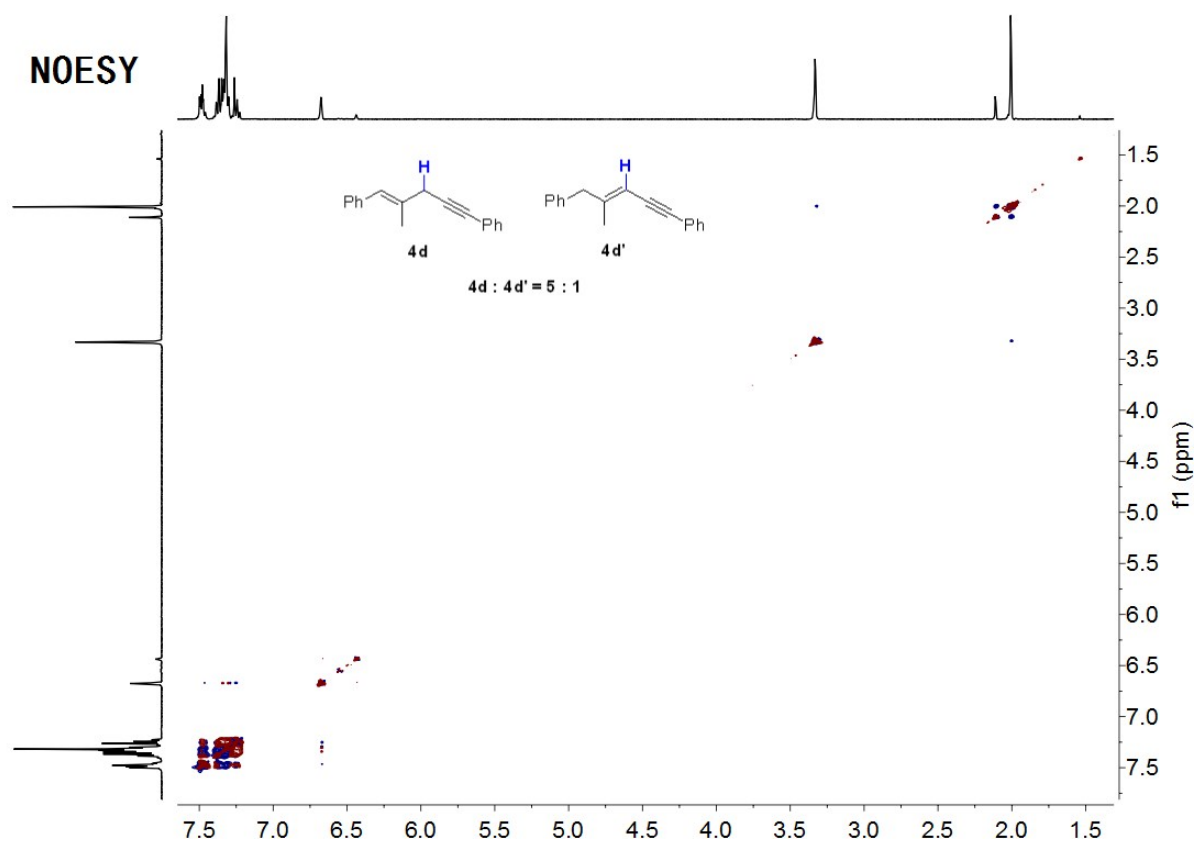
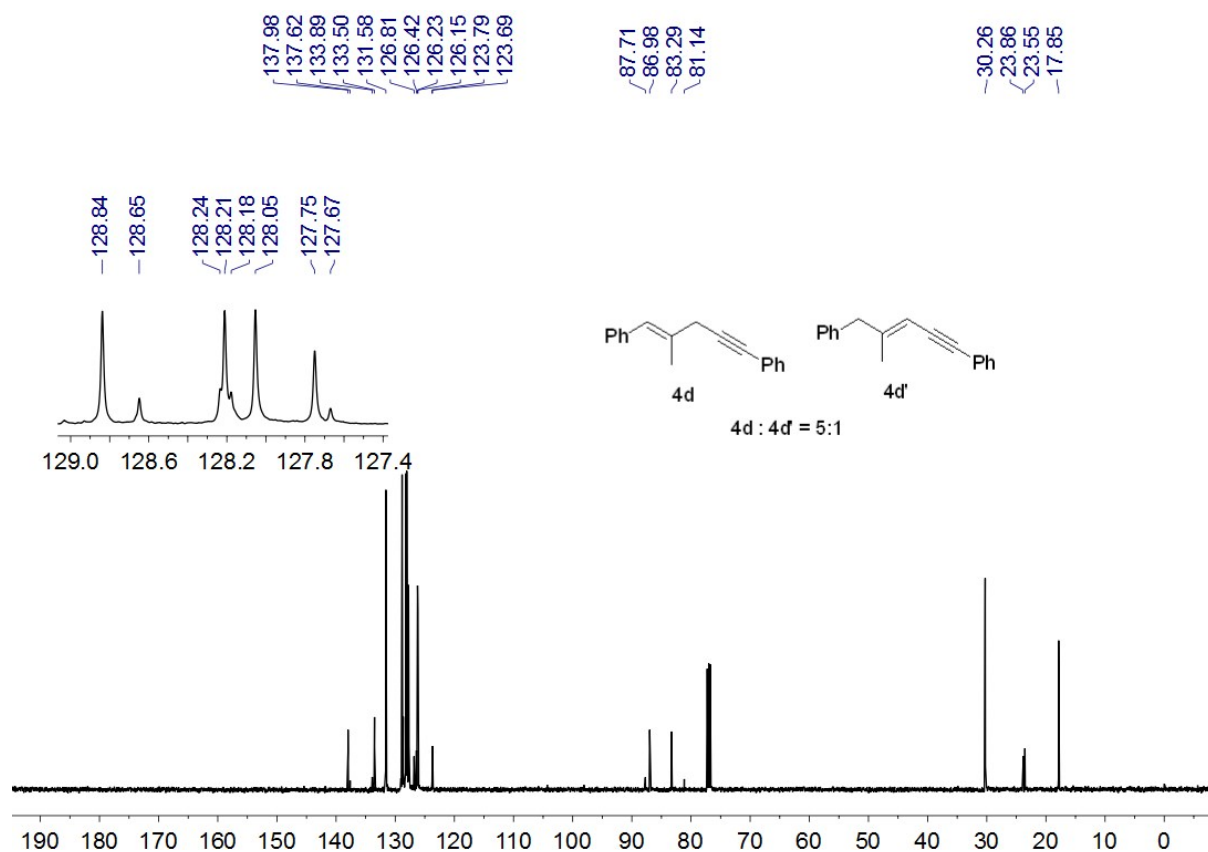


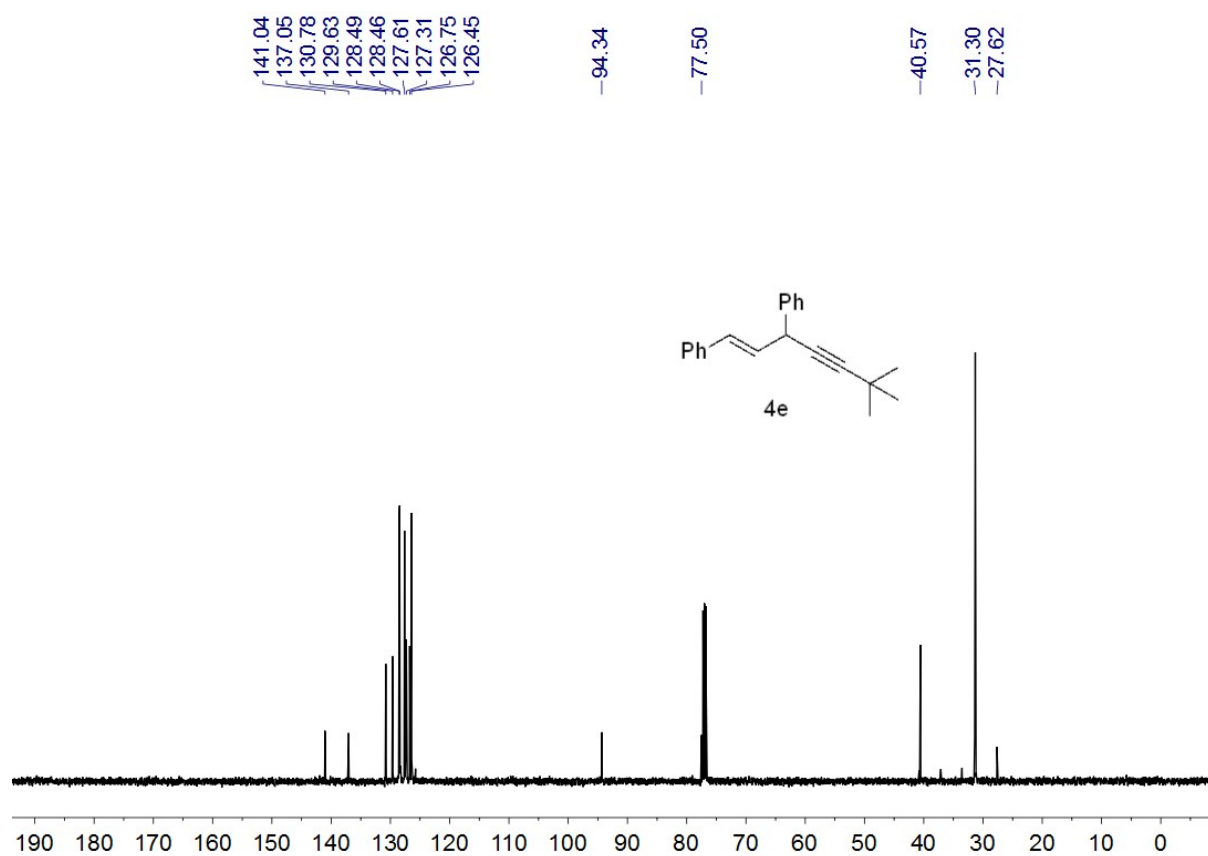
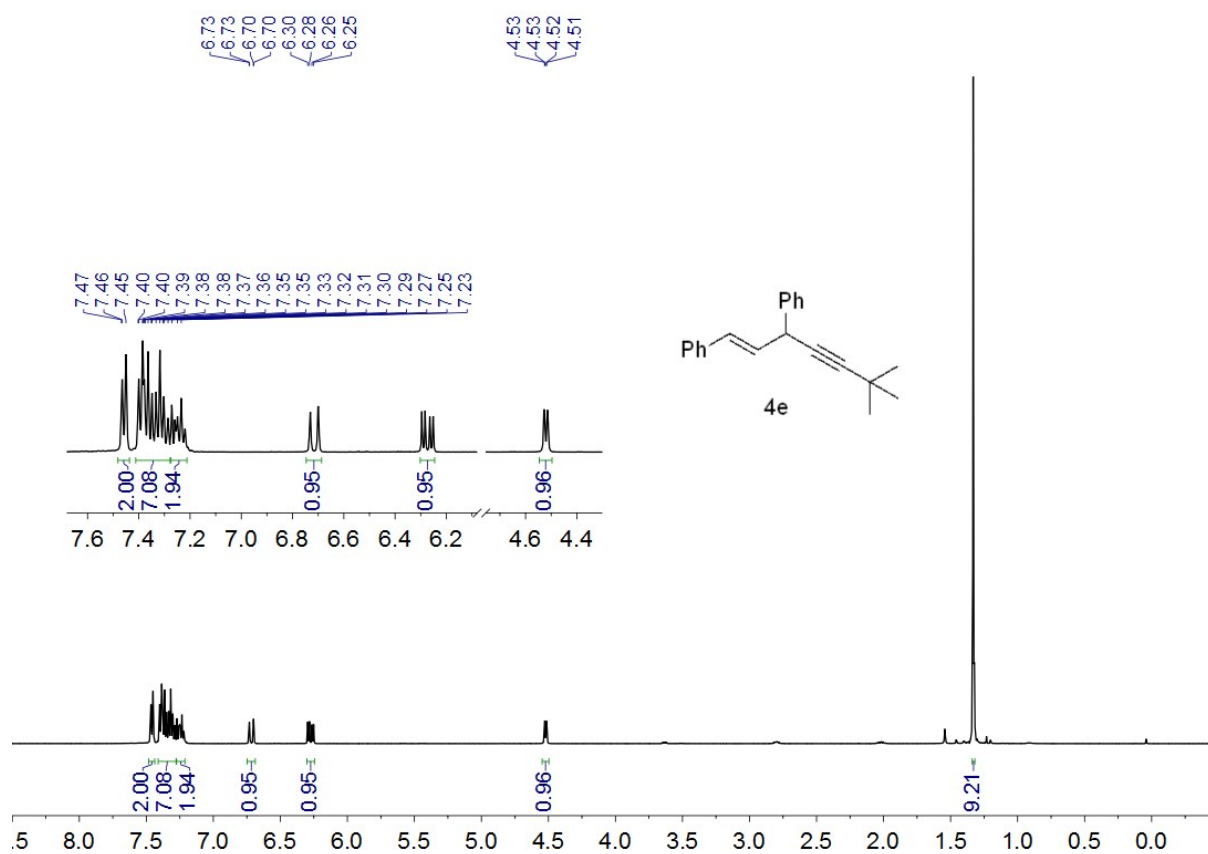


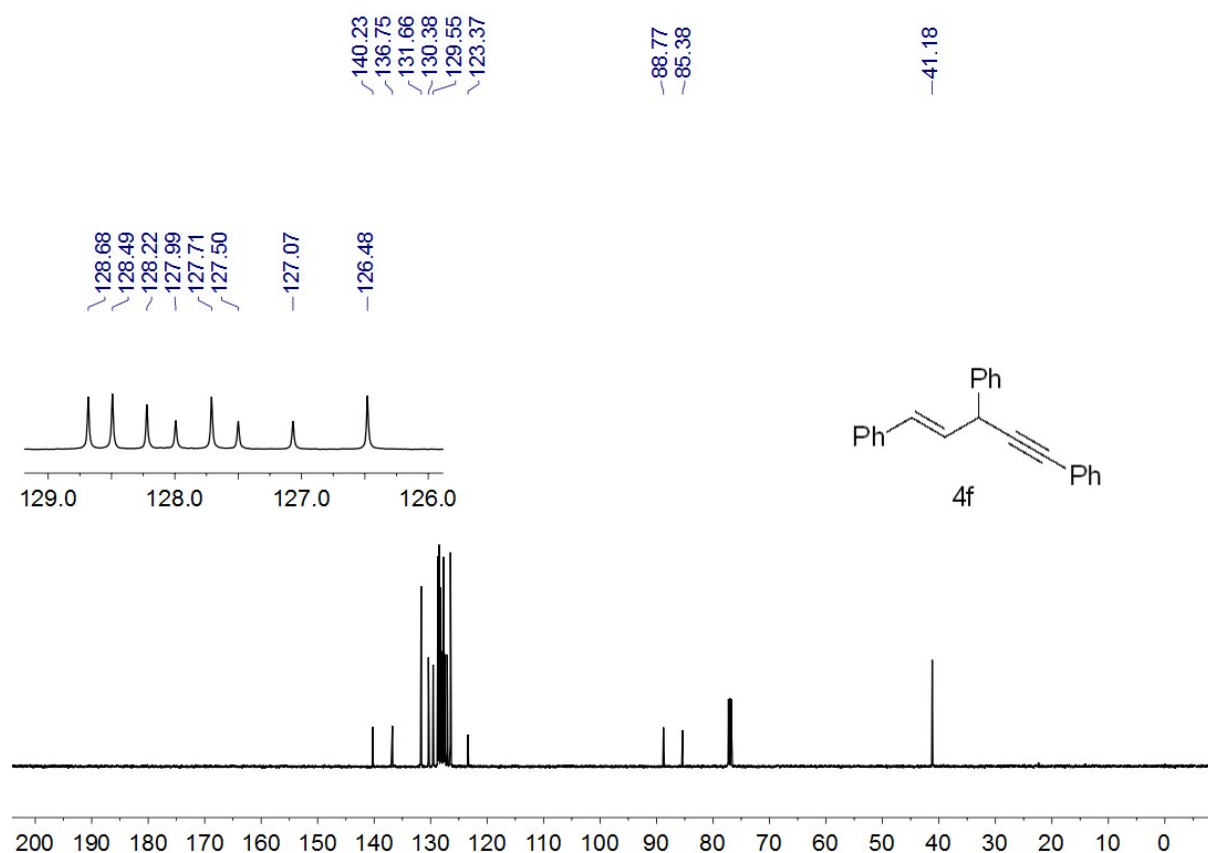
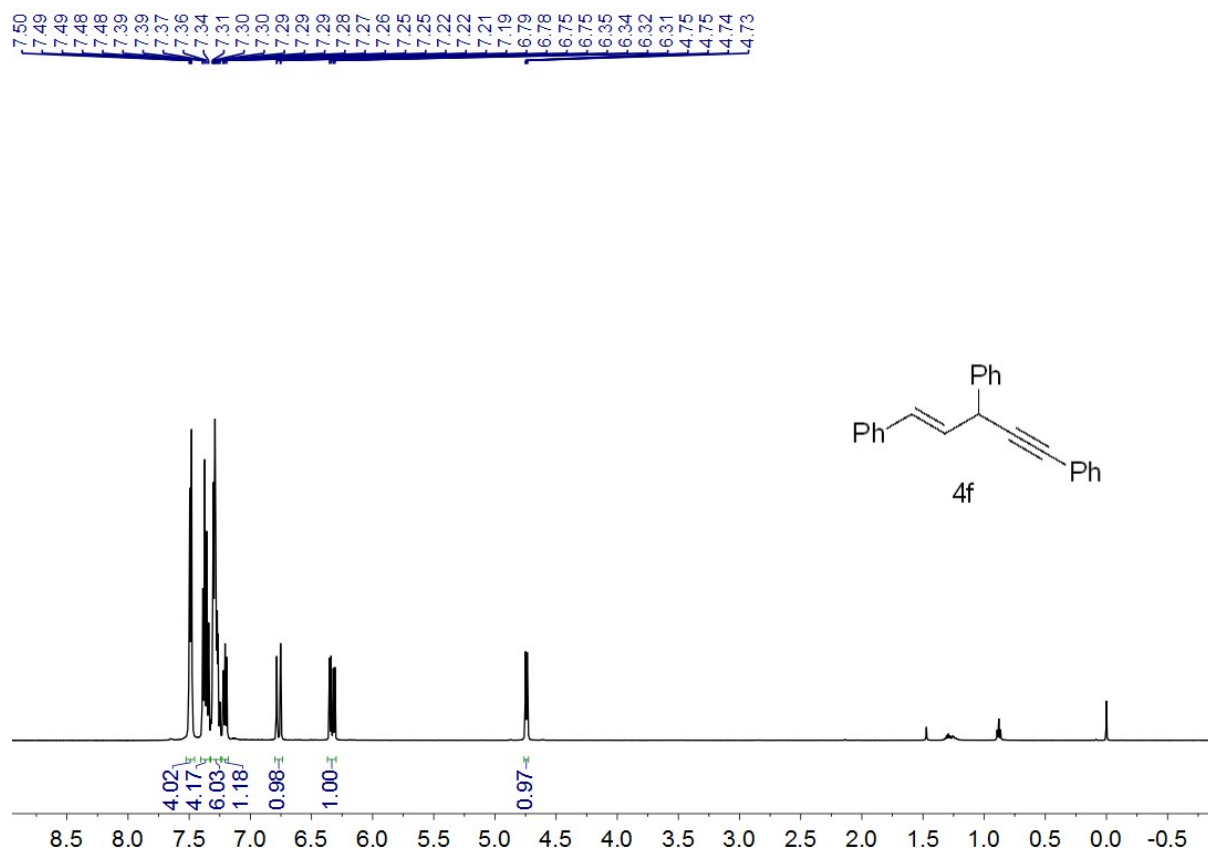


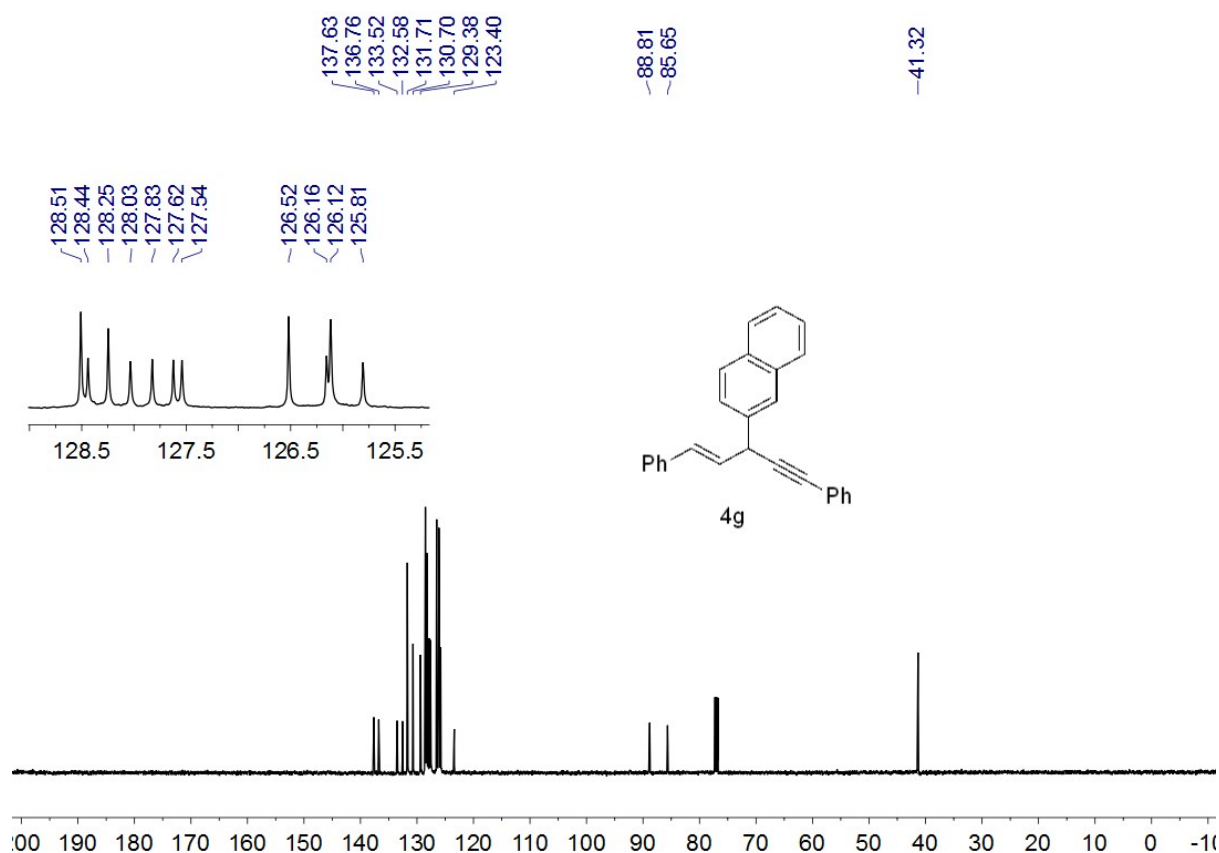
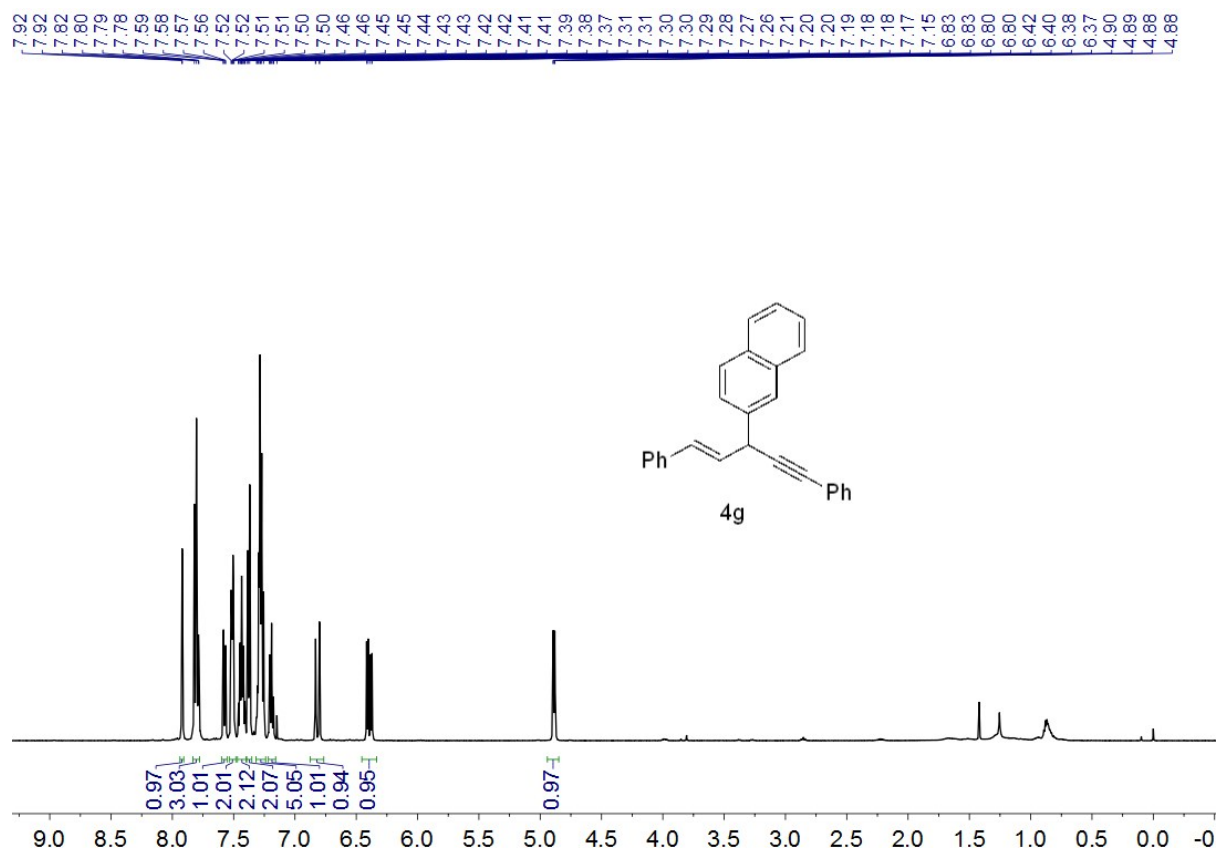




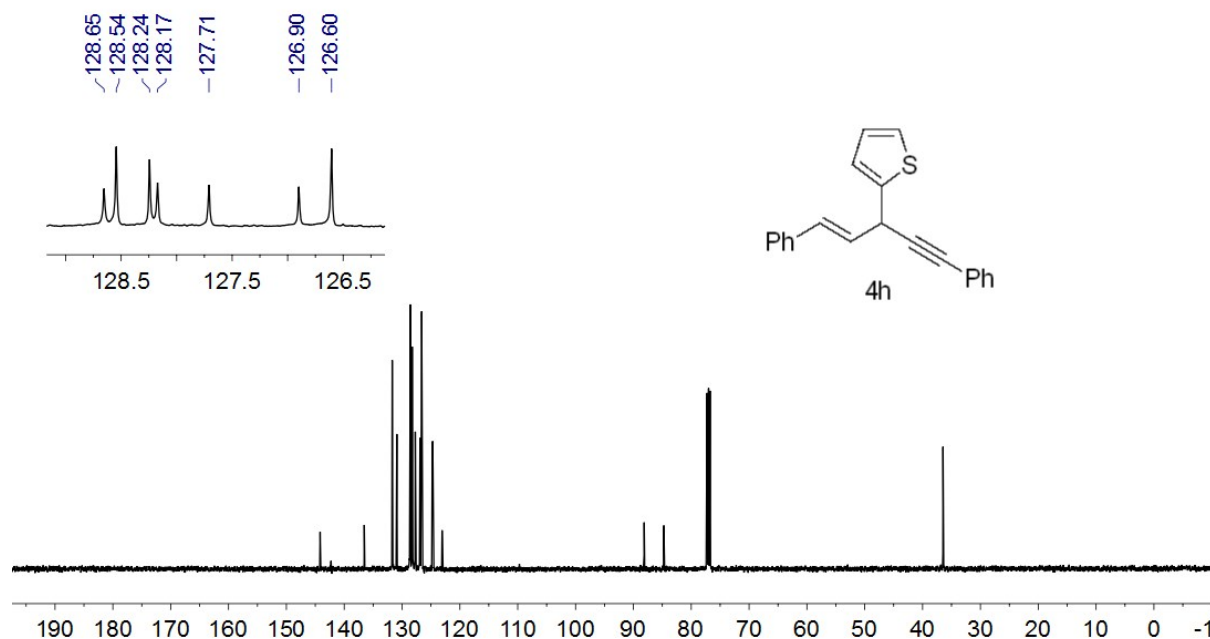
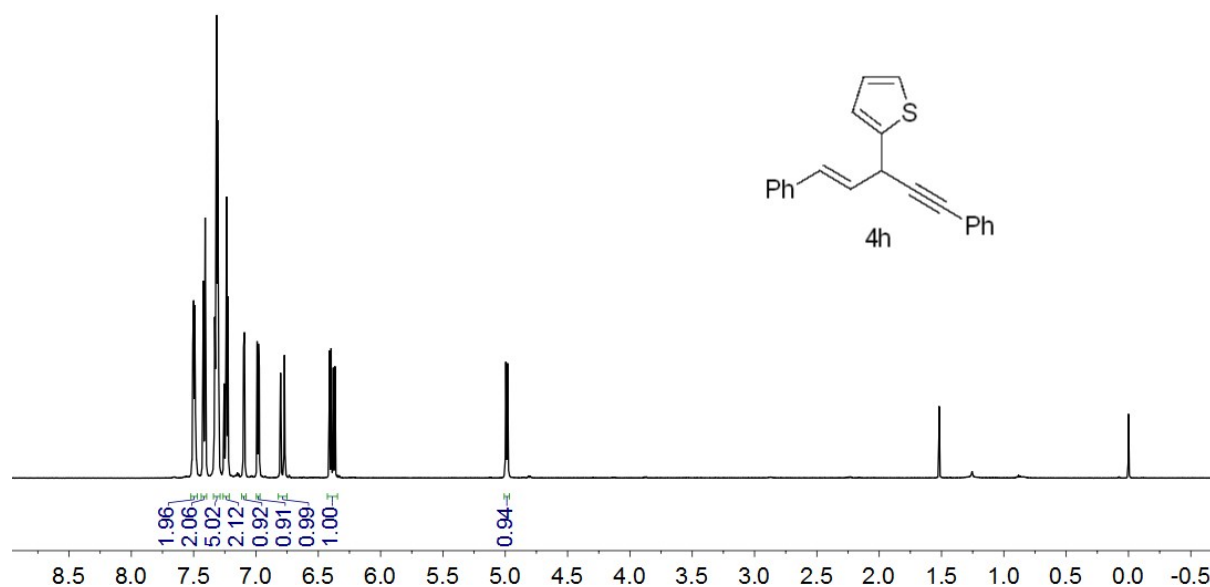


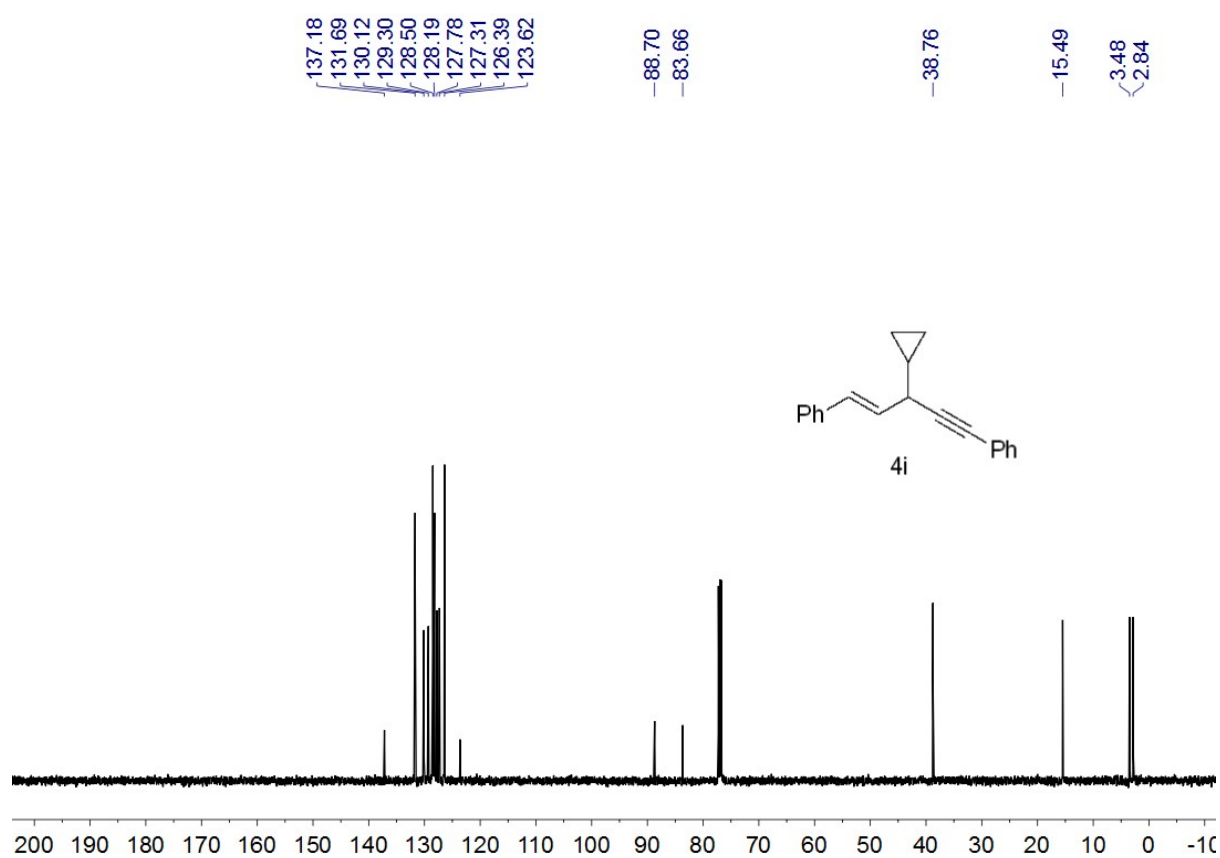
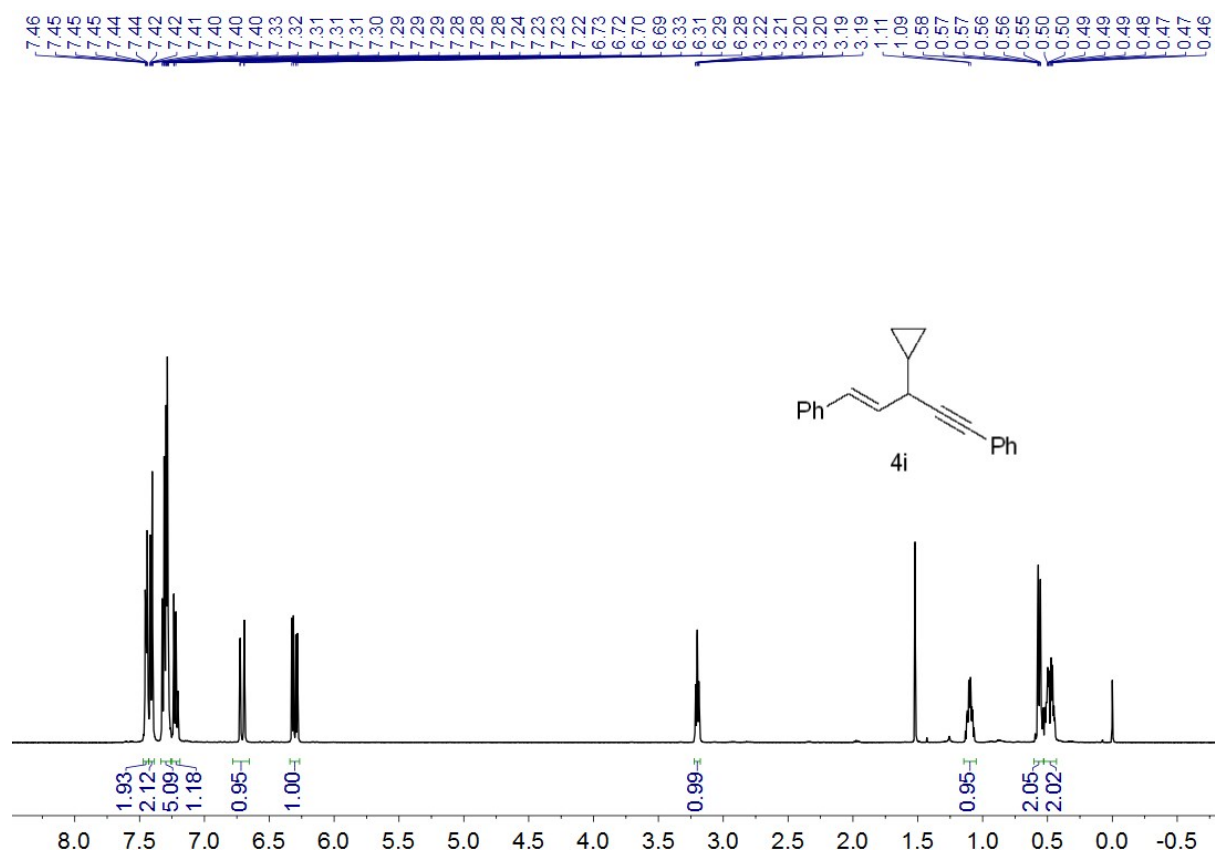


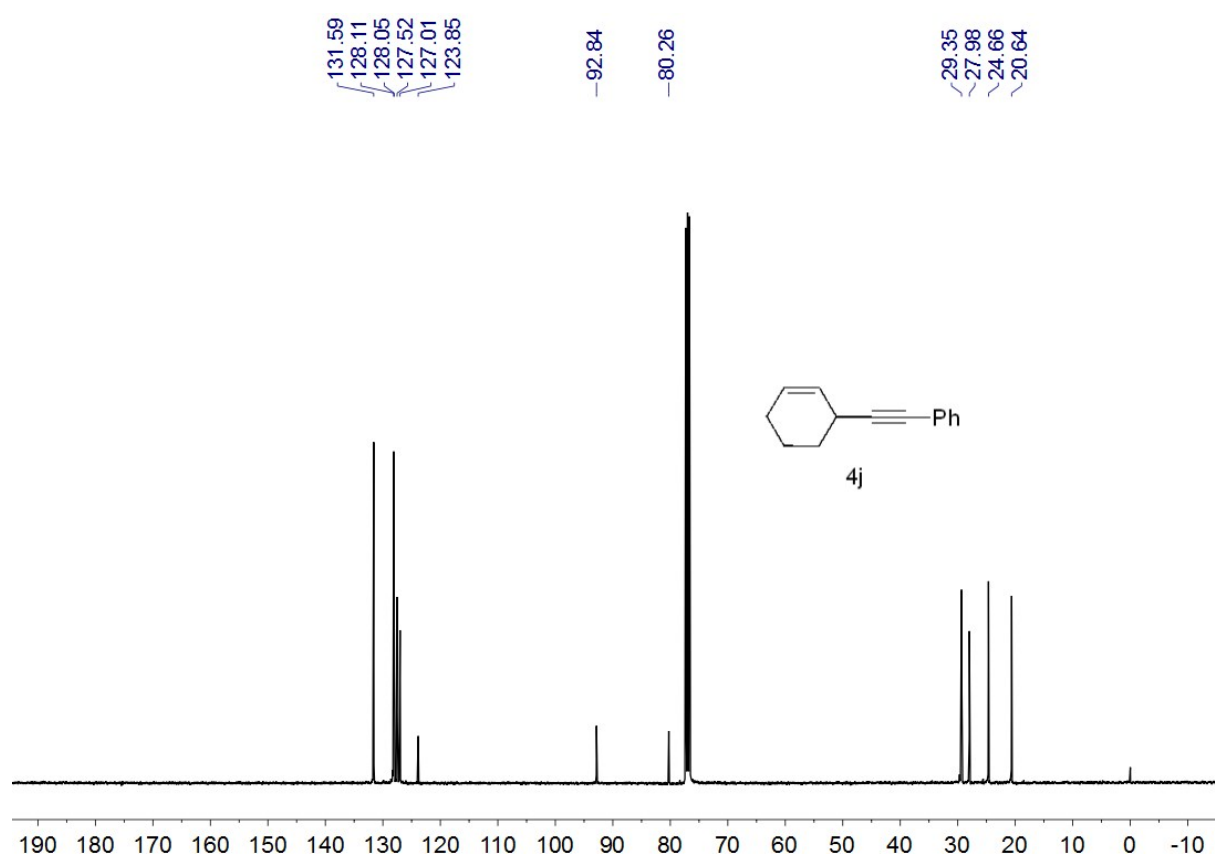
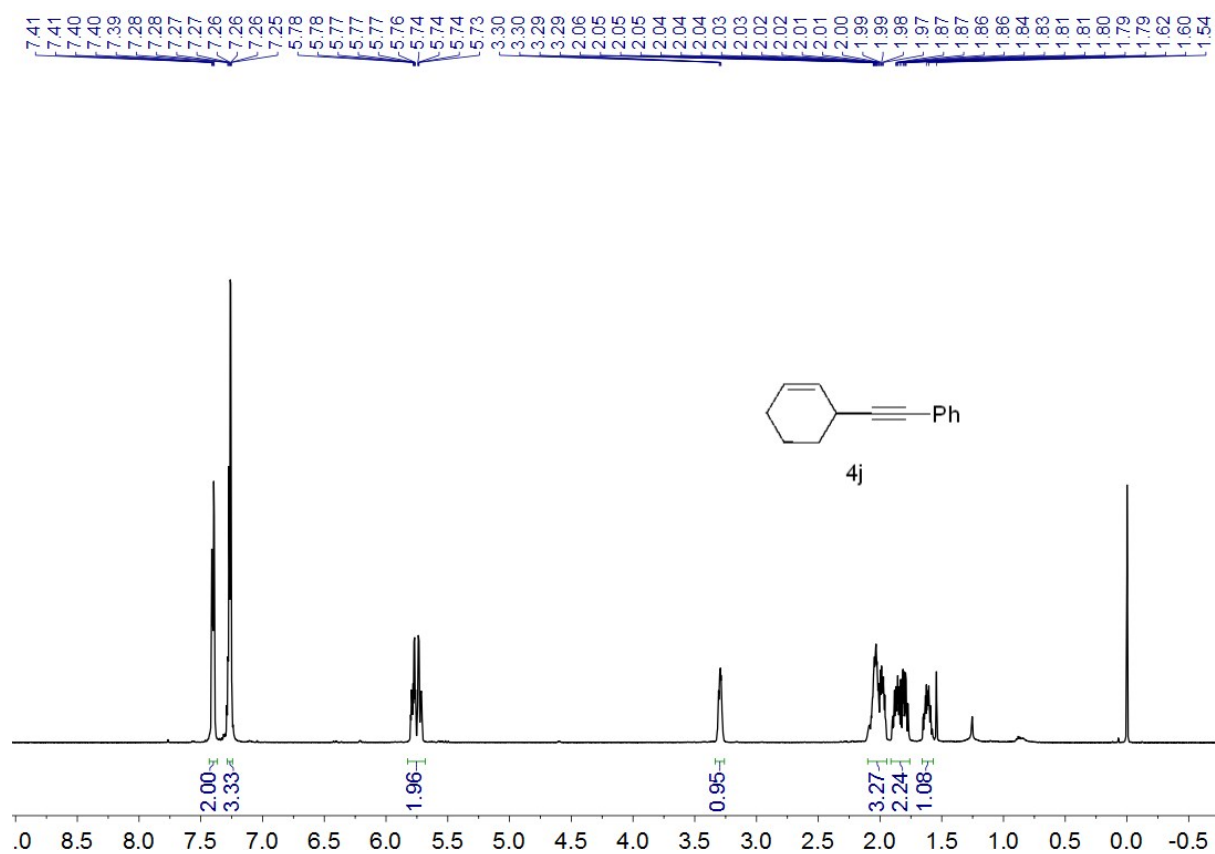


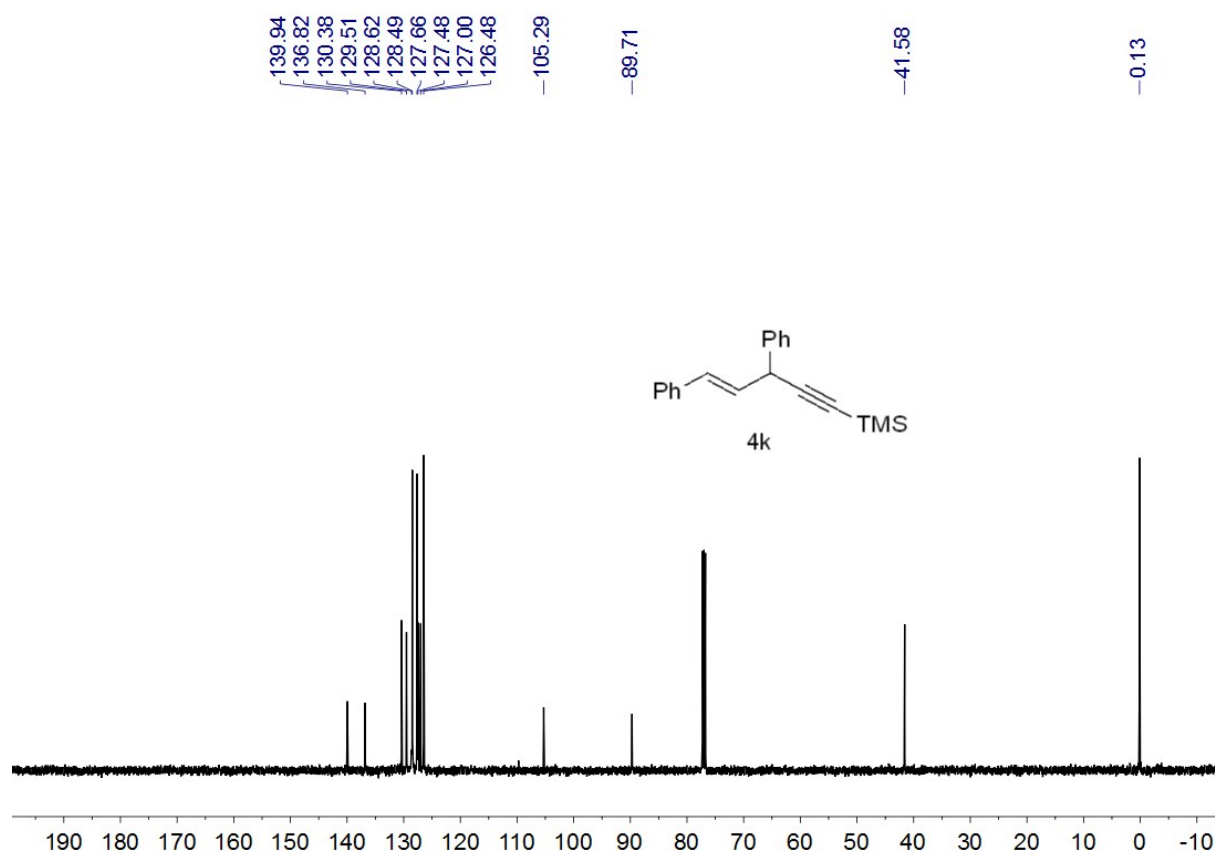
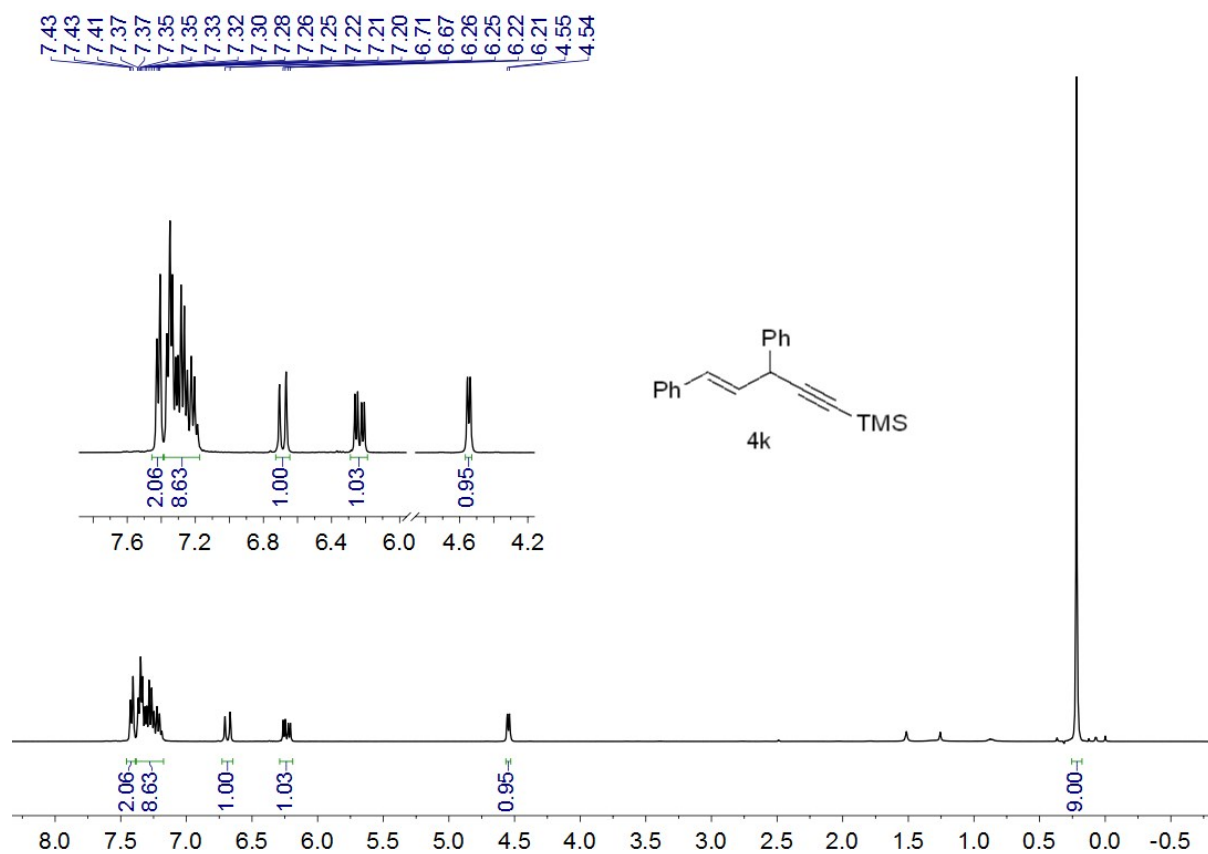


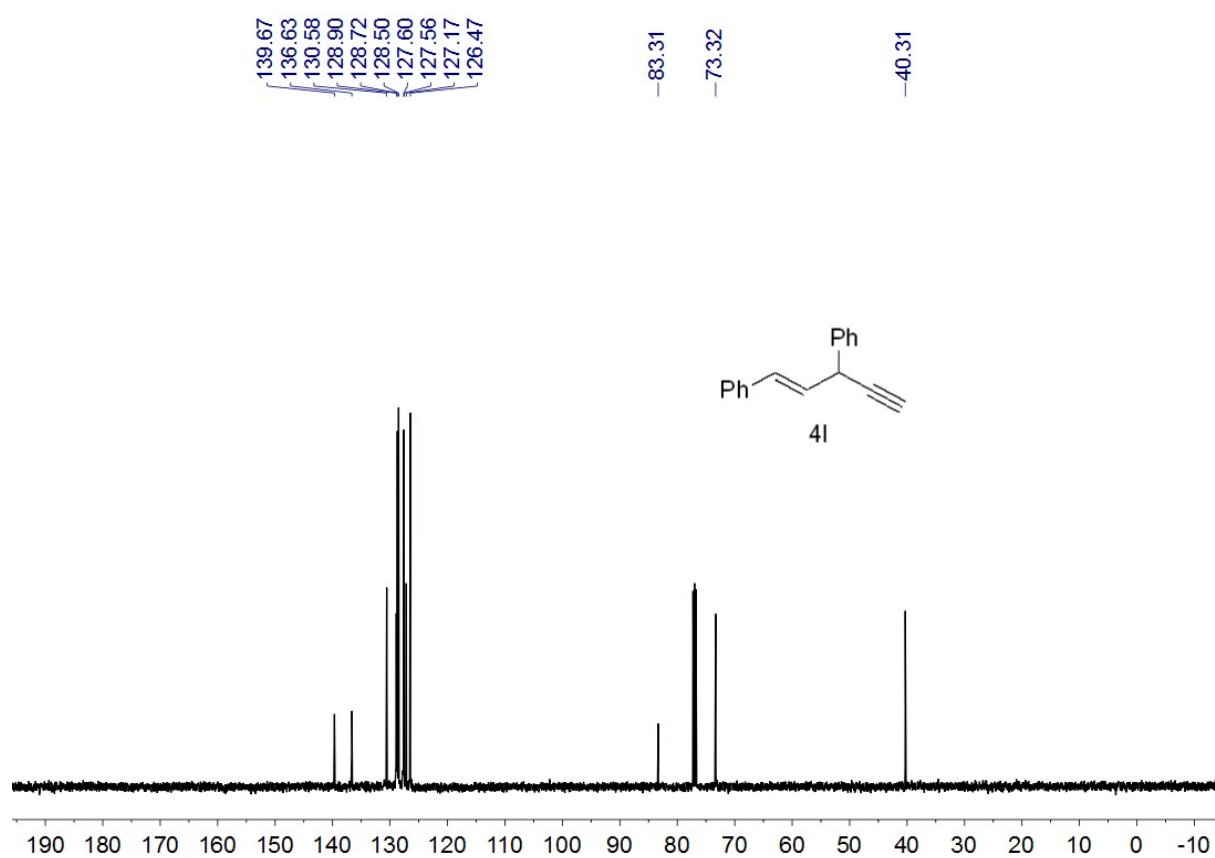
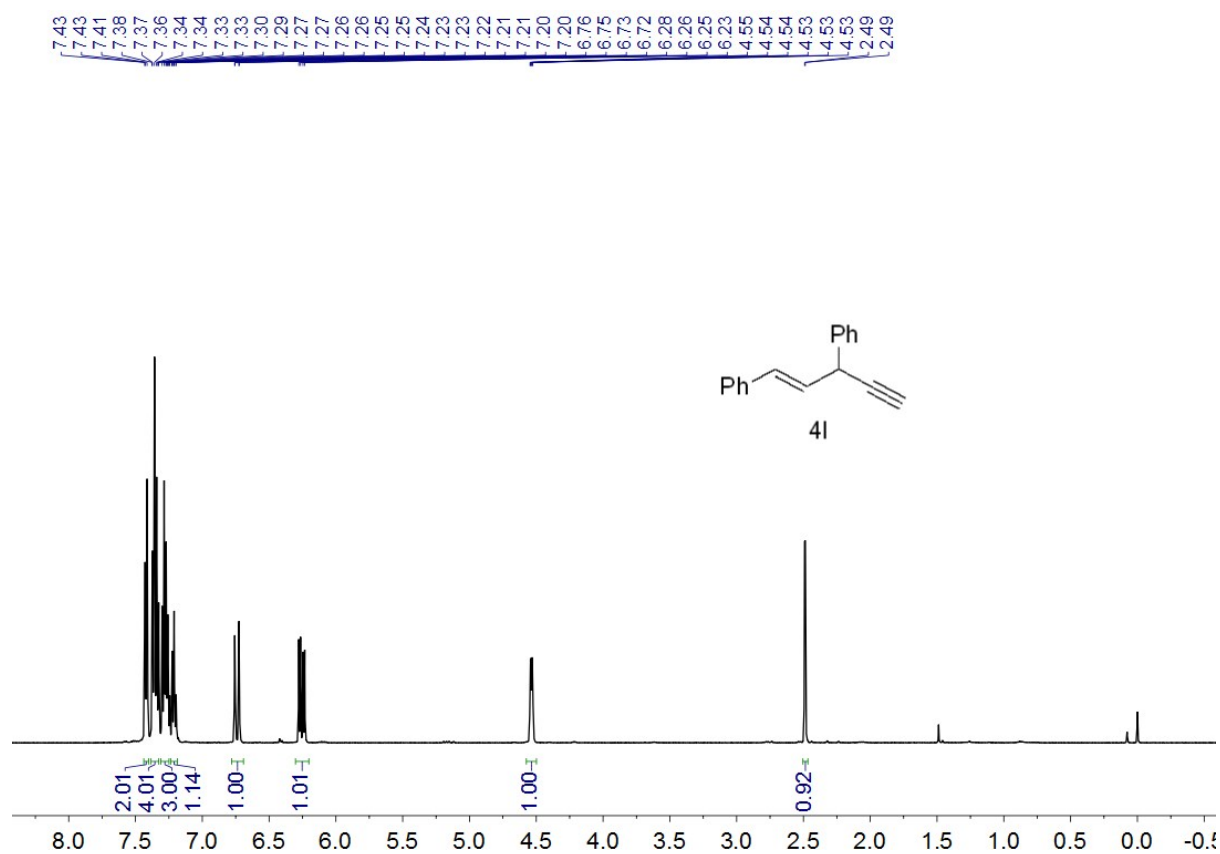
7.51
7.51
7.50
7.50
7.50
7.49
7.49
7.48
7.43
7.42
7.42
7.41
7.41
7.41
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.10
7.10
7.09
7.09
7.09
6.99
6.98
6.98
6.97
6.80
6.80
6.77
6.77
6.41
6.40
6.38
6.37
5.00
5.00
4.99
4.98
4.98



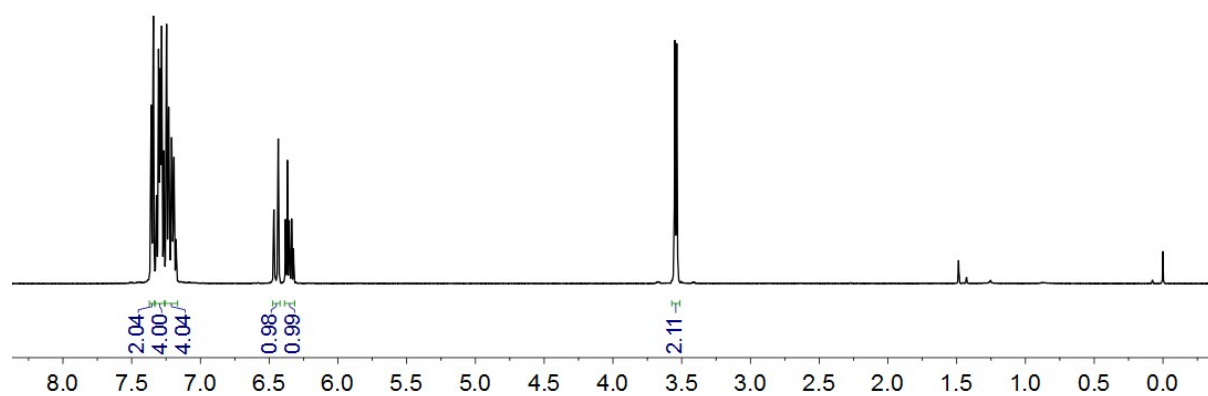
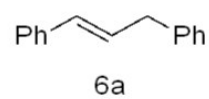








7.36
7.36
7.34
7.32
7.32
7.30
7.30
7.29
7.28
7.27
7.27
7.25
7.25
7.23
7.23
7.21
7.21
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
6.47
6.43
6.38
6.37
6.35
6.35
6.34
6.32
3.55
3.54



140.11
137.40
131.01
129.18
128.64
128.47
128.46
127.07
126.15
126.08

39.33

