

Gold-catalyzed intermolecular reaction of 2-(1-alkynyl)-2-alken-1-ones with diarylethenes to construct polysubstituted cyclopenta[*c*]furans through a cascade heterocyclization/[3+2] cycloaddition sequence

Ting He, Pin Gao, Yi-feng Qiu, Xiao-biao Yan, Xue-yuan Liu and Yong-min Liang*
State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China
liangym@lzu.edu.cn

Table of Contents

1. General Remarks	S2
2. Typical procedure for the preparation of 2-(1-alkynyl)-2-alken-1-ones 1a-1r	S2
3. Characterization data of 2-(1-alkynyl)-2-alken-1-ones 1a-1r	S2-S7
4. Characterization data of highly substituted 4 <i>H</i> -cyclopenta[<i>c</i>]furans 3aa-3ra , 3ab-3af	S8-S16
5. Characterization data of trisubstituted furans 4ag , 4ah	S16-S17
6. Crystal structure of 3ad	S17
7. ¹ H NMR and ¹³ C NMR spectra for compounds 1a-1r	S18-S53
8. ¹ H NMR and ¹³ C NMR spectra for compounds 3aa-3ra , 3ab-3af	S54-S99
9. ¹ H NMR and ¹³ C NMR spectra for compounds 4ag , 4ah	S100-S103

1. General Remarks

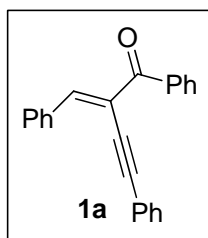
Column chromatography was carried out on silica gel. Unless noted ^1H NMR spectra were recorded on 400 MHz and ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . All new compounds were further characterized by (ESI)HRMS, HRMS was obtained using a Q-TOF instrument equipped with APCI. Copies of their ^1H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification. THF was distilled from Na/benzophenone and used immediately.

2. Typical procedure for the preparation of 2-(1-alkynyl)-2-alken-1-one 1a-1r according to references 1-3.

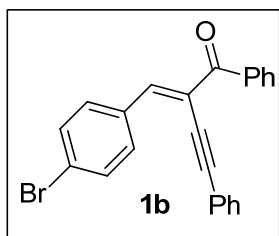
References:

- (1) F. Liu, Y.-H. Yu, J.-L. Zhang, *Angew. Chem. Int. Ed.* 2009, **48**, 5505.
- (2) F. Liu, D.- Y. Qian, L. Li, X.-L. Zhao, J.-L. Zhang, *Angew. Chem. Int. Ed.* 2010, **49**, 6669.
- (3) T. He, P. Gao, S.-C. Zhao, Y.-D. Shi, X.-Y. Liu, Y.-M. Liang, *Adv. Synth. Catal.* 2013, **355**, 365.

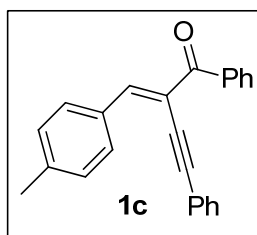
3. Characterization data of 2-(1-alkynyl)-2-alken-1-ones 1a-1r



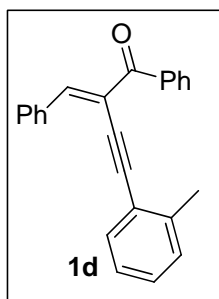
1a: ^1H NMR (400 MHz, CDCl_3): δ 8.13-8.11 (m, 2H), 8.02-7.99 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 2H), 7.63 (s, 1H), 7.58-7.56 (m, 1H), 7.50-7.43 (m, 5H), 7.41-7.38 (m, 2H), 7.34-7.32 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.4, 145.0, 137.2, 134.8, 132.5, 131.3, 130.6, 130.4, 129.7, 128.8, 128.6, 128.4, 128.1, 122.9, 120.9, 100.8, 87.2; IR (neat, cm^{-1}) 3435.2, 3059.0, 2922.5, 2197.2, 1663.2, 1594.2, 1489.3, 1445.3, 1262.2, 1070.6, 755.4, 689.9.



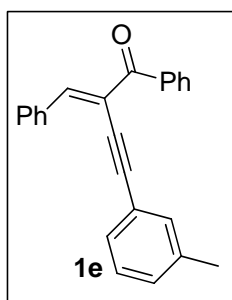
1b: ^1H NMR (400 MHz, CDCl_3): δ 8.03-7.99 (m, 3H), 7.81-7.72 (m, 1H), 7.62-7.57 (m, 4H), 7.52-7.48 (m, 3H), 7.41-7.35 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.0, 143.3, 138.0, 136.9, 133.7, 132.6, 132.0, 131.9, 131.8, 131.6, 131.3, 129.7, 129.5, 129.0, 128.5, 128.1, 124.8, 122.6, 121.5; IR (neat, cm^{-1}) 3432.7, 3058.8, 2923.3, 2194.0, 1624.7, 1580.1, 1485.0, 1384.1, 1260.4, 1171.3, 1083.3, 962.5, 816.9, 755.0, 690.2.



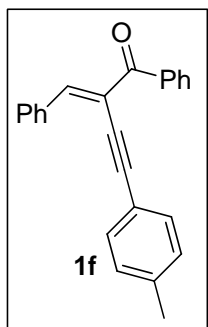
1c: Compound **1c** was prepared according to the method B. ^1H NMR (400 MHz, CDCl_3): δ 8.03-7.97 (dd, $J_1 = 17.2$ Hz, $J_2 = 7.6$ Hz, 4H), 7.63 (s, 1H), 7.57-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.39-7.38 (m, 2H), 7.32-7.31 (m, 3H), 7.26-7.24 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.4, 145.4, 141.2, 137.3, 132.3, 132.1, 131.2, 130.4, 129.6, 129.3, 128.7, 128.4, 128.0, 123.0, 119.7, 100.6, 87.4, 21.6; IR (neat, cm^{-1}) 3393.4, 3057.4, 3027.7, 2920.6, 2851.5, 2198.7, 1624.5, 1598.1, 1578.8, 1445.0, 1319.1, 1275.3, 1180.6, 1095.8, 755.5, 691.5.



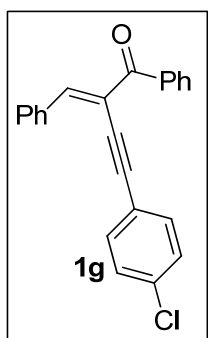
1d: Compound **1d** was prepared according to the method A. ^1H NMR (400 MHz, CDCl_3): δ 8.14-8.11 (d, $J = 5.6$ Hz, 2H), 8.00-7.98 (d, $J = 7.6$ Hz, 2H), 7.61 (s, 1H), 7.58-7.54 (m, 1H), 7.48-7.43 (m, 5H), 7.34-7.33 (d, $J = 7.6$ Hz, 1H), 7.23-7.11 (m, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.7, 144.3, 140.3, 137.3, 134.9, 132.4, 131.9, 130.5, 130.3, 129.7, 129.6, 128.8, 128.6, 128.1, 125.6, 122.6, 121.2, 100.4, 90.7, 20.5; IR (neat, cm^{-1}) 3441.4, 3060.0, 2921.6, 2362.0, 2190.2, 1612.7, 1598.0, 1447.6, 1263.2, 1206.0, 1070.5, 785.6, 718.3, 690.4.



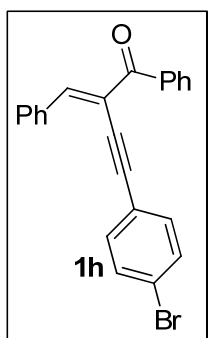
1e: Compound **1e** was prepared according to the method A. ^1H NMR (400 MHz, CDCl_3): δ 8.13-8.11 (m, 2H), 8.01-7.99 (d, $J = 8.0$ Hz, 2H), 7.61-7.56 (m, 2H), 7.50-7.43 (m, 5H), 7.21-7.20 (m, 3H), 7.16-7.14 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.4, 144.9, 138.1, 137.2, 134.9, 132.5, 131.9, 130.5, 130.4, 129.7, 128.6, 128.4, 128.3, 128.0, 122.7, 121.0, 101.1, 86.8, 21.2; IR (neat, cm^{-1}) 3395.6, 3058.0, 2921.3, 2361.8, 2197.2, 1621.5, 1595.9, 1446.7, 1384.1, 1250.7, 1071.1, 1026.8, 783.6, 719.1, 693.7, 670.0.



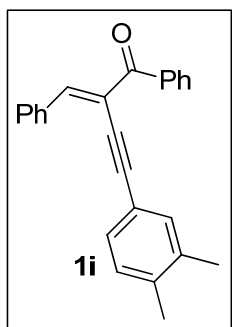
1f: ^1H NMR (400 MHz, CDCl_3): δ 8.11-8.10 (m, 2H), 8.00-7.98 (m, 2H), 7.59 (s, 1H), 7.57-7.54 (m, 1H), 7.47-7.40 (m, 5H), 7.29-7.27 (d, $J = 8.0$ Hz, 2H), 7.13-7.11 (d, $J = 8.0$ Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.4, 144.5, 139.1, 137.1, 134.9, 132.4, 131.2, 130.4, 130.3, 129.7, 129.2, 128.5, 128.0, 125.6, 121.0, 119.8, 101.2, 86.6, 21.5; IR (neat, cm^{-1}) 3334.6, 3058.4, 2921.6, 2194.8, 1662.4, 1594.2, 1446.3, 1262.9, 1178.8, 1097.0, 1026.2, 962.1, 815.1, 753.8, 690.5.



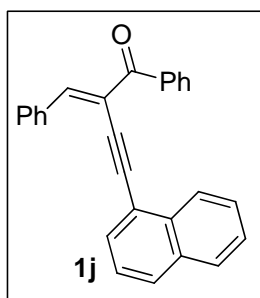
1g: ^1H NMR (400 MHz, CDCl_3): δ 8.07-7.97 (m, 4H), 7.63-7.57 (m, 2H), 7.50-7.45 (m, 5H), 7.31-7.25 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 145.5, 137.1, 134.9, 134.7, 132.5, 130.7, 130.3, 129.7, 128.8, 128.6, 128.1, 121.3, 120.7, 99.5, 88.0; IR (neat, cm^{-1}) 3402.0, 3064.4, 2923.7, 1663.7, 1595.7, 1488.8, 1383.6, 1263.8, 1157.3, 1018.8, 962.6, 826.6, 691.3.



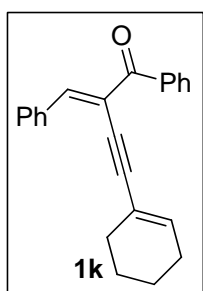
1h: ^1H NMR (400 MHz, CDCl_3): δ 8.08-8.07 (m, 2H), 7.98-7.96 (m, 2H), 7.63 (s, 1H), 7.61-7.57 (m, 1H), 7.50-7.45 (m, 7H), 7.25-7.23 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.2, 145.6, 137.1, 134.7, 132.7, 132.6, 131.8, 130.7, 130.3, 129.7, 128.6, 128.1, 123.2, 121.8, 120.6, 99.5, 88.2; IR (neat, cm^{-1}) 3383.1, 2923.0, 1662.6, 1594.6, 1484.9, 1384.7, 1263.3, 1069.2, 1017.5, 822.9, 756.9, 691.4.



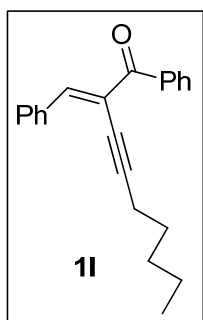
1i: ^1H NMR (400 MHz, CDCl_3): δ 8.12-8.10 (m, 2H), 8.00-7.98 (m, 2H), 7.62-7.54 (m, 2H), 7.48-7.40 (m, 5H), 7.16-7.13 (m, 2H), 7.08-7.06 (m, 1H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.4, 144.4, 137.9, 137.1, 136.7, 134.9, 132.4, 130.4, 130.3, 129.9, 129.7, 129.3, 128.9, 128.5, 128.0, 121.0, 120.0, 101.4, 86.4, 19.7, 19.6; IR (neat, cm^{-1}) 3310.3, 2920.1, 2196.0, 1634.8, 1594.4, 1495.9, 1447.2, 1317.8, 1263.6, 1207.1, 1071.9, 1024.2, 819.4, 754.5, 691.8.



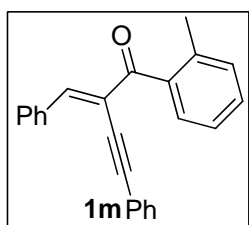
1j: ^1H NMR (400 MHz, CDCl_3): δ 8.22-8.21 (m, 2H), 8.07-7.05 (d, $J = 8.8$ Hz, 2H), 8.00-7.96 (m, 1H), 7.84-7.82 (d, $J = 8.4$ Hz, 2H), 7.71-7.70 (m, 1H), 7.64-7.59 (m, 2H), 7.53-7.47 (m, 6H), 7.45-7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.7, 144.9, 137.5, 134.9, 133.2, 133.1, 132.5, 130.6, 130.5, 130.4, 129.7, 129.3, 128.6, 128.2, 126.9, 126.5, 126.2, 125.2, 121.3, 120.6, 99.6, 91.8; IR (neat, cm^{-1}) 3403.5, 2923.0, 1660.6, 1590.2, 1449.8, 1383.6, 1256.4, 1152.3, 1066.9, 1017.5, 800.1, 771.7, 691.6.



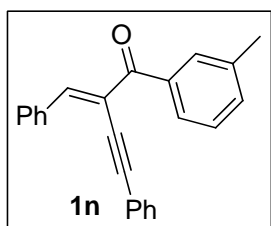
1k: ^1H NMR (400 MHz, CDCl_3): δ 8.06-8.04 (m, 2H), 7.95-7.94 (d, $J = 7.6$ Hz, 2H), 7.80-7.76 (m, 1H), 7.58-7.38 (m, 6H), 6.12 (s, 1H), 2.14-2.11 (m, 4H), 1.67-1.56 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.6, 143.6, 137.1, 136.4, 135.0, 132.3, 130.2, 130.1, 129.6, 128.4, 127.9, 121.2, 120.7, 103.1, 84.7, 28.3, 25.8, 22.1, 21.3; IR (neat, cm^{-1}) 3394.1, 3058.9, 2929.6, 2859.4, 2182.6, 1643.7, 1594.4, 1446.3, 1316.5, 1258.8, 1178.3, 1069.1, 755.8, 691.8.



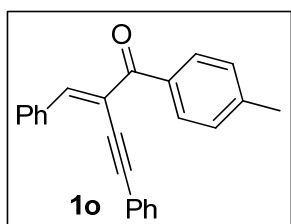
1l: ^1H NMR (400 MHz, CDCl_3): δ 8.05-8.03 (m, 2H), 7.92-7.90 (m, 2H), 7.55-7.51 (m, 1H), 7.45-7.37 (m, 6H), 2.46-2.42 (t, $J = 7.2$ Hz, 2H), 1.59-1.52 (m, 2H), 1.36-1.26 (m, 4H), 0.89-0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.1, 143.8, 137.2, 134.8, 132.2, 130.1, 129.9, 129.6, 128.3, 127.9, 121.7, 103.2, 78.0, 31.0, 27.8, 22.1, 19.9, 13.9; IR (neat, cm^{-1}) 3060.2, 2955.8, 2930.4, 2860.6, 2216.5, 1624.3, 1594.2, 1447.6, 1319.0, 1284.7, 1210.4, 1179.7, 1015.8, 932.4, 757.3, 721.5, 692.0.



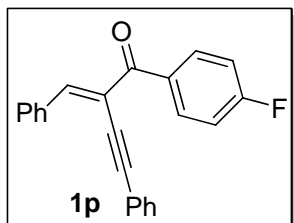
1m: ^1H NMR (400 MHz, CDCl_3): δ 8.10-8.08 (m, 2H), 7.63 (s, 1H), 7.48-7.46 (m, 1H), 7.43-7.42 (m, 3H), 7.39-7.34 (m, 3H), 7.31-7.29 (m, 3H), 7.27-7.25 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 145.9, 138.6, 136.3, 134.5, 131.4, 130.9, 130.7, 130.5, 130.1, 128.7, 128.5, 128.3, 128.0, 125.1, 122.8, 121.9, 100.3, 86.4, 19.8; IR (neat, cm^{-1}) 3059.6, 3023.8, 2924.7, 2200.1, 1624.5, 1595.9, 1489.2, 1446.4, 1290.1, 1264.8, 1070.9, 931.3, 793.4, 661.2.



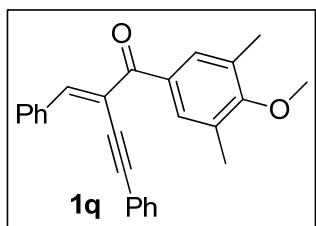
1n: ^1H NMR (400 MHz, CDCl_3): δ 8.10-8.09 (d, $J = 6.8$ Hz, 2H), 7.80 (s, 2H), 7.61 (s, 1H), 7.45-7.35 (m, 7H), 7.33-7.28 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.3, 144.8, 137.7, 137.0, 134.7, 133.2, 131.2, 130.4, 130.2, 130.1, 128.7, 128.4, 128.3, 127.8, 126.8, 122.8, 120.9, 100.6, 87.1, 21.2; IR (neat, cm^{-1}) 3057.9, 3014.0, 2921.0, 2195.1, 1618.4, 1598.6, 1489.2, 1445.1, 1297.4, 1178.8, 1071.9, 793.5, 673.9.



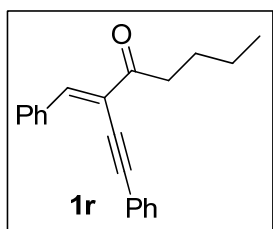
1o: ^1H NMR (400 MHz, CDCl_3): δ 8.11-8.09 (d, $J = 7.6$ Hz, 2H), 7.95-7.93 (d, $J = 8.0$ Hz, 2H), 7.58 (s, 1H), 7.44-7.40 (m, 5H), 7.33-7.31 (m, 3H), 7.28-7.26 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.9, 144.6, 143.3, 134.9, 134.3, 131.3, 130.4, 130.2, 130.0, 128.8, 128.4, 122.9, 121.1, 100.6, 87.2, 21.7; IR (neat, cm^{-1}) 3440.1, 3057.6, 2921.5, 2196.7, 1674.8, 1604.0, 1489.8, 1445.1, 1275.9, 1179.3, 1095.7, 960.5, 754.3, 689.4.



1p: ^1H NMR (400 MHz, CDCl_3): δ 8.11-8.04 (m, 4H), 7.62 (s, 1H), 7.44-7.38 (m, 5H), 7.32-7.31 (m, 3H), 7.15-7.11 (t, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.6, 166.6, 164.1, 145.0, 134.7, 133.2, 133.1, 132.4, 132.3, 131.2, 130.6, 130.3, 128.9, 128.4, 122.6, 120.4, 115.2, 115.0, 101.0, 87.0; IR (neat, cm^{-1}) 3395.3, 3060.3, 2195.9, 1663.1, 1597.4, 1503.9, 1384.6, 1262.4, 1231.6, 1155.5, 1093.3, 847.9, 757.5, 689.2.

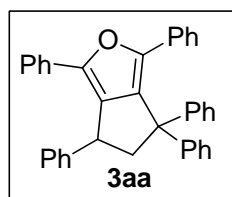


1q: ^1H NMR (400 MHz, CDCl_3): δ 8.11-8.10 (d, $J = 4.8$ Hz, 2H), 7.72 (s, 2H), 7.57 (s, 1H), 7.43-7.34 (m, 8H), 3.78 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 192.6, 160.9, 144.4, 134.9, 132.4, 131.3, 130.9, 130.7, 130.4, 130.2, 128.7, 128.5, 128.4, 122.9, 121.1, 100.6, 87.3, 59.7, 16.2, 16.1; IR (neat, cm^{-1}) 3439.8, 2925.3, 2360.7, 1658.8, 1595.1, 1486.7, 1382.6, 1280.7, 1180.9, 1010.6, 756.4, 689.8.

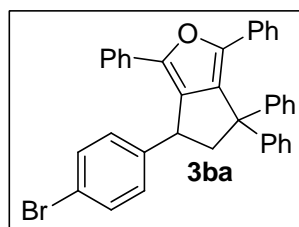


1r: ^1H NMR (400 MHz, CDCl_3): δ 8.10-8.08 (m, 2H), 7.84 (s, 1H), 7.55-7.53 (m, 2H), 7.43-7.38 (m, 6H), 3.02-2.99 (t, $J = 7.6$ Hz, 2H), 1.76-1.69 (m, 2H), 1.47-1.38 (m, 2H), 0.98-0.94 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.5, 142.7, 134.6, 131.3, 130.7, 130.6, 128.8, 128.6, 128.5, 122.9, 119.8, 99.0, 86.9, 40.0, 26.4, 22.4, 13.9; IR (neat, cm^{-1}) 3371.7, 2957.4, 2929.1, 2869.3, 2360.9, 1680.4, 1563.6, 1489.7, 1446.2, 1381.8, 1140.7, 1069.9, 1031.3, 779.2, 683.8.

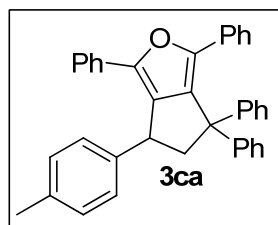
4. Characterization data of highly substituted 4*H*-cyclopenta[*c*]furans 3aa-3ra, 3ab-3af



3aa: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 87.8 mg (90%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.38 (m, 2H), 7.28-7.20 (m, 7H), 7.17-7.14 (t, $J = 6.0$ Hz, 4H), 7.11-7.02 (m, 8H), 7.01-6.98 (m, 4H), 4.26-4.22 (t, $J = 7.2$ Hz, 1H), 3.63-3.58 (dd, $J_1 = 13.2$ Hz, $J_2 = 7.2$ Hz, 1H), 3.18-3.12 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 144.4, 143.7, 143.0, 142.1, 138.1, 132.6, 130.2, 130.1, 128.9, 128.5, 128.4, 128.1, 128.1, 127.8, 126.8, 126.6, 126.5, 126.4, 126.3, 125.0, 124.8, 64.4, 57.1, 43.4; IR (neat, cm^{-1}) 3401.3, 3057.5, 2923.6, 1663.2, 1598.1, 1489.8, 1446.3, 1383.2, 1068.4, 1026.4, 761.1, 693.5; (ESI)HRMS: Found: m/z 489.2217. Calcd for $\text{C}_{37}\text{H}_{29}\text{O}$: $\text{M}+\text{H}^+$: 489.2213.

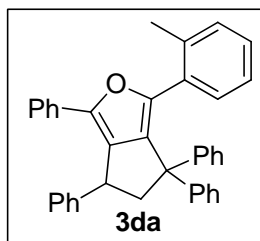


3ba: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 107.5 mg (95%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3): δ 7.78-7.76 (d, $J = 8.0$ Hz, 0.5H), 7.68-7.66 (d, $J = 8.4$ Hz, 0.5H), 7.54-7.51 (m, 1H), 7.48-7.41 (m, 3H), 7.33-7.30 (m, 4H), 7.27-7.22 (m, 6H), 7.19-7.10 (m, 5H), 7.05-7.03 (m, 4H), 4.32-4.28 (t, $J = 7.6$ Hz, 1H), 3.68-3.63 (dd, $J_1 = 12.8$ Hz, $J_2 = 7.2$ Hz, 1H), 3.19-3.13 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 143.8, 143.1, 141.1, 138.0, 132.0, 131.9, 131.8, 131.5, 130.1, 130.0, 129.5, 129.4, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 126.8, 126.7, 126.4, 125.0, 124.7, 120.1, 64.0, 57.1, 42.8; IR (neat, cm^{-1}) 3395.1, 2969.2, 2924.8, 2360.2, 1744.6, 1660.8, 1595.8, 1448.4, 1383.5, 1260.7, 1070.4, 1027.8, 810.9, 775.7, 698.7; (ESI)HRMS: Found: m/z 567.1311. Calcd for $\text{C}_{37}\text{H}_{28}\text{BrO}$: $\text{M}+\text{H}^+$: 567.1318.

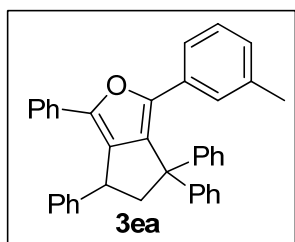


3ca: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 88.4 mg (88%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.46 (m, 2H), 7.35-7.28 (m, 9H), 7.25-7.23 (m, 7H), 7.20-7.04 (m, 4H), 7.00-6.98 (m, 2H), 4.29-4.26 (m, 1H), 3.68-3.63 (m, 1H), 3.22-3.16 (m, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 144.3, 143.7, 143.0, 139.1, 138.2, 135.9,

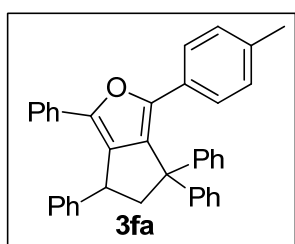
132.8, 130.3, 130.2, 129.2, 128.9, 128.5, 128.3, 128.1, 128.0, 127.9, 127.6, 126.7, 126.6, 126.5, 126.2, 125.0, 124.8, 64.5, 57.1, 43.0, 21.0; IR (neat, cm^{-1}) 3421.8, 3056.5, 2924.2, 2359.6, 1598.5, 1490.1, 1445.2, 1383.6, 1067.9, 1025.3, 793.7, 694.2; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.



3da: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 94.4 mg (94%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.14 (m, 14H), 7.10-7.01 (m, 8H), 6.73-6.67 (m, 1H), 6.61-6.56 (m, 1H), 4.36-4.30 (m, 1H), 3.53-3.46 (m, 1H), 3.37-3.29 (m, 1H), 2.40-2.38 (d, $J = 12.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.7, 145.6, 145.2, 143.8, 142.4, 138.2, 137.1, 131.0, 130.4, 130.3, 129.8, 129.7, 128.6, 128.5, 128.1, 127.9, 127.7, 126.5, 126.4, 126.3, 126.0, 124.8, 124.6, 62.8, 56.3, 43.2, 21.2; IR (neat, cm^{-1}) 3385.2, 3058.8, 2926.6, 1599.3, 1490.5, 1447.1, 1384.1, 1069.3, 1027.9, 758.6, 697.6; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.

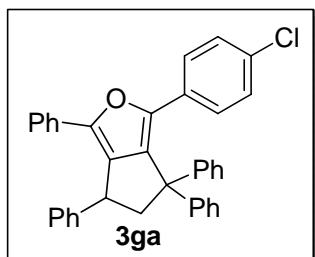


3ea: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 89.4 mg (89%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.45 (s, 2H), 7.30-7.21 (m, 7H), 7.16-7.05 (m, 12H), 7.01-6.97 (m, 1H), 6.91-6.86 (m, 2H), 4.30 (s, 1H), 3.70-3.66 (dd, $J_1 = 12.4$ Hz, $J_2 = 6.8$ Hz, 1H), 3.25-3.20 (t, $J = 12.0$ Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 144.5, 143.6, 142.1, 138.0, 137.5, 132.5, 130.3, 130.1, 128.9, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.5, 126.7, 126.5, 126.4, 126.2, 125.8, 124.8, 122.1, 64.1, 57.1, 43.4, 21.2; IR (neat, cm^{-1}) 3436.5, 2924.0, 2360.9, 1601.6, 1490.9, 1447.3, 1383.7, 1093.3, 1068.2, 757.9, 697.0; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.

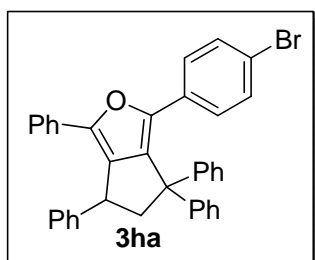


3fa: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford

86.5 mg (86%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.47-7.45 (d, $J = 7.2$ Hz, 2H), 7.36-7.31 (m, 8H), 7.29-7.26 (t, $J = 7.2$ Hz, 2H), 7.24-7.13 (m, 9H), 7.08-7.04 (m, 1H), 6.89-6.87 (d, $J = 8.0$ Hz, 2H), 4.33-4.29 (t, $J = 8.0$ Hz, 1H), 3.70-3.65 (dd, $J_1 = 12.8$ Hz, $J_2 = 7.2$ Hz, 1H), 3.24-3.18 (dd, $J_1 = 12.8$ Hz, $J_2 = 8.8$ Hz, 1H), 2.23(s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 144.7, 143.4, 142.3, 137.4, 136.6, 132.6, 130.4, 129.0, 128.8, 128.6, 128.4, 128.2, 128.1, 127.9, 127.6, 126.8, 126.5, 126.3, 125.0, 124.8, 64.4, 57.2, 43.5, 21.2; IR (neat, cm^{-1}) 3403.6, 2922.6, 2359.0, 1659.6, 1600.0, 1490.8, 1447.6, 1383.2, 1068.4, 1026.3, 757.4, 697.0; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.

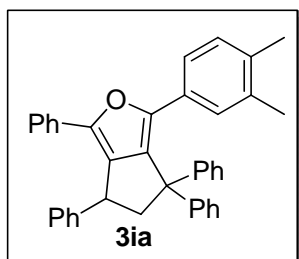


3ga: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 29.3 mg (28%) of the indicated compound after 1 h at 0°C . ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.80 (m, 2H), 7.62-7.57 (m, 1H), 7.50-7.46 (m, 2H), 7.44-7.42 (m, 2H), 7.35-7.25 (m, 7H), 7.21-7.12 (m, 8H), 7.04-7.02 (d, $J = 8.8$ Hz, 2H), 4.33-4.30 (m, 1H), 3.71-3.66 (dd, $J_1 = 13.2$ Hz, $J_2 = 6.8$ Hz, 1H), 3.25-3.20 (dd, $J_1 = 13.2$ Hz, $J_2 = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 144.1, 143.4, 142.7, 141.9, 138.7, 137.6, 132.7, 132.4, 130.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 126.9, 126.8, 126.5, 126.4, 126.1, 124.8, 64.3, 57.1, 43.4; IR (neat, cm^{-1}) 3419.0, 2958.0, 2924.4, 2360.0, 1659.5, 1449.0, 1383.6, 1260.1, 1091.6, 1070.9, 1026.3, 801.3, 699.0; (ESI)HRMS: Found: m/z 523.1809. Calcd for $\text{C}_{37}\text{H}_{28}\text{ClO}$: $\text{M}+\text{H}^+$: 523.1823.

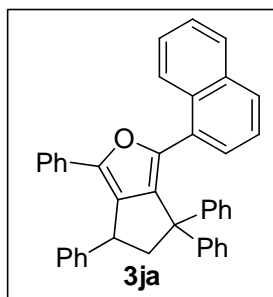


3ha: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 39.6 mg (35%) of the indicated compound after 1 h at 0°C . ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.80 (d, $J = 7.2$ Hz, 1H), 7.59-7.55 (m, 1H), 7.50-7.46 (m, 2H), 7.44-7.42 (m, 2H), 7.37-7.29 (m, 2H), 7.27-7.23 (m, 4H), 7.21-7.17 (m, 7H), 7.14-7.11 (m, 3H), 7.08-7.06 (m, 2H), 4.34-4.30 (t, $J = 8.0$ Hz, 1H), 3.71-3.66 (dd, $J_1 = 13.2$ Hz, $J_2 = 7.2$ Hz, 1H), 3.25-3.19 (dd, $J_1 = 13.2$ Hz, $J_2 = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.9, 144.1, 143.4, 142.7, 141.9, 138.9, 137.6, 132.7, 132.4, 131.2, 130.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 126.9, 126.8, 126.5, 126.4, 124.8, 120.6, 64.2, 57.1, 43.4; IR (neat, cm^{-1}) 3397.0, 2969.2, 2924.2, 2360.2, 1657.9, 1448.4, 1383.5, 1260.7, 1087.7, 1070.4, 1027.1, 801.9, 713.7, 698.7;

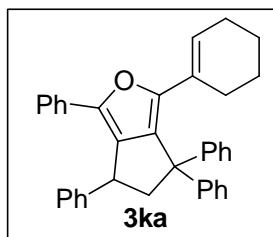
(ESI)HRMS: Found: m/z 567.1311. Calcd for $C_{37}H_{28}BrO$: $M+H^+$: 567.1318.



3ia: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 81.5 mg (79%) of the indicated compound after 1 h. 1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.45 (m, 3H), 7.41-7.28 (m, 7H), 7.23-7.04 (m, 11H), 6.88-6.86 (m, 2H), 4.32-4.28 (t, $J = 7.2$ Hz, 1H), 3.70-3.65 (dd, $J_1 = 12.8$ Hz, $J_2 = 7.2$ Hz, 1H), 3.24-3.19 (dd, $J_1 = 12.4$ Hz, $J_2 = 9.6$ Hz, 1H), 2.13 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.7, 143.2, 142.2, 137.3, 136.1, 135.2, 132.5, 130.4, 130.0, 129.9, 129.4, 129.3, 128.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 126.7, 126.4, 126.2, 124.7, 122.5, 64.1, 57.1, 43.4, 19.5, 19.4; IR (neat, cm^{-1}) 3420.7, 3058.8, 2922.3, 2360.4, 1660.0, 1599.2, 1492.2, 1447.7, 1383.7, 1068.1, 1022.9, 757.2, 697.2; (ESI)HRMS: Found: m/z 517.2529. Calcd for $C_{39}H_{33}O$: $M+H^+$: 517.2526.

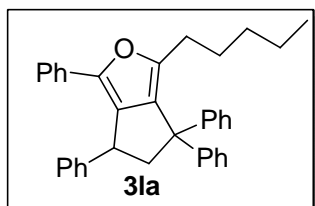


3ja: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 98.6 mg (92%) of the indicated compound after 12 h. 1H NMR (400 MHz, $CDCl_3$): δ 8.26-8.25 (d, $J = 5.6$ Hz, 1H), 7.78-7.76 (d, $J = 7.6$ Hz, 1H), 7.65-7.63 (d, $J = 8.4$ Hz, 1H), 7.47-7.44 (t, $J = 6.4$ Hz, 2H), 7.34-7.05 (m, 17H), 7.00-6.99 (m, 4H), 6.68-6.67 (m, 1H), 4.41-4.39 (m, 1H), 3.58-3.53 (m, 1H), 3.45-3.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 145.2, 145.0, 144.4, 142.4, 139.5, 133.6, 132.2, 131.2, 130.4, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.7, 126.6, 126.5, 126.4, 126.3, 126.2, 126.0, 125.6, 124.8, 124.6, 62.7, 56.3, 43.3; IR (neat, cm^{-1}) 3405.2, 3057.8, 2930.3, 1949.6, 1598.1, 1491.5, 1446.4, 1385.5, 1216.7, 1069.7, 1023.9, 795.6, 687.9; (ESI)HRMS: Found: m/z 539.2379. Calcd for $C_{41}H_{31}O$: $M+H^+$: 539.2369.

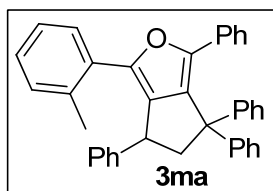


3ka: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 38.4 mg (39%) of the indicated compound after 1 h. 1H NMR (400 MHz, $CDCl_3$): δ

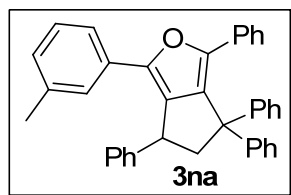
7.44-7.39 (m, 4H), 7.33-7.31 (m, 1H), 7.28-7.26 (m, 2H), 7.24-7.22 (m, 7H), 7.19-7.09 (m, 5H), 7.06-7.03 (m, 1H), 5.63-5.61 (t, $J = 4.0\text{Hz}$, 1H), 4.28-4.24 (t, $J = 7.6\text{Hz}$, 1H), 3.63-3.58 (dd, $J_1 = 13.2\text{ Hz}$, $J_2 = 7.2\text{ Hz}$, 1H), 3.24-3.19 (dd, $J_1 = 12.8\text{ Hz}$, $J_2 = 8.8\text{ Hz}$, 1H), 2.07-2.04 (m, 2H), 1.53-1.38 (m, 4H), 1.30-1.27 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 145.5, 143.7, 142.4, 142.2, 136.2, 132.0, 130.6, 129.1, 128.6, 128.4, 128.1, 128.0, 127.8, 127.7, 127.4, 126.5, 126.3, 126.2, 126.0, 124.5, 64.7, 56.8, 43.3, 25.4, 22.4, 21.8; IR (neat, cm^{-1}) 3421.6, 3025.5, 2930.8, 1659.1, 1599.3, 1491.7, 1447.0, 1217.6, 1070.9, 754.7, 698.5; (ESI)HRMS: Found: m/z 493.2524. Calcd for $\text{C}_{37}\text{H}_{33}\text{O}$: $\text{M}+\text{H}^+$: 493.2526.



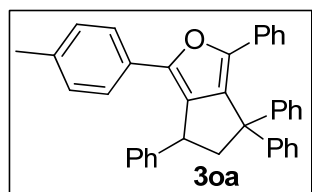
3la: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 55.9 mg (58%) of the indicated compound after 3 h at 50°C . ^1H NMR (400 MHz, CDCl_3): δ 7.34-7.33 (m, 4H), 7.24-7.19 (m, 9H), 7.17-7.13 (m, 4H), 7.09-7.01 (m, 2H), 7.00-6.98 (m, 1H), 4.36-4.32 (t, $J = 8.0\text{Hz}$, 1H), 3.53-3.48 (dd, $J_1 = 13.2\text{ Hz}$, $J_2 = 7.2\text{ Hz}$, 1H), 3.16-3.10 (dd, $J_1 = 13.2\text{ Hz}$, $J_2 = 9.2\text{ Hz}$, 1H), 2.35-2.31 (t, $J = 7.6\text{Hz}$, 2H), 1.52-1.47 (m, 2H), 1.22-1.16 (m, 4H), 0.85-0.82 (t, $J = 6.8\text{Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.3, 146.5, 145.8, 142.7, 142.6, 135.9, 130.8, 130.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 126.4, 126.3, 126.0, 125.8, 124.2, 62.0, 55.5, 43.6, 31.6, 27.6, 27.2, 22.3, 14.0; IR (neat, cm^{-1}) 3058.8, 2928.5, 2863.7, 1600.5, 1491.8, 1447.4, 1382.9, 1217.9, 1069.6, 758.4, 697.3; (ESI)HRMS: Found: m/z 483.2684. Calcd for $\text{C}_{36}\text{H}_{35}\text{O}$: $\text{M}+\text{H}^+$: 483.2682.



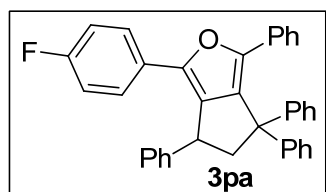
3ma: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 86.3 mg (86%) of the indicated compound after 5 h at 50°C . ^1H NMR (400 MHz, CDCl_3): δ 7.52-7.51 (m, 2H), 7.39-7.35 (m, 2H), 7.32-7.28 (m, 3H), 7.20-7.15 (m, 5H), 7.10-7.00 (m, 11H), 6.91-6.88 (m, 1H), 4.25-4.21 (m, 1H), 3.66-3.61 (dd, $J_1 = 12.8\text{ Hz}$, $J_2 = 6.4\text{ Hz}$, 1H), 3.18-3.12 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 144.9, 144.8, 142.7, 141.7, 137.2, 135.4, 133.3, 130.7, 130.3, 129.6, 129.0, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.6, 127.3, 126.8, 126.5, 126.2, 125.1, 124.8, 64.2, 57.1, 43.6, 21.6; IR (neat, cm^{-1}) 3434.4, 3053.2, 2926.8, 1600.1, 1489.1, 1447.5, 1383.8, 1099.0, 1068.7, 1026.0, 758.9, 697.5; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.



3na: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 84.3mg (84%) of the indicated compound after 3 h. ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.47 (d, $J = 7.6\text{Hz}$, 2H), 7.36-7.31 (m, 5H), 7.29-7.24 (m, 4H), 7.21-7.15 (m, 6H), 7.12-7.10 (m, 1H), 7.05-7.01-6.88 (m, 5H), 6.88-6.86 (d, $J = 7.6\text{Hz}$, 1H), 4.30-4.26 (t, $J = 8.8\text{Hz}$, 1H), 3.70-3.65 (dd, $J_1 = 13.2\text{ Hz}$, $J_2 = 6.8\text{ Hz}$, 1H), 3.24-3.19 (dd, $J_1 = 12.8\text{ Hz}$, $J_2 = 9.6\text{ Hz}$, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 144.2, 143.8, 142.8, 142.3, 138.0, 137.6, 132.6, 130.2, 130.1, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.4, 126.8, 126.6, 126.5, 126.3, 125.7, 125.0, 121.8, 64.4, 57.1, 43.5, 21.2; IR (neat, cm^{-1}) 3397.0, 3058.3, 2923.2, 1663.6, 1600.7, 1489.5, 1446.8, 1383.4, 1070.8, 743.9, 692.7; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.

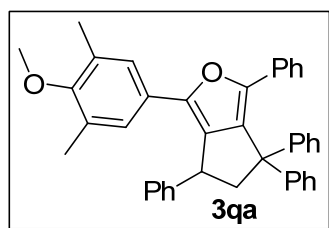


3oa: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 86.3mg (86%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.46 (m, 2H), 7.34-7.27 (m, 5H), 7.23-7.09 (m, 12H), 7.06-7.04 (m, 3H), 6.96-6.93 (m, 2H), 4.33-4.28 (m, 1H), 3.71-3.65 (m, 1H), 3.25-3.18 (m, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.2, 144.0, 143.0, 142.3, 138.1, 136.4, 131.8, 130.3, 128.9, 128.5, 128.3, 128.1, 128.0, 127.8, 127.6, 126.7, 126.5, 126.4, 126.2, 124.9, 124.7, 64.4, 57.1, 43.4, 21.2; IR (neat, cm^{-1}) 3402.0, 3032.3, 2877.2, 1663.6, 1519.2, 1489.5, 1446.8, 1383.4, 1107.2, 1070.8, 757.9, 676.8; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.

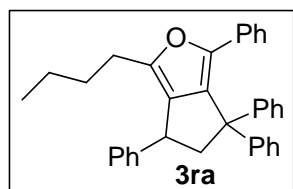


3pa: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 74.9 mg (74%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.47 (m, 2H), 7.37-7.31 (m, 2H), 7.29-7.14 (m, 15H), 7.12-7.06 (m, 3H), 6.84-6.79 (m, 2H), 4.29-4.25 (t, $J = 8.4\text{ Hz}$, 1H), 3.70-3.65 (dd, $J_1 = 13.2\text{ Hz}$, $J_2 = 6.8\text{ Hz}$, 1H), 3.23-3.18 (dd, $J_1 = 12.8\text{ Hz}$, $J_2 = 5.6\text{ Hz}$, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.8, 160.3, 145.2, 144.4, 142.9, 142.7, 141.9, 138.1, 132.2, 130.1, 128.9, 128.6, 128.4, 128.1, 128.0, 127.8, 126.8, 126.6, 126.5, 126.3, 125.0, 115.2, 115.1, 64.4, 57.1, 43.3, 43.2; IR (neat, cm^{-1}) 3401.9, 3059.2, 2931.1, 1662.3, 1599.7, 1496.8, 1447.0, 1383.9, 1231.0, 1156.6, 1092.1, 1029.9, 834.9, 784.2, 697.4; (ESI)HRMS: Found:

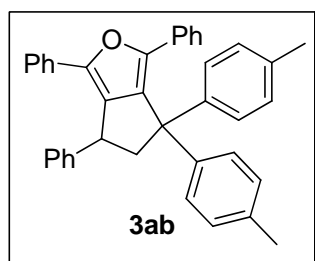
m/z 507.2098. Calcd for $C_{37}H_{28}FO$: $M+H^+$: 507.2119.



3qa: The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 74.2 mg (68%) of the indicated compound after 1 h. 1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.36-7.11 (m, 15H), 7.06-7.04 (m, 3H), 6.91 (s, 2H), 4.24-4.20 (m, 1H), 3.69-3.62 (m, 4H), 3.24-3.18 (dd, $J_1 = 12.8$ Hz, $J_2 = 9.2$ Hz, 1H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 145.5, 143.9, 143.7, 142.6, 142.5, 137.9, 132.0, 130.5, 130.3, 129.0, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 126.8, 126.5, 126.4, 126.2, 125.8, 124.9, 64.4, 59.7, 57.1, 43.6, 15.9, 15.9; IR (neat, cm^{-1}) 3396.2, 2927.4, 1657.5, 1599.4, 1487.3, 1447.3, 1395.3, 1238.0, 1078.9, 1016.9, 759.6, 697.4; (ESI)HRMS: Found: m/z 547.2614. Calcd for $C_{40}H_{35}O_2$: $M+H^+$: 547.2632.

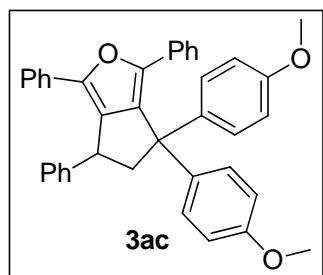


3ra: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 45.9 mg (49%) of the indicated compound after 12 h at 80°C. 1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, $J = 8.0$ Hz, 2H), 7.39-7.32 (m, 2H), 7.30-7.26 (m, 5H), 7.24-7.22 (m, 3H), 7.21-6.15 (m, 2H), 7.12-7.09 (m, 3H), 7.02-7.00 (m, 3H), 3.97-3.92 (dd, $J_1 = 10.4$ Hz, $J_2 = 6.4$ Hz, 1H), 3.55-3.50 (dd, $J_1 = 12.8$ Hz, $J_2 = 6.4$ Hz, 1H), 3.13-3.07 (t, $J = 12.0$ Hz, 1H), 2.33-2.16 (m, 2H), 1.51-1.41 (m, 2H), 1.26-1.14 (m, 2H), 0.79-0.75 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 146.2, 143.2, 142.6, 142.4, 135.7, 131.8, 130.7, 129.1, 128.4, 128.3, 128.1, 127.9, 126.7, 126.5, 126.1, 125.9, 124.4, 63.7, 57.3, 42.2, 30.2, 26.4, 22.2, 13.7; IR (neat, cm^{-1}) 3058.9, 2956.3, 2869.2, 1600.6, 1491.2, 1447.9, 1381.7, 1071.1, 762.2, 739.2, 697.3; (ESI)HRMS: Found: m/z 469.2527. Calcd for $C_{35}H_{33}O$: $M+H^+$: 469.2526.

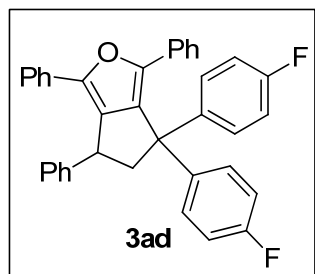


3ab: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 99.1 mg (96%) of the indicated compound after 2 h. 1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 2H), 7.30-7.23 (m, 6H), 7.20-7.10 (m, 9H), 7.07-7.06 (m, 4H), 6.99-6.97 (m, 2H), 4.31-4.27 (t, $J = 6.8$ Hz, 1H), 3.66-3.60 (m, 1H), 3.19-3.12 (m,

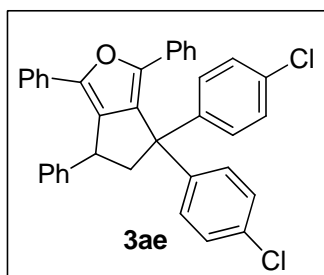
1H), 2.35 (s, 3H), 2,24(s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 143.6, 142.5, 142.3, 140.0, 138.4, 136.3, 135.7, 132.7, 130.3, 129.0, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.8, 126.5, 126.4, 125.0, 124.8, 64.5, 56.4, 43.4, 21.0, 20.8; IR (neat, cm^{-1}) 3436.4, 3025.8, 2921.2, 1672.4, 1598.9, 1489.5, 1448.4, 1382.9, 1261.9, 1225.7, 1179.9, 1023.8, 821.2, 762.3, 697.5; (ESI)HRMS: Found: m/z 517.2529. Calcd for $\text{C}_{39}\text{H}_{33}\text{O}$: $\text{M}+\text{H}^+$: 517.2526.



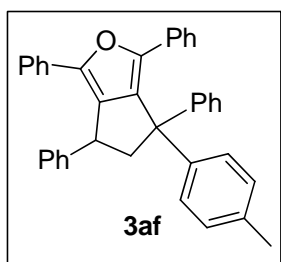
3ac: The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 100.8 mg (92%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.36 (d, $J = 7.2$ Hz, 2H), 7.31-7.28 (m, 4H), 7.23-7.16 (m, 6H), 7.13-7.06 (m, 7H), 6.87-6.86 (d, $J = 7.2$ Hz, 2H), 6.72-6.70 (d, $J = 7.2$ Hz, 2H), 4.30-4.27 (t, $J = 7.2$ Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.61-3.57 (dd, $J_1 = 11.6$ Hz, $J_2 = 6.8$ Hz, 1H), 3.16-3.11 (t, $J = 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.2, 157.9, 144.1, 143.6, 142.2, 138.5, 137.6, 135.1, 132.6, 130.2, 129.8, 129.4, 128.5, 128.1, 128.0, 127.8, 126.5, 126.4, 125.0, 124.8, 113.6, 113.4, 64.4, 55.8, 55.2, 43.3; IR (neat, cm^{-1}) 3058.6, 2932.5, 2835.0, 1604.1, 1510.3, 1486.3, 1446.8, 1295.6, 1242.7, 1180.1, 1035.3, 828.1, 764.1, 693.9; (ESI)HRMS: Found: m/z 549.2413. Calcd for $\text{C}_{39}\text{H}_{33}\text{O}_3$: $\text{M}+\text{H}^+$: 549.2424.



3ad: The reaction mixture was chromatographed using 100:1 hexane/EtOAc to afford 102.7 mg (98%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.38 (m, 2H), 7.34-7.32 (m, 2H), 7.24-7.21 (m, 4H), 7.18-7.14 (m, 4H), 7.13-7.06 (m, 7H), 7.03-6.99 (t, $J = 8.4$ Hz, 2H), 6.87-6.82 (t, $J = 8.8$ Hz, 2H), 4.34-4.30 (t, $J = 7.6$ Hz, 1H), 3.62-3.57 (dd, $J_1 = 12.8$ Hz, $J_2 = 6.8$ Hz, 1H), 3.20-3.14 (dd, $J_1 = 13.2$ Hz, $J_2 = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 162.6, 160.4, 160.1, 144.3, 144.0, 141.7, 140.4, 140.3, 138.8, 137.7, 132.1, 130.4, 130.3, 130.1, 130.0, 129.9, 128.5, 128.2, 128.1, 127.7, 126.9, 126.8, 126.6, 124.9, 124.8, 115.3, 115.1, 115.0, 114.8, 64.5, 56.0, 43.2; IR (neat, cm^{-1}) 3397.7, 2925.4, 1600.1, 1512.4, 1447.7, 1383.9, 1232.1, 1161.2, 1068.0, 1022.2, 831.7, 762.7, 693.3; (ESI)HRMS: Found: m/z 525.2024. Calcd for $\text{C}_{37}\text{H}_{27}\text{F}_2\text{O}$: $\text{M}+\text{H}^+$: 525.2013.

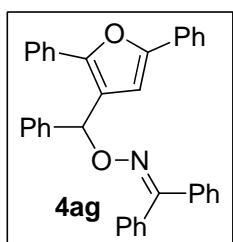


3ae: The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 109.0 mg (98%) of the indicated compound after 2 h. ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.19 (m, 6H), 7.14-7.07 (m, 8H), 7.05-7.01 (m, 9H), 4.24-4.23 (d, $J = 5.2$ Hz, 1H), 3.51-3.46 (m, 1H), 3.08-3.03 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 144.1, 143.0, 141.6, 141.4, 137.1, 132.9, 132.4, 132.1, 130.1, 130.0, 129.8, 128.6, 128.3, 128.2, 127.7, 127.0, 126.8, 126.6, 124.9, 124.8, 64.4, 56.2, 43.2; IR (neat, cm^{-1}) 3416.2, 3062.1, 2924.8, 1674.4, 1596.7, 1490.2, 1449.3, 1384.7, 1227.7, 1091.5, 1016.0, 830.6, 745.7, 699.2; (ESI)HRMS: Found: m/z 557.1433. Calcd for $\text{C}_{37}\text{H}_{27}\text{Cl}_2\text{O}$: $\text{M}+\text{H}^+$: 557.1407.



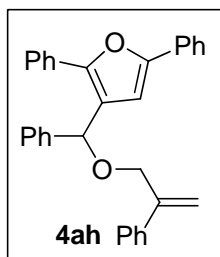
3af: The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 95.4 mg (95%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3): δ 7.58-7.56 (d, $J = 7.2$ Hz, 1H), 7.48-7.15 (m, 22H), 7.09-7.07 (d, $J = 7.6$ Hz, 1H), 4.30-4.29 (t, $J = 8.0$ Hz, 1H), 3.79-3.74 (dd, $J_1 = 12.8$ Hz, $J_2 = 6.8$ Hz, 1H), 3.33-3.26 (m, 1H), 2.45-2.34 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.4, 144.3, 143.7, 143.3, 142.2, 139.8, 138.2, 136.4, 135.7, 132.7, 130.2, 129.1, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 126.7, 126.6, 126.5, 126.4, 125.1, 124.8, 64.4, 56.8, 43.3, 20.8; IR (neat, cm^{-1}) 3398.1, 2923.1, 1599.1, 1490.0, 1446.5, 1383.7, 1070.9, 1025.7, 760.2, 694.0; (ESI)HRMS: Found: m/z 503.2358. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}$: $\text{M}+\text{H}^+$: 503.2369.

5. Characterization data of trisubstituted furans **4ag**, **4ah**



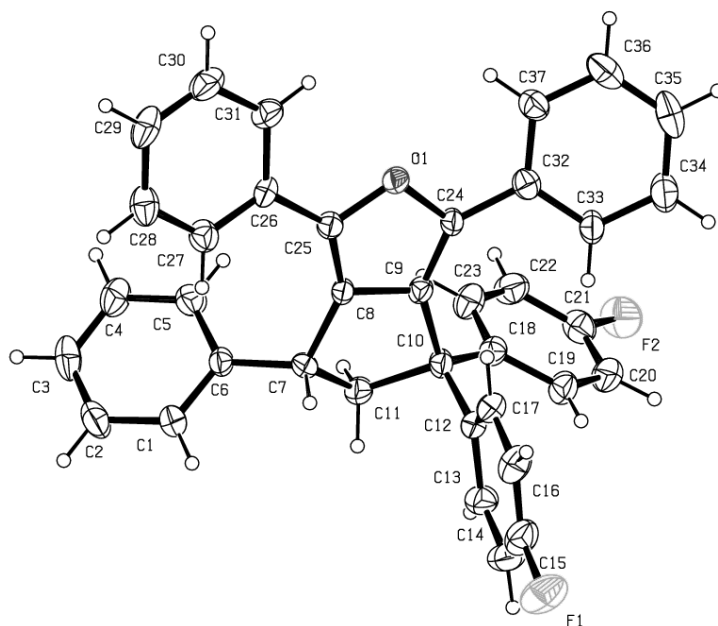
4ag: The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 75.8 mg (75%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3):

δ 7.84-7.82 (d, $J = 8.4$ Hz, 2H), 7.65-7.63 (d, $J = 8.0$ Hz, 2H), 7.44-7.38 (m, 11H), 7.36-7.30 (m, 5H), 7.29-7.19 (m, 5H), 6.66 (s, 1H), 6.48 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.5, 152.3, 150.2, 140.8, 136.4, 133.4, 130.8, 130.6, 129.3, 129.2, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.7, 127.5, 127.3, 127.1, 126.6, 123.7, 123.5, 108.0, 79.9; IR (neat, cm^{-1}) 3388.6, 3059.8, 2923.2, 2347.3, 1953.8, 1596.4, 1489.6, 1446.2, 1384.6, 1165.4, 1025.4, 966.0, 906.5, 763.8, 689.2; (ESI)HRMS: Found: m/z 528.1934. Calcd for $\text{C}_{36}\text{H}_{27}\text{NNaO}_2$: $M+\text{Na}^+$: 528.1956.



4ah: The reaction mixture was chromatographed using 50:1 hexane/EtOAc to afford 49.5 mg (56%) of the indicated compound after 1 h. ^1H NMR (400 MHz, CDCl_3): δ 7.72-7.70 (d, $J = 8.4$ Hz, 2H), 7.65-7.63 (d, $J = 8.0$ Hz, 2H), 7.43-7.33 (m, 7H), 7.32-7.23 (m, 9H), 6.75 (s, 1H), 5.79 (s, 1H), 5.45 (s, 1H), 5.23 (s, 1H), 4.51-4.48 (d, $J = 12.8$ Hz, 1H), 4.34-4.31 (d, $J = 12.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 150.4, 144.0, 140.9, 138.8, 130.8, 130.5, 128.7, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 127.2, 126.5, 126.2, 123.8, 123.6, 114.9, 107.3, 74.6, 70.4; IR (neat, cm^{-1}) 3435.2, 3058.6, 2923.6, 2358.2, 1951.2, 1597.8, 1489.8, 1448.2, 1384.0, 1261.0, 1082.9, 1027.0, 911.3, 793.6, 684.3; (ESI)HRMS: Found: m/z 465.1825. Calcd for $\text{C}_{32}\text{H}_{26}\text{NaO}_2$: $M+\text{Na}^+$: 465.1847.

6. Crystal structure of 3ad

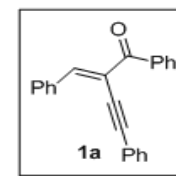


X-ray structure of **3ad**

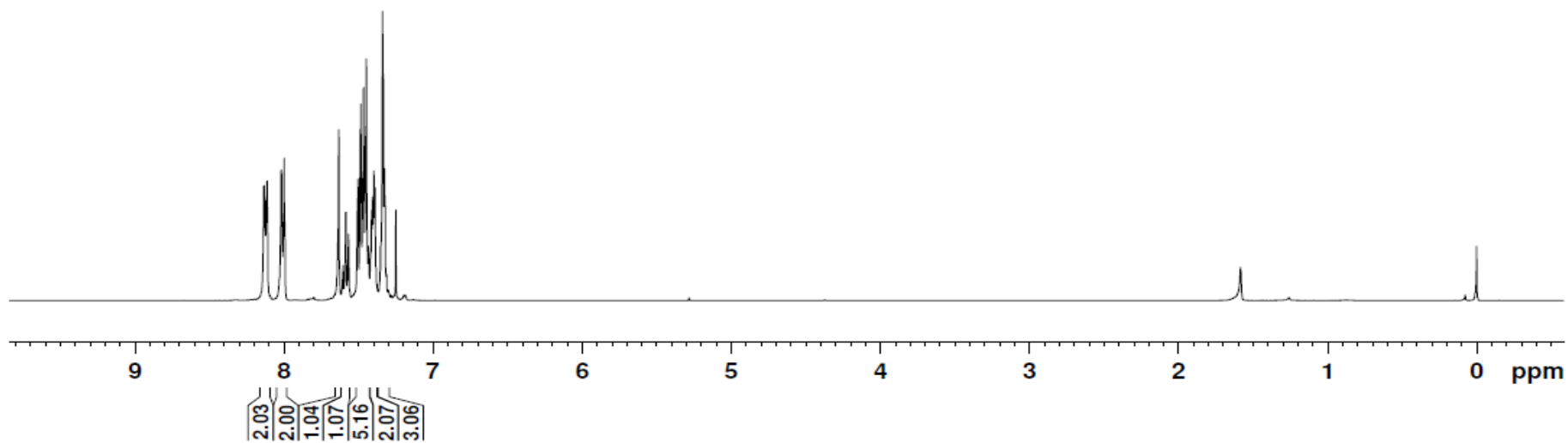
7. ^1H NMR and ^{13}C NMR spectra for compounds 1a-1r

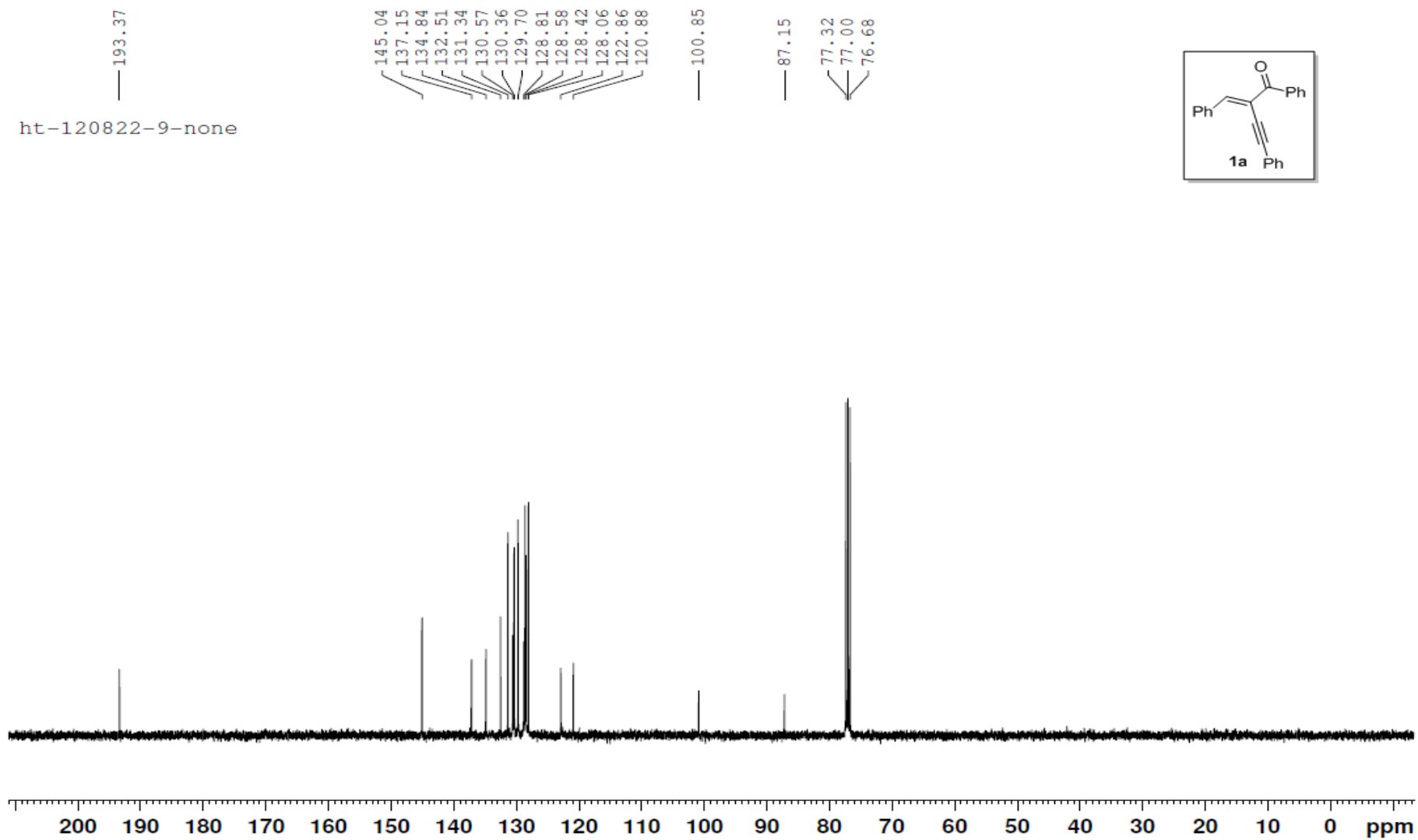
8.131
8.126
8.111
8.015
8.013
7.995
7.992
7.628
7.600
7.582
7.577
7.566
7.563
7.560
7.501
7.482
7.463
7.449
7.444
7.431
7.409
7.403
7.394
7.391
7.386
7.384
7.338
7.332
7.326
7.321

ht-120822-9-none



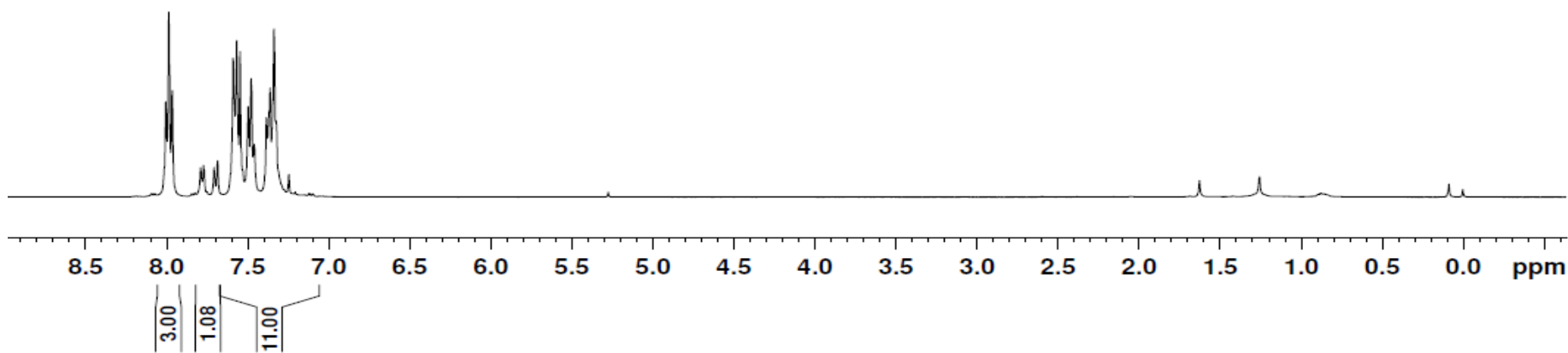
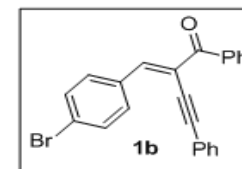
0.000

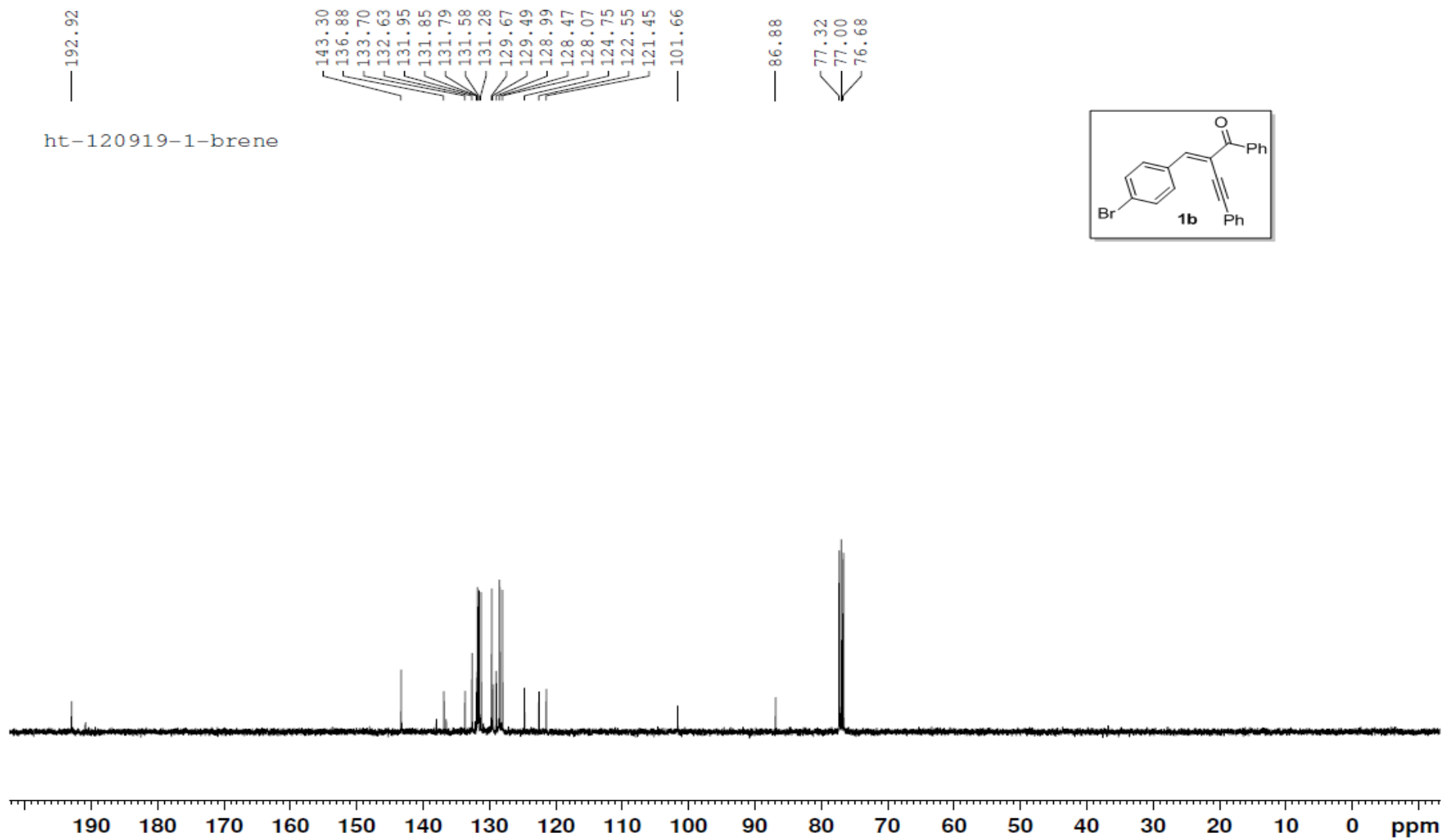


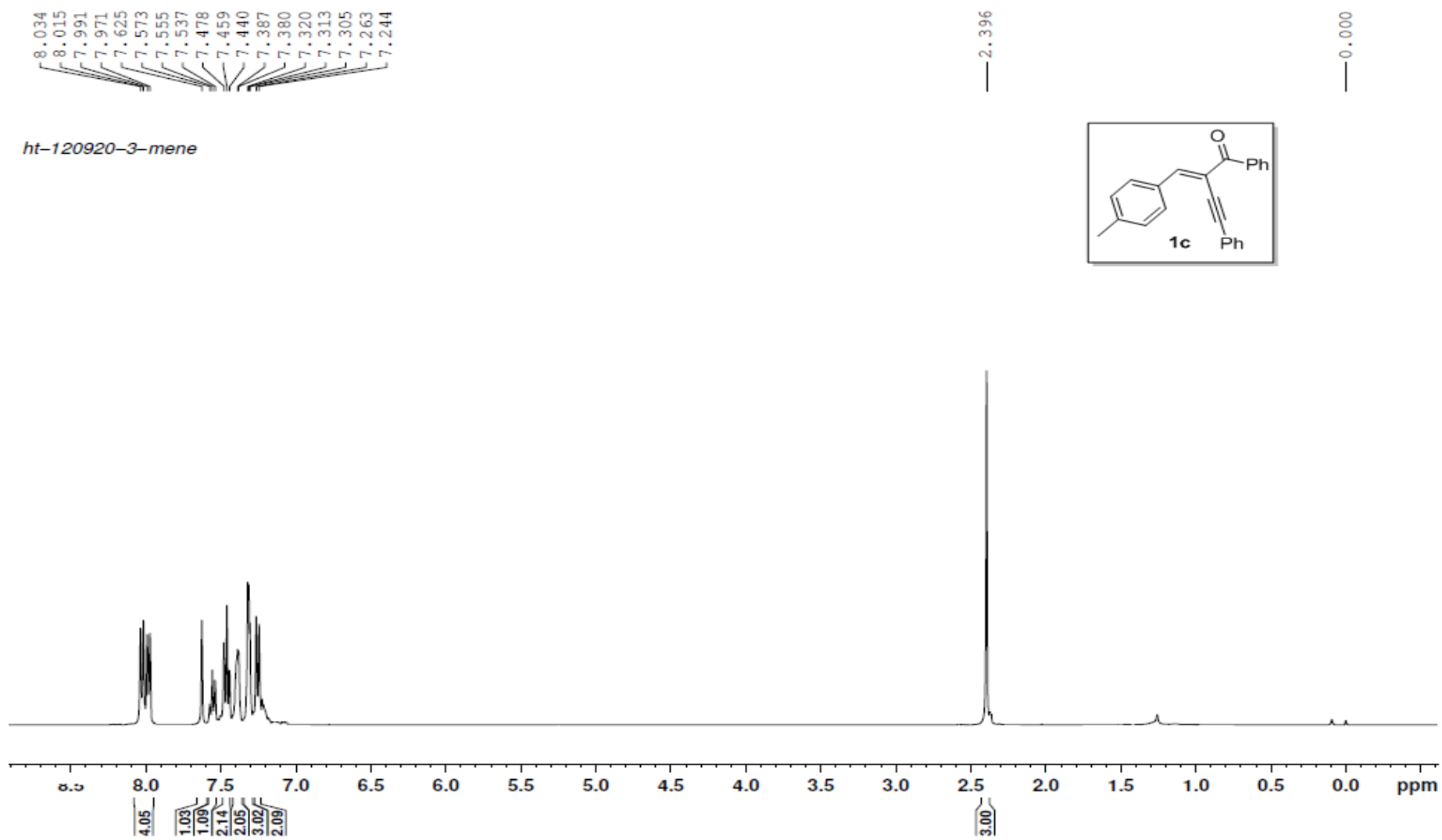


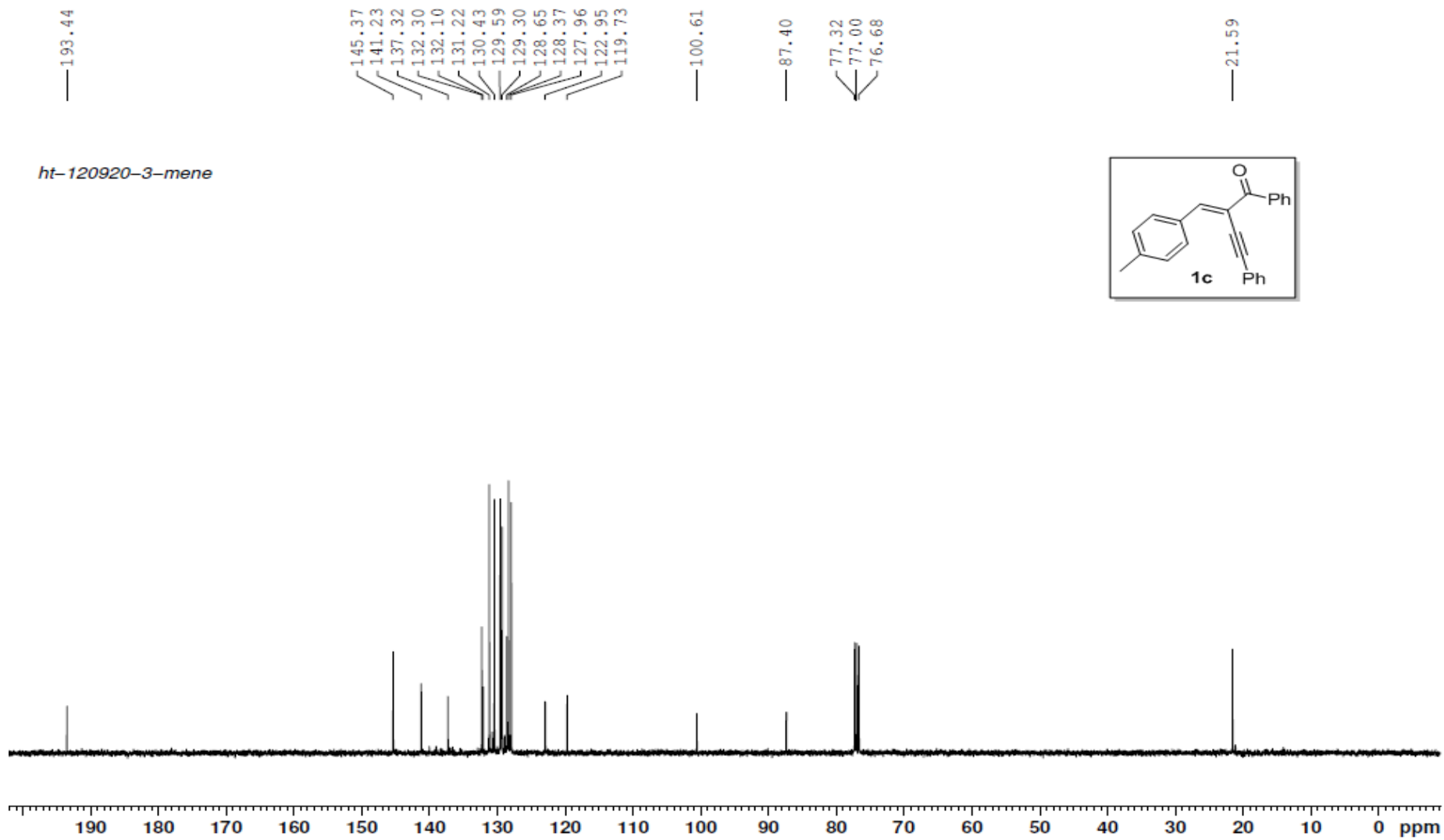
8.004
7.985
7.964
7.788
7.770
7.706
7.684
7.588
7.566
7.545
7.495
7.476
7.458
7.383
7.367
7.360
7.337
7.324

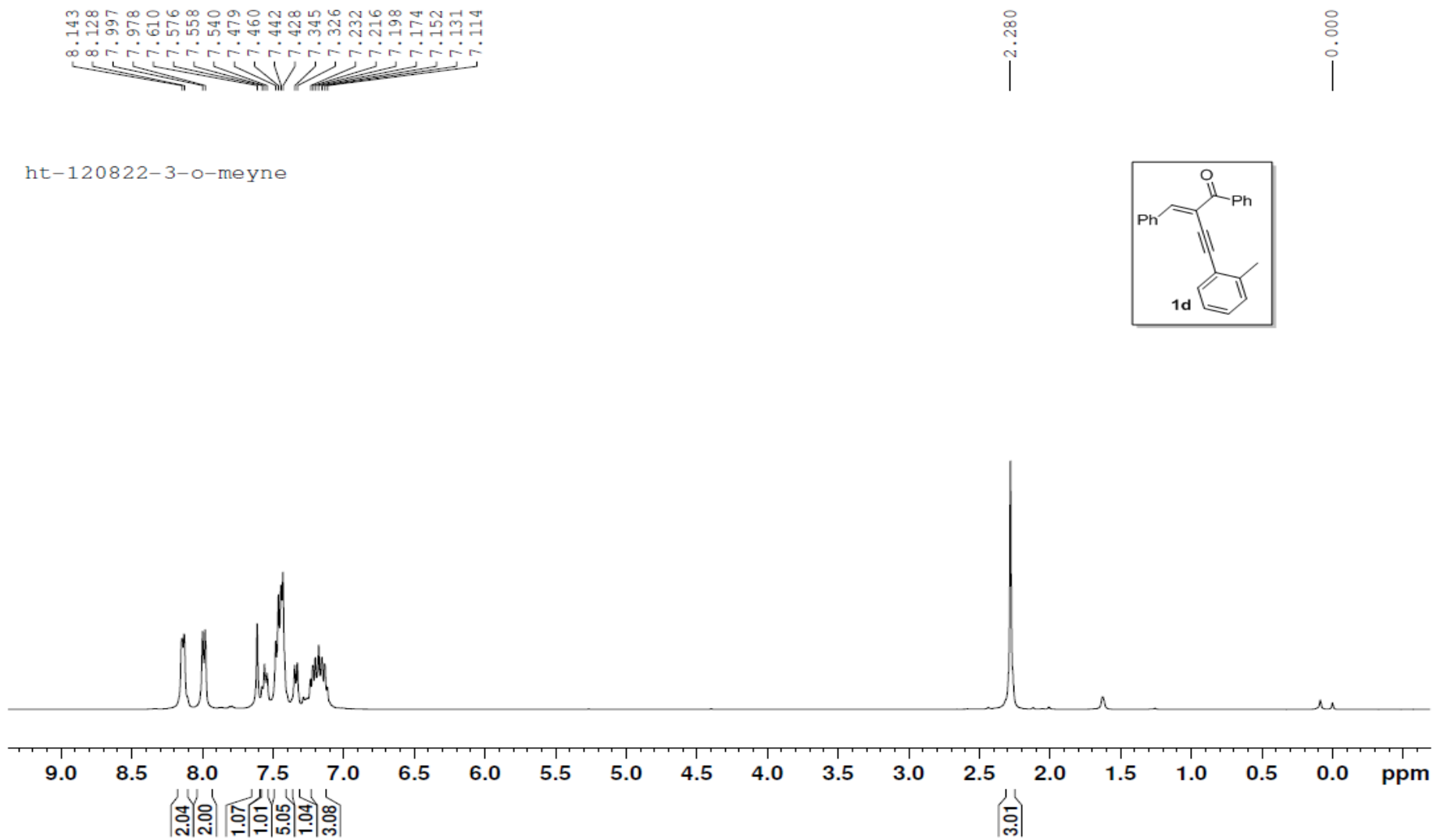
ht-120919-1-brene

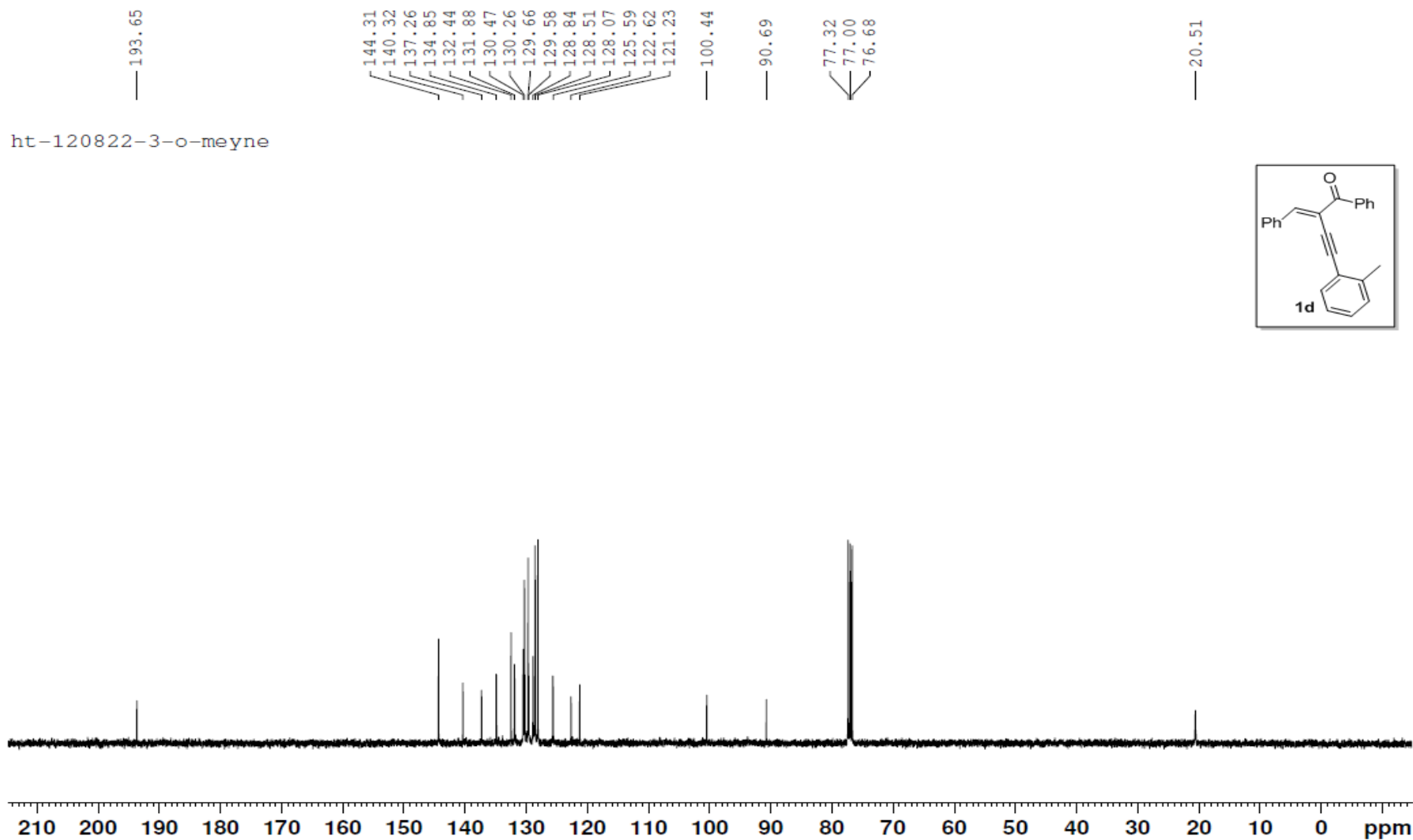


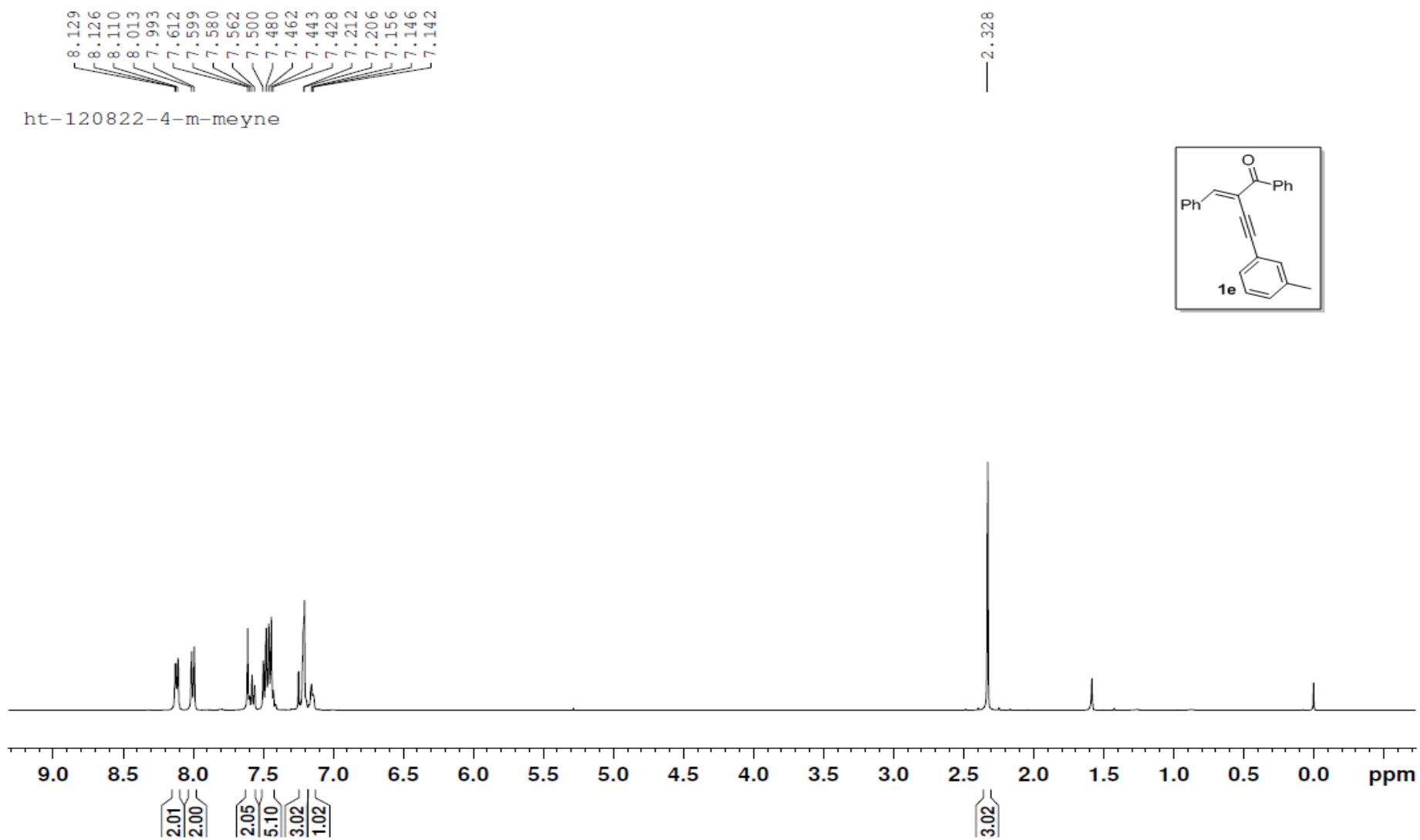


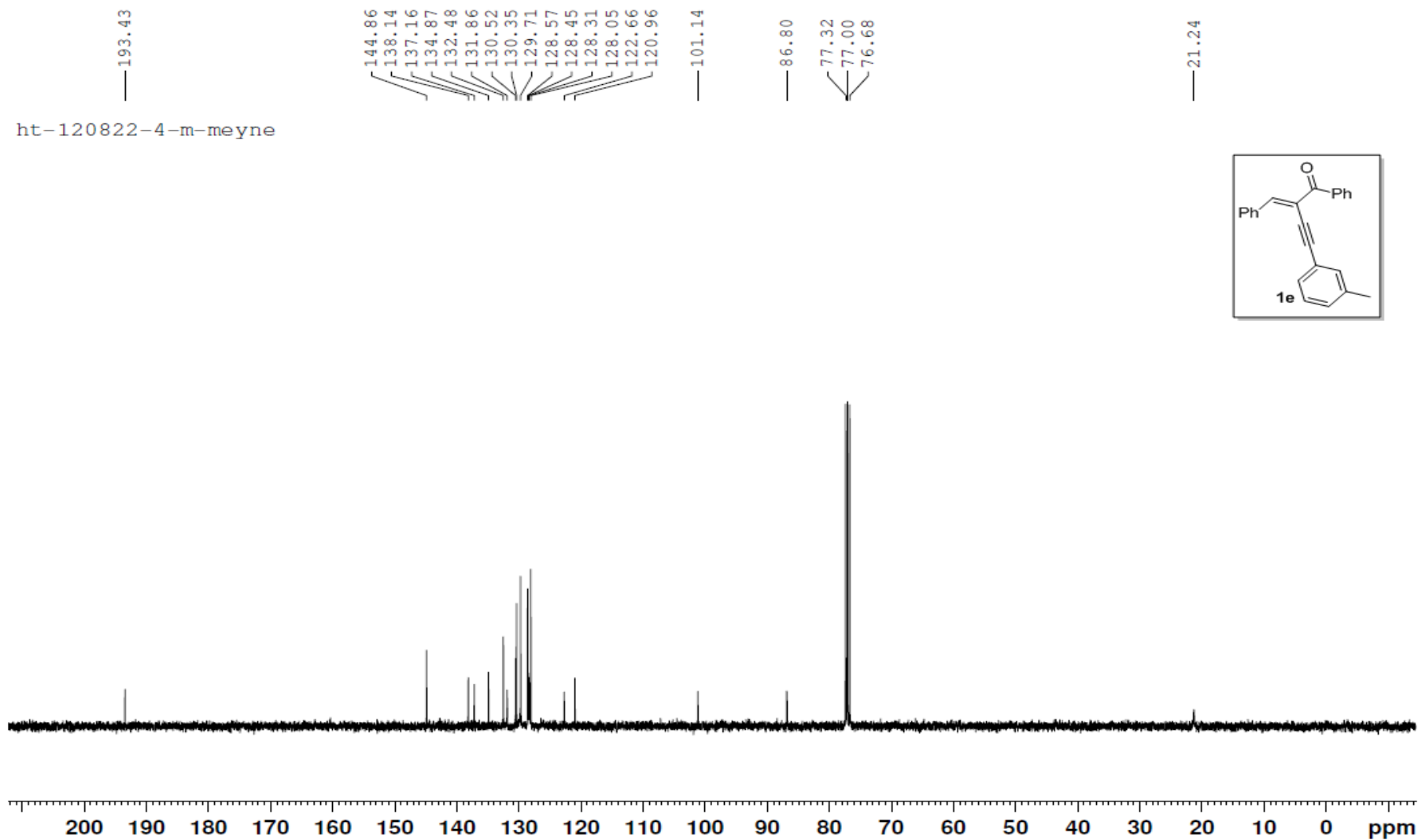








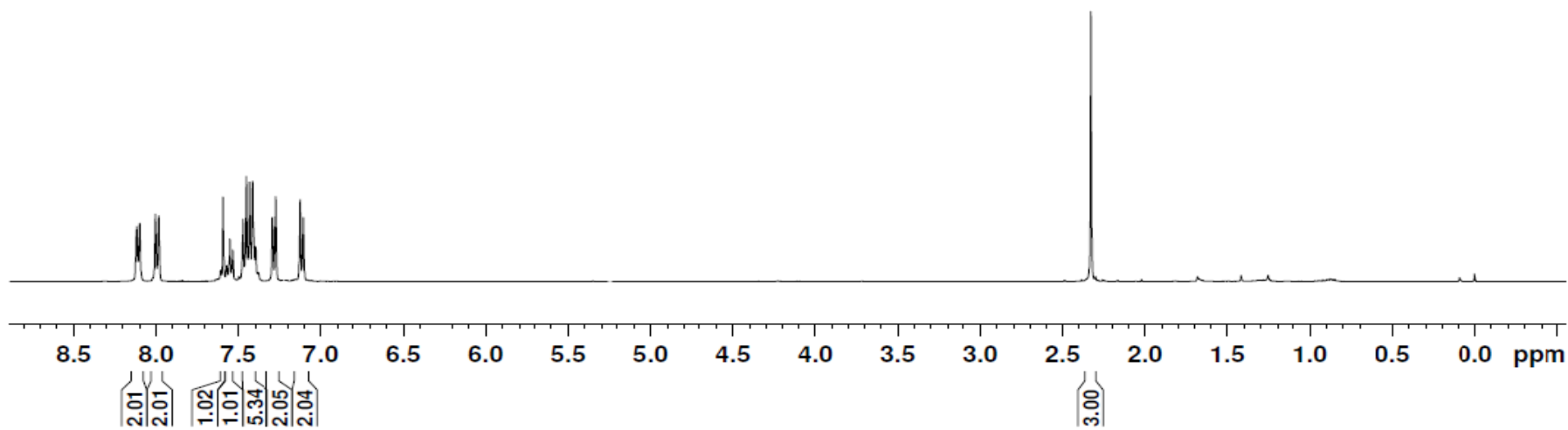
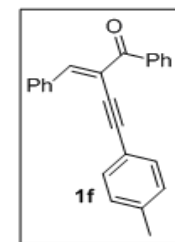


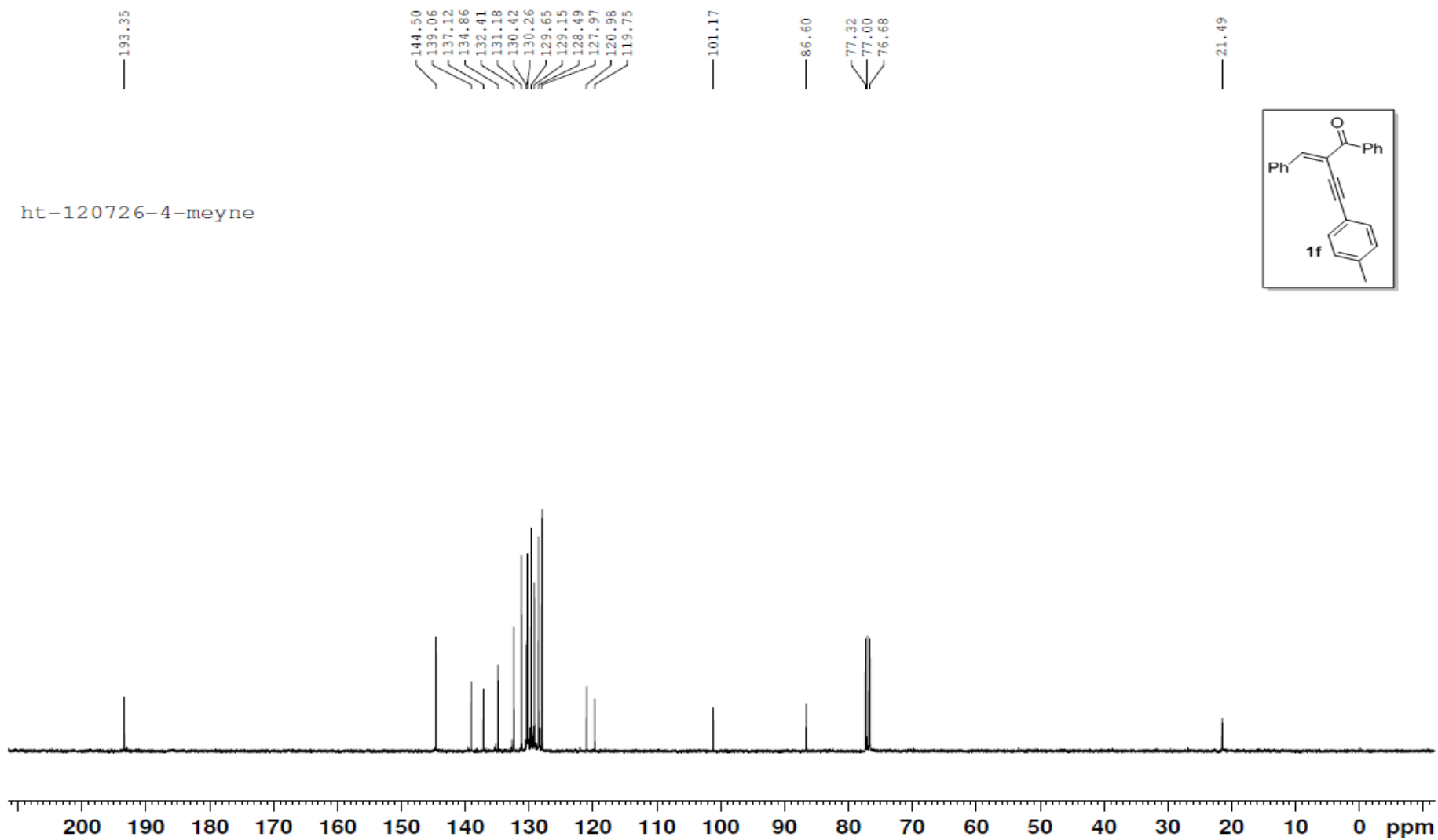


8.096
8.003
7.985
7.982
7.593
7.572
7.558
7.553
7.535
7.474
7.455
7.436
7.416
7.411
7.400
7.398
7.291
7.271
7.126
7.106

ht-120726-4-meyne

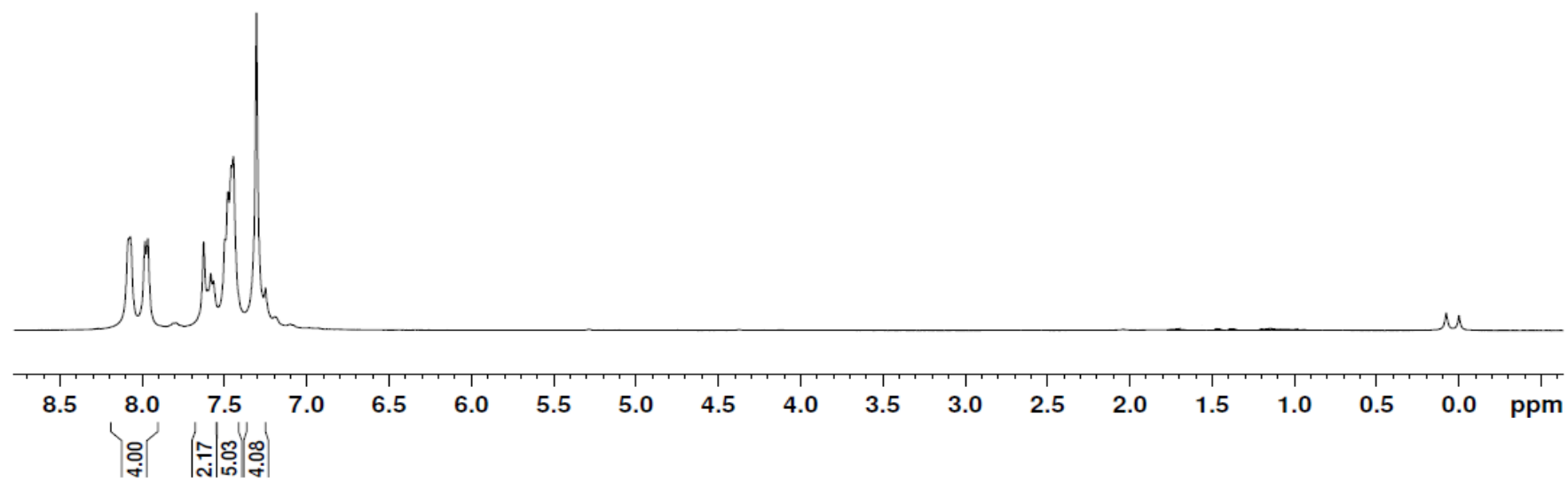
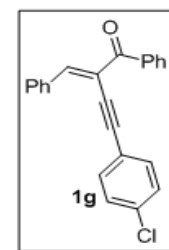
2.330

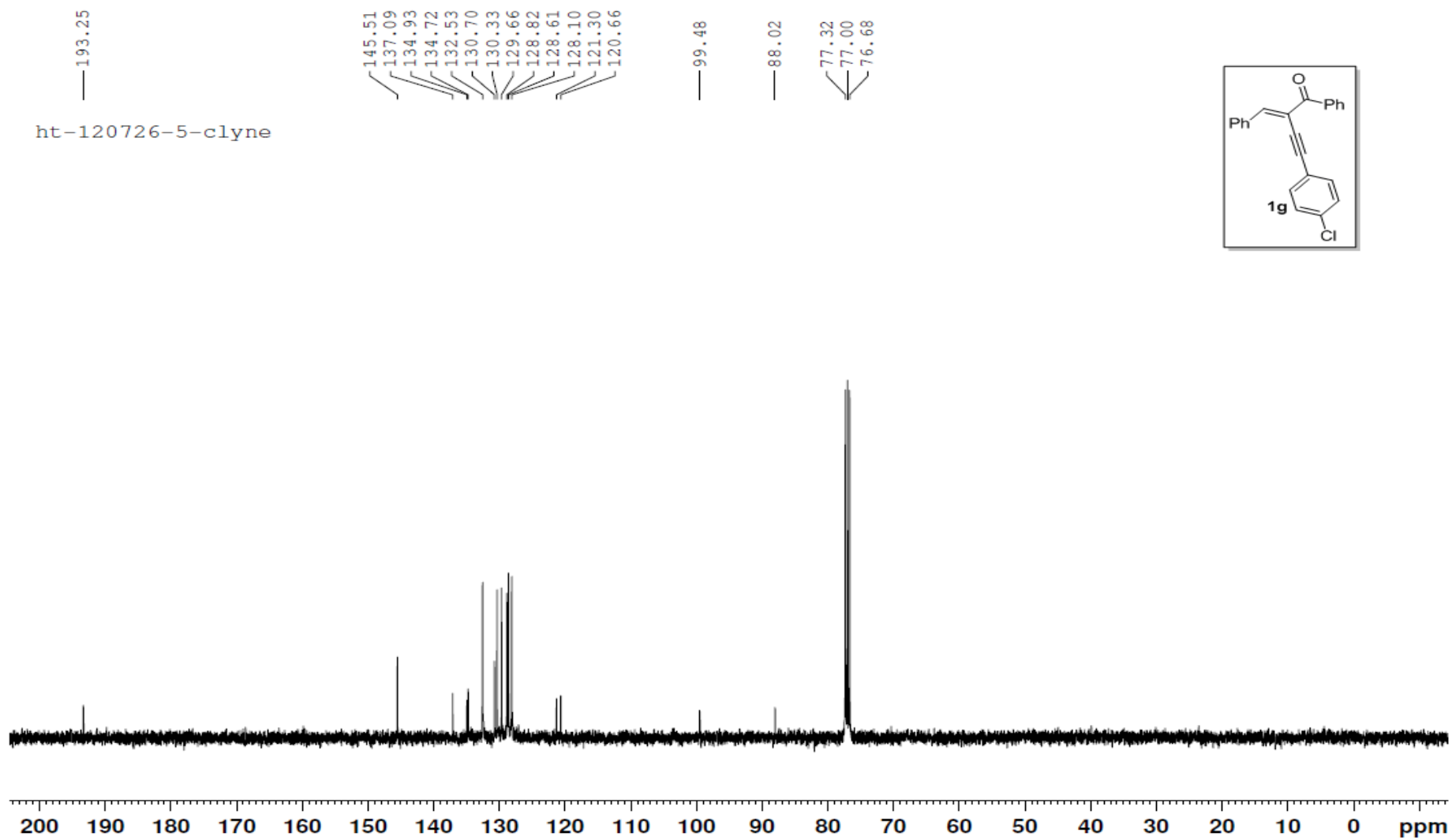




8.073
7.985
7.968
7.628
7.604
7.585
7.569
7.498
7.481
7.461
7.448
7.307
7.253

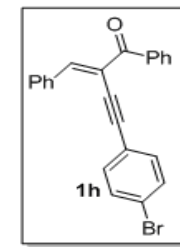
ht-120726-5-clyne



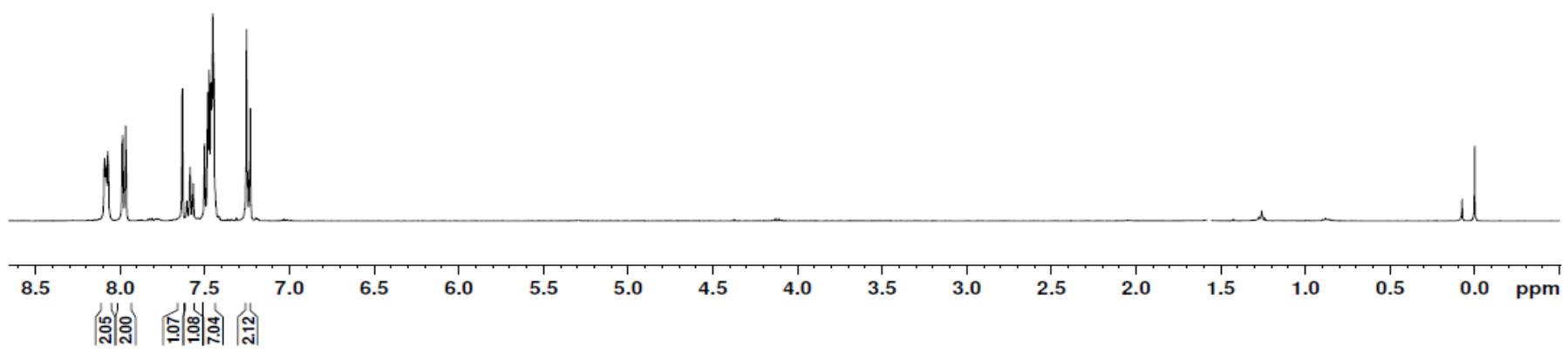


8.085
8.072
8.068
7.985
7.967
7.963
7.634
7.607
7.589
7.570
7.503
7.484
7.476
7.472
7.465
7.460
7.455
7.448
7.255
7.233

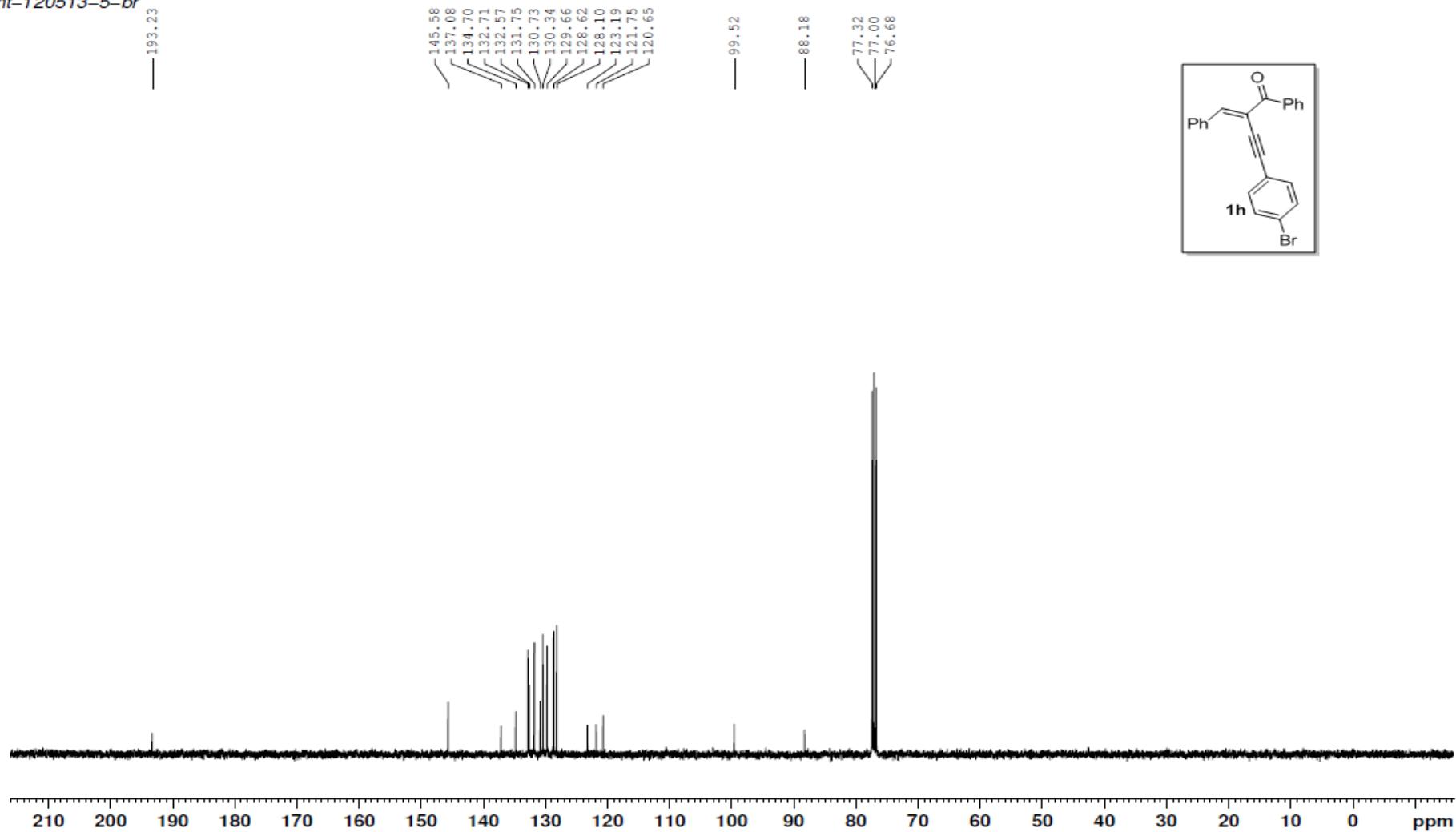
ht-120513-5-br



0.000



ht-120513-5-br

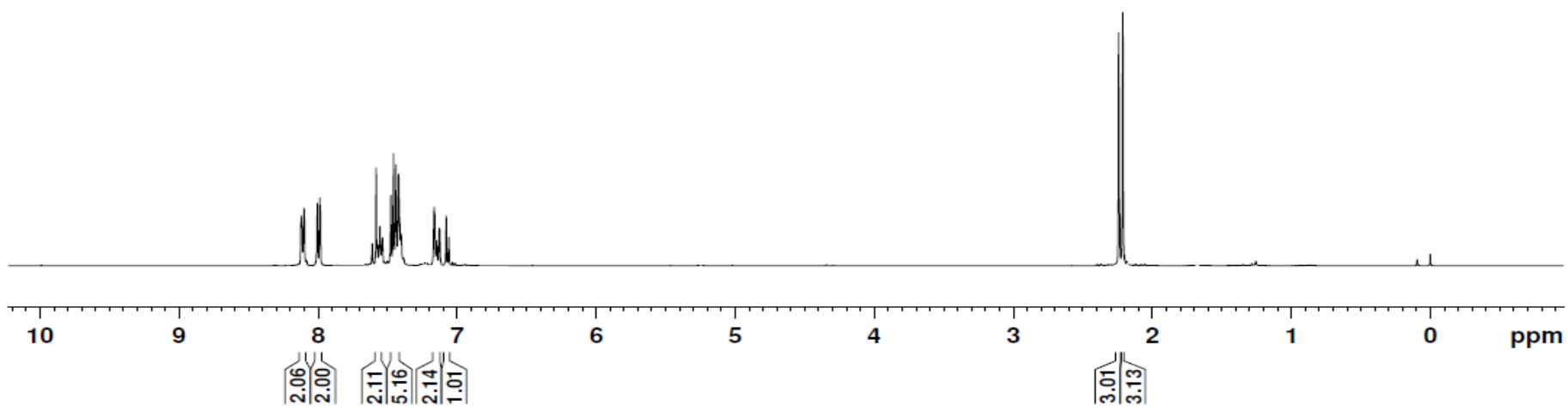
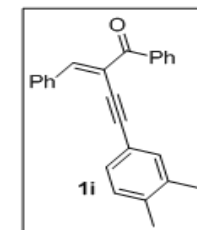


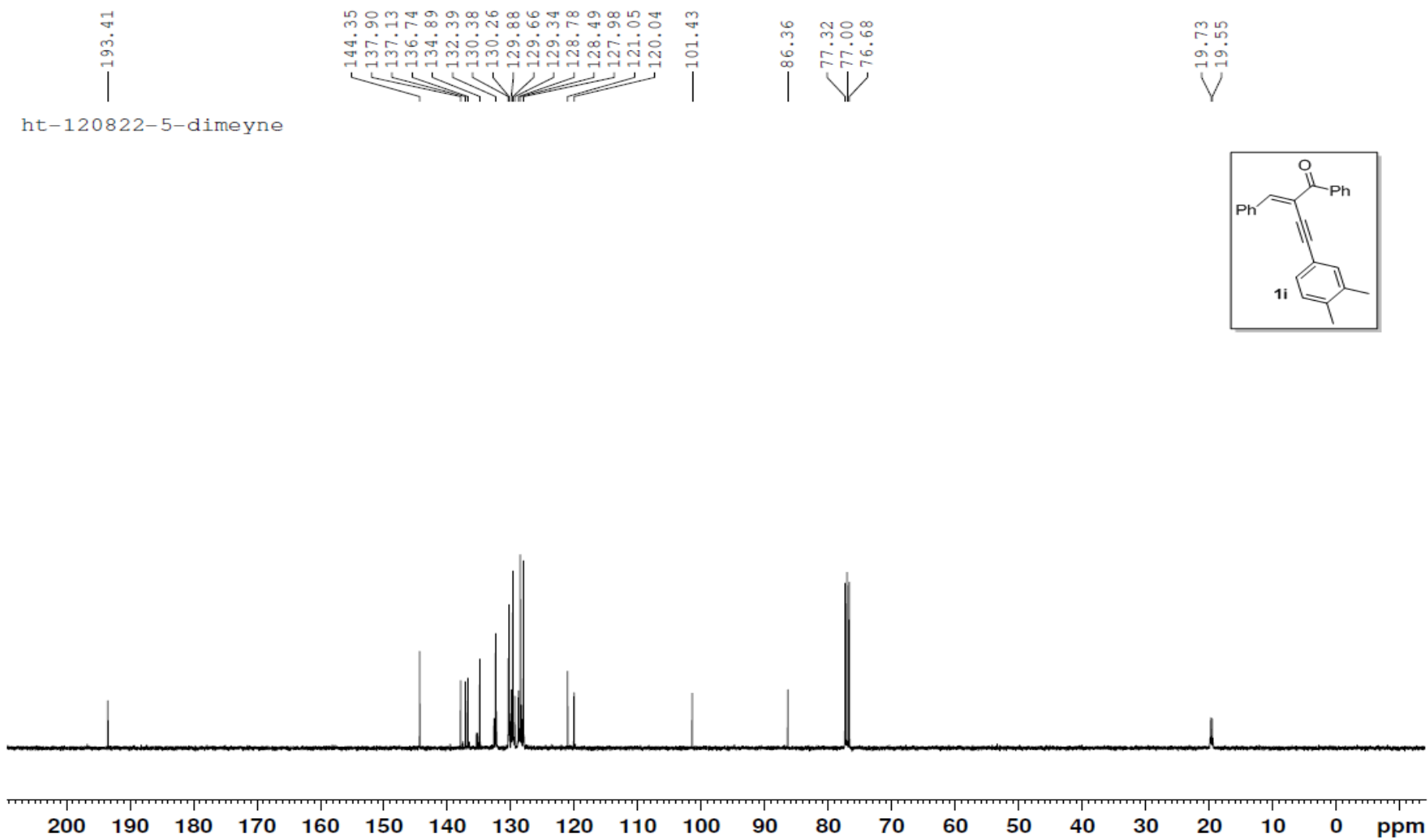
8.124
8.120
8.104
8.007
7.989
7.985
7.816
7.798
7.795
7.782
7.778
7.764
7.755
7.751
7.612
7.584
7.563
7.557
7.542
7.539
7.479
7.459
7.441
7.422
7.414
7.407
7.404
7.165
7.149
7.129
7.080
7.061

ht-120822-5-dimeyne

2.241
2.213

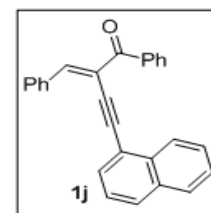
0.000



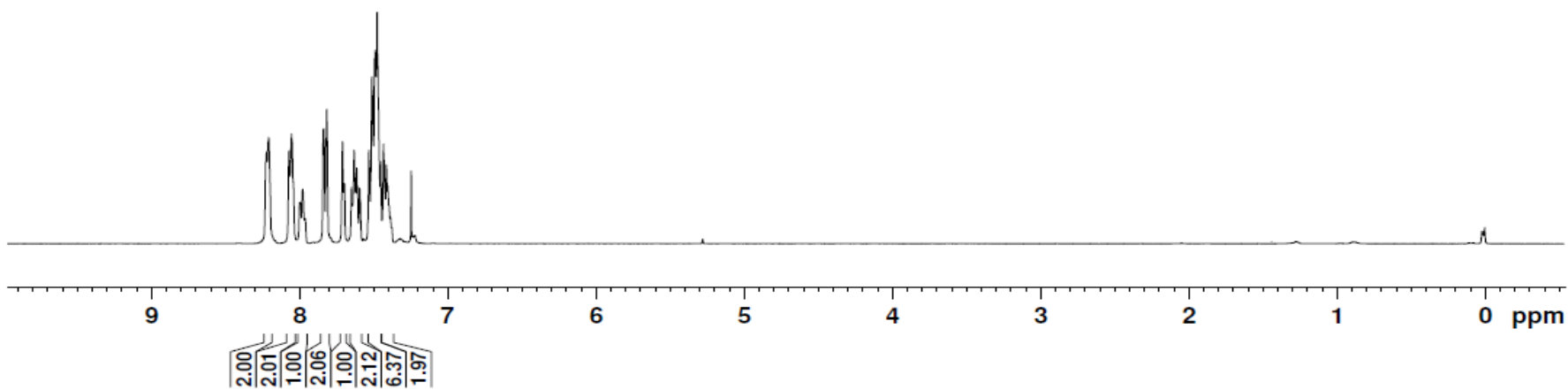


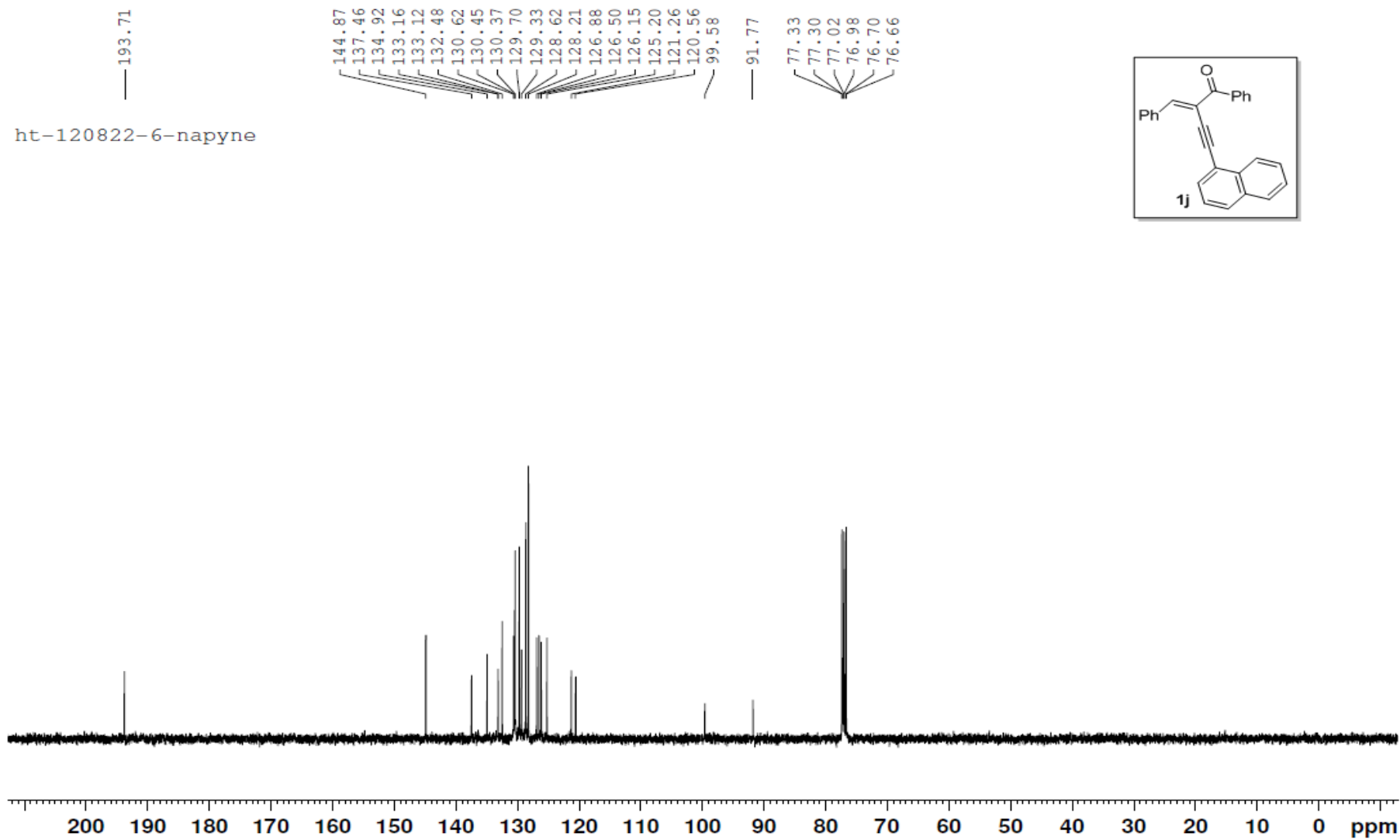
8.223
8.209
8.071
8.053
7.998
7.979
7.963
7.838
7.817
7.710
7.698
7.649
7.631
7.622
7.618
7.613
7.609
7.594
7.532
7.529
7.513
7.508
7.494
7.489
7.476
7.471
7.453
7.432
7.415
7.404

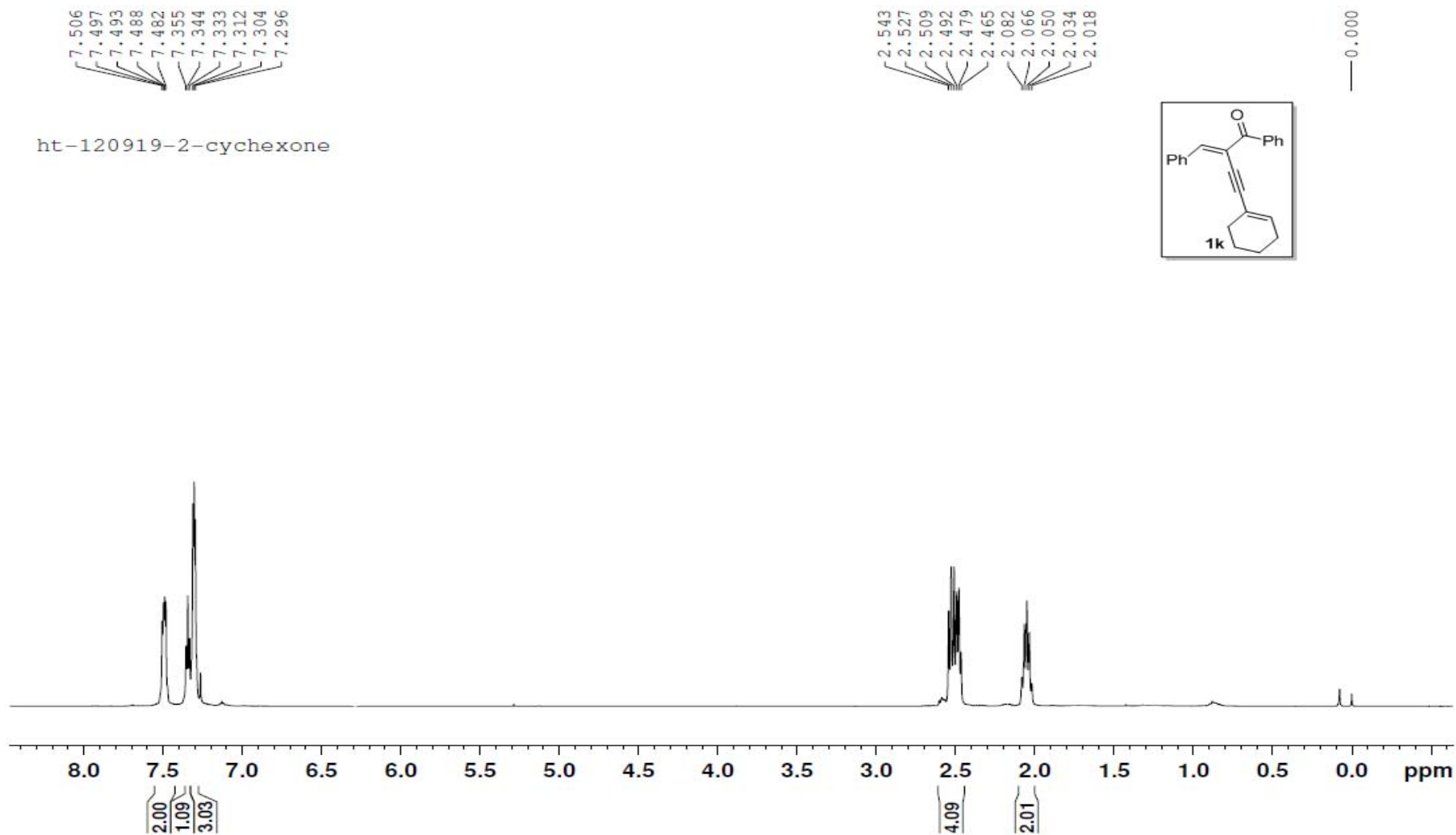
ht-120822-6-napyne|

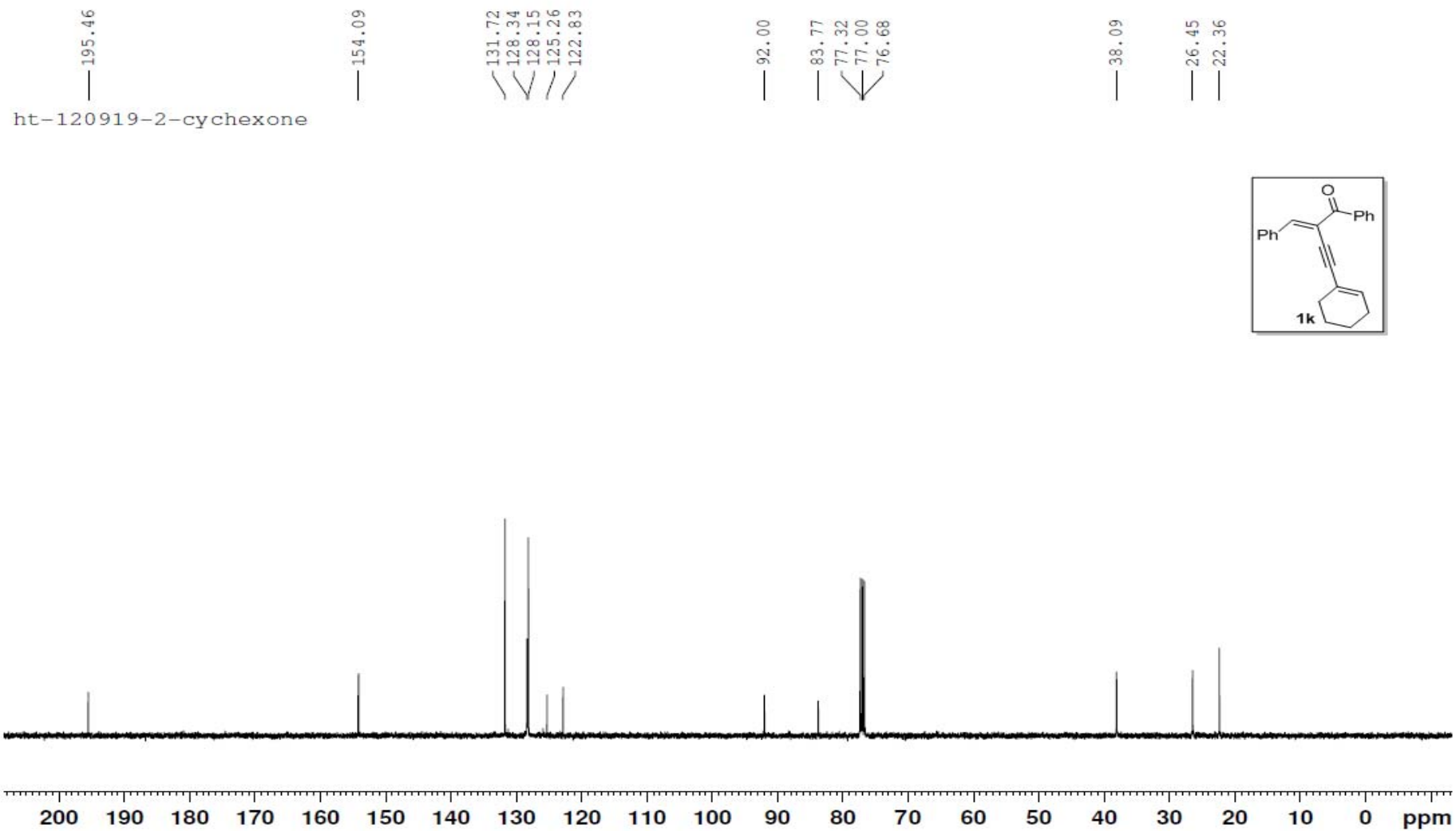


0.000





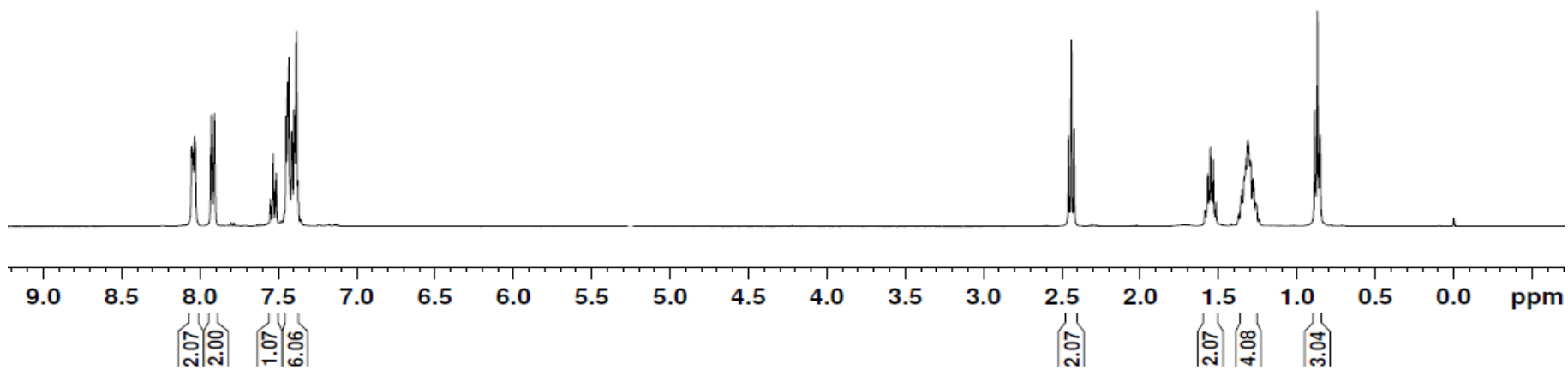
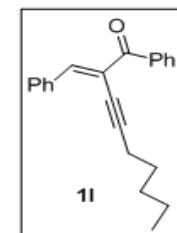


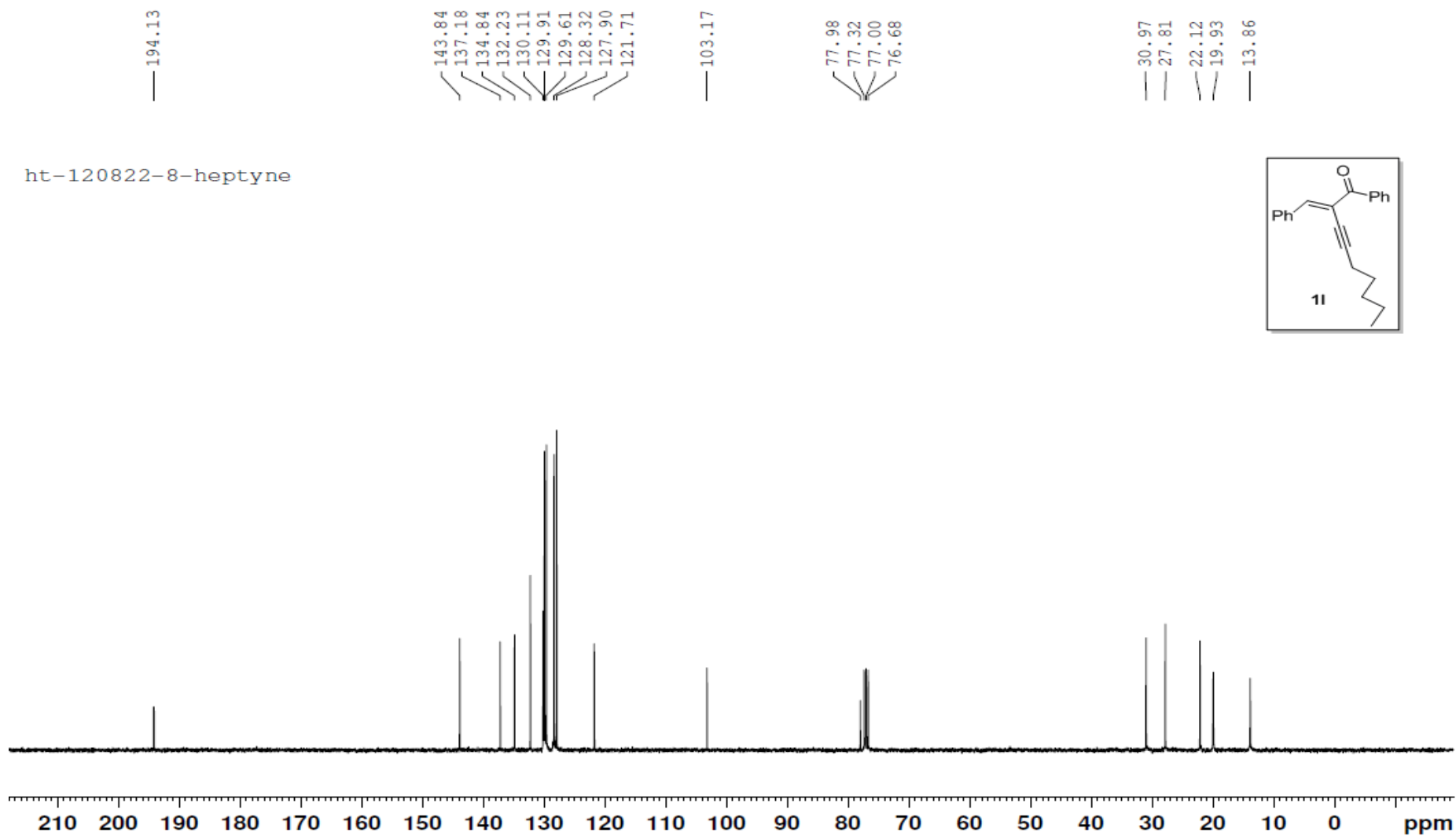


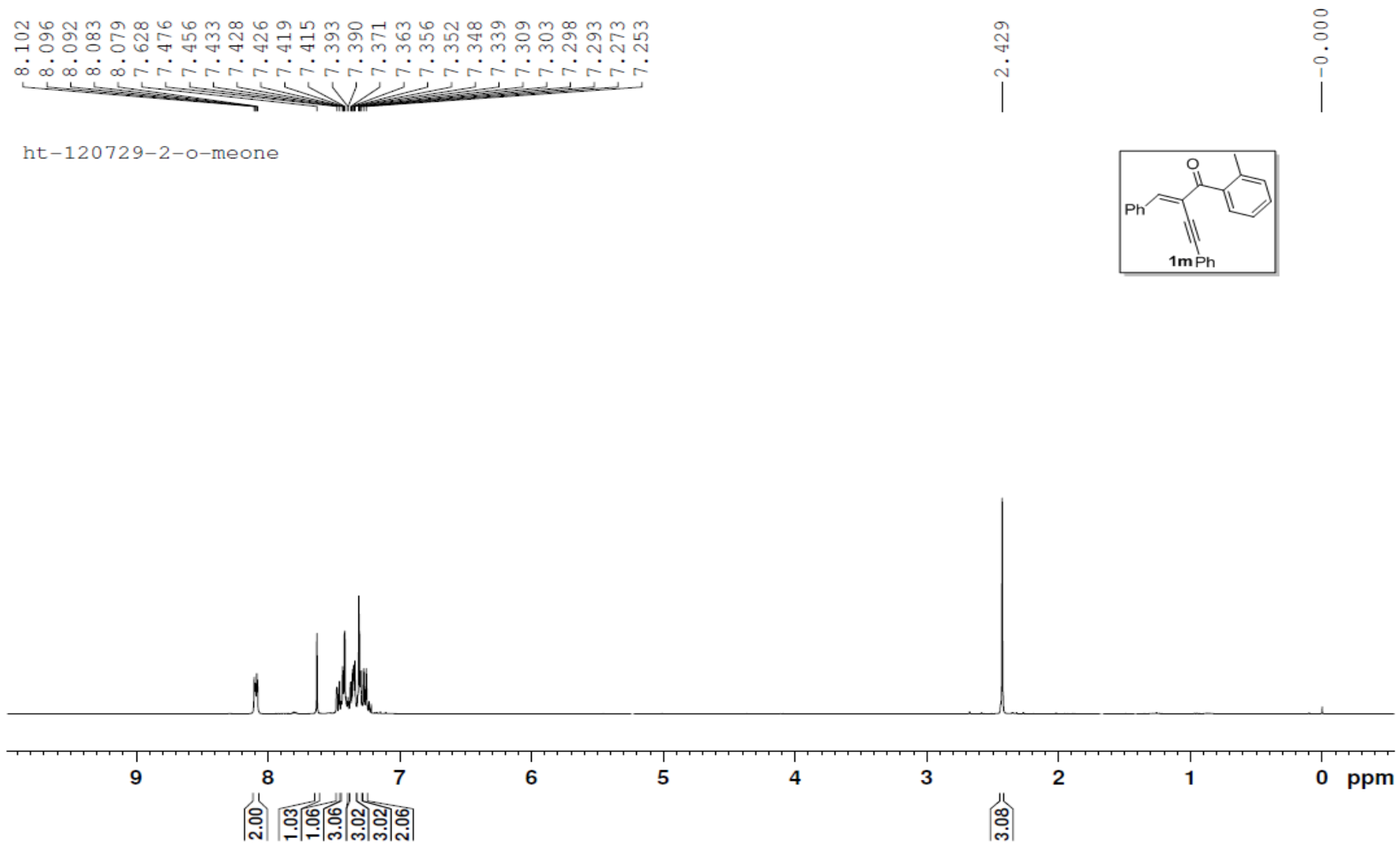
8.051
8.045
8.032
8.028
7.925
7.907
7.904
7.547
7.529
7.513
7.510
7.448
7.445
7.439
7.429
7.421
7.411
7.398
7.391
7.384
7.380
7.373

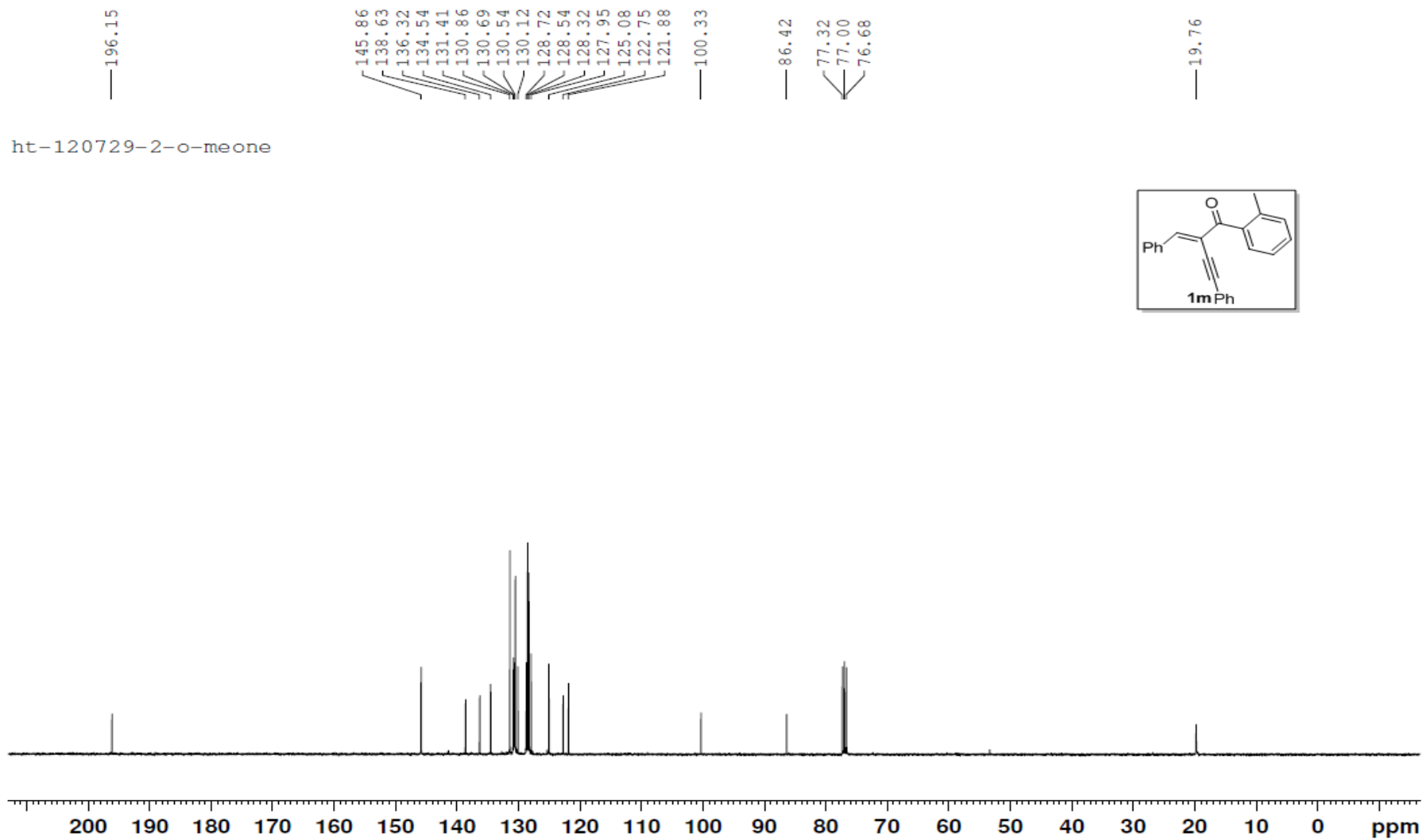
ht-120822-8-heptyne

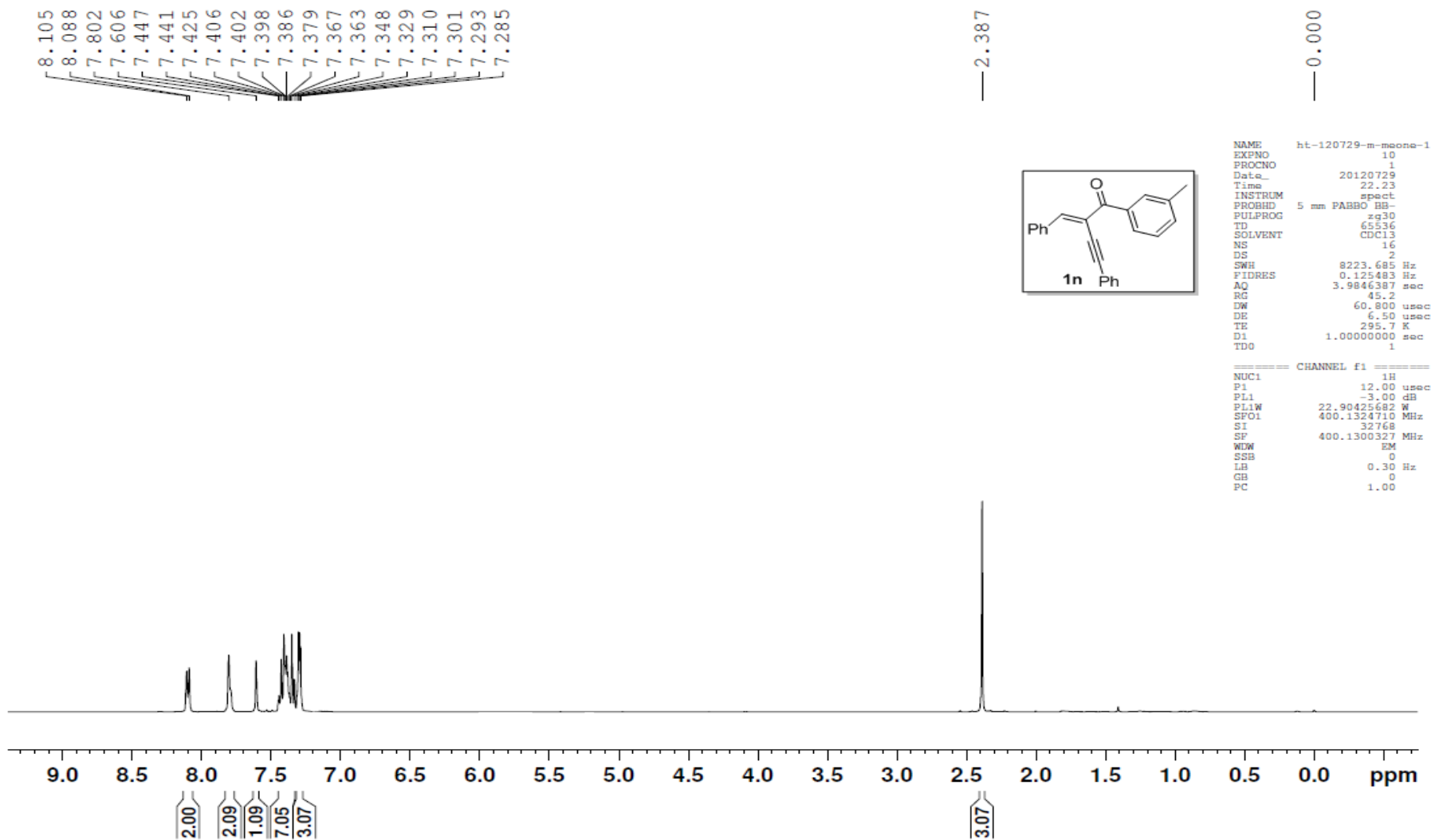
2.457
2.440
2.422
1.588
1.570
1.552
1.534
1.516
1.356
1.348
1.339
1.333
1.325
1.312
1.307
1.298
1.295
1.280
1.262
0.887
0.870
0.852
-0.000

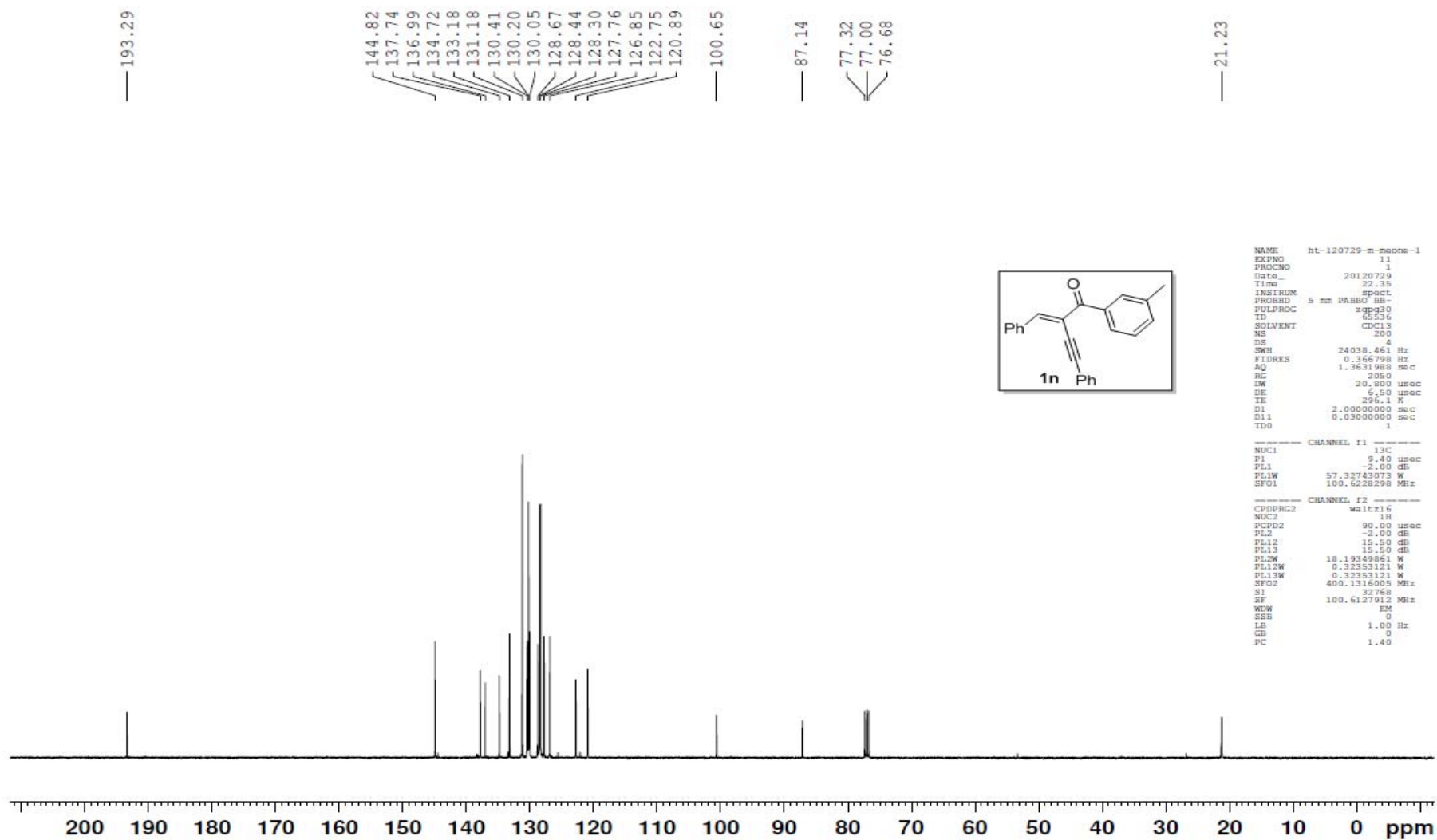






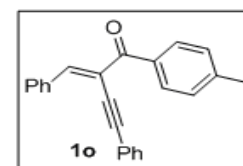






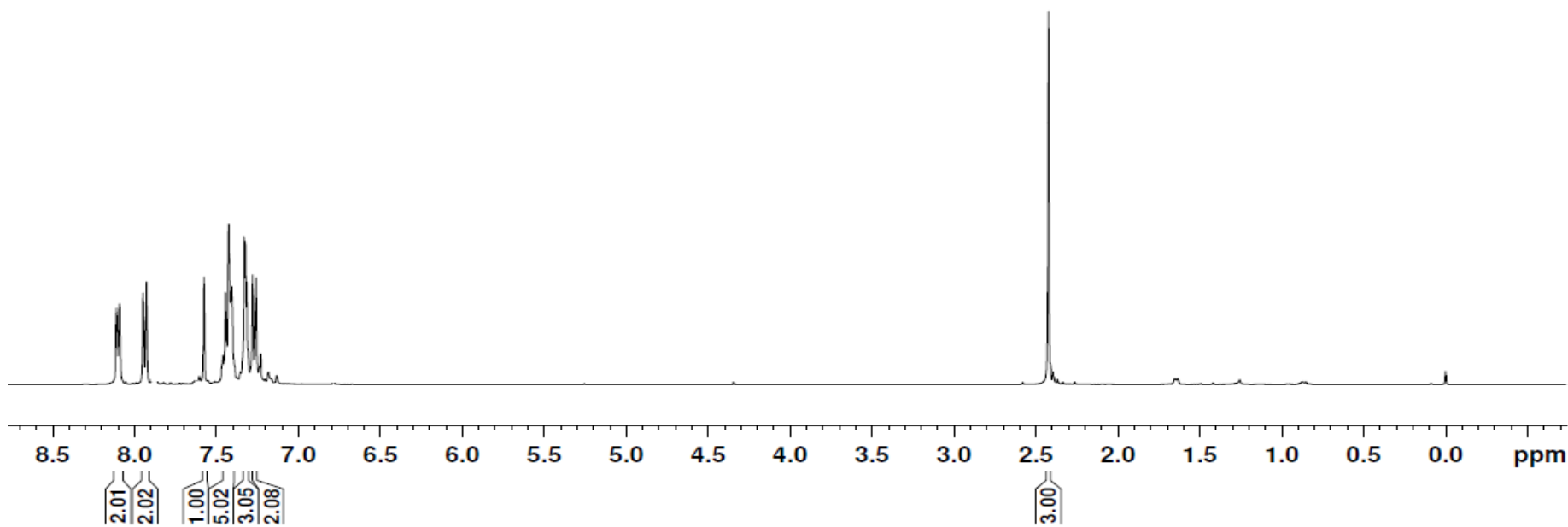
8.107
8.088
7.946
7.926
7.575
7.443
7.423
7.412
7.411
7.409
7.406
7.403
7.329
7.322
7.313
7.277
7.257

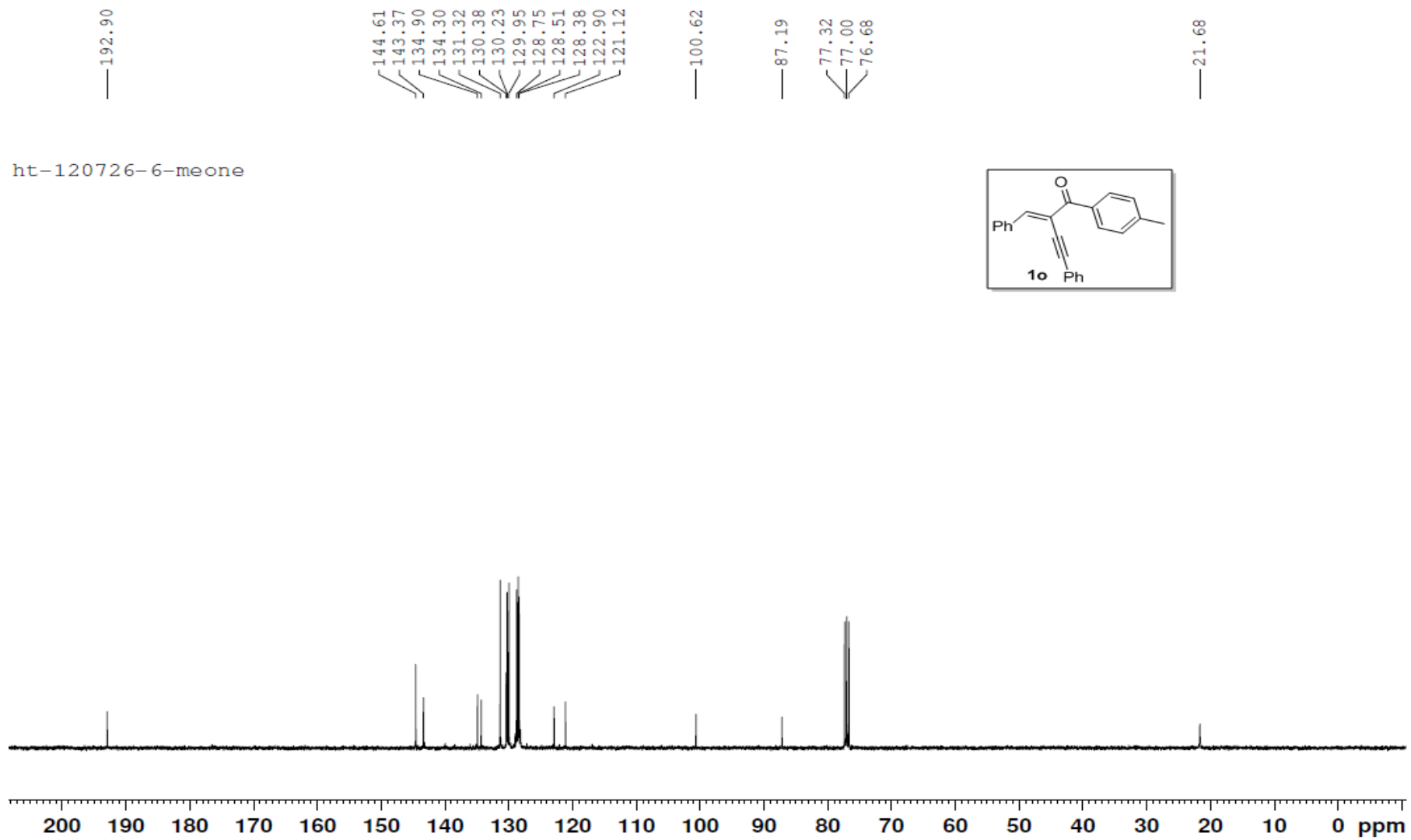
ht-120726-6-meone

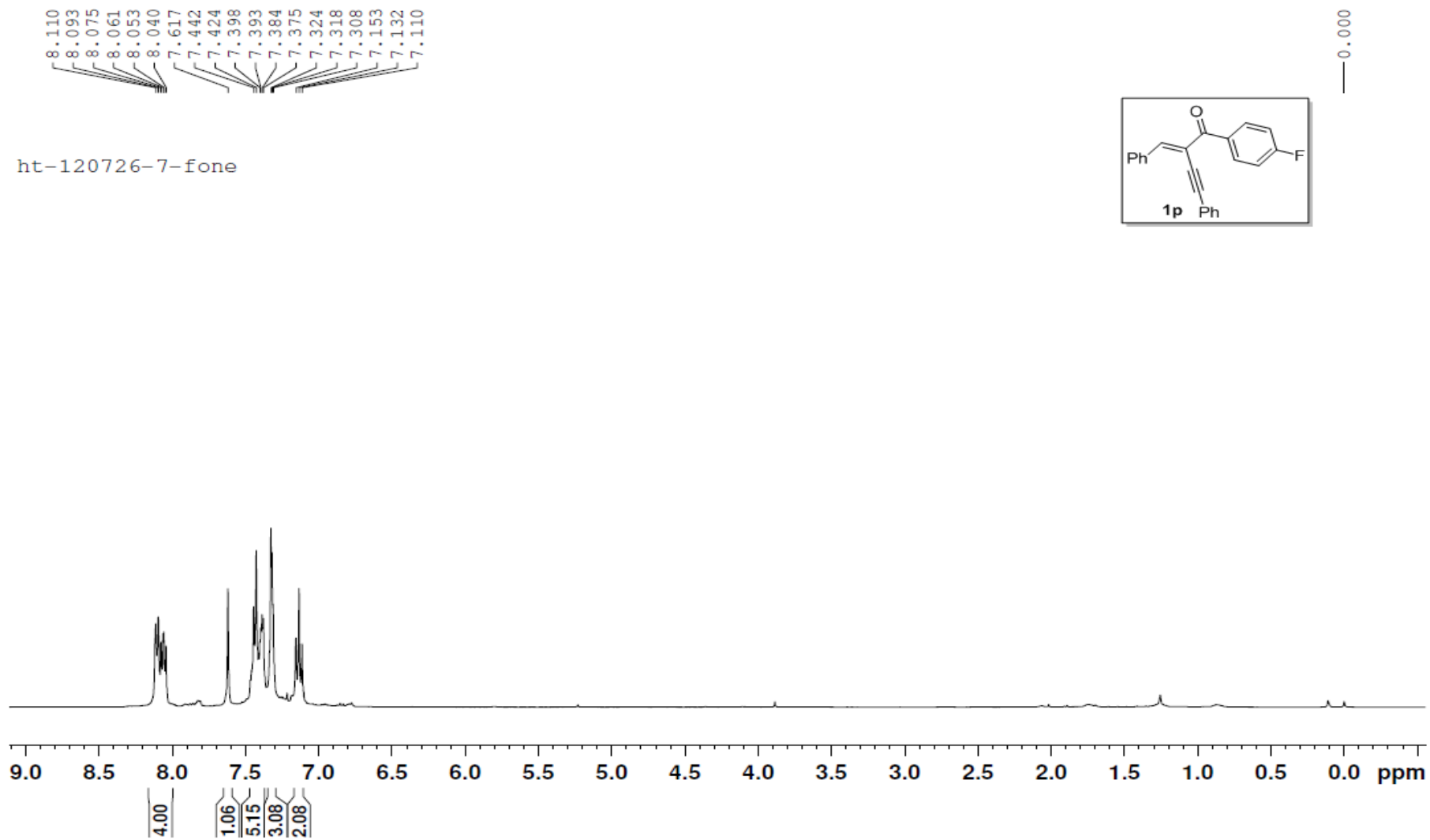


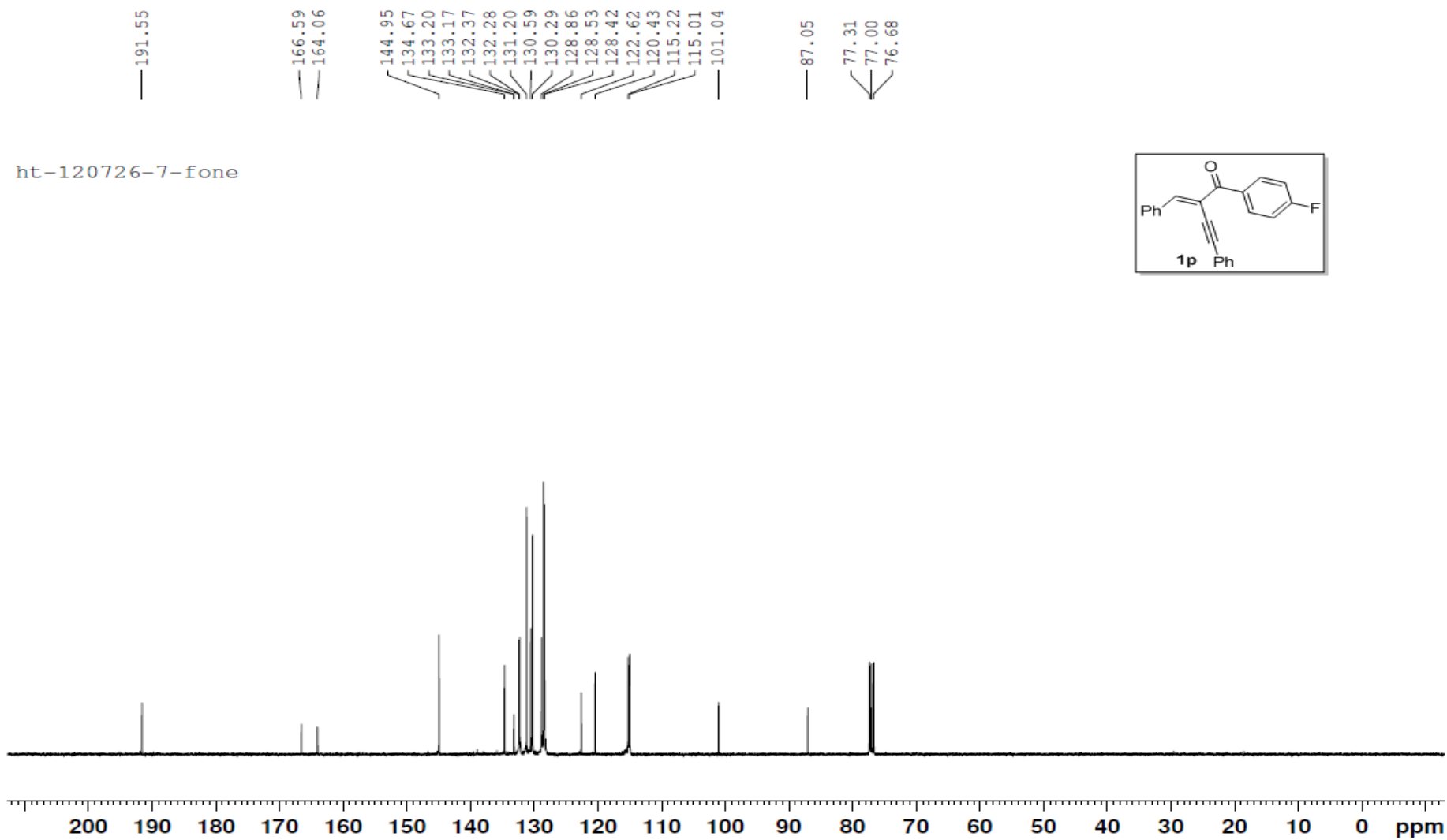
2.423

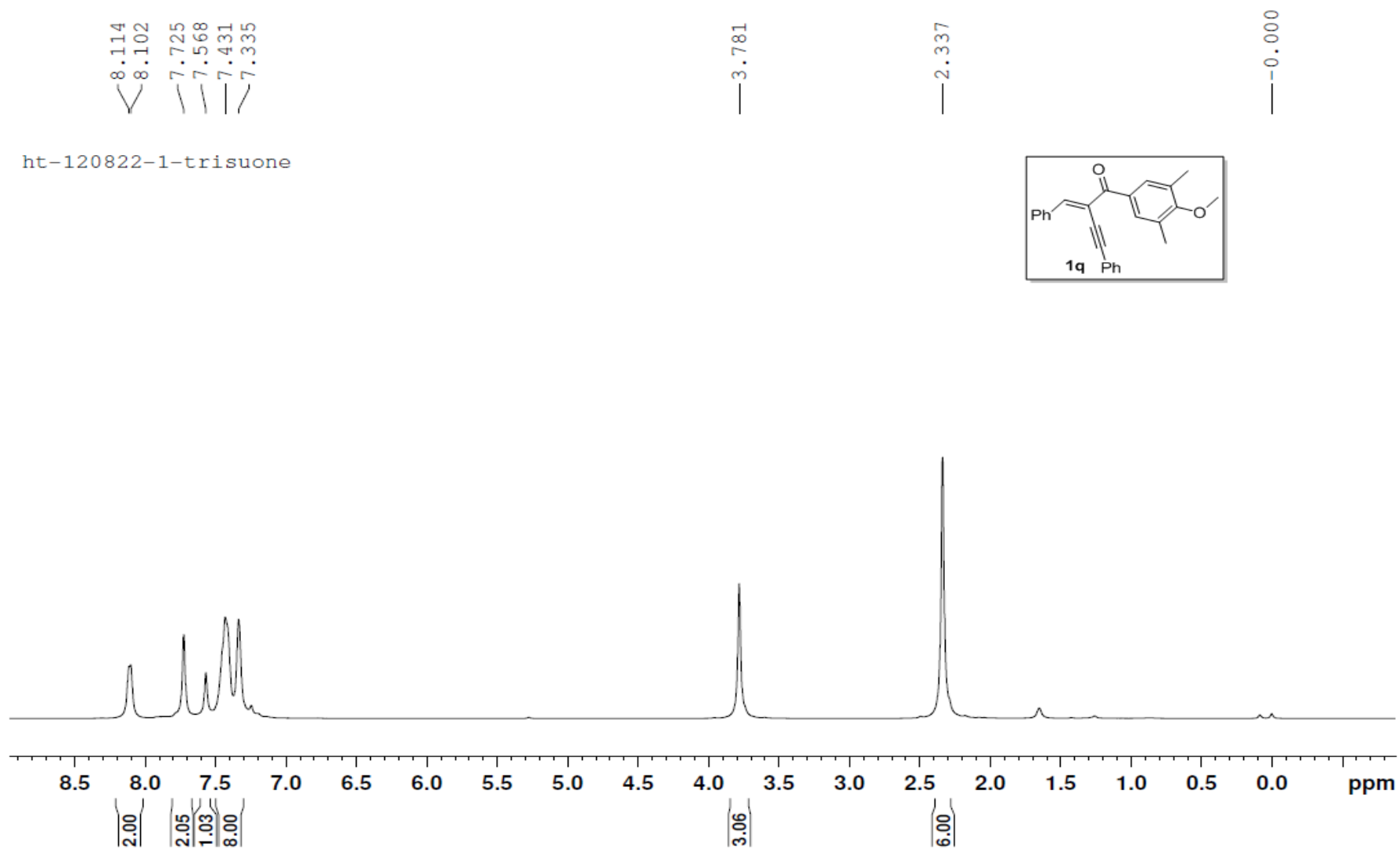
0.000

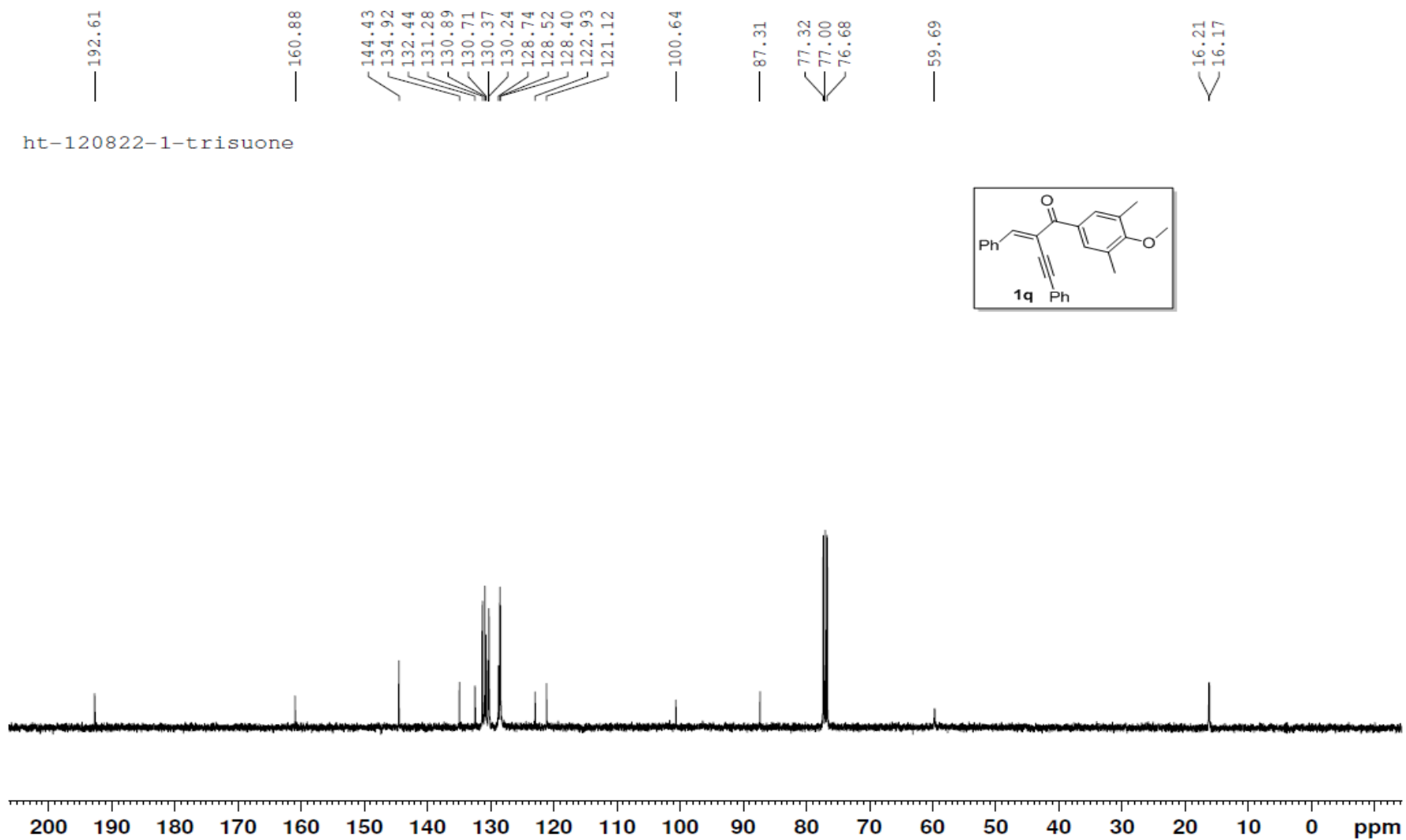








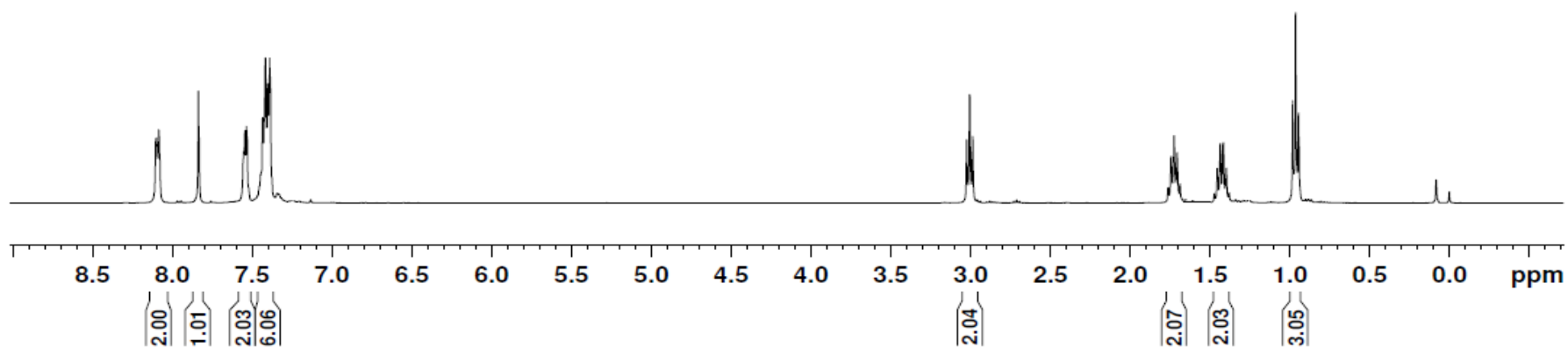
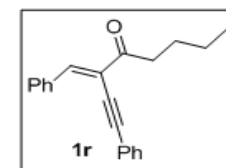


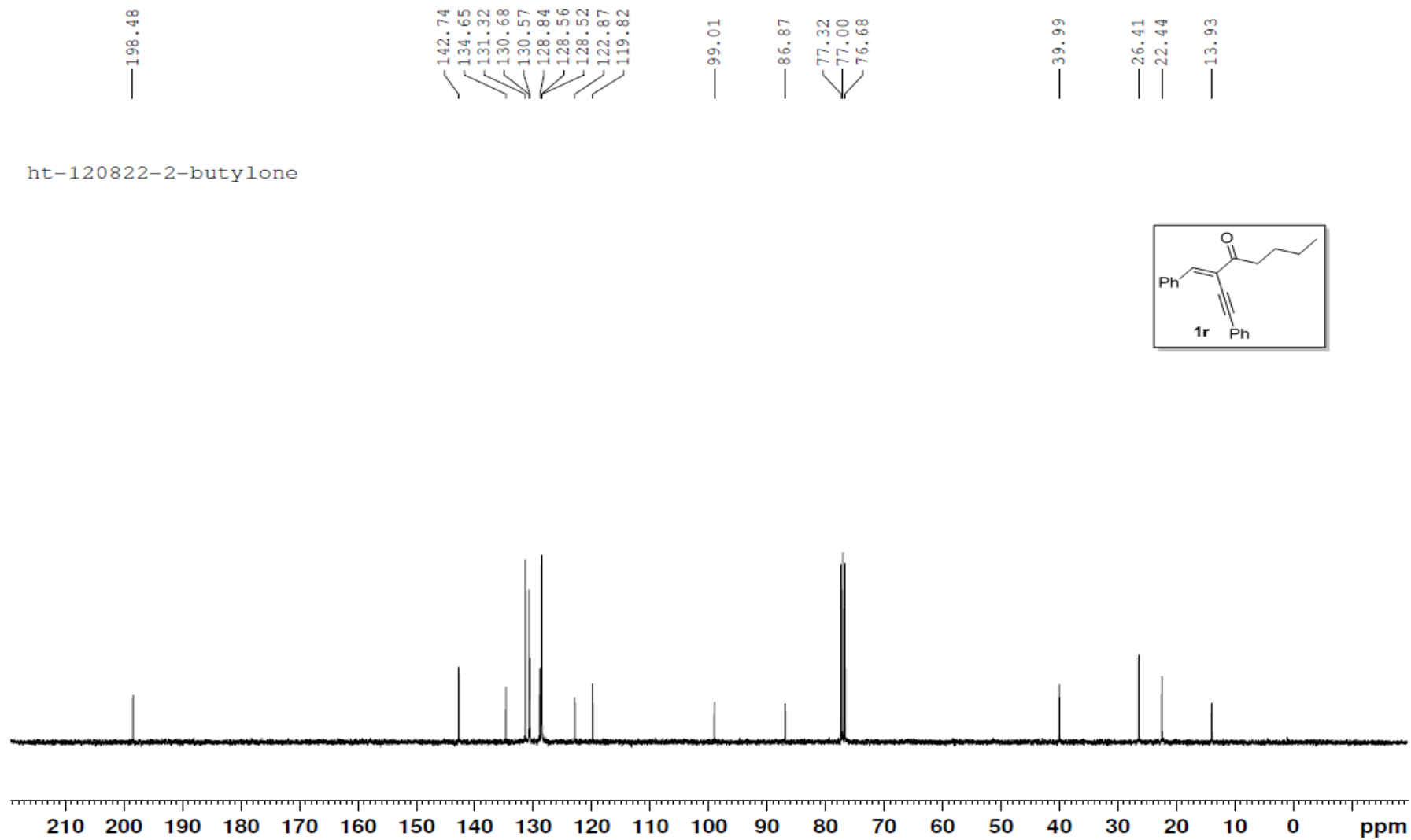


8.100
8.095
8.081
7.835
7.554
7.544
7.535
7.530
7.434
7.416
7.402
7.390
7.385

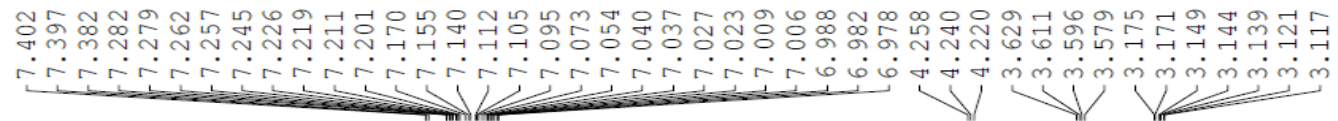
3.023
3.004
2.986
1.761
1.743
1.724
1.706
1.687
1.472
1.453
1.434
1.416
1.397
1.379
0.981
0.962
0.944

ht-120822-2-butylone

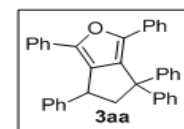




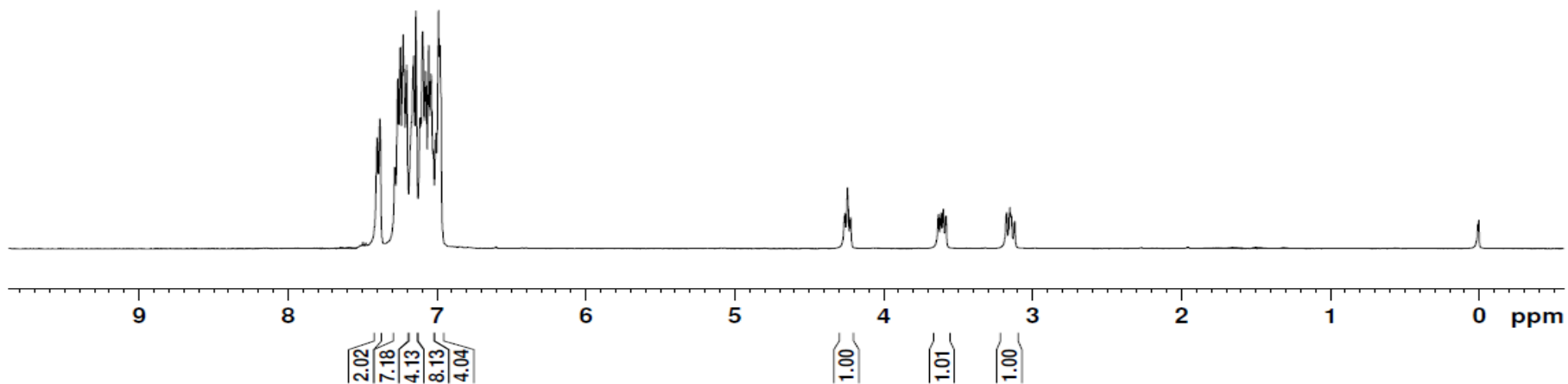
8. ^1H NMR and ^{13}C NMR spectra for compounds 3aa-3ra, 3ab-3af



ht-120513-1-rt



0.000



145.11
144.38
143.73
143.01
142.11
138.12
132.60
130.24
130.17
128.89
128.50
128.36
128.13
128.08
127.99
127.81
126.76
126.63
126.56
126.45
126.28
125.00
124.79

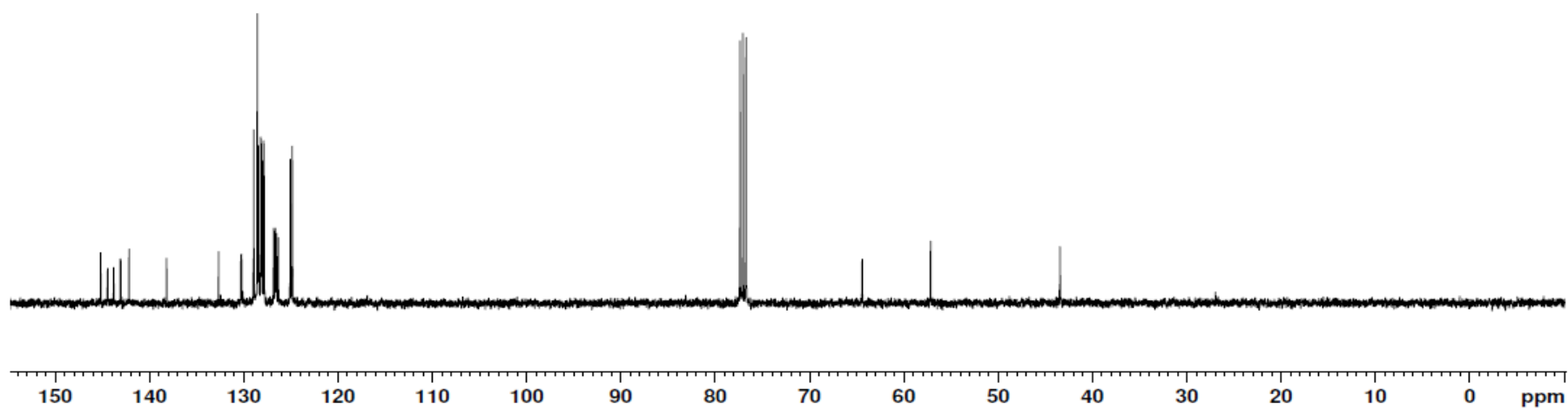
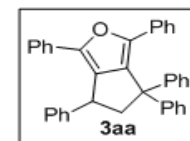
77.32
77.00
76.68

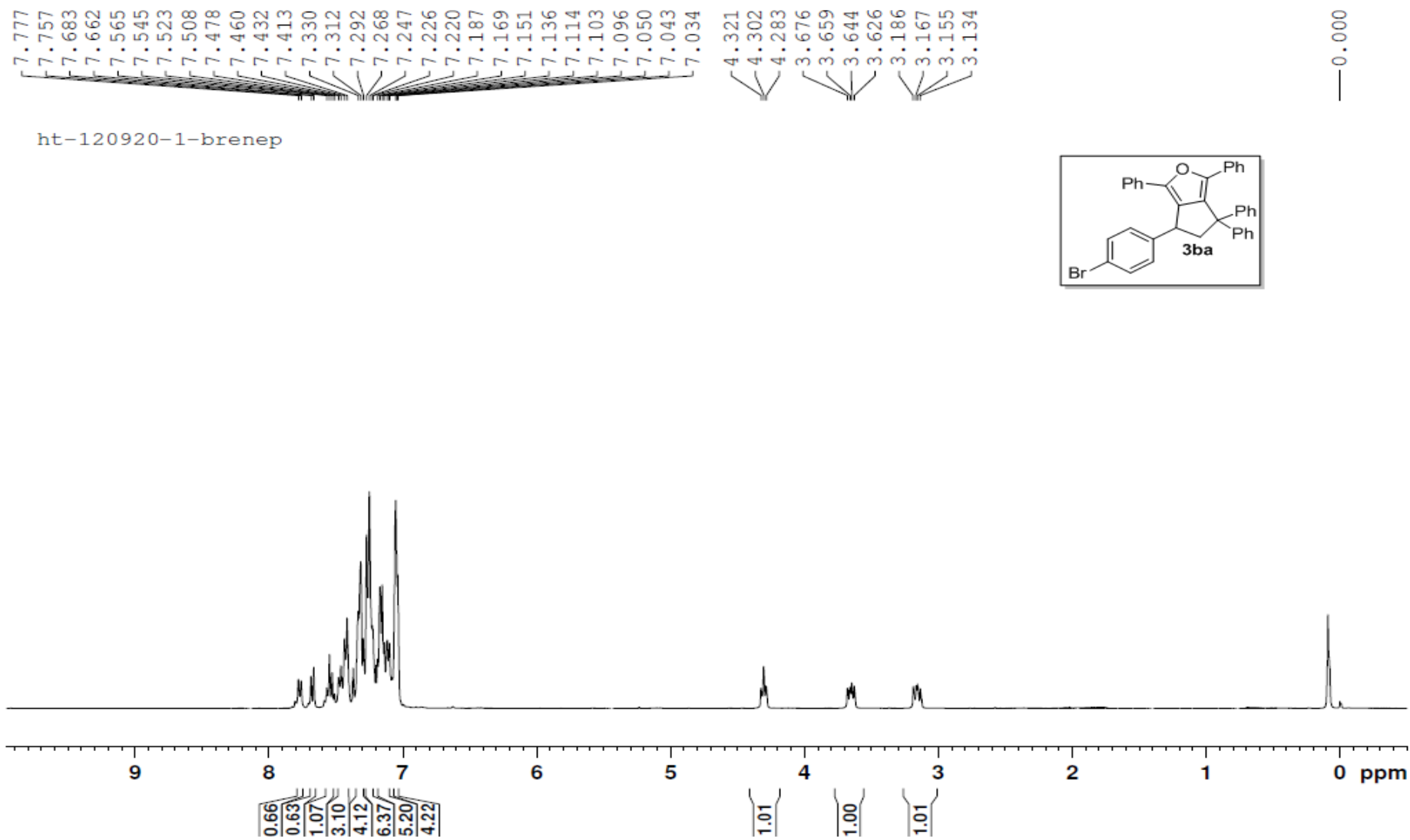
64.37

57.11

43.40

ht-120513-1-rt





144.52
143.78
143.09
141.13
137.95
131.95
131.86
131.79
131.48
130.06
130.00
129.50
129.44
128.75
128.48
128.37
128.28
128.12
128.00
126.78
126.73
126.38
124.98
124.68
120.10

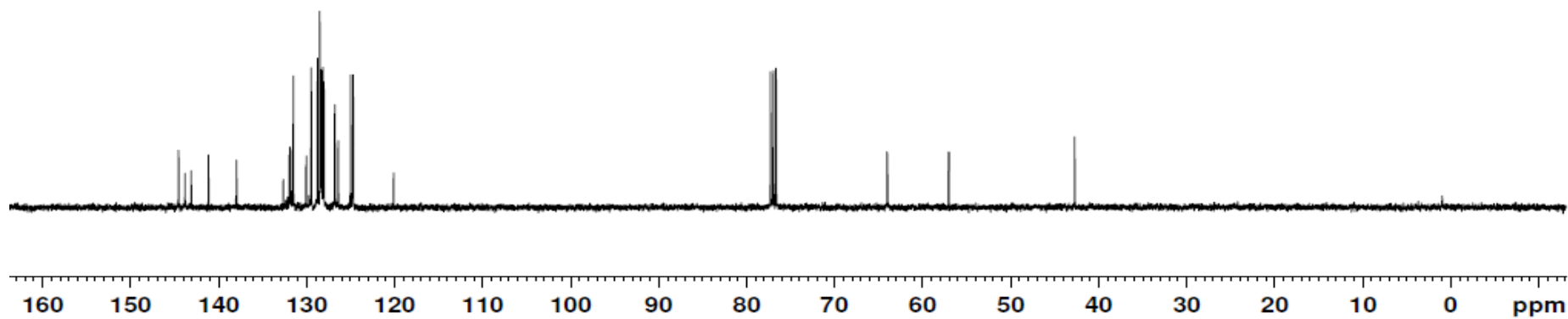
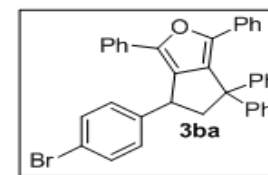
77.31
77.00
76.68

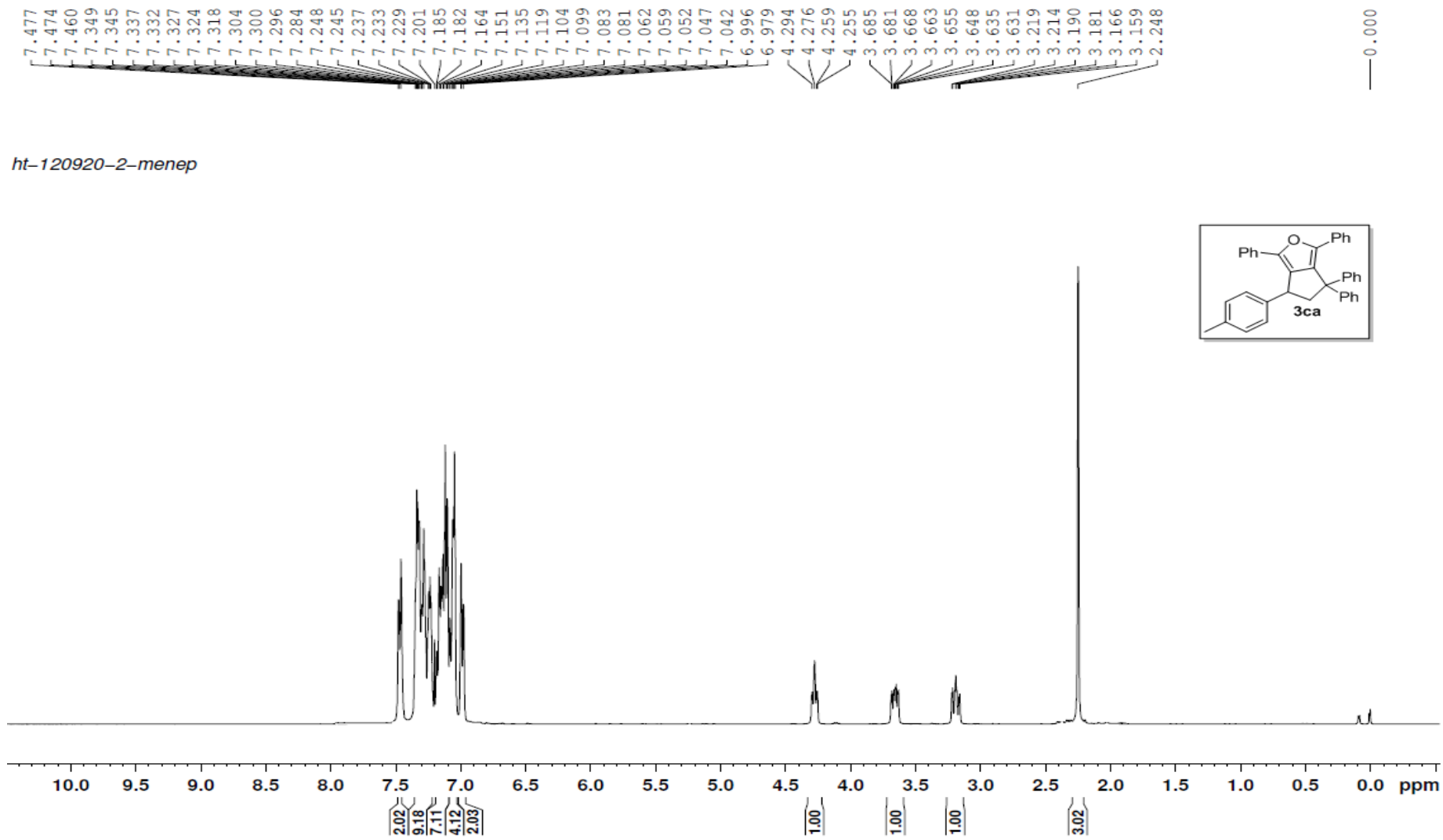
64.04

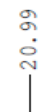
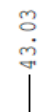
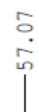
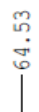
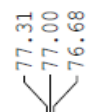
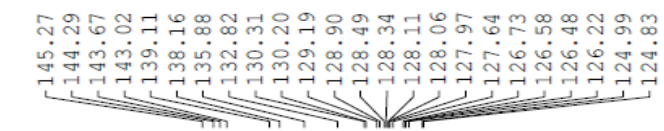
57.06

42.76

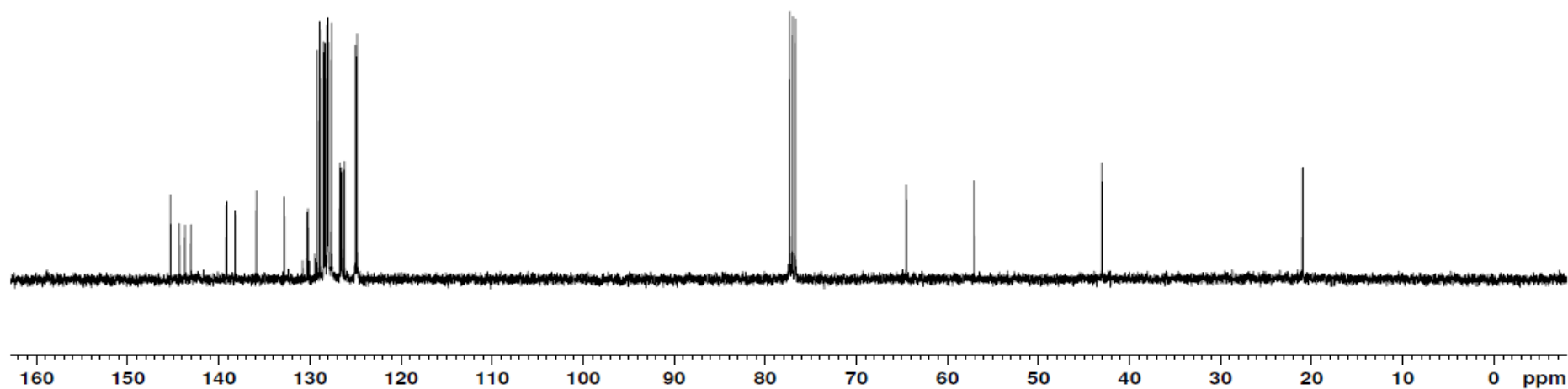
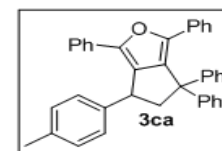
ht-120920-1-bresep



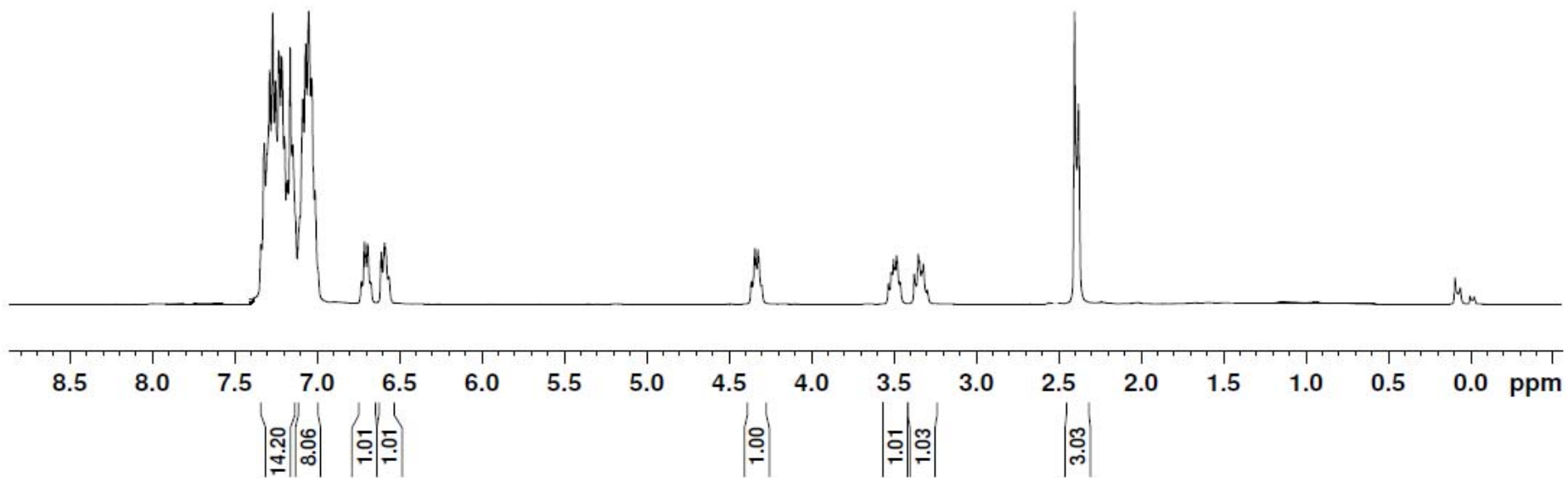
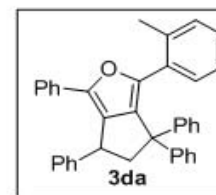


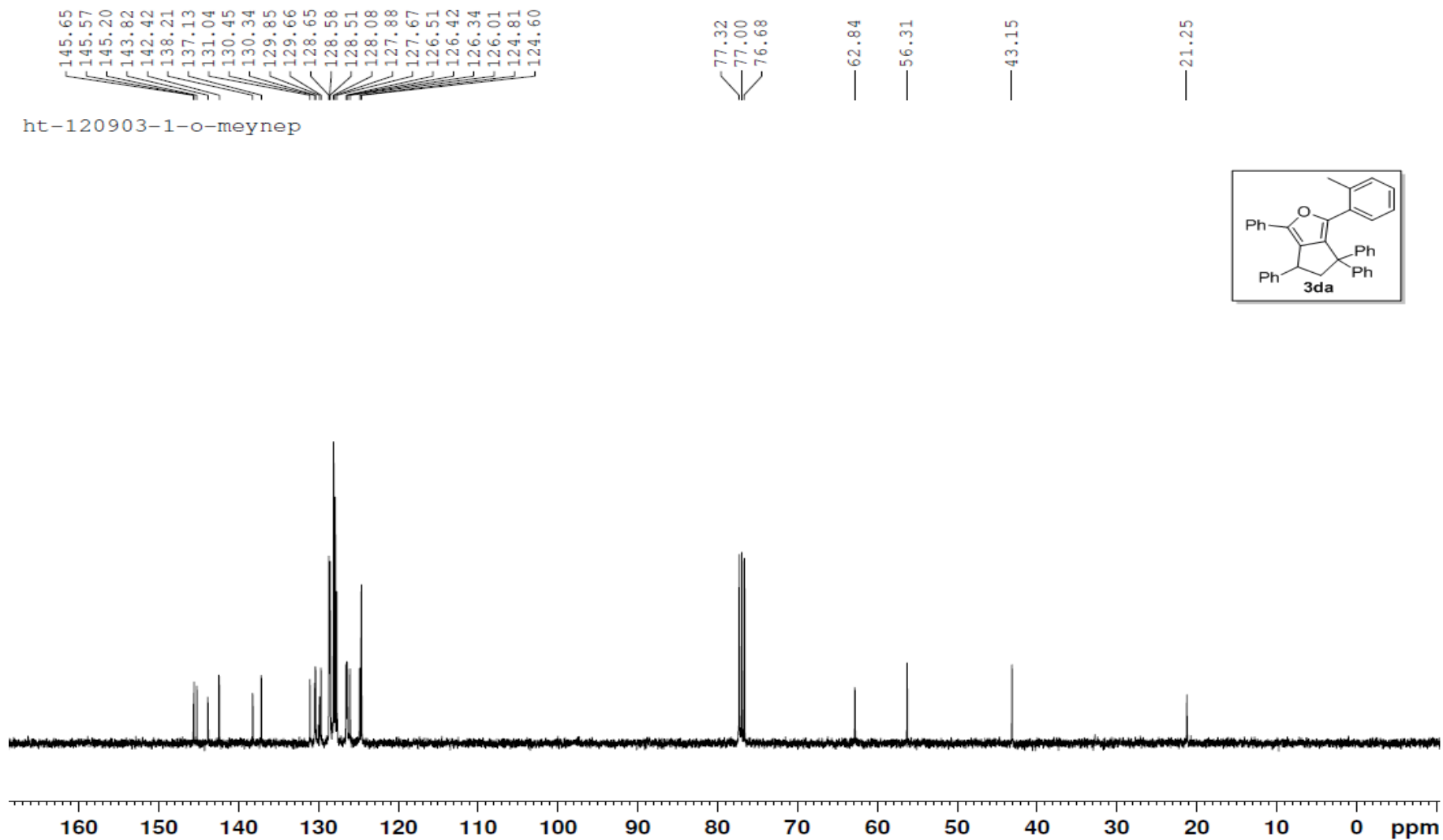


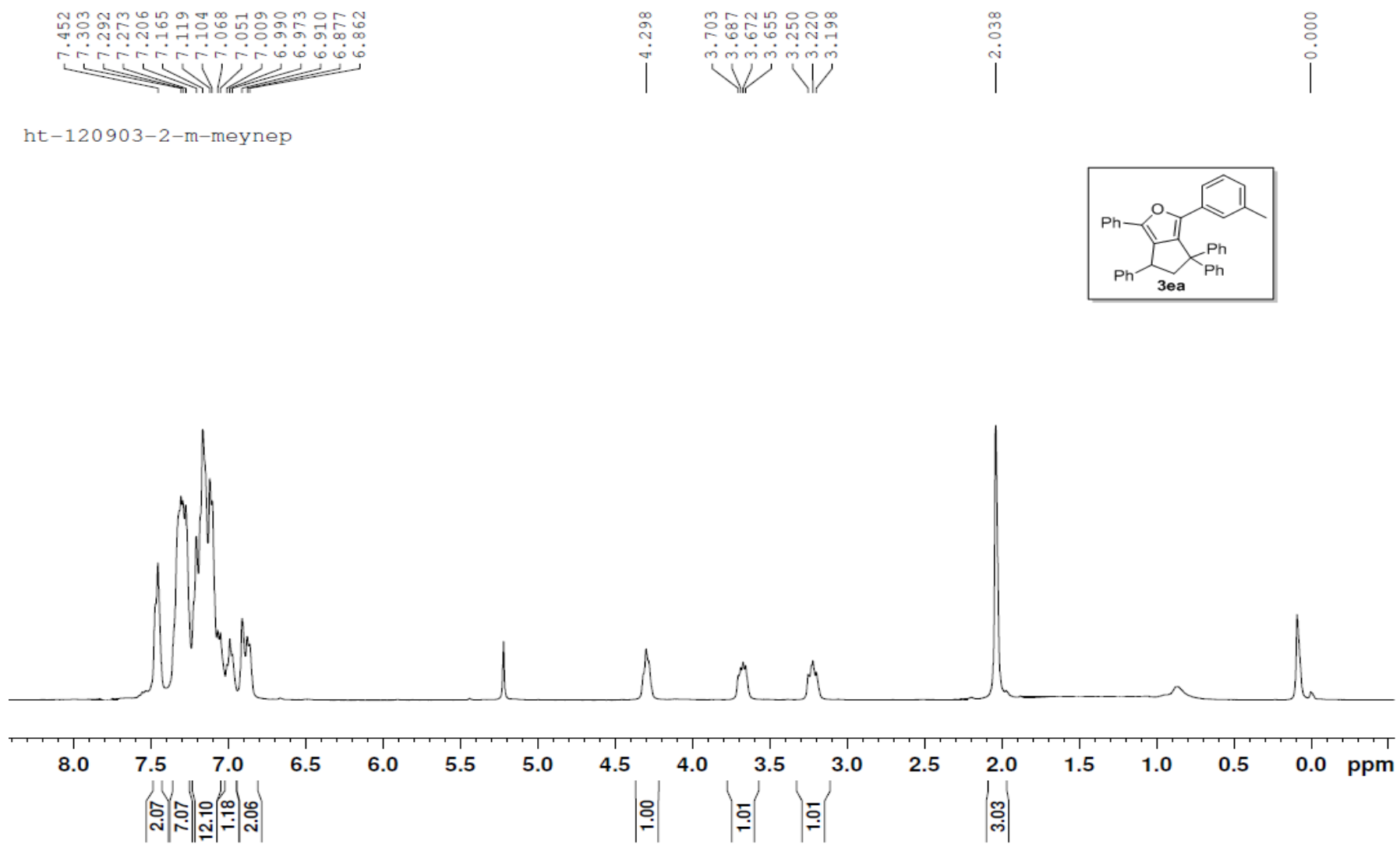
ht-120920-2-menep



ht-120903-1-o-meynep







145.30
144.53
143.60
143.03
142.11
138.02
137.52
132.52
130.27
130.08
128.92
128.55
128.48
128.35
128.09
127.90
127.80
127.46
126.72
126.49
126.42
126.23
125.80
124.77
122.09

77.32
77.00
76.68

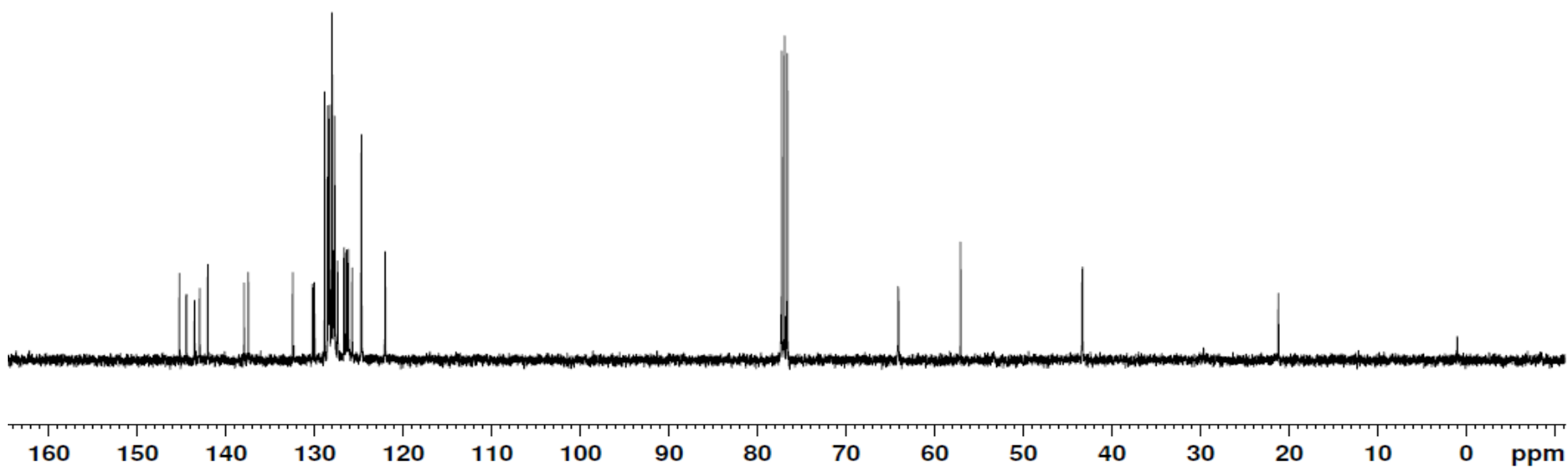
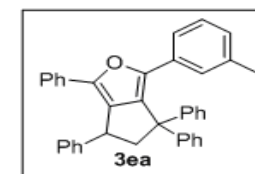
64.14

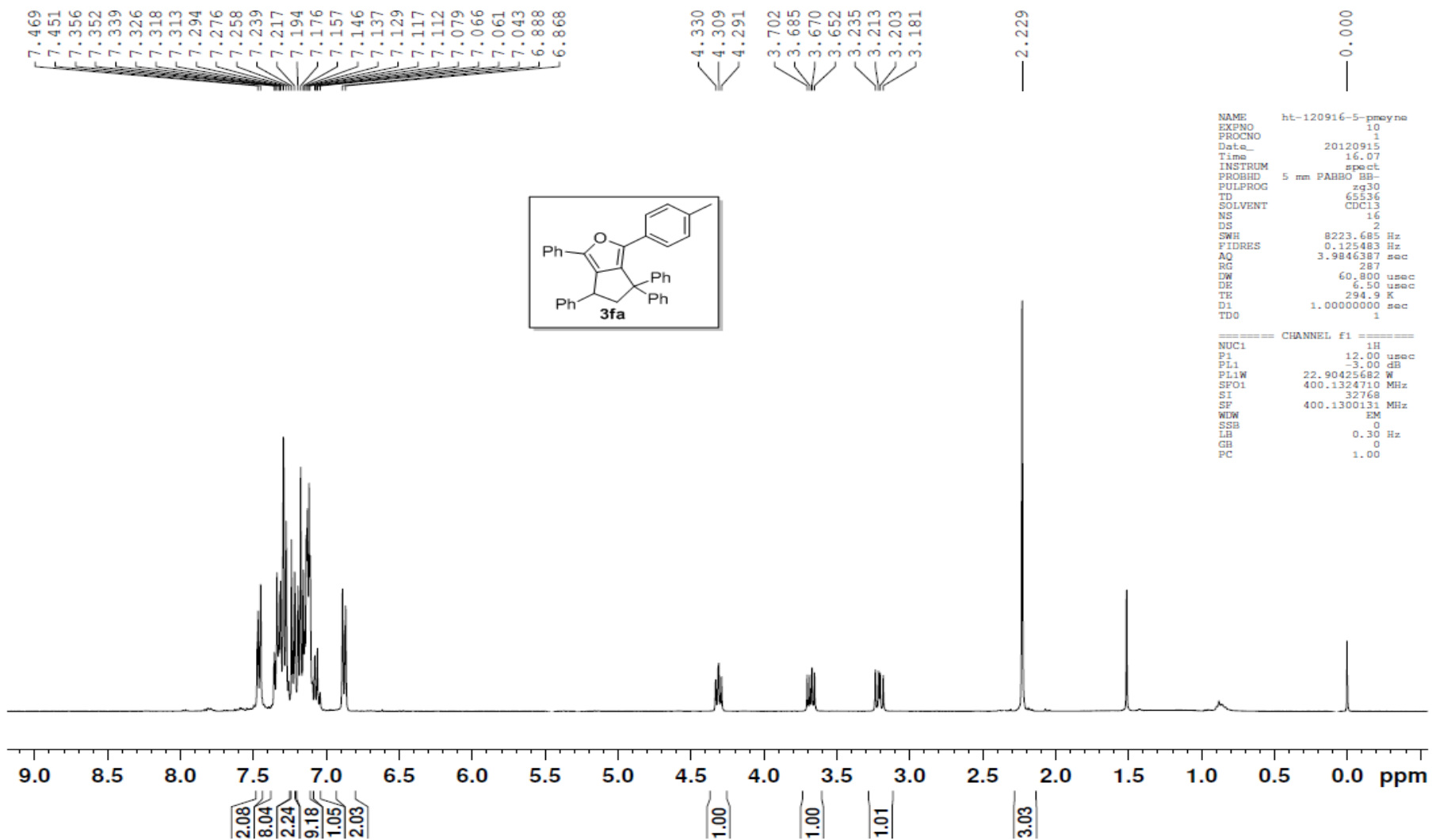
57.13

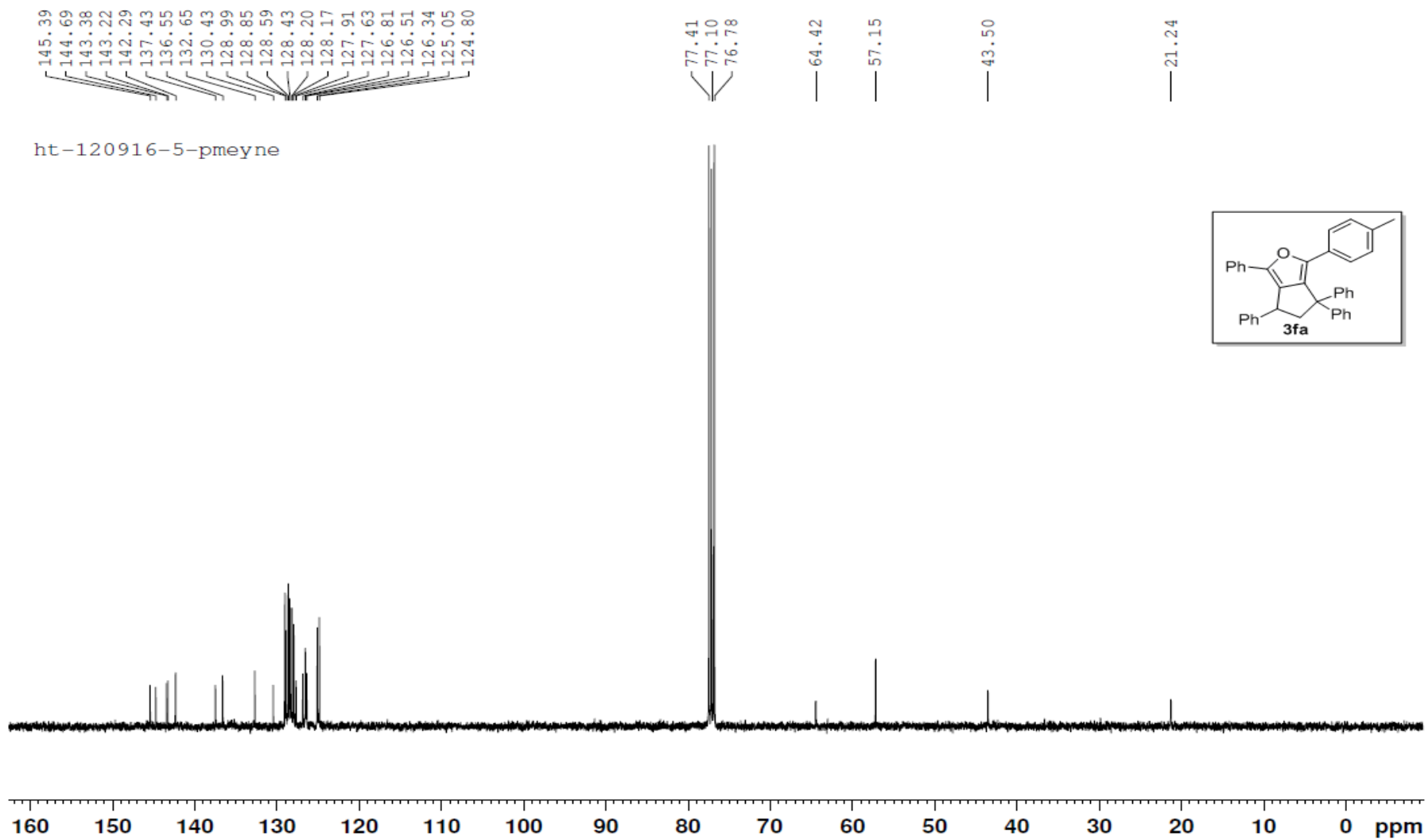
43.36

21.23

ht-120903-2-m-meynep

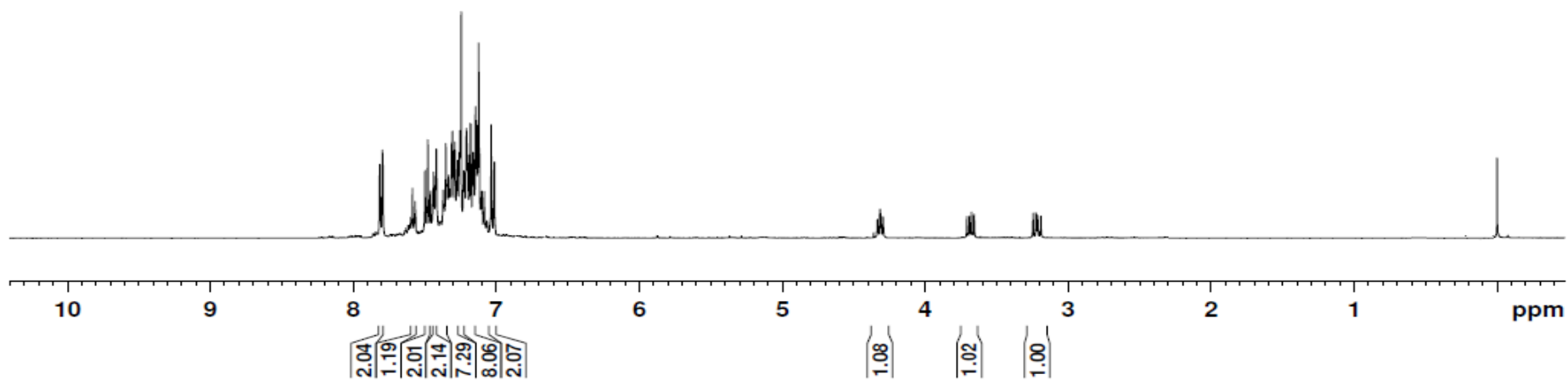
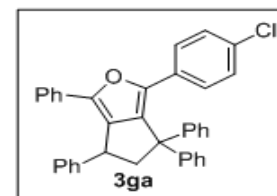






7.815
7.797
7.794
7.617
7.606
7.592
7.587
7.582
7.572
7.569
7.566
7.500
7.480
7.462
7.443
7.439
7.421
7.354
7.334
7.312
7.309
7.295
7.291
7.272
7.260
7.254
7.248
7.211
7.208
7.201
7.183
7.180
7.164
7.147
7.142
7.125
7.037
7.015
4.335
4.317
4.314
4.296
3.709
3.692
3.676
3.659
3.248
3.226
3.215
3.193

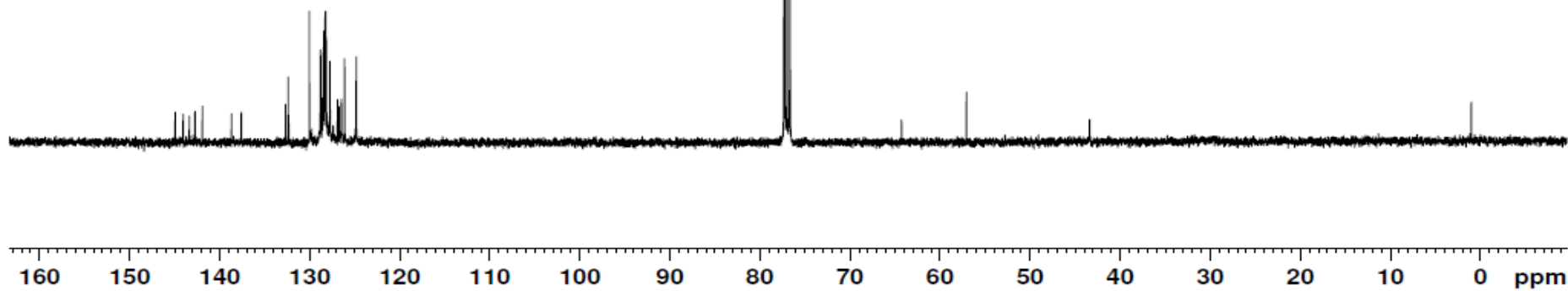
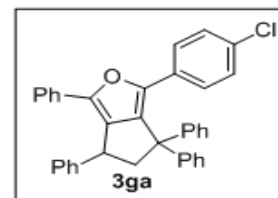
ht-120916-3-clyne

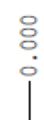
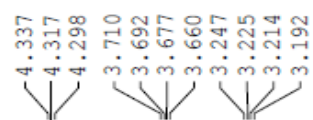
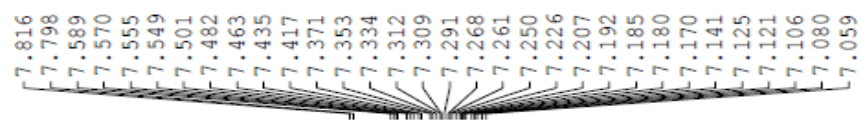


144.94
144.06
143.36
142.74
141.91
138.68
137.60
132.67
132.40
130.05
128.78
128.52
128.45
128.41
128.26
128.23
128.19
128.16
127.77
126.90
126.76
126.51
126.46
126.11
124.83

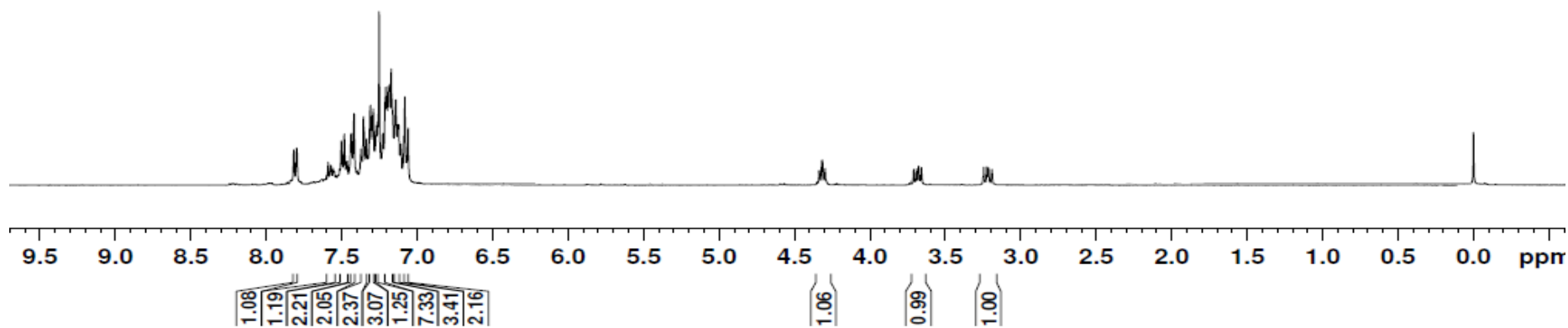
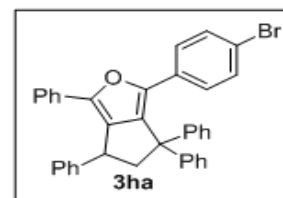
77.32
77.00
76.68
64.27
57.07
43.40

ht-120916-3-clyne





ht-120916-4-bryne



144.93
144.12
143.37
142.70
141.91
138.86
137.61
132.71
132.40
131.16
130.05
128.77
128.53
128.46
128.40
128.26
128.21
128.17
127.78
126.91
126.80
126.48
126.38
124.85
120.58

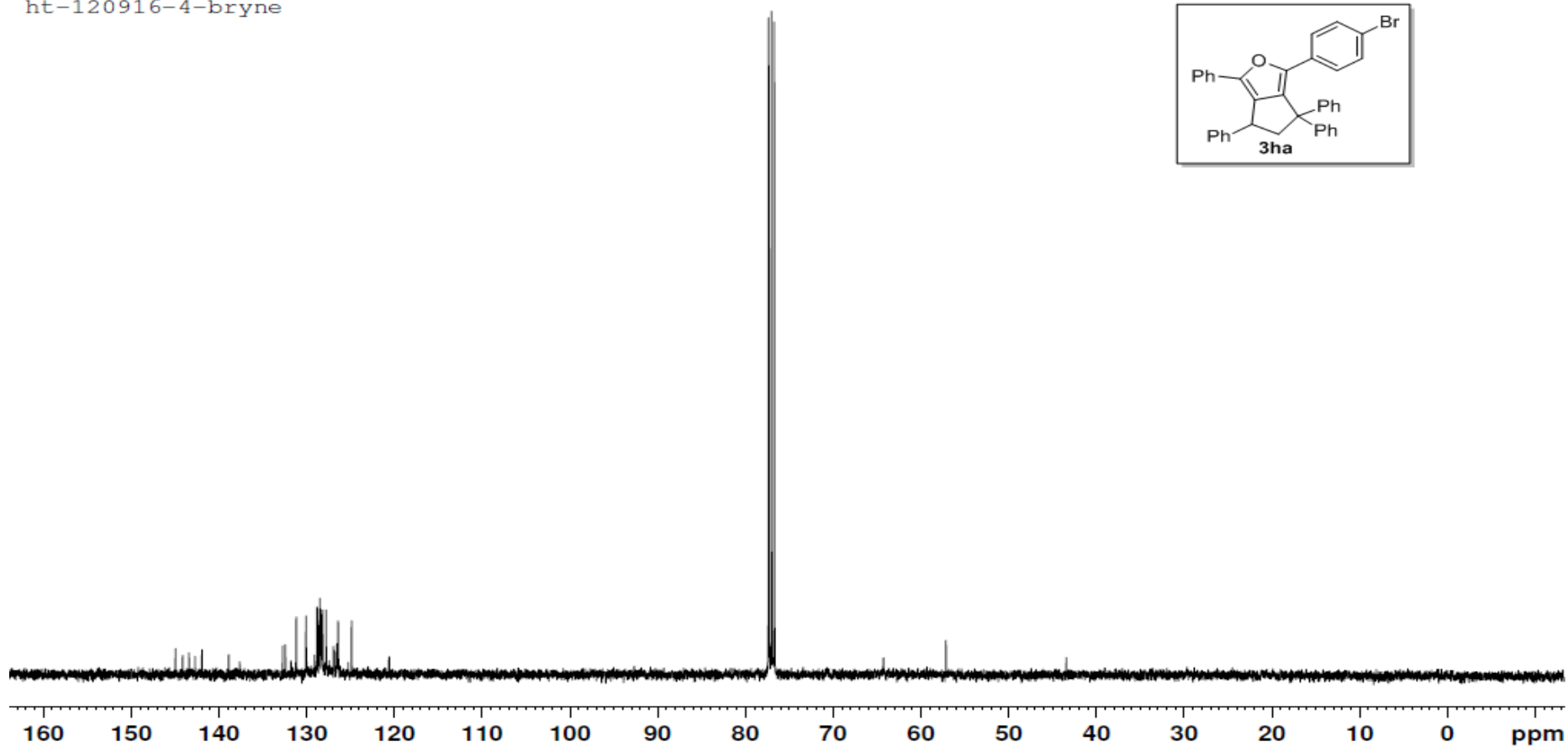
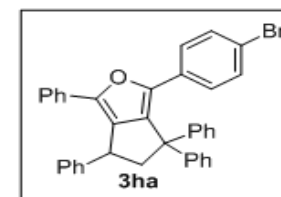
77.32
77.00
76.68

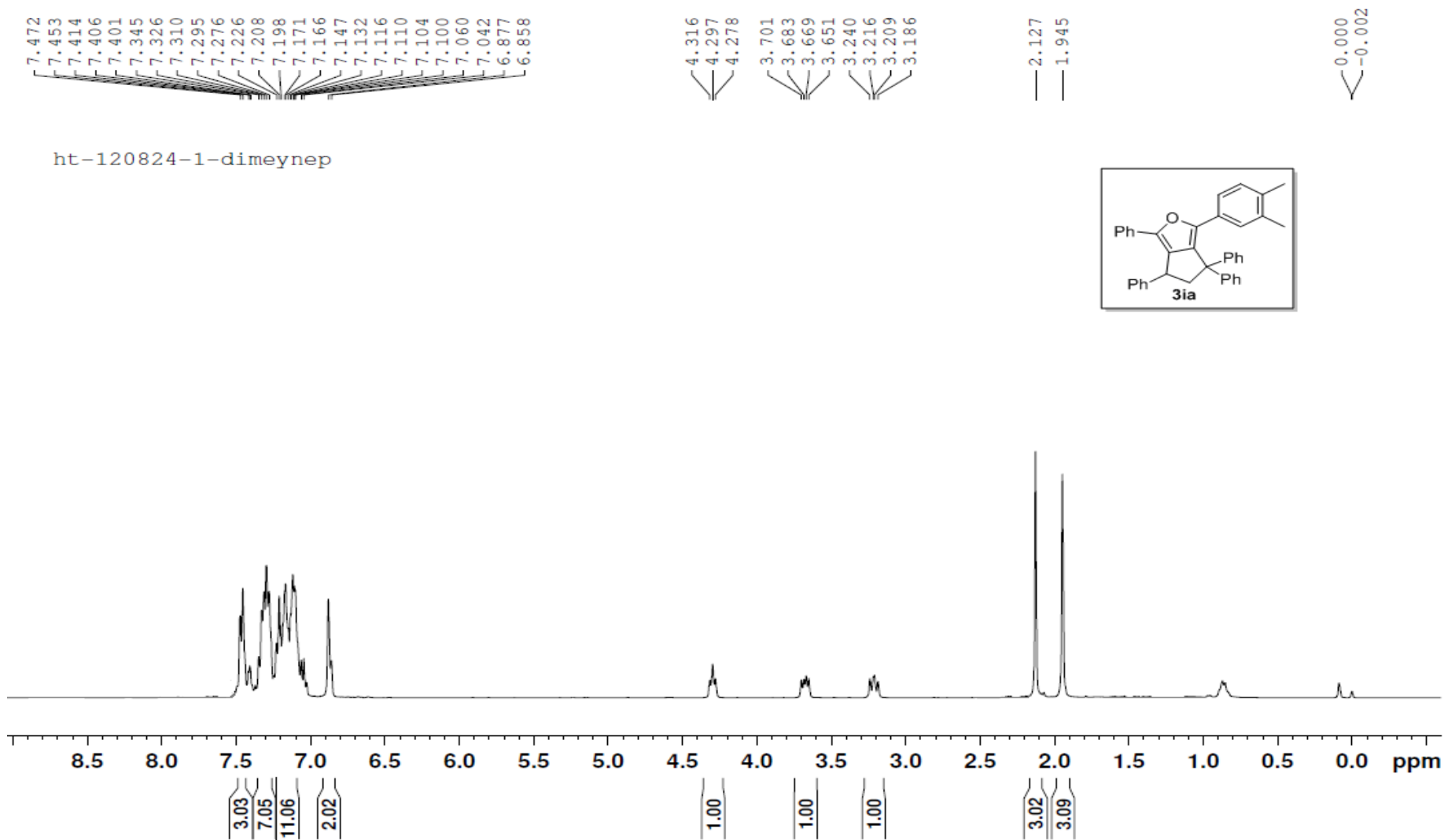
64.25

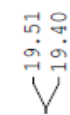
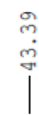
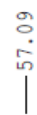
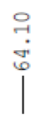
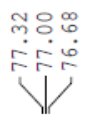
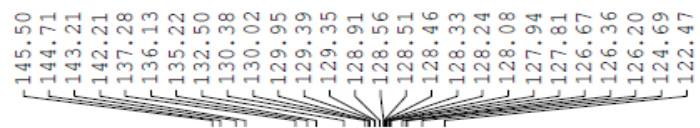
57.10

43.40

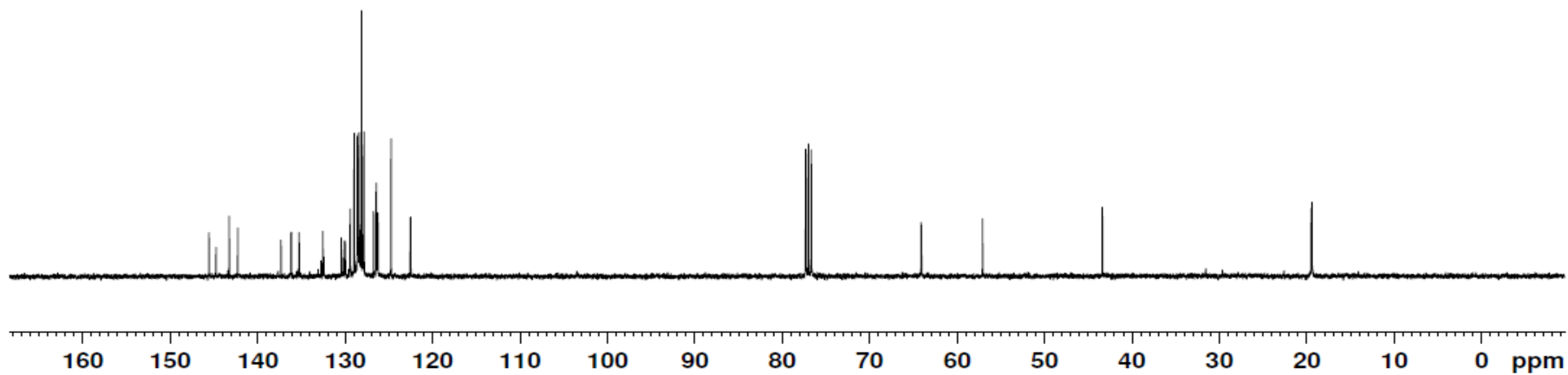
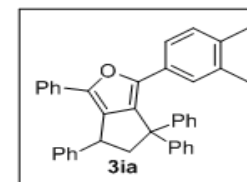
ht-120916-4-bryne

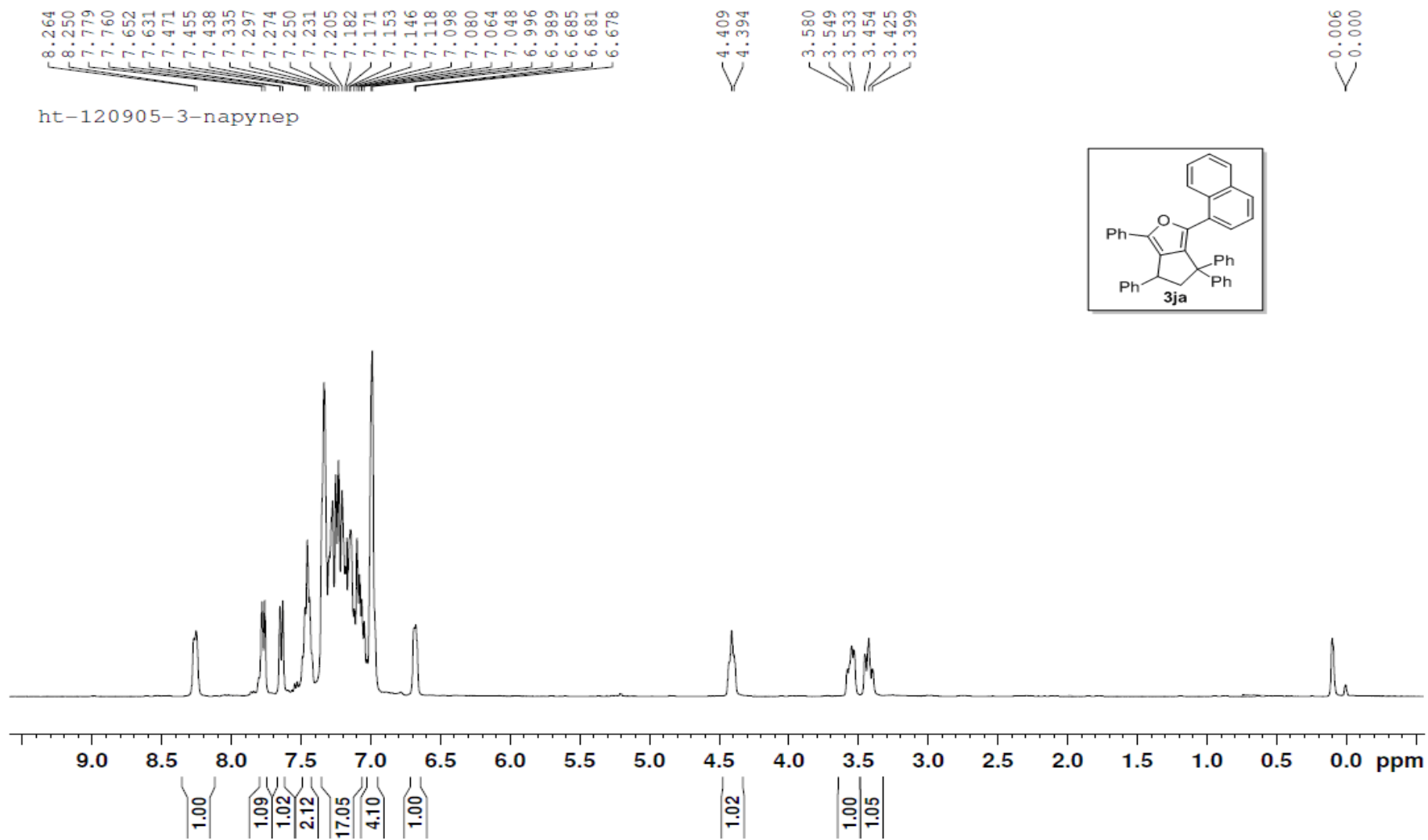


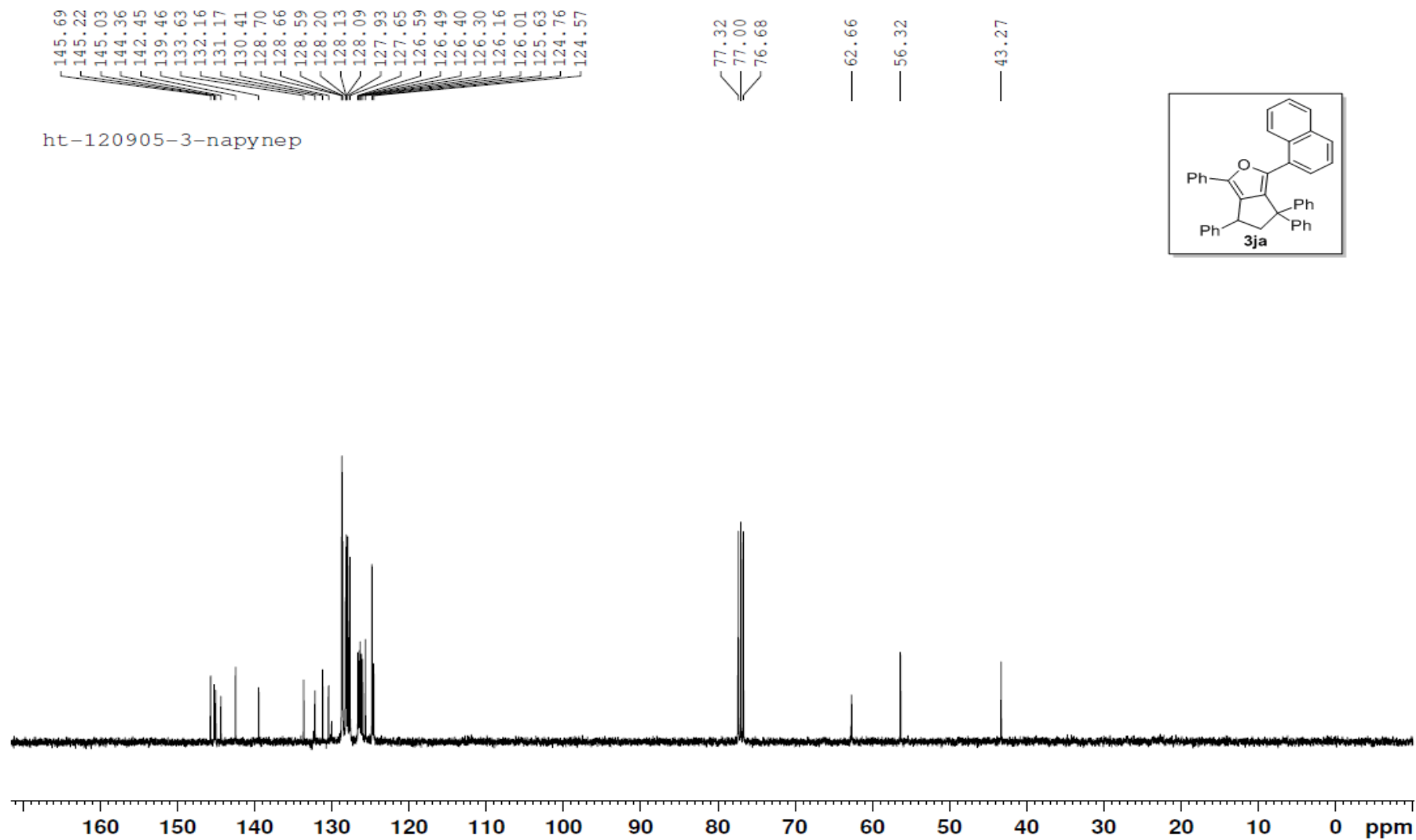




ht-120824-1-dimeynep



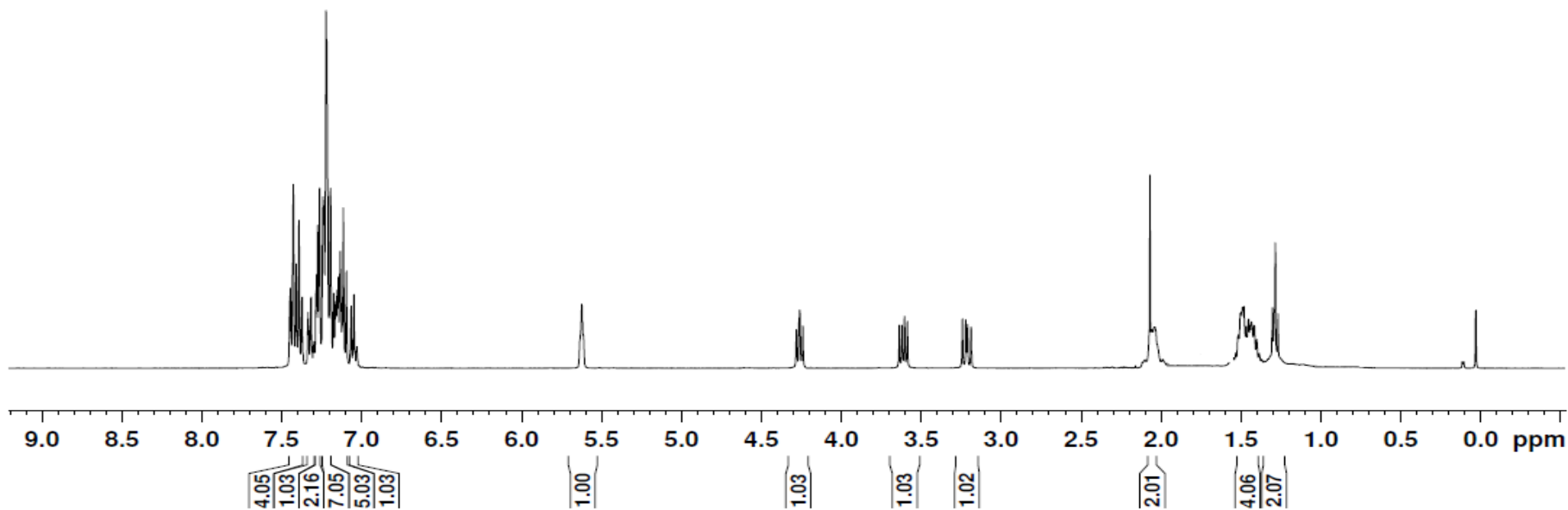
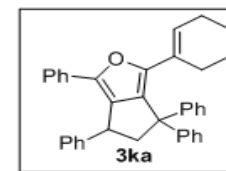


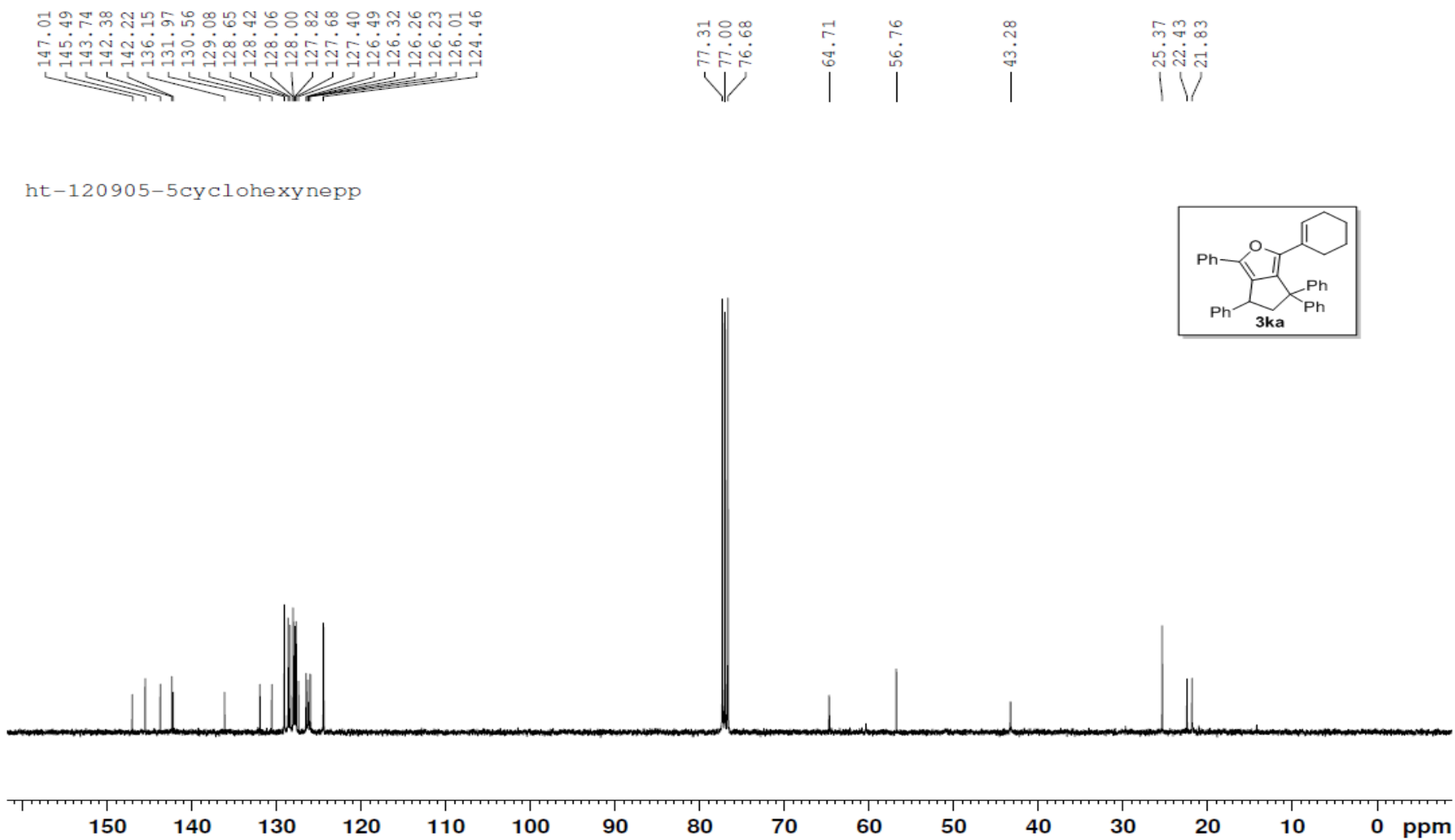


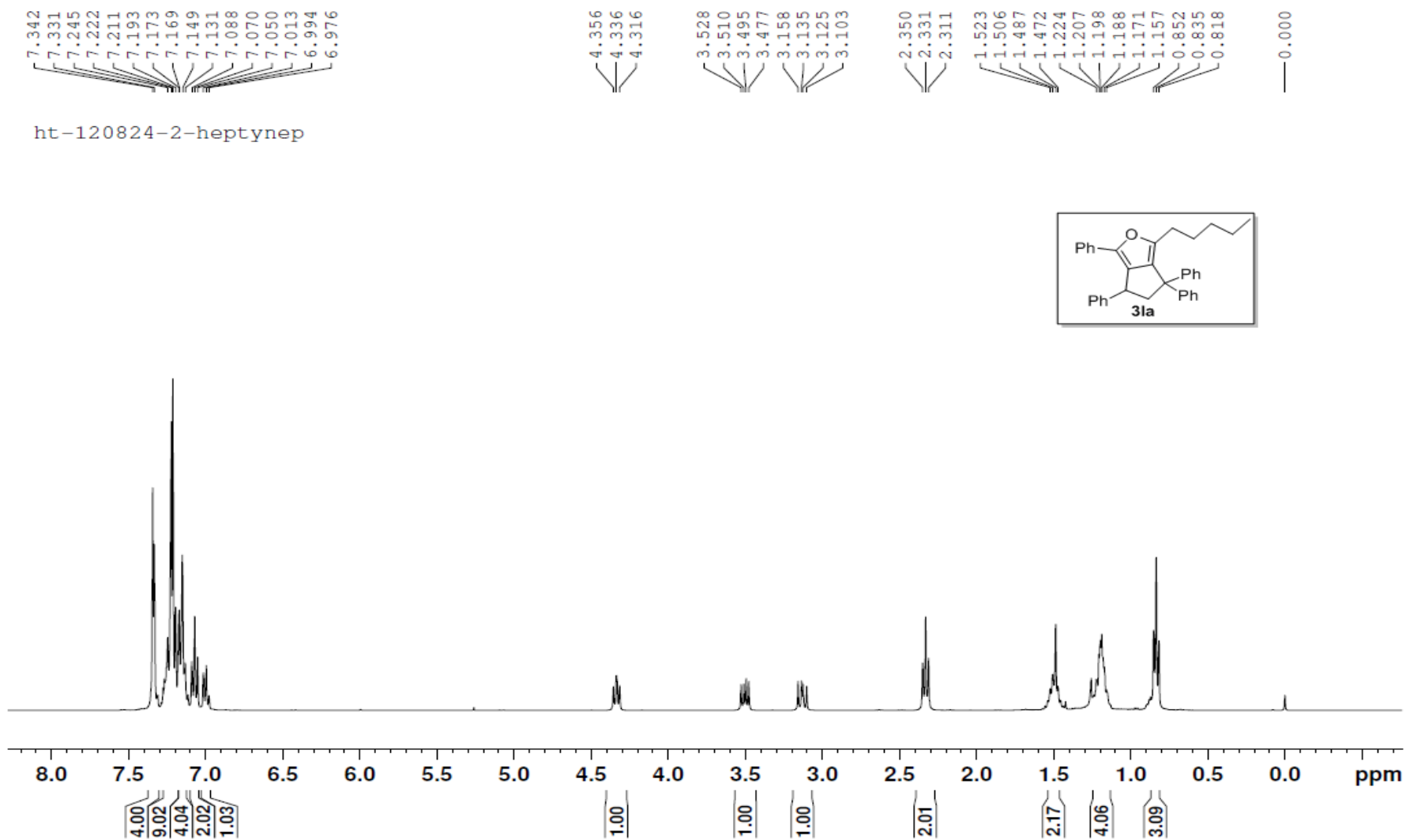
7.444
7.426
7.407
7.390
7.370
7.331
7.314
7.280
7.272
7.261
7.239
7.236
7.234
7.220
7.192
7.172
7.160
7.156
7.150
7.143
7.133
7.126
7.112
7.093
7.063
7.045
7.027
5.630
5.620
5.611

4.277
4.258
4.238
3.634
3.616
3.601
3.584
3.239
3.217
3.207
3.185
2.069
2.059
2.040
1.532
1.516
1.497
1.488
1.481
1.466
1.451
1.442
1.434
1.416
1.401
1.386
1.302
1.284
1.266

ht-120905-5cyclohexynepp







147.30
146.46
145.82
142.74
142.68
135.94
130.81
130.06
128.50
128.39
128.15
128.13
128.00
127.90
127.88
126.41
126.35
126.05
125.80
124.20

77.32
77.00
76.68

61.99

55.49

43.62

31.60

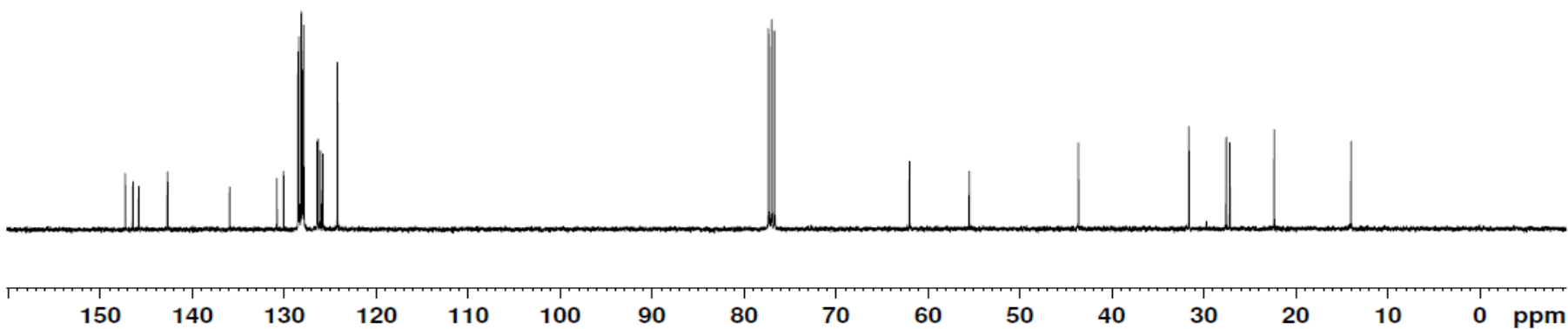
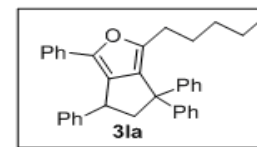
27.55

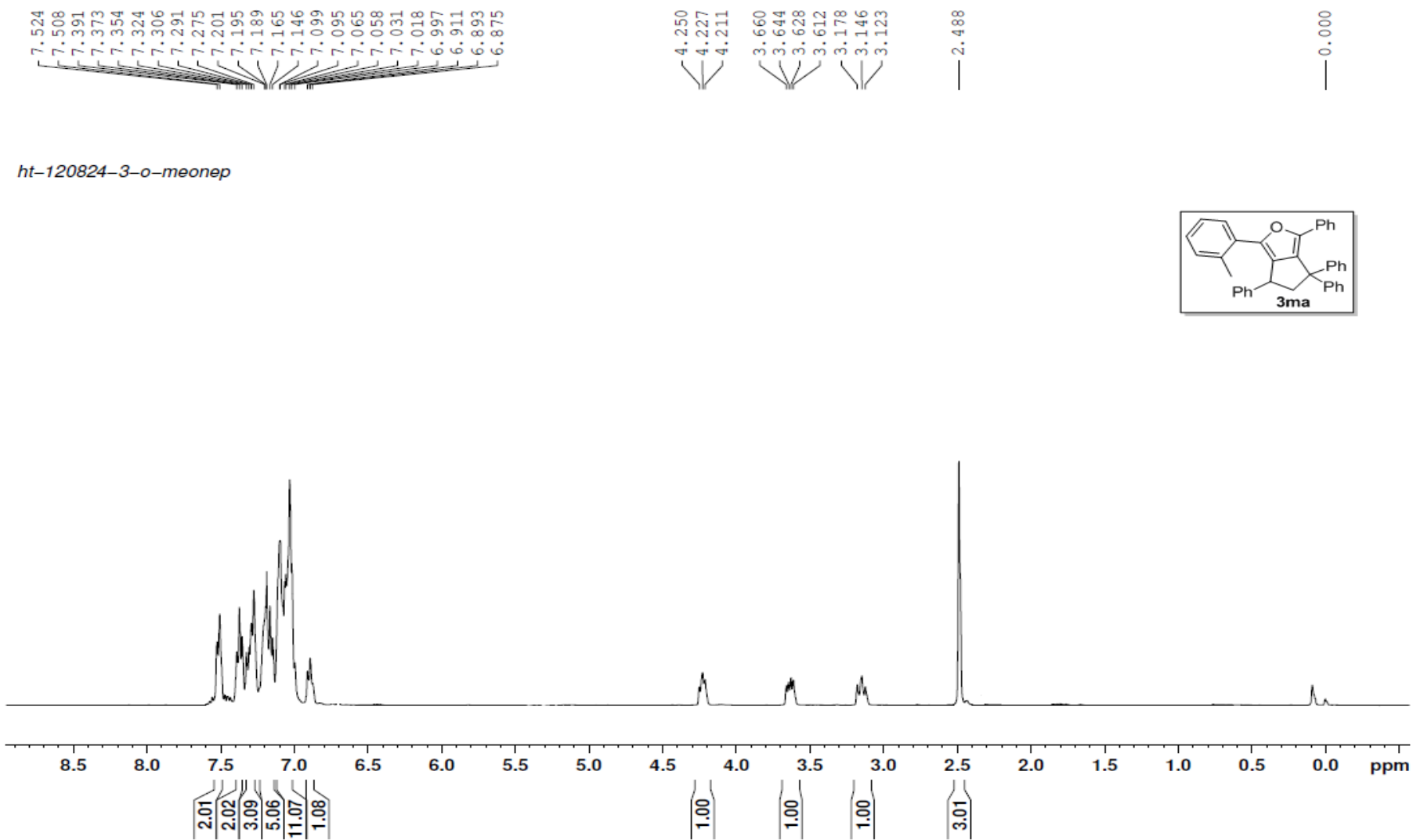
27.17

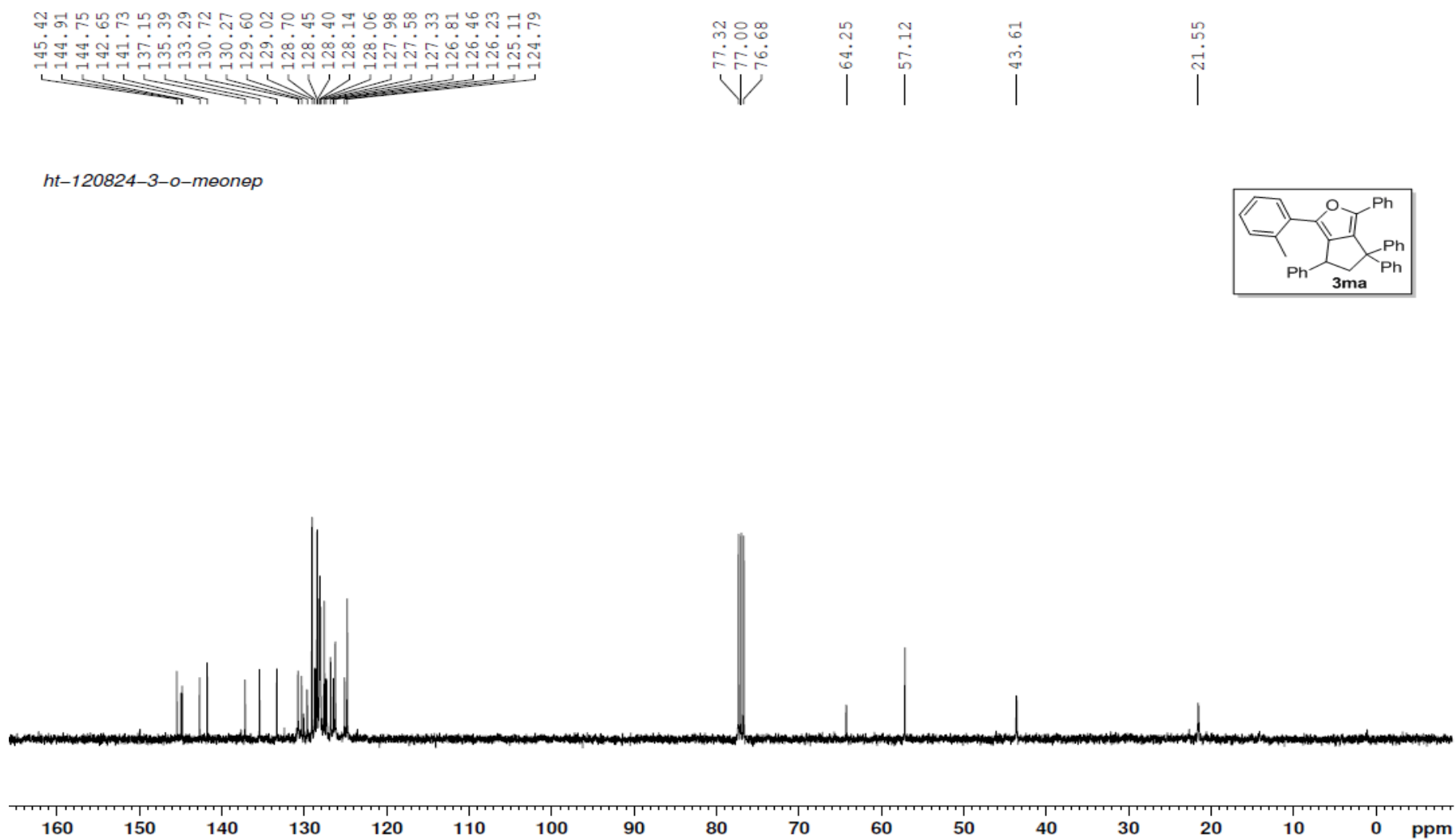
22.32

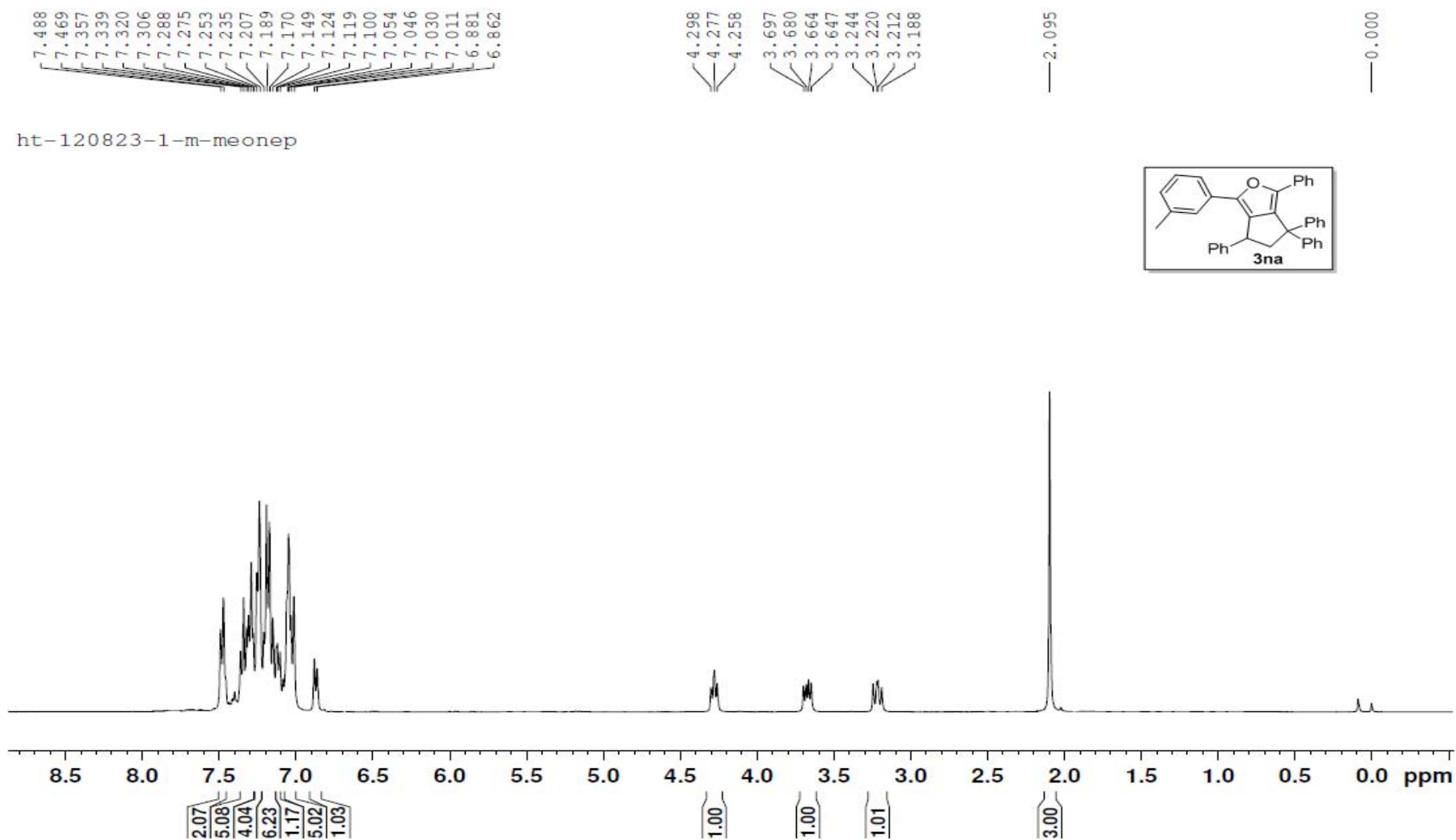
13.96

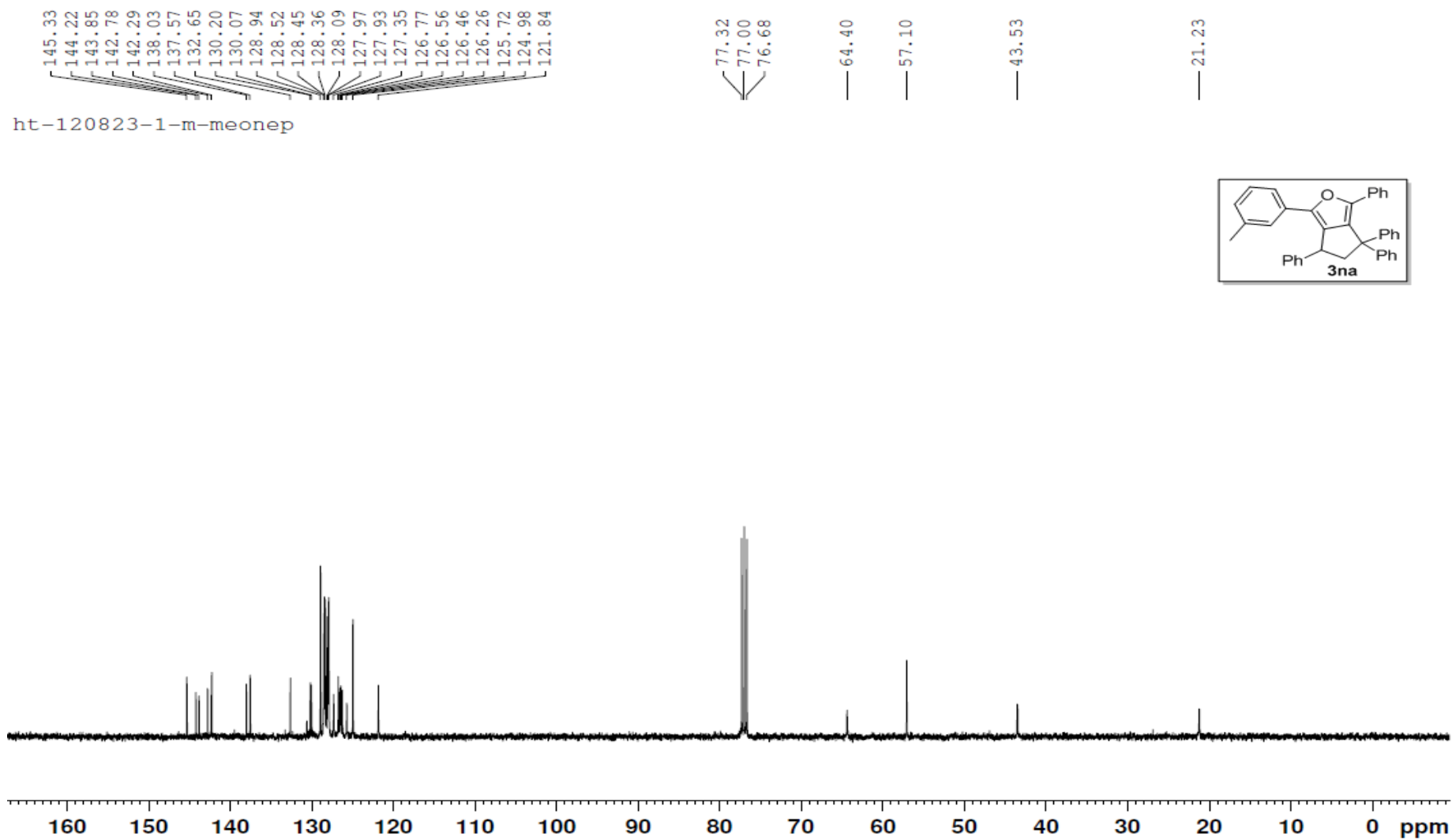
ht-120824-2-heptynep

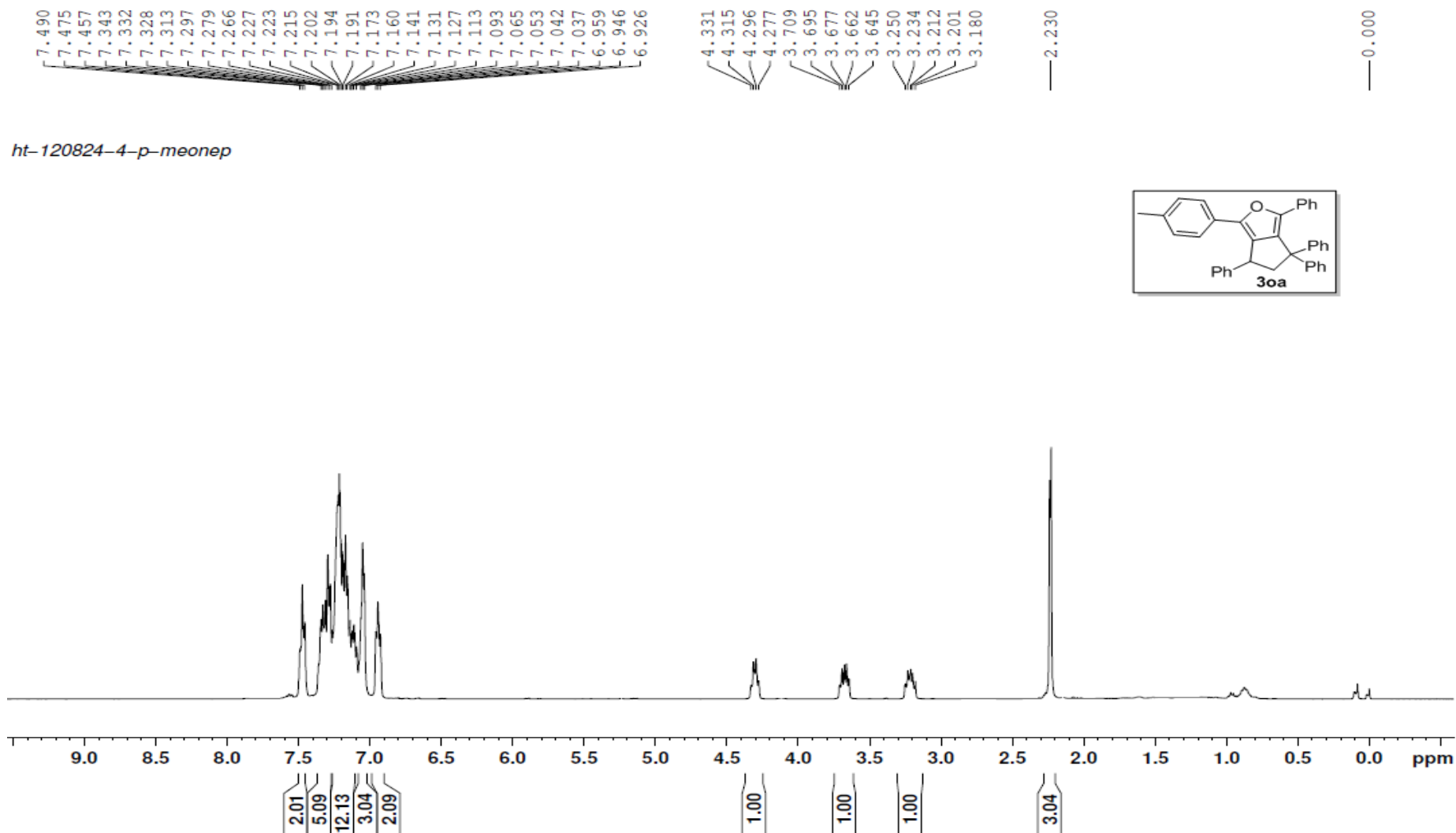


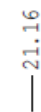
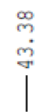
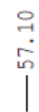
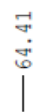
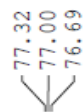
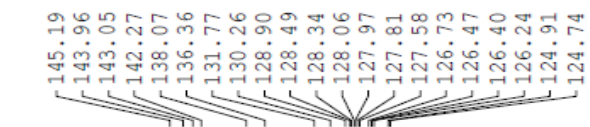




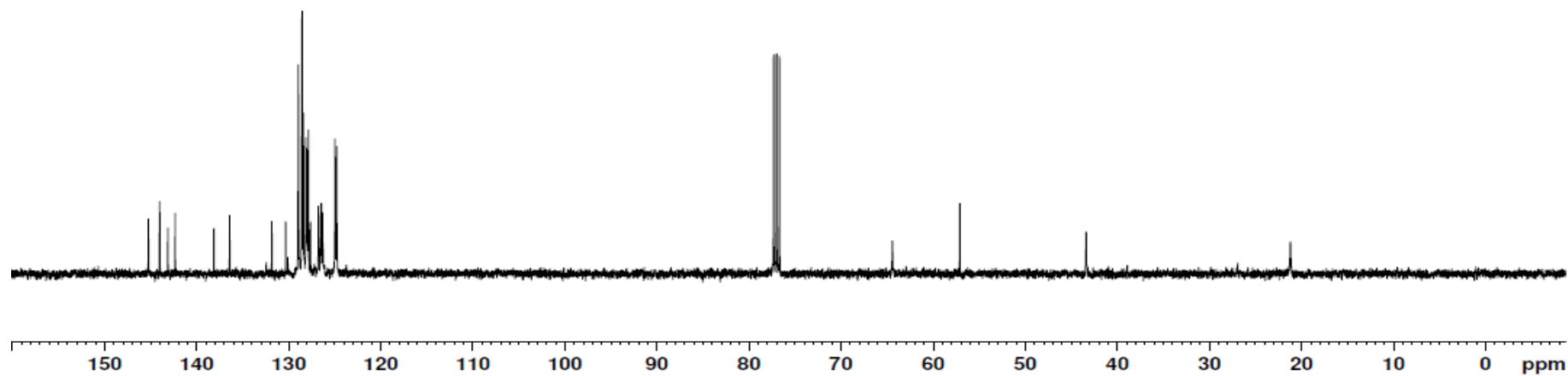
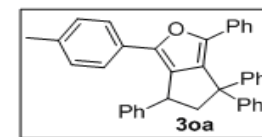


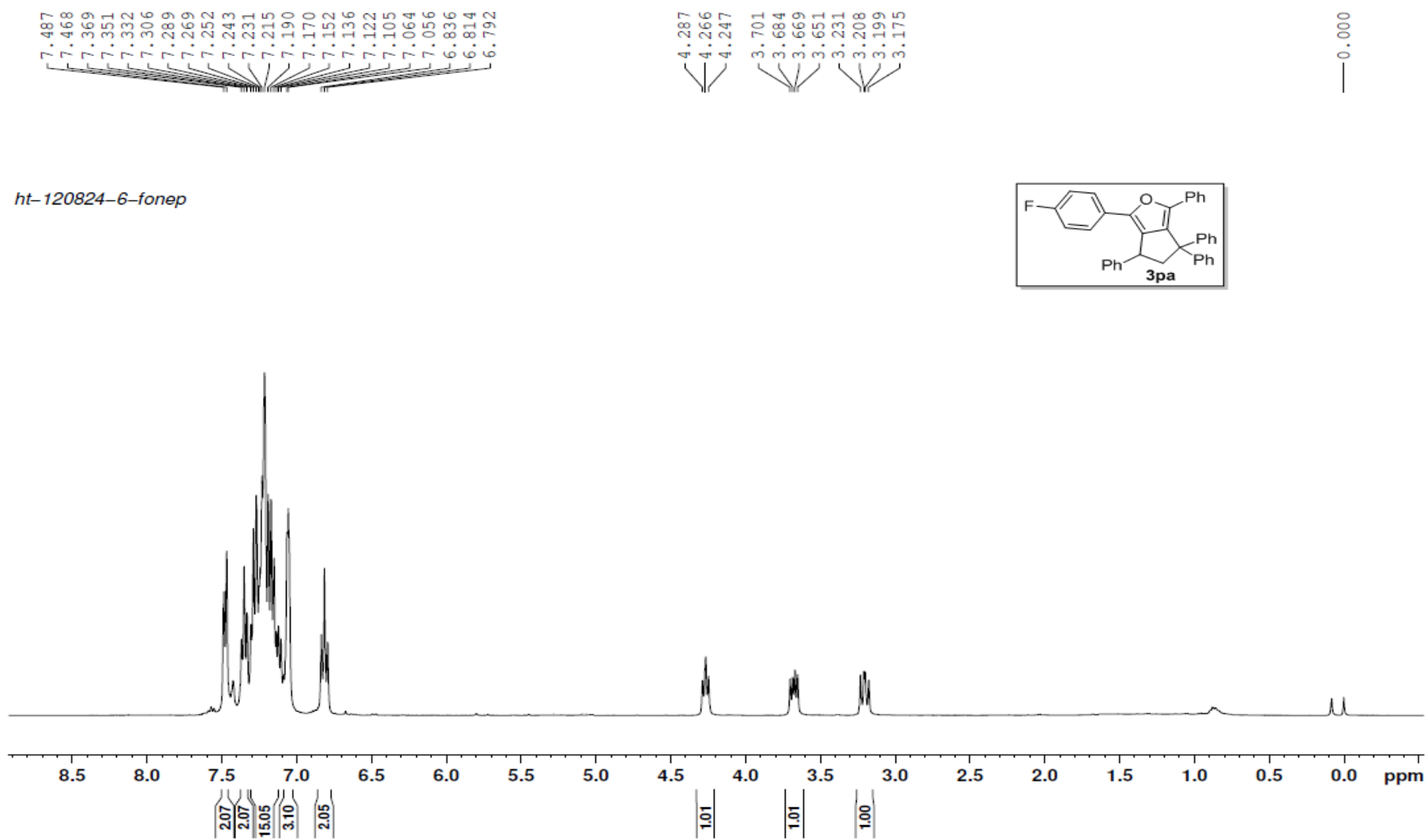


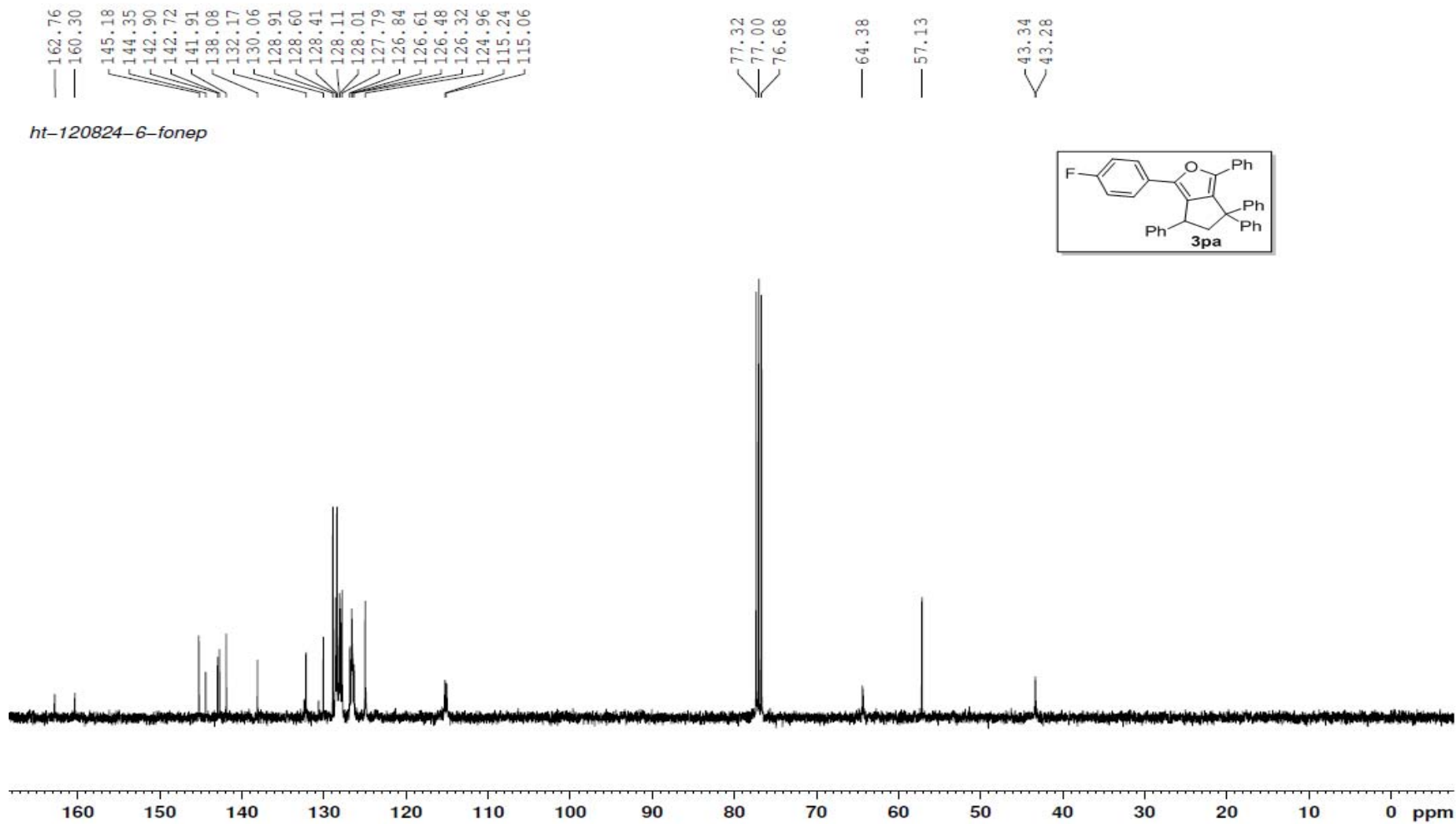


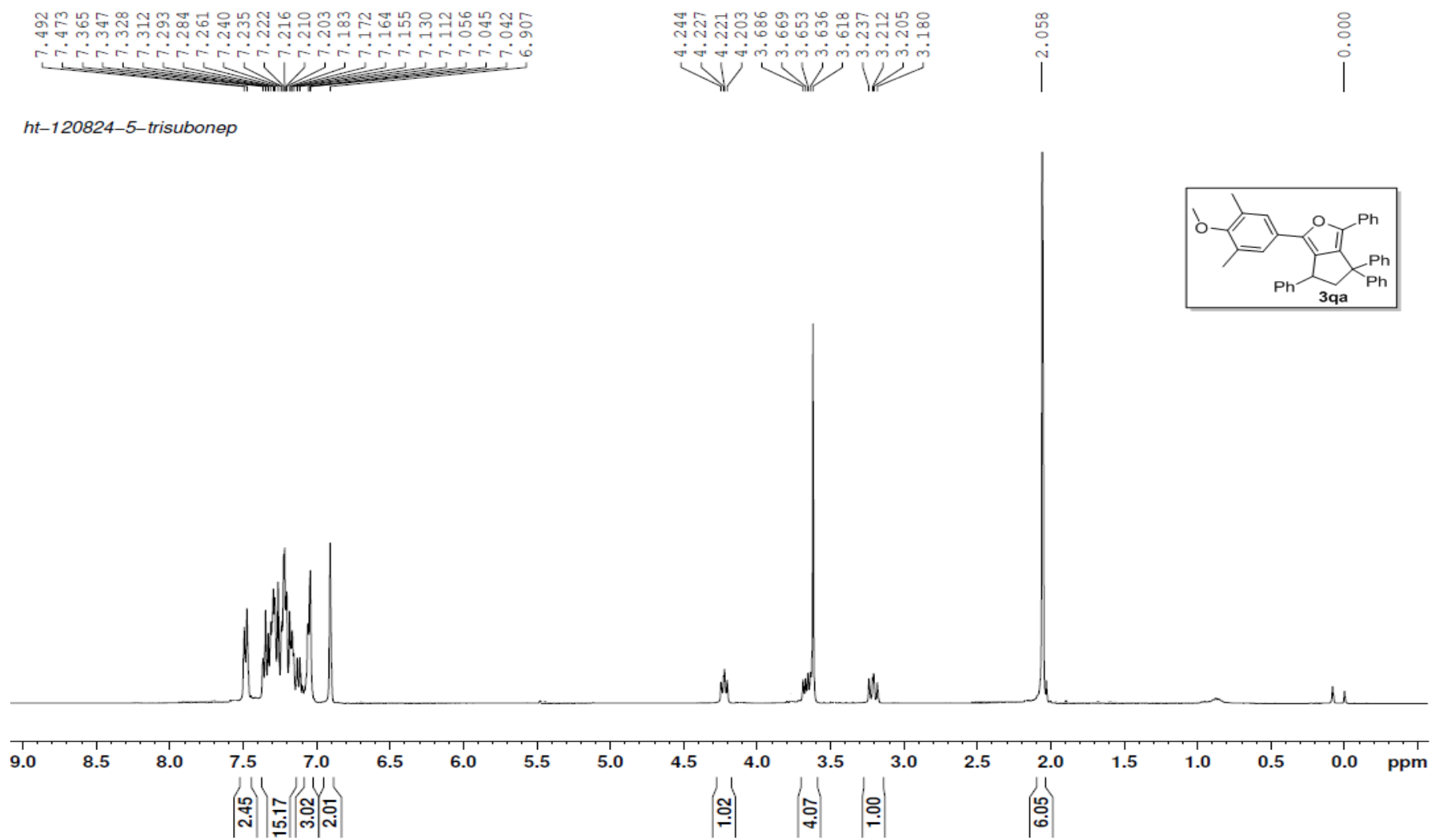


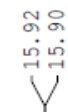
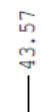
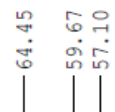
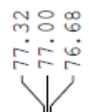
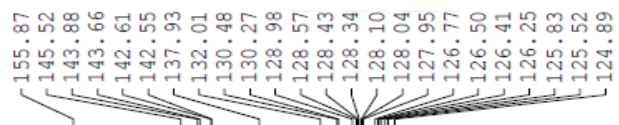
ht-120824-4-p-meonep



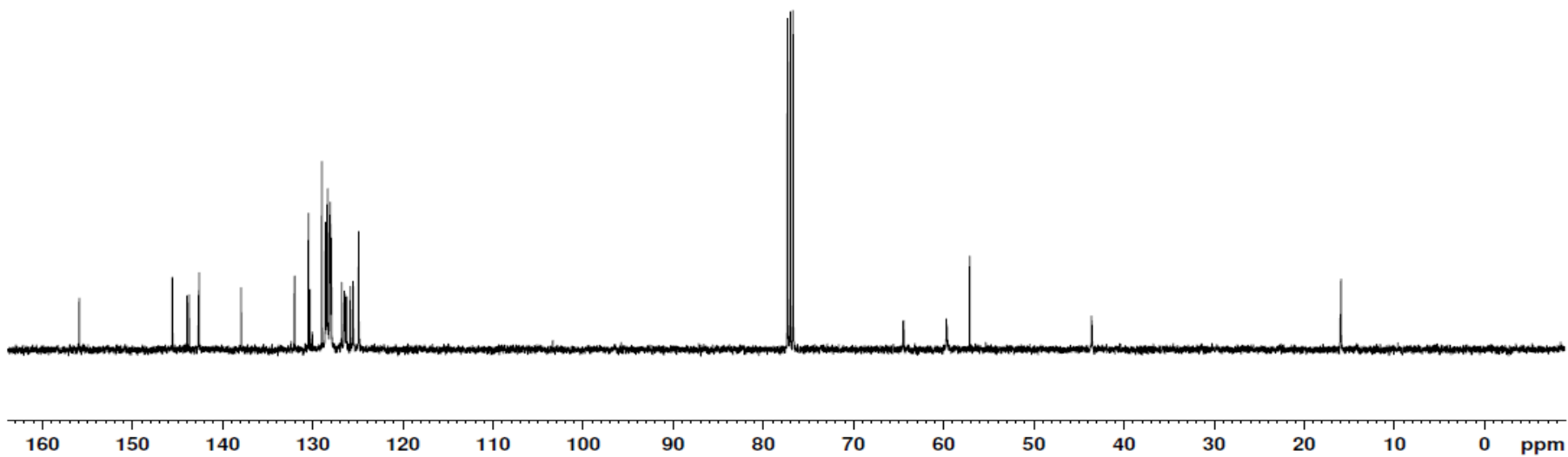
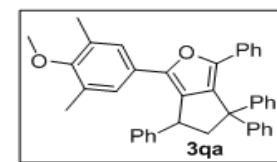


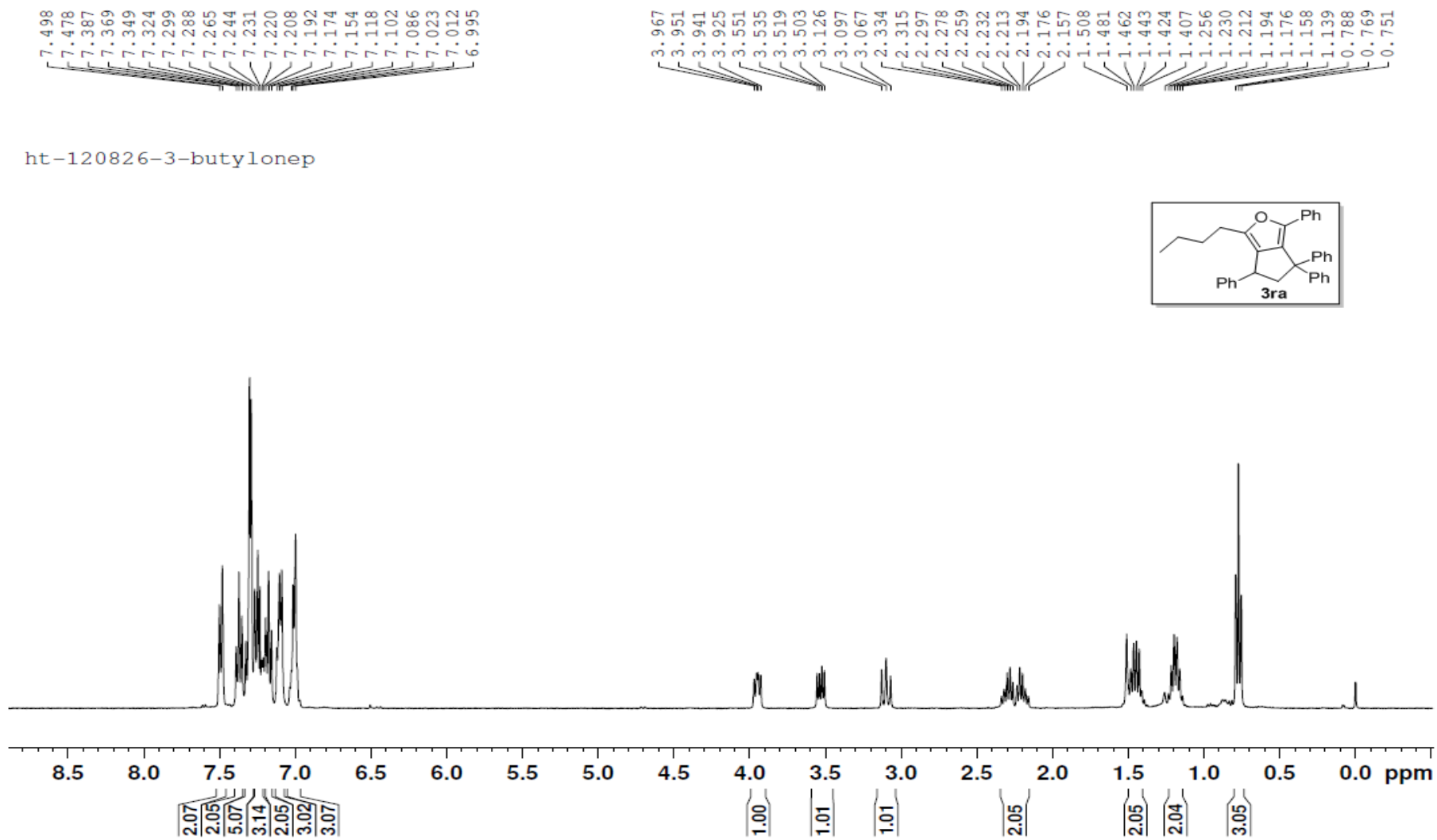


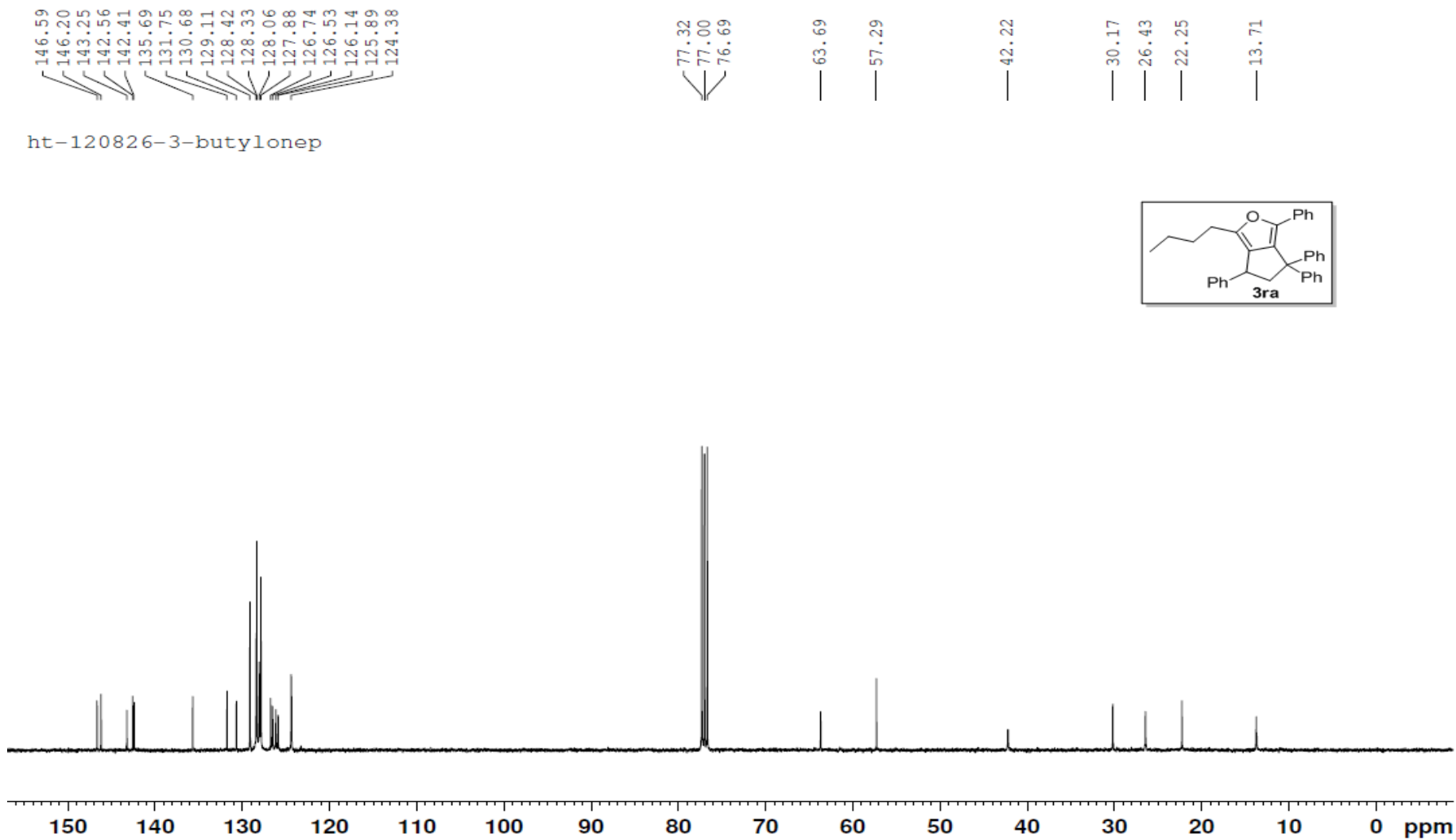


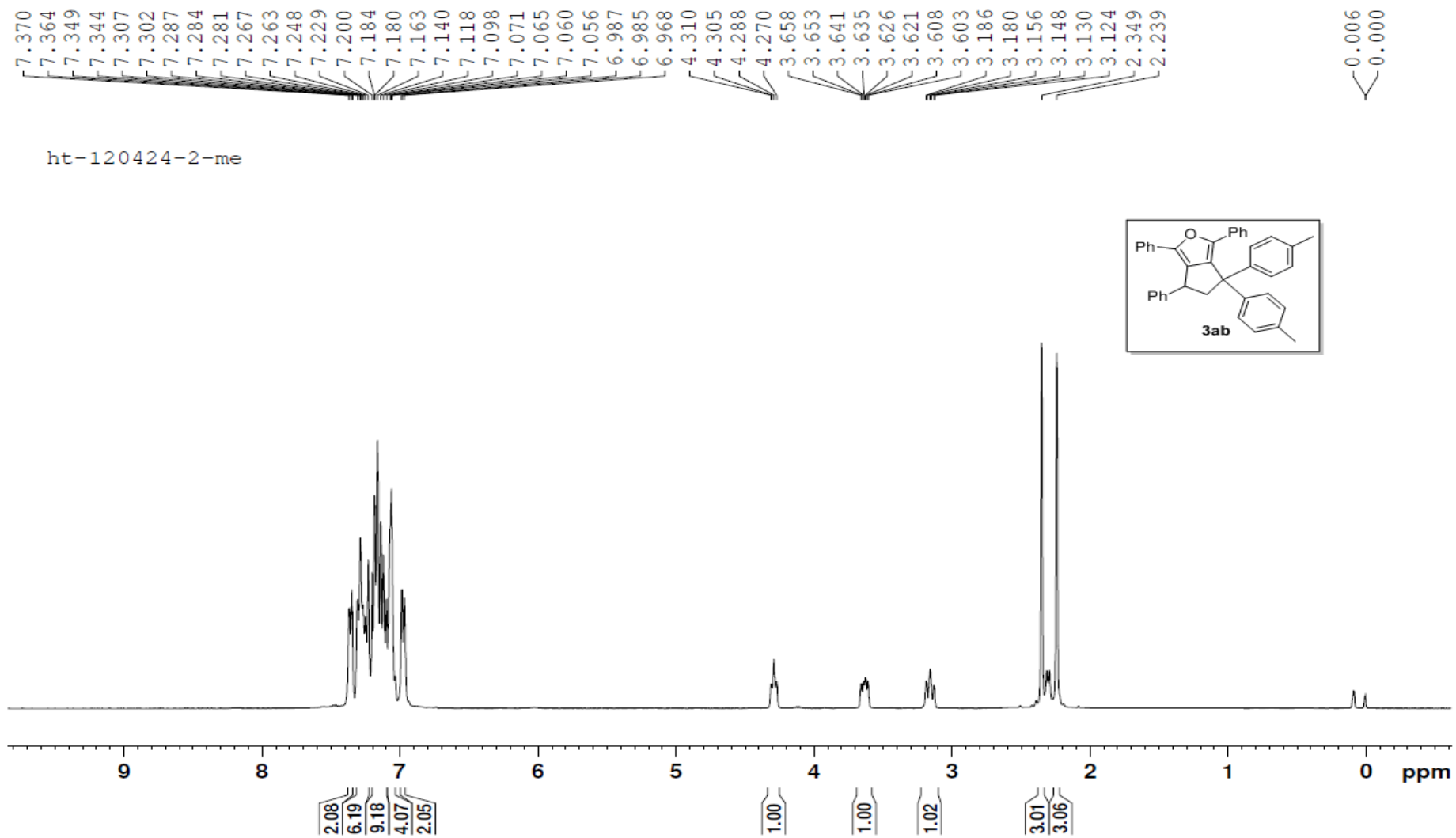


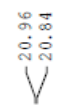
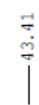
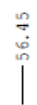
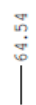
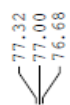
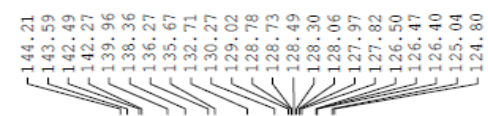
ht-120824-5-trisubonep



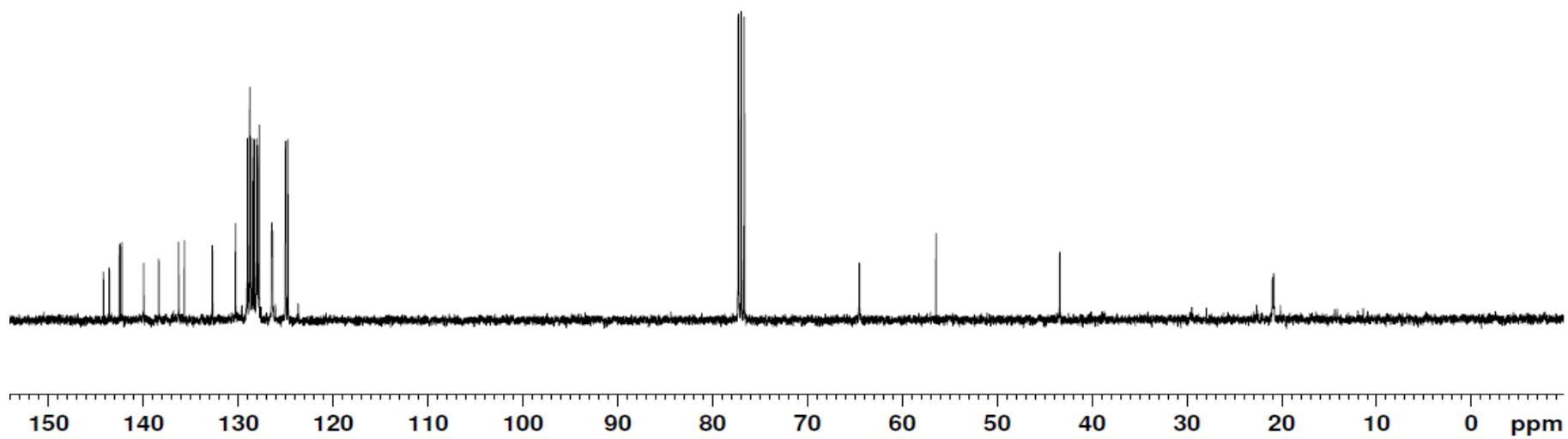
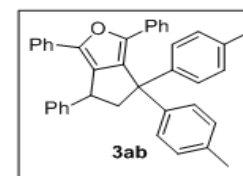


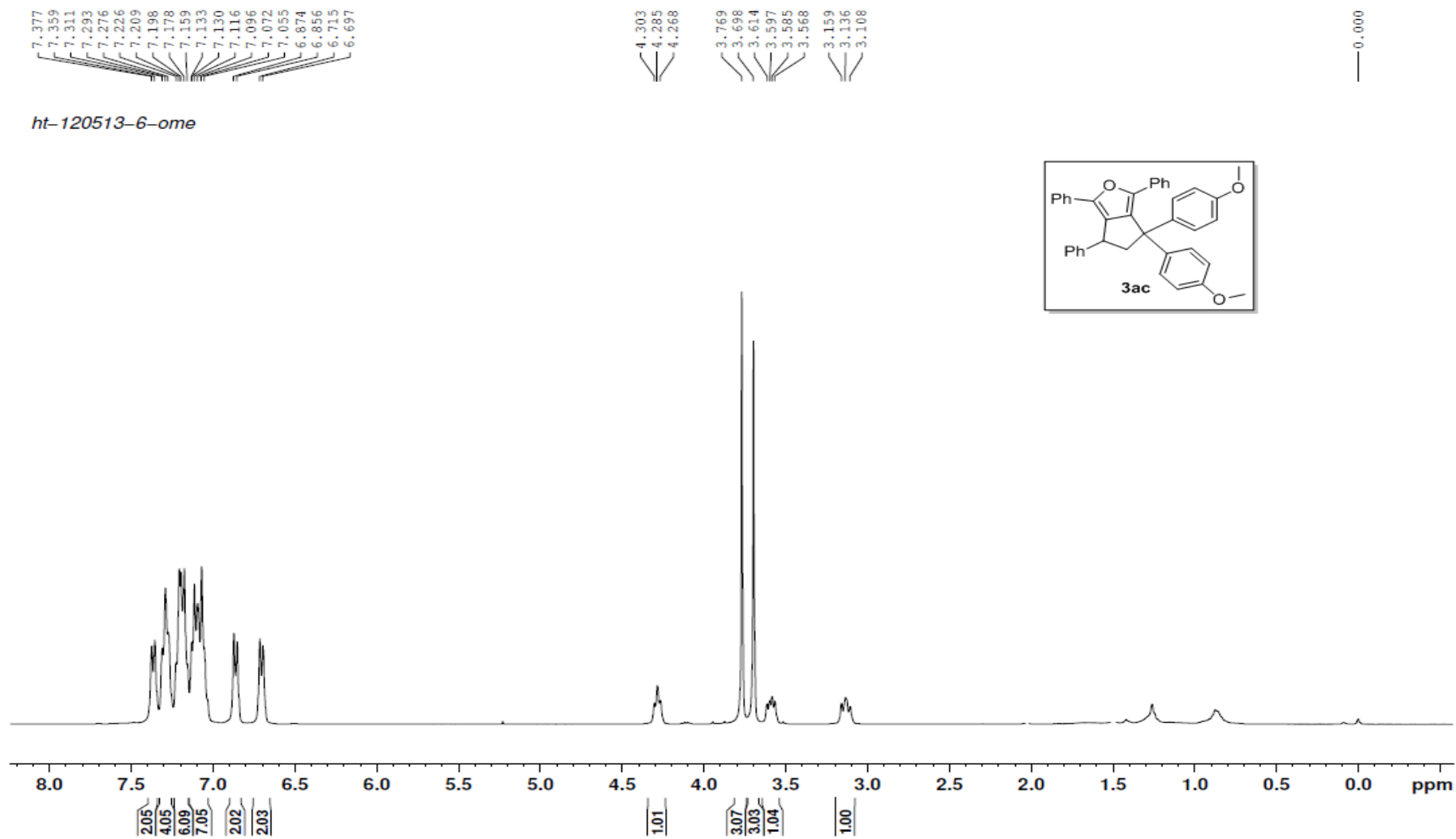


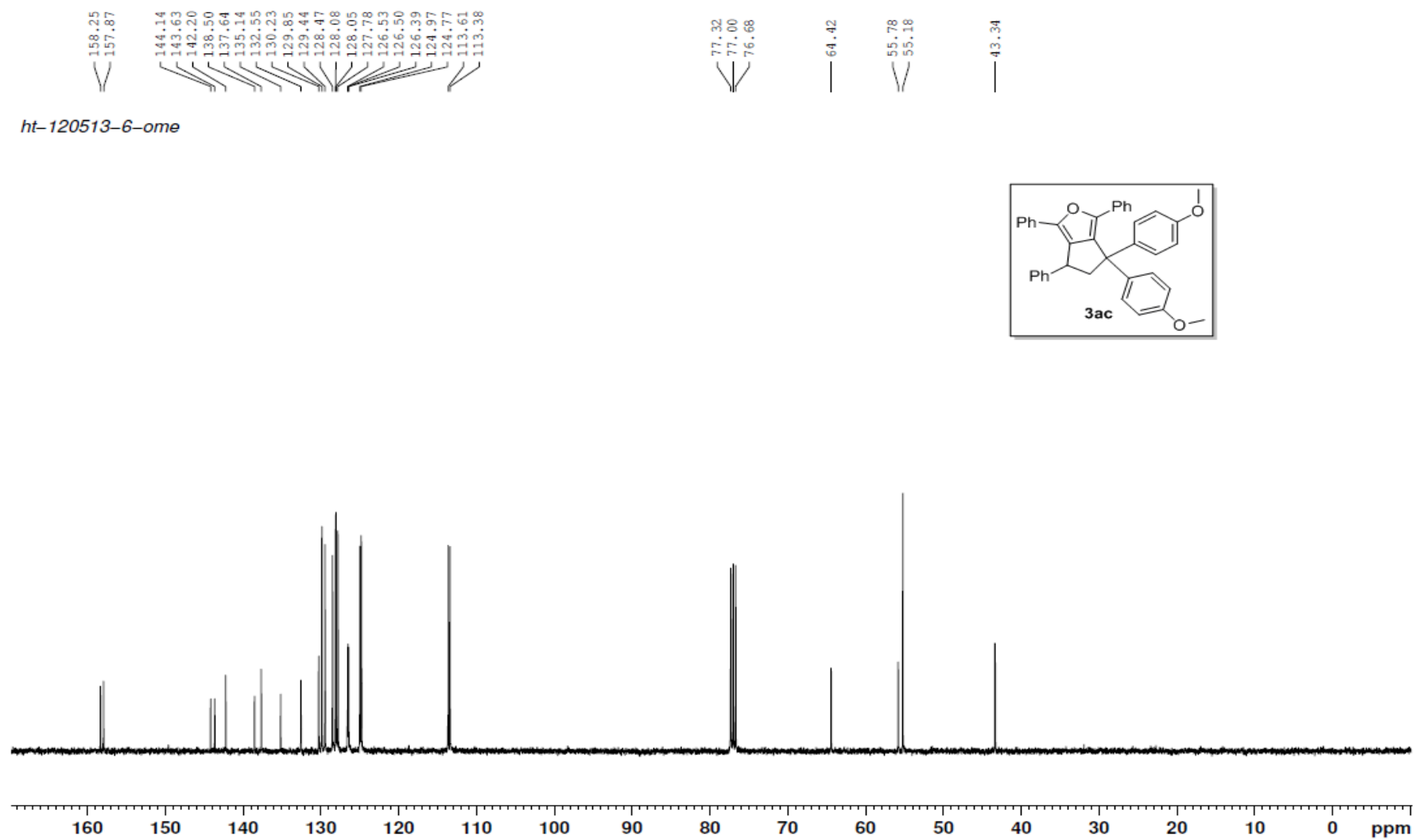




ht-120424-2-me





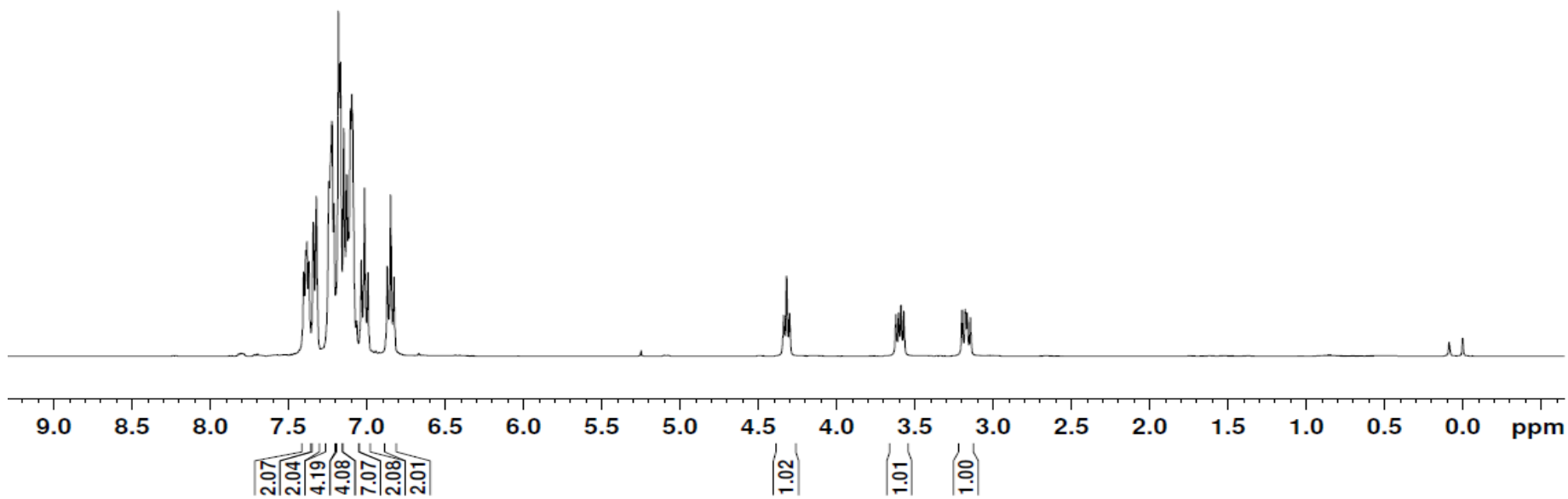
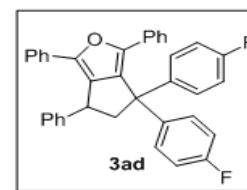


7.401
7.388
7.380
7.367
7.339
7.320
7.241
7.221
7.207
7.179
7.174
7.165
7.145
7.126
7.115
7.100
7.093
7.063
7.033
7.012
6.990
6.867
6.845
6.824

4.338
4.319
4.300
3.620
3.603
3.588
3.570
3.198
3.177
3.165
3.145

0.000

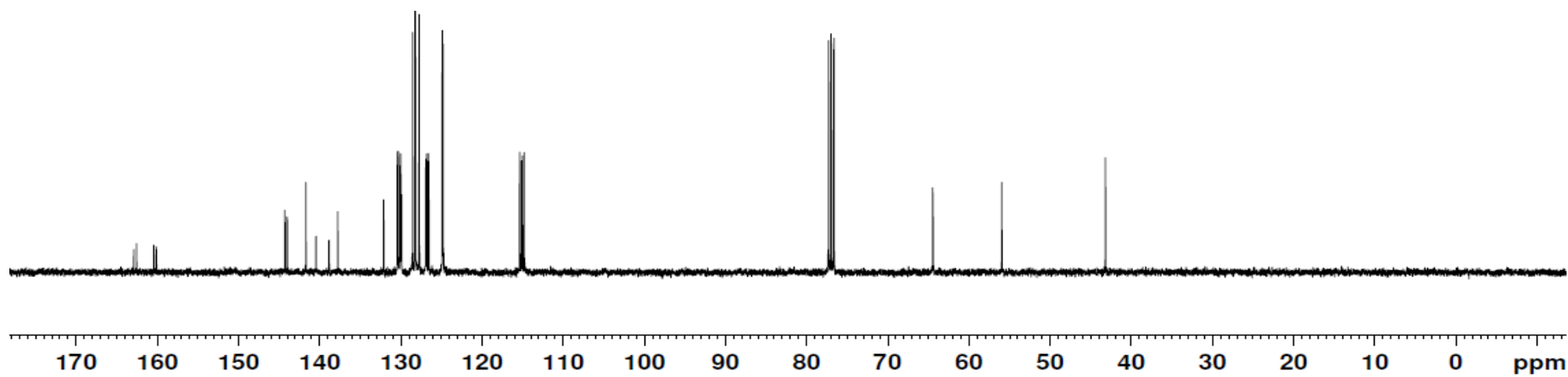
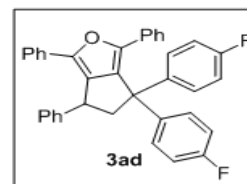
ht-120515-1-f

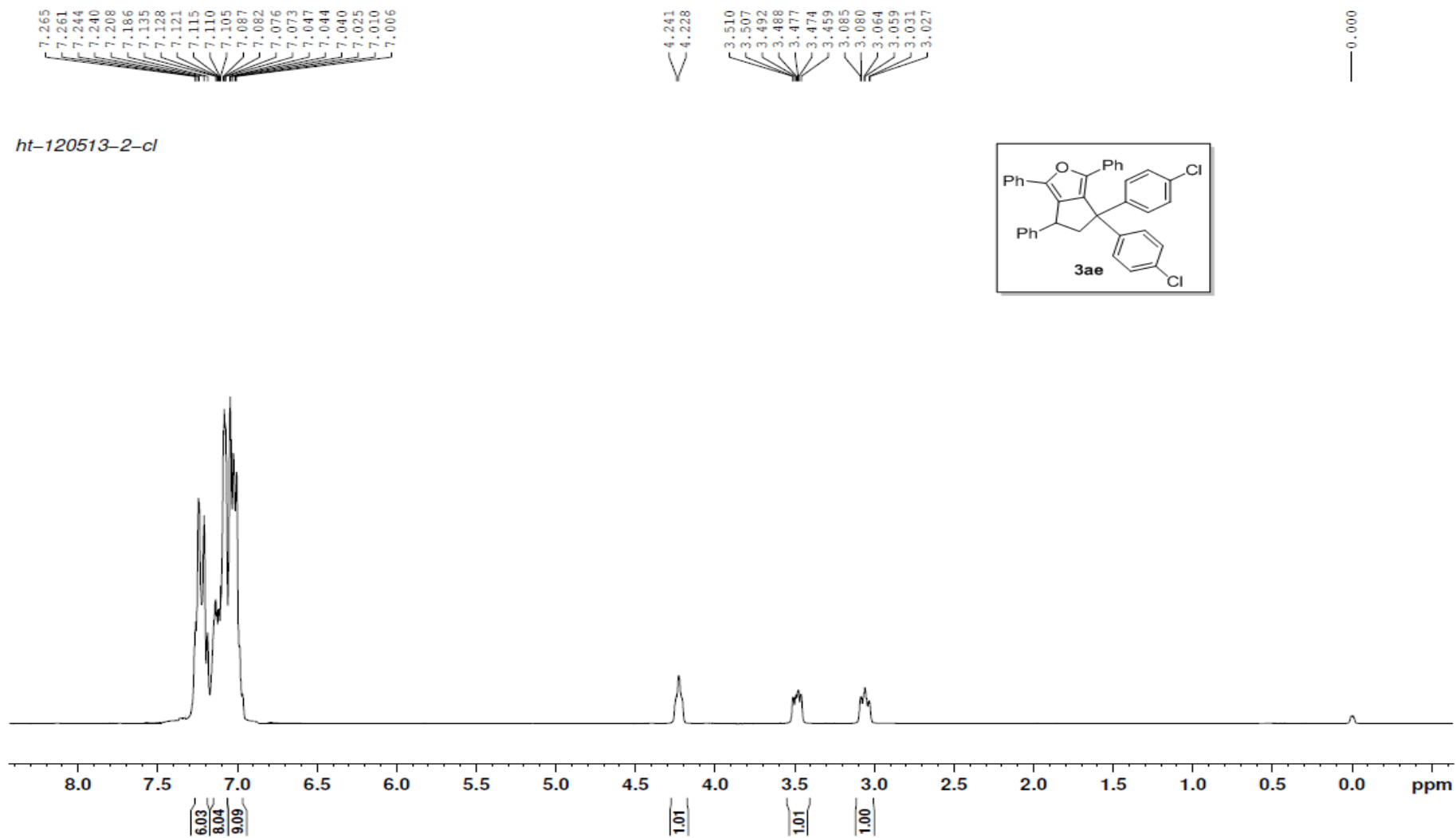


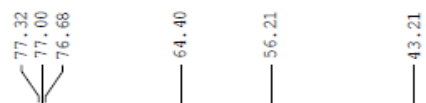
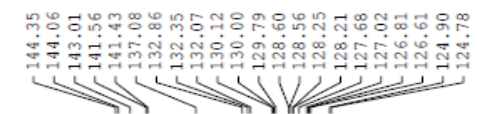
162.88
162.55
160.43
160.11
144.26
143.99
141.68
140.43
140.40
138.79
137.74
132.09
130.37
130.30
130.06
129.98
129.89
128.52
128.21
128.16
127.71
126.90
126.76
126.55
124.88
124.77
115.33
115.12
114.98
114.77

77.32
77.00
76.68
64.48
56.00
43.22

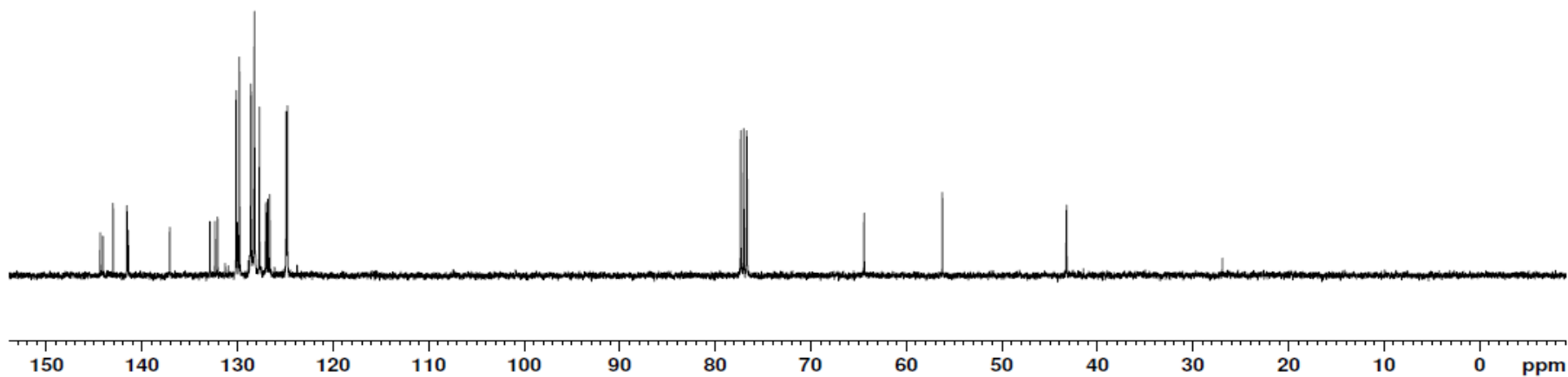
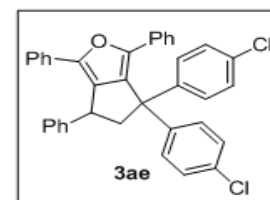
ht-120515-1-f

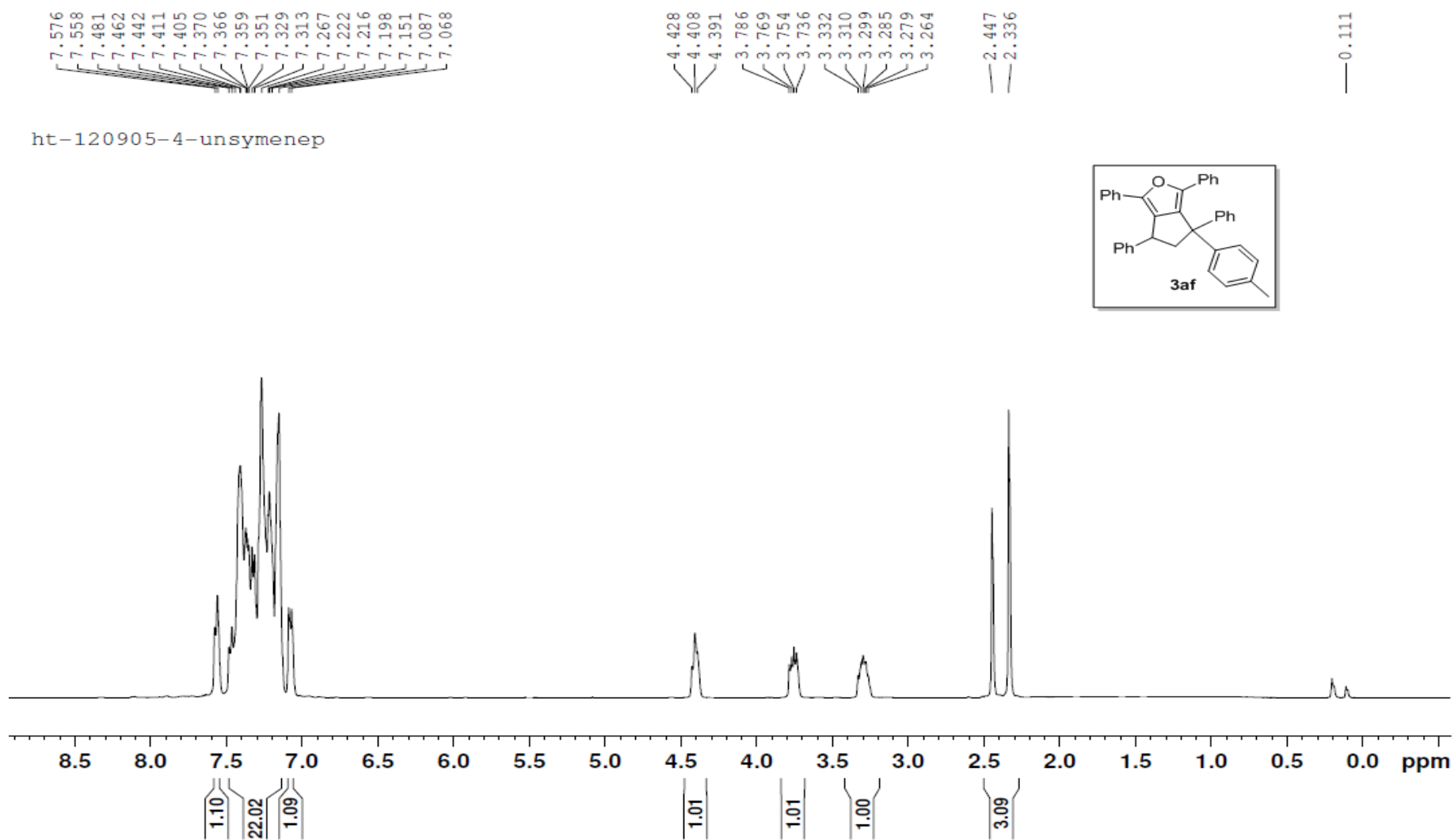


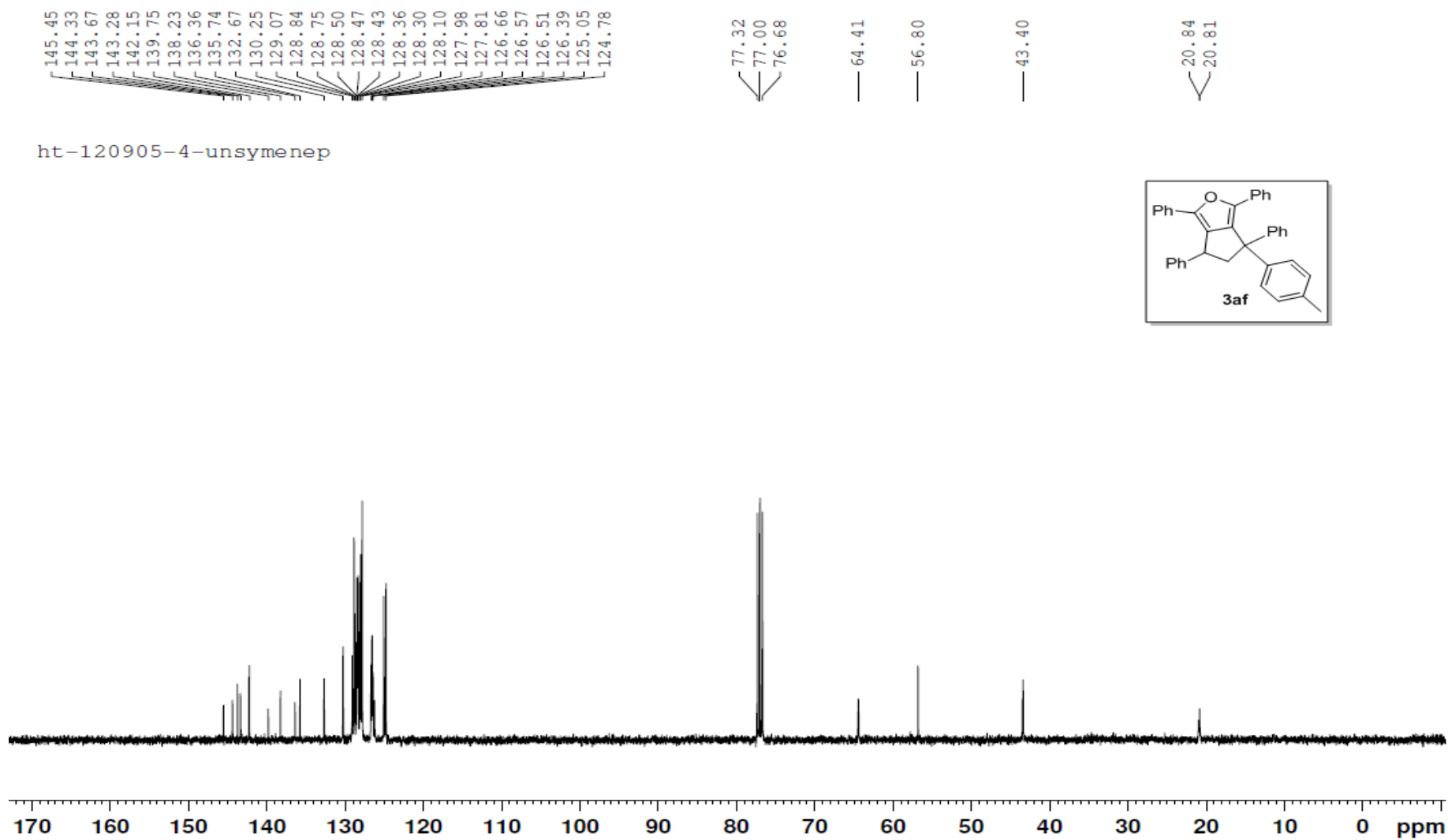




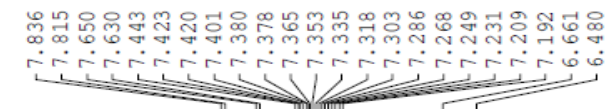
ht-120513-2-d



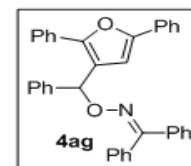




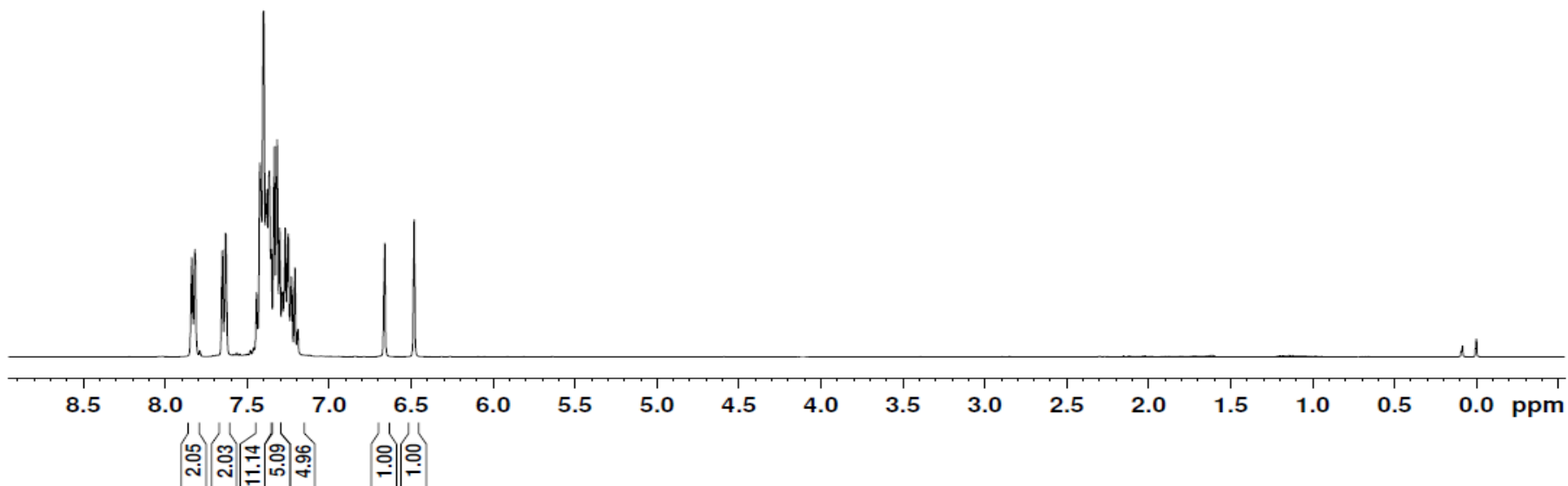
9. ^1H NMR and ^{13}C NMR spectra for compounds 4ag, 4ah



ht-120913-1-xifubase



0.000



157.51
152.29
150.19
140.76
136.42
133.38
130.85
130.56
129.29
129.26
128.73
128.61
128.58
128.26
128.11
128.00
127.97
127.71
127.49
127.33
127.13
126.59
123.71
123.54
107.98

79.91
77.32
77.00
76.68

ht-120913-1-xifubase

