Supplementary Material (ESI) for Chemical Communications

Stereoselective Ir(III)-Catalyzed Dimerization Reaction of Enynes: an Entry to Functionalized Polyunsaturated and Cyclic Systems

Supporting Information

Mehdi Ez-Zoubir, Florent Le Boucher d'Herouville, Jack Brown, Virginie Ratovelomanana-Vidal* and Véronique Michelet*

General information

All manipulations were carried out under an argon atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV 300 instrument. All signals were expressed as ppm (δ) and internally referenced to residual protio solvent signals. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicities. Mass spectrometry analyses (direct introduction by chemical ionization with ammoniac or electrospray) were performed at the Ecole Nationale Supérieure de Chimie de Paris. High resolution mass spectra were performed at the Ecole Normale Supérieure (Paris) and University Pierre and Marie Curie (Paris). Infrared spectra were recorded on a FTIR-4100 Jasco.
Toluene was distilled over sodium benzophenone and degassed prior to use. Dichloromethane was distilled from calcium hydride. $Rh(cod)_2OTf$ was purchased from Aldrich. $[Ir(cod)Cl]_2$ was prepared according to the literature.[1] Enynes **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j** were prepared in analogy with published procedures. [2] Enyne **1k** was prepared according to published procedure.[3]
$[Ir_2H_2I_3(rac\text{-BINAP})_2]I$ was prepared according to the published procedure [4] and the spectral characterizations of $[Ir_2H_2I_3(rac\text{-BINAP})_2]I$,[4]and **4a,** [5] are identical to those published in the literature.

Iridium catalyzed dimerization reaction

In a typical experiment, a Schlenk tube was charged with Ir-catalyst (0.014mmol) under Ar. Then the enyne **1a** (0.35 mmol) in distilled and degassed toluene (0.12-0.19 M) was added. The reaction mixture was stirred at 80°C. The progress of the reaction was monitored by TLC. Then, the solvent was removed under reduced pressure and the product was purified by column chromatography on silica gel.

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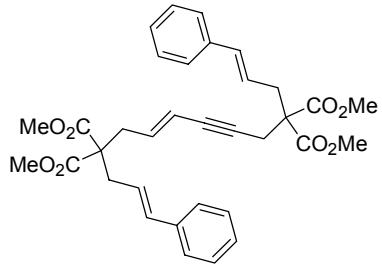
[3] M. Hatano, K. J. Mikami, *J. Am. Chem. Soc.*, 2003, **125**, 4704.
[4]T. Yamagata, H. Tadaoka, M. Nagata, Y. Hirao, Y. Kataoka, V. Ratovelomanana-Vidal, J. P. Genet, K. Mashima, *Organometallics*, 2006, **25**, 2505.
[5] Diethyl ester: (a) N. Chatani, T. Morimoto, S. Murai, *J. Am. Chem. Soc.*, 1994, **116**, 6049. (b) N. Chatani, N. Furukawa, H. Sakurai, S. Murai, *Organometallics*, 1996, **15**, 901. (c) N. Chatani, H. Inoue, T. Ikeda, S. Murai, *J. Org. Chem*., 2000, **65**, 4913.

Rhodium catalyzed reductive C-C bond formation

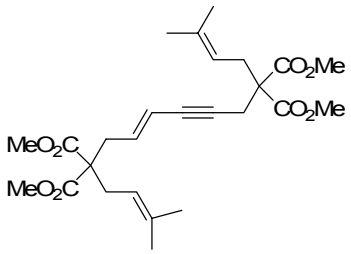
In a typical experiment, the trienyne derivative **2c** (0.20 mmol) was placed in a Schlenk tube under Ar and distilled dichloromethane (0.1 M) was added. $Rh(cod)_2OTf$ (0.01 mmol) and *rac*-Binap (0.01 mmol) was added at room temperature. The system was then purged with hydrogen gas and the reaction mixture was allowed to stir under an atmosphere of hydrogen until completion of the reaction. The crude reaction mixture was then evaporated and the product was purified by column chromatography on silica gel.

(1*E*, 6*E*, 13*E*)-tetramethyl 1,14-diphenyltetradeca-1,6,13-trien-8-yne-4,4,11,11-tetracarboxylate (2a)



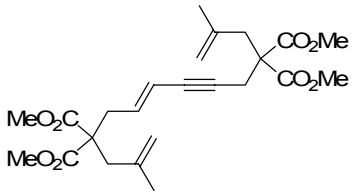
TLC (cyclohexane/ethyl acetate: 80/20) R_f = 0.3.White solid, m.p. = 122°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.70 (dd, *J* = 1.1, 7.6 Hz, 2H), 2.73 (dd, *J* = 1.1, 7.6 Hz, 2H), 2.95 (m, 4H), 3.74 (s, 6H), 3.75 (s, 6H), 5.55 (d, *J* = 15.6 Hz, 1H), 5.89-6.08 (m, 3H), 6.43-6.53 (2d, *J* = 15.3 Hz, 2H), 7.18-7.35 (m, 10H). ^{13}C-NMR (75MHz, $CDCl_3$) 23.9, 36.1, 36.5, 36.6, 52.6, 52.8, 57.5, 57.9, 81.7, 84.0, 113.7, 123.3, 123.5, 126.2, 127.5, 128.5, 134.3, 134.5, 137.0, 137.3, 170.3, 170.9. IR (neat, cm^{-1}) 1730.3, 1436.7, 1276.2, 1194.7, 1072.2, 979.2. CI-MS (NH_3) *m/z* 590 $[M+NH_4]^+$ 573 $[M+H]^+$.HRMS (CI-CH_4) calculated for $C_{34}H_{37}O_8$: 573.2488; found 573.2495.

(*E*)-tetramethyl 2,15-dimethylhexadeca-2, 7,14-trien-9-yne-5,5,12,12-tetracarboxylate (2b)



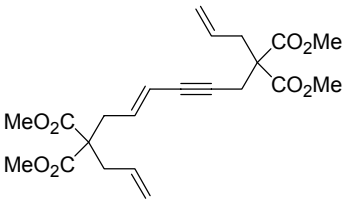
TLC (cyclohexane/ethyl acetate : 80/20) R_f = 0.3. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.59 (s, 3H), 1.63 (s, 3H), 1.68 (s, 6H), 2.55 (d, *J* = 7.5 Hz, 2H), 2.60 (dd, *J* = 1.3, 7.5 Hz, 2H), 2.72 (d, *J* = 7.5 Hz, 2H), 2.84 (d, *J* = 2.0 Hz, 2H), 3.70 (s, 6H), 3.72 (s, 6H), 4.88 (m, 2H), 5.39 (d, *J* = 15.6 Hz, 1H), 5.81 (dt, *J* = 7.5, 15.6, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) 17.8, 17.9, 23.4, 25.9, 26.0, 30.9, 31.3, 36.1, 52.4, 52.6, 57.3, 57.8, 81.4, 84.2, 113.5, 117.1, 117.2, 136.0, 136.7, 137.4, 170.6, 171.2. CI-MS (CH_4) *m/z* 577 $[M+H]^+$. HRMS (ESI) calculated for $C_{26}H_{36}O_8Na$: 499.2302; found 499.2286.

(*E*)-tetramethyl 2, 13-dimethyltetradeca- 1,6, 13-trien-8-yne-4,4,11,11-tetracarboxylate (2c)



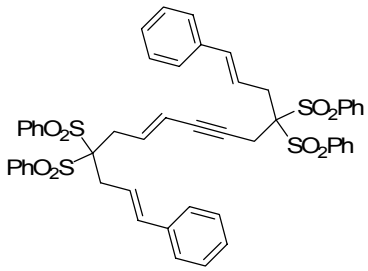
TLC (cyclohexane/ethyl acetate: 80/20) R_f = 0.3.Colorless oil. ^{1}H-NMR (300 MHz $CDCl_3$) 1.58 (s, 3H), 1.60 (s, 3H), 2.59-2.63 (m, 4H), 2.75 (s, 2H), 2.86 (d, *J* = 2.1 Hz, 2H), 3.66 (s, 6H), 3.67 (s, 6H), 4.68 (d, *J* = 1.0 Hz, 1H), 4.75 (d, *J* = 1.0 Hz, 1H), 4.82 (t, *J* = 1.6 Hz, 1H), 4.84 (t, *J* = 1.6 Hz, 1H), 5.41 (d, *J* = 15.7 Hz, 1H), 5.83 (dt, *J* = 7.7, 15.7 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) 22.0, 22.1, 22.6, 35.2, 38.7, 39.6, 51.4, 51.7, 55.7, 56.2, 80.8, 83.1, 112.5, 114.9, 115.2, 136.5, 138.8, 139.1, 169.6, 170.3. IR (neat, cm^{-1}) 1731.3, 1435.3, 1250.6, 1205.8, 1181.2. HRMS (CI-CH_4) calculated for $C_{24}H_{33}O_8$: 449.2175; found 449.2166.

(*E*)-tetramethyl tetradeca-1,6,13-trien-8-yne-4,4,11,11-tetracarboxylate (2d)



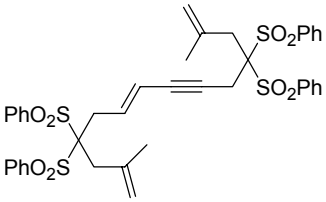
TLC (cyclohexane/ethyl acetate : 80/20) R_f = 0.3. White solid, m.p. = 62°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.63 (m, 4H), 2.76 (d, *J* = 7.5 Hz, 2H), 2.88 (d, *J* = 2.0 Hz, 2H), 3.71 (s, 6H), 3.72 (s, 6H), 5.10-5.19 (m, 4H), 5.45 (d, *J* = 15.5 Hz, 1H), 5.55-5.71 (m, 2H), 5.80-5.92 (dt, *J* = 7.7, 15.5, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) 23.6, 36.2, 36.7, 37.2, 52.5, 52.7, 57.2, 57.6, 81.5, 83.9, 113.7, 119.5, 119.7, 131.8, 132.0, 137.2, 170.2, 170.9. IR (neat, cm^{-1}) 1729.3, 1436.7, 1297.4, 1202.9, 940.6. HRMS (ESI) calculated for $C_{22}H_{28}O_8Na$: 443.1676; found: 443.1676.

(1*E*,6*E*,13*E*)-1,14-diphenyl-4,4,11,11-tetrakis(phenylsulfonyl)tetradeca-1,6,13-trien-8-yne (2e)



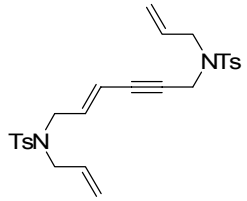
TLC (cyclohexane/ethyl acetate : 80/20) R_f = 0.1. Brown solid, m.p. = 220°C. ^{1}H-NMR (300 MHz $CDCl_3$) 3.04 (d, *J* = 7.0 Hz, 2H), 3.13 (d, *J* = 7.0 Hz, 2H), 3.23 (d, *J* = 7.0 Hz, 2H), 3.34 (s, 2H), 5.33 (d, *J* = 15.6 Hz, 1H), 6.18-6.26 (m, 2H), 6.40-6.51 (m, 3H), 7.27-7.35 (m, 9H), 7.54-7.59 (m, 9H), 7.67-7.69 (m, 4H), 8.03-8.13 (m, 8H). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.0, 32.3, 33.5, 32.7, 81.5, 82.7, 88.1, 89.0, 113.7, 119.7, 119.9, 125.4, 125.5, 126.8, 126.9, 127.6, 130.6, 133.8, 134.5, 134.9, 135.0, 135.4, 135.6. IR (neat, cm^{-1}) 1447.8, 1332.6, 1313.8, 1145.0, 1082.8. HRMS (ESI) calculated for $C_{50}H_{44}O_8NaS_4$: 923.1811; found: 923.1814.

(*E*)- 2,13-dimethyl 1,8,13-triene tetradec-6-yne 4,4',11,11'-tetraphenylsulfone (2f)



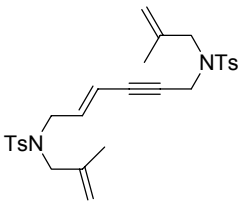
TLC (cyclohexane/ethyl acetate : 70/30) R_f= 0.2. Brown solid, m.p. = 118°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.77 (s, 3H), 1.95 (s, 3H), 2.97 (s, 2H), 3.09 (s, 2H), 3.15 (dd, *J* = 1.3, 6.0 Hz, 2H), 3.55 (d, *J* = 2.0 Hz, 2H), 4.90 (s, 1H), 5.02 (t, *J* = 1.4 Hz, 1H), 5.07 (t, *J* = 1.4 Hz, 1H), 5.11 (s, 1H), 5.40 (d, *J* = 15.6 Hz, 1H), 6.0 (dt, *J* = 7.0, 15.6, 1H), 7.52-7.59 (m, 8H), 7.66-7.70 (m, 4H), 7.98-8.05 (m, 8H). ^{13}C-NMR (75 MHz, $CDCl_3$) 23.1, 24.0, 24.7, 33.9, 36.9, 37.4, 83.6, 84.4, 90.2, 91.3, 114.1, 119.1, 119.3, 128.5, 128.6, 131.6, 131.7, 134.7, 134.8, 136.1, 136.9, 137.3, 137.8, 138.1. IR (neat, cm^{-1}) 1446.8, 1331.6, 1309.4, 1143.1, 1073.2. HRMS (ESI) calculated for $C_{40}H_{40}O_8NaS_4$: 799.1498; found: 799.1511.

***(E)*-*N*, *N*-diallyl-*N*, *N*-ditosylhex-2-en-4-yne-1,6-diamine (2g)**



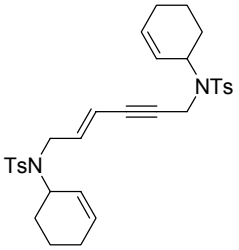
TLC (petroleum ether/ethyl acetate : 80/20) R_f = 0.3. Brown solid, m.p. = 90°C. ^{1}H-NMR (300 MHz $CDCl_3$) 2.43 (s, 6H), 3.73 (d, *J* = 6.3 Hz, 4H), 3.78 (d, *J* = 6.4 Hz, 2H), 4.17 (d, *J* = 1.7 Hz, 2H), 5.06-5.30 (m, 4H), 5.33 (d, *J* = 16.0 Hz, 1H), 5.50-5.80 (m, 3H), 7.27-7.31 (m, 4H), 7.66-7.73 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.5, 36.6, 48.2, 49.2, 49.9, 82.9, 83.0, 112.5, 119.4, 119.8, 127.2, 127.8, 129.5, 129.8, 132.0, 132.3, 136.0, 137.0, 138.2, 143.5, 143.6. IR (neat, cm^{-1}) 1343.7, 1161.4, 1092.9, 938.7. CI-MS (NH_3) *m/z* 516 $[M+NH_4]^+$ 499 $[M+H]^+$. HRMS (ESI) calculated for $C_{26}H_{30}O_4N_2NaS_2$: 521.1539; found: 521.1541.

***(E)*-*N*, *N*-di(2'-methylallyl)-*N*, *N*-ditosylhex-2-en-4-yne-1,6-diamine (2h)**



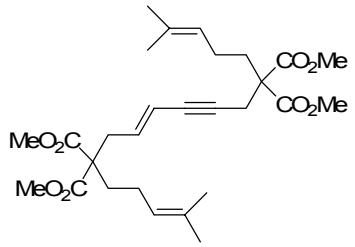
TLC (cyclohexane/ethyl acetate : 70/30) R_f= 0.4. White solid, m.p. = 126°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.63 (s, 3H), 1.75 (s, 3H), 2.42 (s, 6H), 3.62 (s, 2H), 3.66 (s, 3H), 3.69 (s, 1H), 4.12 (d, *J* = 2 Hz, 2H), 4.77 (s, 1H), 4.89 (d, *J* = 1.5 Hz, 1H), 4.91 (s, 1H), 4.95 (d, *J*= 1.5 Hz, 1H), 5.26 (d, *J* = 15.8 Hz, 1H), 5.58 (dt, *J* = 6.8, 15.8 Hz, 1H), 7.25-7.31 (m, 4H), 7.65-7.73 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) 19.6, 19.7, 21.5, 36.3, 48.3, 52.6, 53.5, 82.9, 112.8, 114.9, 115.4, 127.2, 127.8, 129.4, 129.7, 135.9, 136.9, 137.8, 139.3, 139.9, 143.5. IR (neat, cm^{-1}) 1594.4, 1342.7, 1330.2, 1157.6, 1096.3, 1002.8, 963.2, 908.3, 820.0, 759.8. HRMS (ESI) calculated for $C_{28}H_{34}O_4N_2NaS_2$: 549.1852; found: 549.1844.

(*E*)-*N*, *N*'-(hex-2-en-4-yne-1,6-diyl)bis(*N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide) (2i)



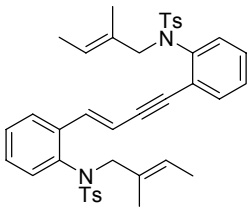
TLC (cyclohexane/ethyl acetate : 80/20) R_f= 0.3. Brown solid, m.p. = 74°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.48-1.87 (m, 12H), 2.35 (s, 6H), 3.66 (dd, *J* = 5.4, 17.1, 1H), 3.86 (dd, *J* = 5.4, 17.1 Hz, 1H), 4.05 (d, *J* = 13.9 Hz, 1H), 4.24 (d, *J* = 13.9 Hz, 1H), 4.43 (m, 2H), 4.93 (d, *J* = 10.0 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 5.50 (d, *J* = 15.9 Hz, 1H), 5.70-5.82 (m, 2H), 5.87-5.94 (dt, *J* = 5.7, 15.9 Hz, 1H), 7.26-7.31(m, 4H), 7.72 (d, *J* = 6.2 Hz, 2H), 7.83 (d, *J* = 6.2 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) 21.4, 21.5, 21.6, 24.3, 27.9, 28.9, 33.5, 45.4, 55.0, 55.3, 81.7, 86.7, 111.3, 127.1, 127.4, 129.4, 129.7, 132.9, 138.0, 138.1, 141.0, 143.2. IR (neat, cm^{-1}) 1339.3, 1331.6, 1161.9, 1088.6, 1032.7. CI-MS (NH_3) *m/z* 596 $[M+NH_4]^+$ 579 $[M+H]^+$. HRMS (ESI) calculated for $C_{32}H_{38}O_4N_2NaS_2$: 601.2165; found: 601.2151.

(*E*)-tetramethyl 2,17-dimethyloctadeca-2, 9, 16-trien-7-yne-5,5,12,12-tetracarboxylate (2j)



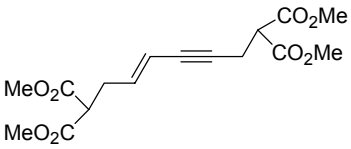
TLC (petroleum ether/ethyl acetate : 80/20) R_f= 0.5. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.56 (s, 3H), 1.58 (s, 3H), 1.67 (s, 6H), 1.85-1.89 (m, 6H), 2.01-2.05 (m, 2H), 2.65 (dd, *J* = 1.0, 7.6 Hz, 2H), 2.90 (d, *J* = 2 Hz, 2H), 3.69 (s, 6H), 3.72 (s, 6H), 5.05-5.08 (m, 2H), 5.43 (d, *J*= 15.6 Hz, 1H), 5.81 (dt, *J* = 7.5, 15.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) 17.5, 22.7, 23.7, 25.6, 32.2, 32.7, 36.4, 52.2, 52.6, 56.9, 57.4, 81.3, 83.9, 113.4 , 122.7, 132.6, 137.3, 170.8, 171.3. IR (neat, cm^{-1}) 1735.6, 1438.1, 1274.2, 1217.3, 1174.4. CI-MS (NH_3) *m/z* 522 $[M+NH_4]^+$ 505 $[M+H]^+$. HRMS (CI-CH_4) calculated for $C_{28}H_{41}O_8$: 505.2801; found 505.2798.

2-((3*E*)-4-(2-(*N*-((*E*)-2-methylbut-2-enyl)-*N*-tosylamino)phenyl)but-3-en-1-ynyl)-*N*-((*E*)-2-methylbut-2-enyl)-*N*-tosylbenzenamine (2k)



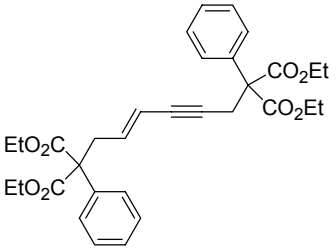
TLC (petroleum ether/ethyl acetate : 80/20) R_f= 0.4. White solid, m.p. = 142°C.^{1}H-NMR (300 MHz, $CDCl_3$) 1.37 (d, *J* = 6.7 Hz, 3H), 1.44 (d, *J* = 6.7 Hz, 3H), 1.66 (s, 3H), 1.70 (s, 3H), 2.32 (s, 3H), 2.41 (s, 3H), 3.70 (m, 1H), 4.29 (s, 3H), 5.0 (m, 1H), 5.24 (m, 1H), 5.90 (d, *J* = 16.3 Hz, 1H), 6.6 (dd, *J* = 0.8, 6.0 Hz, 1H), 6.61-7.18 (m, 2H), 7.21-7.29 (m, 8H), 7.40-7.43 (m, 1H), 7.52-7.61 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$) 13.4, 14.1, 14.6, 21.5, 21.6, 58.0, 60.3, 89.2, 93.7, 109.2, 123.8, 124.6, 125.3, 125.7, 127.8, 128.0, 128.3, 128.5, 128.6, 128.9, 129.4, 129.5, 129.9, 130.6, 132.0, 133.5, 135.7, 137.1, 137.2, 137.5, 139.5, 143.1, 143.6. IR (neat, cm^{-1}) 1339.8, 1332.0, 1159.5, 1034.1. HRMS (CI-CH_4) calculated for $C_{40}H_{43}O_4N_2S_2$: 679.2664; found 679.2660.

2,9-Bis-methoxycarbonyl-dec-4-en-6-ynedioic acid dimethyl ester (2l)



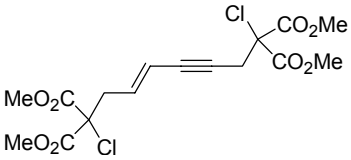
TLC (cyclohexane/ethyl acetate : 70/30) R_f= 0.2. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.62 (m, 2H), 2.86 (dd, *J* = 1.8, 7.8 Hz , 2H), 3.40 (t, *J* = 7.5 Hz, 1H), 3.56 (t, *J* = 7.6 Hz, 1H), 3. 74 (2s, 12H), 5.50 (d, *J* = 16.2 Hz, 1H), 5.91 (dt, *J* = 7.2, 16.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) 19.3, 31.9, 51.0, 52.6, 52.7, 80.4, 85.0, 112.6, 138.6, 168.3, 168.9. IR (neat, cm^{-1}) 1734.7, 1437.2, 1342.7, 1284.8, 1239.5, 1154.2, 1026.9. HRMS (ESI) calculated for $C_{16}H_{20}O_8Na$: 363.1050; found: 363.1046.

2,9-Bis-ethoxycarbonyl-2,9-diphenyl-dec-4-en-6-ynedioic acid diethyl ester (2m)



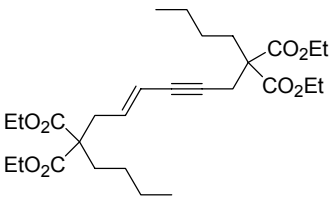
TLC (cyclohexane/ethyl acetate : 70/30) R_f= 0.3 .Yellow solid, m.p. = 100°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.19-1.29 (m, 12H), 3.03 (dd, *J* = 1.1, 7.4 Hz, 2H), 3.25 (d, *J* = 1.9 Hz, 2H), 4.15-4.29 (m, 8H), 5.38 (d, *J* = 15.8 Hz, 1H), 5.88-5.96 (dt, *J* = 7.6, 15.8 Hz, 1H), 7.28-7.46 (m, 10H). ^{13}C-NMR (75 MHz, $CDCl_3$) 14.0, 27.2, 39.6, 61.7, 61.9, 62.1, 62.3, 62.97, 81.9, 84.7, 113.4, 127.6 ,127.8, 127.9, 128.0, 128.1, 135.9, 136.6, 137.9, 169.5, 170.0. IR (neat, cm^{-1}) 1725.9, 1445.4, 1295.4, 1231.3, 1181.2, 1021.6. HRMS (ESI) calculated for $C_{32}H_{36}O_8Na$: 571.2302; found: 571.2298.

2,9-Dichloro-2,9-bis-methoxycarbonyl-dec-4-en-6-ynedioic acid dimethyl ester (2n)



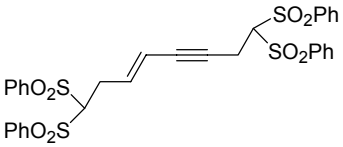
TLC (cyclohexane/ethyl acetate : 80/20) R_f= 0.3. Brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$) 3.01 (dd, *J* = 1.3 , *J* = 7.3 Hz, 2H), 3.27 (d, *J* = 1.7 Hz, 2H), 3.81 (s, 6H), 3.84 (s, 6H), 5.60 (d, *J* = 15.8 Hz, 1H), 6.00 (dt, *J*= 7.4, 15.8, 1H). ^{13}C-NMR 30.2, 41.2, 53.9, 54.1, 68.3, 69.0, 82.0, 82.6, 114.8, 135.6, 166.1, 166.6. IR (neat, cm^{-1}) 1749.1, 1435.7, 1271.8, 1246.3, 1201.9, 1094.9, 1040.4, 1013.9, 963.7. HRMS (CI-CH_4) calculated for $C_{16}H_{19}O_8Cl_2$: 409.0457; found 409.0460.

2-Butyl-2,9,9-tris-ethoxycarbonyl-tridec-4-en-6-ynoic acid ethyl ester (2o)



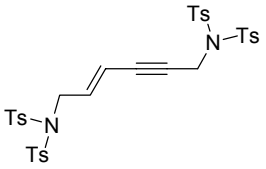
TLC (petroleum ether/ethyl acetate: 80/20) R_f= 0.6. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) 0.88 (m, 6H), 1.11-1.14 (m, 4H), 1.14-1.21 (t, *J* = 7.1 Hz, 12 H), 1.24-1.33 (m, 4H), 1.78-1.84 (m, 2H), 1.95-2.00 (m, 2H), 2.62 (dd, *J* = 1.1, 7.6 Hz, 2H), 2. 87 (d, *J* = 1.8 Hz, 2H), 4.11-4.20 (m, 8H), 5.40 (d, *J* = 15.8 Hz, 1H), 5.83 (dt, *J* = 7.6, 15.8 Hz, 1H). ^{13}C-NMR 13.7, 14.0, 22.8, 23.5, 26.0, 30.8, 31.6, 32.0, 36.0, 57.0, 57.4, 61.1, 61.5, 81.2, 83.9, 113.2, 137.4, 170.4, 171.0. IR (neat, cm^{-1}) 2958.7, 2928.4, 1733.2, 1462.7, 1210.6, 1037.0. HRMS (CI-CH_4) calculated for $C_{28}H_{45}O_8$: 509.3114; found 509.3113.

(*E*)-(oct-3-en-5-yne-1,8,8-tetrayltetrasulfonyl)tetrabenzene (2p)



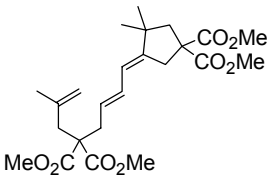
TLC (cyclohexane/ethyl acetate : 50/50) R_f= 0.5. Brown solid, m.p. = 188°C. ^{1}H-NMR (300 MHz, DMSO-d_6) 2.90-2.95 (t, *J* = 5.6 Hz, 2H), 3.21 (d, *J* = 3.9 Hz, 2H), 5.37 (d, *J* = 15.9 Hz, 1H), 5.82-5.88 (m, 1H), 5.93 (t, *J* = 5.6 Hz, 1H), 6.01 (t, *J* = 5.6 Hz, 1H), 7.69-8.01 (m, 20H). ^{13}C-NMR 16.7, 28.3, 78.5, 79.2, 81.5, 83.3, 112.0, 128.9, 129.2, 134.6, 134.7, 137.6, 137.8, 138.0. IR (neat, cm^{-1}) 1451.2, 1322.9, 1312.3, 1151.8, 1074.6, 729.9. HRMS (CI-CH_4) calculated for $C_{32}H_{29}O_8S_4$: 669.0745; found 669.0740.

(*E*)-N, N'-(hex-2-en-4-yne-1,6-diyl)bis(4-methyl-*N*-tosylbenzenesulfonamide) (2q)



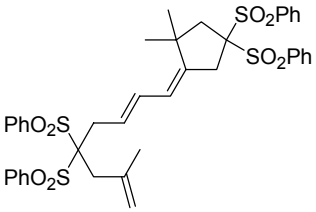
TLC (cyclohexane/ethyl acetate : 80/20) R_f= 0.3. Brown solid, m.p. = 220°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.40 (s, 6H), 2.42 (s, 6H), 4.28 (dd, *J* = 0.9, 6.6 Hz, 2H), 4.62 (d, *J* = 1.8 Hz, 1H), 5.57 (d, *J*= 15.8 Hz, 1H), 5.82-5.88 (dt, *J* = 6.7, 15.8 Hz, 1H), 7.19-7.27 (m, 8H), 7.78-7.85 (m, 8H). ^{13}C-NMR 21.6, 38.7, 50.1, 82.1, 85.0, 114,1, 128.2, 128.3, 129.6, 129.7, 136.5, 136.7, 137.9, 145.2, 145.3. IR (neat, cm^{-1}) 1599.2, 1367.8, 1165.3, 1083.8, 1041.4, 816.7, 787.8. HRMS (ESI) calculated for $C_{34}H_{34}O_8N_2NaS_4$: 749.1090; found 749.1098.

(4*E*)-dimethyl 4-((*E*)-5,5-di(methoxycarbonyl)-7-methylocta-2,7-dienylidene)-3,3-dimethylcyclopentane-1,1-dicarboxylate (7)



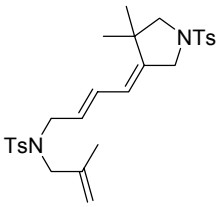
TLC (cyclohexane/ethyl acetate : 80/20) R_f= 0.3. Colorless oil. ^{1}H-NMR (300 MHz $CDCl_3$) 1.05 (s, 6H), 1.66 (s, 3H), 2.29 (s, 2H), 2.69 (s, 2H), 2.70 (d, J = 6.0 Hz, 2H), 3.13 (d, *J* = 2.3 Hz, 2H), 3.70 (s, 12H), 4.74 (s, 1H), 4.88 (s, 1H), 5.36-5.44 (m, 1H), 5.74 (d, *J* = 11.0 Hz, 1H), 6.13 (dd, *J* = 11.0, 15.0 Hz, 1H).^{13}C-NMR (75MHz, $CDCl_3$) 23.1, 29.3, 36.2, 37.4 , 40.4, 42.2, 48.1, 52.3, 52.8, 57.6, 58.0, 115.8, 119.5, 125.8, 131.5, 140.5, 150.1, 171.6, 172.5. IR (neat, cm^{-1}) 1729.8, 1432.8, 1258.3, 1199.0, 1172.5, 1077.0. HRMS (ESI) calculated for $C_{24}H_{34}O_8Na$: 473.2145; found: 473.2131.

(4*E*)-dimethyl 4-((*E*)-5,5-di(phenylsulfonyl)-7-methylocta-2,7-dienylidene)-3,3-dimethylcyclopentane-1,1-dicarboxylate (8)



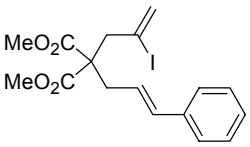
TLC (cyclohexane/ethyl acetate : 70/30) R_f= 0.2 . Yellow solid, m.p. = 94°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.12 (s, 6H), 1.86 (s, 3H), 2.61 (s, 2H), 3.03 (s, 2H), 3.22 (d, *J* = 6.7 Hz, 2H), 3.50 (s, 2H), 4.93 (s, 1H), 5.06 (s, 1H), 5.58-5.71 (m, 2H), 6.17 (dd, *J* = 11.1, 14.8 Hz, 1H), 7.54- 7.69 (m, 12H), 8.00-8.05 (m, 8H). ^{13}C-NMR (75 MHz, $CDCl_3$) 24.7, 29.3, 34.5, 35.2, 37.6, 43.4, 44.0, 91.6, 91.9, 119.3, 125.3, 128.6, 128.9, 131.5, 131.8, 134.5, 134.7, 136.2, 137.4, 138.0, 148.9. IR (neat, cm^{-1}) 1449.7, 1326.8, 1307.5, 1141.6, 1076.6. HRMS (ESI) calculated for $C_{40}H_{42}O_8NaS_4$: 801.1655; found: 801.1664.

3-[4(2-methyl-*N*-tosylallyl-but-2-enylidène]-4,4 dimethyl-*N*-tosyl-pyrrolidine (9)



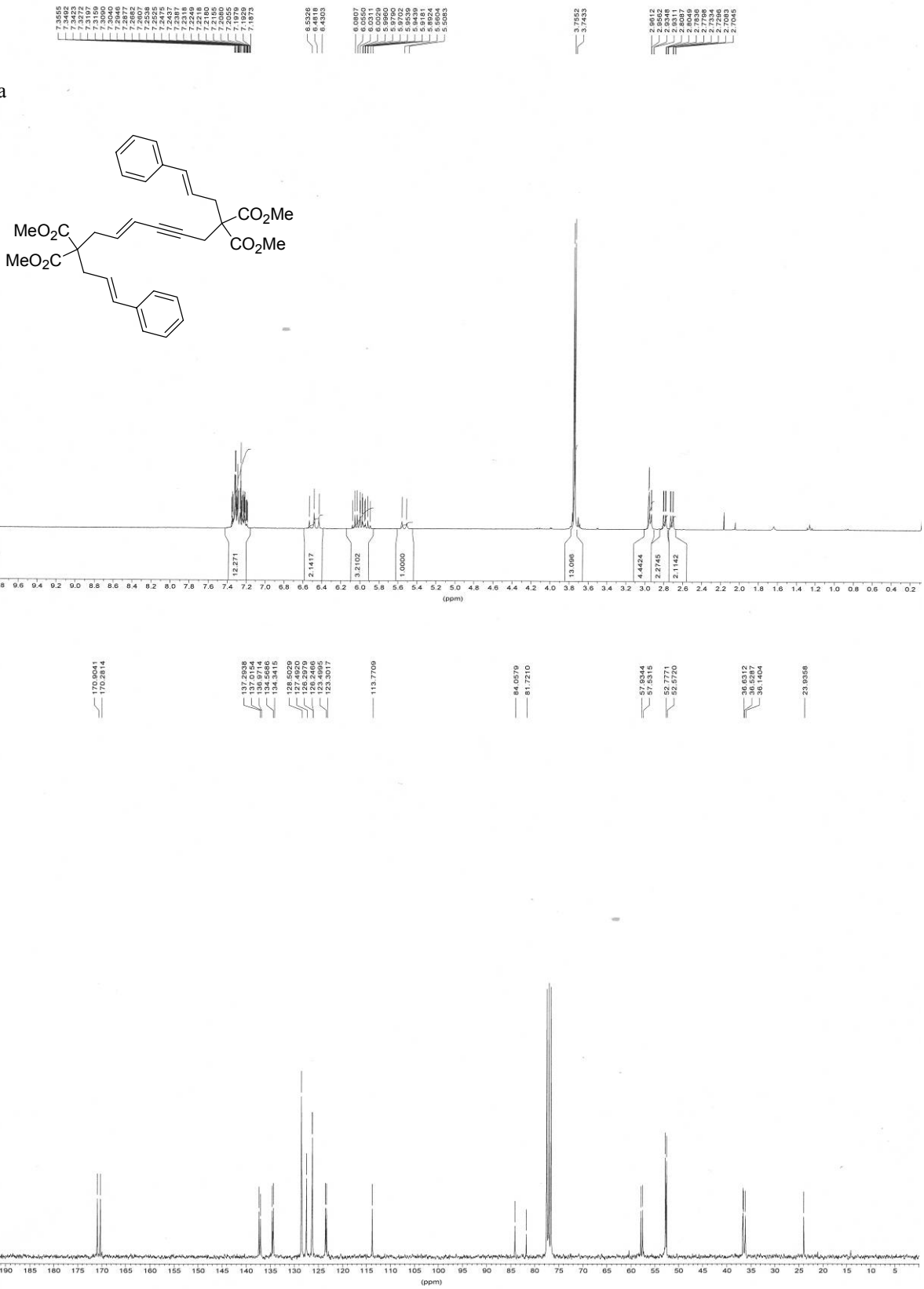
TLC (cyclohexane/ethyl acetate : 70/30) R_f= 0.4. Yellow solid, m.p. = 80°C. ^{1}H-NMR (300 MHz, $CDCl_3$) 1.07 (s, 6H), 1.67 (s, 3H), 2.41 (s, 3H), 2.42 (s, 3H), 2.98 (s, 2H), 3.66 (s, 2H), 3.76 (d, *J* = 6.7 Hz, 2H), 3.88 (d, *J* = 2.2 Hz, 2H), 4.81 (s, 1H), 4.91 (s, 1H), 5.33 (dt, *J* = 7.0, 14.8 Hz, 1H), 5.62 (d, *J* = 10.9 Hz, 1H), 5.83 (dd, *J* = 10.9, 14.8 Hz, 1H), 7.26-7.35 (m, 4H), 7.66-7.72 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) 19.8, 21.5, 26.3, 42.2, 48.6, 49.9, 53.0, 60.6, 114.6, 118.3, 127.2, 127.8, 129.6, 129.7, 129.9, 132.5, 137.2, 140.2, 143.2, 143.7, 146.8. IR (neat, cm^{-1}) 1446.8, 1338.8, 1156.1, 1094.4, 1034.6, 823.9, 816.2. HRMS (ESI) calculated for $C_{28}H_{36}O_4N_2NaS_2$: 551.2008; found: 551.2007.

dimethyl 2-cinnamyl-2-(2-iodoallyl)malonate (5a)



TLC (cyclohexane/ethyl acetate: 80/20) R_f= 0.5. Brown oil. ^{1}H-NMR (300 MHz, $CDCl_3$) 2.91 (dd, *J* = 1.3, 7.5 Hz, 2H), 3.21 (d, *J* = 0.9 Hz, 2H), 3.7 (s, 6H), 5.97 (d, *J* = 1.5 Hz, 1H), 6.0 (dt, *J* = 7.5, 15.8 Hz, 1H), 6.20 (d, *J* = 1.5 Hz, 1H), 6.45 (d, *J*= 15.8 Hz, 1H), 7.21-7.36 (m, 5H) ^{13}C-NMR (75 MHz, $CDCl_3$) 35.6, 46.5, 52.7, 57.8, 100.9, 123.5, 126.2, 127.5, 128.5, 131.4, 134.4, 136.9, 170.4. IR (neat, cm^{-1}) 1733.2, 1433.3, 1288.2, 1246.3, 1208.7, 1183.1, 970.0. CI-MS (NH_3) *m/z* 432 $[M+NH_4]^+$ 415 $[M+H]^+$.

2a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CO2Me
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MeO2C
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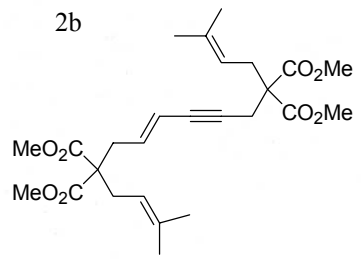
(ppm)

(ppm)

2b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CO2Me
MeO2C
MeO2C

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2.6304
2.6260
2.6047
2.6009
2.5640
2.5589
1.6864
1.6350
1.6318
1.5923
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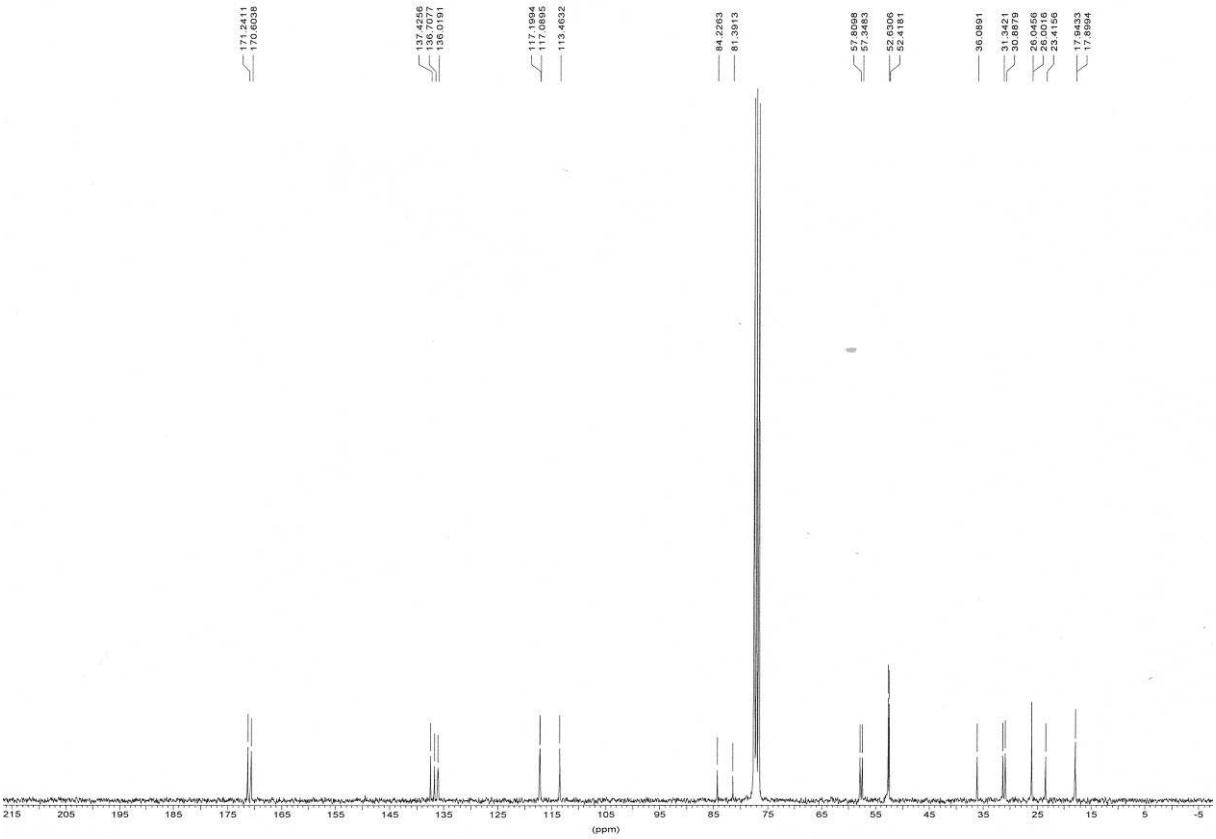
(ppm)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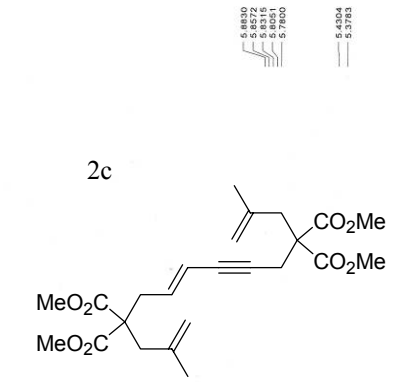
(ppm)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MeO2C

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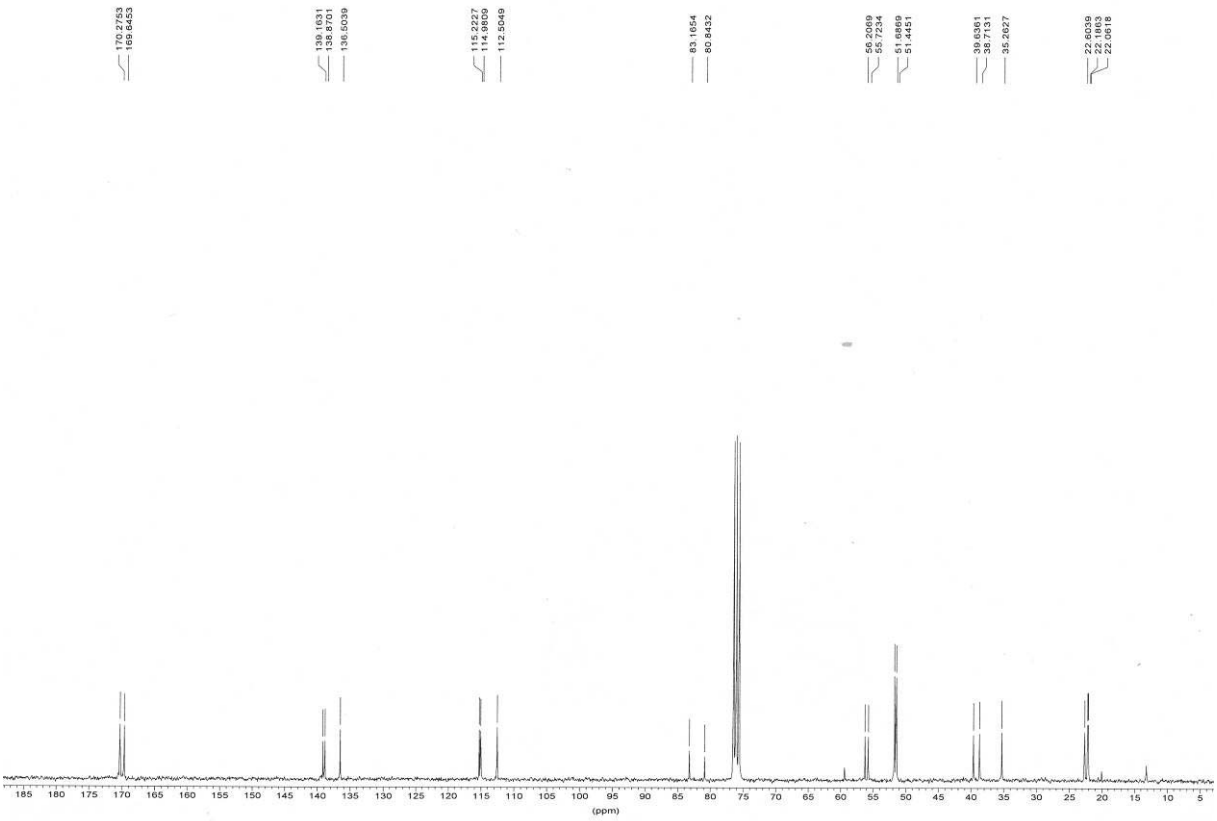
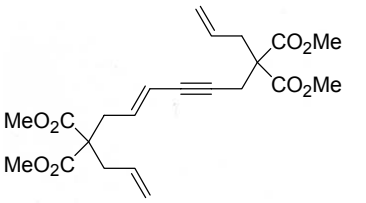
(ppm)


(ppm)

2d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MeO2C

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2.77906
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2.65435
2.65016
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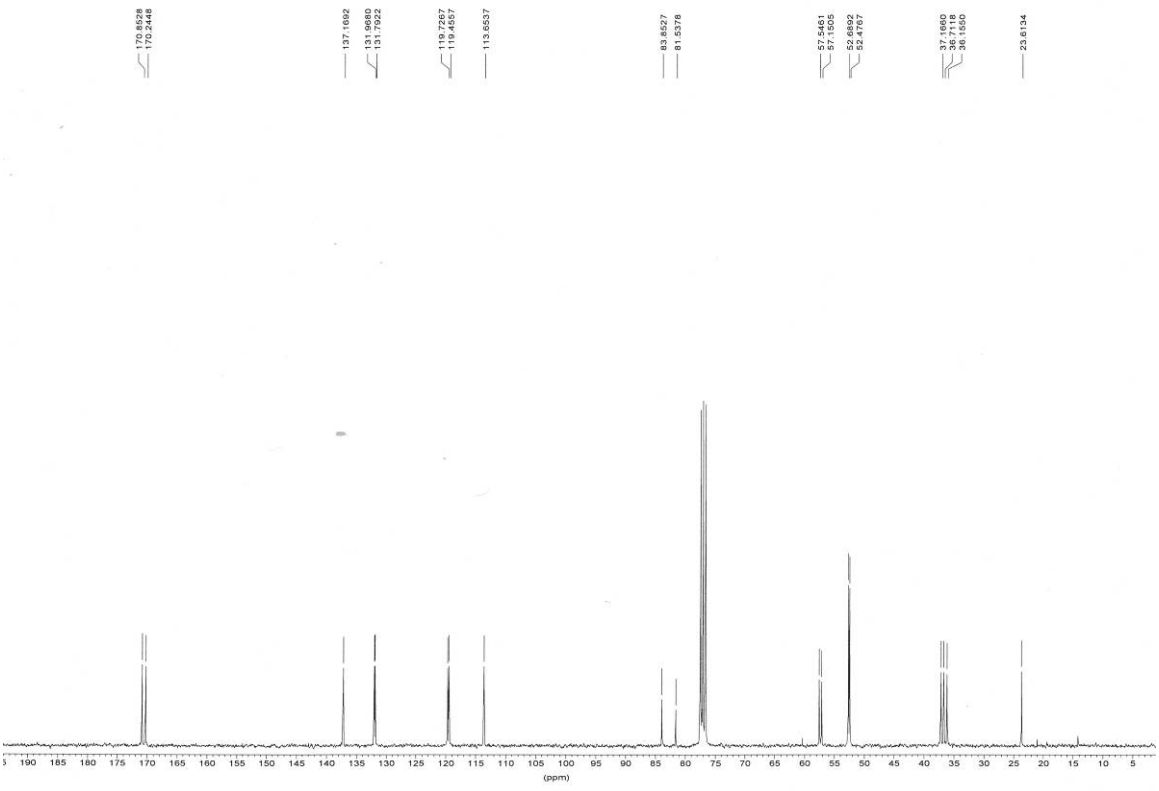
ppm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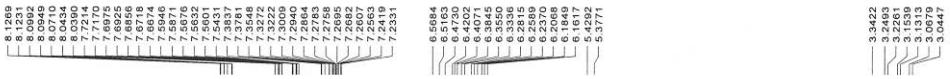
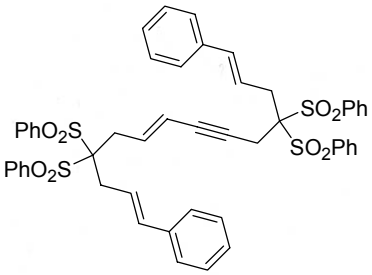
(ppm)



2e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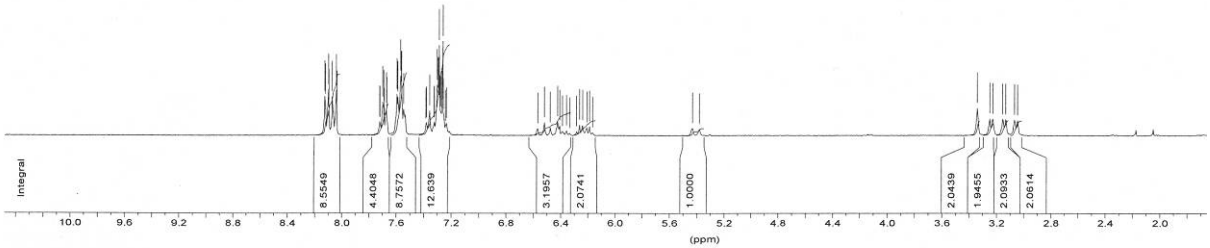
PhO2S
PhO2S
SO2Ph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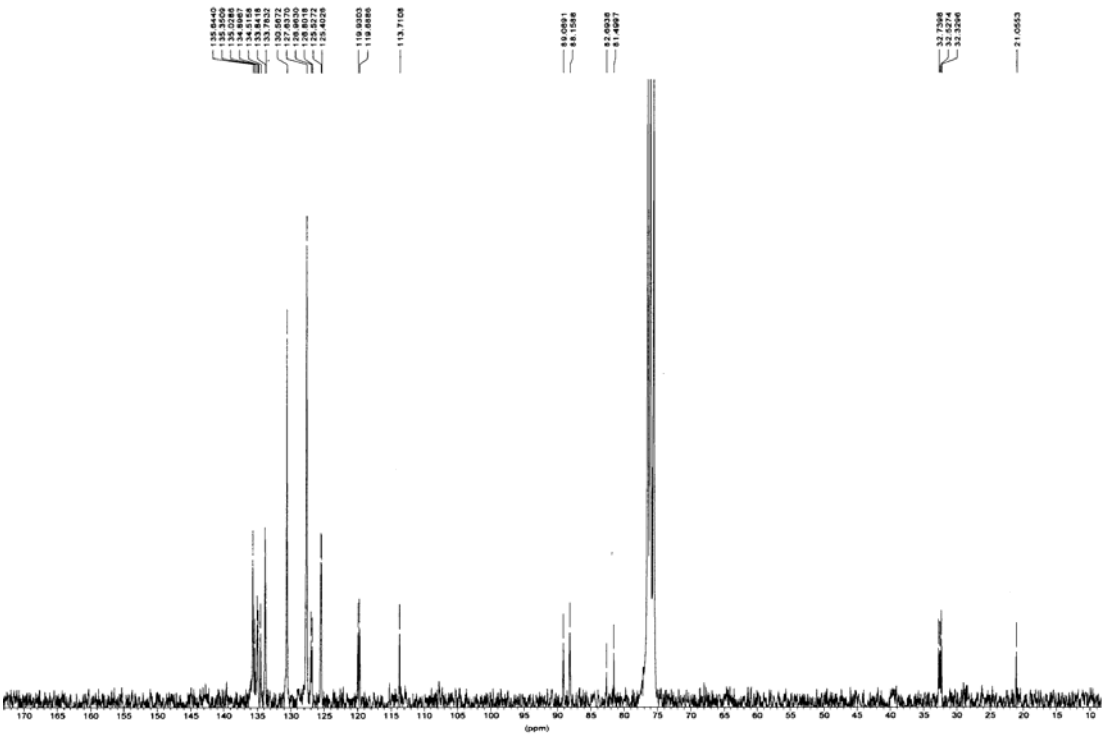
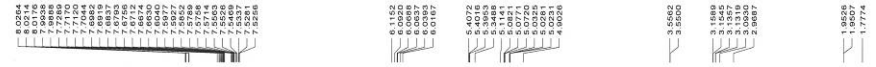
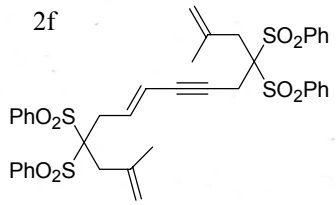
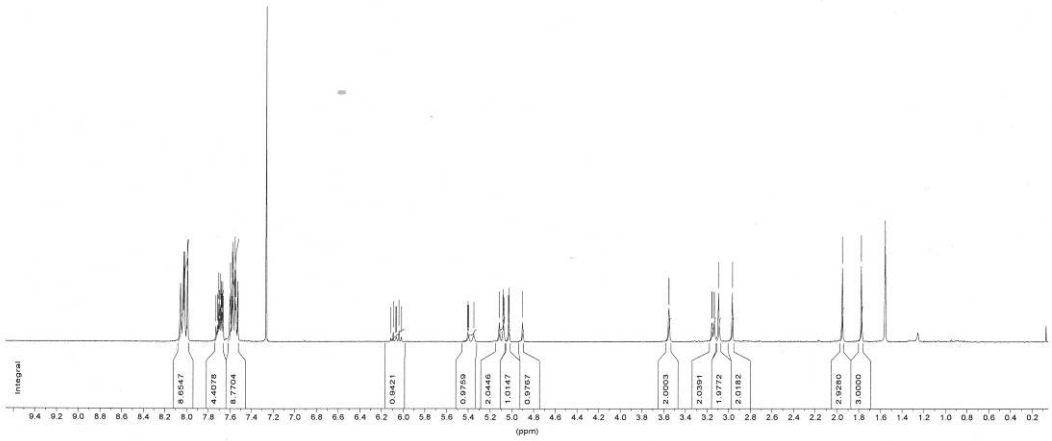
2.0614
(ppm)

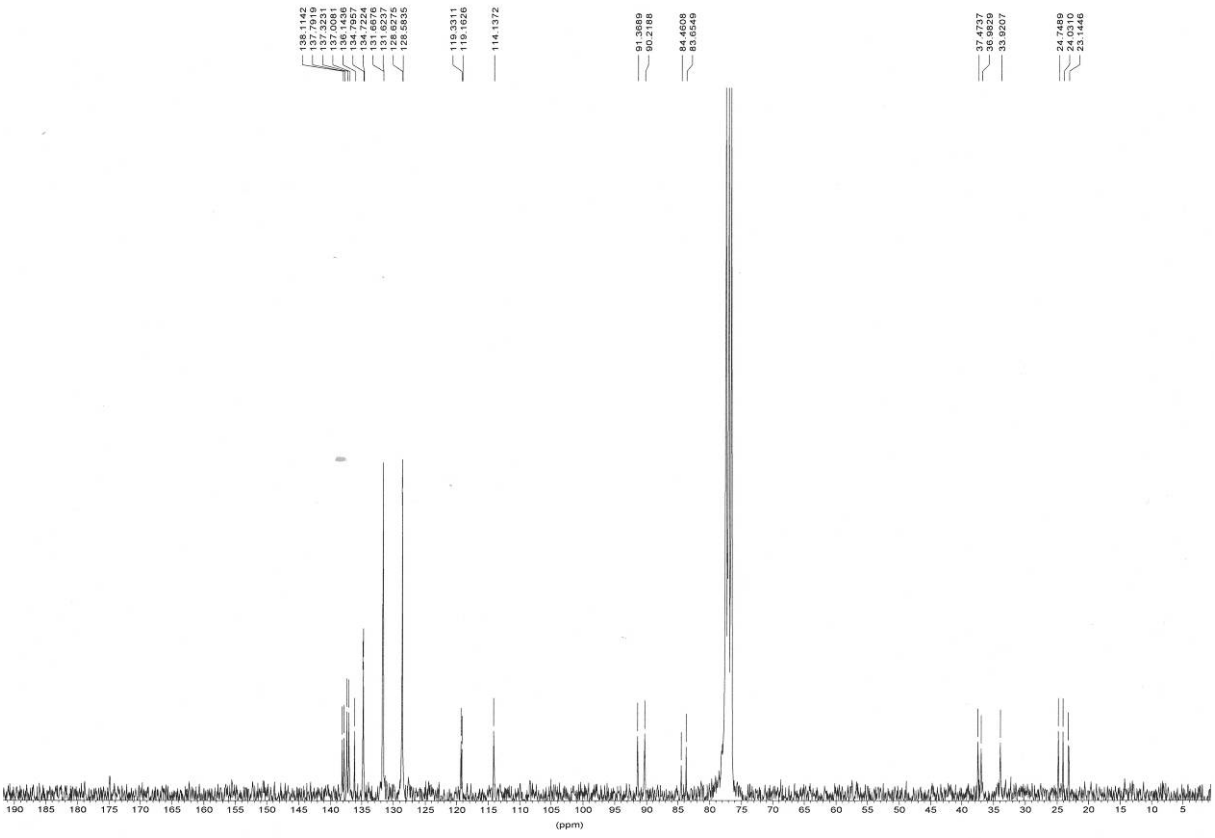

(ppm)

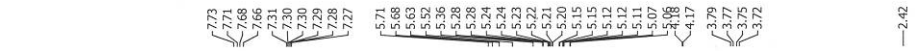


2f

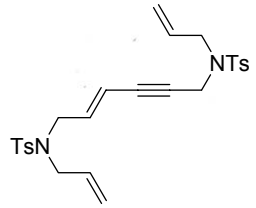

SO2Ph
SO2Ph
PhO2S
PhO2S

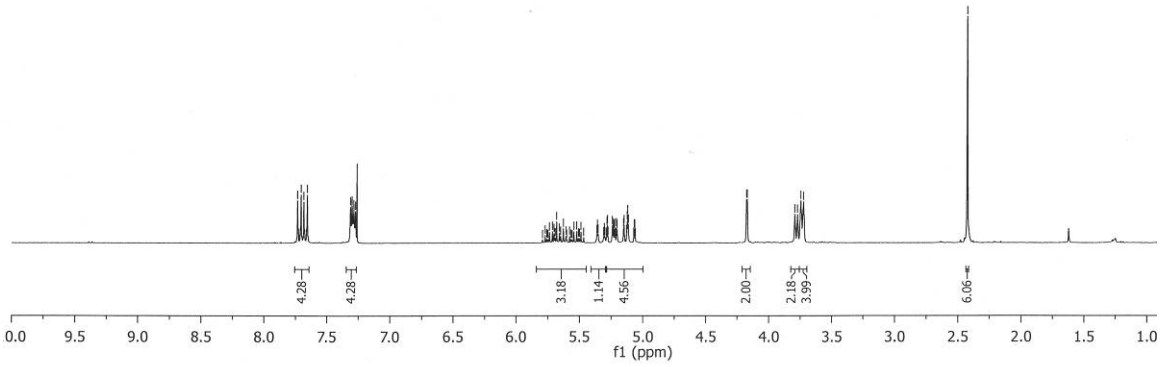

Integral
8.6547
4.4078
8.7704
0.9421
0.9759
2.0446
1.0147
0.9767
2.0003
2.0351
1.9772
2.0182
2.9280
3.0000
(ppm)

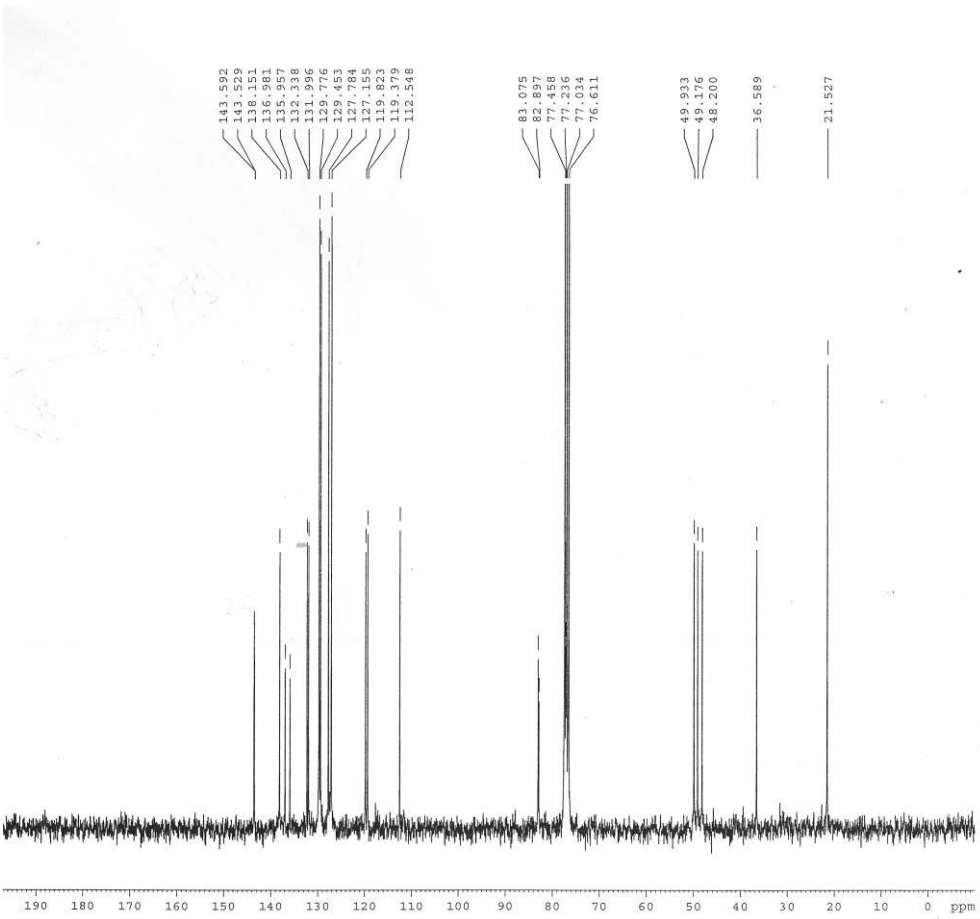

138.1142
137.7919
137.3231
137.0041
136.1436
134.7957
134.7224
131.6460
131.6237
128.6275
128.5835
119.3311
119.1626
114.1372
91.3689
90.2188
84.4608
83.6549
37.4737
36.5529
33.9207
24.7489
24.0310
23.1446
(ppm)


7.73
7.71
7.68
7.66
7.31
7.30
7.30
7.29
7.28
7.27
5.71
5.68
5.63
5.52
5.36
5.28
5.28
5.24
5.24
5.23
5.22
5.21
5.20
5.15
5.15
5.12
5.12
5.11
5.07
5.06
4.18
4.17
3.79
3.77
3.75
3.72
2.42

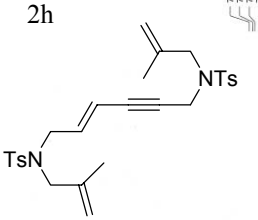
2g


NTs
TsN

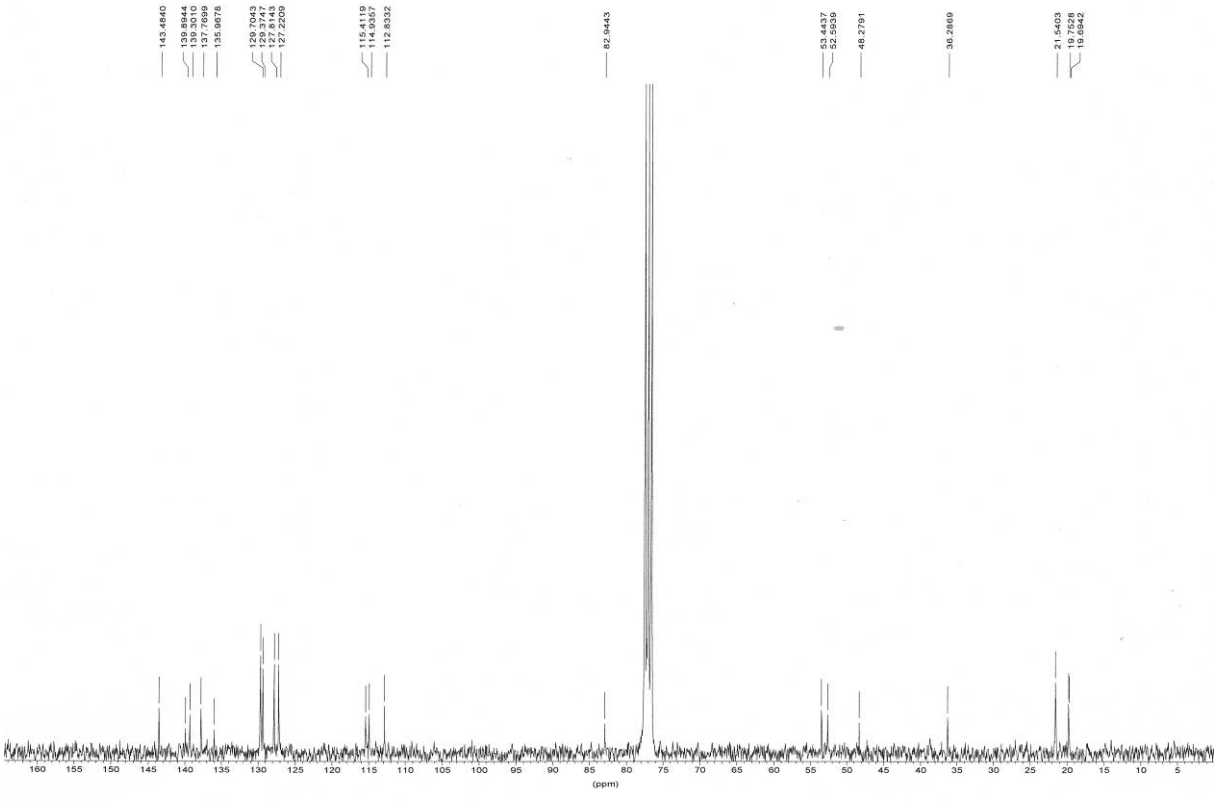

4.28
4.28
3.18
1.14
4.56
2.00
2.18
3.99
6.06
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

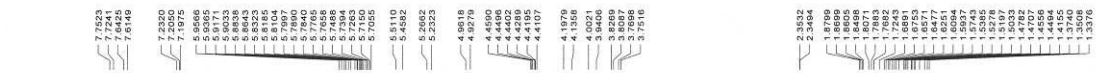

143.592
143.529
138.151
136.981
135.957
132.338
131.996
129.776
129.453
127.784
127.155
119.823
119.379
112.548
83.075
82.897
77.458
77.236
77.034
76.611
49.933
49.176
48.200
36.589
21.527
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2h

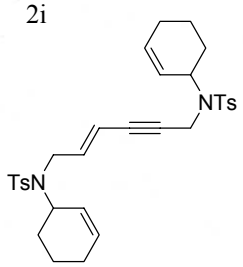

NTs
TsN

7.7358
7.7068
7.6894
7.6618
7.3159
7.2952
5.6394
5.6186
5.5936
5.5861
5.5729
5.5409
5.2754
5.2227
4.9691
4.9151
4.8963
4.7668
4.1261
2.4266
1.7599
1.6368
Integral
5.0321
7.3860
1.0000
1.0667
3.4849
1.0911
2.2100
6.8170
6.8266
2.9534
2.9230
(ppm)

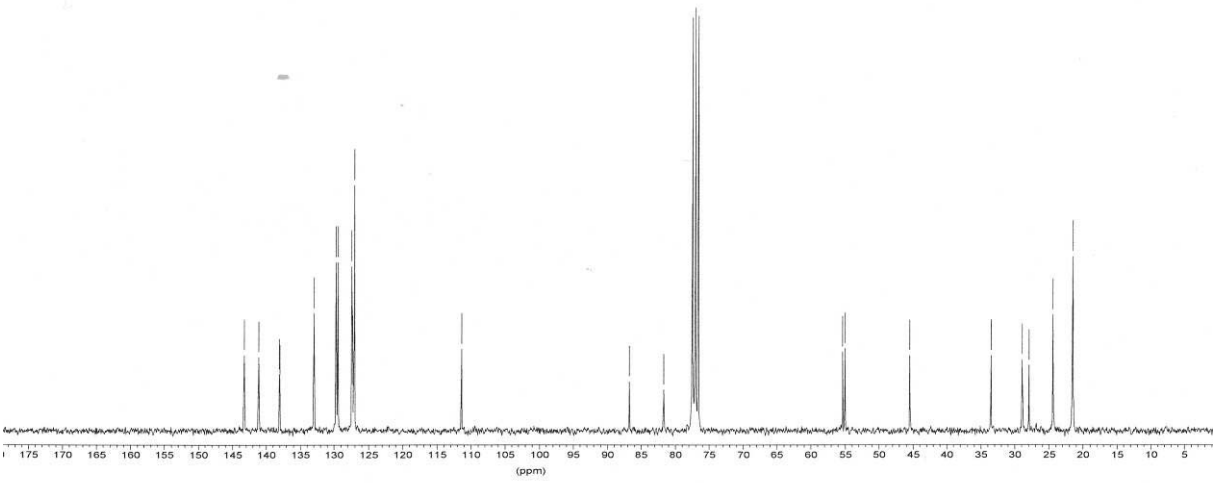

143.4840
139.8944
139.5010
137.7699
135.9678
129.7043
128.2477
127.8143
127.2209
115.4119
114.0357
112.8332
82.9443
53.4437
52.5939
48.2791
36.2869
21.5403
19.7528
19.6842
(ppm)

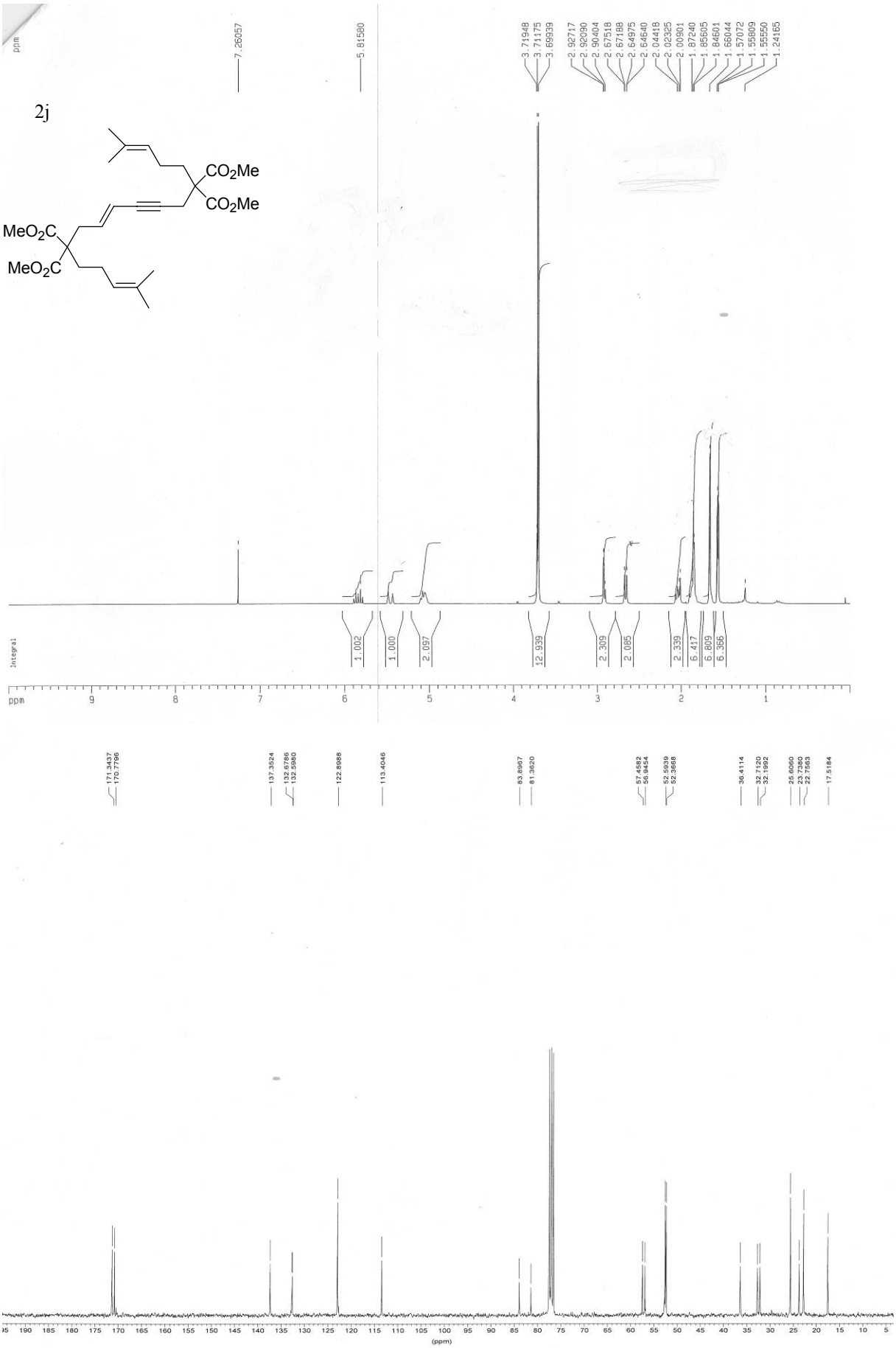


2i

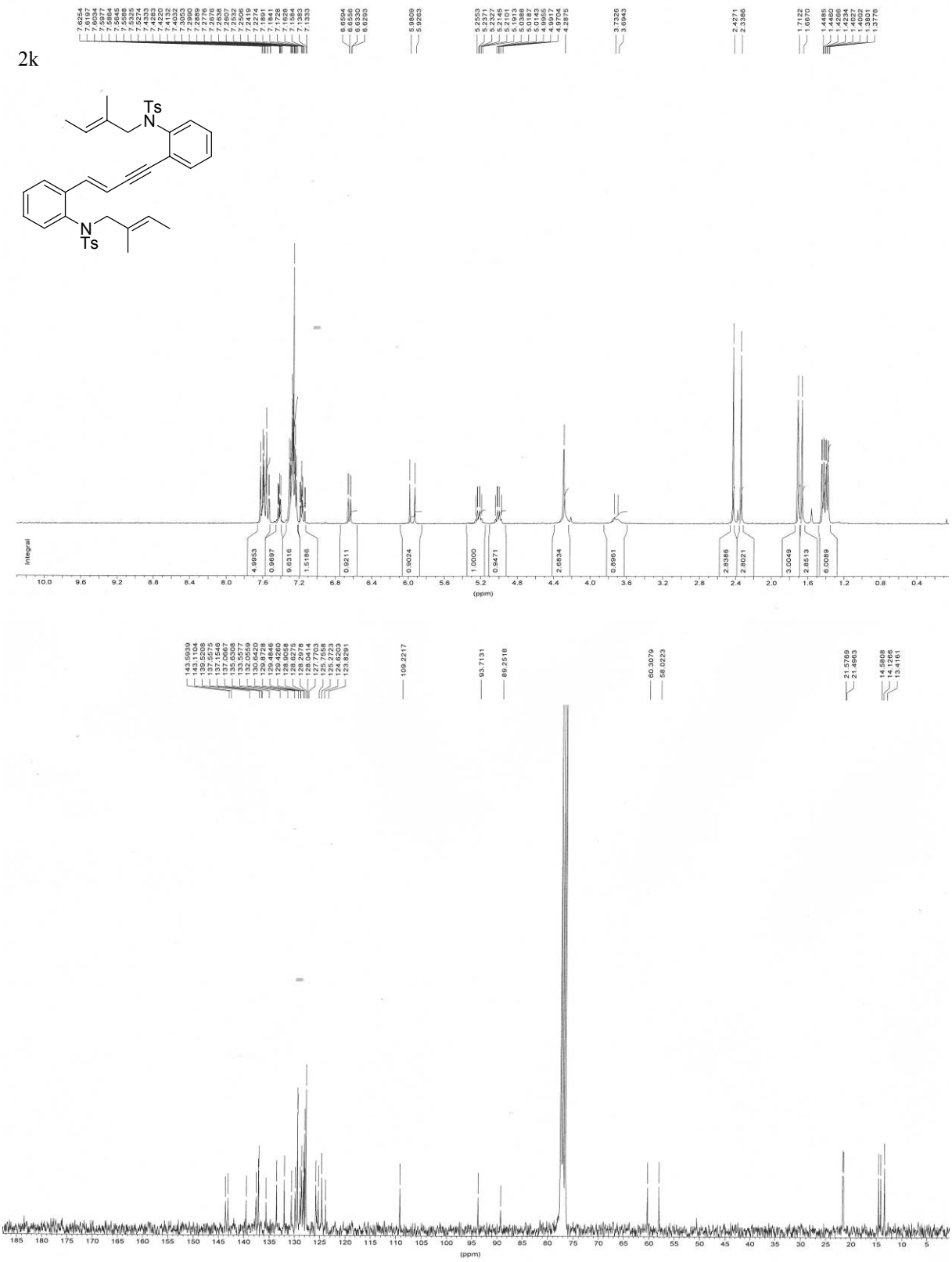

NTs
TsN

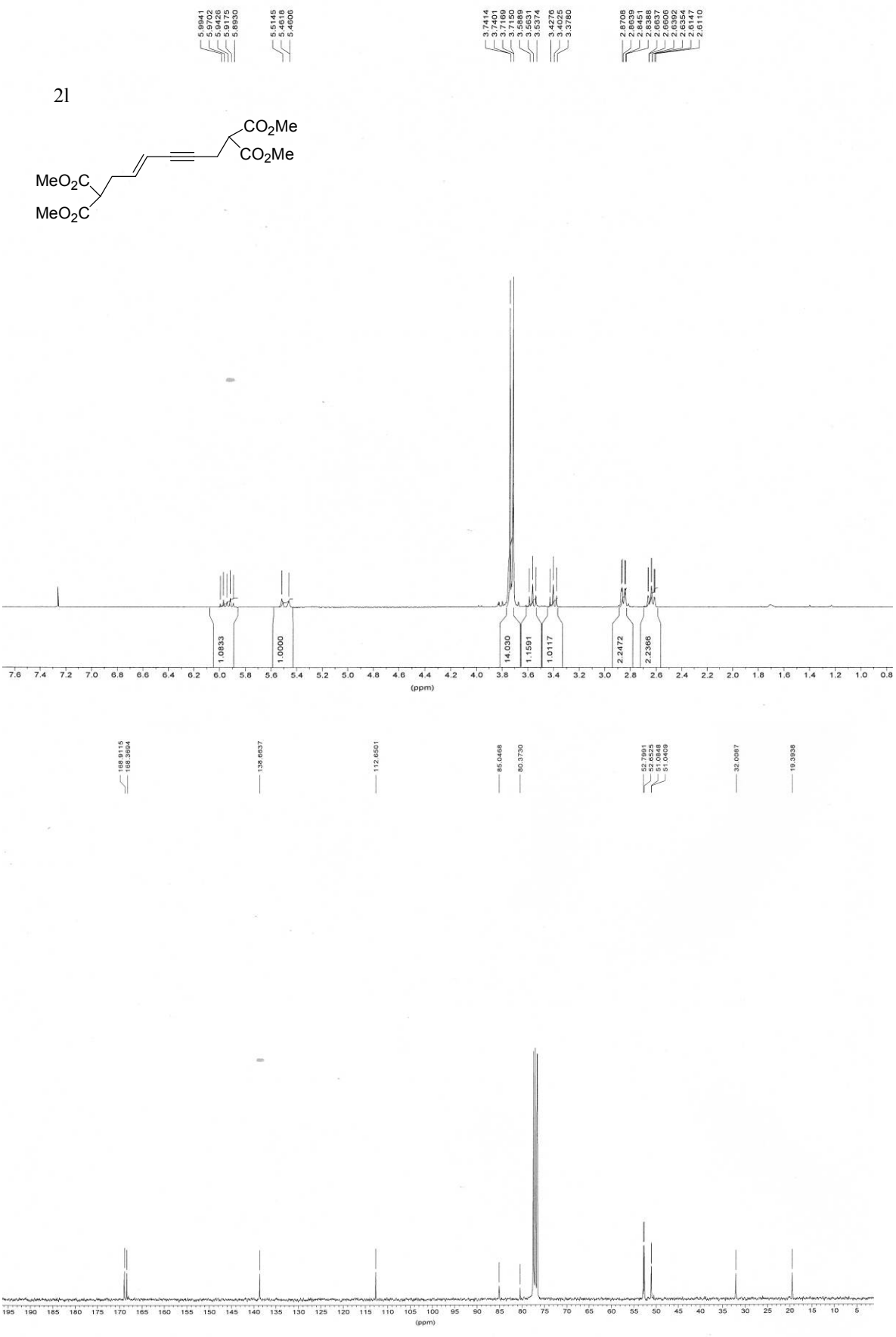
4.4642
4.9718
1.0162
2.1464
1.0000
1.1255
1.0488
2.1719
2.2326
2.2410
6.6351
14.284
(ppm)

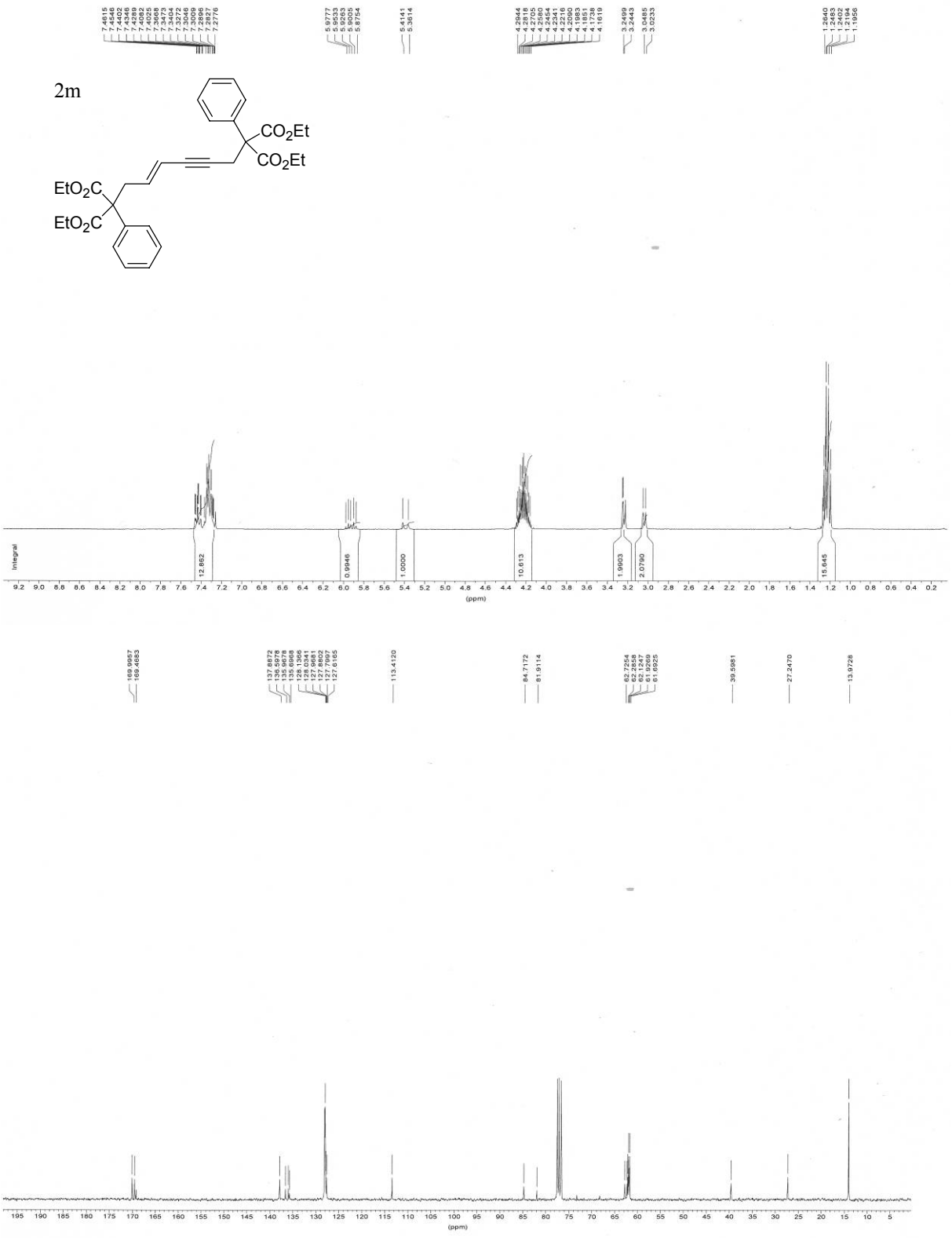

(ppm)


2j
CO2Me
CO2Me
MeO2C
MeO2C
ppm
7.26057
5.81560
3.71948
3.71175
3.69939
2.92717
2.92090
2.90404
2.67518
2.67188
2.64975
2.64640
2.04418
2.02325
2.00901
1.87240
1.85605
1.84601
1.66044
1.57072
1.55809
1.55550
1.24165
integral
1.002
1.000
2.097
12.939
2.309
2.085
2.339
6.417
6.809
6.366
171.3437
170.7796
137.3524
132.6786
132.5980
122.8988
113.4046
83.8967
81.3820
57.4852
56.4844
52.5939
52.3668
36.4114
32.7120
32.1992
25.6060
23.7350
22.7563
17.5184
(ppm)

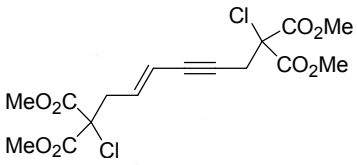
2k



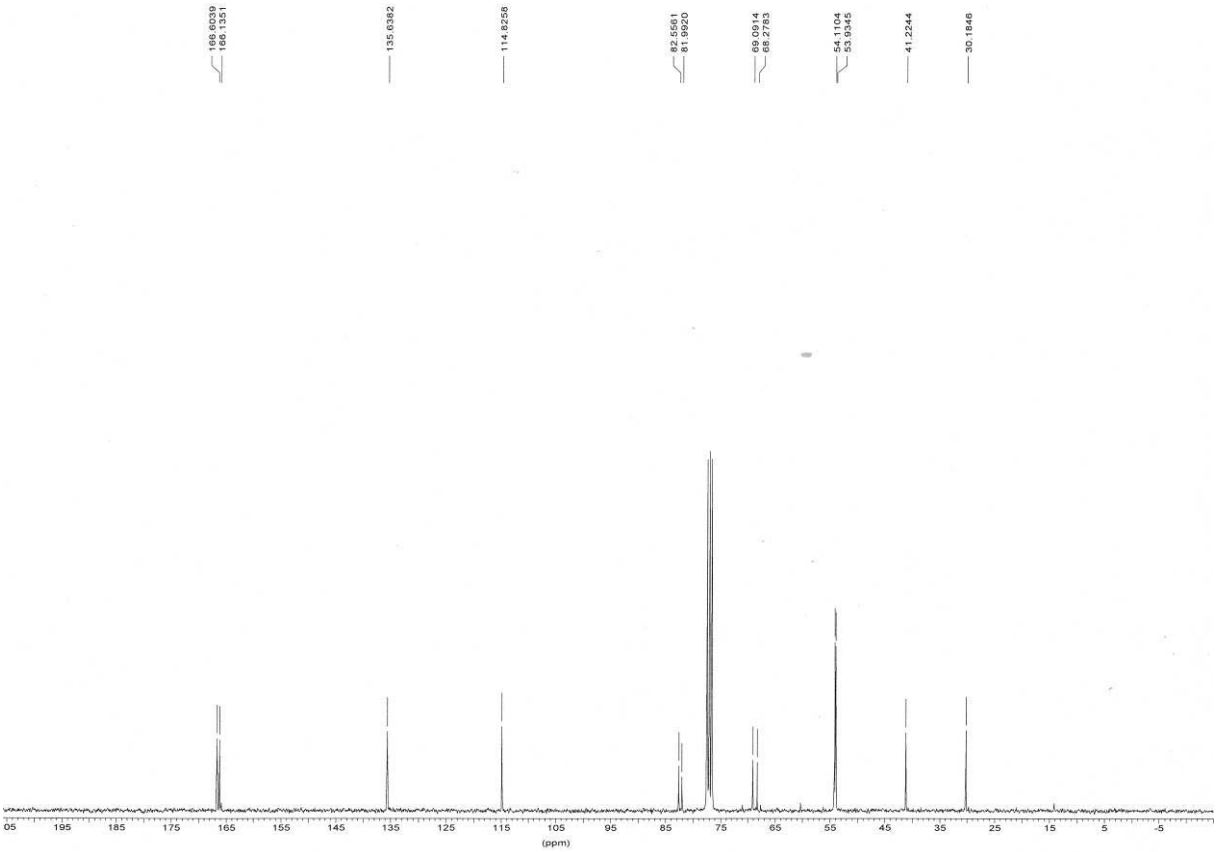

5.9941
5.9702
5.9426
5.9175
5.8930
5.5145
5.4618
5.4606
3.7414
3.7401
3.7169
3.7150
3.5889
3.5631
3.5374
3.4276
3.4025
3.3780
2.8708
2.8639
2.8451
2.8388
2.6637
2.6606
2.6492
2.6354
2.6147
2.6110
21
CO2Me
CO2Me
MeO2C
MeO2C
1.0833
1.0000
14.030
1.1591
1.0117
2.2472
2.2366
(ppm)
168.9115
168.3694
138.6637
112.6501
85.0468
80.3730
53.7091
52.6525
51.0848
51.0409
32.0587
19.3938
(ppm)


2m
CO2Et
CO2Et
EtO2C
EtO2C
Integral
12.862
0.9946
1.0000
10.613
1.9963
2.0790
15.645
(ppm)

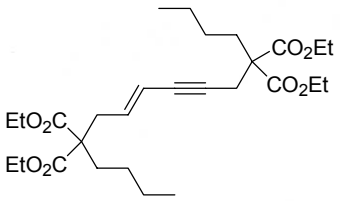
2n

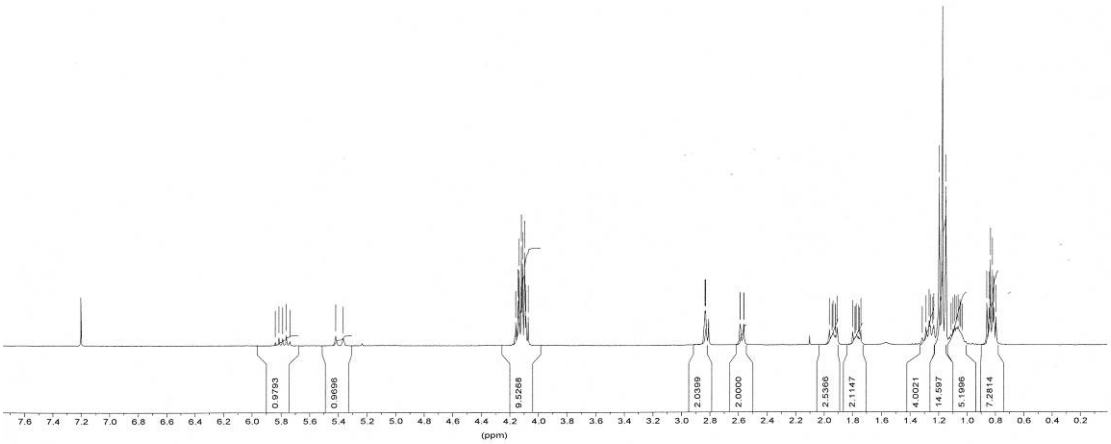

Cl
CO2Me
CO2Me
MeO2C
MeO2C
Cl

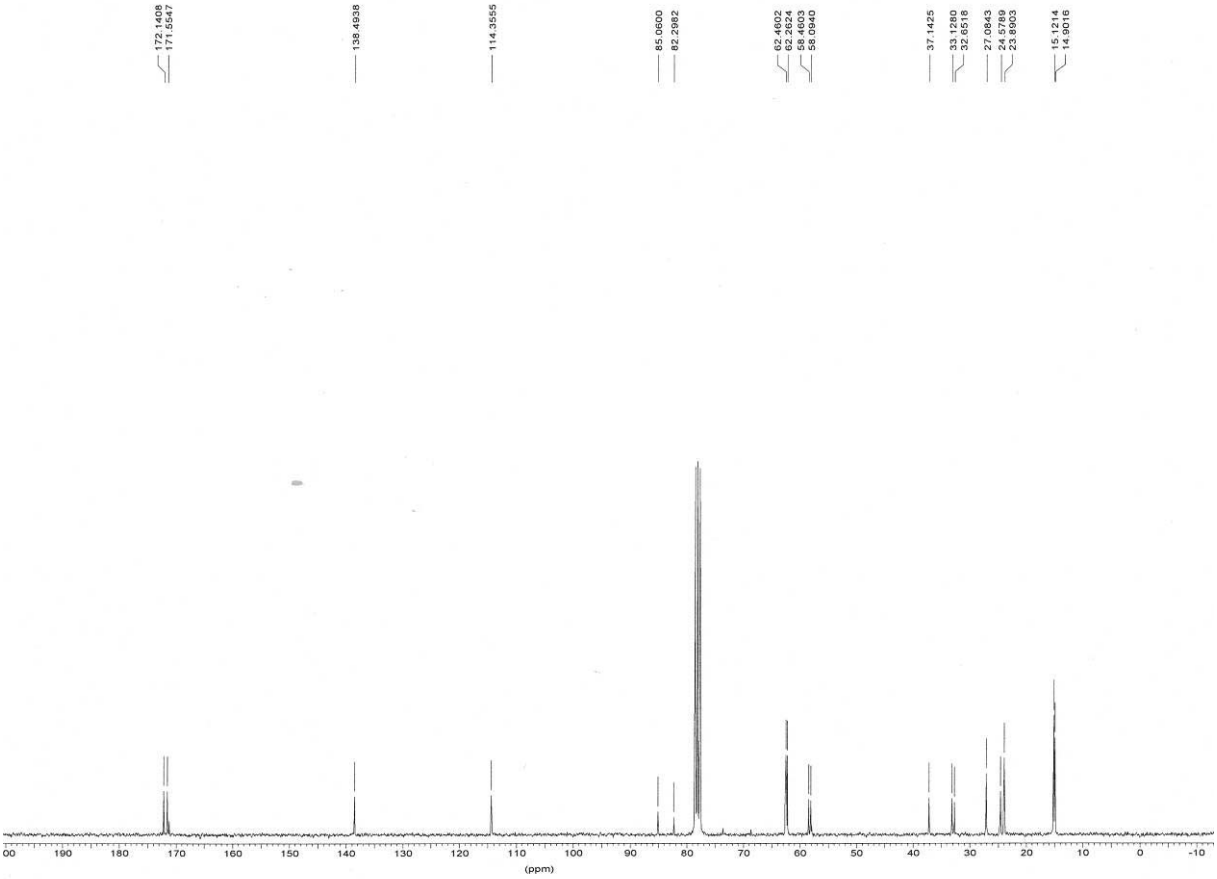
6.0732
6.0487
6.0236
6.0004
5.9850
5.9715
5.5999
5.5472
3.8393
3.8161
3.2703
3.2706
3.0152
3.0108
2.9907
2.9663
1.0065
1.0000
12.343
2.0328
2.1152
(ppm)

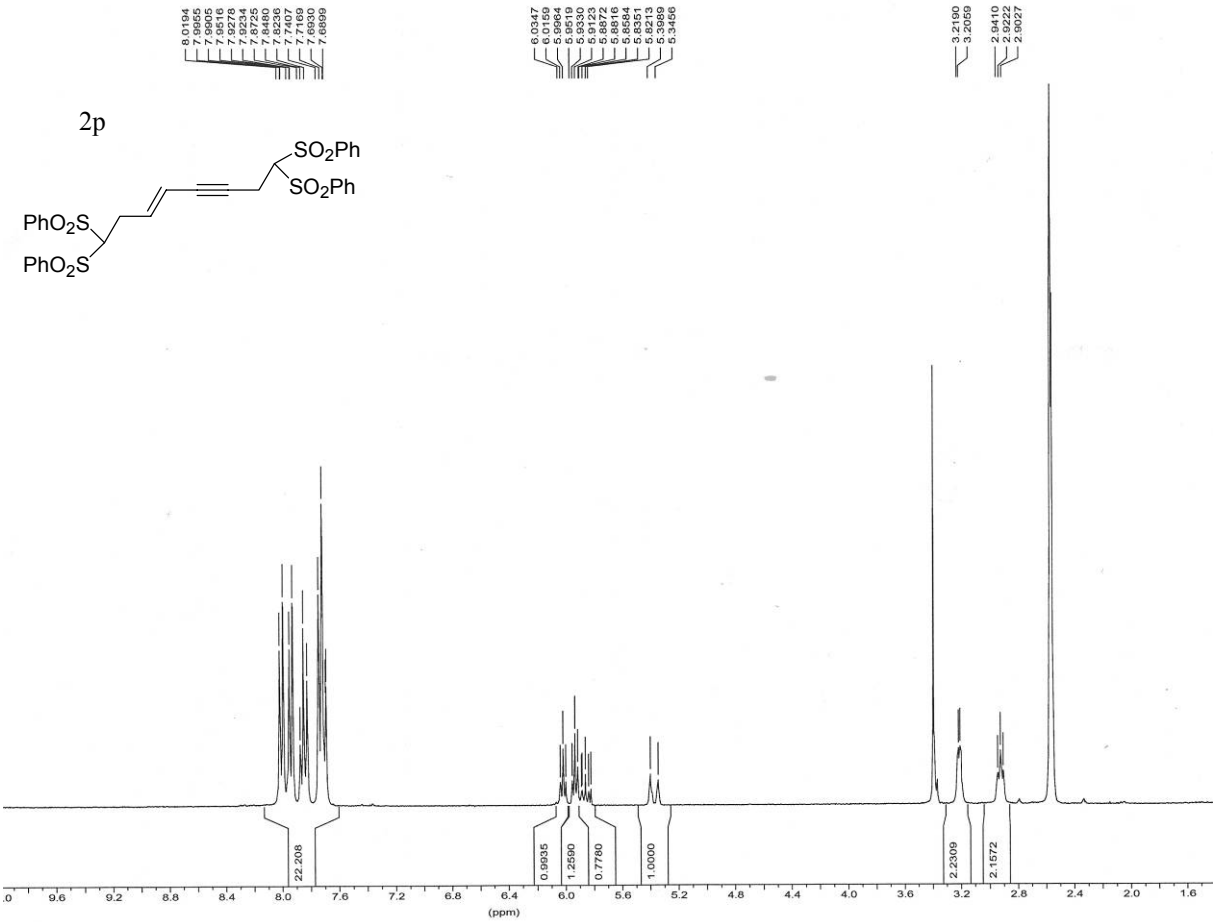

166.6039
166.1351
135.6362
114.8258
82.5561
81.9920
69.0914
68.2793
54.1104
53.9345
41.2244
30.1846
(ppm)

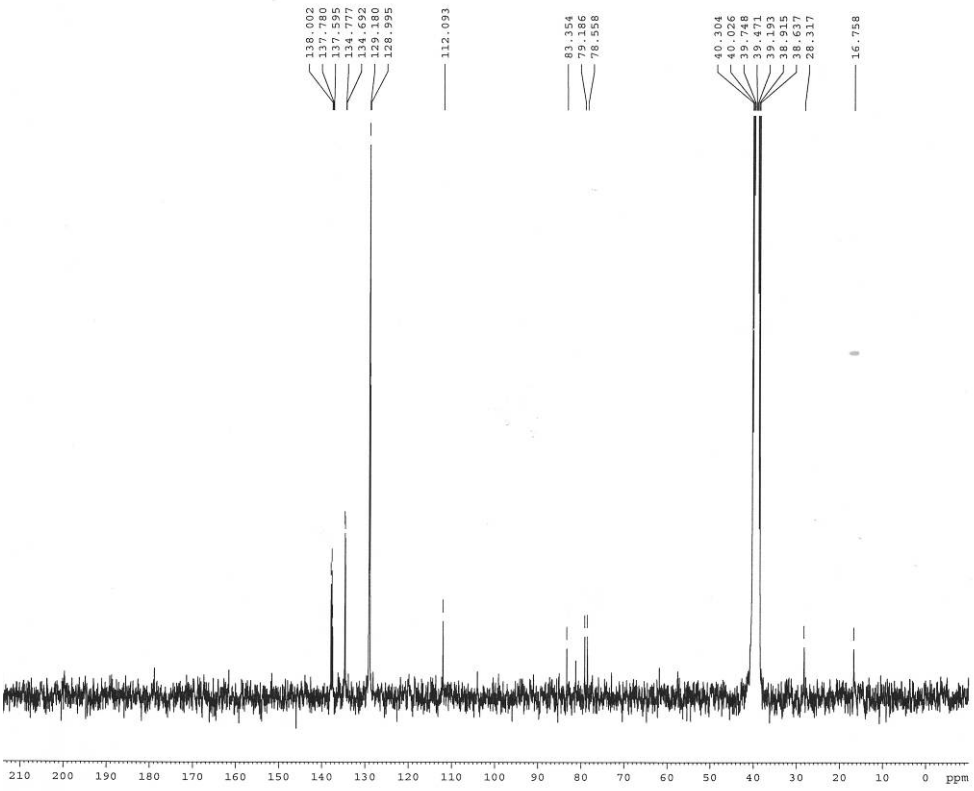
2o

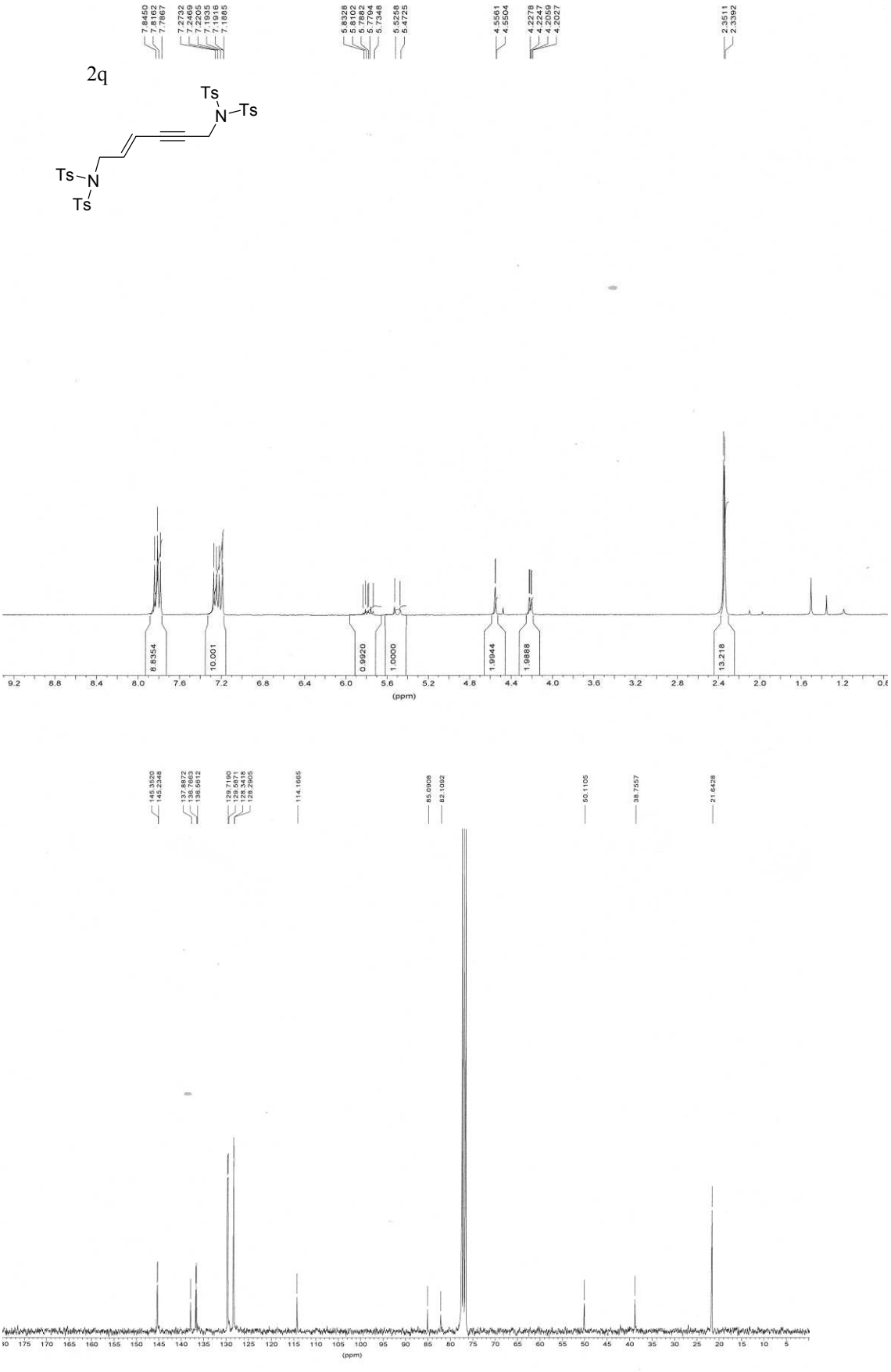

CO2Et
CO2Et
EtO2C
EtO2C


0.9793
0.9696
9.5288
2.0399
2.0000
2.5366
2.1147
4.0021
14.597
5.1996
7.2814
(ppm)

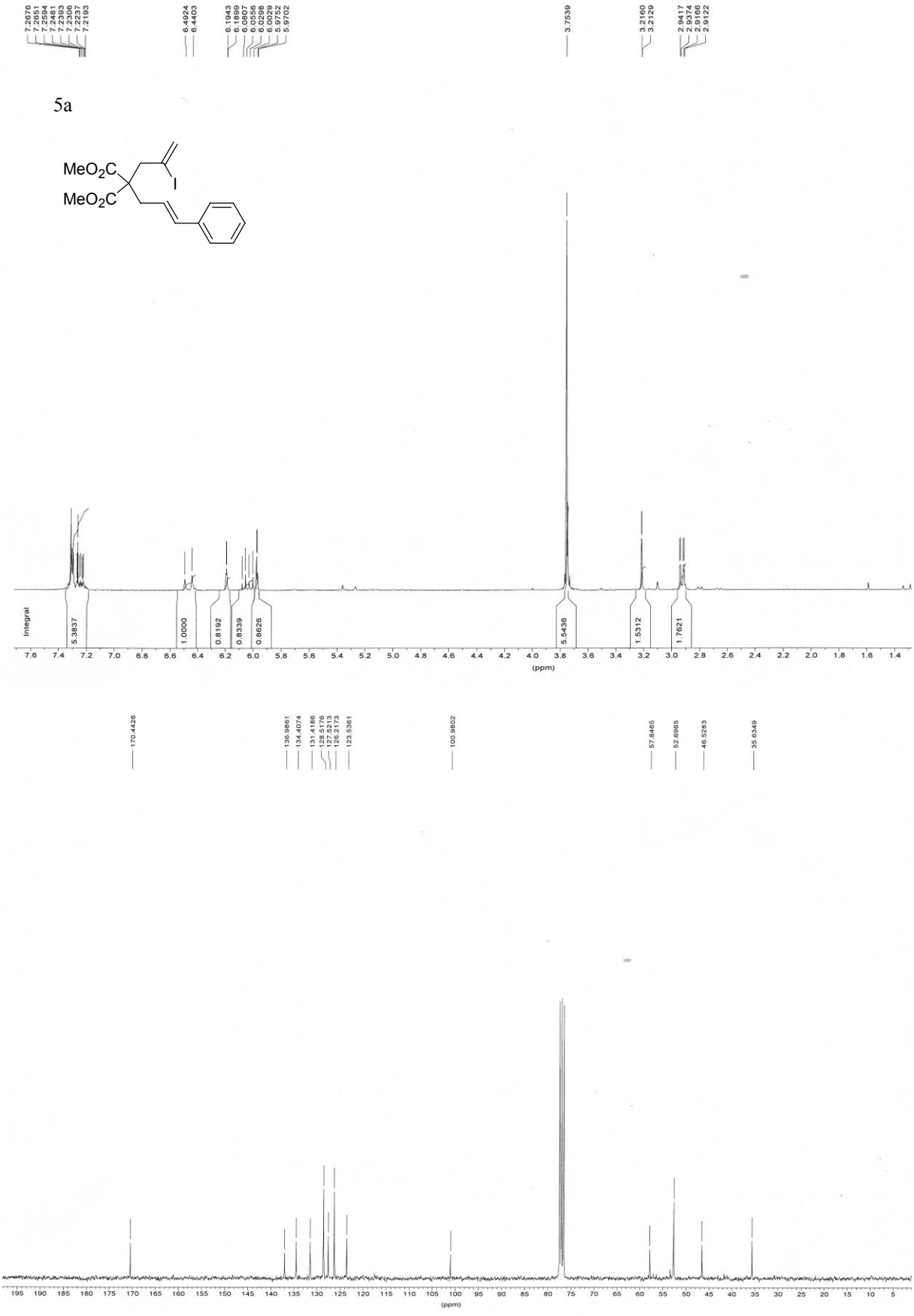

172.1408
171.6547
138.4938
114.3555
85.0600
82.2982
62.4602
62.2624
58.4603
58.0940
37.1425
33.1280
32.6518
27.0843
24.5789
23.8903
15.1214
14.9016
(ppm)


2p
SO_2Ph
SO_2Ph
PhO_2S
PhO_2S
(ppm)

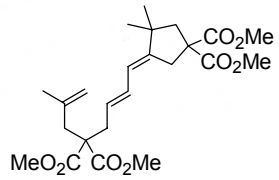

ppm


2q
Ts
N
Ts
Ts
N
Ts
7.8450
7.8162
7.7867
7.2732
7.2469
7.2205
7.1936
7.1665
7.1685
5.8328
5.8102
5.7882
5.7734
5.7548
5.5258
5.4725
4.5561
4.5504
4.2278
4.2247
4.2059
4.2027
2.3511
2.3392
8.8354
10.001
0.9920
1.0000
1.9944
1.9888
13.218
(ppm)
145.3529
145.2344
137.8872
136.7663
136.5612
129.7190
129.5871
128.3418
128.2905
114.1665
85.0908
82.1092
50.1105
38.7557
21.6428
(ppm)

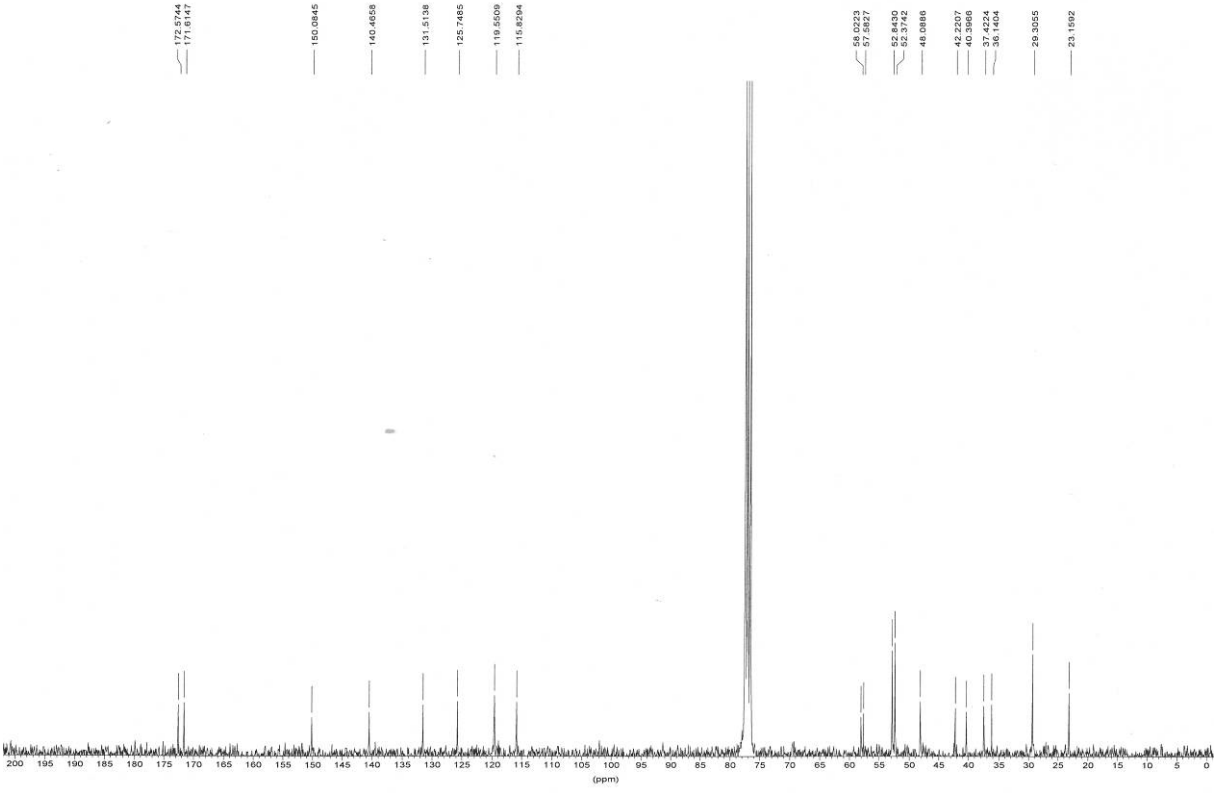
5a


7.2676
7.2651
7.2584
7.2481
7.2393
7.2306
7.2237
7.2193
6.4924
6.4403
6.1943
6.1899
6.0807
6.0556
6.0298
6.0039
5.9752
5.9702
3.7539
3.2160
3.2129
2.9417
2.8374
2.9166
2.9122
MeO2C
MeO2C
I
Integral
5.3837
1.0000
0.8192
0.8339
0.8626
5.5436
1.5312
1.7621
(ppm)
170.4426
136.9861
134.4074
131.4186
128.5176
127.5213
126.2173
123.5361
100.9802
57.8465
52.6965
46.5283
35.6349
(ppm)

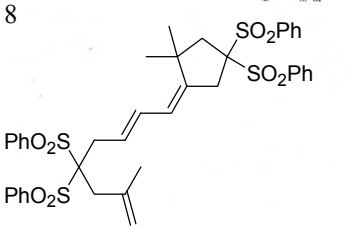
7

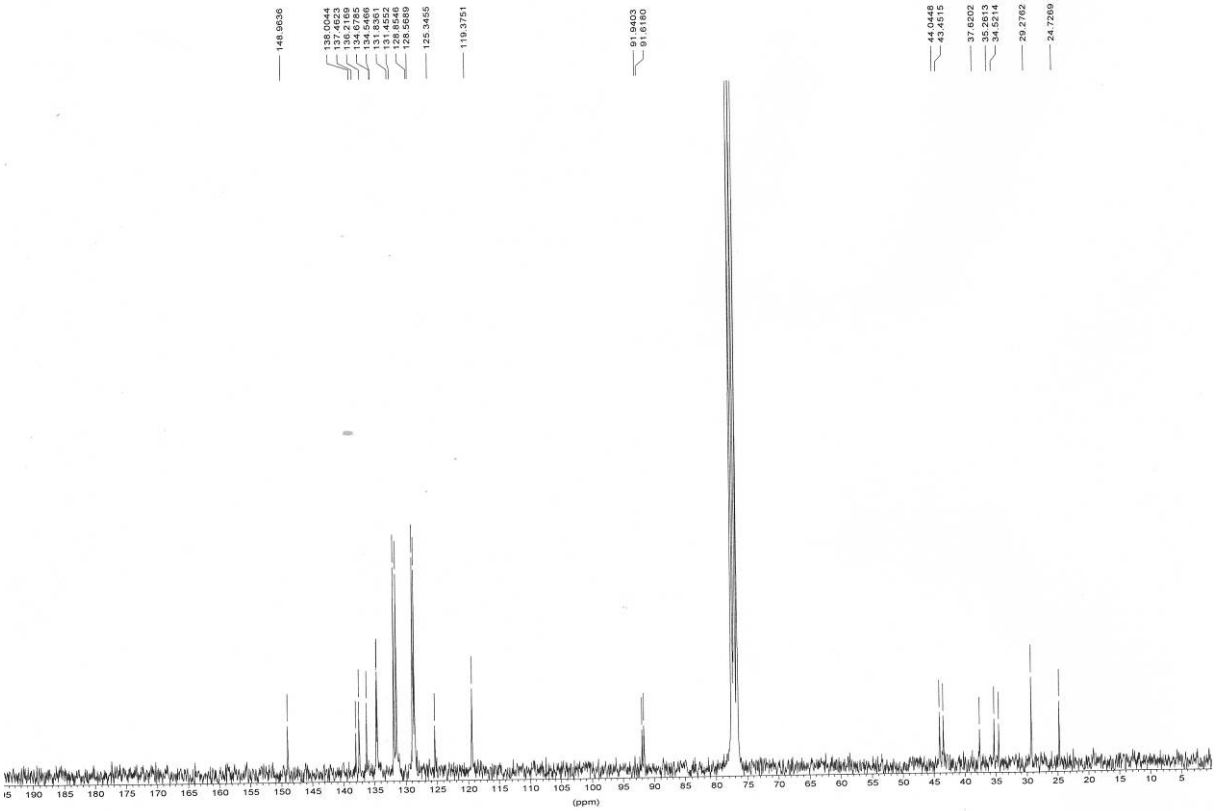

CO2Me
CO2Me
MeO2C CO2Me

6.1038
6.0673
6.0455
6.0171
5.6928
5.6562
5.3832
5.3581
5.3330
5.3085
5.2828
4.8163
4.6852
4.6821
3.6565
3.6471
3.0684
3.0615
2.6485
2.6080
2.2223
1.5821
0.9814
Integral
1.0196
1.0000
1.0842
1.0686
1.0440
13.595
2.0640
4.3589
2.1565
3.2266
5.9750
(ppm)

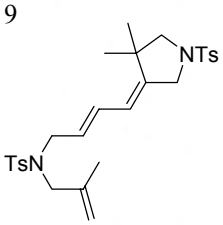

172.5744
171.6147
150.0845
140.4658
131.5138
125.7465
119.5509
115.8294
58.0223
57.5827
52.8410
52.3142
48.0886
42.2207
40.3966
37.4224
36.1404
29.3055
23.1592
(ppm)

8

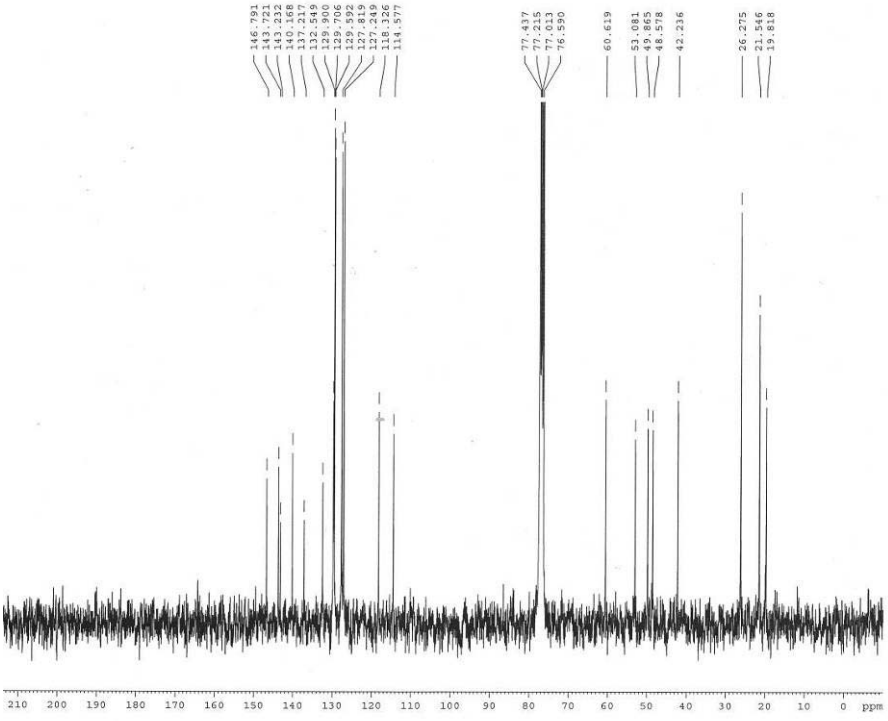




9


NTs
TsN

7.6549
7.6423
7.6210
7.5934
7.2814
7.2551
7.2155
7.1892
5.8121
5.7757
5.7605
5.7254
5.5616
5.5252
5.3156
5.2924
5.2679
5.2428
5.2309
5.2196
4.8455
4.7432
3.8111
3.8035
3.7931
3.6805
3.5989
2.9116
2.3599
2.3455
1.6048
1.0023
4.7792
5.8029
1.0320
1.0000
1.0429
2.2368
2.0842
2.0363
2.0318
2.1499
7.0349
3.1804
6.6708
(ppm)


146.791
143.721
143.232
140.668
137.217
132.549
129.900
129.706
129.592
127.849
127.419
118.326
114.577
77.437
77.215
77.013
76.590
60.619
53.081
49.865
48.578
42.236
26.275
21.546
19.818
ppm