Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Nickel-Catalyzed Alkyl-Zincation and Carboxylation of Diynes

Tao Cao[a] and Shengming Ma*[a,b]

[a] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

[b] Department of Chemistry, Fudan University, 220 Handan Lu, Shanghai 200433, P. R. China

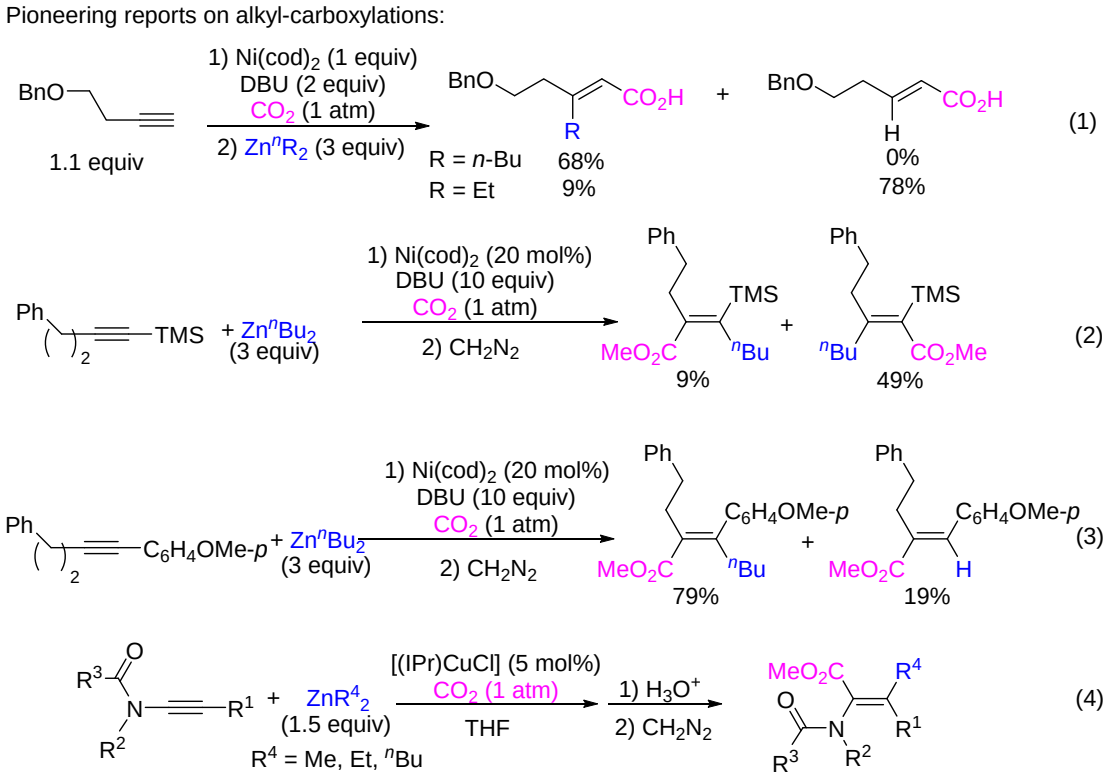
Email: masm@ sioc.ac.cn

Fax: 86-21-64167510

Supporting Information

Index

General Information: All reactions were carried out in oven dried Schlenk tubes. $Ni(cod)_2$ was purchased from Strem Chemicals and kept in a glove box at -30 °C. $ZnMe_2$ was purchased from J&K Scientific. $ZnEt_2$ was purchased from Acros. Zn^nBu_2 was purchased from Energy Chemical. DMSO was dried over calcium hydride before distillation. Toluene was dried over sodium before distillation. Other reagents were used without further treatment. All the temperatures are referred to the oil baths used.

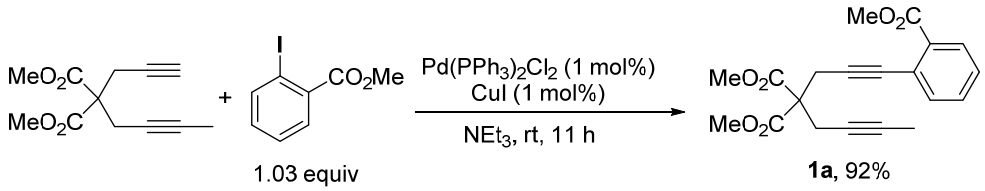


Scheme S1

1. Preparation of starting materials.

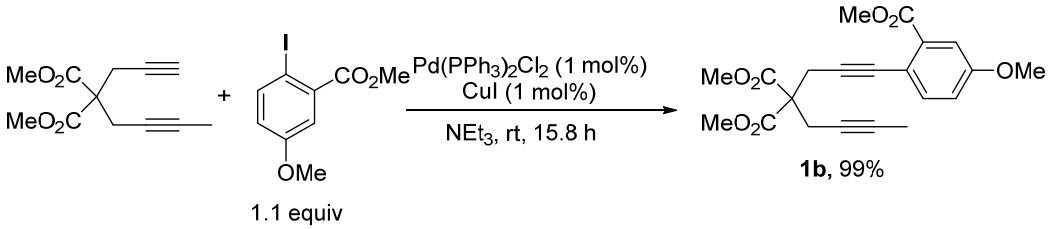
The starting materials were synthesized via Sonogashira reactions of aryl iodides with corresponding terminal alkynes.[1] The starting material **1a'** was prepared according to literature.[2]

(1) Preparation of **1a** (ct-8-127)



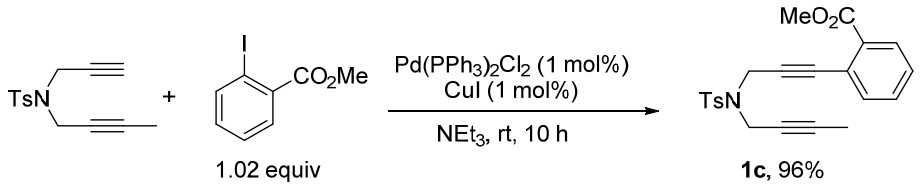
Typical procedure A: Under Ar atmosphere, to a 50 mL three-neck flask were added $Pd(PPh_3)_2Cl_2$ (0.0697 g, 0.1 mmol), dimethyl 2-(2-butynyl)-2-(2-propynyl)malonate (2.1528 g, 9.7 mmol), methyl 2-iodobenzoate (2.6412 g, 10 mmol), and 30 mL of NEt_3 sequentially. After being stirred for 5 min at room temperature, to this resulting mixture was added CuI (0.0185 g, 0.1 mmol). After being stirred at room temperature for 11 h, the reaction was complete as monitored by TLC. The mixture was filtered and eluted with 30 mL of ethyl acetate. The mixture was concentrated in vacuo. **1a** (3.1867 g, 92%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 7/1) as a solid: m.p. 42-44 ^{o}C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1 H, ArH), 7.49 (d, J = 7.6 Hz, 1 H, ArH), 7.42 (t, J = 7.4 Hz, 1 H, ArH), 7.33 (t, J = 7.4 Hz, 1 H, ArH), 3.93 (s, 3 H, OCH_3), 3.78 (s, 6 H, $OCH_3 \times 2$), 3.27 (s, 2 H, CH_2), 3.04 (s, 2 H, CH_2), 1.77 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.6, 134.5, 131.9, 131.4, 130.0, 127.6, 123.4, 89.3, 82.0, 79.1, 73.0, 57.0, 52.9, 52.1, 23.8, 23.1, 3.5; MS (ESI) 374 ($[M+NH_4]^+$), 357 ($[M+H]^+$); IR (neat, cm^{-1}) 1726, 1595, 1568, 1487, 1435, 1327, 1289, 1256, 1212, 1193, 1136, 1076, 1051; Anal. calcd for $C_{20}H_{20}O_6$ (%): C 67.41, H 5.66; found: C 67.37, H 5.57.

(2) Preparation of **1b** (ct-7-67)



Following **Typical Procedure A**, the reaction of dimethyl 2-(2-butynyl)-2-(2-propynyl)malonate (1.8019 g, 8.1 mmol), methyl 2-iodo-5-methoxybenzoate (2.6179 g, 9.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.0547 g, 0.08 mmol), CuI (0.0151 g, 0.08 mmol) in 20 mL of NEt_3 for 15.8 h afforded **1b** (3.0940 g, 99%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 5/1) as a solid: m.p. 74-75 ^oC (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 1 H, ArH), 7.38 (d, J = 2.8 Hz, 1 H, ArH), 6.96 (dd, J = 8.8, 2.8 Hz, 1 H, ArH), 3.93 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 3.77 (s, 6 H, OCH_3 × 2), 3.25 (s, 2 H, CH_2), 3.03 (q, J = 2.4 Hz, 2 H, CH_2), 1.77 (t, J = 2.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 166.5, 158.7, 135.7, 133.1, 118.0, 115.5, 114.5, 87.2, 81.8, 79.1, 73.0, 57.0, 55.4, 52.9, 52.2, 23.8, 23.0, 3.4; MS (ESI) 409 ($[M+Na]^+$), 404 ($[M+NH_4]^+$), 387 ($[M+H]^+$); IR (neat, cm^{-1}) 1734, 1701, 1603, 1496, 1431, 1320, 1287, 1217, 1148, 1128, 1079, 1036; Anal. calcd for $C_{21}H_{22}O_7$ (%): C 65.28, H 5.74; found: C 64.96, H 5.65.

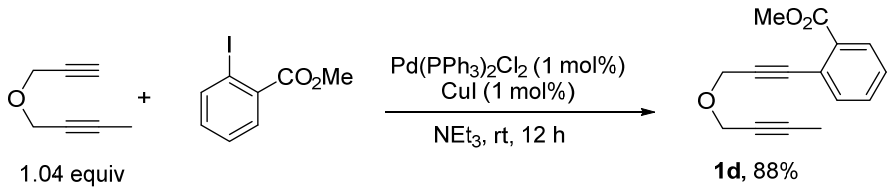
(3) Preparation of **1c** (ct-6-47)



Following **Typical Procedure A**, the reaction of *N*-(2-butynyl)-*N*-(2-propynyl)-*p*-toluenesulfonamide (2.5412 g, 9.7 mmol), methyl 2-iodobenzoate (2.6068 g, 9.9 mmol), $Pd(PPh_3)_2Cl_2$ (0.0712 g, 0.1 mmol), CuI (0.0194 g, 0.1 mmol) in 20 mL of NEt_3 for 10 h afforded **1c** (3.7065 g, 96%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 7/1 to petroleum ether/ ethyl acetate/dichloromethane = 5/1/1) as a solid: m.p. 84-85 ^oC (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.6 Hz, 1

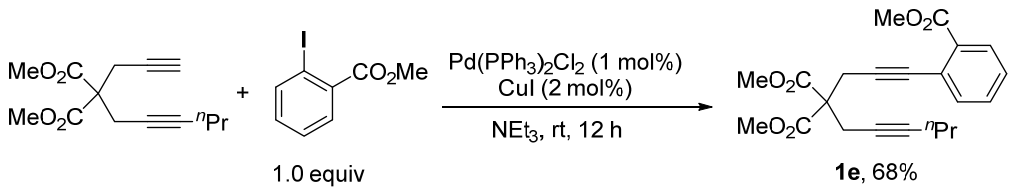
H, ArH), 7.74 (d, J = 8.4 Hz, 2 H, ArH), 7.41 (t, J = 7.2 Hz, 1 H, ArH), 7.34 (t, J = 7.4 Hz, 1 H, ArH), 7.24 (d, J = 7.2 Hz, 1 H, ArH), 7.20 (d, J = 8.0 Hz, 2 H, ArH), 4.44 (s, 2 H, NCH_2), 4.23 (s, 2 H, NCH_2), 3.88 (s, 3 H, OCH_3), 2.29 (s, 3 H, CH_3), 1.67 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 143.5, 135.2, 134.0, 131.6, 131.4, 130.1, 129.2, 127.9, 127.8, 122.6, 86.9, 84.2, 81.7, 71.5, 52.0, 37.2, 36.9, 21.2, 3.3; MS (ESI) (m/z) 396 ($[M+H]^+$); IR (neat, cm^{-1}) 1710, 1595, 1486, 1442, 1401, 1336, 1294, 1249, 1189, 1164, 1127, 1089, 1064, 1040; Anal. calcd for $C_{22}H_{21}NO_4S$ (%): C 66.82, H 5.35, N 3.54; found: C 66.33, H 5.26, N 3.46.

(4) Preparation of **1d** (ct-6-115)



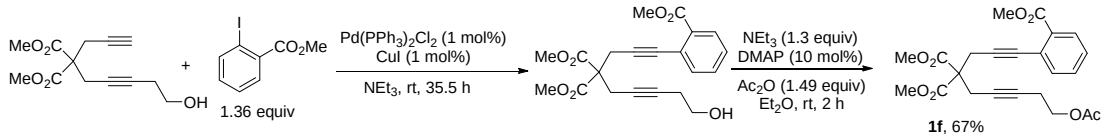
Following **Typical Procedure A**, the reaction of 1-(2-propynyloxy)-2-butyne (2.2245 g, 20.6 mmol), methyl 2-iodobenzoate (5.1804 g, 19.8 mmol), $Pd(PPh_3)_2Cl_2$ (0.1402 g, 0.2 mmol), CuI (0.0382 g, 0.2 mmol) in 50 mL of NEt_3 for 12 h afforded **1d** (4.4049 g, 88%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10/1) as a solid: m.p. 31-33 ^oC (petroleum ether/ ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.8, 1.4 Hz, 1 H, ArH), 7.56 (dd, J = 7.6, 1.4 Hz, 1 H, ArH), 7.46 (td, J = 7.6, 1.3 Hz, 1 H, ArH), 7.37 (td, J = 7.6, 1.3 Hz, 1 H, ArH), 4.53 (s, 2 H, OCH_2), 4.34 (q, J = 2.3 Hz, 2 H, OCH_2), 3.92 (s, 3 H, OCH_3), 1.87 (t, J = 2.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 134.0, 131.7, 131.5, 130.1, 127.9, 122.8, 89.7, 85.0, 82.9, 74.3, 57.0, 56.9, 52.0, 3.4; MS (ESI) 260 ($[M+NH_4]^+$), 243 ($[M+H]^+$); IR (neat, cm^{-1}) 1723, 1594, 1566, 1484, 1437, 1375, 1352, 1297, 1278, 1255, 1195, 1166, 1066; Anal. calcd for $C_{15}H_{14}O_3$ (%): C 74.36, H 5.82; found: C 74.02, H 5.78.

(5) Preparation of **1e** (ct-6-151)



Following **Typical Procedure A**, the reaction of dimethyl 2-(2-pentynyl)-2-(2-propynyl)malonate (1.0018 g, 4 mmol), methyl 2-iodobenzoate (1.0536 g, 4 mmol), $Pd(PPh_3)_2Cl_2$ (0.0266 g, 0.04 mmol), CuI (0.0154 g, 0.08 mmol) in 10 mL of NEt_3 for 12 h afforded **1e** (1.0407 g, 68%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.0, 1.2 Hz, 1 H, ArH), 7.49 (dd, *J* = 7.7, 1.1 Hz, 1 H, ArH), 7.42 (td, *J* = 7.6, 1.5 Hz, 1 H, ArH), 7.33 (td, *J* = 7.6, 1.4 Hz, 1 H, ArH), 3.93 (s, 3 H, OCH_3), 3.78 (s, 6 H, OCH_3 × 2), 3.28 (s, 2 H, CH_2), 3.06 (t, *J* = 2.4 Hz, 2 H, CH_2), 2.11 (tt, *J* = 7.0, 2.4 Hz, 2 H, CH_2), 1.48 (sext, *J* = 7.2 Hz, 2 H, CH_2), 0.95 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.6, 134.4, 131.8, 131.4, 130.0, 127.6, 123.4, 89.3, 83.7, 82.0, 74.1, 57.1, 52.9, 52.1, 23.8, 23.1, 22.1, 20.5, 13.2; MS (ESI) (m/z) 402 ($[M+NH_4]^+$), 385 ($[M+H]^+$); IR (neat, cm^{-1}) 1734, 1596, 1568, 1485, 1434, 1380, 1328, 1291, 1251, 1201, 1130, 1079, 1052; HRMS calcd for $C_{22}H_{28}NO_6$ ($[M+NH_4^+]$): 402.1911; found: 402.1912.

(6) Preparation of **1f** (ct-6-164, ct-6-169)

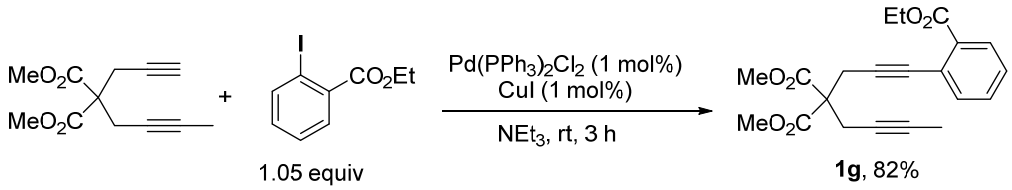


Following **Typical Procedure A**, the reaction of dimethyl 2-(5-hydroxy-2-pentynyl)-2-(2-propynyl)malonate (3.2090 g, 12.7 mmol), methyl 2-iodobenzoate (4.5219 g, 17.3 mmol), $Pd(PPh_3)_2Cl_2$ (0.0896 g, 0.13 mmol), CuI (0.0238 g, 0.12 mmol) in 30 mL of NEt_3 for 35.5 h afforded dimethyl 2-(5-hydroxy-2-pentynyl)-2-(3-(2-(methoxycarbonyl)phenyl)-2-propynyl)malonate (3.7599 g) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 2/1) as an oil and used directly in the next step.

To a round bottom flask were added dimethyl

2-(5-hydroxy-2-pentynyl)-2-(3-(2-(methoxycarbonyl)phenyl)-2-propynyl)malonate (2.9660 g, 7.7 mmol) prepared above, diethyl ether (20 mL), NEt_3 (1.4 mL, d = 0.73 g/mL, 1.022 g, 10.0 mmol), DMAP (93.7 mg, 0.77 mmol), and Ac_2O (1.1 mL, d = 1.08 g/mL, 1.188 g, 11.5 mmol). After being stirred at room temperature for 2 h, the reaction was complete as monitored by TLC. The mixture was concentrated in vacuo. **1f** (2.9080 g, 67% for two steps) was afforded via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 2/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1 H, ArH), 7.49 (d, *J* = 7.6 Hz, 1 H, ArH), 7.42 (t, *J* = 7.6 Hz, 1 H, ArH), 7.33 (t, *J* = 7.6 Hz, 1 H, ArH), 4.11 (t, *J* = 6.6 Hz, 2 H, OCH_2), 3.92 (s, 3 H, OCH_3), 3.78 (s, 6 H, OCH_3 × 2), 3.26 (s, 2 H, CH_2), 3.06 (s, 2 H, CH_2), 2.48 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.08 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 169.2, 166.5, 134.4, 131.9, 131.4, 130.0, 127.6, 123.3, 89.2, 82.1, 79.3, 75.9, 62.4, 57.0, 53.0, 52.1, 23.8, 23.0, 20.7, 19.1; MS (ESI) (m/z) 451 ($[M+Na]^+$), 429 ($[M+H]^+$); IR (neat, cm^{-1}) 1733, 1596, 1568, 1485, 1434, 1386, 1365, 1329, 1292, 1237, 1208, 1130, 1079, 1043; HRMS calcd for $C_{23}H_{28}NO_8$ ($[M+NH_4^+]$): 446.1809; found: 446.1811.

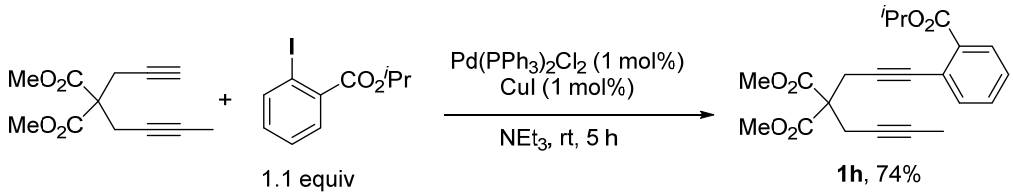
(7) Preparation of **1g** (ct-7-87)



Following **Typical Procedure A**, the reaction of dimethyl 2-(2-butynyl)-2-(2-propynyl)malonate (1.6742 g, 7.5 mmol), ethyl 2-iodobenzoate (2.2193 g, 7.9 mmol), $Pd(PPh_3)_2Cl_2$ (0.0488 g, 0.07 mmol), CuI (0.0135 g, 0.07 mmol) in 20 mL of NEt_3 for 3 h afforded **1g** (2.2975 g, 82%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 7/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1 H, ArH), 7.48 (d, *J* = 7.6 Hz, 1 H, ArH), 7.41 (t, *J* = 7.4 Hz, 1 H, ArH), 7.33 (t, *J* = 7.4 Hz, 1 H, ArH), 4.39 (q, *J* = 7.1 Hz, 2 H, OCH_2), 3.78 (s, 6 H, OCH_3 × 2), 3.26 (s, 2 H, CH_2), 3.03 (s, 2 H, CH_2), 1.76 (s, 3 H, CH_3), 1.40 (t, *J* = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 166.0, 134.4,

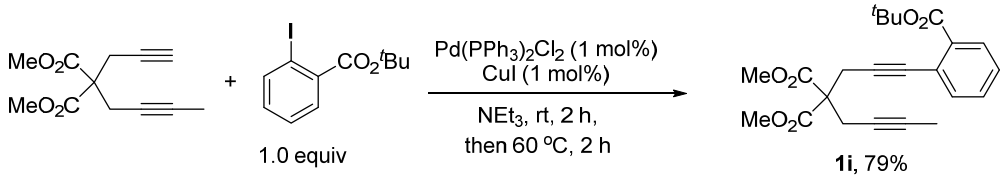
132.1, 131.3, 129.9, 127.5, 123.2, 89.2, 82.1, 79.1, 72.9, 61.0, 57.0, 52.9, 23.7, 23.1, 14.1, 3.4; MS (ESI) (m/z) 371 ($[M+H]^+$); IR (neat, cm^{-1}) 1734, 1596, 1568, 1483, 1437, 1390, 1367, 1328, 1290, 1248, 1203, 1132, 1077, 1050, 1018; HRMS calcd for $C_{21}H_{26}NO_6$ ($[M+NH_4^+]$): 388.1755; found: 388.1756.

(8) Preparation of **1h** (ct-7-93)



Following **Typical Procedure A**, the reaction of dimethyl 2-(2-butynyl)-2-(2-propynyl)malonate (1.5465 g, 7.0 mmol), *iso*-propyl 2-iodobenzoate (2.2415 g, 7.7 mmol), $Pd(PPh_3)_2Cl_2$ (0.0488 g, 0.07 mmol), CuI (0.0135 g, 0.07 mmol) in 20 mL of NEt_3 for 5 h afforded **1h** (1.9750 g, 74%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 7/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1 H, ArH), 7.46 (d, *J* = 7.6 Hz, 1 H, ArH), 7.40 (t, *J* = 7.4 Hz, 1 H, ArH), 7.32 (t, *J* = 7.4 Hz, 1 H, ArH), 5.26 (hept, *J* = 6.2 Hz, 1 H, OCH), 3.78 (s, 6 H, OCH_3 × 2), 3.26 (s, 2 H, CH_2), 3.03 (s, 2 H, CH_2), 1.76 (s, 3 H, CH_3), 1.38 (d, *J* = 6.4 Hz, 6 H, CH_3 × 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 165.6, 134.3, 132.6, 131.1, 129.8, 127.5, 123.2, 89.1, 82.1, 79.1, 73.0, 68.5, 57.0, 52.9, 23.7, 23.1, 21.7, 3.4; MS (ESI) (m/z) 407 ($[M+Na]^+$), 385 ($[M+H]^+$); IR (neat, cm^{-1}) 1738, 1596, 1569, 1484, 1436, 1375, 1329, 1289, 1251, 1203, 1139, 1107, 1075, 1054; HRMS calcd for $C_{22}H_{28}NO_6$ ($[M+NH_4^+]$): 402.1911; found: 402.1911.

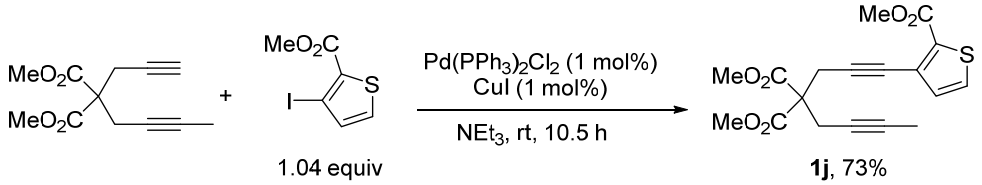
(9) Preparation of **1i** (ct-7-95)



Following **Typical Procedure A**, the reaction of dimethyl

2-(2-butynyl)-2-(2-propynyl)malonate (1.7690 g, 8.0 mmol), *tert*-butyl 2-iodobenzoate (2.4518 g, 8.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.0557 g, 0.08 mmol), CuI (0.0155 g, 0.08 mmol) in 20 mL of NEt_3 for 2 h at room temperature and then at 60 ^oC for 2 h afforded **1i** (2.4991 g, 79%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 7/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1 H, ArH), 7.44 (d, *J* = 7.6 Hz, 1 H, ArH), 7.38 (t, *J* = 7.4 Hz, 1 H, ArH), 7.31 (t, *J* = 7.8 Hz, 1 H, ArH), 3.78 (s, 6 H, OCH_3 × 2), 3.25 (s, 2 H, CH_2), 3.03 (s, 2 H, CH_2), 1.76 (s, 3 H, CH_3), 1.61 (s, 9 H, CH_3 × 3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 165.5, 134.4, 133.7, 130.9, 129.8, 127.5, 122.9, 88.7, 82.4, 81.4, 79.1, 73.0, 57.0, 52.9, 28.0, 23.8, 23.1, 3.4; MS (ESI) (m/z) 421 ($[M+Na]^+$); IR (neat, cm^{-1}) 1738, 1596, 1568, 1481, 1437, 1392, 1368, 1291, 1250, 1203, 1178, 1131, 1077, 1053; HRMS calcd for $C_{23}H_{30}NO_6$ ($[M+NH_4^+]$): 416.2068; found: 416.2069.

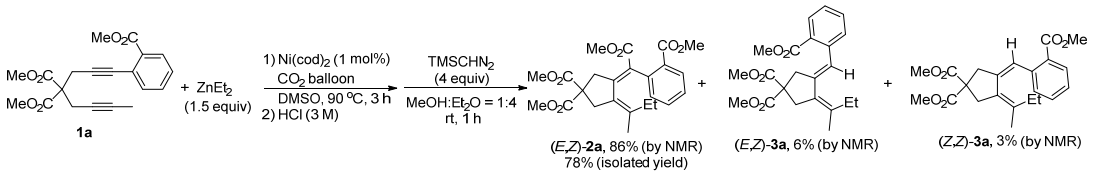
(10) Preparation of **1j** (ct-7-57)



Following **Typical Procedure A**, the reaction of dimethyl 2-(2-butynyl)-2-(2-propynyl)malonate (1.5191 g, 6.8 mmol), methyl 3-iodothiophene-2-carboxylate (1.8943 g, 7.1 mmol), $Pd(PPh_3)_2Cl_2$ (0.0420 g, 0.06 mmol), CuI (0.0117 g, 0.06 mmol) in 20 mL of NEt_3 for 10.5 h afforded **1j** (1.8066 g, 73%) via column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 10/1) as a solid: m.p. 92-93 ^oC (petroleum ether/ ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 4.0, 1 H, ArH), 7.08-7.04 (m, 1 H, ArH), 3.90 (s, 3 H, OCH_3), 3.78 (s, 6 H, OCH_3 × 2), 3.27 (s, 2 H, CH_2), 3.05 (s, 2 H, CH_2), 1.77 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 161.6, 133.4, 132.5, 130.2, 126.9, 90.4, 79.1, 77.8, 72.9, 56.9, 52.9, 52.0, 23.8, 23.0, 3.4; MS (ESI) 380 ($[M+NH_4]^+$), 363 ($[M+H]^+$); IR (neat, cm^{-1}) 1737, 1696, 1522, 1433, 1380, 1325, 1290, 1227, 1211, 1152, 1112, 1083, 1052; Anal. calcd for $C_{18}H_{18}O_6S$ (%): C 59.66, H 5.01; found: C 59.30, H 5.00.

2. Ni(cod)$_2$-catalyzed reaction of 1 with carbon dioxide and ZnR_2

(1) Preparation of (*E*,*Z*)-**2a** (ct-9-142, ct-6-113).

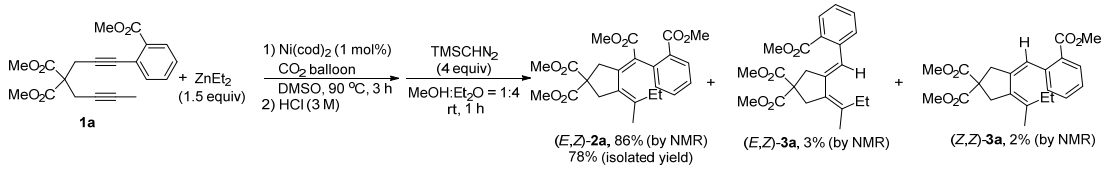


Typical procedure I: To a 50 mL flame-dried Schlenk tube was added Ni(cod)$_2$ (2.8 mg, 0.01 mmol) inside a glove box. Compound **1a** (356.7 mg, 1.0 mmol) and DMSO (10 mL) were sequentially added under argon outside the glove box. The Schlenk tube was then frozen with a liquid nitrogen bath. The argon inside the tube was completely replaced with CO_2 by using a balloon of CO_2 (about 1 L). The Schlenk tube was allowed to stand until the temperature was above 0 ^oC. Then the Schlenk tube was placed in an oil bath pre-heated at 90 ^oC. After completely thawed, to the mixture was added $ZnEt_2$ (1.5 M in toluene, 1.0 mL, 1.5 mmol) with a syringe. After being vigorously stirred for 3 h, the reaction was complete as monitored by TLC. HCl (3 M, 10 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (10 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo.

To the crude product were added MeOH (1 mL) and Et_2O (4 mL). To the resulting mixture was dropwise added $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) with a syringe. After being stirred for 1 h at room temperature, the reaction was complete as monitored by TLC. The reaction mixture was concentrated to afford a mixture of (*E*,*Z*)-**2a**, (*E*,*Z*)-**3a**, and (*Z*,*Z*)-**3a**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2a** (86%), (*E*,*Z*)-**3a** (6%), and (*Z*,*Z*)-**3a** (3%)). (*E*,*Z*)-**2a** (347.4 mg, 78%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as a white solid: m.p. 106-107 ^oC (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 1 H, ArH), 7.40 (t, *J* = 7.4 Hz, 1 H, ArH), 7.31 (t, *J* = 7.6 Hz, 1 H, ArH), 7.13 (d, *J* = 7.7 Hz, 1 H, ArH), 3.84 (s, 3 H,

OCH_3), 3.75 (s, 6 H, OCH_3 × 2), 3.62 (s, 3 H, OCH_3), 3.56 (d, J = 16.9 Hz, 1 H, one proton of CH_2), 3.46 (d, J = 17.1 Hz, 1 H, one proton of CH_2), 3.06 (d, J = 15.1 Hz, 1 H, one proton of CH_2), 2.93 (d, J = 15.1 Hz, 1 H, one proton of CH_2), 1.76-1.65 (m, 1 H, one proton of CH_2), 1.51 (s, 3 H, CH_3), 1.33-1.22 (m, 1 H, one proton of CH_2), 0.17 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 167.7, 167.2, 149.8, 140.9, 138.7, 132.8, 132.1, 130.3, 129.8, 129.6, 128.8, 127.3, 56.0, 52.8, 52.7, 51.8, 51.4, 40.8, 37.0, 27.9, 18.3, 10.6; MS (EI) (m/z) (%) 444 (M^+, 9.2), 320 (100); IR (neat, cm^{-1}) 1729, 1611, 1566, 1483, 1432, 1263, 1210, 1162, 1133, 1078, 1049, 1011; Anal. calcd for $C_{24}H_{28}O_8$ (%): C 64.85, H 6.35; found: C 64.87, H 6.25.

Gram scale preparation of (*E*,*Z*)-**2a** (ct-8-134).



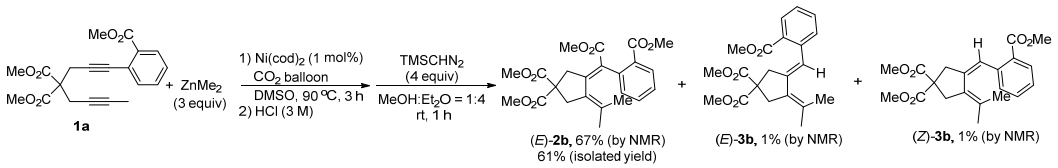
To a 100 mL flame-dried Schlenk flask was added $Ni(cod)_2$ (8.3 mg, 0.03 mmol) inside a glove box. Compound **1a** (1.0687 g, 3.0 mmol) and DMSO (30 mL) were sequentially added under argon outside the glove box. The Schlenk flask was then frozen with a liquid nitrogen bath. The argon inside the flask was completely replaced with CO_2 by using a balloon of CO_2 (about 1.5 L). The Schlenk flask was allowed to stand until the temperature was above 0 ^oC. Then the Schlenk flask was placed in an oil bath pre-heated at 90 ^oC. After completely thawed, to the mixture was added $ZnEt_2$ (1.5 M in toluene, 3.0 mL, 4.5 mmol) with a syringe. After being vigorously stirred for 3 h, the reaction was complete as monitored by TLC. HCl (3 M, 30 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (10 mL × 5) and the combined organic layer was washed with brine (30 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo.

To the crude product were added MeOH (3 mL) and Et_2O (12 mL). To the resulting mixture was dropwise added $TMSCHN_2$ (2.0 M in hexane, 6.0 mL, 12.0 mmol) with a syringe in 2 min. After being stirred for 1 h at room temperature, the reaction was complete as monitored by TLC. The reaction mixture was concentrated

to afford a mixture of (*E*,*Z*)-**2a**, (*E*,*Z*)-**3a**, and (*Z*,*Z*)-**3a**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2a** (86%), (*E*,*Z*)-**3a** (3%), and (*Z*,*Z*)-**3a** (2%)). (*E*,*Z*)-**2a** (1.0403 g, 78%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1 H, ArH), 7.40 (t, *J* = 7.2 Hz, 1 H, ArH), 7.31 (t, *J* = 7.4 Hz, 1 H, ArH), 7.13 (d, *J* = 7.6 Hz, 1 H, ArH), 3.84 (s, 3 H, OCH_3), 3.75 (s, 6 H, OCH_3 × 2), 3.62 (s, 3 H, OCH_3), 3.56 (d, *J* = 17.0 Hz, 1 H, one proton of CH_2), 3.47 (d, *J* = 17.0 Hz, 1 H, one proton of CH_2), 3.06 (d, *J* = 15.0 Hz, 1 H, one proton of CH_2), 2.93 (d, *J* = 15.2 Hz, 1 H, one proton of CH_2), 1.76-1.64 (m, 1 H, one proton of CH_2), 1.51 (s, 3 H, CH_3), 1.33-1.21 (m, 1 H, one proton of CH_2), 0.17 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 167.7, 167.2, 149.8, 140.9, 138.6, 132.8, 132.1, 130.3, 129.7, 129.5, 128.8, 127.3, 56.0, 52.8, 52.7, 51.9, 51.4, 40.7, 37.0, 27.8, 18.3, 10.5.

The following compounds were prepared according to **Typical Procedure I**.

(2) Preparation of (*E*)-**2b** (ct-6-111).

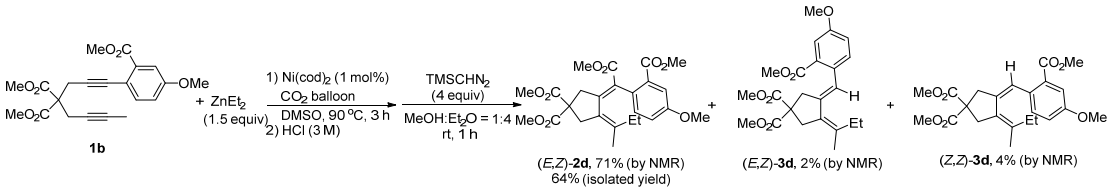


The reaction of Ni(cod)$_2$ (2.8 mg, 0.01 mmol), **1a** (355.8 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*)-**2b**, (*E*)-**3b**, and (*Z*)-**3b**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*)-**2b** (67%), (*E*)-**3b** (1%), and (*Z*)-**3b** (1%)). (*E*)-**2b** (260.5 mg, 61%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1 H, ArH), 7.39 (t, *J* = 7.5 Hz, 1 H, ArH), 7.30 (t, *J* =

6.9 Hz, 1 H, ArH), 7.12 (d, J = 7.7 Hz, 1 H, ArH), 3.83 (s, 3 H, OCH_3), 3.75 (s, 6 H, OCH_3 × 2), 3.63 (s, 3 H, OCH_3), 3.58 (d, J = 17.3 Hz, 1 H, one proton of CH_2), 3.50 (d, J = 17.1 Hz, 1 H, one proton of CH_2), 3.06 (d, J = 15.1 Hz, 1 H, one proton of CH_2), 2.95 (d, J = 15.3 Hz, 1 H, one proton of CH_2), 1.54 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.8, 167.7, 167.4, 150.2, 141.1, 134.3, 132.6, 132.0, 130.3, 130.2, 129.2, 128.8, 127.1, 56.2, 52.9, 52.8, 51.9, 51.5, 40.9, 37.1, 22.4, 22.2; MS (EI) (m/z) (%) 430 (M^+, 15.86), 306 (100); IR (neat, cm^{-1}) 1723, 1611, 1433, 1375, 1281, 1267, 1243, 1209, 1121, 1084, 1049; HRMS calcd for $C_{23}H_{26}O_8$ (M^+): 430.1628; found: 430.1624.

(3) Preparation of (*E*,*Z*)-**2d** (ct-9-107, ct-7-73).

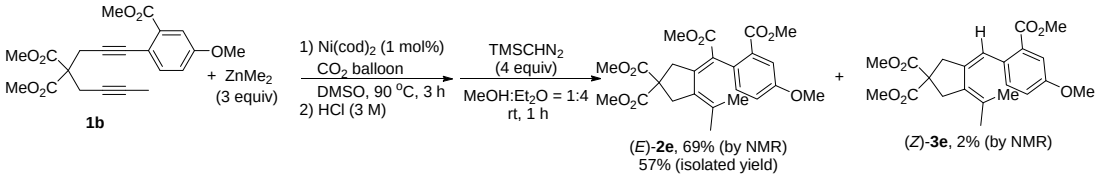


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1b** (386.4 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 1.0 mL, 1.5 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*Z*)-**2d**, (*E*,*Z*)-**3d**, and (*Z*,*Z*)-**3d**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2d** (71%), (*E*,*Z*)-**3d** (2%), and (*Z*,*Z*)-**3d** (4%)). (*E*,*Z*)-**2d** (301.4 mg, 64%) was obtained via recrystallization (petroleum ether/dichloromethane = 5/1) as a white solid: m.p.163-164 °C (petroleum ether/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1 H, ArH), 7.04 (d, J = 8.6 Hz, 1 H, ArH), 6.95 (d, J = 8.6 Hz, 1 H, ArH), 3.84 (s, 6 H, OCH_3 × 2), 3.75 (s, 6 H, OCH_3 × 2), 3.62 (s, 3 H, OCH_3), 3.52 (d, J = 17.0 Hz, 1 H, one proton of CH_2), 3.44 (d, J = 16.7 Hz, 1 H, one proton of CH_2), 3.04 (d, J = 15.0 Hz, 1 H, one proton of CH_2), 2.93 (d, J = 15.0 Hz, 1 H, one proton of CH_2), 1.79-1.67 (m, 1 H, one proton of CH_2), 1.52 (s, 3 H, CH_3), 1.34-1.21 (m, 1 H, one proton of CH_2), 0.25 (t, J = 7.4 Hz, 3

H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 168.0, 167.0, 158.5, 149.3, 138.4, 134.0, 133.2, 130.4, 129.8, 128.4, 118.4, 114.7, 56.0, 55.3, 52.8, 52.7, 51.9, 51.4, 40.8, 36.9, 27.8, 18.2, 10.8; MS (EI) (m/z) (%) 474 (M^+, 17.68), 350 (100); IR (neat, cm^{-1}) 1719, 1602, 1497, 1431, 1378, 1317, 1292, 1248, 1212, 1178, 1116, 1067, 1031; Anal. calcd for $C_{25}H_{30}O_9$ (%): C 63.28, H 6.37; found: C 63.33, H 6.33.

(4) Preparation of (*E*)-**2e** (ct-7-69).

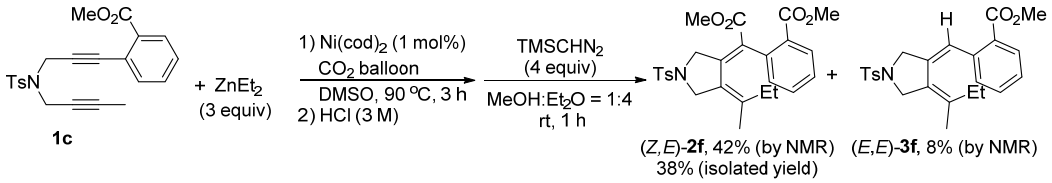


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1b** (385.7 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*)-**2e** and (*Z*)-**3e**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*)-**2e** (69%) and (*Z*)-**3e** (2%)). (*E*)-**2e** was obtained via column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 4/2/1) to afford 314.3 mg of impure product, which was then recrystallized (petroleum ether/dichloromethane = 7/1) to afford 261.9 mg of pure (*E*)-**2e** (57%) as a white solid: m.p. 161-162 ^oC (petroleum ether/dichloromethane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.0 Hz, 1 H, ArH), 7.10 (d, *J* = 8.5 Hz, 1 H, ArH), 7.01 (dd, *J* = 8.6, 2.2 Hz, 1 H, ArH), 3.91 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 3.822 (s, 3 H, OCH_3), 3.815 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.62 (d, *J* = 17.0 Hz, 1 H, one proton of CH_2), 3.54 (d, *J* = 17.2 Hz, 1 H, one proton of CH_2), 3.11 (d, *J* = 15.1 Hz, 1 H, one proton of CH_2), 3.02 (d, *J* = 15.2 Hz, 1 H, one proton of CH_2), 1.63 (s, 3 H, CH_3), 1.03 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 167.9, 167.1, 158.1, 149.6, 133.9, 133.8, 133.4, 130.3, 130.1, 128.4, 118.3, 114.4, 56.2, 55.2, 52.8, 52.7, 51.9, 51.4, 40.9, 37.0, 22.3, 22.2; MS (EI)

(m/z) (%) 460 (M^+, 24.91), 337 (100); IR (neat, cm^{-1}) 1721, 1603, 1498, 1431, 1374, 1289, 1252, 1215, 1180, 1122, 1071, 1034; Anal. calcd for $C_{24}H_{28}O_9$ (%): C 62.60, H 6.13; found: C 62.40, H 6.16.

(5) Preparation of (*Z*,*E*)-**2f** (ct-6-127).

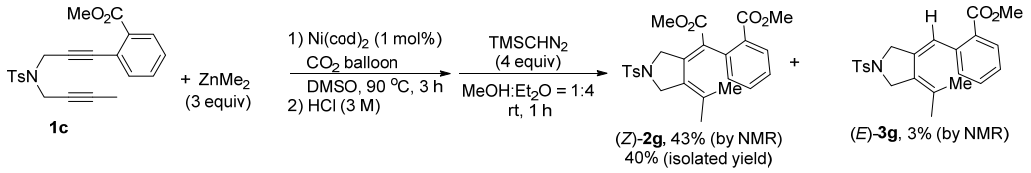


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1c** (394.4 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 2.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*Z*,*E*)-**2f** and (*E*,*E*)-**3f**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*Z*,*E*)-**2f** (42%) and (*E*,*E*)-**3f** (8%)). (*Z*,*E*)-**2f** was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford 207.6 mg of impure product, which was then recrystallized from petroleum ether/dichloromethane = 6/1 to afford 182.0 mg of pure (*Z*,*E*)-**2f** (38%) as a white solid: m.p. 157-158 ^oC (petroleum ether/dichloromethane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02-7.95 (m, 1 H, ArH), 7.75 (d, *J* = 7.8 Hz, 2 H, ArH), 7.36-7.25 (m, 4 H, ArH), 6.65-6.57 (m, 1 H, ArH), 4.65 (d, *J* = 15.0 Hz, 1 H, one proton of CH_2), 4.23 (d, *J* = 15.0 Hz, 1 H, one proton of CH_2), 4.07 (d, *J* = 12.7 Hz, 1 H, one proton of CH_2), 3.93 (d, *J* = 12.7 Hz, 1 H, one proton of CH_2), 3.81 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 2.39 (s, 3 H, CH_3), 1.64-1.52 (m, 1 H, one proton of CH_2), 1.45 (s, 3 H, CH_3), 1.19-1.08 (m, 1 H, one proton of CH_2), 0.10 (t, *J* = 7.3 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 167.0, 144.4, 143.6, 140.7, 139.6, 133.7, 132.3, 132.1, 130.5, 129.7, 129.65, 129.55, 127.9, 127.6, 126.6, 53.4, 52.0, 51.8, 49.9, 27.8, 21.4, 18.7, 10.1; MS (EI) (m/z) (%) 483 (M^+, 3.97), 264 (100); IR (neat, cm^{-1}) 1718, 1647, 1612, 1597, 1569, 1488, 1450, 1430, 1339, 1291, 1249, 1217,

1192, 1156, 1132, 1083, 1040, 1016; Anal. calcd for $C_{26}H_{29}NO_6S$ (%): C 64.58, H 6.04, N 2.90; found: C 64.48, H 6.00, N 2.92.

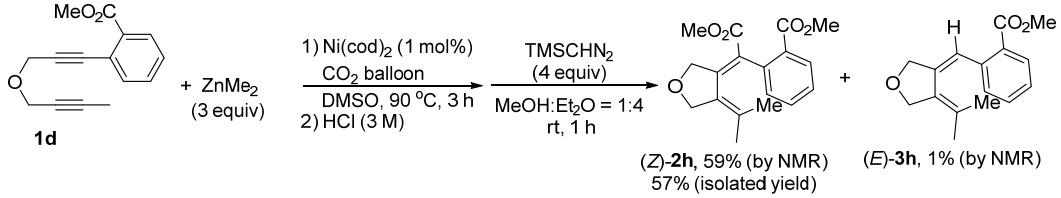
(6) Preparation of (*Z*)-**2g** (ct-6-112).



The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1c** (395.0 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*Z*)-**2g** and (*E*)-**3g**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*Z*)-**2g** (43%) and (*E*)-**3g** (3%)). (*Z*)-**2g** was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford 201.3 mg of impure product, which was then recrystallized (petroleum ether/dichloromethane = 4/1) to afford 189.0 mg of pure (*Z*)-**2g** (40%) as a white solid: m.p. 150-151 ^oC (petroleum ether/dichloromethane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01-7.95 (m, 1 H, ArH), 7.75 (d, *J* = 8.1 Hz, 2 H, ArH), 7.36-7.28 (m, 4 H, ArH), 6.71-6.64 (m, 1 H, ArH), 4.65 (d, *J* = 15.3 Hz, 1 H, one proton of CH_2), 4.26 (d, *J* = 15.2 Hz, 1 H, one proton of CH_2), 4.04 (d, *J* = 12.8 Hz, 1 H, one proton of CH_2), 3.96 (d, *J* = 12.8 Hz, 1 H, one proton of CH_2), 3.80 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 2.40 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 0.80 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 167.0, 144.8, 143.7, 139.7, 136.3, 133.4, 132.0, 130.4, 129.7, 129.3, 129.2, 127.59, 127.57, 127.1, 53.5, 52.0, 51.8, 50.0, 22.6, 22.3, 21.4; MS (EI) (m/z) (%) 469 (M^+, 12.93), 250 (100); IR (neat, cm^{-1}) 1720, 1654, 1612, 1569, 1488, 1448, 1429, 1370, 1339, 1295, 1252, 1219, 1190, 1157, 1131, 1081, 1039, 1006; Anal. calcd for $C_{25}H_{27}NO_6S$ (%): C 63.95, H 5.80, N 2.98; found: C 63.67, H 5.76, N 2.98.

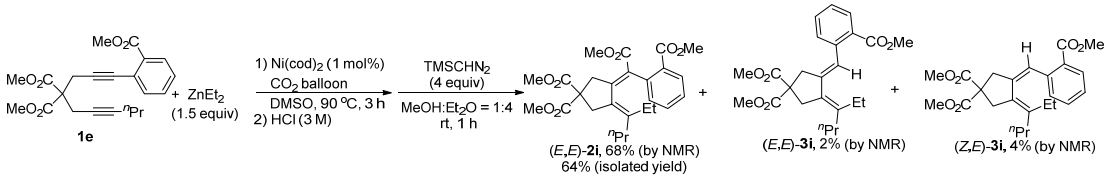
(7) Preparation of (*Z*)-**2h** (ct-6-117).



The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1d** (242.6 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*Z*)-**2h** and (*E*)-**3h**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*Z*)-**2h** (59%) and (*E*)-**3h** (1%)). (*Z*)-**2h** (180.3 mg, 57%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1 H, ArH), 7.44 (t, *J* = 7.6 Hz, 1 H, ArH), 7.35 (t, *J* = 7.6 Hz, 1 H, ArH), 7.21 (d, *J* = 7.7 Hz, 1 H, ArH), 4.91 (d, *J* = 15.5 Hz, 1 H, one proton of CH_2), 4.87 (d, *J* = 14.8 Hz, 1 H, one proton of CH_2), 4.56 (d, *J* = 10.8 Hz, 1 H, one proton of CH_2), 4.40 (d, *J* = 10.8 Hz, 1 H, one proton of CH_2), 3.84 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 1.57 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.2, 149.5, 140.3, 134.8, 132.2, 132.1, 130.4, 130.0, 129.6, 127.3, 126.9, 72.7, 69.4, 51.9, 51.6, 22.8, 22.5; MS (EI) (m/z) (%) 316 (M^+, 33.28), 224 (100); IR (neat, cm^{-1}) 1712, 1654, 1601, 1571, 1434, 1375, 1289, 1256, 1216, 1128, 1084, 1059, 1019; HRMS calcd for $C_{18}H_{20}O_5$ (M^+): 316.1311; found: 316.1313.

(8) Preparation of (*E*,*E*)-**2i** (ct-9-127, ct-8-86).

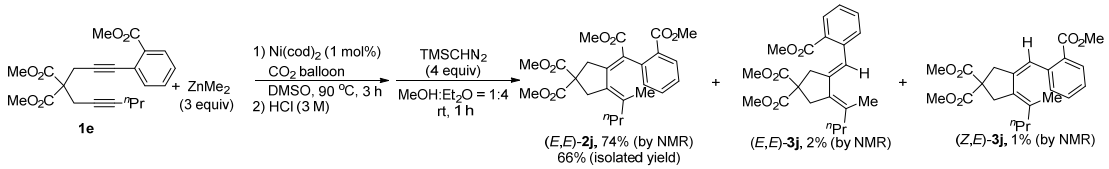


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1e** (384.3 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 1.0 mL, 1.5 mmol), and carbon dioxide (about 1 L) in 10 mL of

DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*E*)-**2i**, (*E*,*E*)-**3i**, and (*Z*,*E*)-**3i**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*E*)-**2i** (68%), (*E*,*E*)-**3i** (2%), and (*Z*,*E*)-**3i** (4%)). (*E*,*E*)-**2i** (303.0 mg, 64%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1 H, ArH), 7.37 (t, *J* = 7.0 Hz, 1 H, ArH), 7.31 (t, *J* = 7.3 Hz, 1 H, ArH), 7.13 (d, *J* = 7.4 Hz, 1 H, ArH), 3.84 (s, 3 H, OCH_3), 3.74 (s, 6 H, OCH_3 × 2), 3.62 (s, 3 H, OCH_3), 3.52 (s, 2 H, CH_2), 3.12 (d, *J* = 14.7 Hz, 1 H, one proton of CH_2), 2.92 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 2.00-1.71 (m, 3 H, CH_2 + one proton of CH_2), 1.28-1.08 (m, 3 H, CH_2 + one proton of CH_2), 0.77 (t, *J* = 7.2 Hz, 3 H, CH_3), 0.26 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.6, 167.5, 167.0, 150.2, 142.7, 140.7, 132.8, 131.9, 130.2, 129.9, 129.3, 128.6, 127.2, 55.8, 52.7, 52.6, 51.7, 51.3, 40.1, 36.6, 33.7, 25.6, 20.8, 14.0, 10.9; MS (EI) (m/z) (%) 472 (M^+, 32.00), 443 (100); IR (neat, cm^{-1}) 2955, 2873, 1719, 1601, 1434, 1374, 1243, 1205, 1171, 1129, 1081, 1045, 1009; HRMS calcd for $C_{26}H_{32}O_8$ (M^+): 472.2097; found: 472.2100.

(9) Preparation of (*E*,*E*)-**2j** (ct-6-155).

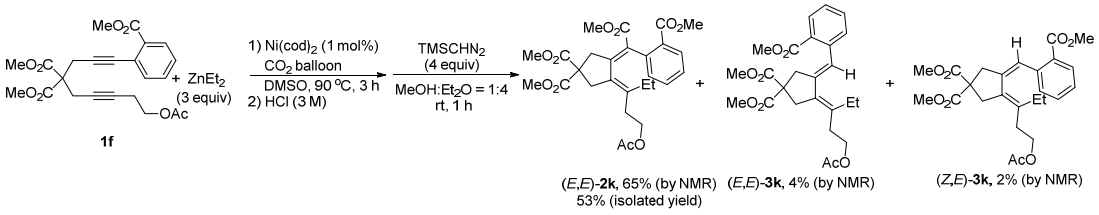


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1e** (384.9 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*E*)-**2j**, (*E*,*E*)-**3j**, and (*Z*,*E*)-**3j**. The NMR yields were determined by ^1H NMR analysis of the

crude products using CH_2Br_2 as the internal standard ((*E*,*E*)-**2j** (74%), (*E*,*E*)-**3j** (2%), and (*Z*,*E*)-**3j** (1%)). (*E*,*E*)-**2j** (304.2 mg, 66%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.5 Hz, 1 H, ArH), 7.37 (t, *J* = 7.2 Hz, 1 H, ArH), 7.30 (t, *J* = 7.1 Hz, 1 H, ArH), 7.13 (d, *J* = 7.5 Hz, 1 H, ArH), 3.84 (s, 3 H, OCH_3), 3.75 (s, 6 H, OCH_3 × 2), 3.63 (s, 3 H, OCH_3), 3.54 (s, 2 H, CH_2), 3.12 (d, *J* = 15.3 Hz, 1 H, one proton of CH_2), 2.94 (d, *J* = 15.0 Hz, 1 H, one proton of CH_2), 2.02-1.91 (m, 1 H, one proton of CH_2), 1.86-1.74 (m, 1 H, one proton of CH_2), 1.24-1.06 (m, 2 H, CH_2), 0.91 (s, 3 H, CH_3), 0.75 (t, *J* = 7.3 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.8, 167.6, 167.3, 150.5, 141.1, 138.3, 132.8, 132.0, 130.5, 130.2, 129.1, 128.9, 127.1, 56.0, 52.85, 52.75, 51.9, 51.5, 40.5, 38.3, 36.7, 20.6, 20.4, 14.0; MS (EI) (m/z) (%) 458 (M^+, 8.14), 334 (100); IR (neat, cm^{-1}) 2954, 1718, 1599, 1434, 1377, 1249, 1207, 1173, 1130, 1081, 1052, 1021; HRMS calcd for $C_{25}H_{30}O_8$ (M^+): 458.1941; found: 458.1944.

(10) Preparation of (*E*,*E*)-**2k** (ct-6-172).

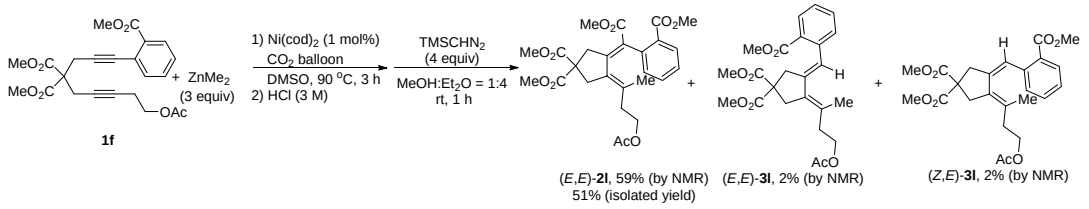


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1f** (427.8 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 2.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*E*)-**2k**, (*E*,*E*)-**3k**, and (*Z*,*E*)-**3k**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*E*)-**2k** (65%), (*E*,*E*)-**3k** (4%), and (*Z*,*E*)-**3k** (2%)). (*E*,*E*)-**2k** (288.7 mg, purity of 94%, 53%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 1 H, ArH), 7.40-7.28 (m, 2

H, ArH), 7.10 (d, J = 7.4 Hz, 1 H, ArH), 3.88-3.79 (m, 5 H, OCH_3 + OCH_2), 3.75 (s, 6 H, OCH_3 × 2), 3.63 (s, 3 H, OCH_3), 3.56 (d, J = 17.4 Hz, 1 H, one proton of CH_2), 3.48 (d, J = 17.3 Hz, 1 H, one proton of CH_2), 3.15 (d, J = 15.1 Hz, 1 H, one proton of CH_2), 2.95 (d, J = 14.9 Hz, 1 H, one proton of CH_2), 2.41-2.31 (m, 1 H, one proton of CH_2), 2.26-2.17 (m, 1 H, one proton of CH_2), 2.02 (s, 3 H, CH_3), 1.84-1.72 (m, 1 H, one proton of CH_2), 1.31-1.20 (m, 1 H, one proton of CH_2), 0.26 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 171.6, 170.7, 167.4, 167.1, 149.4, 140.5, 137.6, 132.8, 132.6, 132.0, 130.3, 129.54, 129.46, 127.6, 62.3, 55.9, 52.9, 52.8, 51.9, 51.5, 40.0, 36.8, 30.8, 26.1, 20.8, 10.9; MS (EI) (m/z) (%) 516 (M^+, 10.61), 332 (100); IR (neat, cm^{-1}) 2954, 1718, 1602, 1570, 1434, 1384, 1365, 1239, 1205, 1170, 1132, 1080, 1044; HRMS calcd for $C_{27}H_{32}O_{10}$ (M^+): 516.1995; found: 519.1990.

(11) Preparation of (*E*,*E*)-**2l** (ct-6-173).

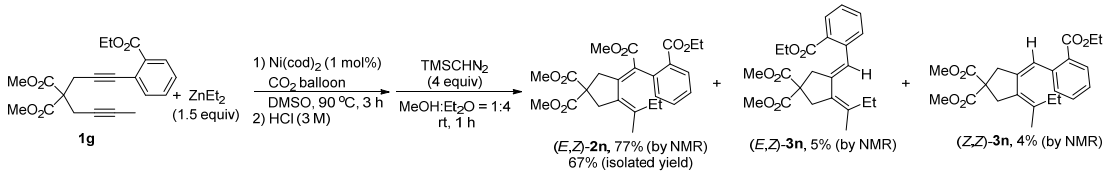


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1f** (428.4 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*E*)-**2l**, (*E*,*E*)-**3l**, and (*Z*,*E*)-**3l**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*E*)-**2l** (59%), (*E*,*E*)-**3l** (2%), and (*Z*,*E*)-**3l** (2%)). (*E*,*E*)-**2l** (257.1 mg, 51%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.7 Hz, 1 H, ArH), 7.39-7.28 (m, 2 H, ArH), 7.09 (d, J = 7.4 Hz, 1 H, ArH), 3.96-3.79 (m, 5 H, OCH_3 + OCH_2), 3.75 (s, 6 H, OCH_3 × 2), 3.63 (s, 3 H, OCH_3), 3.59 (d, J = 17.4 Hz, 1 H, one proton of CH_2), 3.50 (d, J = 17.4 Hz, 1 H, one proton of CH_2), 3.13 (d, J = 15.3 Hz, 1 H, one proton of

CH_2), 2.98 (d, J = 15.4 Hz, 1 H, one proton of CH_2), 2.43-2.32 (m, 1 H, one proton of CH_2), 2.19-2.09 (m, 1 H, one proton of CH_2), 2.02 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.6, 170.7, 167.4, 167.2, 149.6, 140.7, 133.2, 133.1, 132.5, 131.9, 130.3, 129.8, 129.1, 127.4, 62.2, 56.1, 52.9, 52.8, 51.9, 51.5, 40.4, 36.8, 35.3, 20.8, 20.7; MS (EI) (m/z) (%) 502 (M^+, 10.78), 319 (100); IR (neat, cm^{-1}) 2954, 1718, 1600, 1570, 1434, 1382, 1243, 1206, 1131, 1080, 1045; HRMS calcd for $C_{26}H_{30}O_{10}$ (M^+): 502.1839; found: 502.1836.

(12) Preparation of (*E*,*Z*)-**2n** (ct-9-73, ct-7-88).

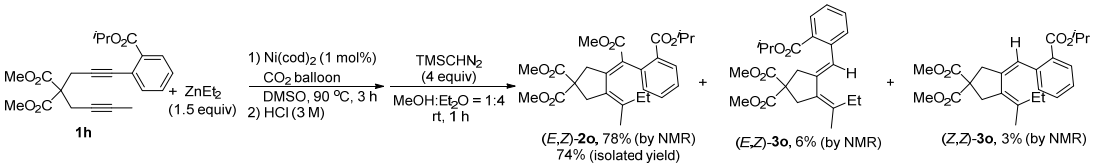


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1g** (370.0 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 1.0 mL, 1.5 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*Z*)-**2n**, (*E*,*Z*)-**3n**, and (*Z*,*Z*)-**3n**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2n** (77%), (*E*,*Z*)-**3n** (5%), and (*Z*,*Z*)-**3n** (4%)). (*E*,*Z*)-**2n** was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford 347.0 mg of impure product, which was then recrystallized (petroleum ether/dichloromethane = 20/1) to afford 307.3 mg of pure (*E*,*Z*)-**2n** (67%) as a white solid: m.p. 101-102 °C (petroleum ether/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 1 H, ArH), 7.39 (t, J = 7.6 Hz, 1 H, ArH), 7.30 (t, J = 7.4 Hz, 1 H, ArH), 7.12 (d, J = 7.5 Hz, 1 H, ArH), 4.39-4.22 (m, 2 H, OCH_2), 3.74 (s, 6 H, OCH_3 × 2), 3.61 (s, 3 H, OCH_3), 3.57 (d, J = 17.2 Hz, 1 H, one proton of CH_2), 3.46 (d, J = 17.2 Hz, 1 H, one proton of CH_2), 3.06 (d, J = 15.2 Hz, 1 H, one proton of CH_2), 2.93 (d, J = 15.0 Hz, 1 H, one proton of CH_2), 1.79-1.65 (m, 1 H, one proton of CH_2), 1.51 (s, 3 H, CH_3), 1.33 (t, J =

7.2 Hz, 3 H, CH_3), 1.37-1.23 (m, 1 H, one proton of CH_2), 0.19 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.7, 167.6, 166.6, 149.6, 140.8, 138.5, 132.7, 131.9, 130.2, 129.8, 129.7, 128.8, 127.2, 60.8, 55.9, 52.7, 52.6, 51.3, 40.6, 36.9, 27.7, 18.2, 14.0, 10.5; MS (EI) (m/z) 458 (%) (M^+, 8.63), 320 (100); IR (neat, cm^{-1}) 2953, 1730, 1712, 1605, 1569, 1484, 1436, 1386, 1368, 1286, 1256, 1207, 1170, 1138, 1119, 1098, 1075, 1051, 1003; Anal. calcd for $C_{25}H_{30}O_8$ (%): C 65.49, H 6.60; found: C 65.47, H 6.63.

(13) Preparation of (*E*,*Z*)-**2o** (ct-9-74, ct-7-94).

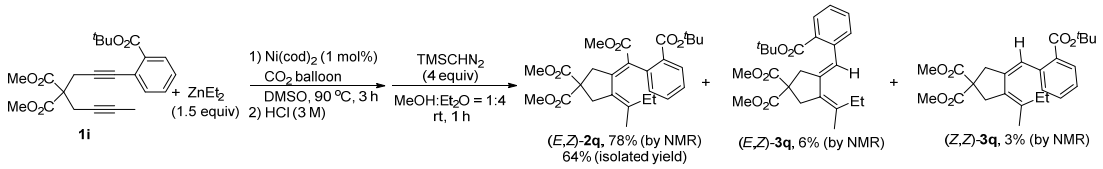


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1h** (384.9 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 1.0 mL, 1.5 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*Z*)-**2o**, (*E*,*Z*)-**3o**, and (*Z*,*Z*)-**3o**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2o** (78%), (*E*,*Z*)-**3o** (6%), and (*Z*,*Z*)-**3o** (3%)). (*E*,*Z*)-**2o** (351.7 mg, 74%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.4 Hz, 1 H, ArH), 7.38 (t, J = 7.2 Hz, 1 H, ArH), 7.30 (t, J = 7.9 Hz, 1 H, ArH), 7.09 (d, J = 7.5 Hz, 1 H, ArH), 5.17 (heptet, J = 6.3 Hz, 1 H, OCH), 3.75 (s, 6 H, OCH_3 × 2), 3.63-3.53 (m, 4 H, OCH_3 + one proton of CH_2), 3.47 (d, J = 17.1 Hz, 1 H, one proton of CH_2), 3.06 (d, J = 14.9 Hz, 1 H, one proton of CH_2), 2.91 (d, J = 14.9 Hz, 1 H, one proton of CH_2), 1.80-1.70 (m, 1 H, one proton of CH_2), 1.50 (s, 3 H, CH_3), 1.35-1.21 (m, 7 H, CH_3 × 2 + one proton of CH_2), 0.19 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 167.6, 166.2, 149.6, 140.8, 138.6, 132.7, 131.9, 130.3, 130.2, 129.8, 129.0, 127.2, 68.5, 56.0, 52.8, 52.7, 51.4, 40.6, 37.1, 27.7, 21.7, 18.2, 10.7; MS (EI) (m/z) (%) 472 (M^+, 7.09),

320 (100); IR (neat, cm^{-1}) 1714, 1603, 1435, 1375, 1340, 1271, 1210, 1153, 1130, 1106, 1078, 1060, 1011; HRMS calcd for $C_{26}H_{32}O_8$ (M^+): 472.2097; found: 472.2090.

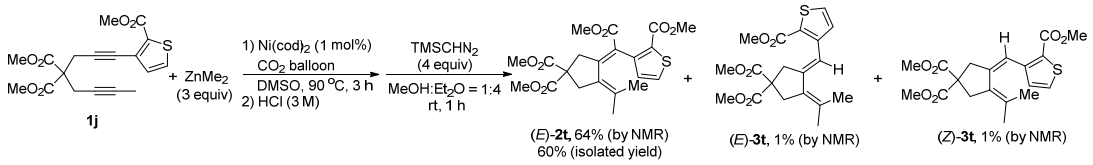
(14) Preparation of (*E*,*Z*)-**2q** (ct-9-75, ct-8-85).



The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1i** (398.9 mg, 1.0 mmol), $ZnEt_2$ (1.5 M in toluene, 1.0 mL, 1.5 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*Z*)-**2q**, (*E*,*Z*)-**3q**, and (*Z*,*Z*)-**3q**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2q** (78%), (*E*,*Z*)-**3q** (6%), and (*Z*,*Z*)-**3q** (3%)). (*E*,*Z*)-**2q** was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford 352.4 mg of impure product, which was then recrystallized (petroleum ether (1.5 mL)) to afford 313.2 mg of pure (*E*,*Z*)-**2q** (64%) as a white solid: m.p. 83-85 ^oC (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 1 H, ArH), 7.35 (t, *J* = 7.0 Hz, 1 H, ArH), 7.28 (t, *J* = 7.6 Hz, 1 H, ArH), 7.08 (d, *J* = 7.4 Hz, 1 H, ArH), 3.743 (s, 3 H, OCH_3), 3.740 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.58 (d, *J* = 19.1 Hz, 1 H, one proton of CH_2), 3.49 (d, *J* = 17.3 Hz, 1 H, one proton of CH_2), 3.07 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 2.92 (d, *J* = 15.1 Hz, 1 H, one proton of CH_2), 1.86-1.76 (m, 1 H, one proton of CH_2), 1.53 (s, 9 H, $CH_3 \times 3$), 1.51 (s, 3 H, CH_3), 1.35-1.22 (m, 1 H, one proton of CH_2), 0.22 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 167.5, 165.9, 149.5, 140.5, 138.6, 132.5, 131.5, 131.4, 130.3, 129.9, 129.1, 127.1, 81.4, 56.0, 52.7, 52.6, 51.4, 40.6, 37.1, 27.8, 27.5, 18.2, 10.7; MS (EI) (m/z) (%) 486 (M^+, 34.67), 401 (100); IR (neat, cm^{-1}) 2966, 1746, 1711, 1603, 1437, 1393, 1370, 1292, 1244, 1209, 1169, 1125, 1074, 1059; Anal. calcd for $C_{27}H_{34}O_8$ (%): C 66.65, H 7.04; found: C 66.89, H 7.08.

(15) Preparation of (*E*)-**2t** (ct-7-59).

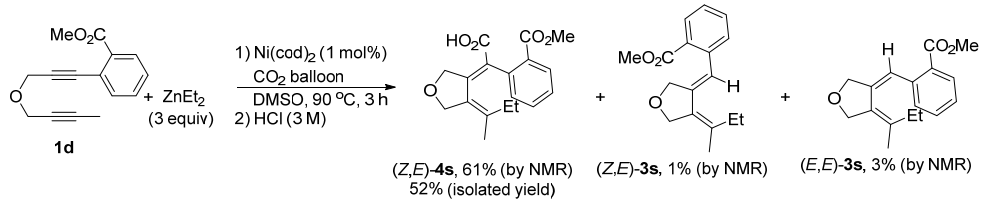


The reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1j** (361.6 mg, 1.0 mmol), $ZnMe_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*)-**2t**, (*E*)-**3t**, and (*Z*)-**3t**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*)-**2t** (64%), (*E*)-**3t** (1%), and (*Z*)-**3t** (1%)). (*E*)-**2t** (259.6 mg, 60%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 5.1 Hz, 1 H, ArH), 6.80 (d, J = 5.0 Hz, 1 H, ArH), 3.82 (s, 3 H, OCH_3), 3.74 (s, 6 H, OCH_3 × 2), 3.68 (s, 3 H, OCH_3), 3.46 (s, 2 H, CH_2), 2.99 (bs, 2 H, CH_2), 1.61 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 167.4, 162.2, 151.8, 145.5, 135.8, 131.6, 130.2, 129.2, 128.2, 123.1, 56.0, 52.7, 51.8, 51.5, 40.8, 36.8, 22.2, 22.1; MS (EI) (m/z) (%) 436 (M^+, 20.96), 313 (100); IR (neat, cm^{-1}) 2949, 1734, 1707, 1643, 1600, 1520, 1437, 1408, 1388, 1273, 1248, 1223, 1160, 1111, 1084, 1051; HRMS calcd for $C_{21}H_{24}O_8S$ (M^+): 436.1192; found: 436.1196.

3. $Ni(cod)_2$-catalyzed reaction of 1 with carbon dioxide and $ZnEt_2$ –preparation of the acids.

(1) Preparation of (*Z*,*E*)-**4s** (ct-6-139).

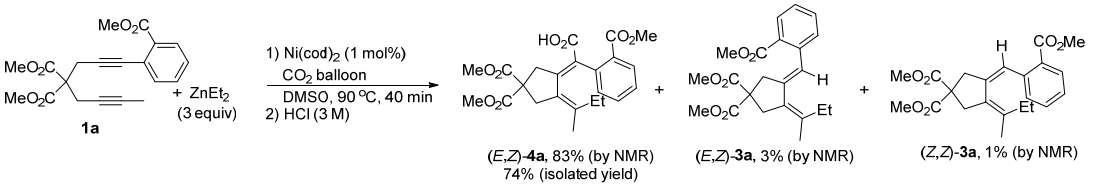


Typical procedure II: To a 50 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (2.8 mg, 0.01 mmol) inside a glove box. Compound **1d** (242.2 mg, 1.0 mmol)

and DMSO (10 mL) were sequentially added under argon outside the glove box. The Schlenk tube was then frozen with a liquid nitrogen bath. The argon inside the tube was completely replaced with CO_2 by using a balloon of CO_2 (about 1 L). The Schlenk tube was allowed to stand until the temperature was above 0 ^oC. Then the Schlenk tube was placed in an oil bath pre-heated at 90 ^oC. After completely thawed, to the mixture was added $ZnEt_2$ (1.5 M in toluene, 2.0 mL, 3.0 mmol) with a syringe. After being vigorously stirred for 3 h, the reaction was complete as monitored by TLC. HCl (3 M, 10 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (10 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford a mixture of (*Z*,*E*)-**4s**, (*Z*,*E*)-**3s**, and (*E*,*E*)-**3s**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*Z*,*E*)-**4s** (61%), (*Z*,*E*)-**3s** (1%), and (*E*,*E*)-**3s** (3%)). (*Z*,*E*)-**4s** was obtained via column chromatography on silica gel (eluent: petroleum ether/acetone = 5/1) to afford 208.5 mg of impure product, which was then recrystallized (petroleum ether/dichloromethane = 7/1) to afford 165.1 mg of pure (*Z*,*E*)-**4s** (52%) as a solid: m.p. 153-155 ^oC (petroleum ether/dichloromethane); ^1H NMR (400 MHz, $CDCl_3$) δ 11.59 (bs, 1 H, CO_2H), 8.05 (d, *J* = 7.6 Hz, 1 H, ArH), 7.43 (t, *J* = 7.2 Hz, 1 H, ArH), 7.35 (t, *J* = 7.5 Hz, 1 H, ArH), 7.18 (d, *J* = 7.4 Hz, 1 H, ArH), 4.92 (d, *J* = 14.6 Hz, 1 H, one proton of CH_2), 4.77 (d, *J* = 14.5 Hz, 1 H, one proton of CH_2), 4.54 (d, *J* = 10.6 Hz, 1 H, one proton of CH_2), 4.37 (d, *J* = 10.8 Hz, 1 H, one proton of CH_2), 3.86 (s, 3 H, OCH_3), 1.76-1.64 (m, 1 H, one proton of CH_2), 1.53 (s, 3 H, CH_3), 1.37-1.25 (m, 1 H, one proton of CH_2), 0.20 (t, *J* = 7.4 Hz, 3 H, CH_3); ^1H NMR (400 MHz, DMSO-d_6) δ 12.37 (s, 1 H, CO_2H), 7.93 (d, *J* = 7.7 Hz, 1 H, ArH), 7.49 (t, *J* = 7.4 Hz, 1 H, ArH), 7.40 (t, *J* = 7.5 Hz, 1 H, ArH), 7.19 (d, *J* = 7.7 Hz, 1 H, ArH), 4.74 (d, *J* = 14.2 Hz, 1 H, one proton of CH_2), 4.58 (d, *J* = 14.3 Hz, 1 H, one proton of CH_2), 4.44 (d, *J* = 11.0 Hz, 1 H, one proton of CH_2), 4.32 (d, *J* = 10.5 Hz, 1 H, one proton of CH_2), 3.76 (s, 3 H, OCH_3), 1.69-1.58 (m, 1 H, one proton of CH_2), 1.50 (s, 3 H, CH_3), 1.42-1.32 (m, 1 H, one proton of CH_2), 0.08 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 167.2, 150.8, 140.4, 140.0, 132.6, 132.4, 130.6, 130.0, 129.5,

127.9, 127.0, 72.5, 69.2, 52.1, 28.3, 19.1, 10.2; MS (EI) (m/z) (%) 316 (M^+, 14.18), 255 (100); IR (neat, cm^{-1}) 3500-2000, 1712, 1675, 1603, 1573, 1482, 1454, 1434, 1409, 1265, 1190, 1136, 1087, 1049; Anal. calcd for $C_{18}H_{20}O_5$ (%): C 68.34, H 6.37; found: C 68.59, H 6.15.

(2) Preparation of (*E*,*Z*)-**4a** (ct-8-101).

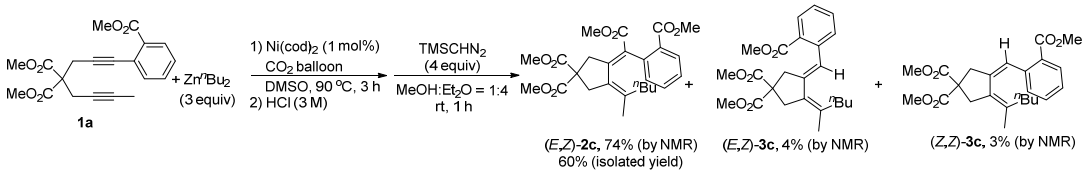


Following **Typical procedure II**, the reaction of $Ni(cod)_2$ (0.8 mg, 0.003 mmol), **1a** (107.5 mg, 0.3 mmol), $ZnEt_2$ (1.5 M in toluene, 0.6 mL, 0.9 mmol) and carbon dioxide (about 1 L) in 3 mL of DMSO for 40 min afforded a mixture of (*E*,*Z*)-**4a**, (*E*,*Z*)-**3a**, and (*Z*,*Z*)-**3a**. The NMR yields were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**4a** (83%), (*E*,*Z*)-**3a** (3%), and (*Z*,*Z*)-**3a** (1%)). (*E*,*Z*)-**4a** (110.4 mg, purity of 87%, 74%) was obtained via column chromatography on silica gel (eluent: dichloromethane/methanol = 40/1) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 11.87 (bs, 1 H, CO_2H), 8.02 (d, J = 7.5 Hz, 1 H, ArH), 7.39 (t, J = 7.1 Hz, 1 H, ArH), 7.31 (t, J = 7.5 Hz, 1 H, ArH), 7.12 (d, J = 7.7 Hz, 1 H, ArH), 3.86 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.64 (d, J = 17.6 Hz, 1 H, one proton of CH_2), 3.44 (d, J = 17.3 Hz, 1 H, one proton of CH_2), 3.06 (d, J = 14.9 Hz, 1 H, one proton of CH_2), 2.91 (d, J = 15.1 Hz, 1 H, one proton of CH_2), 1.75-1.65 (m, 1 H, one proton of CH_2), 1.51 (s, 3 H, CH_3), 1.36-1.24 (m, 1 H, one proton of CH_2), 0.16 (t, J = 7.4 Hz, 3 H, CH_3); ^1H NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1 H, CO_2H), 7.89 (d, J = 7.7 Hz, 1 H, ArH), 7.46 (t, J = 7.6 Hz, 1 H, ArH), 7.36 (t, J = 7.6 Hz, 1 H, ArH), 7.09 (d, J = 7.5 Hz, 1 H, ArH), 3.76 (s, 3 H, OCH_3), 3.69 (s, 6 H, OCH_3 × 2), 3.48 (d, J = 17.0 Hz, 1 H, one proton of CH_2), 3.18 (d, J = 17.0 Hz, 1 H, one proton of CH_2), 2.96 (d, J = 15.7 Hz, 1 H, one proton of CH_2), 2.89 (d, J = 15.2 Hz, 1 H, one proton of CH_2), 1.67-1.55 (m, 1 H, one proton of CH_2), 1.46 (s, 3 H, CH_3), 1.41-1.31 (m, 1 H, one proton of CH_2), 0.04 (t, J = 7.4 Hz, 3 H, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.3, 171.8, 167.2, 151.8, 140.6, 139.5, 132.8, 132.2, 130.4, 129.9, 129.7, 128.4, 127.5, 56.0, 52.9, 52.8, 52.0, 40.9, 37.0, 27.9, 18.4, 10.6; MS (EI) (m/z) (%) 430 (M^+, 10.68), 369 (100); IR (neat, cm^{-1}) 3500-2300, 1718, 1680, 1596, 1483, 1434, 1375, 1256, 1199, 1171, 1137, 1082, 1049; HRMS calcd for $C_{23}H_{26}O_8$ (M^+): 430.1628; found: 430.1623.

4. Ni(cod)$_2$-catalyzed reaction of 1a with carbon dioxide and Zn^{n}Bu$_2$.

(1) preparation of (*E*,*Z*)-**2c** (ct-7-55).

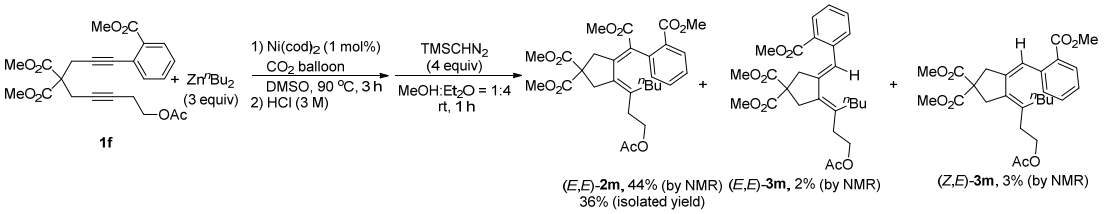


Typical procedure III: To a 50 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (2.8 mg, 0.01 mmol) inside a glove box. Compound **1a** (356.8 mg, 1.0 mmol), DMSO (10 mL) and Zn^{n}Bu$_2$ (1.0 M in hexane, 3.0 mL, 3.0 mmol) were sequentially added under argon outside the glove box. The hexane was then removed by applying a vaccum for 2 min. A balloon of CO_2 (about 1 L) was then placed on the tube with a needle to fulfill the tube with CO_2. Toluene (3 mL) was added to the tube with a syringe. Then the Schlenk tube was placed in an oil bath pre-heated at 90 ^{o}C. After being vigorously stirred for 3 h, the reaction was complete as monitored by TLC. HCl (3 M, 10 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (10 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo.

To the crude product were added MeOH (1 mL) and Et_2O (4 mL). To the resulting mixture was dropwise added $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) with a syringe. After being stirred for 1 h at room temperature, the reaction was complete as monitored by TLC. The reaction mixture was concentrated to afford a mixture of (*E*,*Z*)-**2c**, (*E*,*Z*)-**3c**, and (*Z*,*Z*)-**3c**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2c** (74%), (*E*,*Z*)-**3c** (4%), and (*Z*,*Z*)-**3c** (3%)). (*E*,*Z*)-**2c** was obtained via column

chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1) to afford 340.8 mg of impure product, which was then recrystallized (petroleum ether/dichloromethane = 20/1) to afford 281.5 mg of pure (*E*,*Z*)-**2c** (60%) as a white solid: m.p. 122-123 ^{o}C (petroleum ether/dichloromethane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1 H, ArH), 7.40 (t, *J* = 7.4 Hz, 1 H, ArH), 7.31 (t, *J* = 7.4 Hz, 1 H, ArH), 7.12 (d, *J* = 7.7 Hz, 1 H, ArH), 3.83 (s, 3 H, OCH_3), 3.75 (s, 6 H, OCH_3 × 2), 3.62 (s, 3 H, OCH_3), 3.57 (d, *J* = 17.1 Hz, 1 H, one proton of CH_2), 3.49 (d, *J* = 17.1 Hz, 1 H, one proton of CH_2), 3.07 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 2.92 (d, *J* = 15.1 Hz, 1 H, one proton of CH_2), 1.78-1.67 (m, 1 H, one proton of CH_2), 1.50 (s, 3 H, CH_3), 1.04-0.78 (m, 4 H, CH_2 × 2), 0.68 (t, *J* = 6.9 Hz, 3 H, CH_3), 0.46-0.35 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.7, 167.6, 167.1, 149.8, 141.0, 137.7, 132.7, 132.0, 130.3, 130.2, 129.2, 128.7, 127.2, 56.0, 52.8, 52.7, 51.8, 51.4, 40.7, 37.0, 34.7, 28.4, 22.3, 18.7, 13.6; MS (EI) (m/z) (%) 472 (M^+, 13.37), 415 (100); IR (neat, cm^{-1}) 2958, 2927, 1729, 1711, 1603, 1434, 1380, 1280, 1248, 1210, 1172, 1150, 1125, 1107, 1085, 1051; Anal. calcd for $C_{26}H_{32}O_8$ (%): C 66.09, H 6.83; found: C 65.87, H 6.75.

(2) preparation of (*E*,*E*)-**2m** (ct-7-74).

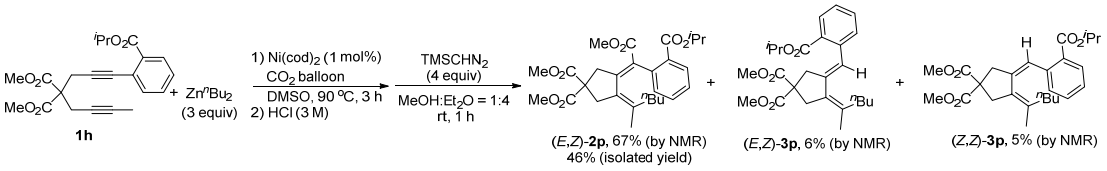


Following **Typical procedure III**, the reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1f** (427.3 mg, 1.0 mmol), Zn^nBu_2 (1.0 M in hexane, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO and 3 mL of toluene afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*E*)-**2m**, (*E*,*E*)-**3m**, and (*Z*,*E*)-**3m**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*E*)-**2m** (44%), (*E*,*E*)-**3m**

(2%), and (*Z*,*E*)-**3m** (3%)). (*E*,*E*)-**2m** (195.2 mg, 36%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.5, 1.8 Hz, 1 H, ArH), 7.39-7.30 (m, 2 H, ArH), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1 H, ArH), 3.83 (s, 3 H, OCH_3), 3.85-3.76 (m, 2 H, OCH_2), 3.749 (s, 3 H, OCH_3), 3.745 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.57 (d, *J* = 17.6 Hz, 1 H, one proton of CH_2), 3.50 (d, *J* = 17.3 Hz, 1 H, one proton of CH_2), 3.16 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 2.93 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 2.44-2.34 (m, 1 H, one proton of CH_2), 2.23-2.14 (m, 1 H, one proton of CH_2), 2.02 (s, 3 H, CH_3), 1.81-1.72 (m, 1 H, one proton of CH_2), 1.05-0.81 (m, 4 H, $CH_2 \times 2$), 0.69 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.57-0.46 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.7, 170.8, 167.4, 167.1, 149.5, 140.6, 136.7, 133.2, 132.6, 132.0, 130.4, 129.6, 129.2, 127.6, 62.5, 56.1, 52.9, 52.8, 51.9, 51.6, 40.0, 37.0, 32.9, 31.1, 28.8, 22.3, 20.9, 13.7; MS (EI) (m/z) (%) 544 (M^+, 24.01), 457 (100); IR (neat, cm^{-1}) 1720, 1601, 1570, 1434, 1373, 1239, 1171, 1127, 1082, 1044; HRMS calcd for $C_{29}H_{36}O_{10}$ (M^+): 544.2308; found: 544.2314.

(3) preparation of (*E*,*Z*)-**2p** (ct-9-84).

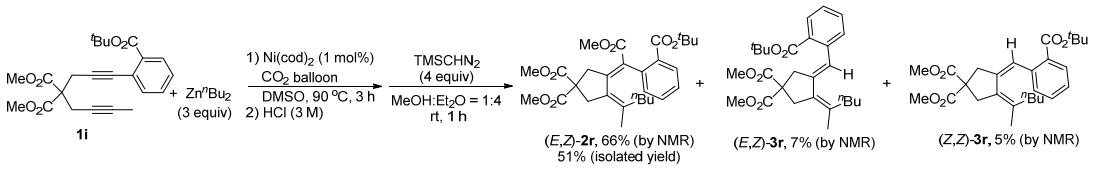


Following **Typical procedure I**, the reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1h** (383.7 mg, 1.0 mmol), Zn^{n}Bu$_2$ (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*Z*)-**2p**, (*E*,*Z*)-**3p**, and (*Z*,*Z*)-**3p**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2p** (67%), (*E*,*Z*)-**3p** (6%), and (*Z*,*Z*)-**3p** (5%)). (*E*,*Z*)-**2p** was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) to afford 330.7 mg of impure product, which was then recrystallized (petroleum ether (2 mL)) to afford 229.7 mg of pure

(*E*,*Z*)-**2p** (46%) as a white solid: m.p. 94-96 ^{o}C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.8, 1.2 Hz, 1 H, ArH), 7.38 (td, *J* = 7.5, 1.4 Hz, 1 H, ArH), 7.30 (td, *J* = 7.5, 1.4 Hz, 1 H, ArH), 7.10 (dd, *J* = 7.6, 1.0 Hz, 1 H, ArH), 5.15 (hept, *J* = 6.3 Hz, 1 H, OCH), 3.74 (s, 6 H, OCH_3 × 2), 3.61 (s, 3 H, OCH_3), 3.59 (d, *J* = 20.6 Hz, 1 H, one proton of CH_2), 3.50 (d, *J* = 17.1 Hz, 1 H, one proton of CH_2), 3.08 (d, *J* = 15.0 Hz, 1 H, one proton of CH_2), 2.90 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 1.76-1.65 (m, 1 H, one proton of CH_2), 1.50 (s, 3 H, CH_3), 1.324 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.317 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.13-1.03 (m, 1 H, one proton of CH_2), 1.00-0.78 (m, 3 H, one proton of CH_2 + CH_2), 0.67 (t, *J* = 6.9 Hz, 3 H, CH_3), 0.32-0.19 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.8, 167.6, 166.1, 149.7, 141.1, 137.7, 132.7, 131.9, 130.29, 130.26, 129.9, 128.9, 127.2, 68.6, 56.1, 52.8, 52.7, 51.4, 40.7, 37.2, 34.8, 28.3, 22.5, 21.8, 21.7, 18.8, 13.8; MS (EI) (m/z) (%) 500 (M^+, 26.34), 443 (100); IR (neat, cm^{-1}) 1745, 1711, 1604, 1452, 1436, 1382, 1344, 1287, 1272, 1247, 1216, 1171, 1131, 1106, 1086, 1058, 1011; Anal. calcd for $C_{28}H_{36}O_8$ (%): C 67.18, H 7.25; found: C 67.16, H 7.23.

(4) preparation of (*E*,*Z*)-**2r** (ct-9-85).

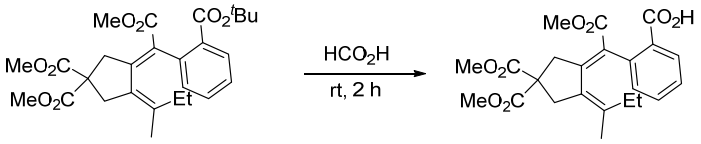


Following **Typical procedure I**, the reaction of $Ni(cod)_2$ (2.8 mg, 0.01 mmol), **1i** (397.6 mg, 1.0 mmol), Zn^nBu_2 (1.0 M in toluene, 3.0 mL, 3.0 mmol), and carbon dioxide (about 1 L) in 10 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 2.0 mL, 4.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O afforded a mixture of (*E*,*Z*)-**2r**, (*E*,*Z*)-**3r**, and (*Z*,*Z*)-**3r**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**2r** (66%), (*E*,*Z*)-**3r** (7%), and (*Z*,*Z*)-**3r** (5%)). Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) afforded 341.0 mg of impure product, which was then recrystallized (petroleum ether (1 mL) for the first round to afford 212.4 mg of pure

(*E*,*Z*)-**2r**; the mother liquid was concentrated and submitted to the second round (petroleum ether (4 mL)) to afford 50.0 mg of (*E*,*Z*)-**2r**) as a white solid: total 262.4 mg (51%); m.p. 83-84 ^{o}C (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.8, 1.0 Hz, 1 H, ArH), 7.35 (td, *J* = 7.5, 1.3 Hz, 1 H, ArH), 7.28 (td, *J* = 7.6, 1.2 Hz, 1 H, ArH), 7.09 (d, *J* = 7.4 Hz, 1 H, ArH), 3.741 (s, 3 H, OCH_3), 3.737 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.59 (d, *J* = 22.4 Hz, 1 H, one proton of CH_2), 3.50 (d, *J* = 17.3 Hz, 1 H, one proton of CH_2), 3.09 (d, *J* = 14.9 Hz, 1 H, one proton of CH_2), 2.90 (d, *J* = 15.1 Hz, 1 H, one proton of CH_2), 1.76-1.67 (m, 1 H, one proton of CH_2), 1.54 (s, 9 H, CH_3 × 3), 1.51 (s, 3 H, CH_3), 1.25-1.15 (m, 1 H, one proton of CH_2), 1.02-0.81 (m, 3 H, one proton of CH_2 + CH_2), 0.66 (t, *J* = 6.9 Hz, 3 H, CH_3), 0.18-0.04 (m, 1 H, one proton of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.8, 167.5, 165.9, 149.5, 140.7, 137.8, 132.6, 131.5, 131.1, 130.25, 130.17, 129.0, 127.1, 81.3, 56.0, 52.8, 52.6, 51.4, 40.7, 37.2, 34.8, 28.2, 27.8, 22.6, 18.8, 13.8; MS (EI) (m/z) (%) 514 (M^+, 14.2), 401 (100); IR (neat, cm^{-1}) 1727, 1711, 1640, 1601, 1453, 1436, 1391, 1367, 1290, 1248, 1205, 1168, 1125, 1080, 1156; Anal. calcd for $C_{29}H_{38}O_8$ (%): C 67.68, H 7.44; found: C 67.67, H 7.43.

5. Selective removal of *tert*-butyl group of (*E*,*Z*)-2q (ct-7-101).



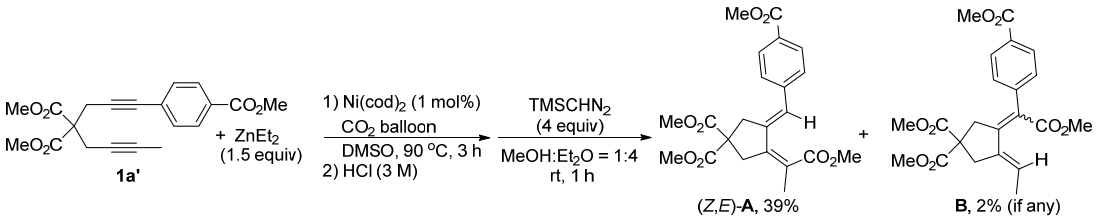
(*E*,*Z*)-**2q** (*E*,*Z*)-**5q**, 98%

To a 25 mL round bottom flask was added (*E*,*Z*)-**2q** (77.3 mg, 0.16 mmol) and 1.6 mL of HCO_2H (98%). After being stirred for 2 h at room temperature, the mixture was concentrated to afford (*E*,*Z*)-**5q** (67.2 mg, 98%) via column chromatography on silica gel (eluent: dichloromethane/methanol = 30/1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (bs, 1 H, CO_2H), 8.12 (d, *J* = 7.9 Hz, 1 H, ArH), 7.44 (t, *J* = 7.5 Hz, 1 H, ArH), 7.34 (t, *J* = 7.6 Hz, 1 H, ArH), 7.16 (d, *J* = 7.7 Hz, 1 H, ArH), 3.76 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.59 (d, *J* = 17.1 Hz, 1 H, one proton of CH_2), 3.46 (d, *J* = 16.8 Hz, 1 H, one proton of CH_2), 3.07 (d, *J* = 15.2 Hz, 1

H, one proton of CH_2), 2.94 (d, J = 15.3 Hz, 1 H, one proton of CH_2), 1.79-1.67 (m, 1 H, one proton of CH_2), 1.52 (s, 3 H, CH_3), 1.39-1.27 (m, 1 H, one proton of CH_2), 0.18 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 172.1, 171.8, 167.6, 150.2, 141.7, 138.9, 133.2, 132.9, 131.2, 129.8, 128.64, 128.63, 127.5, 56.0, 52.9, 52.8, 51.5, 40.8, 37.0, 27.9, 18.3, 10.5; MS (EI) (m/z) (%) 430 (M^+, 23.57), 401 (100); IR (neat, cm^{-1}) 3262, 2953, 1734, 1711, 1595, 1568, 1484, 1434, 1378, 1247, 1222, 1147, 1109, 1078, 1049, 1009; HRMS calcd for $C_{23}H_{26}O_8$ (M^+): 430.1628; found: 430.1622.

6. Control experiments.

(1) Reaction of **1a'** under the standard conditions (ct-9-136).

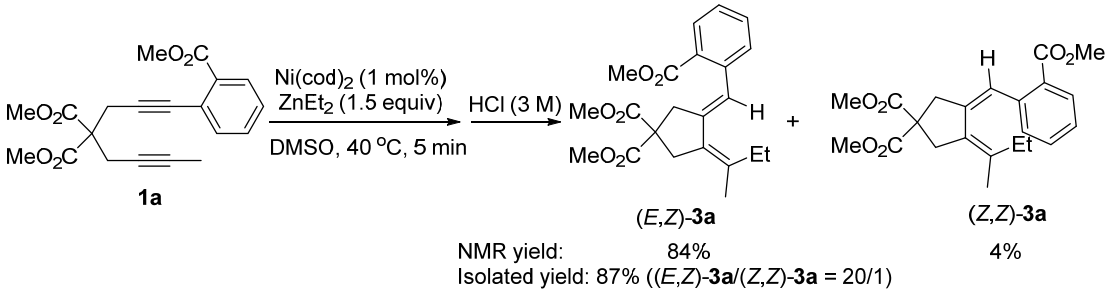


Following **Typical Procedure I**, the reaction of $Ni(cod)_2$ (1.4 mg, 0.005 mmol), **1a'** (178.1 mg, 0.5 mmol), $ZnEt_2$ (1.5 M in toluene, 0.5 mL, 0.75 mmol), and carbon dioxide (about 1 L) in 5 mL of DMSO afforded the crude product.

The crude product was then reacted with $TMSCHN_2$ (2.0 M in hexane, 1.0 mL, 2.0 mmol) in 1 mL of MeOH and 4 mL of Et_2O to afford a mixture of (*E*,*Z*)-**A** and **B**. The NMR yields were determined by ^{1}H NMR analysis of the crude products using CH_2Br_2 as the internal standard ((*E*,*Z*)-**A** (44%) and **B** (2%)). (*E*,*Z*)-**A**[2] (80.2 mg, 39%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) as a white solid: m.p. 126-127 °C (petroleum ether/ethyl acetate) (reported:[2] 126-127 °C (petroleum ether/ethyl acetate)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.9 Hz, 2 H, ArH), 7.35 (d, J = 7.9 Hz, 2 H, ArH), 6.72 (s, 1 H, CH=), 3.91 (s, 3 H, OCH_3), 3.71 (s, 9 H, $OCH_3 \times 3$), 3.33 (s, 2 H, CH_2), 3.09 (s, 2 H, CH_2), 2.00 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.9, 166.6, 141.4, 140.8, 138.4, 129.4, 128.8, 128.5, 126.1, 123.1, 57.0, 52.9, 52.0, 51.8, 39.3, 37.9, 18.3; MS (EI) (m/z) 416 (M^+, 34.01), 297 (100); IR (neat, cm^{-1}) 1743, 1727, 1704, 1637, 1600,

1560, 1433, 1353, 1300, 1257, 1197, 1136, 1115, 1071, 1053, 1015.

(2) Reaction of **1a** without carbon dioxide-quenched with HCl. (ct-9-137)



To a 25 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (0.8 mg, 0.003 mmol) inside a glove box. Compound **1a** (106.5 mg, 0.3 mmol) and DMSO (3 mL) were sequentially added under argon outside the glove box. Then the Schlenck tube was placed in an oil bath pre-heated at 40 °C. To the mixture was added $ZnEt_2$ (1.5 M in toluene, 0.3 mL, 0.45 mmol) with a syringe. After being stirred for 5 min, the reaction was complete as monitored by TLC. HCl (3 M, 5 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford a mixture of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a**. The NMR yields were determined by ^1H NMR analysis of this crude products using CH_2Br_2 as the internal standard (84% ((*E*,*Z*)-**3a**) and 4% ((*Z*,*Z*)-**3a**), respectively). A mixture of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a** (100.8 mg, 87%, (*E*,*Z*)-**3a**/(*Z*,*Z*)-**3a** = 20/1) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) as an oil.

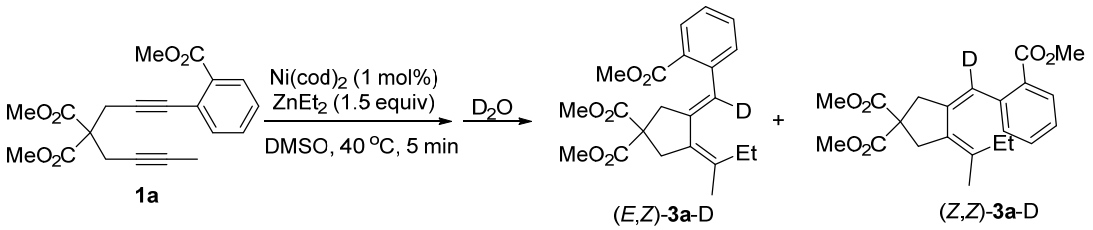
(*E*,*Z*)-**3a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1 H, ArH), 7.47 (t, *J* = 7.3 Hz, 1 H, ArH), 7.35 (d, *J* = 7.7 Hz, 1 H, ArH), 7.28 (t, *J* = 7.6 Hz, 1 H, ArH), 7.08 (s, 1 H, CH=), 3.84 (s, 3 H, OCH_3), 3.66 (s, 6 H, OCH_3 × 2), 3.06-2.99 (m, 4 H, CH_2 × 2), 2.43 (q, *J* = 7.4 Hz, 2 H, CH_2), 1.79 (s, 3 H, CH_3), 1.14 (t, *J* = 7.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 167.6, 139.3, 138.7, 135.4, 131.4, 130.9, 130.4, 130.2, 129.1, 126.3, 124.0, 57.3, 52.5, 51.8, 39.4, 38.4, 28.5, 20.6, 12.8; GC-MS (GC condition: injector: 260 °C; column: DB-5MS column 30 m × 0.25 mm,

temperature programming: 15 °C/min to 285 °C, 285 °C (15 min); detector: 150 °C) (70 ev, EI) (m/z) (%) (retention time: 10.9 min): 386 (M^+, 29.7), 235 (100); HRMS calcd for $C_{22}H_{26}O_6$ (M^+): 386.1729; found: 386.1728.

The following signals are discernible for (*Z*,*Z*)-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.3 Hz, 1 H, ArH), 6.69 (s, 1 H, CH=), 3.88 (s, 3 H, OCH_3), 3.75 (s, 6 H, OCH_3 × 2), 1.57-1.49 (m, 5 H, CH_3 + CH_2), 0.34 (t, *J* = 7.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 167.3, 141.1, 138.0, 134.1, 131.8, 130.7, 127.7, 127.5, 126.2, 124.1, 56.3, 52.6, 51.7, 43.3, 37.9, 28.3, 17.8, 10.6; GC-MS (GC condition: injector: 260 °C; column: DB-5MS column 30 m × 0.25 mm, temperature programming: 15 °C/min to 285 °C, 285 °C (15 min); detector: 150 °C) (70 ev, EI) (m/z) (%) (retention time: 10.5 min): 386 (M^+, 20.38), 235 (100); HRMS calcd for $C_{22}H_{26}O_6$ (M^+): 386.1729; found: 386.1725.

IR (for the mixture of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a**) (neat, cm^{-1}) 2955, 1723, 1596, 1567, 1477, 1433, 1290, 1244, 1201, 1165, 1126, 1074.

(3) Reaction of **1a** without carbon dioxide-quenched with D_2O. (ct-9-138)



To a 25 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (0.8 mg, 0.003 mmol) inside a glove box. Compound **1a** (106.3 mg, 0.3 mmol) and DMSO (3 mL) were sequentially added under argon outside the glove box. Then the Schlenck tube was placed in an oil bath pre-heated at 40 °C. To the mixture was added $ZnEt_2$ (1.5 M in toluene, 0.3 mL, 0.45 mmol) with a syringe. After being stirred for 5 min, the reaction was complete as monitored by TLC. D_2O (1.0 mL) was added to quench the reaction followed by the addition of HCl (3 M, 5 mL). The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (10 mL),

dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to afford a mixture of (*E*,*Z*)-**3a**-D and (*Z*,*Z*)-**3a**-D. The NMR yields were determined by ^{1}H NMR analysis of this crude products using CH_2Br_2 as the internal standard (84% ((*E*,*Z*)-**3a**-D) and 4% ((*Z*,*Z*)-**3a**-D), respectively). A mixture of (*E*,*Z*)-**3a**-D and (*Z*,*Z*)-**3a**-D (99.2 mg, 86%, (*E*,*Z*)-**3a**-D/(*Z*,*Z*)-**3a**-D = 20/1, D-incorporation: (*E*,*Z*)-**3a**-D 81% and (*E*,*Z*)-**3a**-D 97%) was obtained via column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) as an oil.

(*E*,*Z*)-**3a**-D: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1 H, ArH), 7.47 (t, *J* = 7.6 Hz, 1 H, ArH), 7.36 (d, *J* = 7.7 Hz, 1 H, ArH), 7.28 (t, *J* = 7.5 Hz, 1 H, ArH), 3.84 (s, 3 H, OCH_3), 3.66 (s, 6 H, $OCH_3 \times 2$), 3.06-3.00 (m, 4 H, $CH_2 \times 2$), 2.42 (q, *J* = 7.4 Hz, 2 H, CH_2), 1.79 (s, 3 H, CH_3), 1.14 (t, *J* = 7.6 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 167.6, 139.2, 138.6, 135.4, 131.4, 130.9, 130.3, 130.2, 129.1, 126.3, 123.6 (t, $J_{C\text{-}D}$ = 24.6 Hz), 57.25, 52.5, 51.8, 39.34, 38.4, 28.4, 20.6, 12.8; GC-MS (GC condition: injector: 260 ^{o}C; column: DB-5MS column 30 m × 0.25 mm, temperature programming: 15 ^{o}C/min to 285 ^{o}C, 285 ^{o}C (15 min); detector: 150 ^{o}C) (70 ev, EI) (m/z) (%) (retention time: 10.9 min): 387 (M^+ ($C_{22}H_{25}DO_6$), 40.24), 386 (M^+ ($C_{22}H_{26}O_6$), 5.81), 236 (100); HRMS calcd for $C_{22}H_{25}DO_6$ (M^+): 387.1792; found: 387.1790.

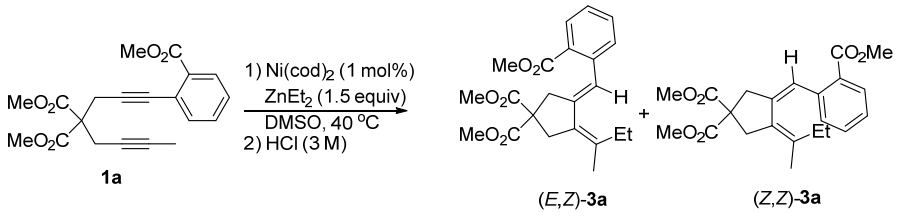
The following signals are discernible for (*E*,*Z*)-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 0.19 H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.7, 123.9, 57.23, 39.37.

The following signals are discernible for (*Z*,*Z*)-**3a**-D: ^{1}H NMR (400 MHz, $CDCl_3$) 7.23-7.18 (m, 1 H, ArH), 6.70 (s, 0.03 H, CH=), 3.88 (s, 3 H, OCH_3), 3.75 (s, 6 H, $OCH_3 \times 2$), 1.57-1.48 (m, 5 H, $CH_3 + CH_2$), 0.35 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 167.3, 141.0, 137.9, 134.1, 131.8, 130.7, 130.1, 127.7, 127.5, 126.2, 56.3, 52.6, 51.7, 43.2, 37.8, 28.3, 17.8, 10.6; GC-MS (GC condition: injector: 260 ^{o}C; column: DB-5MS column 30 m × 0.25 mm, temperature programming: 15 ^{o}C/min to 285 ^{o}C, 285 ^{o}C (15 min); detector: 150 ^{o}C) (70 ev, EI) (m/z) (%) (retention time: 10.5 min): 387 (M^+ ($C_{22}H_{25}DO_6$), 32.09), 386 (M^+ ($C_{22}H_{26}O_6$), 3.95), 236 (100); HRMS calcd for $C_{22}H_{25}DO_6$ (M^+): 387.1792; found:

387.1795.

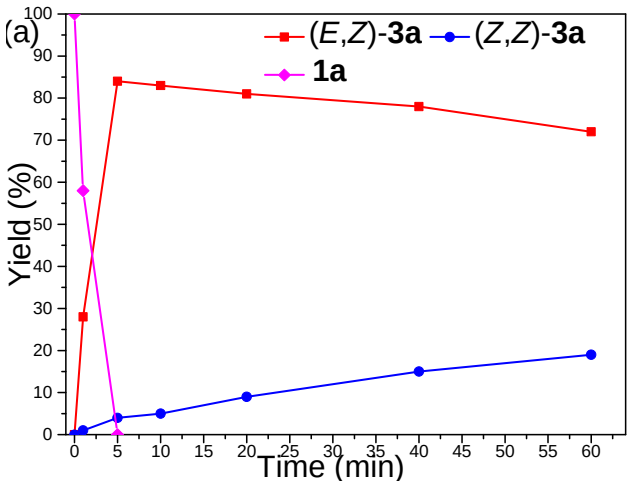
IR (for the mixture of (*E*,*Z*)-**3a**-D and (*Z*,*Z*)-**3a**-D) (neat, cm^{-1}) 1731, 1711, 1639, 1595, 1564, 1476, 1433, 1377, 1273, 1243, 1198, 1161, 1112, 1092, 1074.

(4) Monitoring the yields of (*E*,*Z*)-**3a** and (*Z*,*Z*)-**3a** vs. time at 40 °C without CO_2.

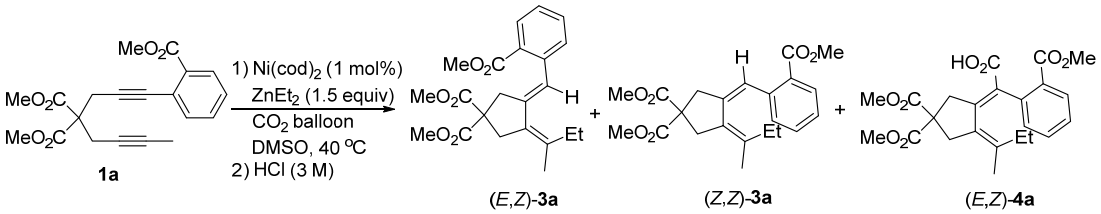


To a 25 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (0.003 mmol) inside a glove box. Compound **1a** (0.3 mmol) and DMSO (3 mL) were sequentially added under argon outside the glove box. Then the Schlenck tube was placed in an oil bath pre-heated at 40 °C. To the mixture was added $ZnEt_2$ (1.5 M in toluene, 0.3 mL, 0.45 mmol) with a syringe. After being stirred for the time specified, HCl (3 M, 5 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The yields of (*E*,*Z*)-**3a**, (*Z*,*Z*)-**3a**, and the recovery of **1a** were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard. Samples were taken for analysis at 1 min, 5 min, 10 min, 20 min, 40 min, and 60 min.

Time (min)	Yield of (*E*,*Z*)-**3a**	Yield of (*Z*,*Z*)-**3a**	Recovery of **1a**	(*E*,*Z*)-**3a**/(*Z*,*Z*)-**3a**
1	28	1	58	28.0
5	84	4	0	21.0
10	83	5	0	16.6
20	81	9	0	9.0
40	78	15	0	5.2
60	72	19	0	3.8

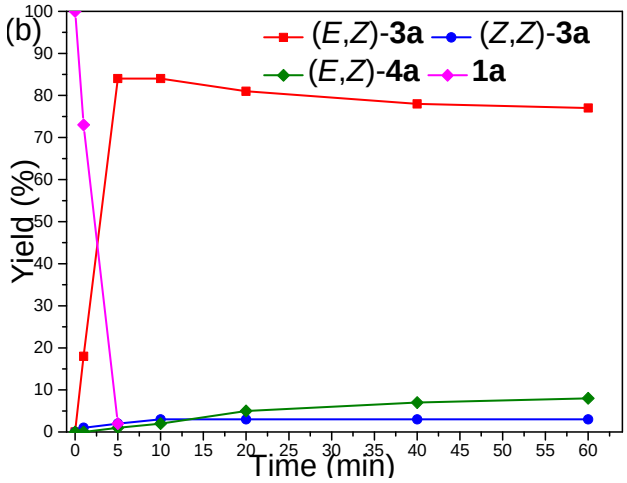


(5) Monitoring the yields of (*E*,*Z*)-**3a**, (*Z*,*Z*)-**3a, and** (*E*,*Z*)-**4a** vs. time at 40 °C with CO_2.

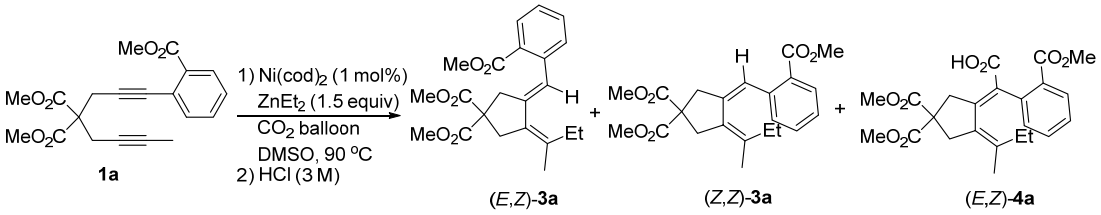


To a 25 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (0.003 mmol) inside a glove box. Compound **1a** (0.3 mmol) and DMSO (3 mL) were sequentially added under argon outside the glove box. The Schlenk tube was then frozen with a liquid nitrogen bath. The argon inside the tube was completely replaced with CO_2 by using a balloon of CO_2 (about 1 L). The Schlenk tube was allowed to stand until the temperature was above 0 °C. Then the Schlenk tube was placed in an oil bath pre-heated at 40 °C. After completely thawed, to the mixture was added $ZnEt_2$ (1.5 M in toluene, 0.3 mL, 0.45 mmol) with a syringe. After being stirred for the time specified, HCl (3 M, 5 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The yields of (*E*,*Z*)-**3a**, (*Z*,*Z*)-**3a**, (*E*,*Z*)-**4a**, and the recovery of **1a** were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard. Samples were taken for analysis at 1 min, 5 min, 10 min, 20 min, 40 min, and 60 min.

Time (min)	Yield of (*E*,*Z*)-**3a**	Yield of (*Z*,*Z*)-**3a**	Yield of (*E*,*Z*)-**4a**	Recovery of **1a**	(*E*,*Z*)-**3a**/(*Z*,*Z*)-**3a**
1	18	1	0	73	18.0
5	84	2	1	0	42.0
10	84	3	2	0	28.0
20	81	3	5	0	27.0
40	78	3	7	0	26.0
60	77	3	8	0	25.7



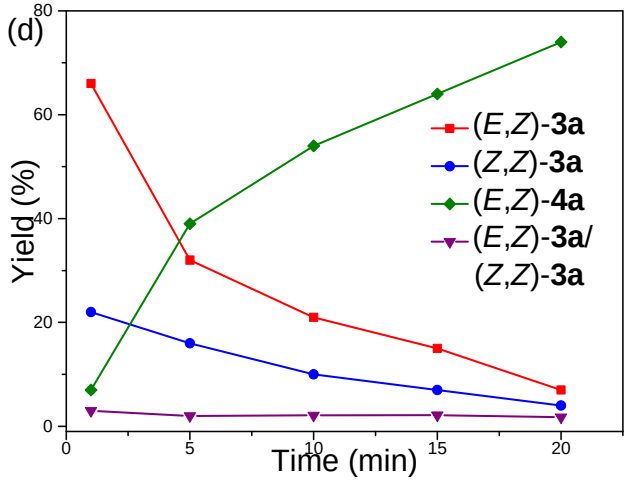
(6) Monitoring the yields of (*E*,*Z*)-**3a**, (*Z*,*Z*)-**3a**, and (*E*,*Z*)-**4a** vs. time at 90 °C with CO_2.



To a 25 mL flame-dried Schlenk tube was added $Ni(cod)_2$ (0.003 mmol) inside a glove box. Compound **1a** (0.3 mmol) and DMSO (3 mL) were sequentially added under argon outside the glove box. The Schlenk tube was then frozen with a liquid nitrogen bath. The argon inside the tube was completely replaced with CO_2 by using a balloon of CO_2 (about 1 L). The Schlenk tube was allowed to stand until the temperature was above 0 °C. Then the Schlenk tube was placed in an oil bath pre-heated at 90 °C. After completely thawed, to the mixture was added $ZnEt_2$ (1.5 M

in toluene, 0.3 mL, 0.45 mmol) with a syringe. After being stirred for the time specified, HCl (3 M, 5 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The yields of (*E*,*Z*)-**3a**, (*Z*,*Z*)-**3a**, and (*E*,*Z*)-**4a** were determined by ^1H NMR analysis of the crude products using CH_2Br_2 as the internal standard. Samples were taken for analysis at 1 min, 5 min, 10 min, 15 min and 20 min.

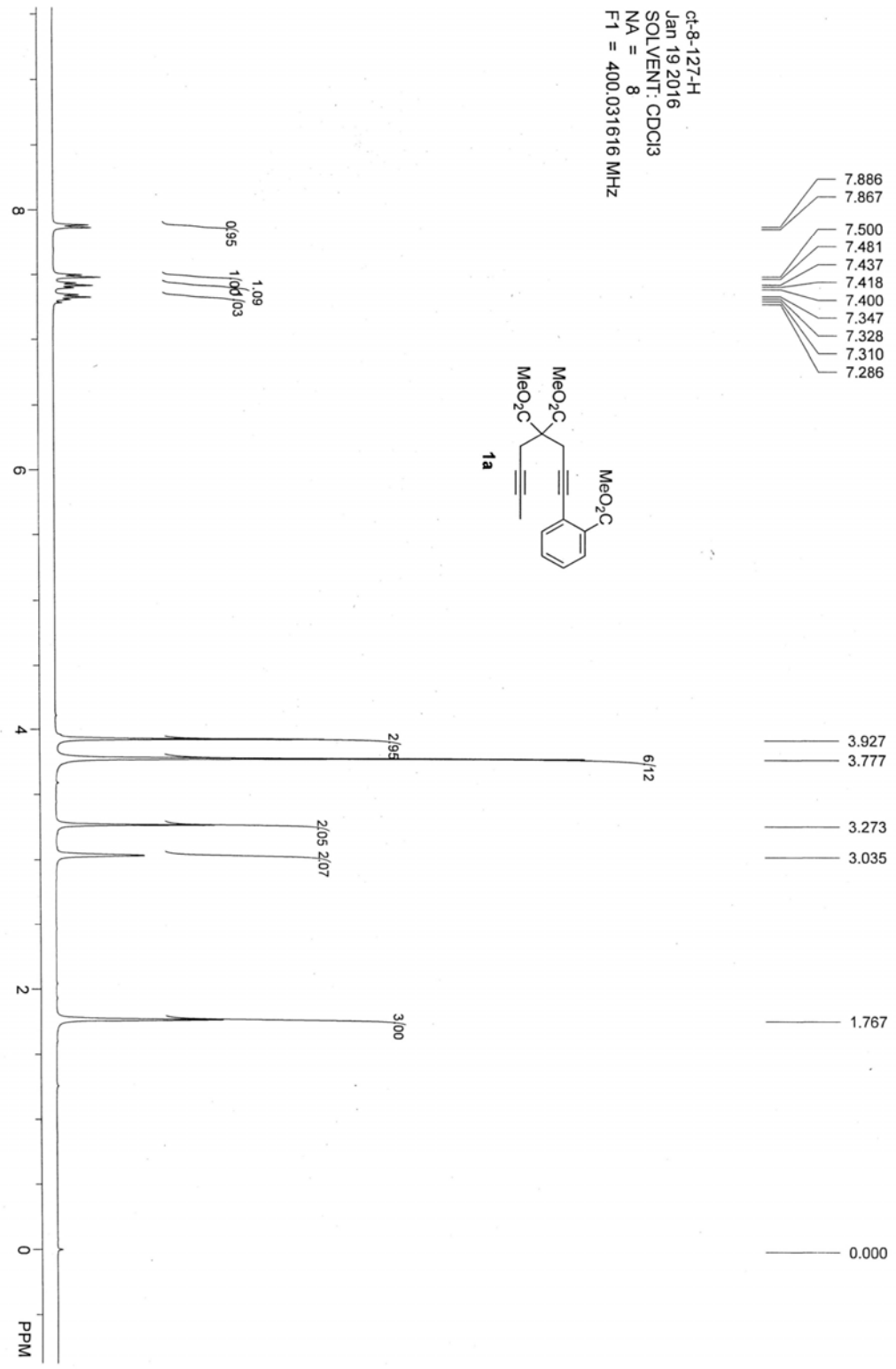
Time (min)	Yield of (*E*,*Z*)-**3a**	Yield of (*Z*,*Z*)-**3a**	Yield of (*E*,*Z*)-**4a**	(*E*,*Z*)-**3a**/(*Z*,*Z*)-**3a**
1	66	22	7	3.0
5	32	16	39	2.0
10	21	10	54	2.1
15	15	7	64	2.1
20	7	4	74	1.8

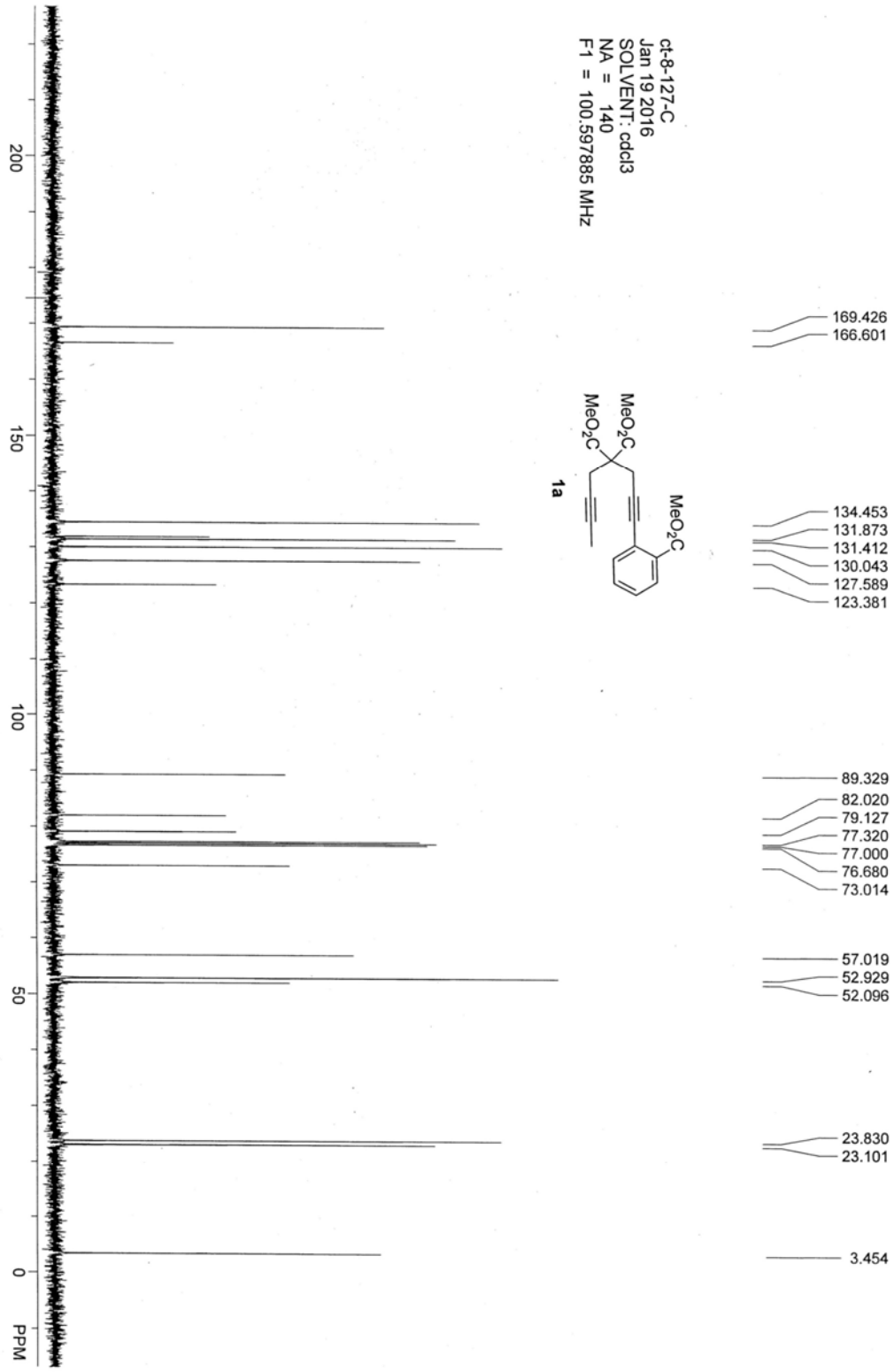


References

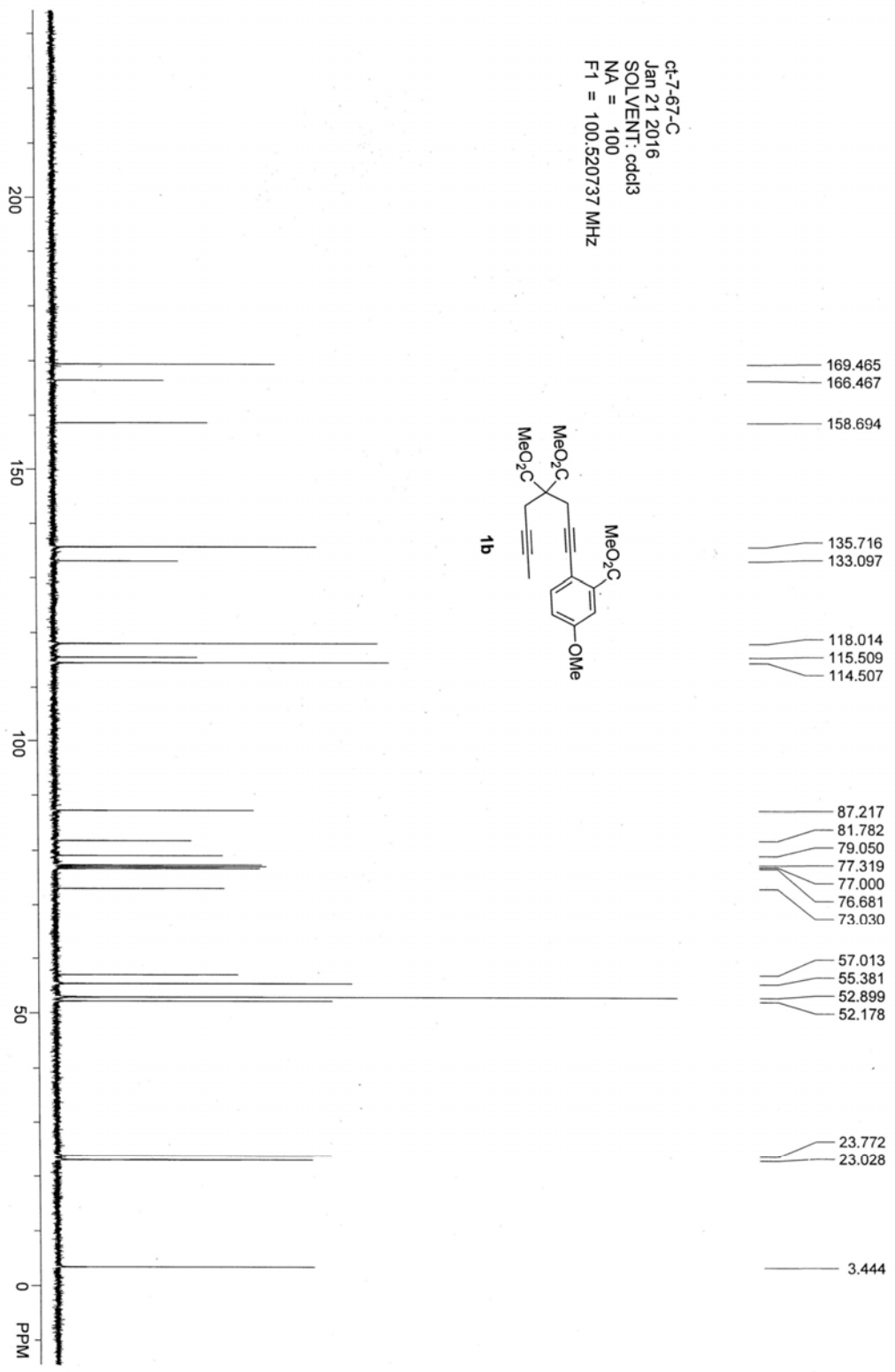
(1) Thorson, M. K.; Klinkel, K. L.; Wang, J.; Williams, T. J. *Eur. J. Inorg. Chem.* **2009**, 295.

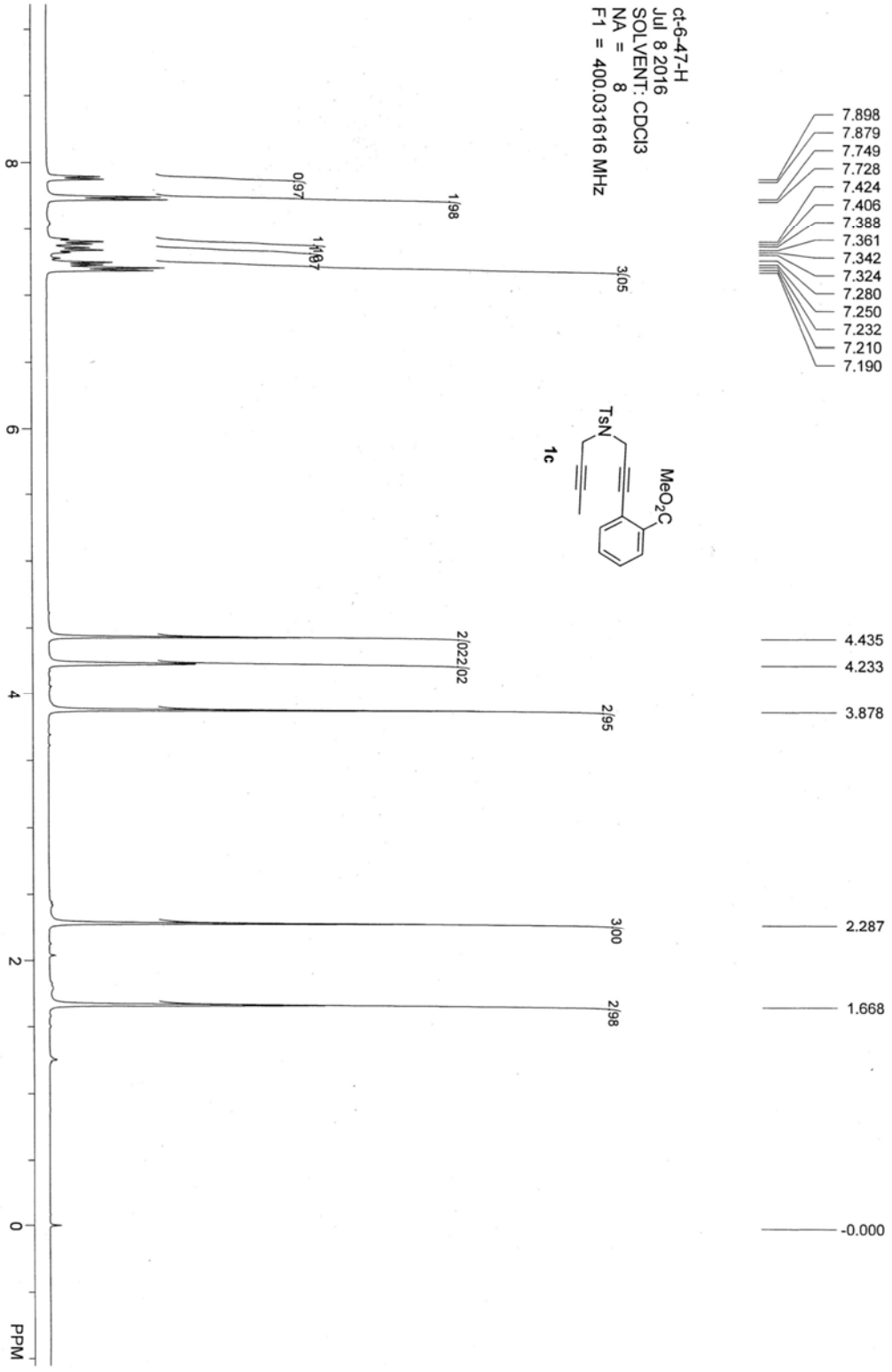
(2) Cao, T.; Ma, S. *Org. Lett.* **2016**, *18*, 1510.

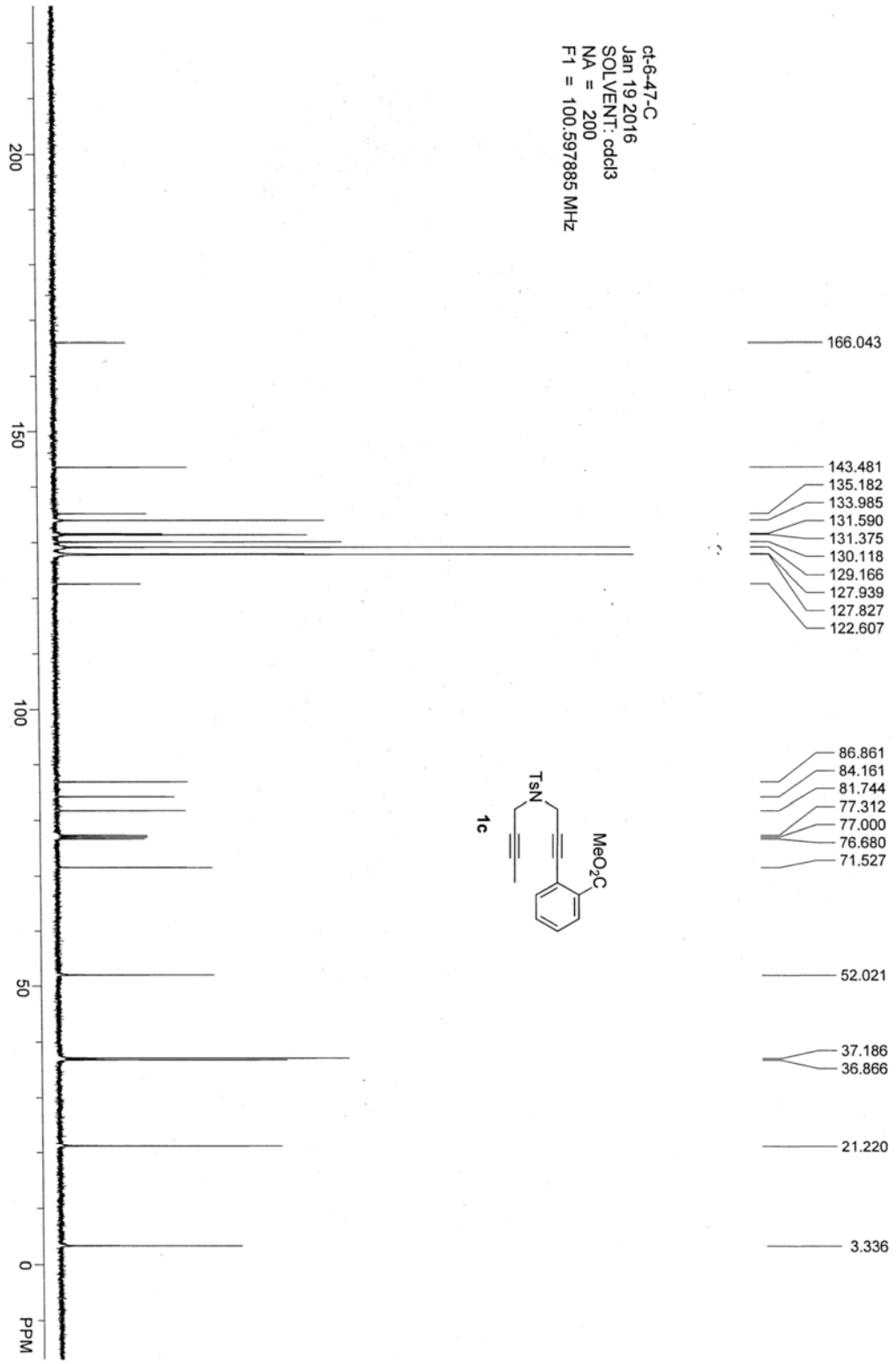

ct-8-127-H
Jan 19 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
MeO2C
MeO2C
MeO2C
1a
7.886
7.867
7.500
7.481
7.437
7.418
7.400
7.347
7.328
7.310
7.286
3.927
3.777
3.273
3.035
1.767
0.000
0.95
1.00
1.03
1.09
2.95
6.12
2.05
2.07
3.00
8
6
4
2
0
PPM

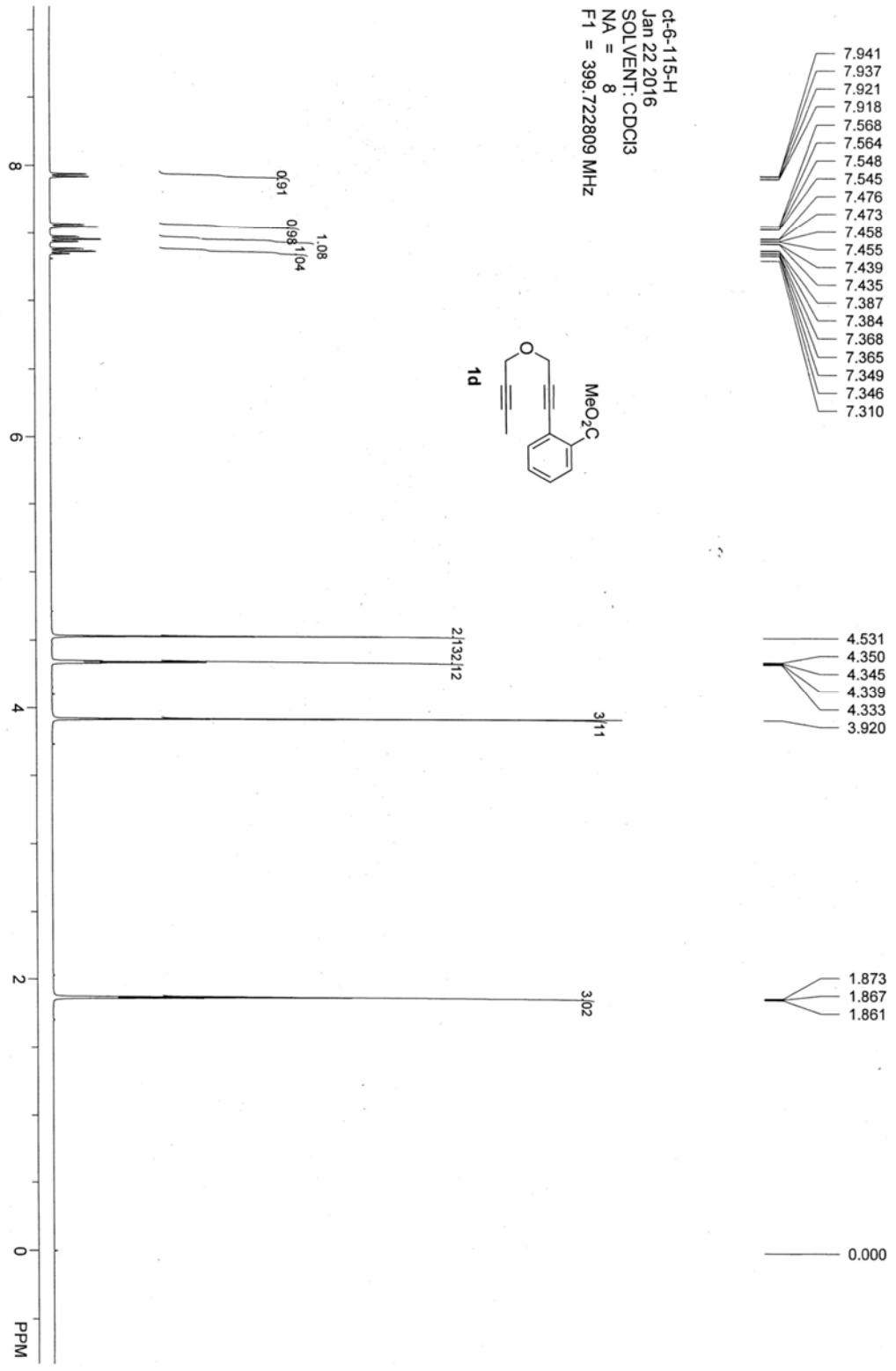

ct-8-127-C
Jan 19 2016
SOLVENT: cdcl3
NA = 140
F1 = 100.597885 MHz
MeO2C
MeO2C
MeO2C
1a
169.426
166.601
134.453
131.873
131.412
130.043
127.589
123.381
89.329
82.020
79.127
77.320
77.000
76.680
73.014
57.019
52.929
52.096
23.830
23.101
3.454
200
150
100
50
0
PPM

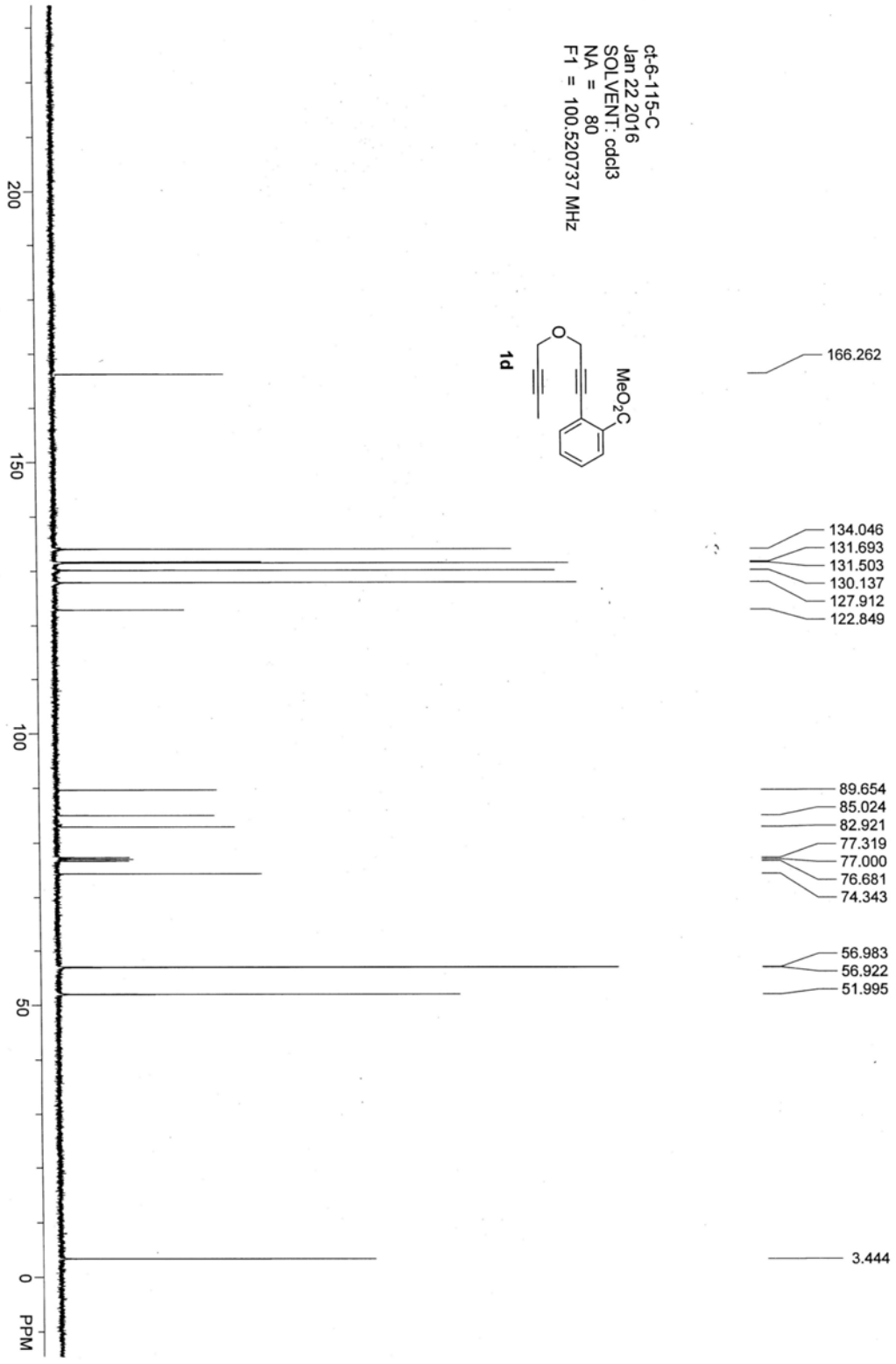

ct-7-67-H
Jan 21 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
1b
MeO2C
MeO2C
MeO2C
OMe
7.414
7.393
7.383
7.376
7.297
6.976
6.969
6.954
6.947
3.929
3.827
3.774
3.245
3.035
3.029
3.023
3.017
1.773
1.767
1.761
-0.000
1.01
0.99
1.01
3.08
3.00
5.97
2.02
2.00
3.00
8
6
4
2
0
PPM

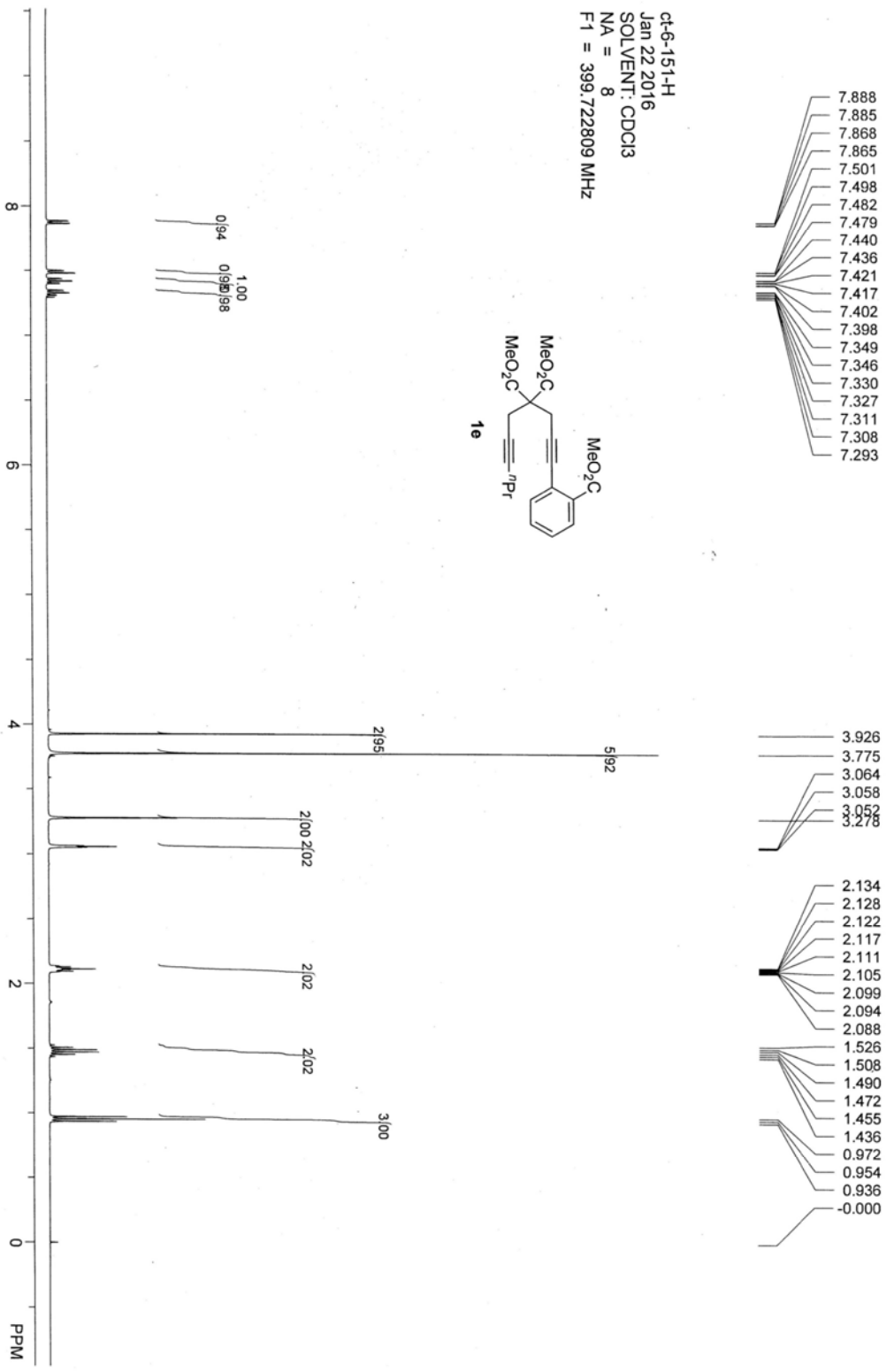

ct-7-67-C
Jan 21 2016
SOLVENT: cdcl3
NA = 100
F1 = 100.520737 MHz
MeO2C
MeO2C
MeO2C
OMe
1b
169.465
166.467
158.694
135.716
133.097
118.014
115.509
114.507
87.217
81.782
79.050
77.319
77.000
76.681
73.030
57.013
55.381
52.899
52.178
23.772
23.028
3.444
200
150
100
50
0
PPM

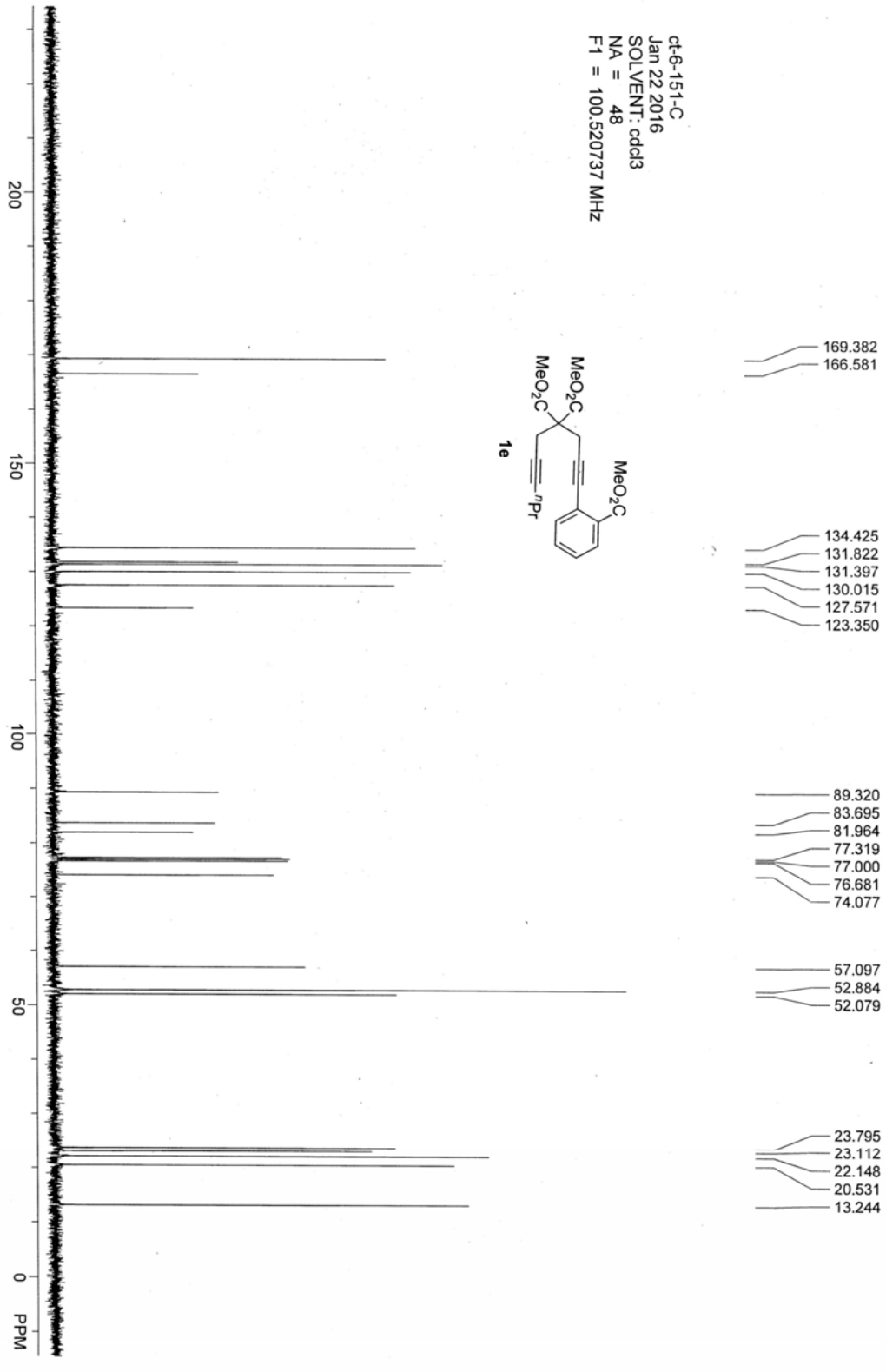

ct-6-47-H
Jul 8 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
TsN
MeO2C
1c
7.898
7.879
7.749
7.728
7.424
7.406
7.388
7.361
7.342
7.324
7.280
7.250
7.232
7.210
7.190
4.435
4.233
3.878
2.287
1.668
-0.000
0.97
1.98
1.97
3.05
2.02
2.02
2.95
3.00
2.98
8
6
4
2
0
PPM

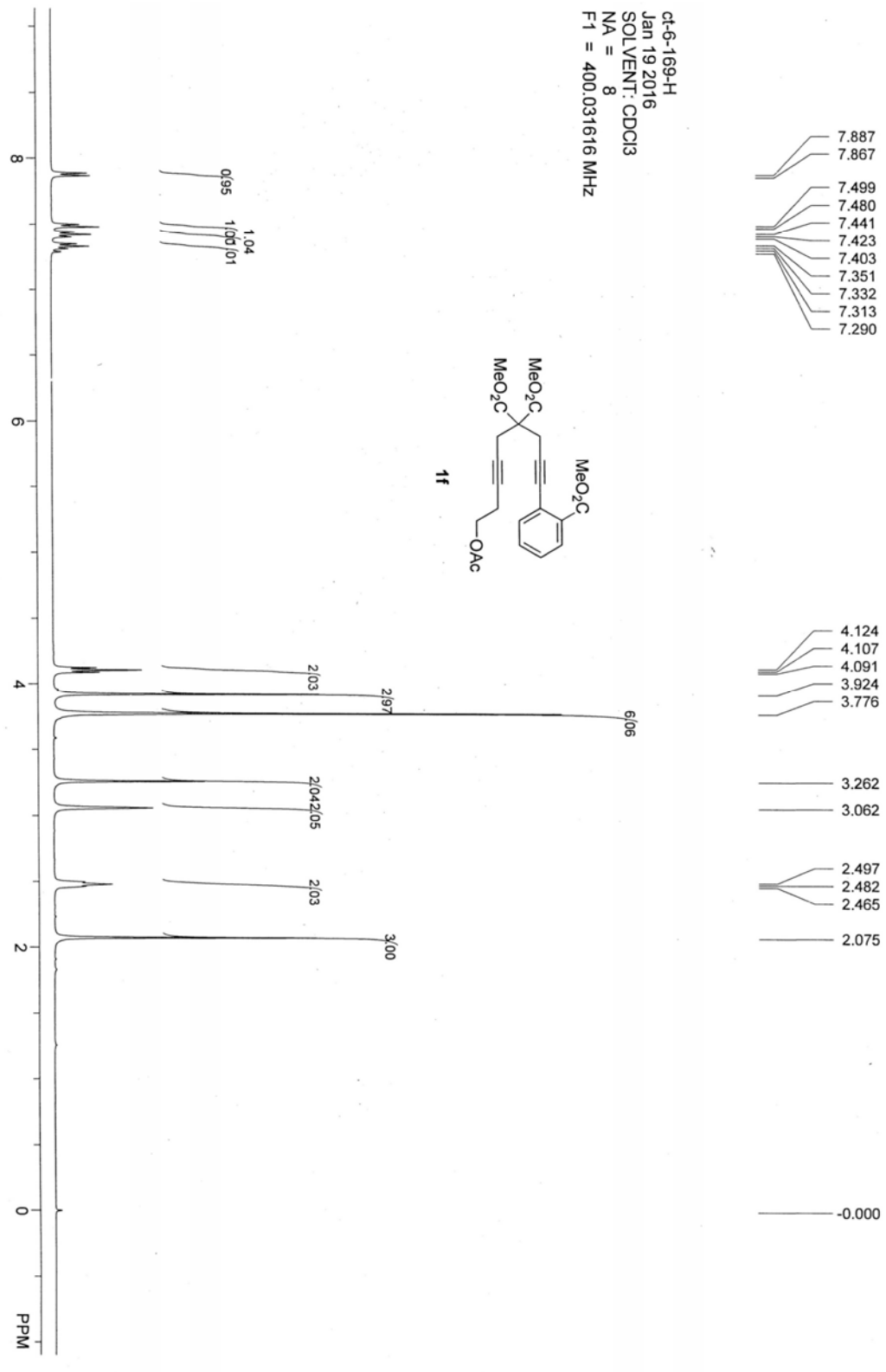

ct-6-47-C
Jan 19 2016
SOLVENT: cdcl3
NA = 200
F1 = 100.597885 MHz
200
150
100
50
0
PPM
166.043
143.481
135.182
133.985
131.590
131.375
130.118
129.166
127.939
127.827
122.607
86.861
84.161
81.744
77.312
77.000
76.680
71.527
52.021
37.186
36.866
21.220
3.336
TsN
MeO2C
1c

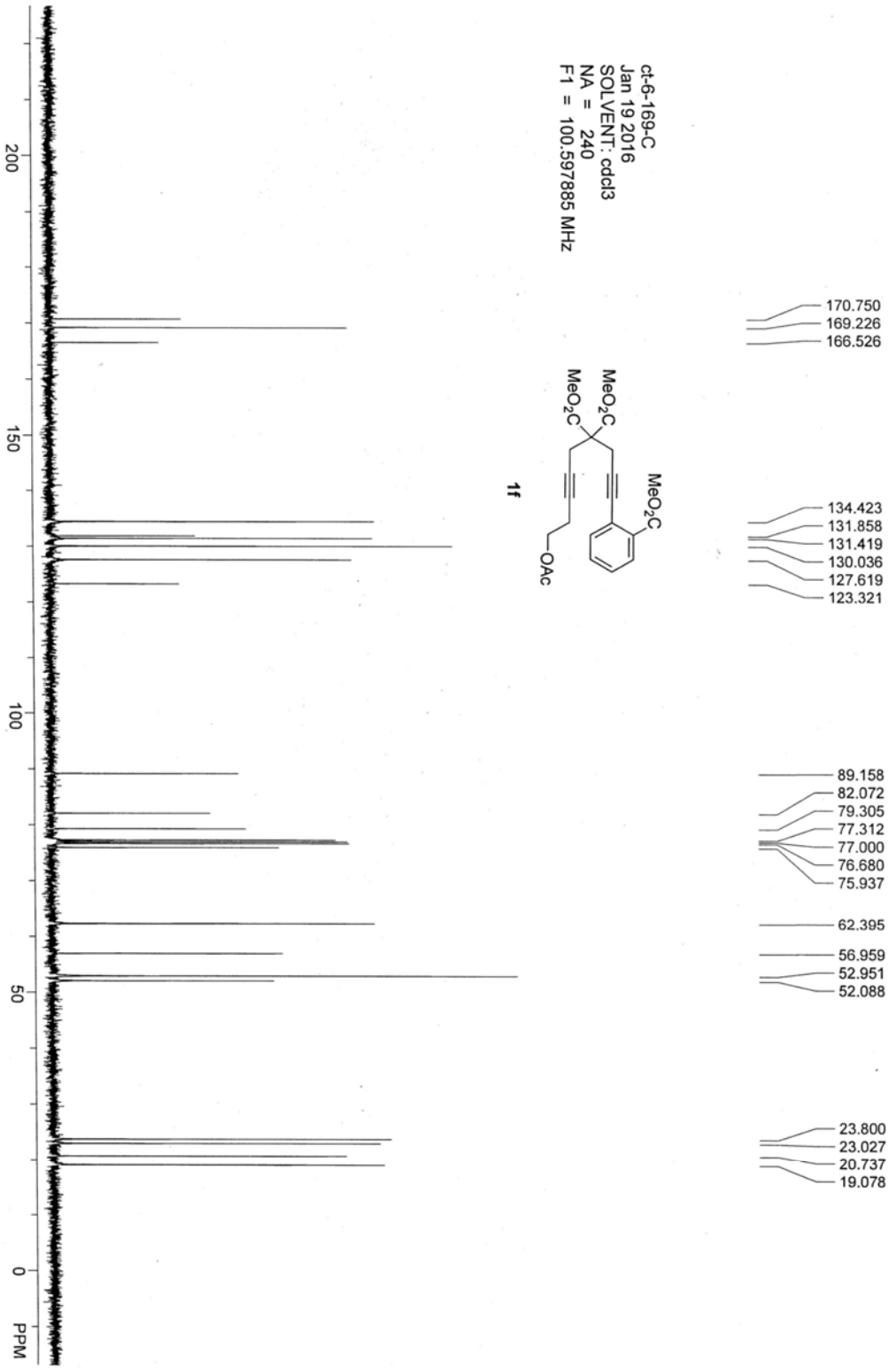

ct-6-115-H
Jan 22 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
1d
MeO2C
7.941
7.937
7.921
7.918
7.568
7.564
7.548
7.545
7.476
7.473
7.458
7.455
7.439
7.435
7.387
7.384
7.368
7.365
7.349
7.346
7.310
4.531
4.350
4.345
4.339
4.333
3.920
1.873
1.867
1.861
0.000
0.91
0.98
1.04
1.08
2.12
2.12
3.11
3.02
8
6
4
2
0
PPM

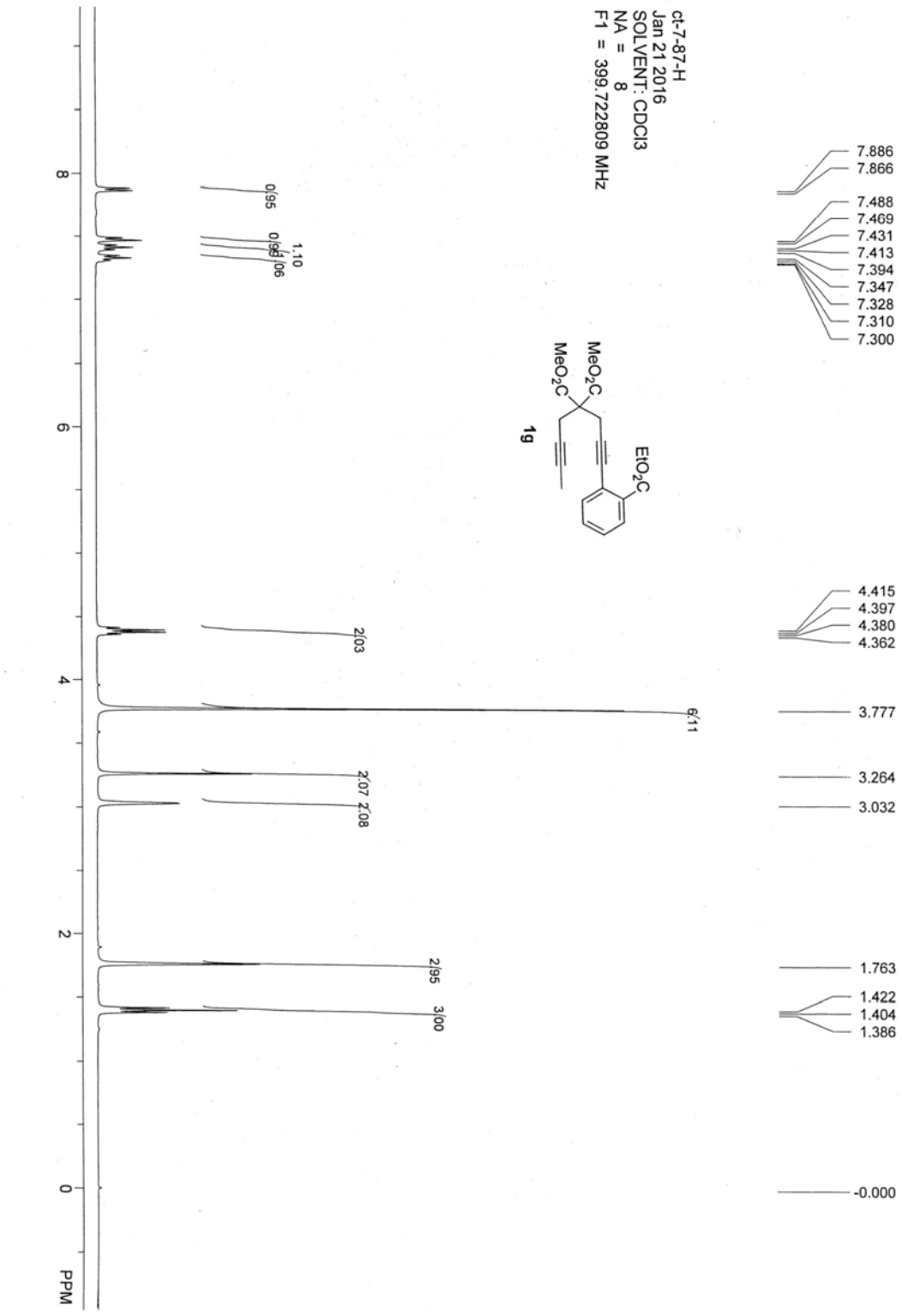

ct-6-115-C
Jan 22 2016
SOLVENT: cdcl3
NA = 80
F1 = 100.520737 MHz
1d
MeO2C
166.262
134.046
131.693
131.503
130.137
127.912
122.849
89.654
85.024
82.921
77.319
77.000
76.681
74.343
56.983
56.922
51.995
3.444
200
150
100
50
0
PPM

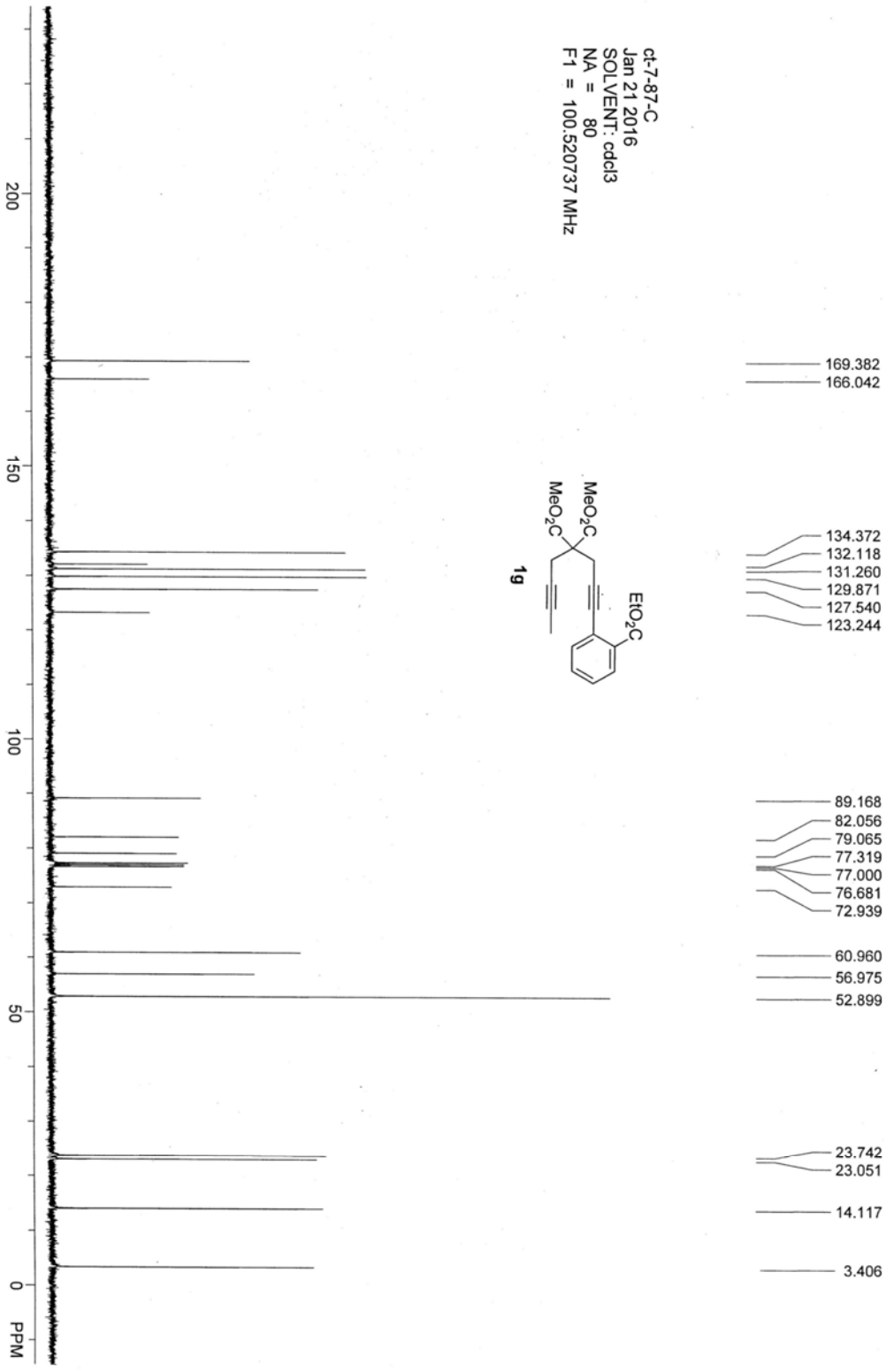

ct-6-151-H
Jan 22 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
MeO2C
MeO2C
MeO2C
nPr
1e
7.888
7.885
7.868
7.865
7.501
7.498
7.482
7.479
7.440
7.436
7.421
7.417
7.402
7.398
7.349
7.346
7.330
7.327
7.311
7.308
7.293
3.926
3.775
3.064
3.058
3.052
3.278
2.134
2.128
2.122
2.117
2.111
2.105
2.099
2.094
2.088
1.526
1.508
1.490
1.472
1.455
1.436
0.972
0.954
0.936
-0.000
0.94
1.00
0.98
2.95
5.92
2.00
2.02
2.02
2.02
3.00
PPM

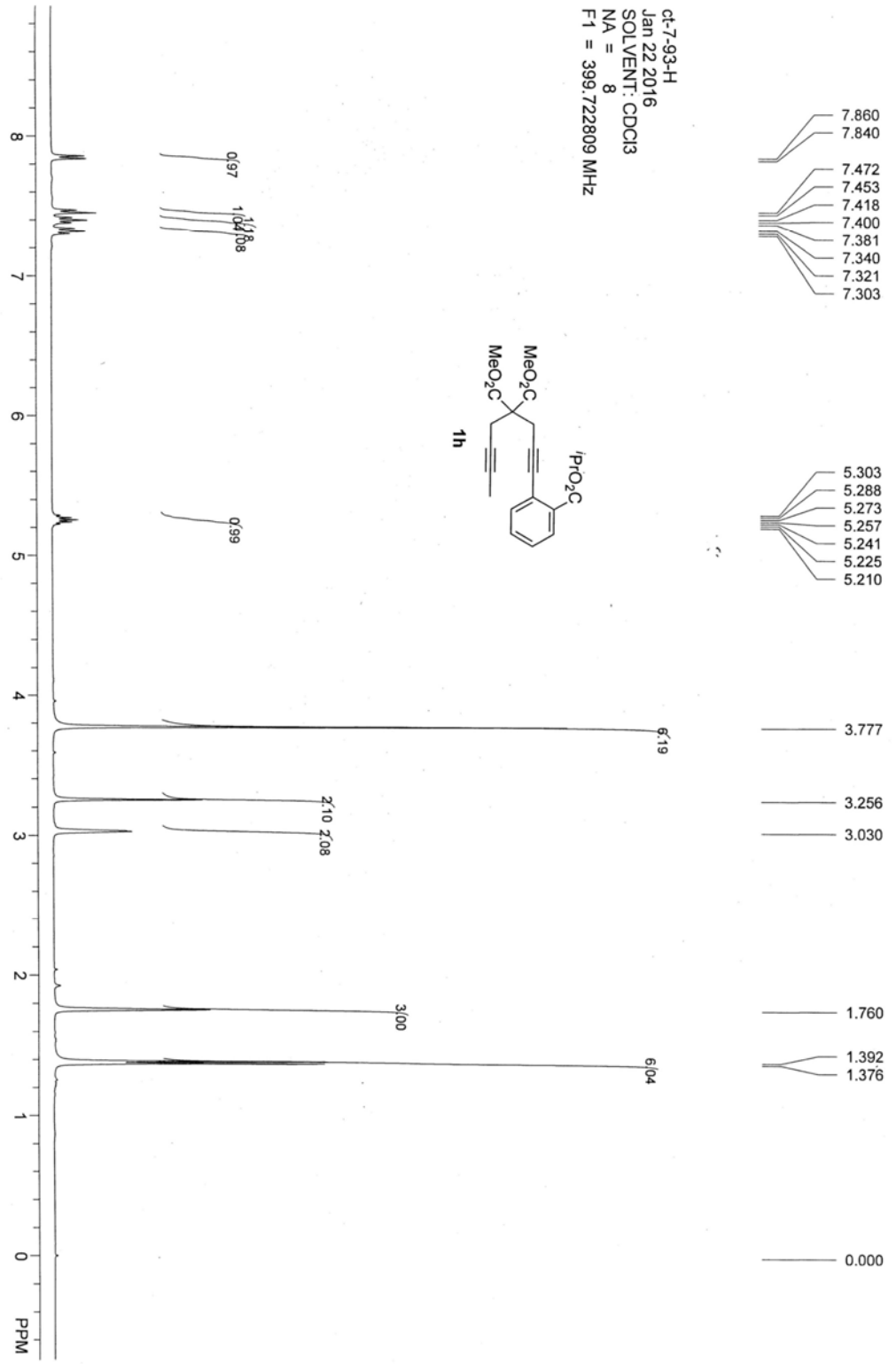

ct-6-151-C
Jan 22 2016
SOLVENT: cdcl3
NA = 48
F1 = 100.520737 MHz
MeO2C
MeO2C
MeO2C
nPr
1e
169.382
166.581
134.425
131.822
131.397
130.015
127.571
123.350
89.320
83.695
81.964
77.319
77.000
76.681
74.077
57.097
52.884
52.079
23.795
23.112
22.148
20.531
13.244
200
150
100
50
0
PPM

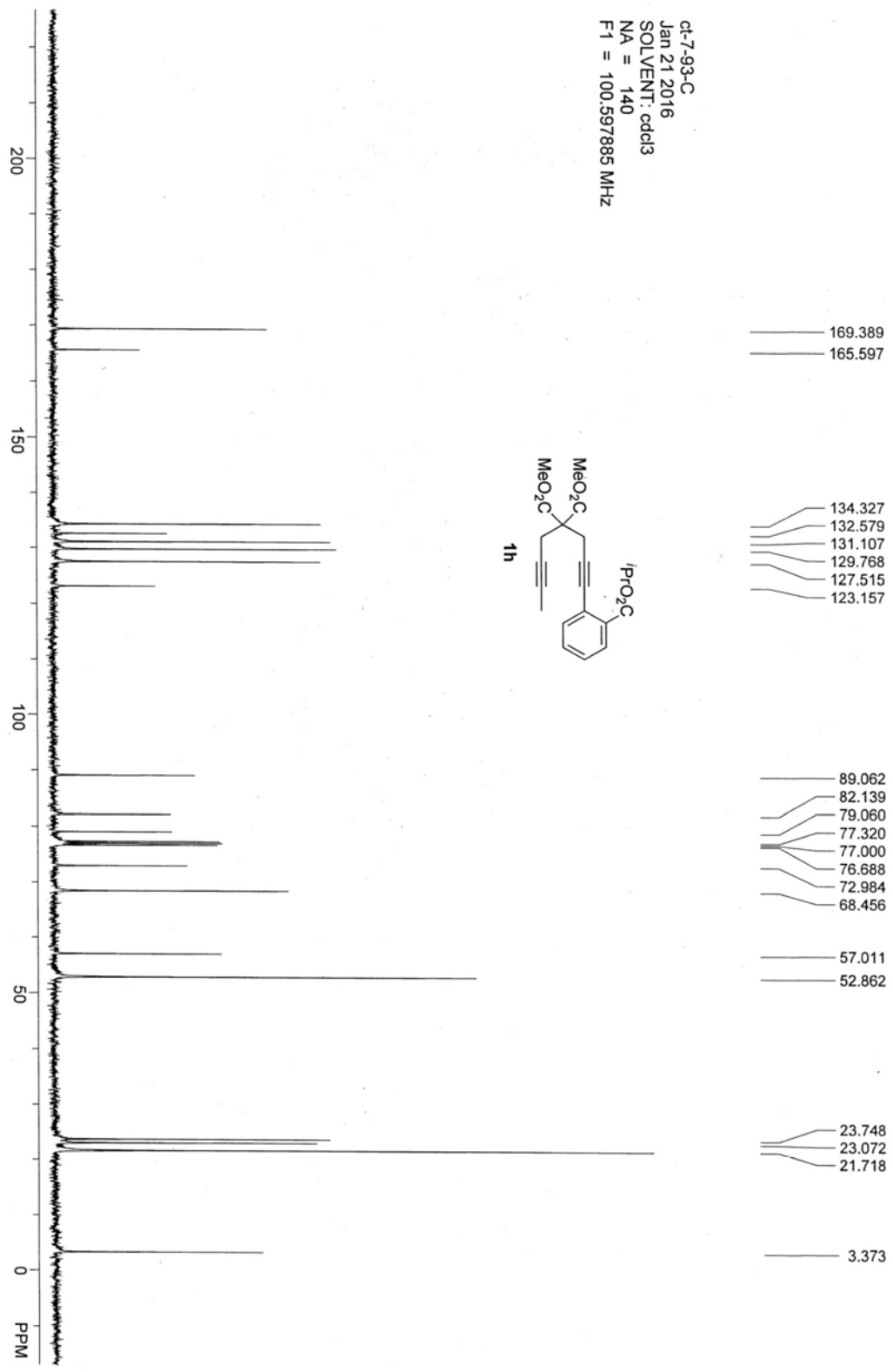

ct-6-169-H
Jan 19 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
1f
MeO2C
MeO2C
MeO2C
OAc
7.887
7.867
7.499
7.480
7.441
7.423
7.403
7.351
7.332
7.313
7.290
4.124
4.107
4.091
3.924
3.776
3.262
3.062
2.497
2.482
2.465
2.075
-0.000
0.95
1.04
1.00
1.01
2.03
2.97
6.06
2.03
2.04
2.05
2.03
3.00
8
6
4
2
0
PPM

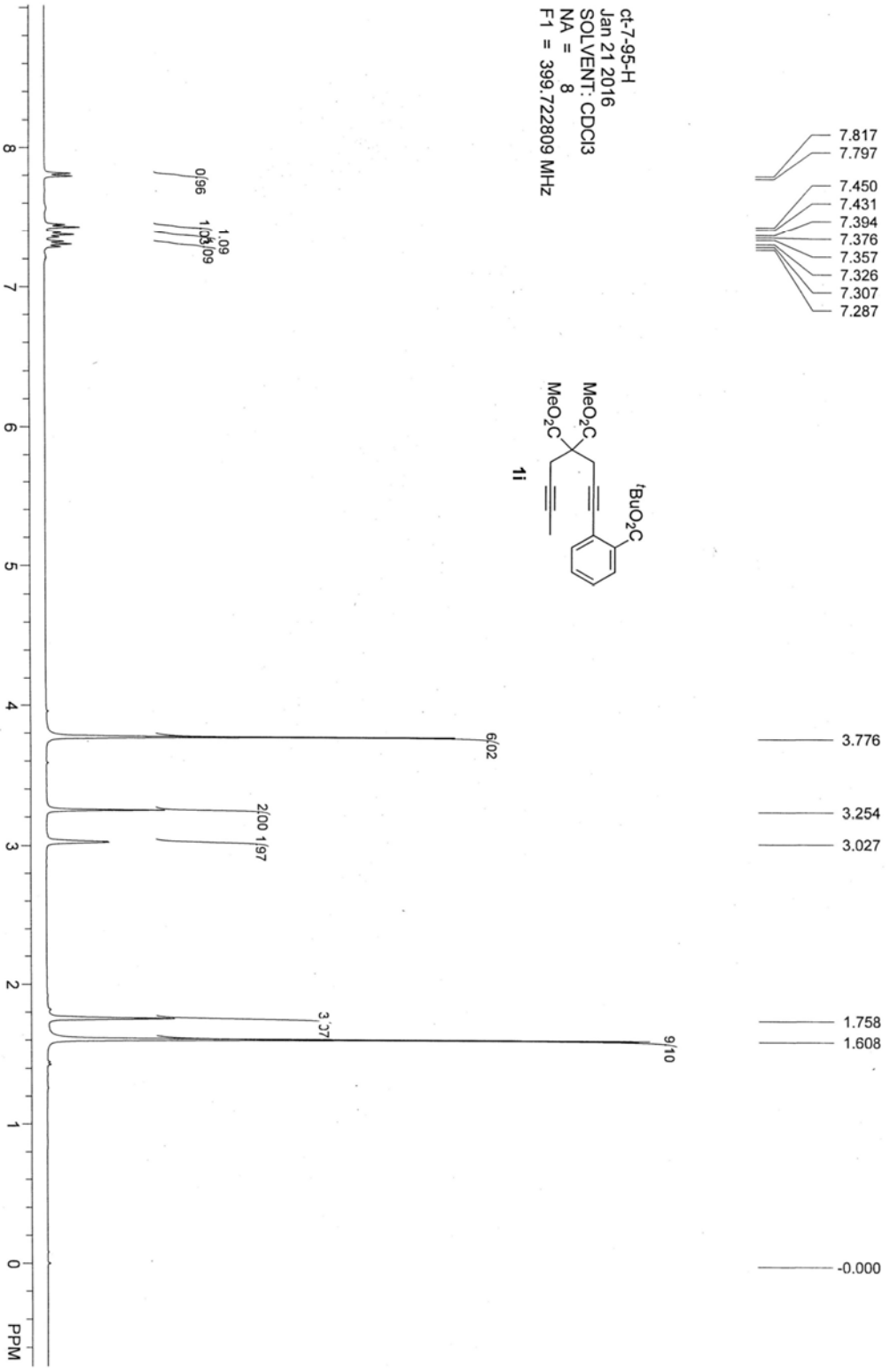

ct-6-169-C
Jan 19 2016
SOLVENT: cdcl3
NA = 240
F1 = 100.597885 MHz
MeO2C
MeO2C
MeO2C
OAc
1f
170.750
169.226
166.526
134.423
131.858
131.419
130.036
127.619
123.321
89.158
82.072
79.305
77.312
77.000
76.680
75.937
62.395
56.959
52.951
52.088
23.800
23.027
20.737
19.078
200
150
100
50
0
PPM

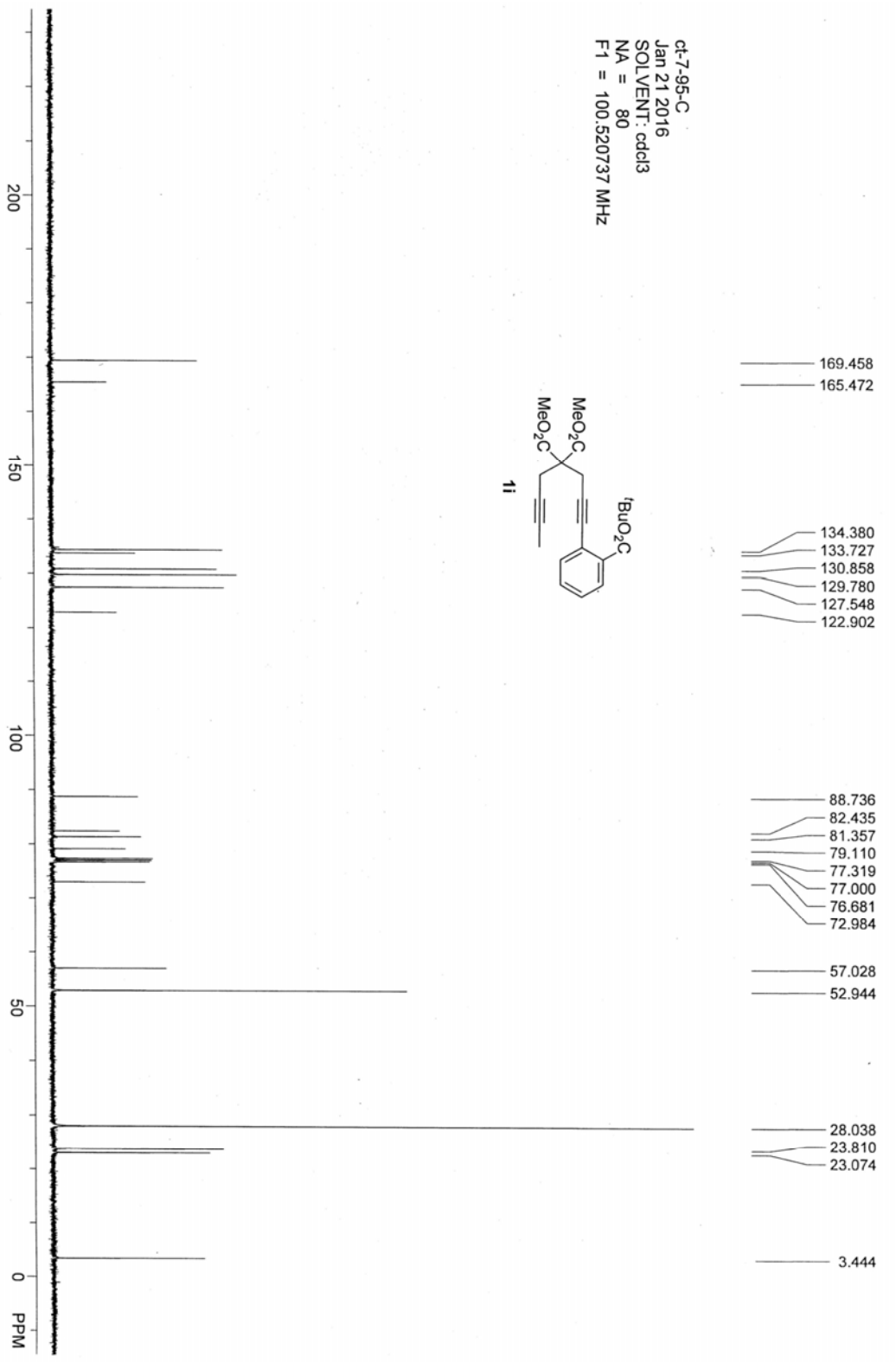

ct-7-87-H
Jan 21 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
MeO2C
MeO2C
EtO2C
1g
7.886
7.866
7.488
7.469
7.431
7.413
7.394
7.347
7.328
7.310
7.300
4.415
4.397
4.380
4.362
3.777
3.264
3.032
1.763
1.422
1.404
1.386
-0.000
0.95
1.10
0.99
1.06
2.03
6.11
2.07
2.08
2.95
3.00
8
6
4
2
0
PPM

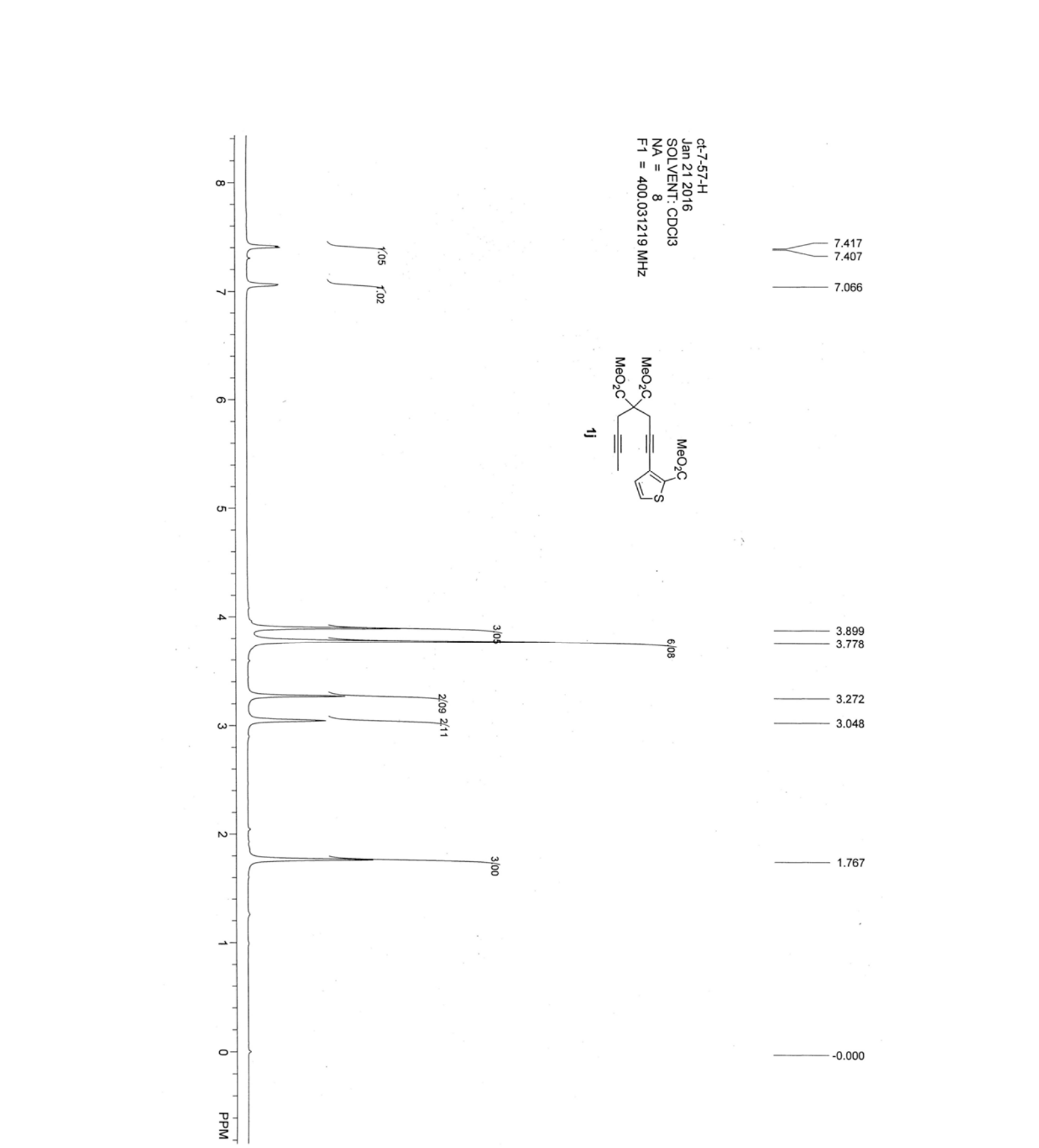

ct-7-87-C
Jan 21 2016
SOLVENT: cdcl3
NA = 80
F1 = 100.520737 MHz
MeO2C
MeO2C
EtO2C
1g
169.382
166.042
134.372
132.118
131.260
129.871
127.540
123.244
89.168
82.056
79.065
77.319
77.000
76.681
72.939
60.960
56.975
52.899
23.742
23.051
14.117
3.406
200
150
100
50
0
PPM

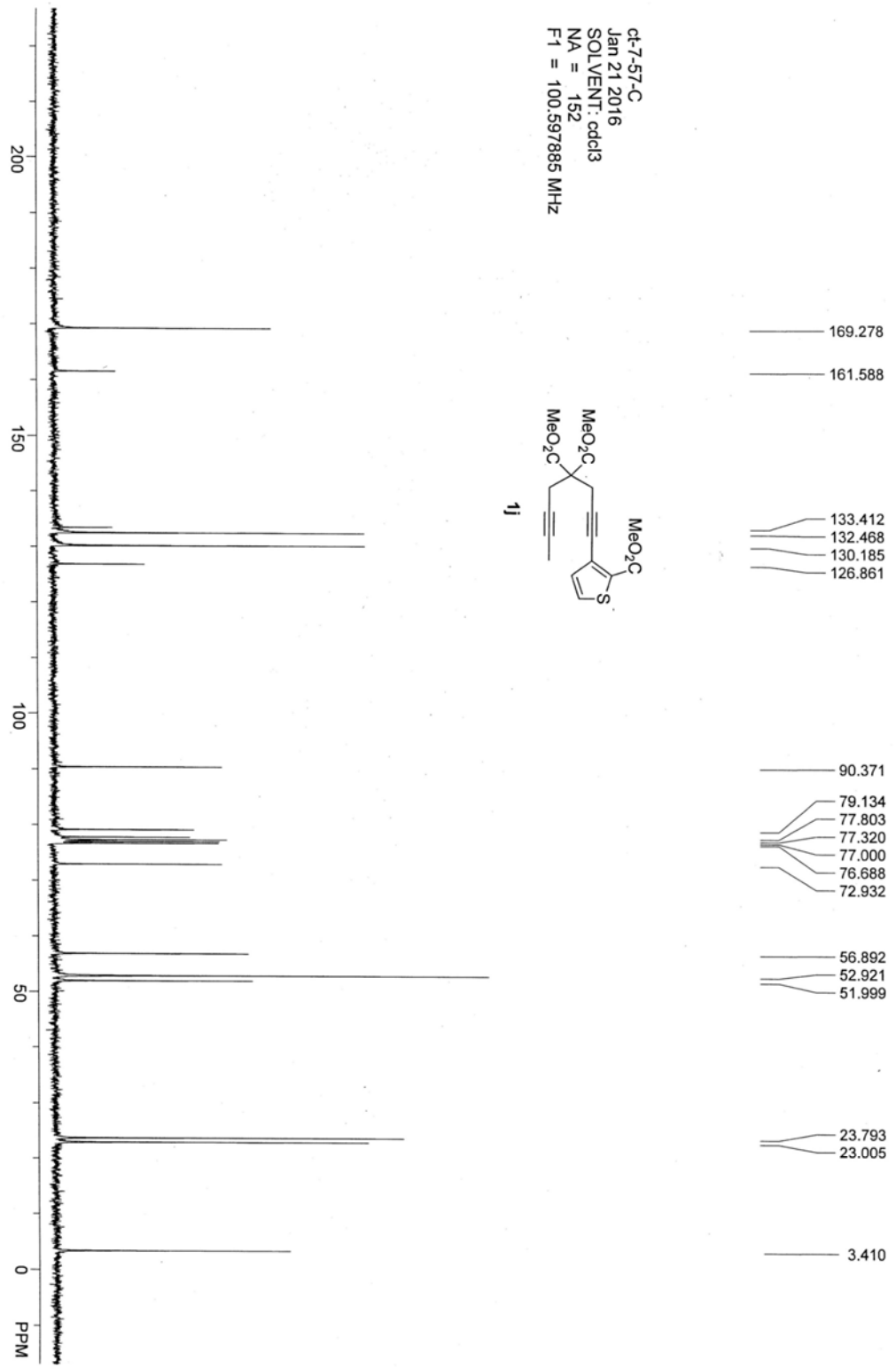

ct-7-93-H
Jan 22 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
1h
MeO2C
MeO2C
iPrO2C
7.860
7.840
7.472
7.453
7.418
7.400
7.381
7.340
7.321
7.303
5.303
5.288
5.273
5.257
5.241
5.225
5.210
3.777
3.256
3.030
1.760
1.392
1.376
0.000
0.97
1.04
1.08
0.99
6.19
2.10
2.08
3.00
6.04
PPM

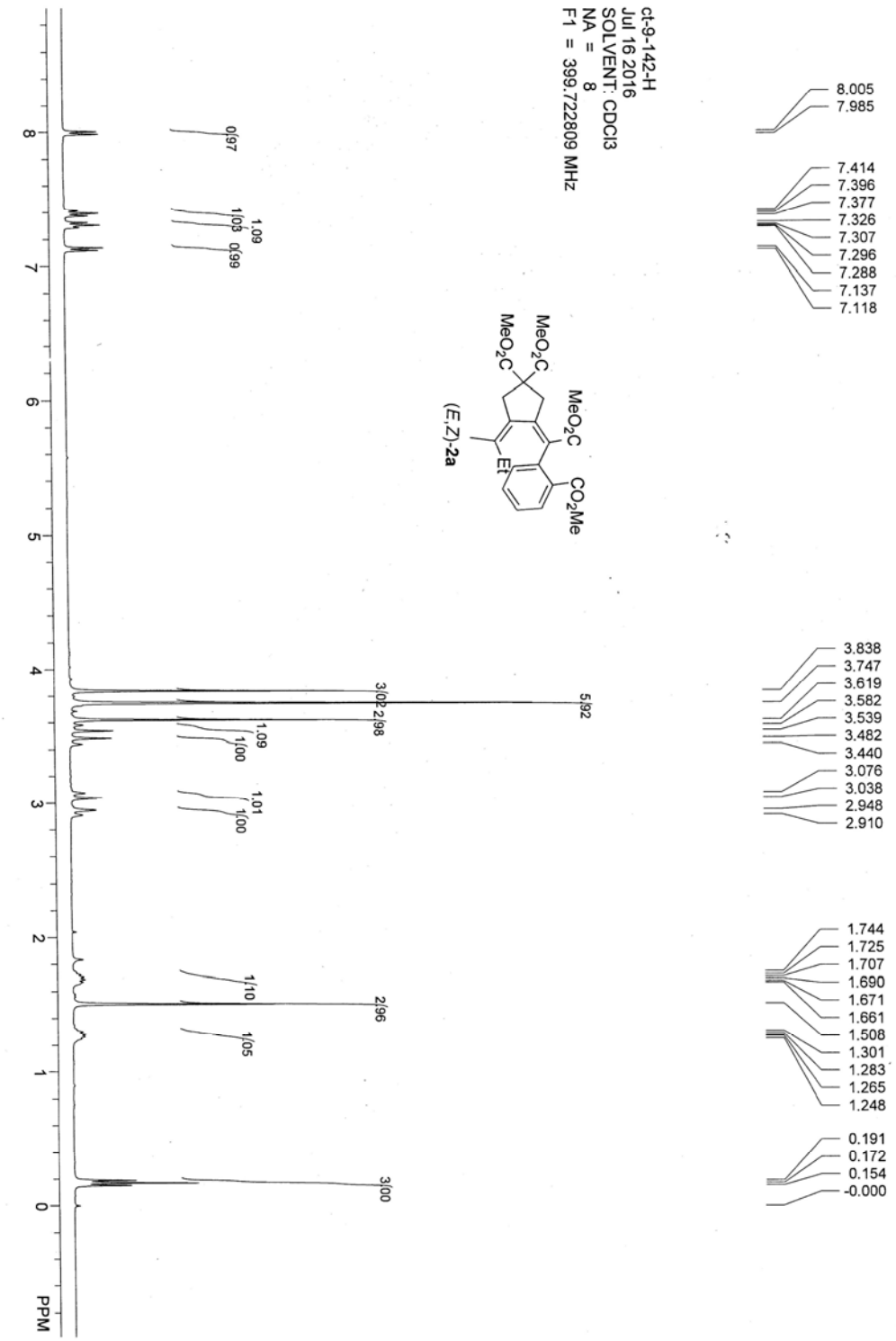

ct-7-93-C
Jan 21 2016
SOLVENT: cdcl3
NA = 140
F1 = 100.597885 MHz
MeO2C
MeO2C
iPrO2C
1h
169.389
165.597
134.327
132.579
131.107
129.768
127.515
123.157
89.062
82.139
79.060
77.320
77.000
76.688
72.984
68.456
57.011
52.862
23.748
23.072
21.718
3.373
200
150
100
50
0
PPM

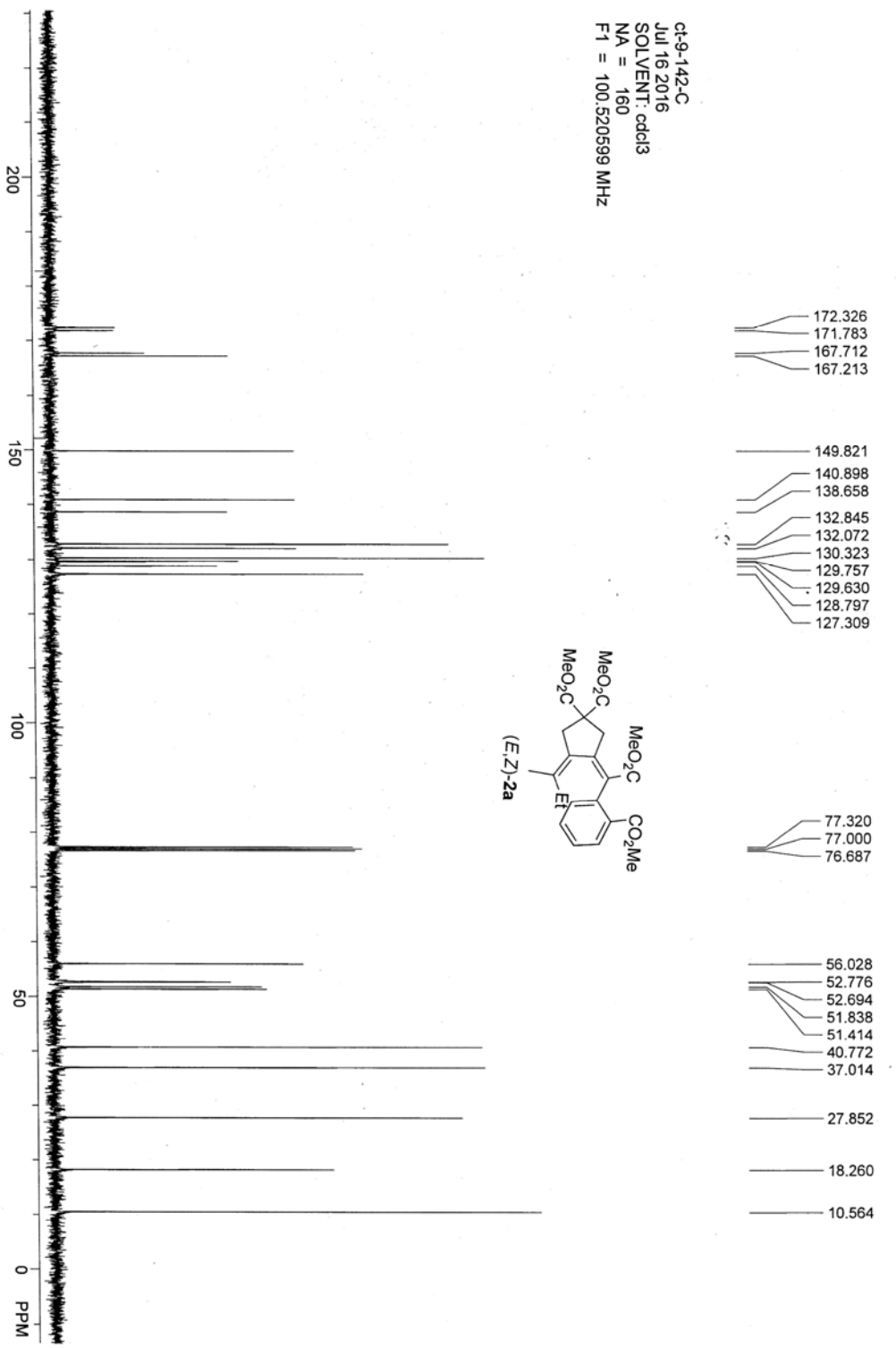

ct-7-95-H
Jan 21 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
MeO2C
MeO2C
tBuO2C
1i
7.817
7.797
7.450
7.431
7.394
7.376
7.357
7.326
7.307
7.287
3.776
3.254
3.027
1.758
1.608
-0.000
0.96
1.09
1.09
6.02
2.00
1.97
3.37
9.10
PPM

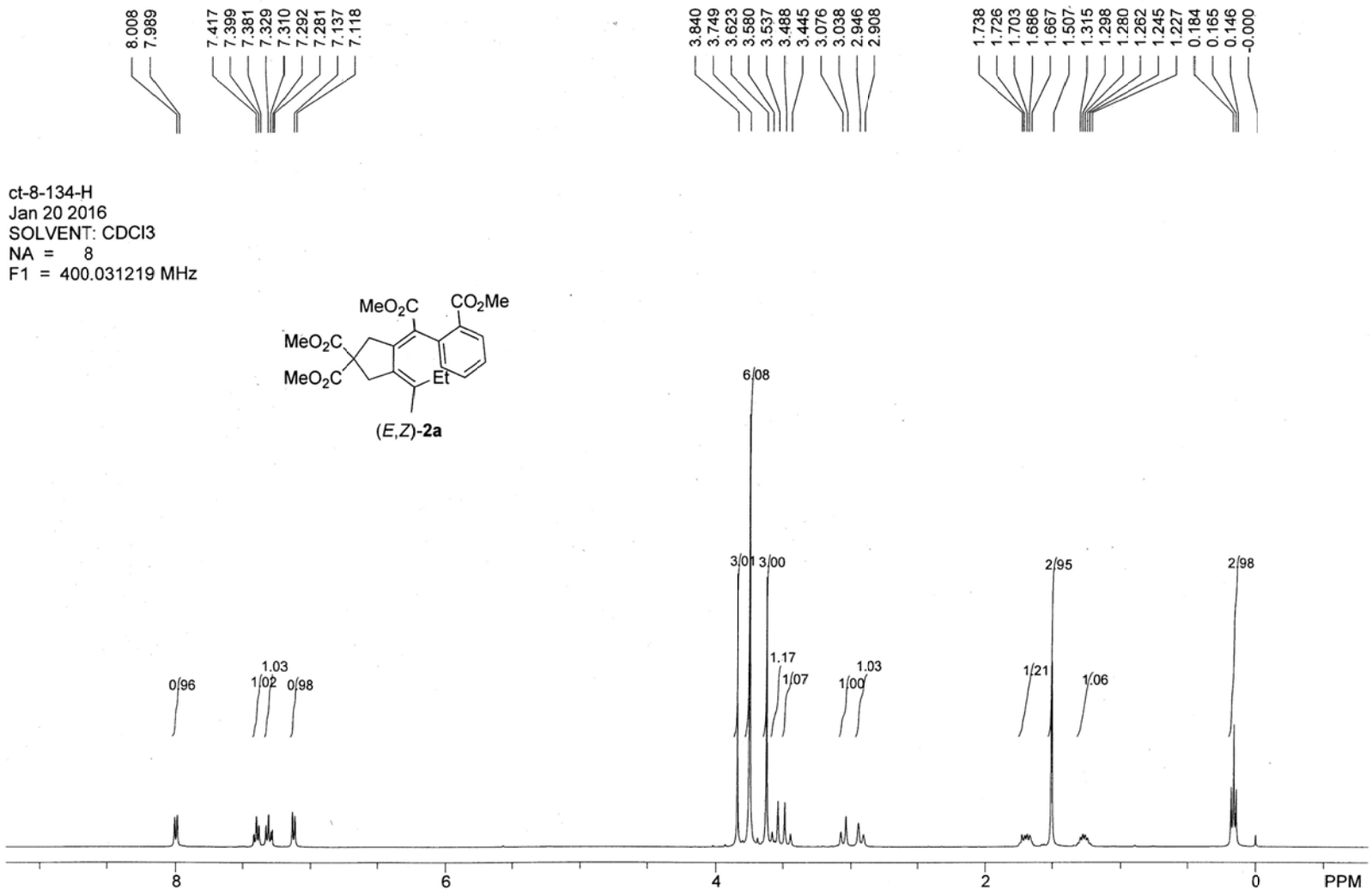

ct-7-95-C
Jan 21 2016
SOLVENT: cdcl3
NA = 80
F1 = 100.520737 MHz
MeO2C
MeO2C
tBuO2C
1i
169.458
165.472
134.380
133.727
130.858
129.780
127.548
122.902
88.736
82.435
81.357
79.110
77.319
77.000
76.681
72.984
57.028
52.944
28.038
23.810
23.074
3.444
200
150
100
50
0
PPM

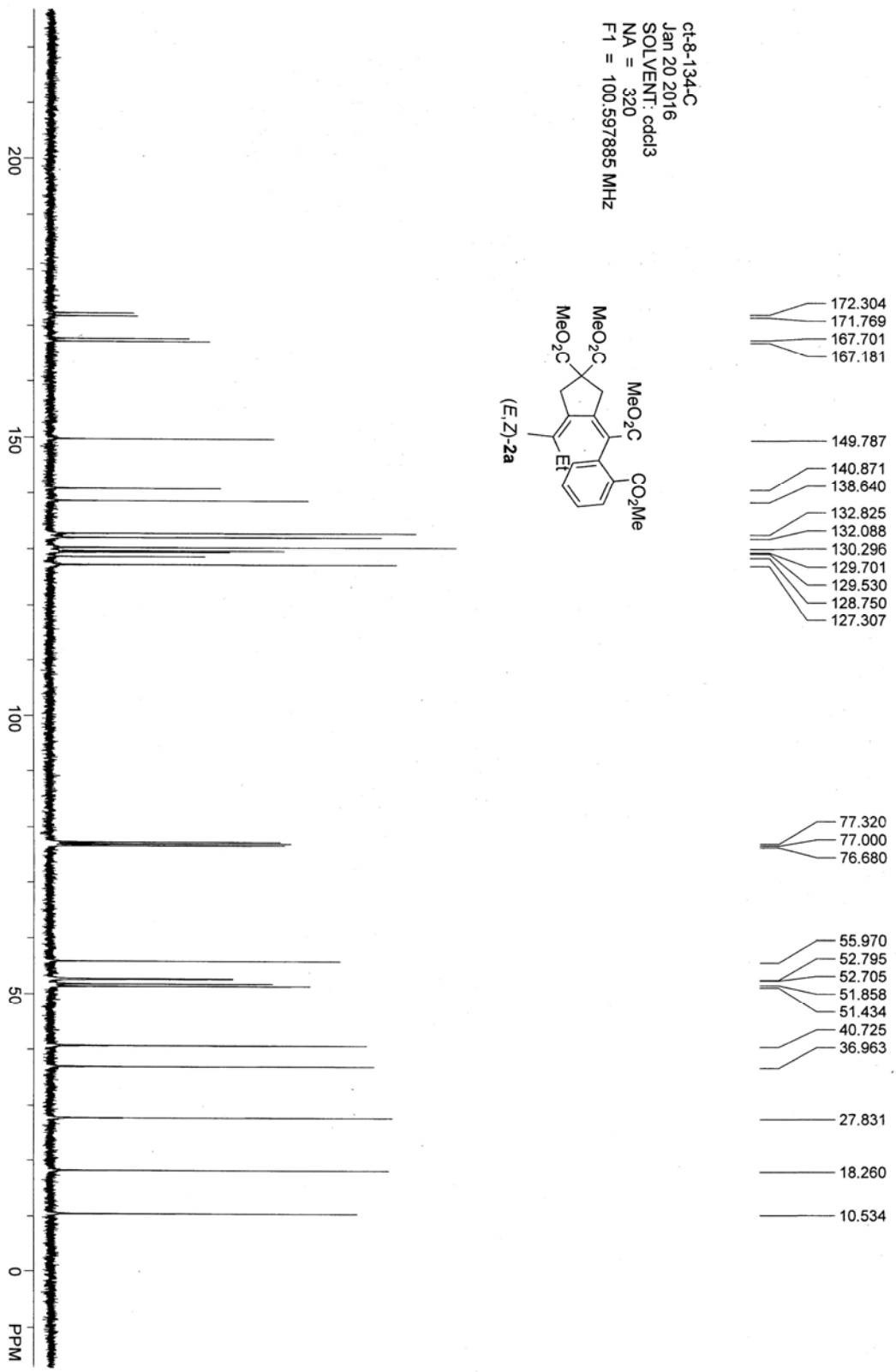

ct-7-57-H
Jan 21 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031219 MHz
MeO2C
MeO2C
MeO2C
S
1j
7.417
7.407
7.066
3.899
3.778
3.272
3.048
1.767
-0.000
1.05
1.02
3.05
6.08
2.09
2.11
3.00
PPM

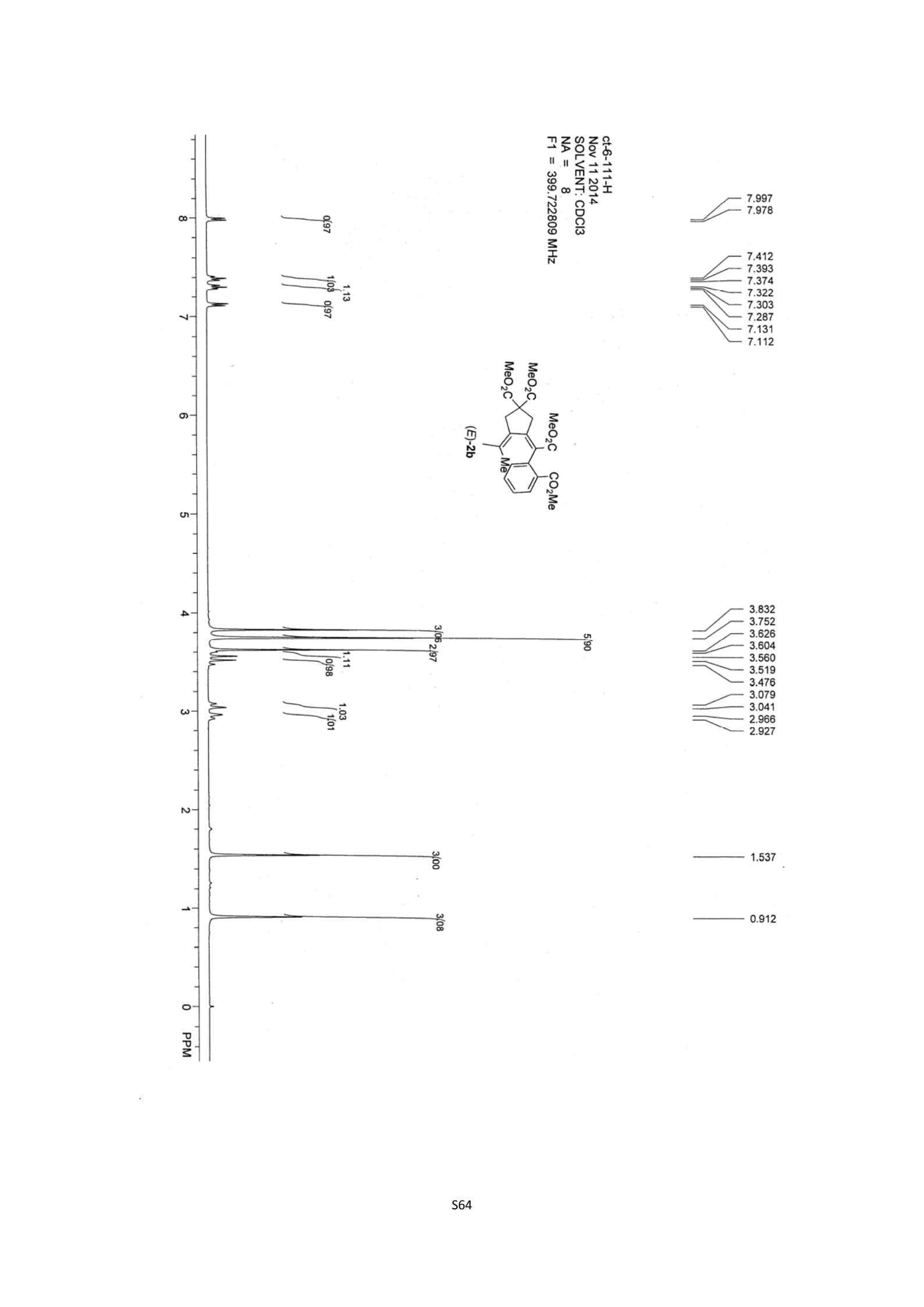

ct-7-57-C
Jan 21 2016
SOLVENT: cdcl3
NA = 152
F1 = 100.597885 MHz
1j
MeO2C
MeO2C
MeO2C
S
169.278
161.588
133.412
132.468
130.185
126.861
90.371
79.134
77.803
77.320
77.000
76.688
72.932
56.892
52.921
51.999
23.793
23.005
3.410
200
150
100
50
0
PPM

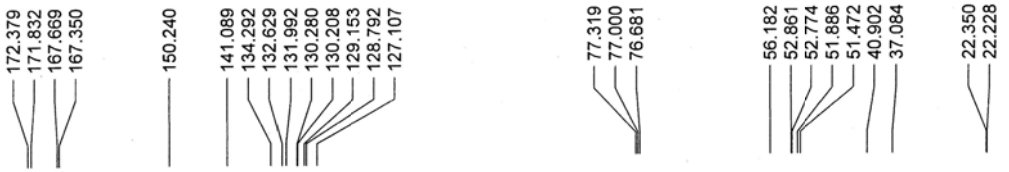

ct-9-142-H
Jul 16 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E,Z)-2a
MeO2C
MeO2C
MeO2C
CO2Me
Et
8.005
7.985
7.414
7.396
7.377
7.326
7.307
7.296
7.288
7.137
7.118
3.838
3.747
3.619
3.582
3.539
3.482
3.440
3.076
3.038
2.948
2.910
1.744
1.725
1.707
1.690
1.671
1.661
1.508
1.301
1.283
1.265
1.248
0.191
0.172
0.154
-0.000
0.97
1.03
0.99
1.09
3.02
2.98
1.09
1.00
1.01
1.00
1.10
1.05
2.96
5.92
3.00
PPM


ct-9-142-C
Jul 16 2016
SOLVENT: cdcl3
NA = 160
F1 = 100.520599 MHz
200
150
100
50
0
PPM
172.326
171.783
167.712
167.213
149.821
140.898
138.658
132.845
132.072
130.323
129.757
129.630
128.797
127.309
77.320
77.000
76.687
56.028
52.776
52.694
51.838
51.414
40.772
37.014
27.852
18.260
10.564
MeO2C
MeO2C
MeO2C
CO2Me
Et
(E,Z)-2a

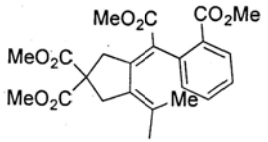

8.008
7.989
7.417
7.399
7.381
7.329
7.310
7.292
7.281
7.137
7.118
3.840
3.749
3.623
3.580
3.537
3.488
3.445
3.076
3.038
2.946
2.908
1.738
1.726
1.703
1.686
1.667
1.507
1.315
1.298
1.280
1.262
1.245
1.227
0.184
0.165
0.146
-0.000
ct-8-134-H
Jan 20 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031219 MHz
MeO2C
CO2Me
MeO2C
MeO2C
Et
(E,Z)-2a
6.08
3.01
3.00
2.95
2.98
1.17
1.03
1.03
0.96
1.02
0.98
1.07
1.00
1.21
1.06
8
6
4
2
0
PPM


ct-8-134-C
Jan 20 2016
SOLVENT: cdcl3
NA = 320
F1 = 100.597885 MHz
MeO2C
MeO2C
MeO2C
CO2Me
Et
(E,Z)-2a
172.304
171.769
167.701
167.181
149.787
140.871
138.640
132.825
132.088
130.296
129.701
129.530
128.750
127.307
77.320
77.000
76.680
55.970
52.795
52.705
51.858
51.434
40.725
36.963
27.831
18.260
10.534
200
150
100
50
0
PPM

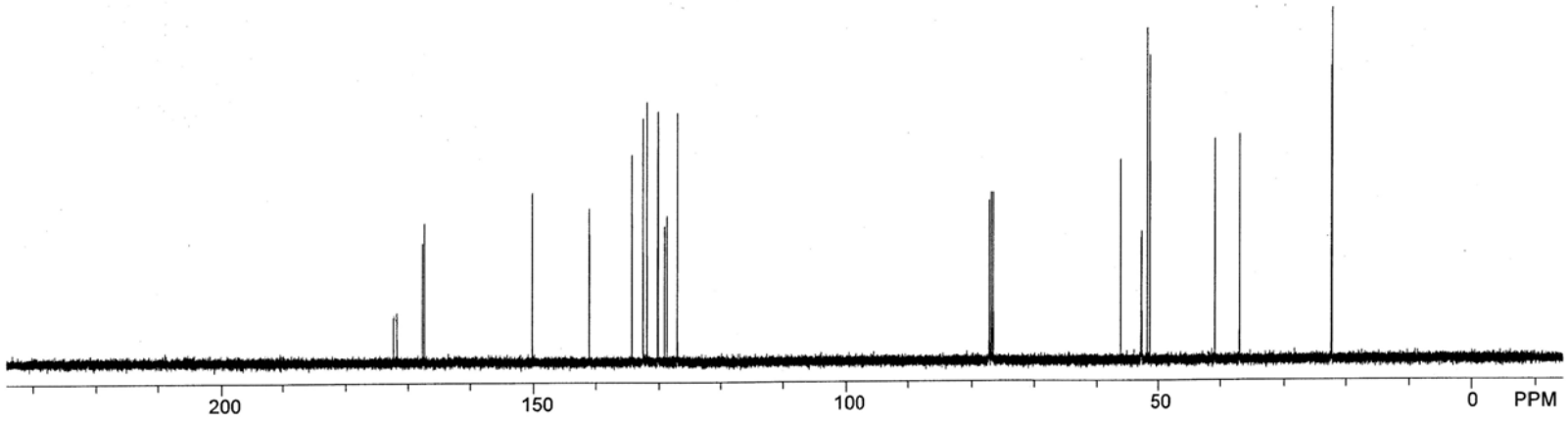

ct-6-111-H
Nov 11 2014
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E)-2b
MeO2C
MeO2C
MeO2C
CO2Me
Me
7.997
7.978
7.412
7.393
7.374
7.322
7.303
7.287
7.131
7.112
3.832
3.752
3.626
3.604
3.560
3.519
3.476
3.079
3.041
2.966
2.927
1.537
0.912
0.97
1.03
1.13
0.97
5.90
3.06
2.97
0.98
1.11
1.03
1.01
3.00
3.08
PPM

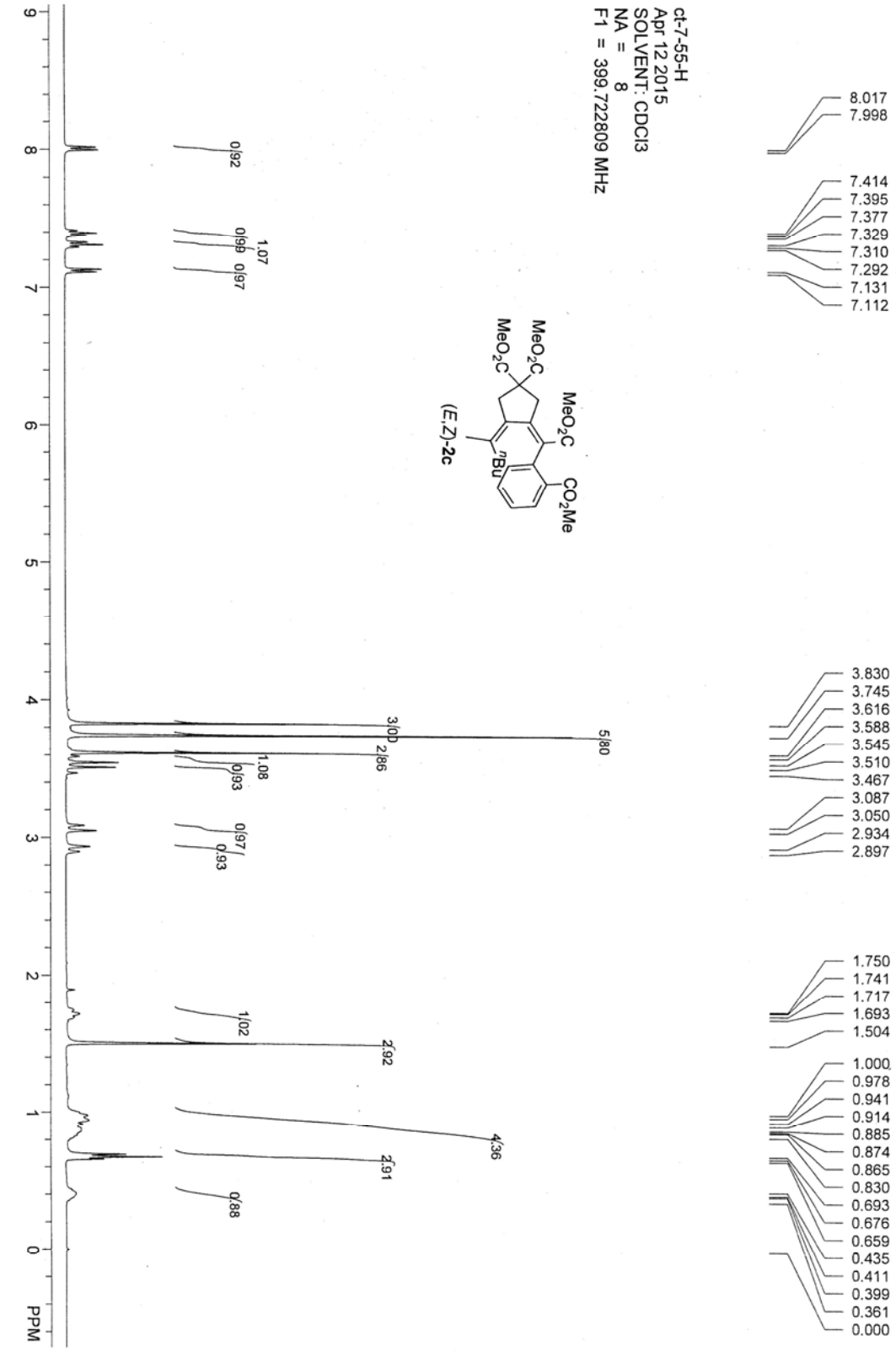


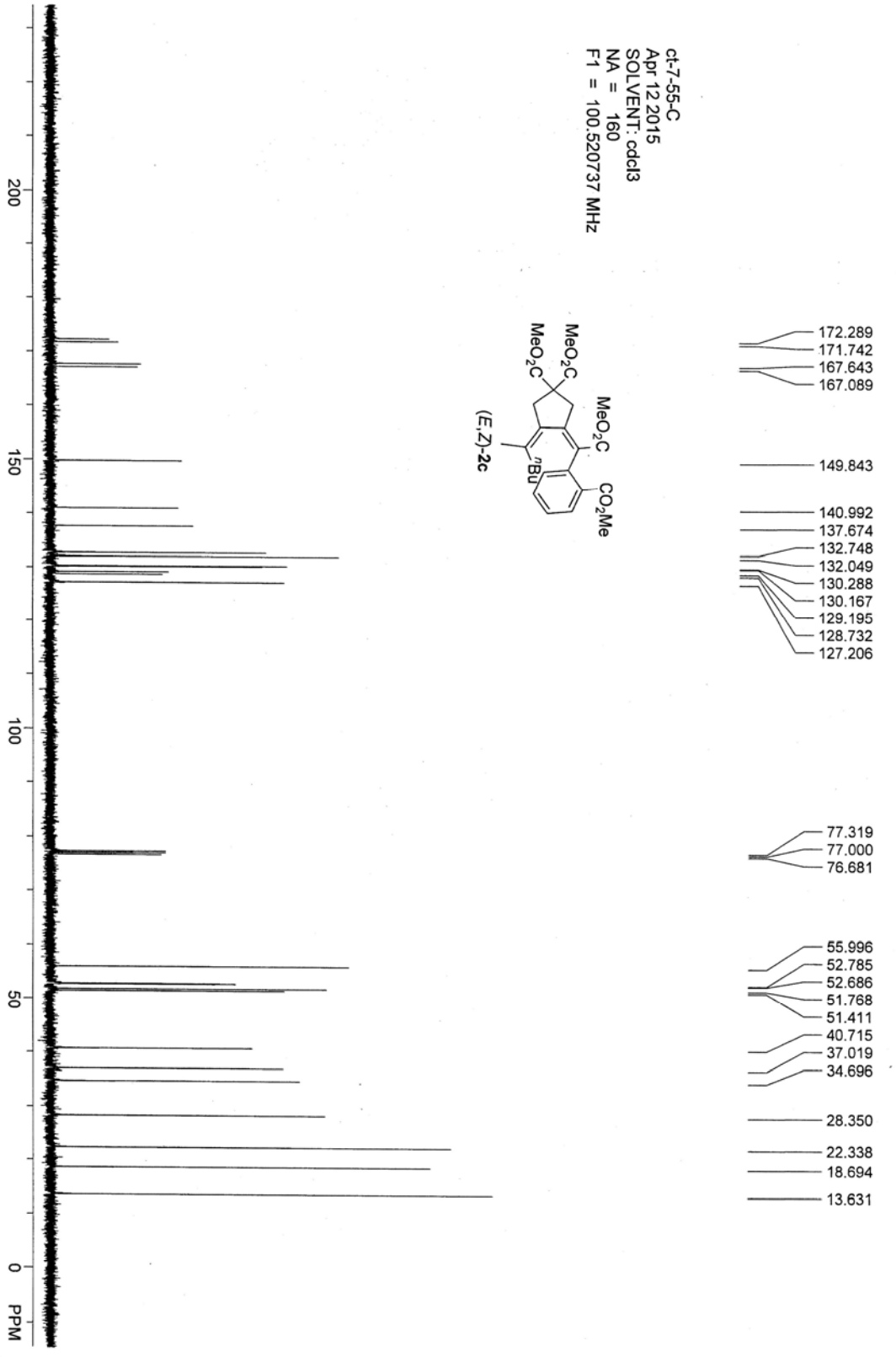
ct-6-111-C
Nov 11 2014
SOLVENT: cdcl3
NA = 240
F1 = 100.520737 MHz

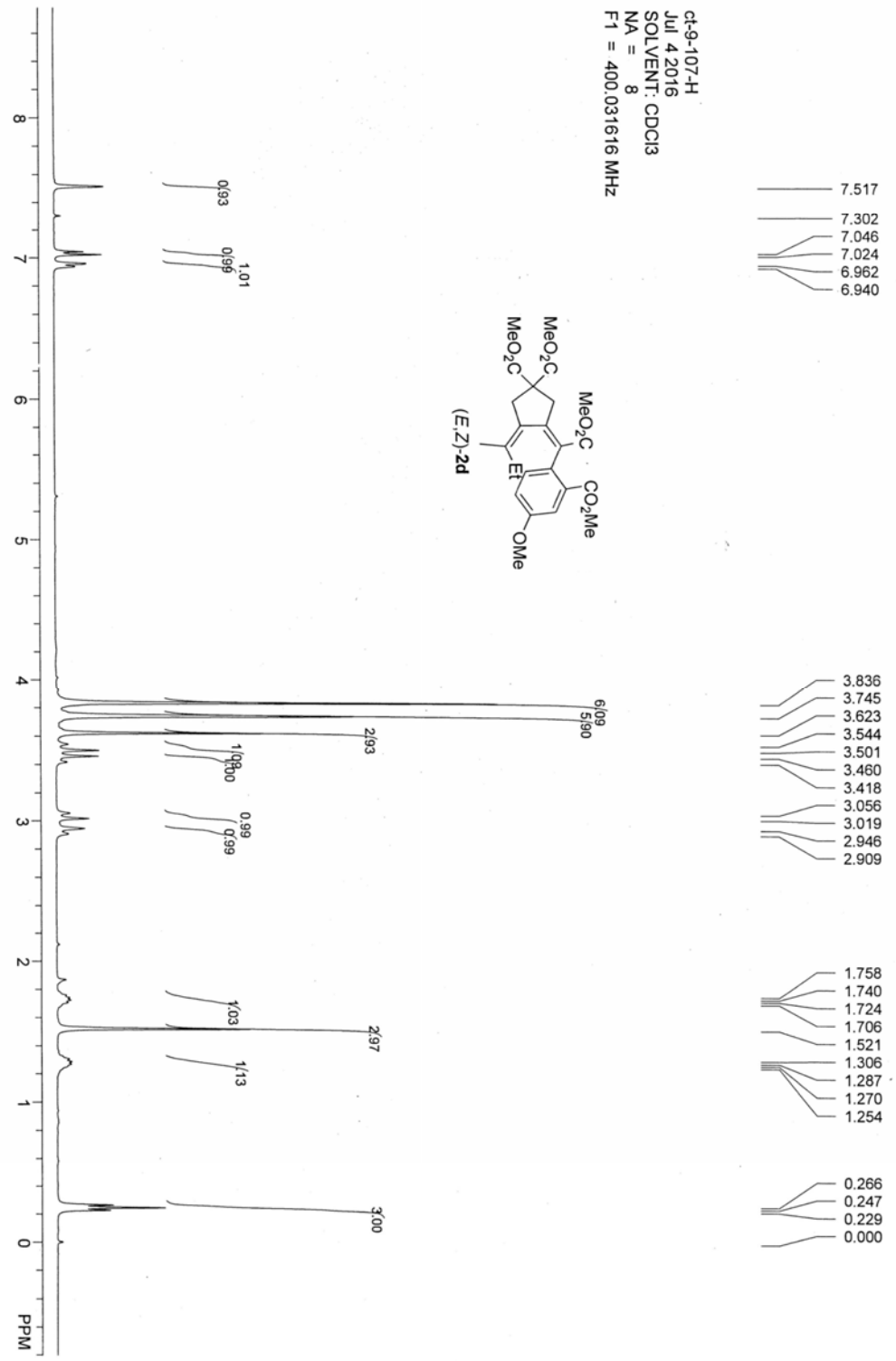


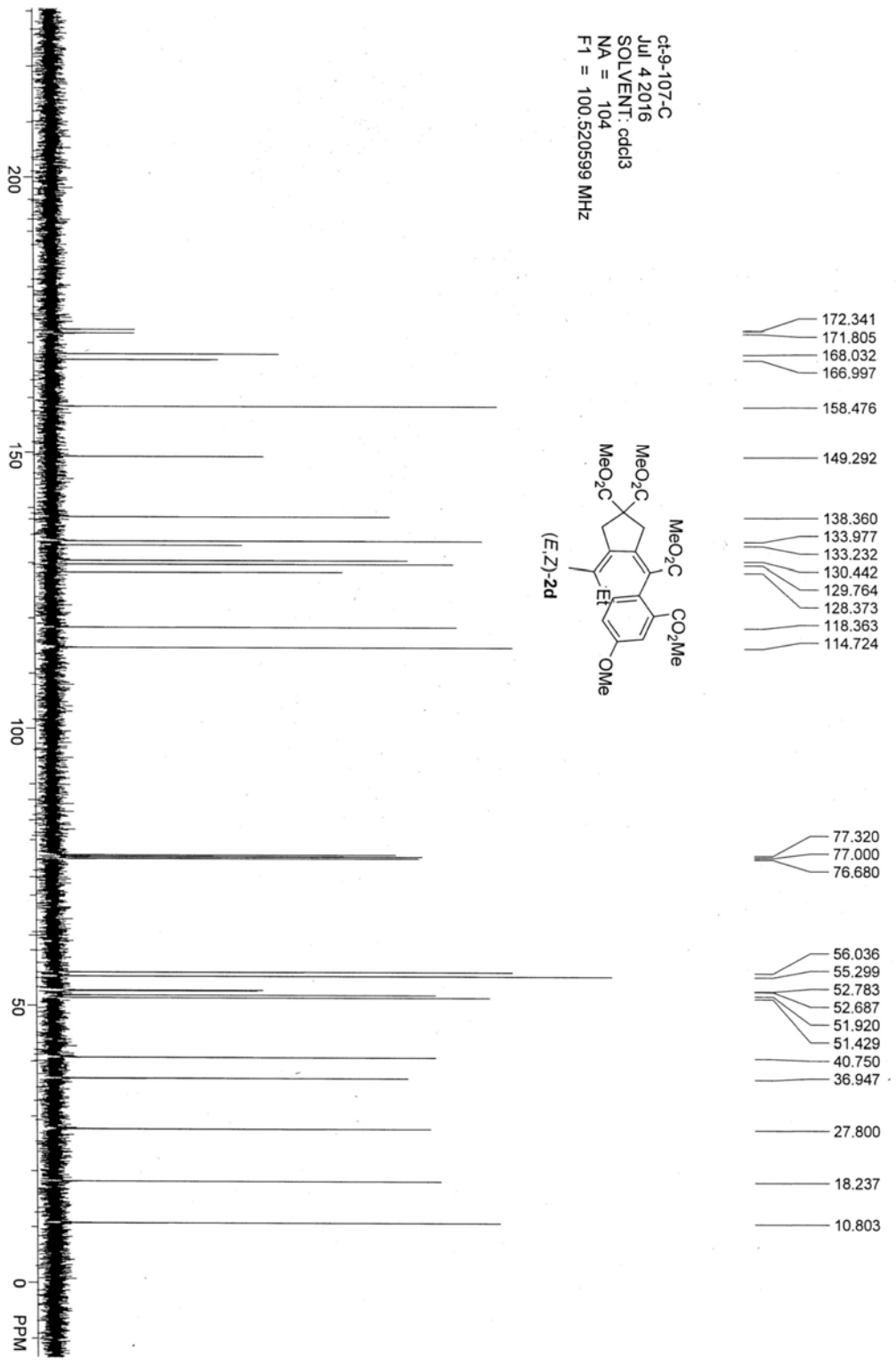
(*E*)-**2b**

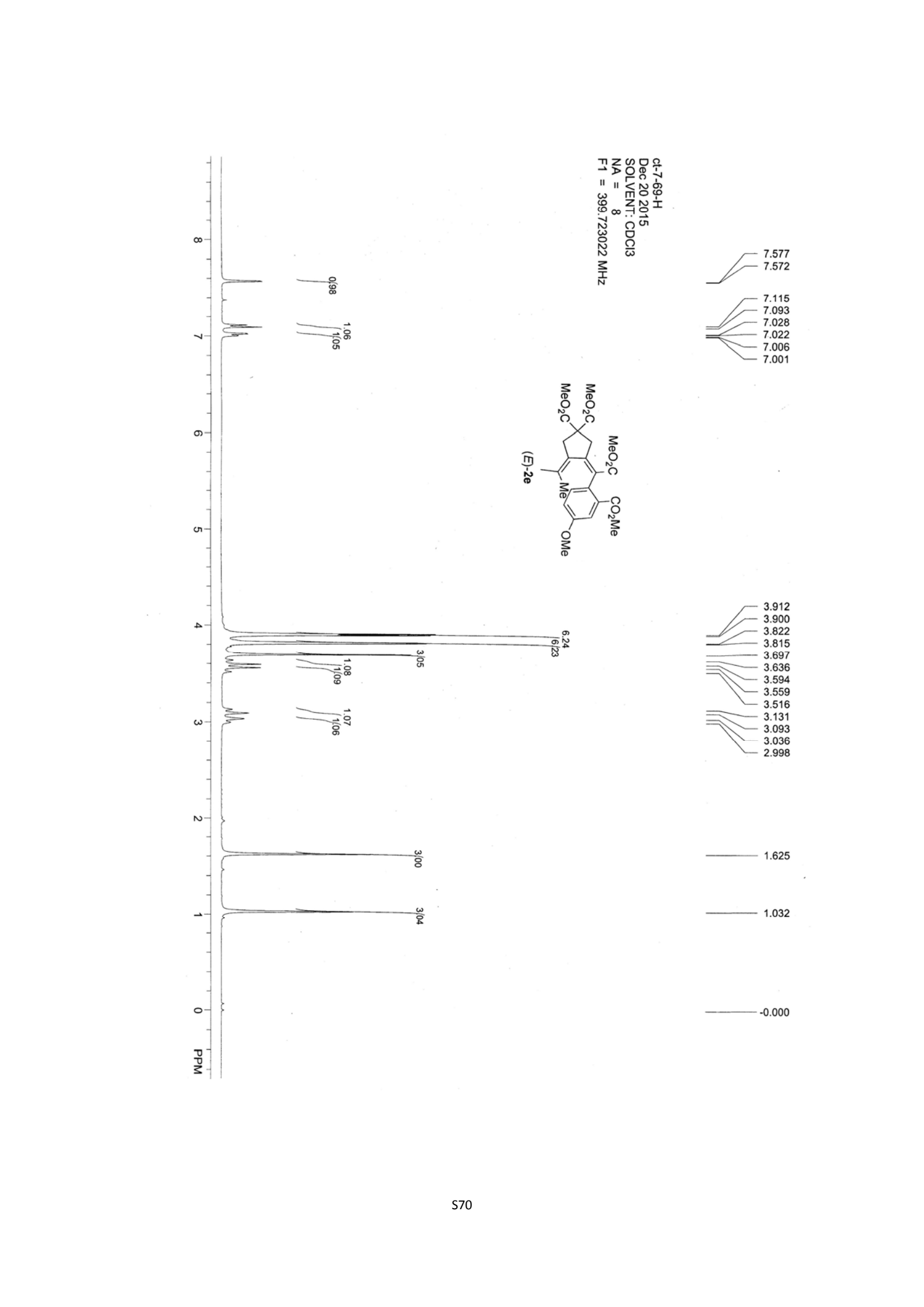


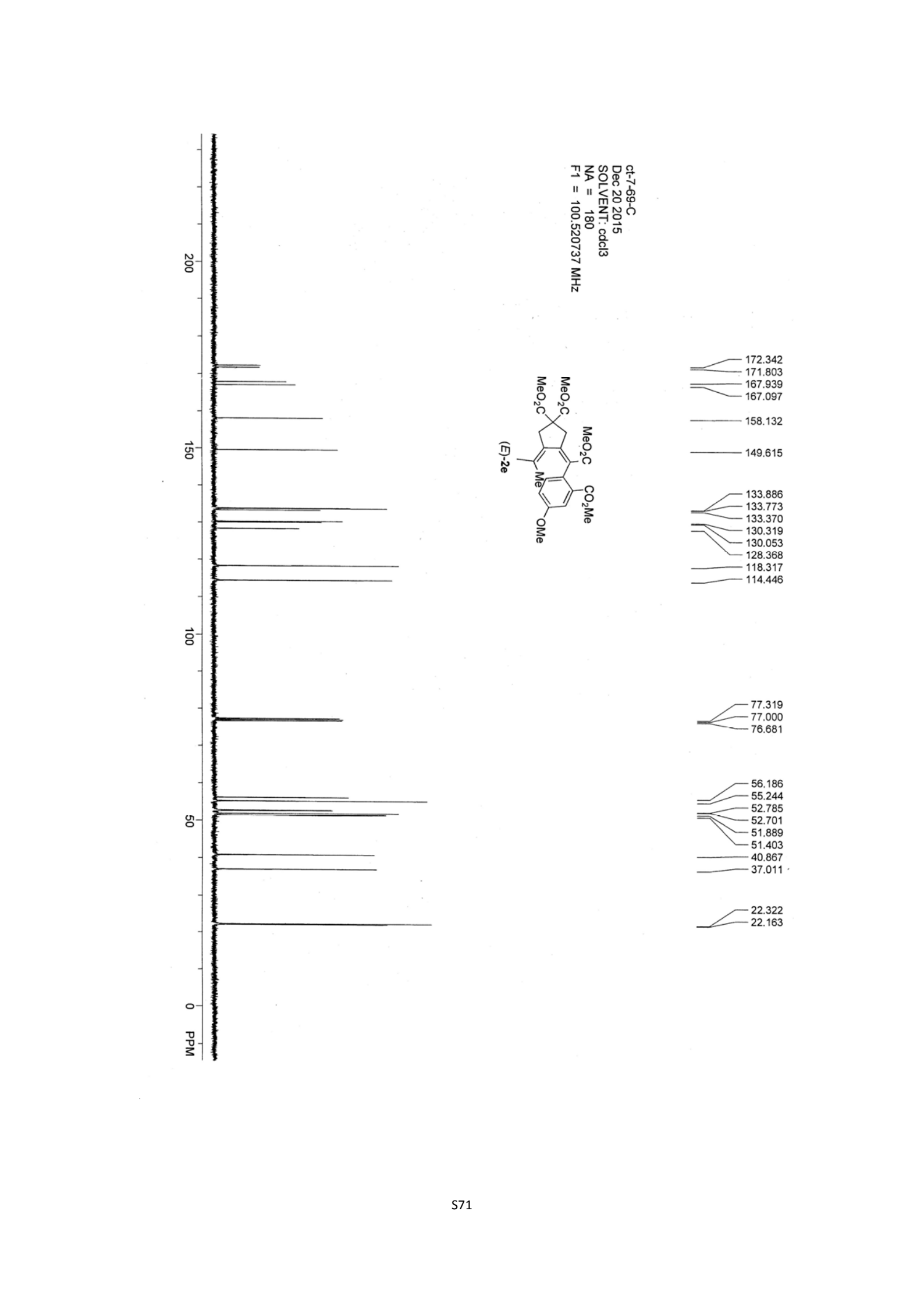

ct-7-55-H
Apr 12 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
MeO2C
MeO2C
MeO2C
CO2Me
nBu
(E,Z)-2c
8.017
7.998
7.414
7.395
7.377
7.329
7.310
7.292
7.131
7.112
3.830
3.745
3.616
3.588
3.545
3.510
3.467
3.087
3.050
2.934
2.897
1.750
1.741
1.717
1.693
1.504
1.000
0.978
0.941
0.914
0.885
0.874
0.865
0.830
0.693
0.676
0.659
0.435
0.411
0.399
0.361
0.000
0.92
1.07
0.99
0.97
3.00
2.86
5.80
1.08
0.93
0.97
0.93
1.02
2.92
4.36
2.91
0.88
9
8
7
6
5
4
3
2
1
0
PPM

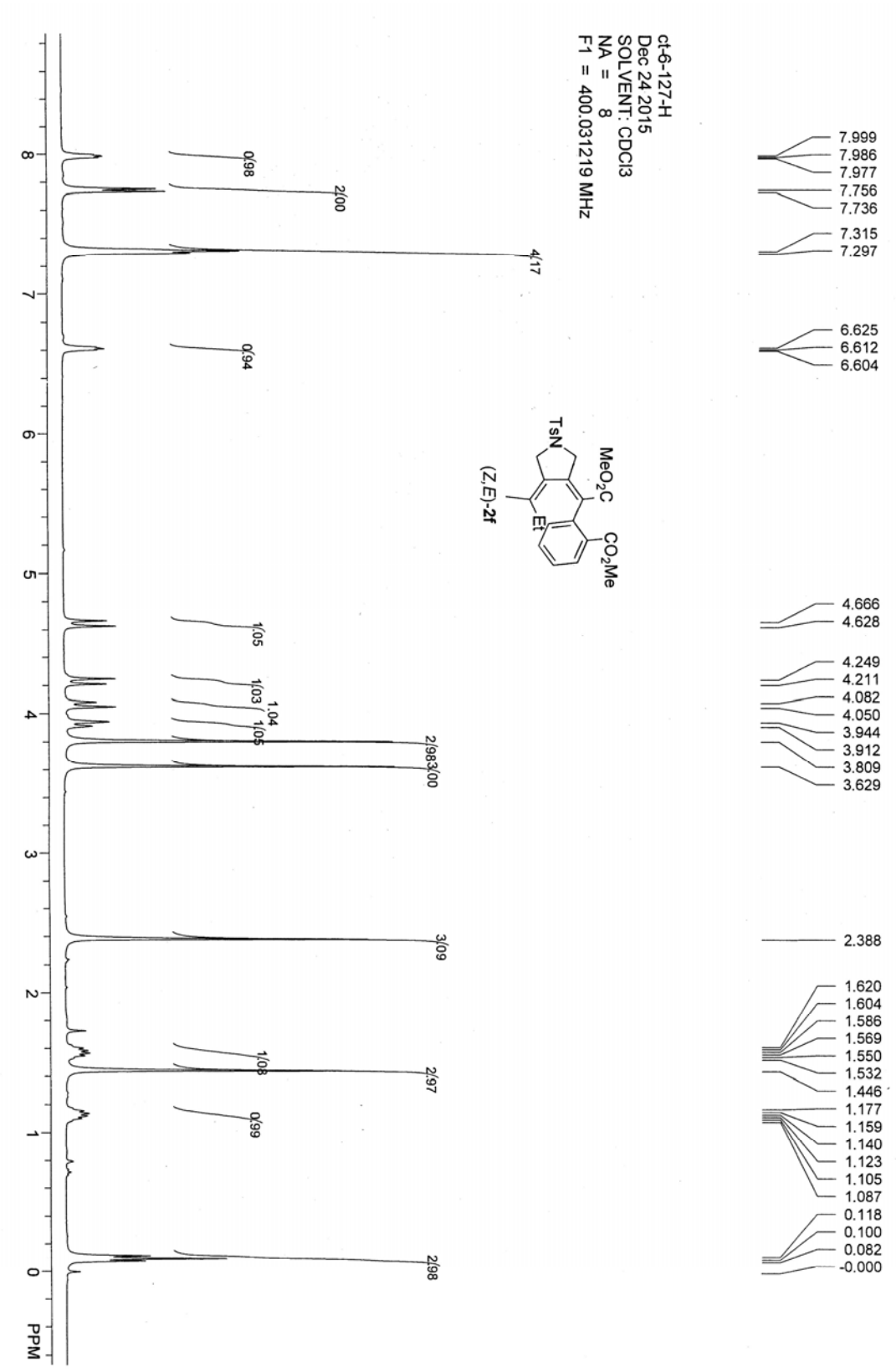

ct-7-55-C
Apr 12 2015
SOLVENT: cdcl3
NA = 160
F1 = 100.520737 MHz
MeO2C
MeO2C
MeO2C
nBu
CO2Me
(E,Z)-2c
172.289
171.742
167.643
167.089
149.843
140.992
137.674
132.748
132.049
130.288
130.167
129.195
128.732
127.206
77.319
77.000
76.681
55.996
52.785
52.686
51.768
51.411
40.715
37.019
34.696
28.350
22.338
18.694
13.631
200
150
100
50
0
PPM

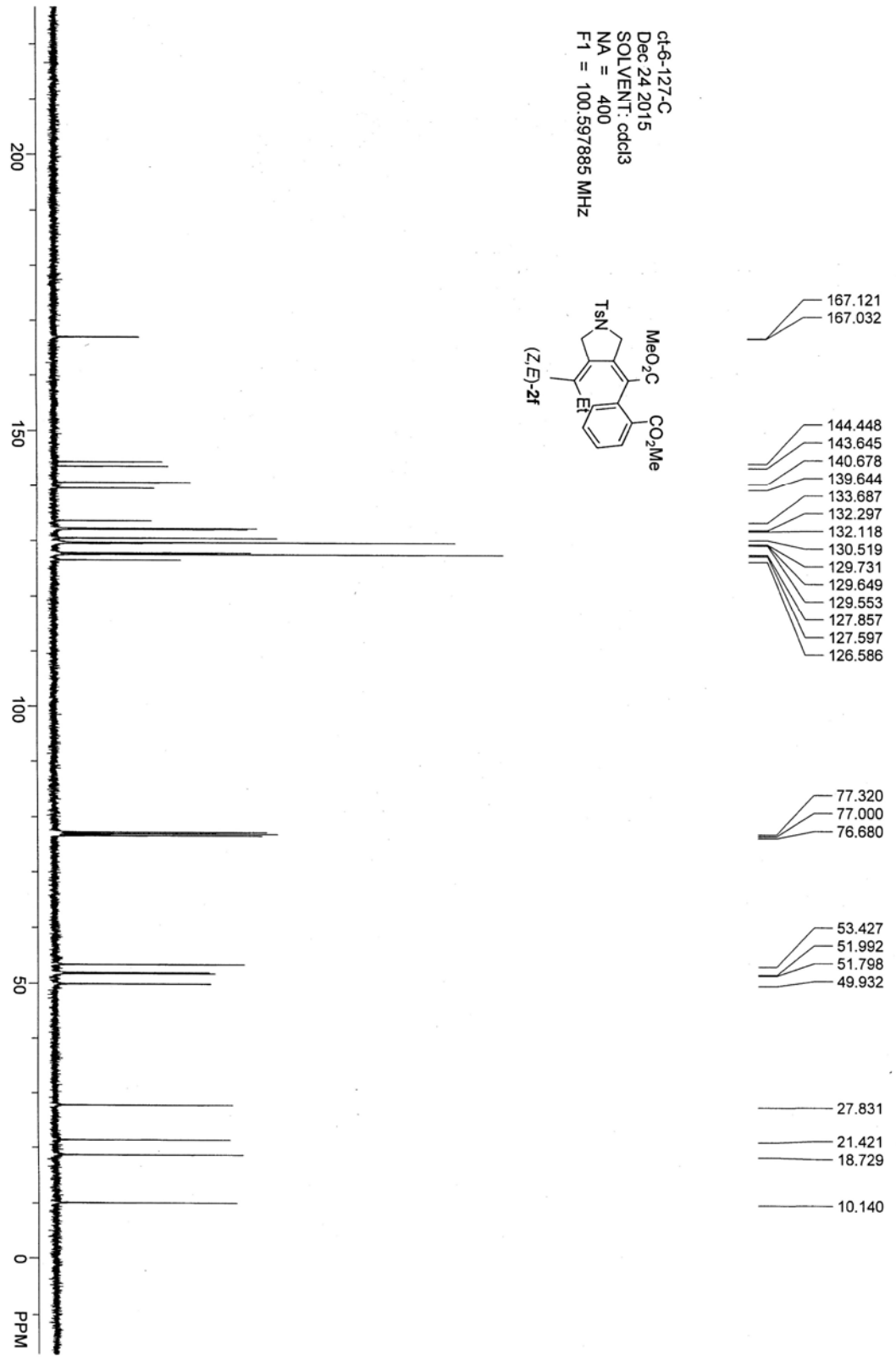

ct-9-107-H
Jul 4 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
(E,Z)-2d
MeO2C
MeO2C
MeO2C
Et
CO2Me
OMe
7.517
7.302
7.046
7.024
6.962
6.940
3.836
3.745
3.623
3.544
3.501
3.460
3.418
3.056
3.019
2.946
2.909
1.758
1.740
1.724
1.706
1.521
1.306
1.287
1.270
1.254
0.266
0.247
0.229
0.000
0.93
0.96
1.01
6.09
5.90
2.93
1.08
1.00
0.99
0.99
1.03
2.97
1.13
3.00
PPM

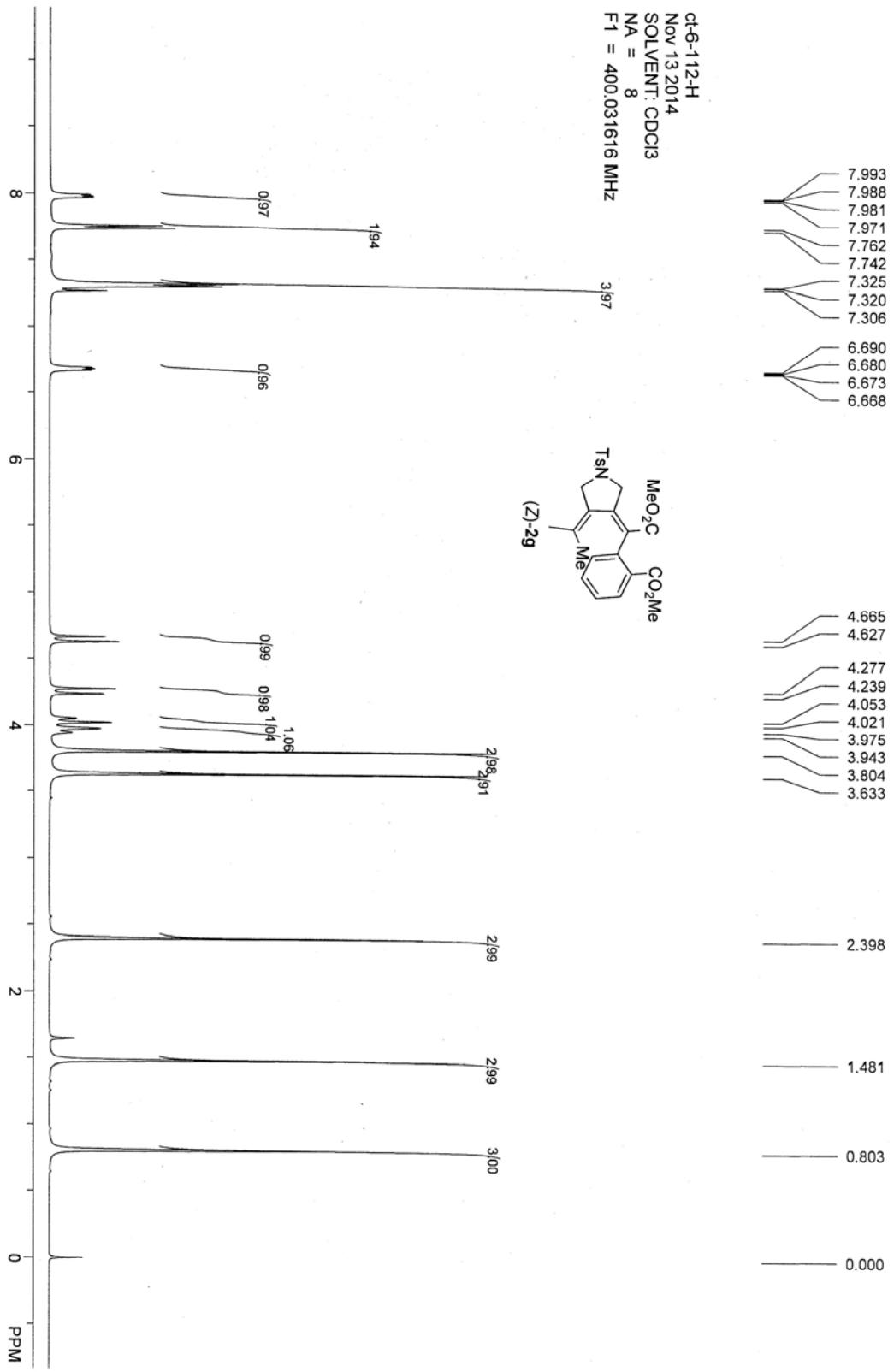

ct-9-107-C
Jul 4 2016
SOLVENT: cdcl3
NA = 104
F1 = 100.520599 MHz
(E,Z)-2d
MeO2C
MeO2C
MeO2C
Et
CO2Me
OMe
172.341
171.805
168.032
166.997
158.476
149.292
138.360
133.977
133.232
130.442
129.764
128.373
118.363
114.724
77.320
77.000
76.680
56.036
55.299
52.783
52.687
51.920
51.429
40.750
36.947
27.800
18.237
10.803
200
150
100
50
0
PPM

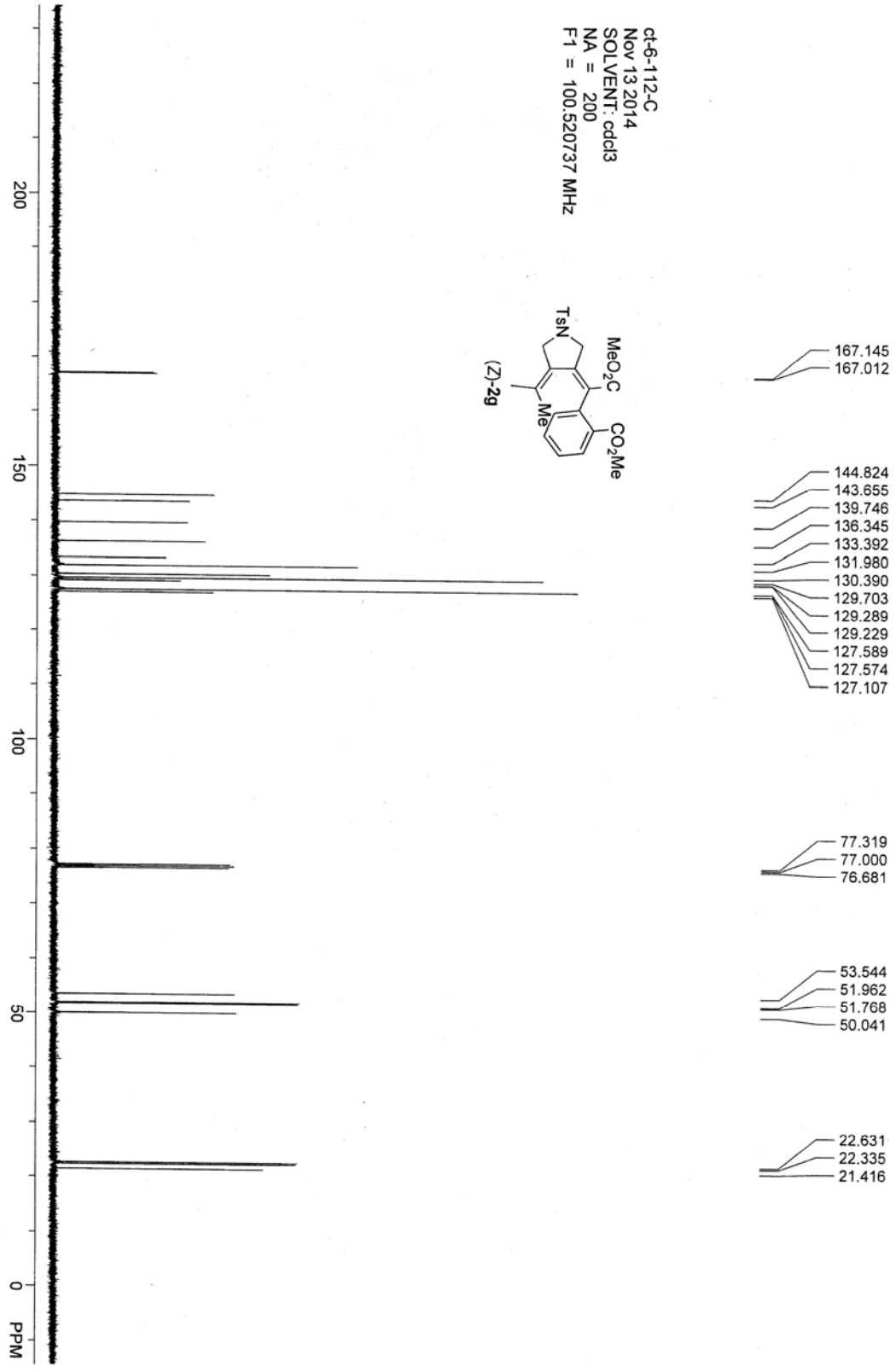

ct-7-69-H
Dec 20 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.723022 MHz
(E)-2e
MeO2C
MeO2C
MeO2C
Me
OMe
CO2Me
7.577
7.572
7.115
7.093
7.028
7.022
7.006
7.001
3.912
3.900
3.822
3.815
3.697
3.636
3.594
3.559
3.516
3.131
3.093
3.036
2.998
1.625
1.032
-0.000
0.98
1.06
1.05
6.24
6.23
3.05
1.08
1.09
1.07
1.06
3.00
3.04
PPM

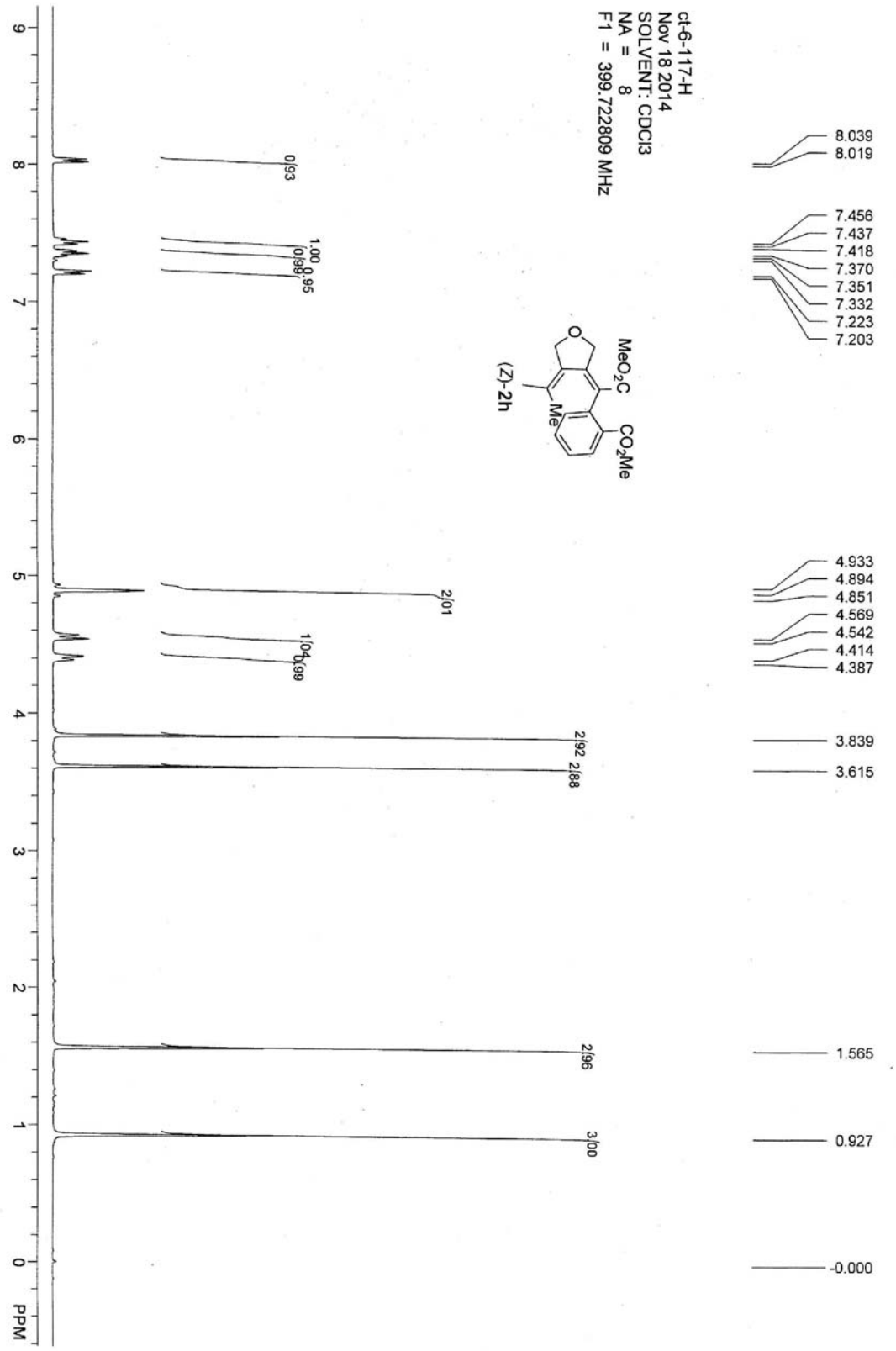

ct-7-69-C
Dec 20 2015
SOLVENT: cdcl3
NA = 180
F1 = 100.520737 MHz
MeO2C
MeO2C
MeO2C
CO2Me
Me
OMe
(E)-2e
172.342
171.803
167.939
167.097
158.132
149.615
133.886
133.773
133.370
130.319
130.053
128.368
118.317
114.446
77.319
77.000
76.681
56.186
55.244
52.785
52.701
51.889
51.403
40.867
37.011
22.322
22.163
200
150
100
50
0
PPM

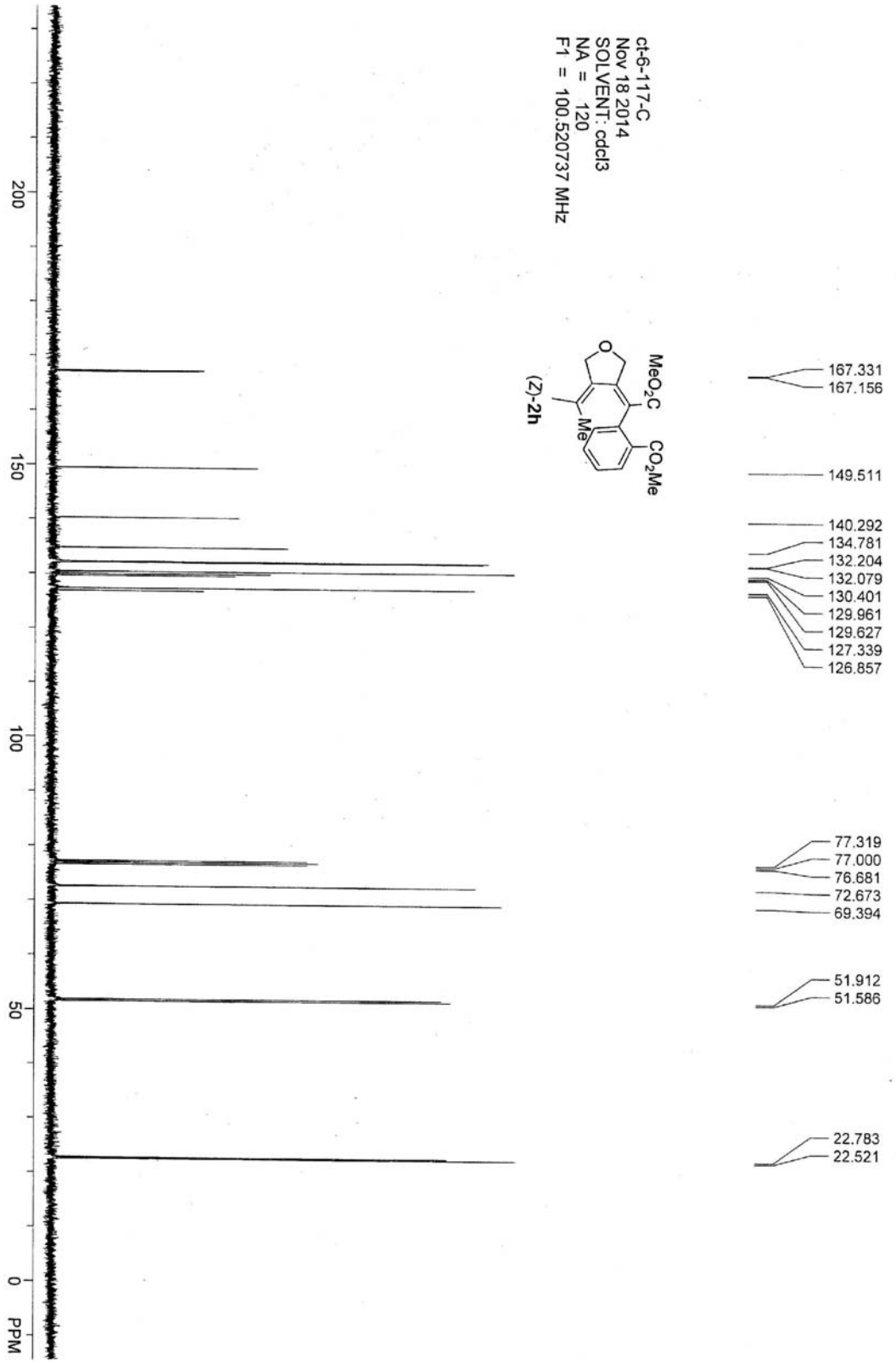

ct-6-127-H
Dec 24 2015
SOLVENT: CDCl3
NA = 8
F1 = 400.031219 MHz
TsN
MeO2C
CO2Me
Et
(Z,E)-2f
7.999
7.986
7.977
7.756
7.736
7.315
7.297
6.625
6.612
6.604
4.666
4.628
4.249
4.211
4.082
4.050
3.944
3.912
3.809
3.629
2.388
1.620
1.604
1.586
1.569
1.550
1.532
1.446
1.177
1.159
1.140
1.123
1.105
1.087
0.118
0.100
0.082
-0.000
4.17
2.00
0.98
0.94
1.05
1.03
1.04
1.05
2.98
3.00
3.09
1.08
2.97
0.99
2.98
PPM

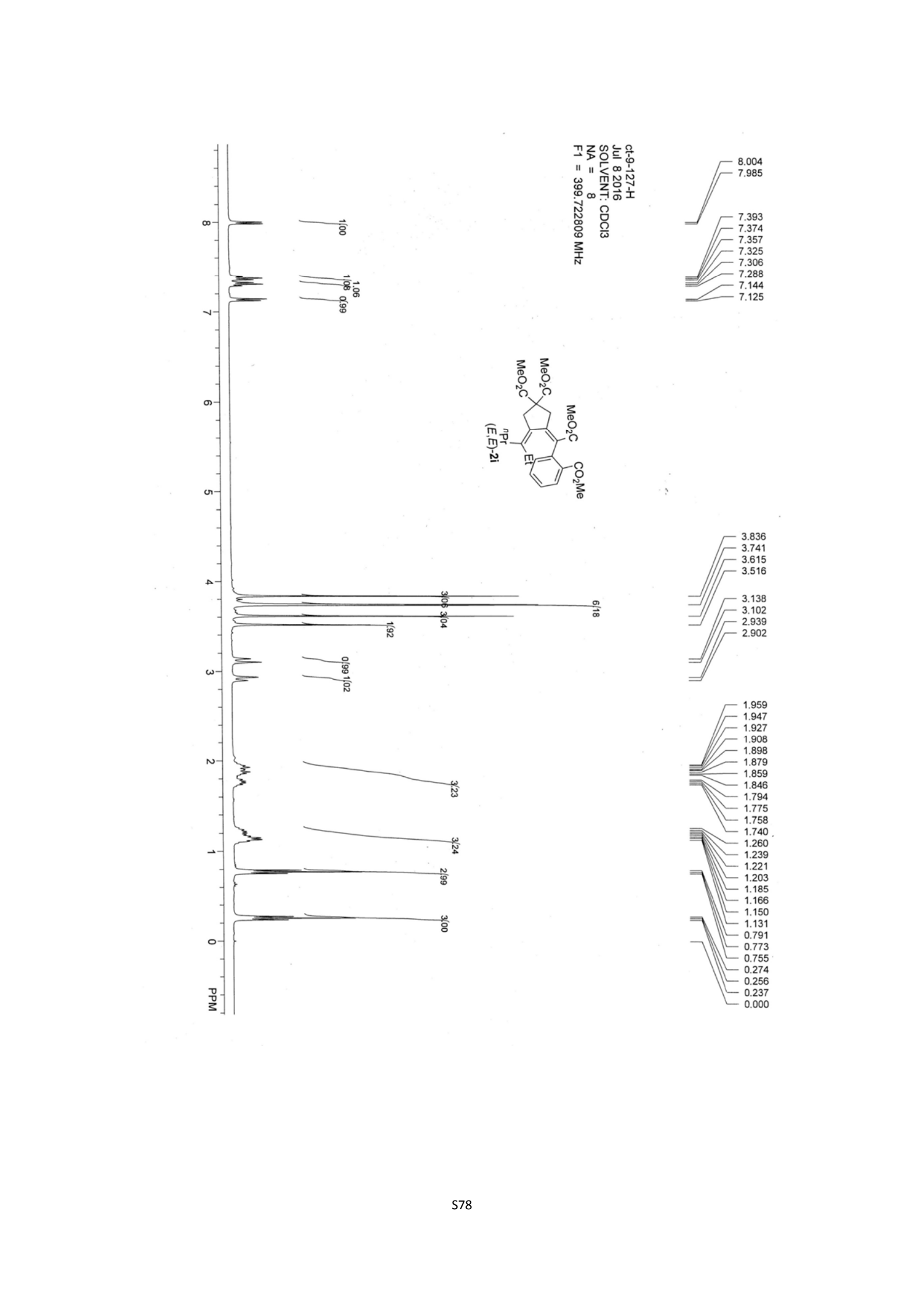

ct-6-127-C
Dec 24 2015
SOLVENT: cdcl3
NA = 400
F1 = 100.597885 MHz
TsN
MeO2C
Et
CO2Me
(Z,E)-2f
167.121
167.032
144.448
143.645
140.678
139.644
133.687
132.297
132.118
130.519
129.731
129.649
129.553
127.857
127.597
126.586
77.320
77.000
76.680
53.427
51.992
51.798
49.932
27.831
21.421
18.729
10.140
200
150
100
50
0
PPM

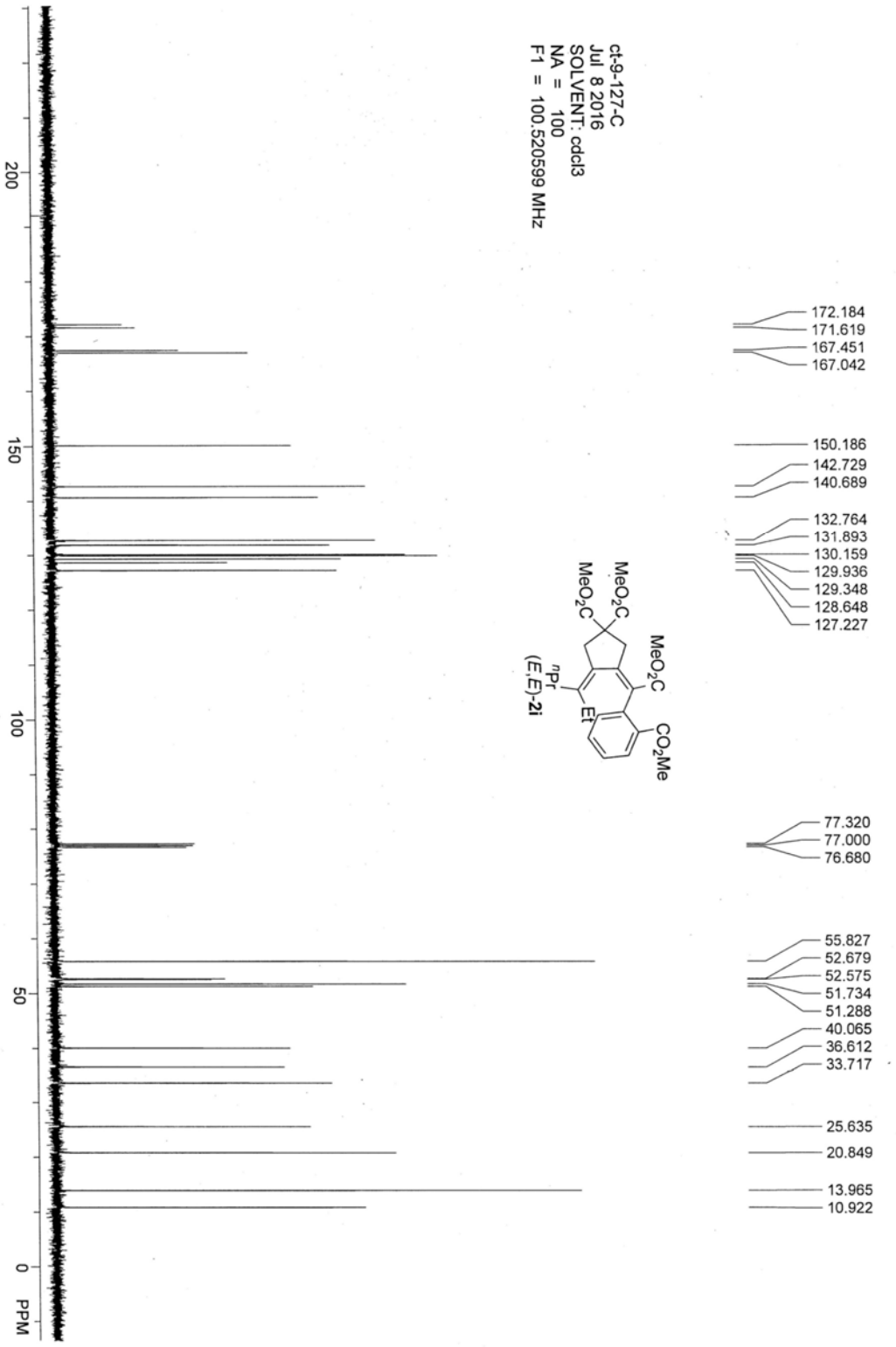

ct-6-112-H
Nov 13 2014
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
TsN
MeO2C
CO2Me
Me
(Z)-2g
7.993
7.988
7.981
7.971
7.762
7.742
7.325
7.320
7.306
6.690
6.680
6.673
6.668
4.665
4.627
4.277
4.239
4.053
4.021
3.975
3.943
3.804
3.633
2.398
1.481
0.803
0.000
0/97
1/94
3/97
0/96
0/99
0/98
1/04
1.06
2/98
2/91
2/99
2/99
3/00
8
6
4
2
0
PPM

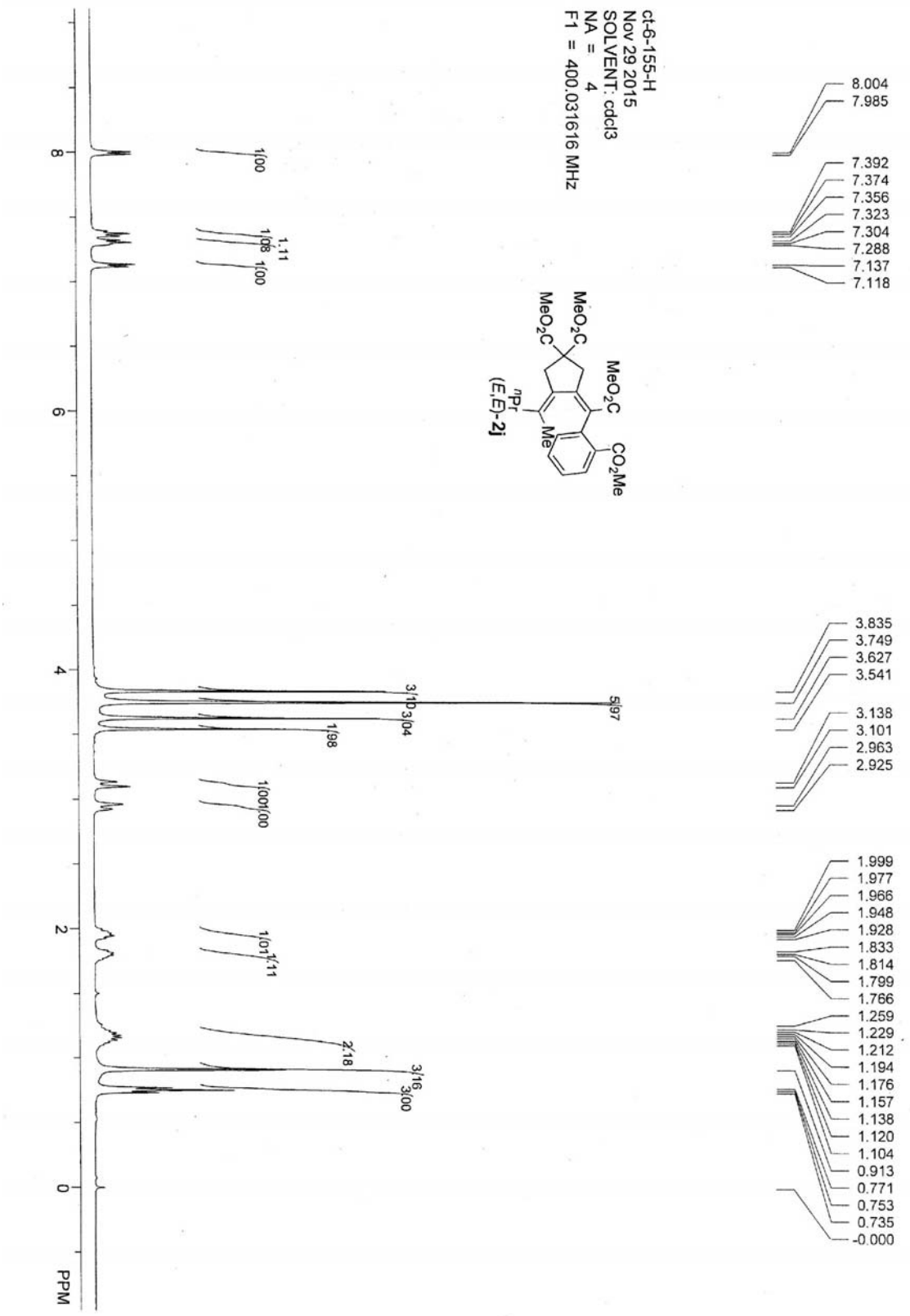

ct-6-112-C
Nov 13 2014
SOLVENT: cdcl3
NA = 200
F1 = 100.520737 MHz
(Z)-2g
TsN
Me
MeO2C
CO2Me
167.145
167.012
144.824
143.655
139.746
136.345
133.392
131.980
130.390
129.703
129.289
129.229
127.589
127.574
127.107
77.319
77.000
76.681
53.544
51.962
51.768
50.041
22.631
22.335
21.416
200
150
100
50
0
PPM

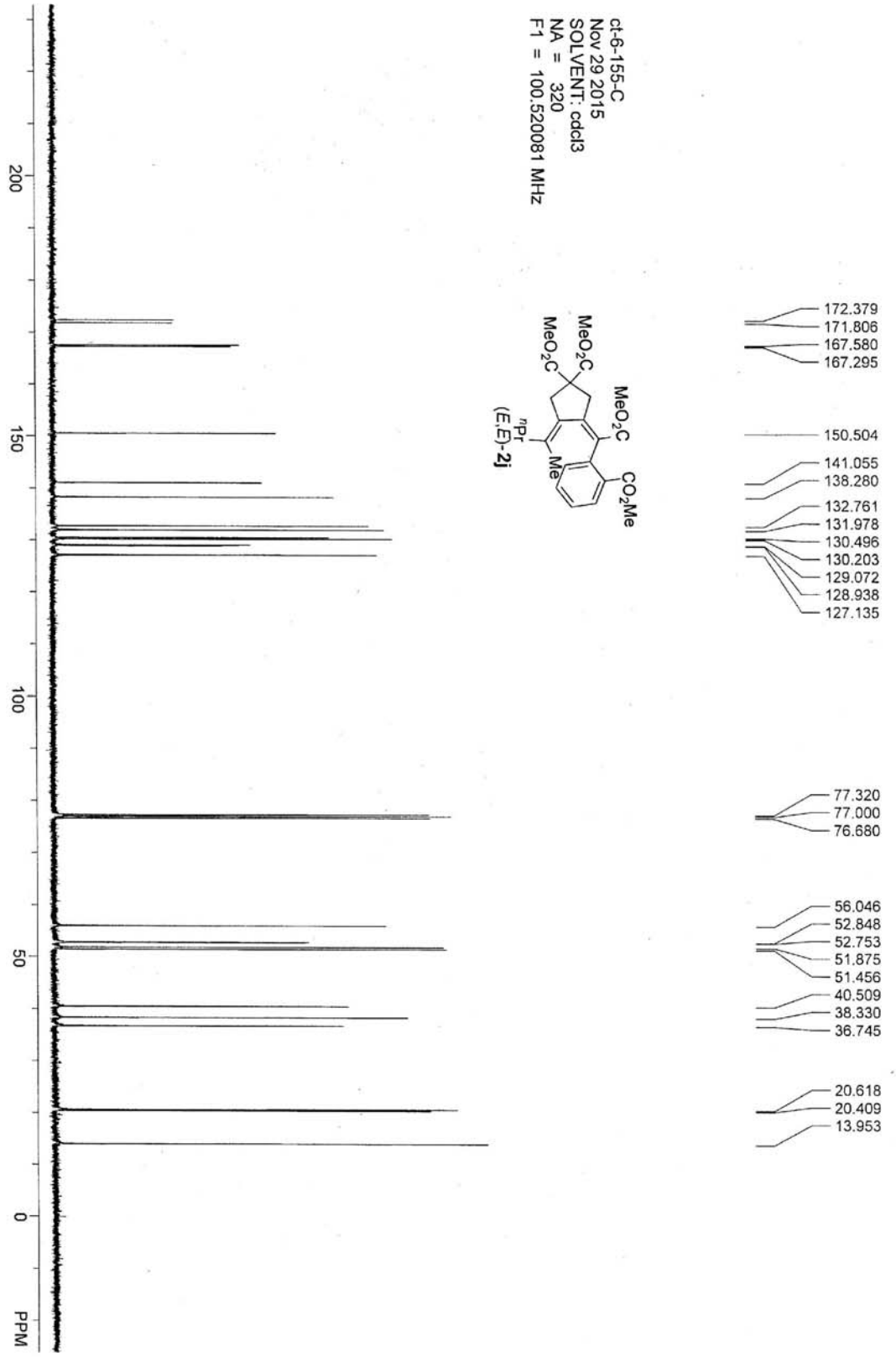

ct-6-117-H
Nov 18 2014
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(Z)-2h
MeO2C
CO2Me
Me
8.039
8.019
7.456
7.437
7.418
7.370
7.351
7.332
7.223
7.203
4.933
4.894
4.851
4.569
4.542
4.414
4.387
3.839
3.615
1.565
0.927
-0.000
0.93
1.00
0.98
0.95
2.01
1.04
0.99
2.92
2.88
2.96
3.00
PPM

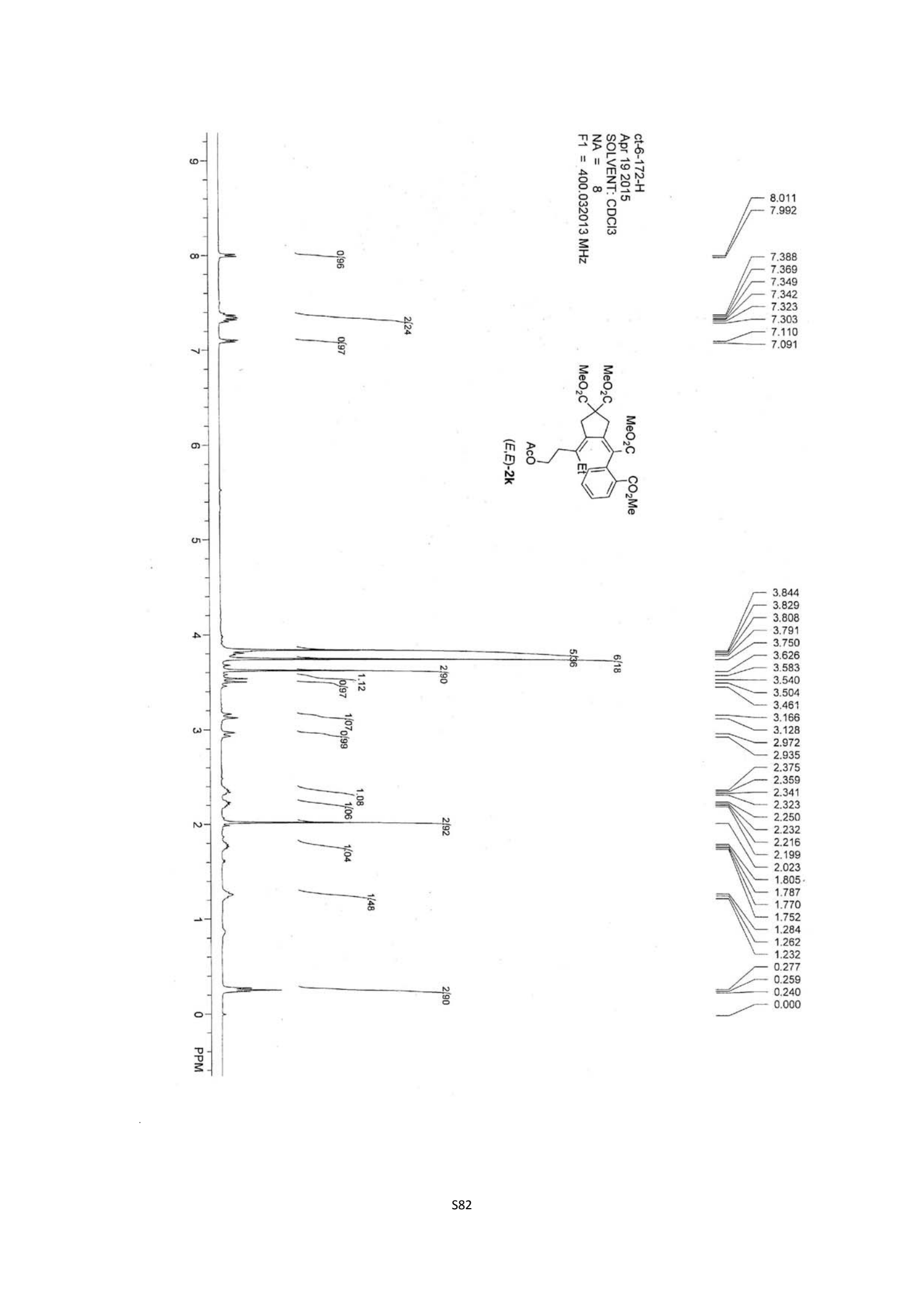

ct-6-117-C
Nov 18 2014
SOLVENT: cdcl3
NA = 120
F1 = 100.520737 MHz
(Z)-2h
MeO2C
CO2Me
Me
167.331
167.156
149.511
140.292
134.781
132.204
132.079
130.401
129.961
129.627
127.339
126.857
77.319
77.000
76.681
72.673
69.394
51.912
51.586
22.783
22.521
200
150
100
50
0
PPM

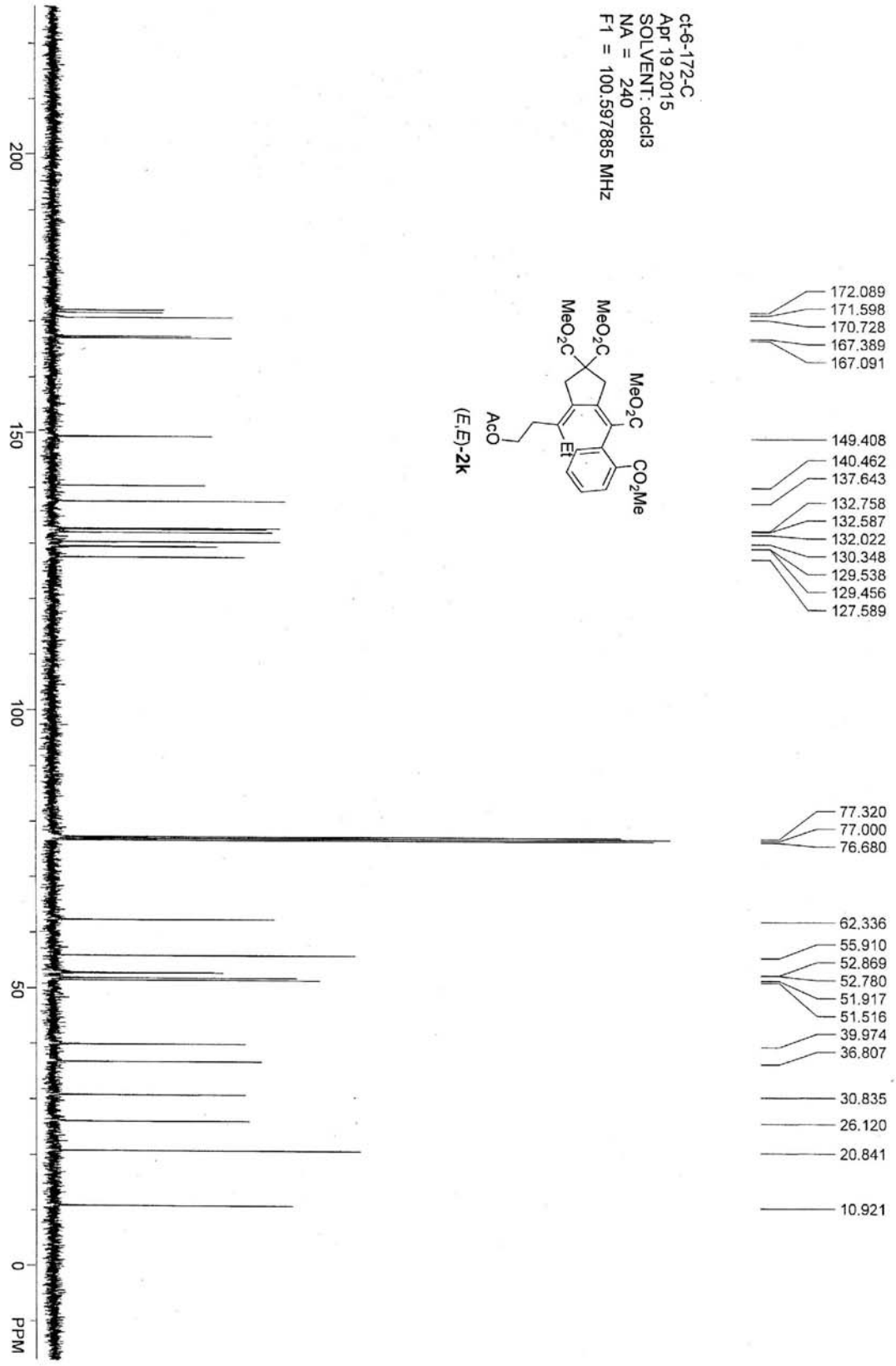

ct-9-127-H
Jul 8 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
8.004
7.985
7.393
7.374
7.357
7.325
7.306
7.288
7.144
7.125
3.836
3.741
3.615
3.516
3.138
3.102
2.939
2.902
1.959
1.947
1.927
1.908
1.898
1.879
1.859
1.846
1.794
1.775
1.758
1.740
1.260
1.239
1.221
1.203
1.185
1.166
1.150
1.131
0.791
0.773
0.755
0.274
0.256
0.237
0.000
1.00
1.08
1.06
0.99
3.06
3.04
6.18
1.92
0.99
1.02
3.23
3.24
2.99
3.00
PPM

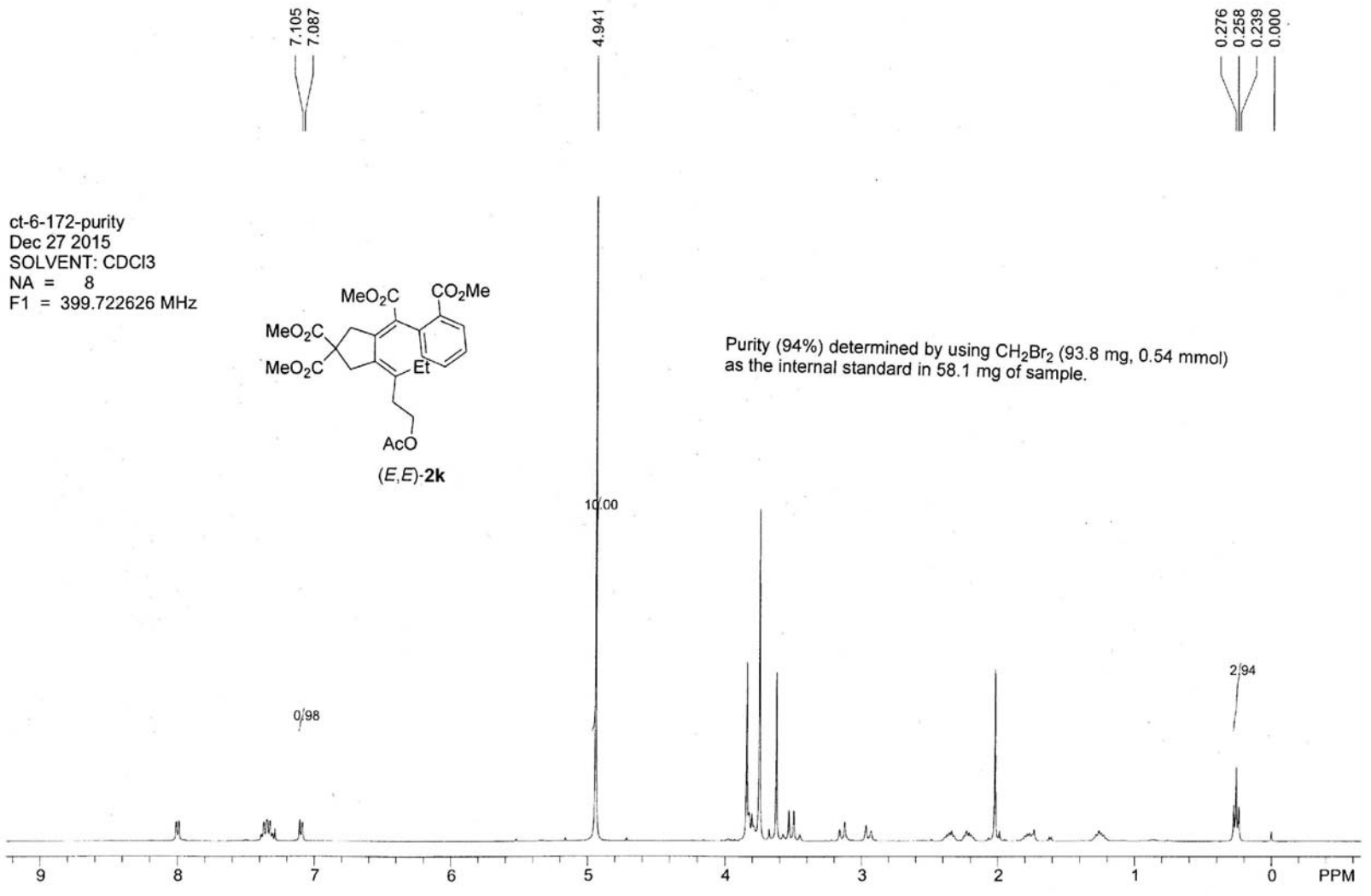

ct-9-127-C
Jul 8 2016
SOLVENT: cdcl3
NA = 100
F1 = 100.520599 MHz
(E,E)-2i
172.184
171.619
167.451
167.042
150.186
142.729
140.689
132.764
131.893
130.159
129.936
129.348
128.648
127.227
77.320
77.000
76.680
55.827
52.679
52.575
51.734
51.288
40.065
36.612
33.717
25.635
20.849
13.965
10.922
200
150
100
50
0
PPM

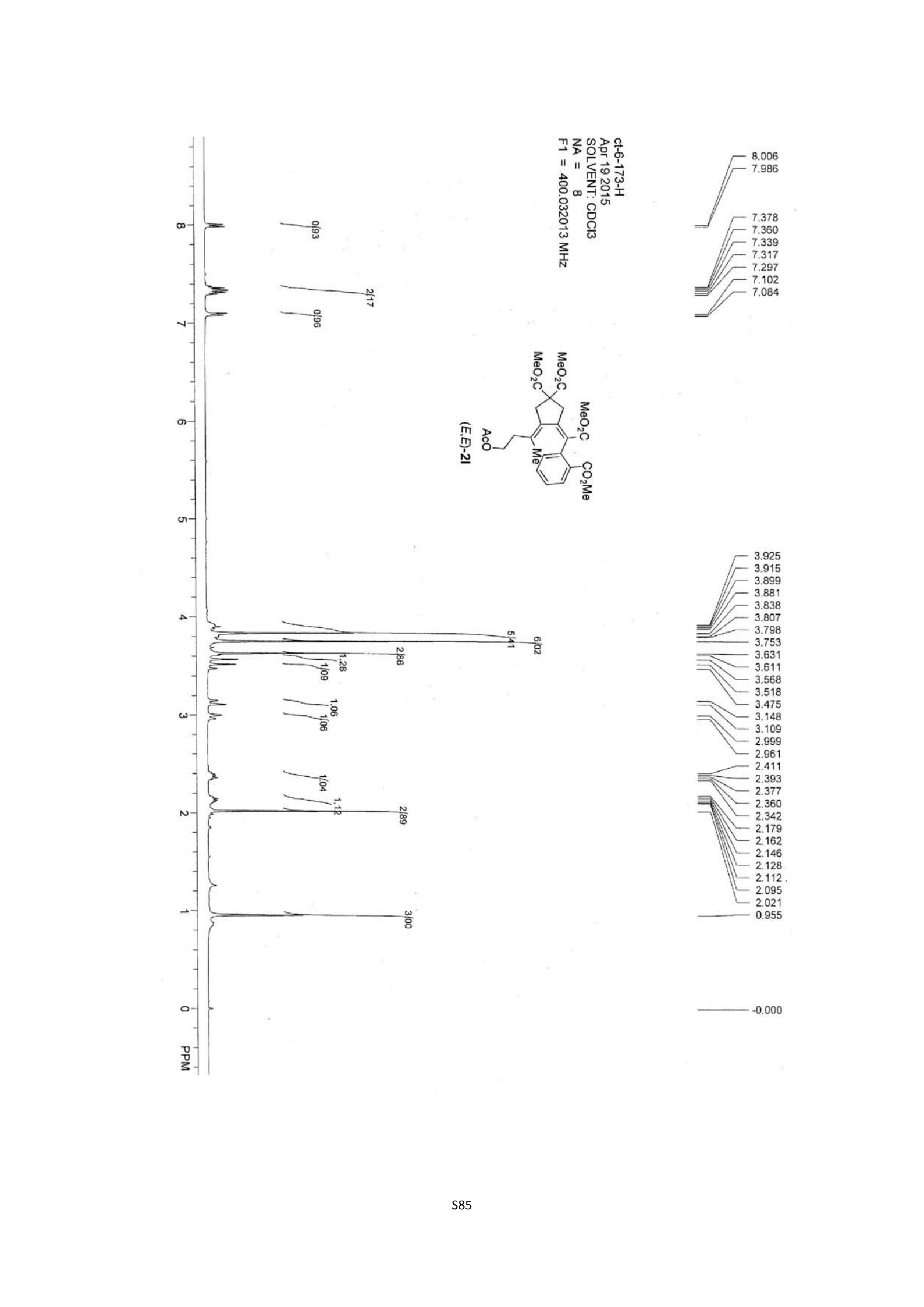

ct-6-155-H
Nov 29 2015
SOLVENT: cdcl3
NA = 4
F1 = 400.031616 MHz
MeO2C
MeO2C
MeO2C
MeO2C
nPr
(E,E)-2j
Me
CO2Me
8.004
7.985
7.392
7.374
7.356
7.323
7.304
7.288
7.137
7.118
3.835
3.749
3.627
3.541
3.138
3.101
2.963
2.925
1.999
1.977
1.966
1.948
1.928
1.833
1.814
1.799
1.766
1.259
1.229
1.212
1.194
1.176
1.157
1.138
1.120
1.104
0.913
0.771
0.753
0.735
-0.000
PPM

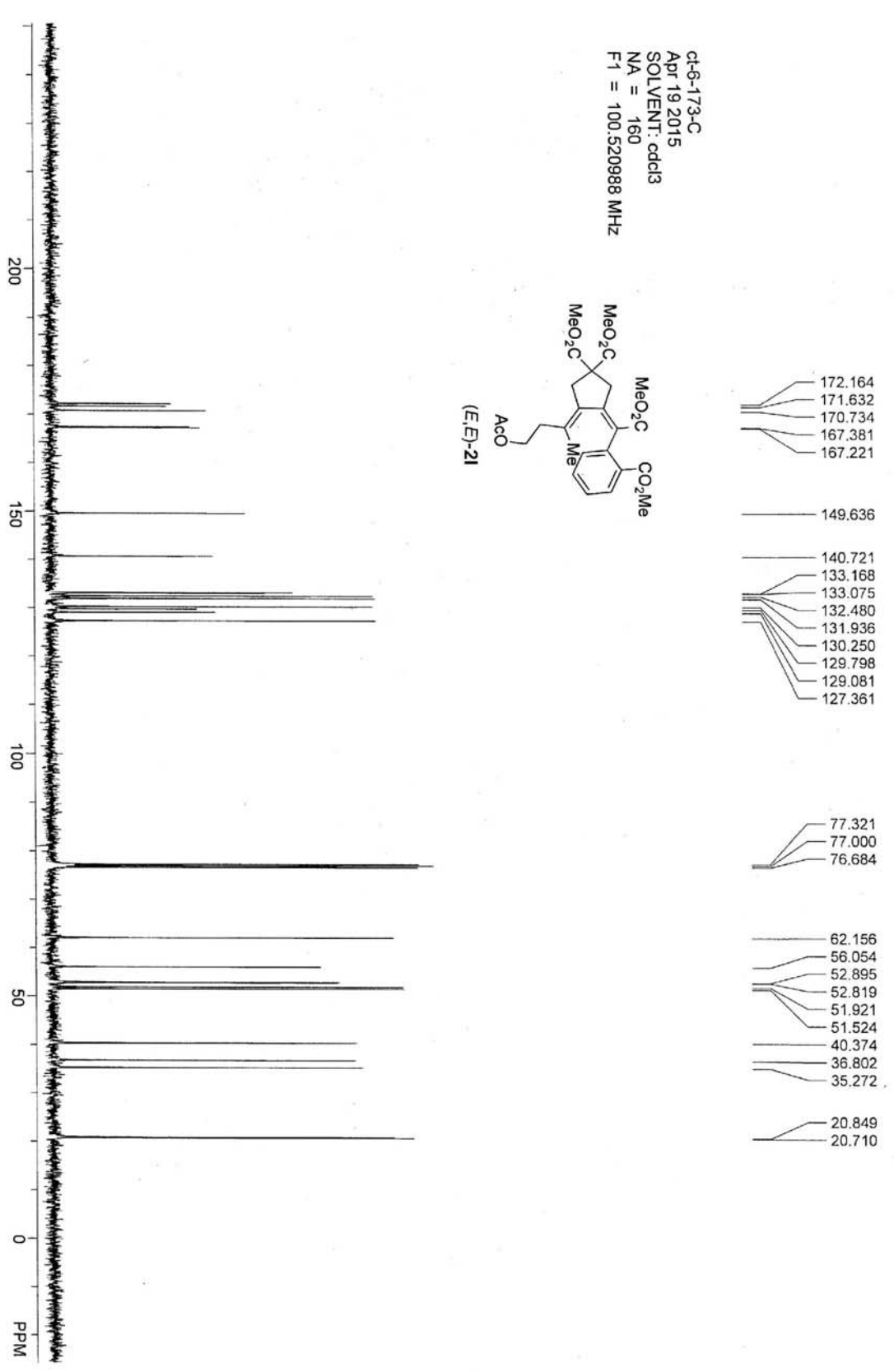

ct-6-155-C
Nov 29 2015
SOLVENT: cdcl3
NA = 320
F1 = 100.520081 MHz
MeO2C
MeO2C
MeO2C
CO2Me
nPr
Me
(E,E)-2j
172.379
171.806
167.580
167.295
150.504
141.055
138.280
132.761
131.978
130.496
130.203
129.072
128.938
127.135
77.320
77.000
76.680
56.046
52.848
52.753
51.875
51.456
40.509
38.330
36.745
20.618
20.409
13.953
200
150
100
50
0
PPM

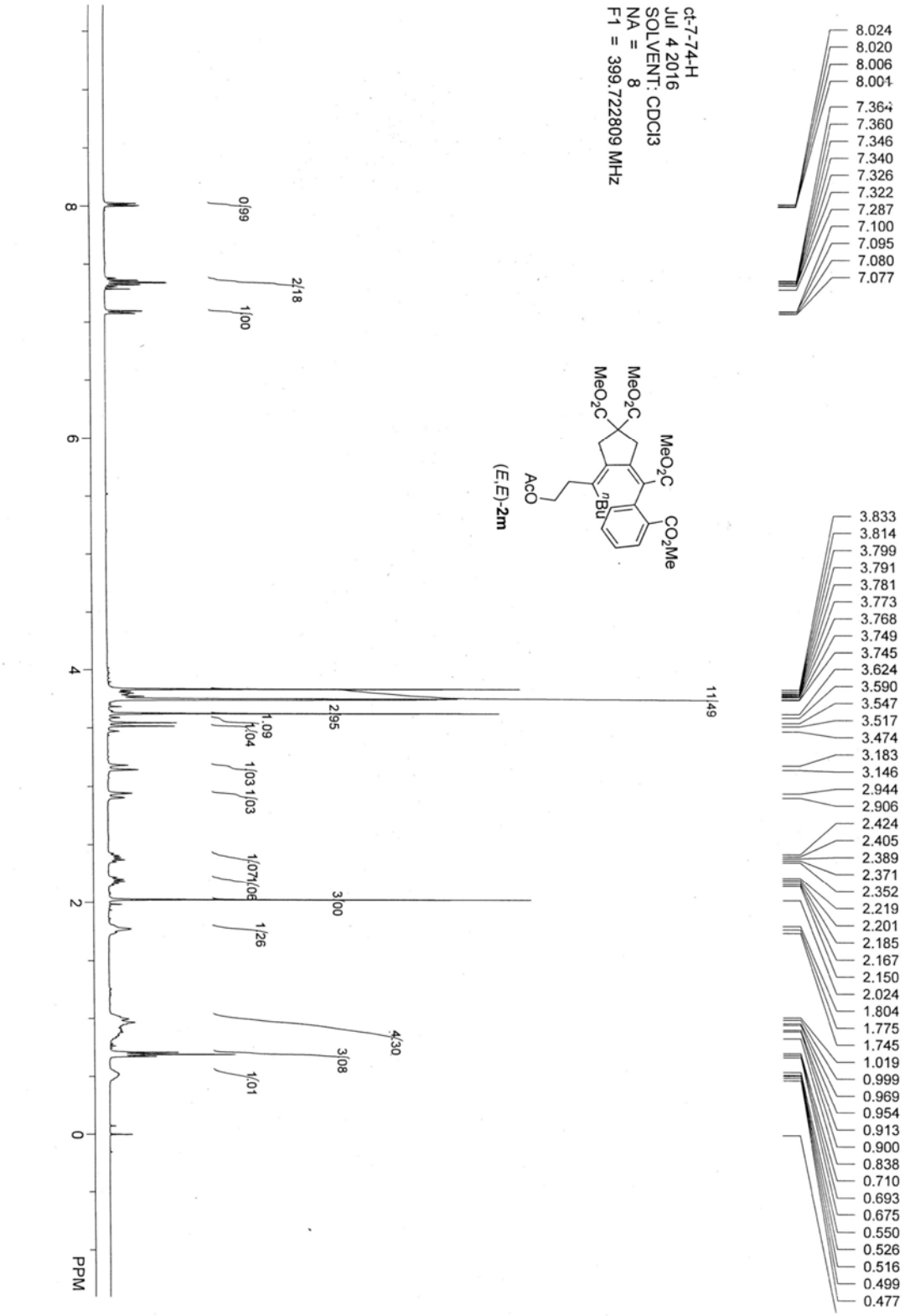

ct-6-172-H
Apr 19 2015
SOLVENT: CDCl3
NA = 8
F1 = 400.032013 MHz
(E,E)-2k
8.011
7.992
7.388
7.369
7.349
7.342
7.323
7.303
7.110
7.091
3.844
3.829
3.808
3.791
3.750
3.626
3.583
3.540
3.504
3.461
3.166
3.128
2.972
2.935
2.375
2.359
2.341
2.323
2.250
2.232
2.216
2.199
2.023
1.805
1.787
1.770
1.752
1.284
1.262
1.232
0.277
0.259
0.240
0.000
PPM

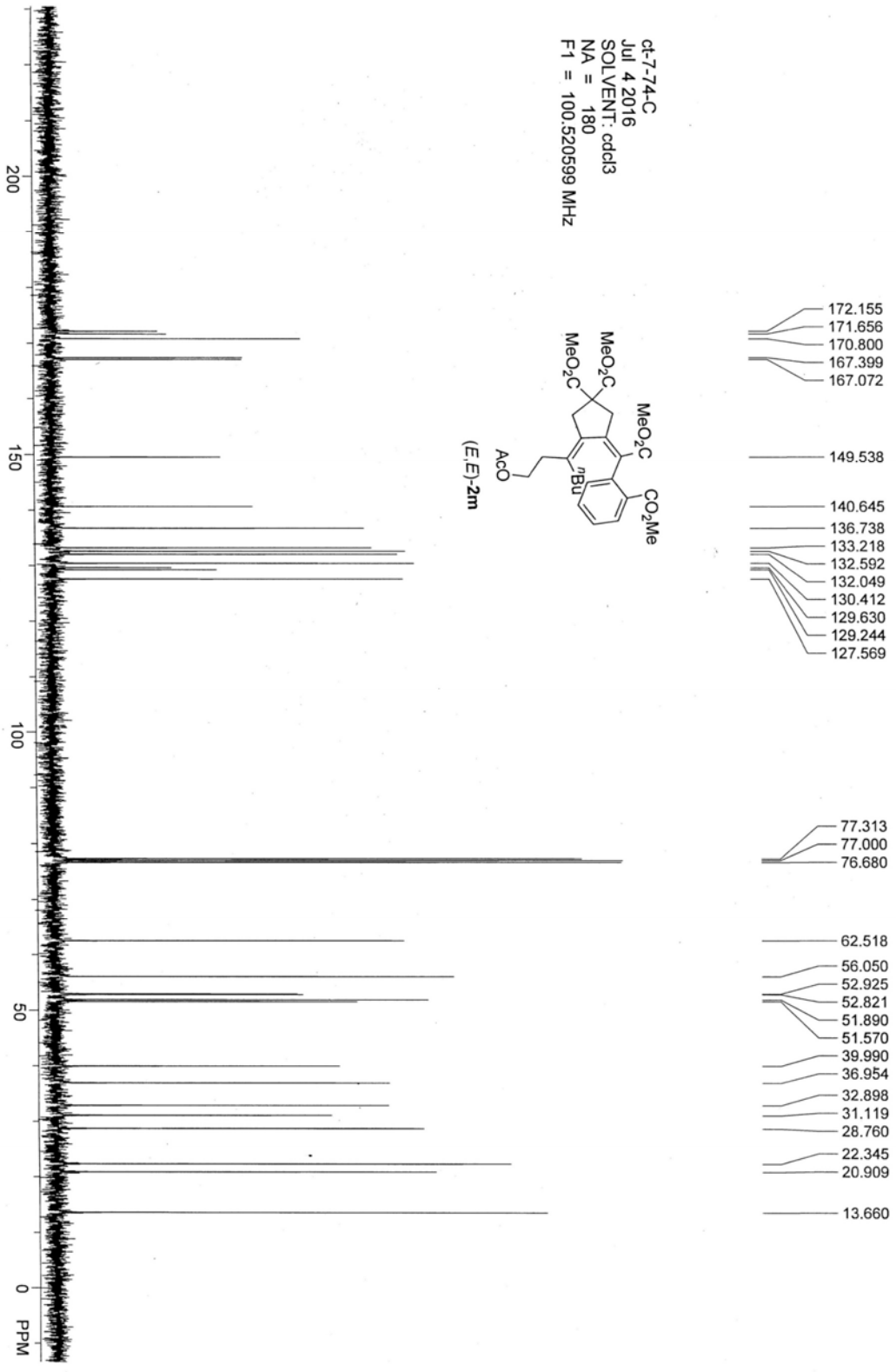

ct-6-172-C
Apr 19 2015
SOLVENT: cdcl3
NA = 240
F1 = 100.597885 MHz
MeO2C
MeO2C
MeO2C
CO2Me
Et
AcO
(E,E)-2k
172.089
171.598
170.728
167.389
167.091
149.408
140.462
137.643
132.758
132.587
132.022
130.348
129.538
129.456
127.589
77.320
77.000
76.680
62.336
55.910
52.869
52.780
51.917
51.516
39.974
36.807
30.835
26.120
20.841
10.921
200
150
100
50
0
PPM

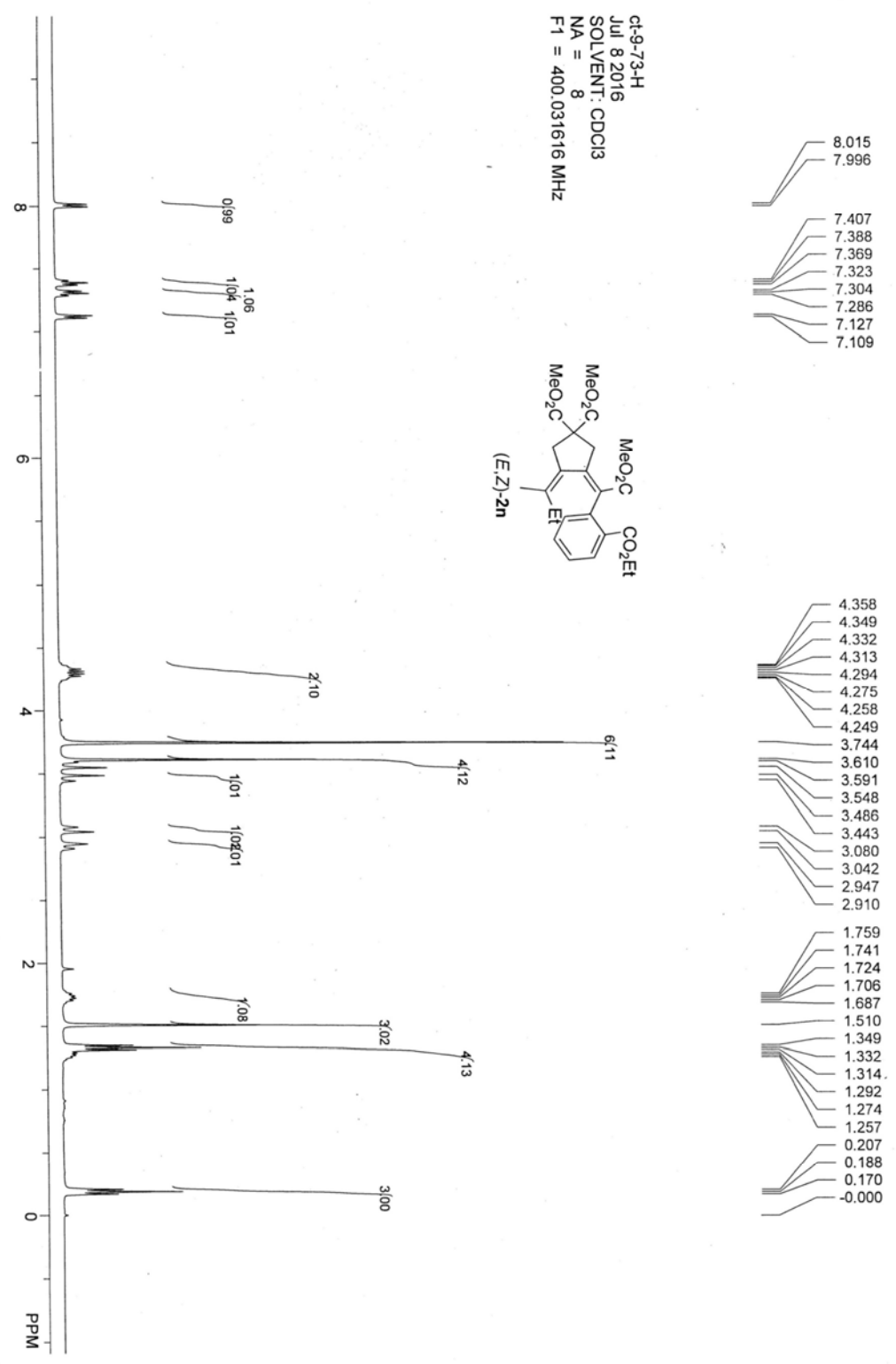

7.105
7.087
4.941
0.276
0.258
0.239
0.000
ct-6-172-purity
Dec 27 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.722626 MHz
MeO2C
CO2Me
MeO2C
MeO2C
Et
AcO
(E,E)-2k
Purity (94%) determined by using CH2Br2 (93.8 mg, 0.54 mmol) as the internal standard in 58.1 mg of sample.
10.00
2.94
0.98
9
8
7
6
5
4
3
2
1
0
PPM

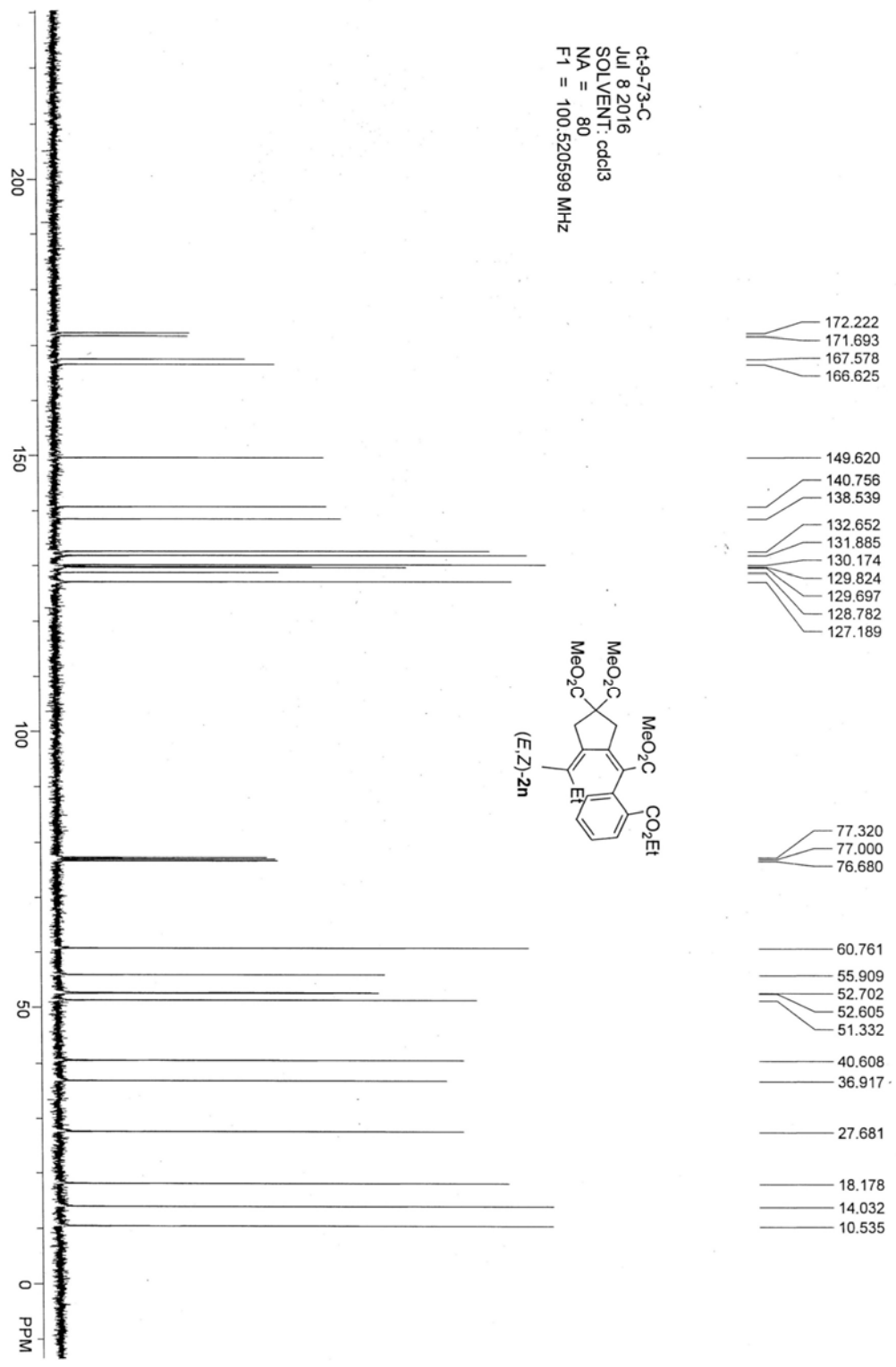

ct-6-173-H
Apr 19 2015
SOLVENT: CDCl3
NA = 8
F1 = 400.032013 MHz
(E,E)-2l
8.006
7.986
7.378
7.360
7.339
7.317
7.297
7.102
7.084
3.925
3.915
3.899
3.881
3.838
3.807
3.798
3.753
3.631
3.611
3.568
3.518
3.475
3.148
3.109
2.999
2.961
2.411
2.393
2.377
2.360
2.342
2.179
2.162
2.146
2.128
2.112
2.095
2.021
0.955
-0.000
0.93
2.17
0.96
6.02
5.41
2.86
1.28
1.09
1.06
1.06
1.04
1.12
2.89
3.00
PPM

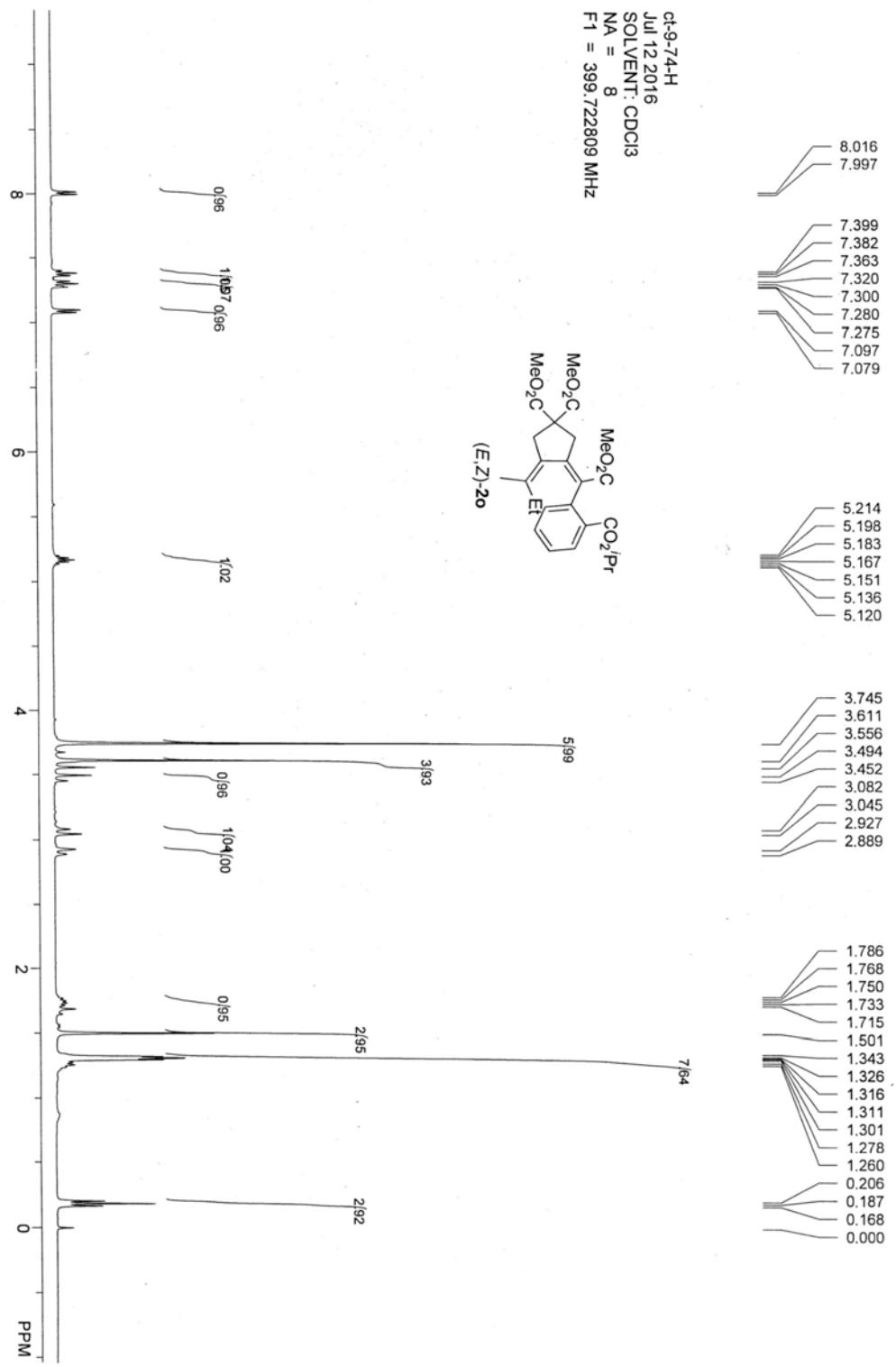

ct-6-173-C
Apr 19 2015
SOLVENT: cdcl3
NA = 160
F1 = 100.520988 MHz
MeO2C
MeO2C
MeO2C
CO2Me
AcO
Me
(E,E)-2l
172.164
171.632
170.734
167.381
167.221
149.636
140.721
133.168
133.075
132.480
131.936
130.250
129.798
129.081
127.361
77.321
77.000
76.684
62.156
56.054
52.895
52.819
51.921
51.524
40.374
36.802
35.272
20.849
20.710
200
150
100
50
0
PPM

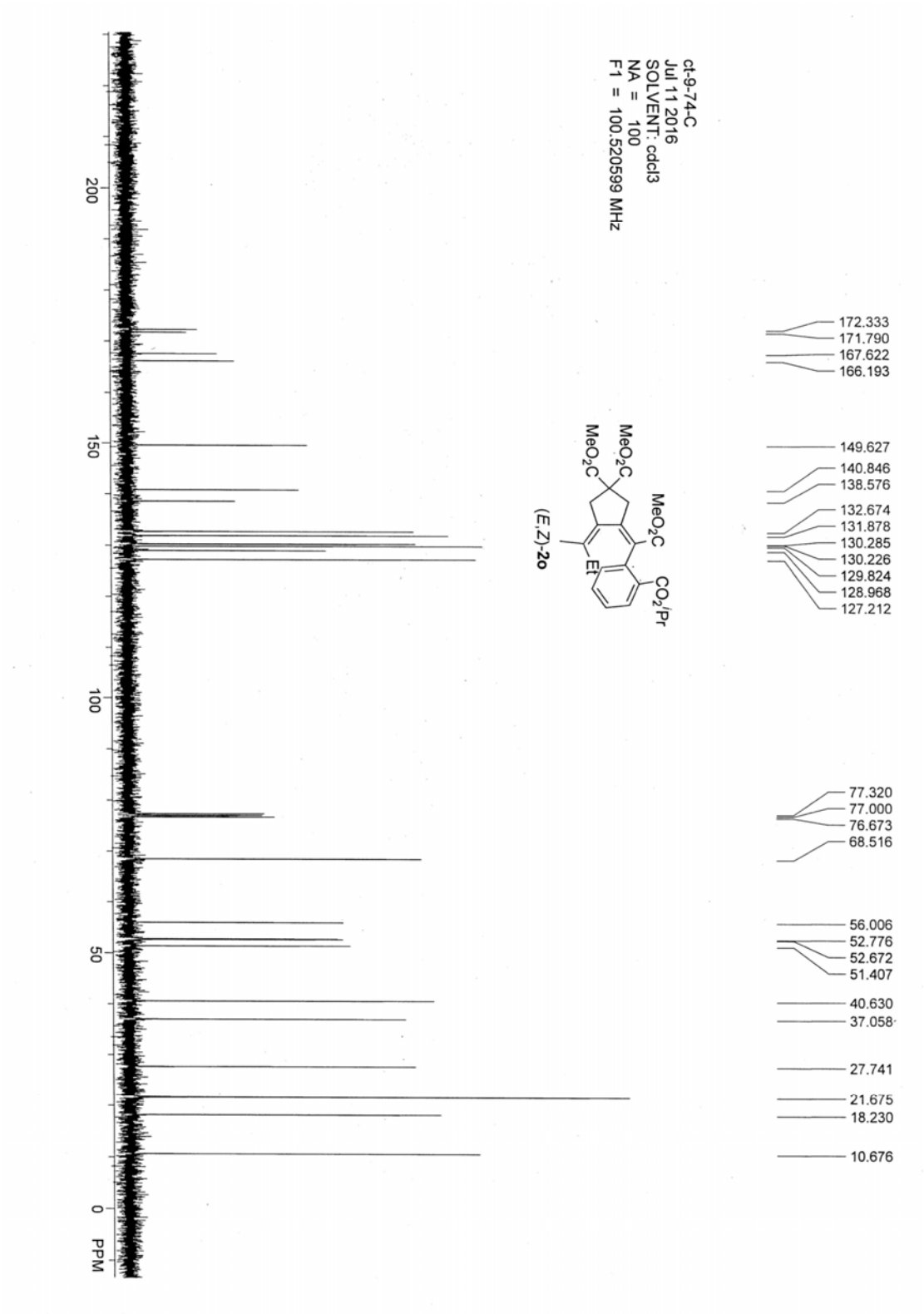

ct-7-74-H
Jul 4 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
MeO2C
MeO2C
MeO2C
CO2Me
nBu
AcO
(E,E)-2m
8.024
8.020
8.006
8.001
7.364
7.360
7.346
7.340
7.326
7.322
7.287
7.100
7.095
7.080
7.077
3.833
3.814
3.799
3.791
3.781
3.773
3.768
3.749
3.745
3.624
3.590
3.547
3.517
3.474
3.183
3.146
2.944
2.906
2.424
2.405
2.389
2.371
2.352
2.219
2.201
2.185
2.167
2.150
2.024
1.804
1.775
1.745
1.019
0.999
0.969
0.954
0.913
0.900
0.838
0.710
0.693
0.675
0.550
0.526
0.516
0.499
0.477
0.99
2.18
1.00
11.49
2.95
1.09
1.04
1.03
1.03
1.03
1.07
1.08
3.00
1.26
4.30
3.08
1.01
8
6
4
2
0
PPM

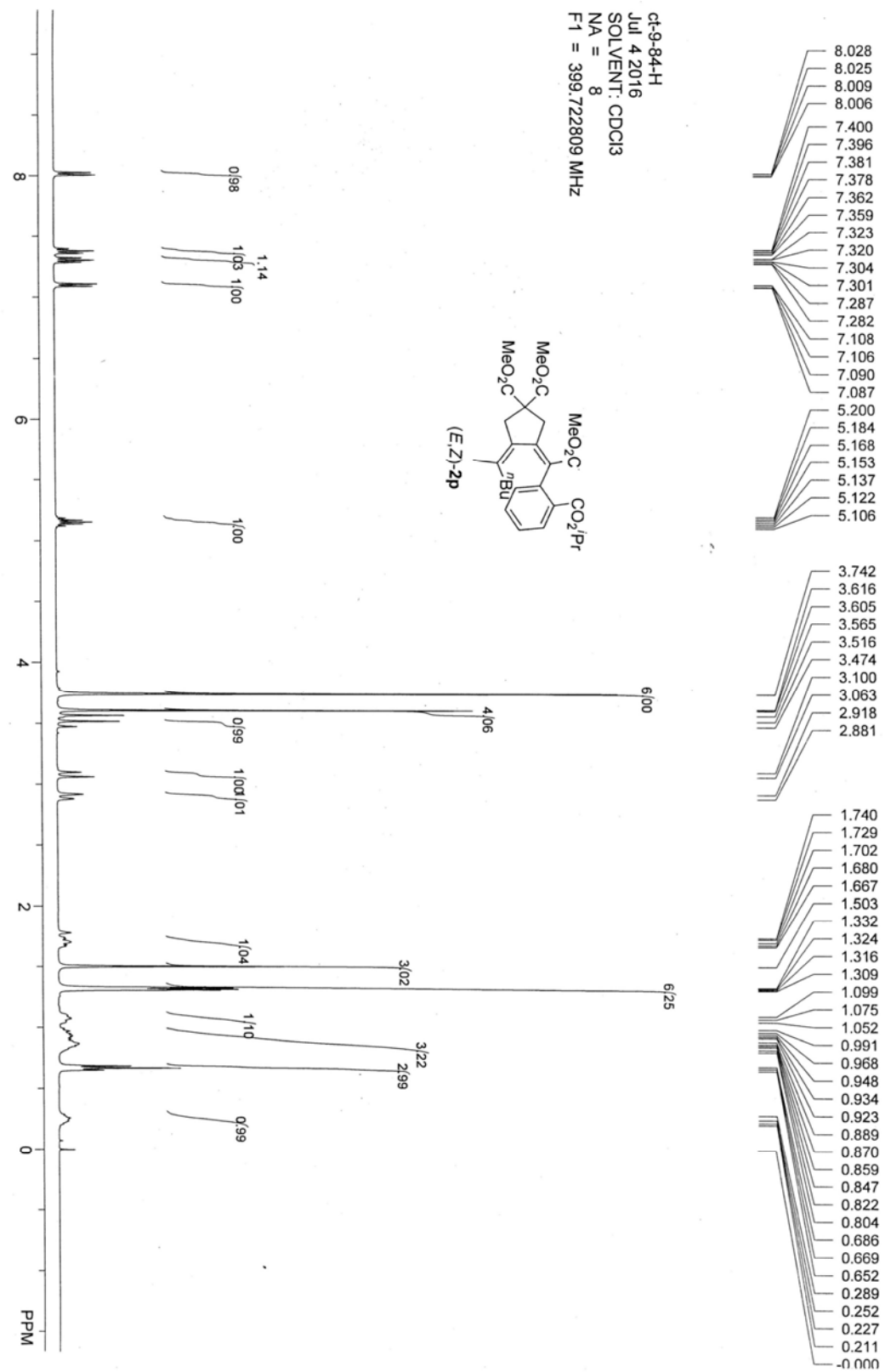

ct-7-74-C
Jul 4 2016
SOLVENT: cdcl3
NA = 180
F1 = 100.520599 MHz
MeO2C
MeO2C
MeO2C
CO2Me
nBu
AcO
(E,E)-2m
172.155
171.656
170.800
167.399
167.072
149.538
140.645
136.738
133.218
132.592
132.049
130.412
129.630
129.244
127.569
77.313
77.000
76.680
62.518
56.050
52.925
52.821
51.890
51.570
39.990
36.954
32.898
31.119
28.760
22.345
20.909
13.660
200
150
100
50
0
PPM

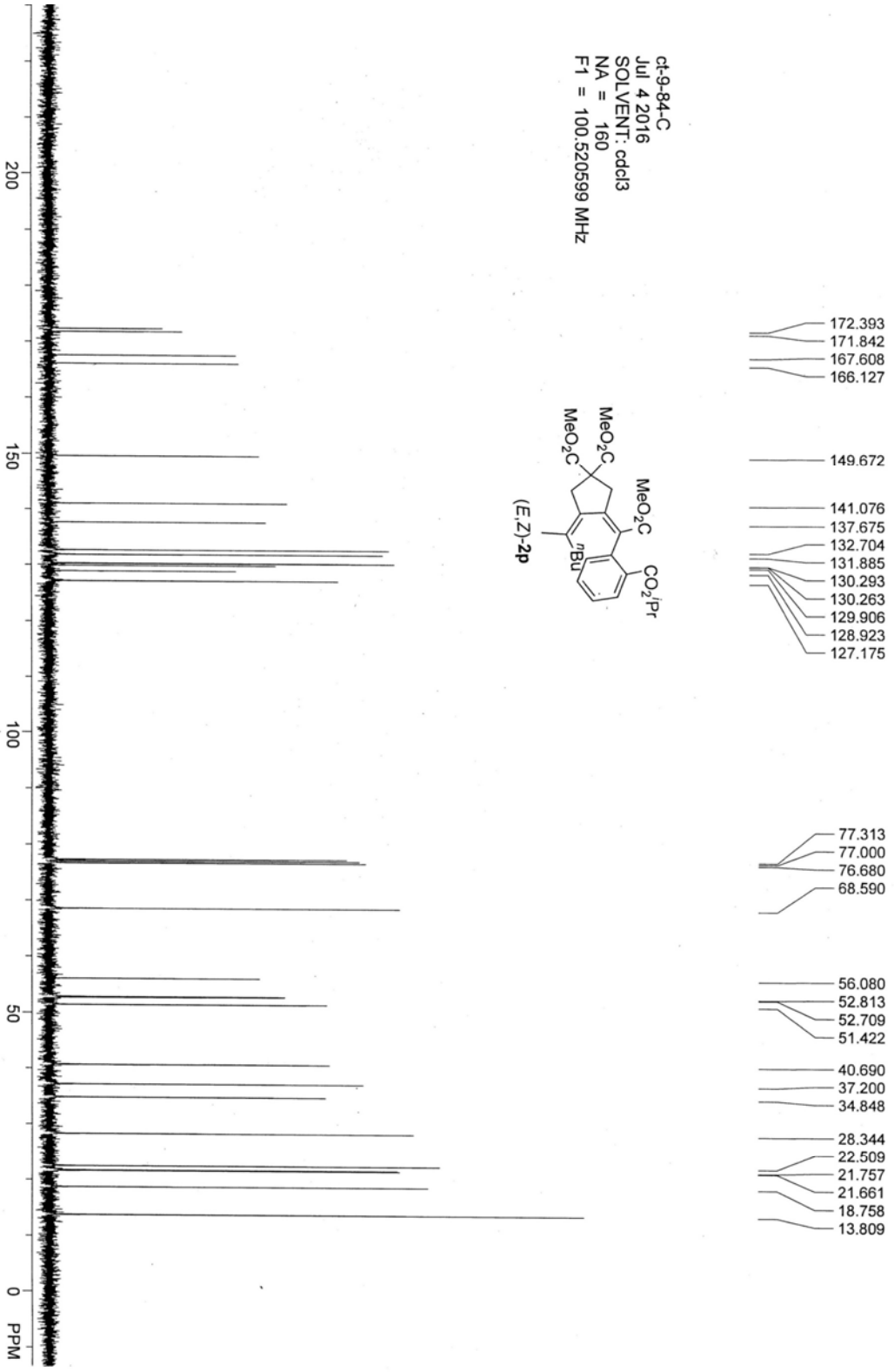

ct-9-73-H
Jul 8 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
(E,Z)-2n
MeO2C
MeO2C
MeO2C
CO2Et
Et
8.015
7.996
7.407
7.388
7.369
7.323
7.304
7.286
7.127
7.109
4.358
4.349
4.332
4.313
4.294
4.275
4.258
4.249
3.744
3.610
3.591
3.548
3.486
3.443
3.080
3.042
2.947
2.910
1.759
1.741
1.724
1.706
1.687
1.510
1.349
1.332
1.314
1.292
1.274
1.257
0.207
0.188
0.170
-0.000
0.99
1.06
1.04
1.01
2.10
6.11
4.12
1.01
1.02
1.01
1.08
3.02
4.13
3.00
8
6
4
2
0
PPM

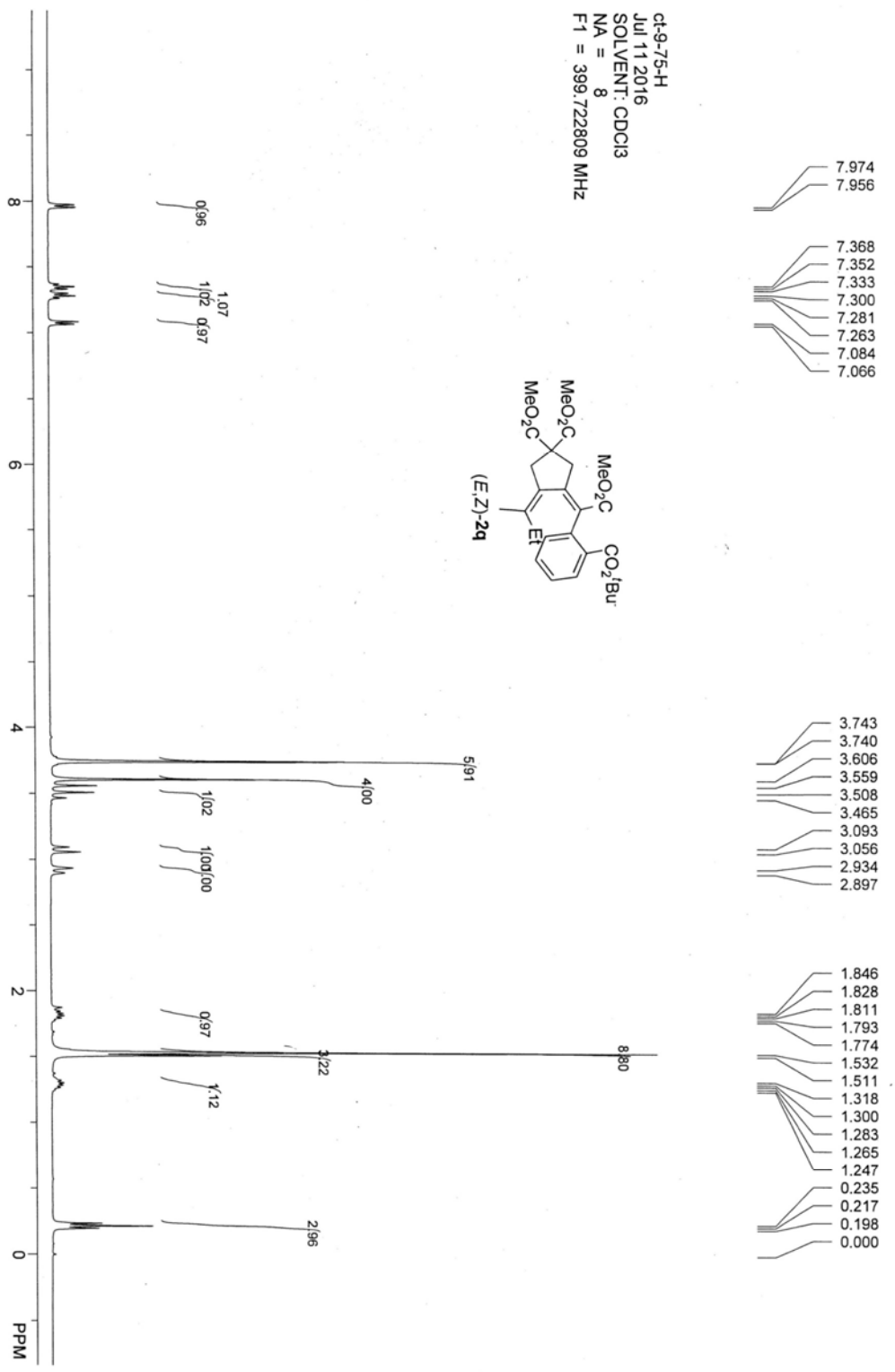

ct-9-73-C
Jul 8 2016
SOLVENT: cdcl3
NA = 80
F1 = 100.520599 MHz
MeO2C
MeO2C
MeO2C
CO2Et
Et
(E,Z)-2n
172.222
171.693
167.578
166.625
149.620
140.756
138.539
132.652
131.885
130.174
129.824
129.697
128.782
127.189
77.320
77.000
76.680
60.761
55.909
52.702
52.605
51.332
40.608
36.917
27.681
18.178
14.032
10.535
200
150
100
50
0
PPM

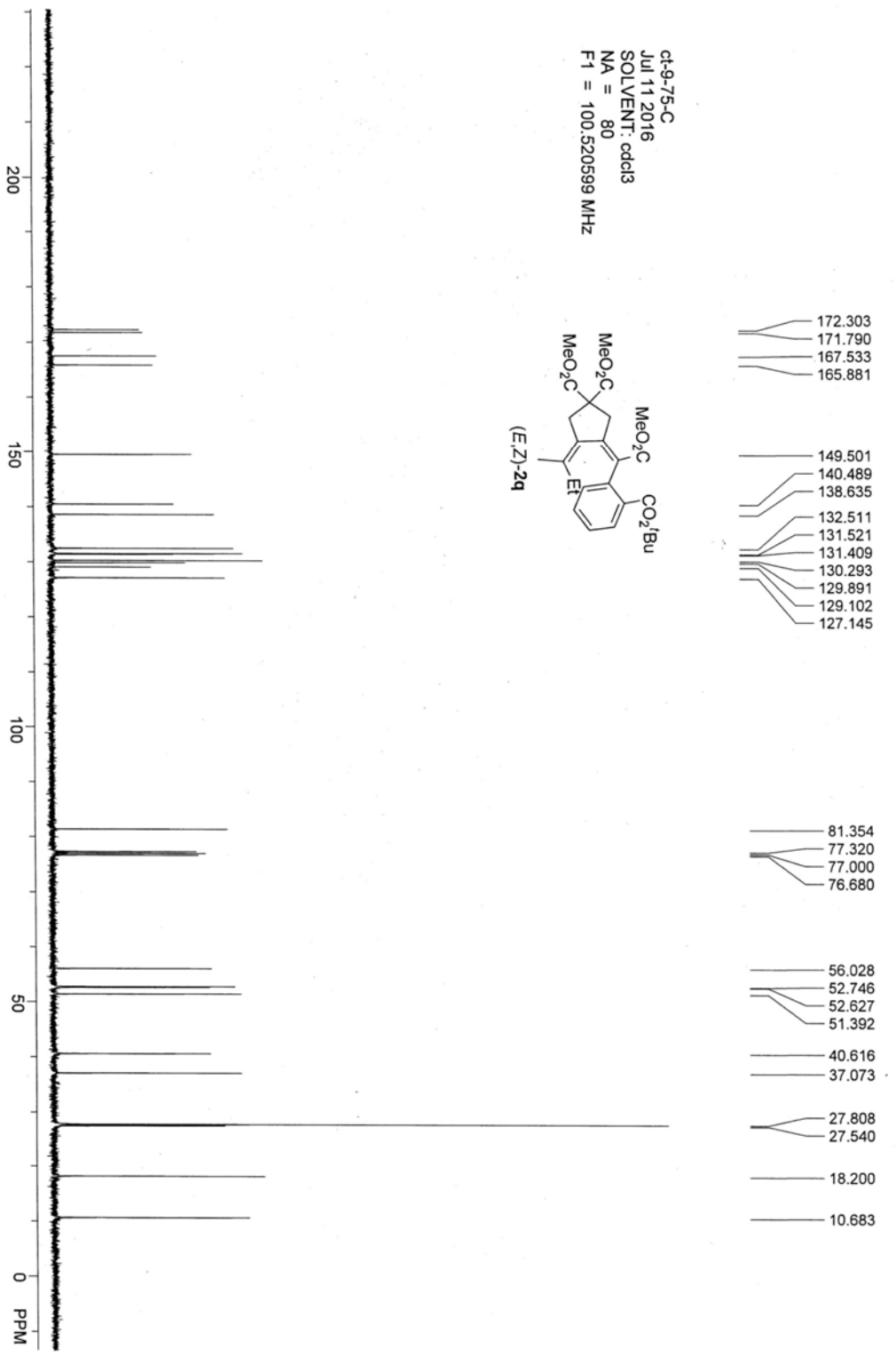

ct-9-74-H
Jul 12 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
MeO2C
MeO2C
MeO2C
Et
CO2iPr
(E,Z)-2o
8.016
7.997
7.399
7.382
7.363
7.320
7.300
7.280
7.275
7.097
7.079
5.214
5.198
5.183
5.167
5.151
5.136
5.120
3.745
3.611
3.556
3.494
3.452
3.082
3.045
2.927
2.889
1.786
1.768
1.750
1.733
1.715
1.501
1.343
1.326
1.316
1.311
1.301
1.278
1.260
0.206
0.187
0.168
0.000
0.96
1.00
0.96
1.02
5.99
3.93
0.96
1.04
1.00
0.95
2.95
7.64
2.92
8
6
4
2
0
PPM

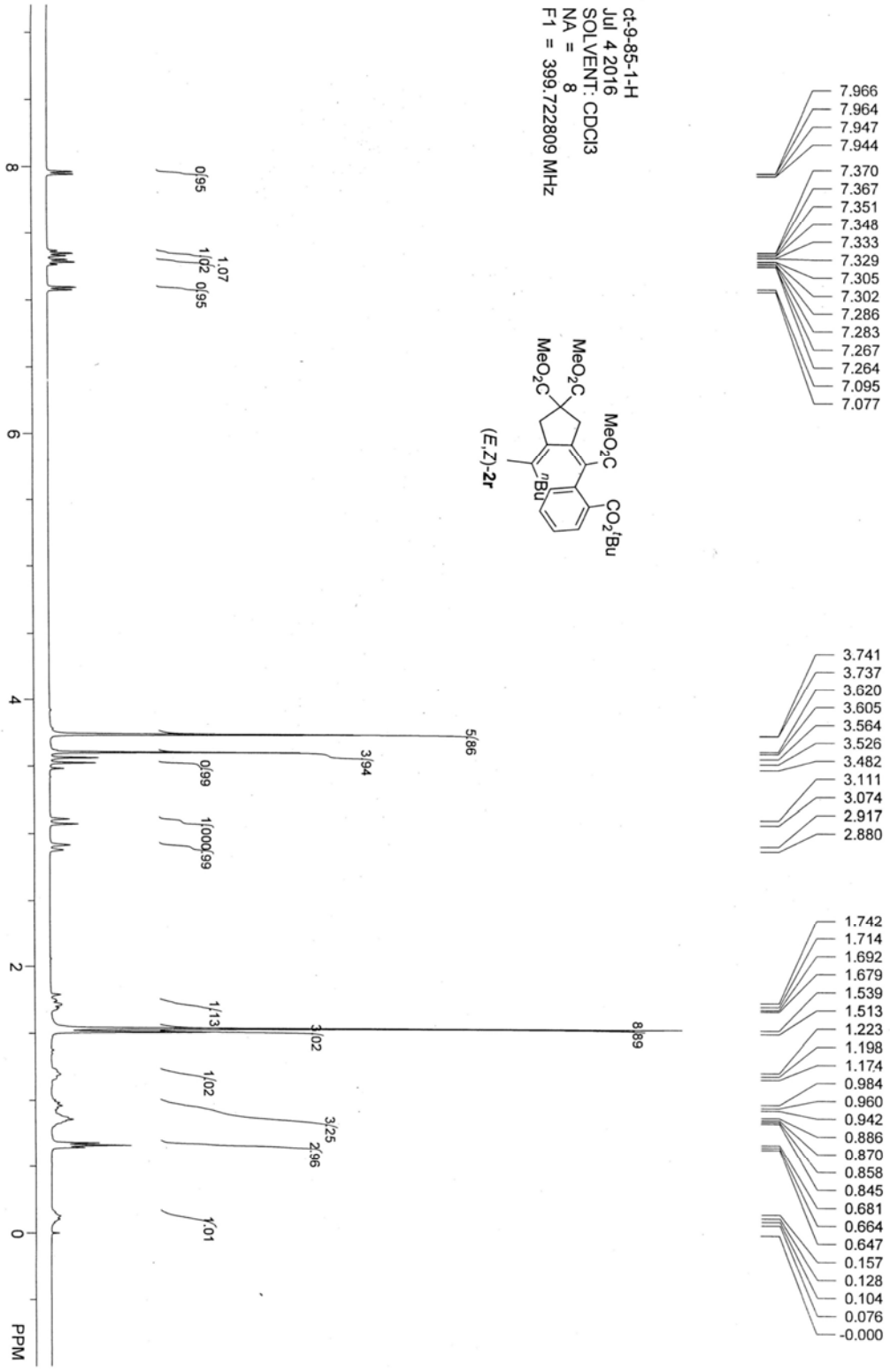

ct-9-74-C
Jul 11 2016
SOLVENT: cdcl3
NA = 100
F1 = 100.520599 MHz
(E,Z)-2o
MeO2C
MeO2C
MeO2C
Et
CO2iPr
172.333
171.790
167.622
166.193
149.627
140.846
138.576
132.674
131.878
130.285
130.226
129.824
128.968
127.212
77.320
77.000
76.673
68.516
56.006
52.776
52.672
51.407
40.630
37.058
27.741
21.675
18.230
10.676
200
150
100
50
0
PPM

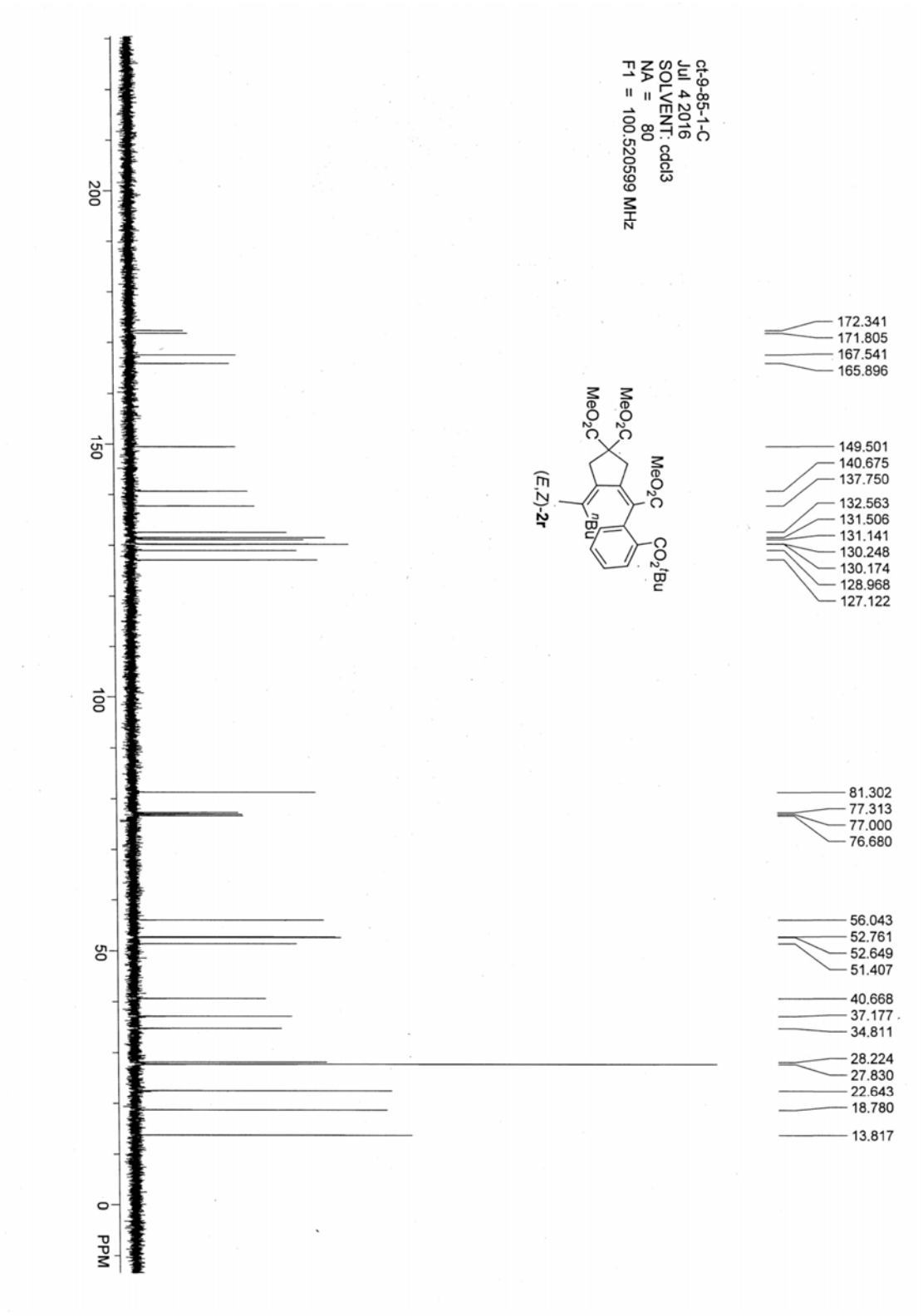

ct-9-84-H
Jul 4 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E,Z)-2p
8.028
8.025
8.009
8.006
7.400
7.396
7.381
7.378
7.362
7.359
7.323
7.320
7.304
7.301
7.287
7.282
7.108
7.106
7.090
7.087
5.200
5.184
5.168
5.153
5.137
5.122
5.106
3.742
3.616
3.605
3.565
3.516
3.474
3.100
3.063
2.918
2.881
1.740
1.729
1.702
1.680
1.667
1.503
1.332
1.324
1.316
1.309
1.099
1.075
1.052
0.991
0.968
0.948
0.934
0.923
0.889
0.870
0.859
0.847
0.822
0.804
0.686
0.669
0.652
0.289
0.252
0.227
0.211
-0.000
0.98
1.03
1.00
1.14
1.00
6.00
4.06
0.99
1.00
1.01
1.04
3.02
6.25
1.10
3.22
2.99
0.99
8
6
4
2
0
PPM

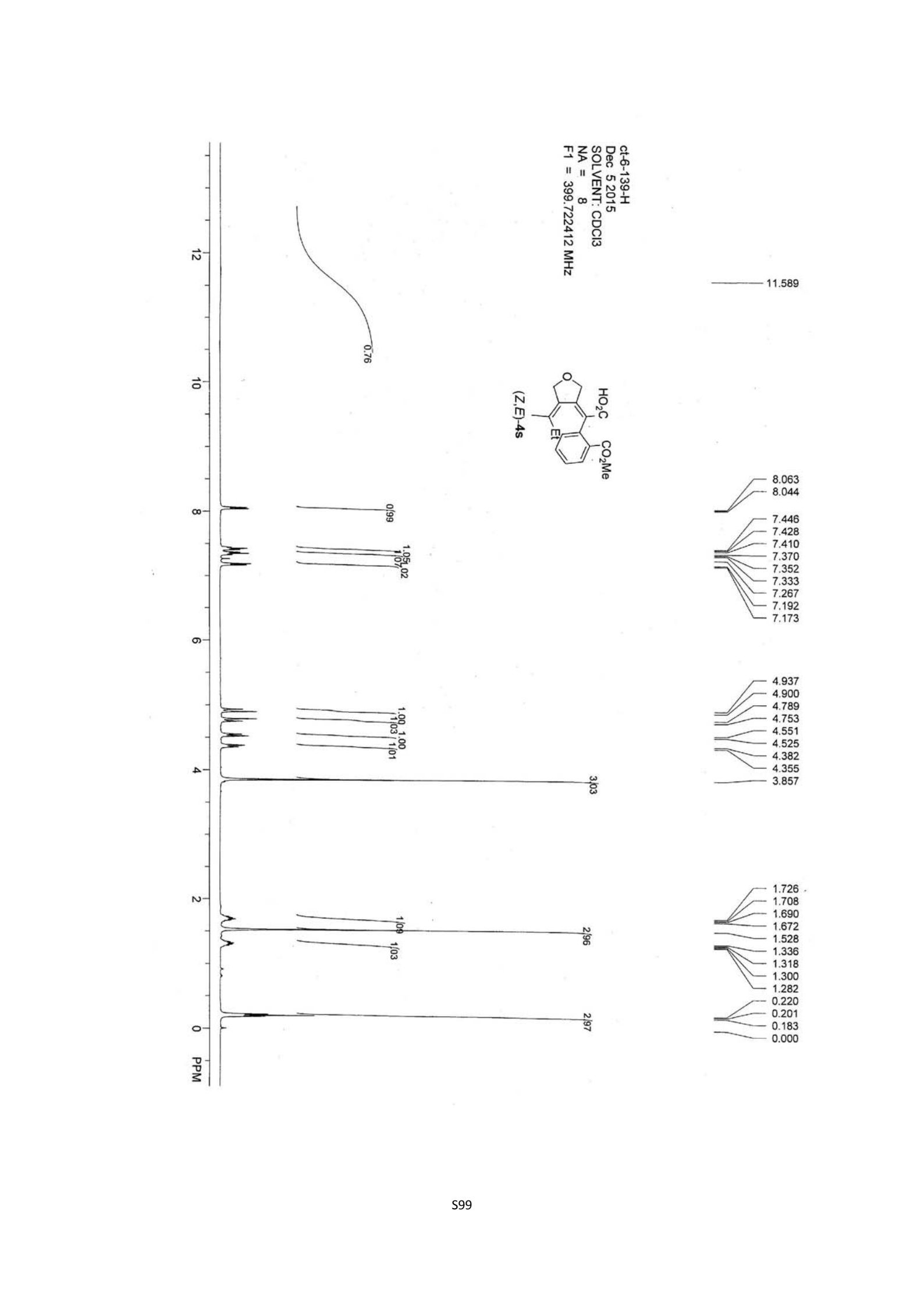

ct-9-84-C
Jul 4 2016
SOLVENT: cdcl3
NA = 160
F1 = 100.520599 MHz
MeO2C
MeO2C
MeO2C
CO2iPr
nBu
(E,Z)-2p
172.393
171.842
167.608
166.127
149.672
141.076
137.675
132.704
131.885
130.293
130.263
129.906
128.923
127.175
77.313
77.000
76.680
68.590
56.080
52.813
52.709
51.422
40.690
37.200
34.848
28.344
22.509
21.757
21.661
18.758
13.809
200
150
100
50
0
PPM

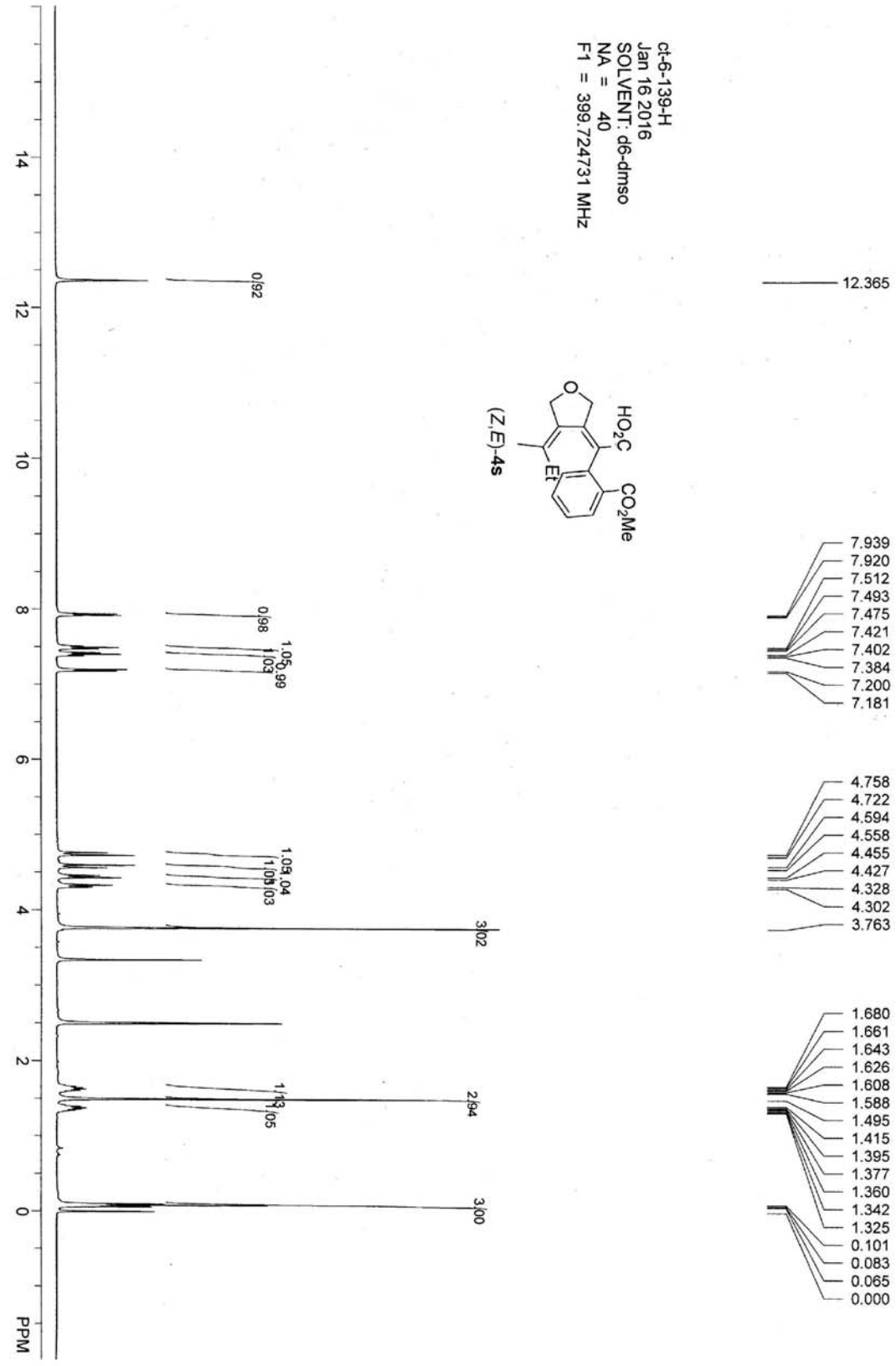

ct-9-75-H
Jul 11 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E,Z)-2q
MeO2C
MeO2C
MeO2C
Et
CO2tBu
7.974
7.956
7.368
7.352
7.333
7.300
7.281
7.263
7.084
7.066
3.743
3.740
3.606
3.559
3.508
3.465
3.093
3.056
2.934
2.897
1.846
1.828
1.811
1.793
1.774
1.532
1.511
1.318
1.300
1.283
1.265
1.247
0.235
0.217
0.198
0.000
0.96
1.07
1.02
0.97
5.91
4.00
1.02
1.00
1.00
0.97
8.80
2.22
1.12
2.96
8
6
4
2
0
PPM

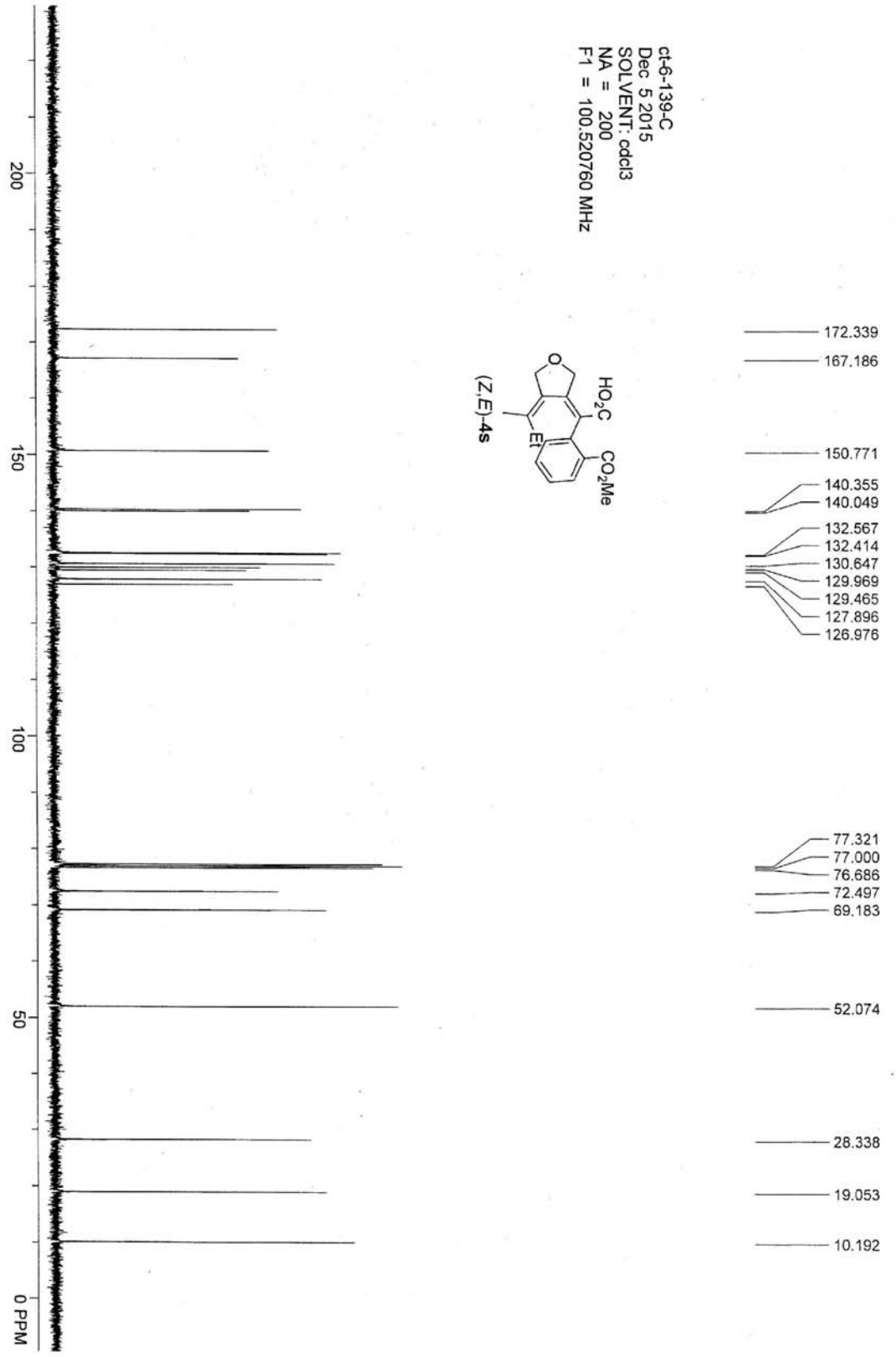

ct-9-75-C
Jul 11 2016
SOLVENT: cdcl3
NA = 80
F1 = 100.520599 MHz
(E,Z)-2q
MeO2C
MeO2C
MeO2C
Et
CO2tBu
172.303
171.790
167.533
165.881
149.501
140.489
138.635
132.511
131.521
131.409
130.293
129.891
129.102
127.145
81.354
77.320
77.000
76.680
56.028
52.746
52.627
51.392
40.616
37.073
27.808
27.540
18.200
10.683
200
150
100
50
0
PPM

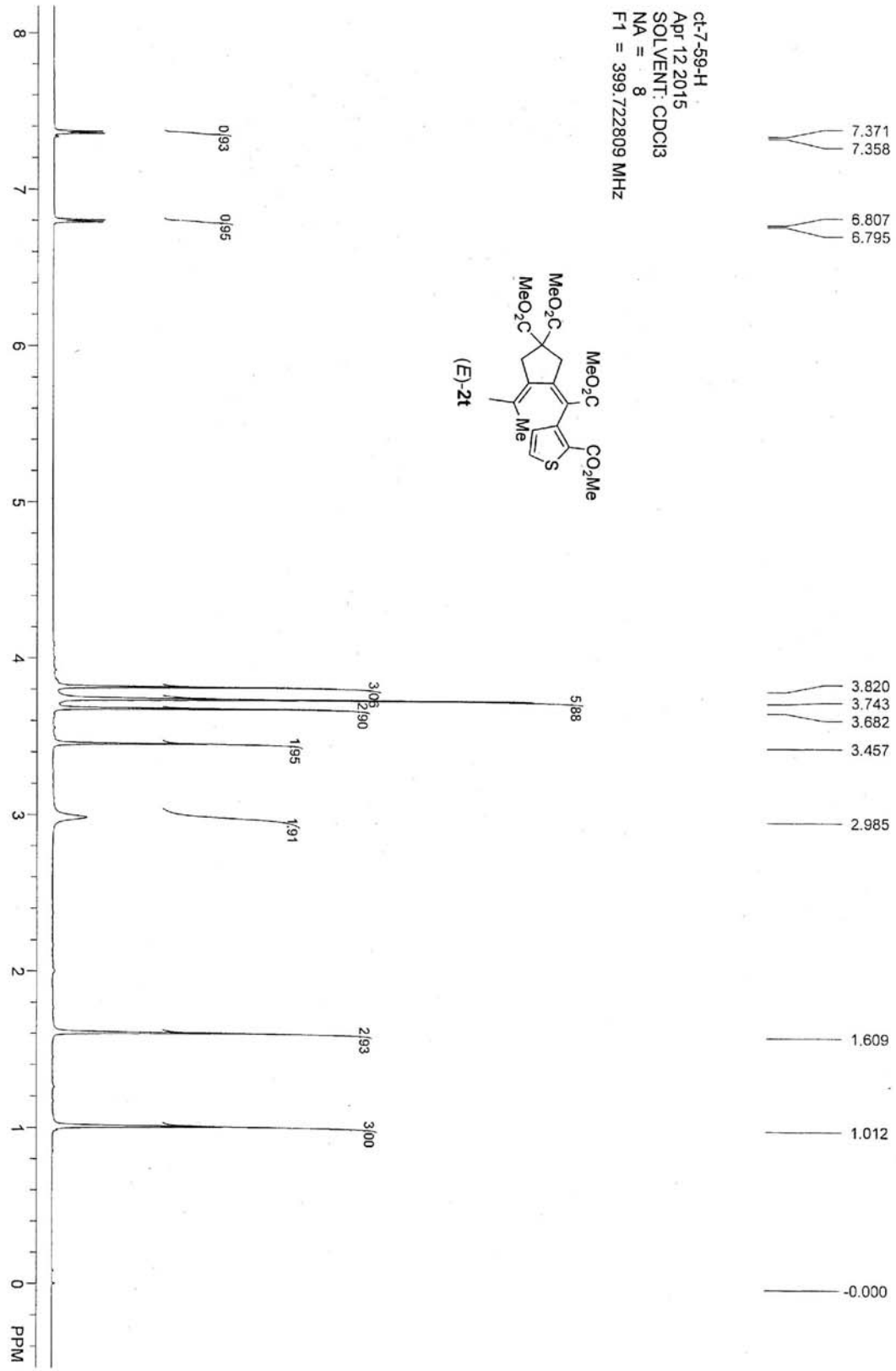

ct-9-85-1-H
Jul 4 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E,Z)-2r
MeO2C
MeO2C
MeO2C
CO2tBu
nBu
7.966
7.964
7.947
7.944
7.370
7.367
7.351
7.348
7.333
7.329
7.305
7.302
7.286
7.283
7.267
7.264
7.095
7.077
3.741
3.737
3.620
3.605
3.564
3.526
3.482
3.111
3.074
2.917
2.880
1.742
1.714
1.692
1.679
1.539
1.513
1.223
1.198
1.174
0.984
0.960
0.942
0.886
0.870
0.858
0.845
0.681
0.664
0.647
0.157
0.128
0.104
0.076
-0.000
0/95
1/02
1.07
0/95
5/86
3/94
0/99
1/000
99
8/89
1/13
3/02
1/02
3/25
2/96
1/01
8
6
4
2
0
PPM

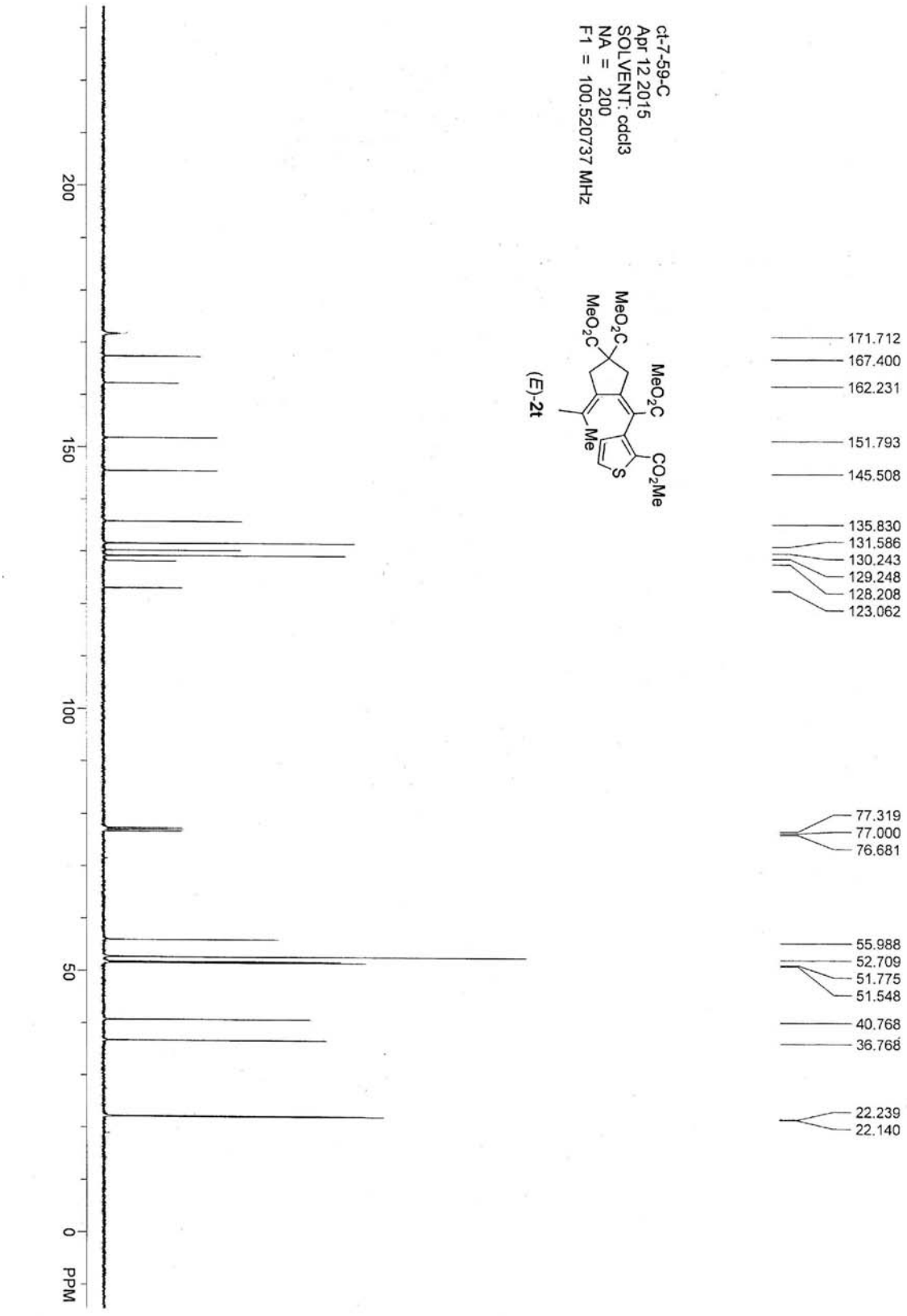

ct-9-85-1-C
Jul 4 2016
SOLVENT: cdcl3
NA = 80
F1 = 100.520599 MHz
(E,Z)-2r
MeO2C
MeO2C
MeO2C
nBu
CO2tBu
172.341
171.805
167.541
165.896
149.501
140.675
137.750
132.563
131.506
131.141
130.248
130.174
128.968
127.122
81.302
77.313
77.000
76.680
56.043
52.761
52.649
51.407
40.668
37.177
34.811
28.224
27.830
22.643
18.780
13.817
200
150
100
50
0
PPM

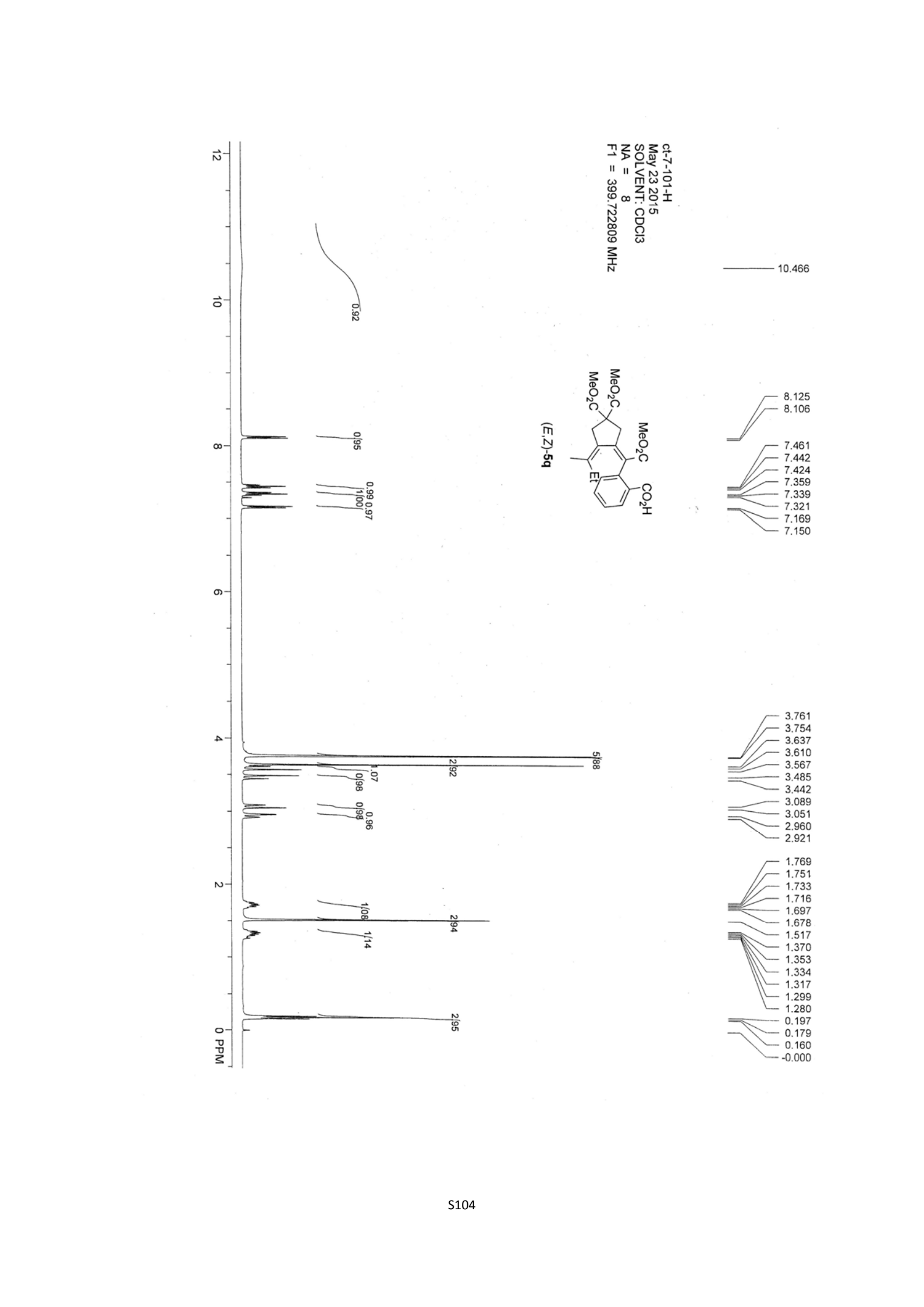

ct-6-139-H
Dec 5 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.722412 MHz
(Z,E)-4s
HO2C
CO2Me
Et
O
11.589
8.063
8.044
7.446
7.428
7.410
7.370
7.352
7.333
7.267
7.192
7.173
4.937
4.900
4.789
4.753
4.551
4.525
4.382
4.355
3.857
1.726
1.708
1.690
1.672
1.528
1.336
1.318
1.300
1.282
0.220
0.201
0.183
0.000
0.76
0.99
1.05
1.02
1.07
1.00
1.03
1.00
1.01
3.03
1.09
1.03
2.96
2.97
12
10
8
6
4
2
0
PPM

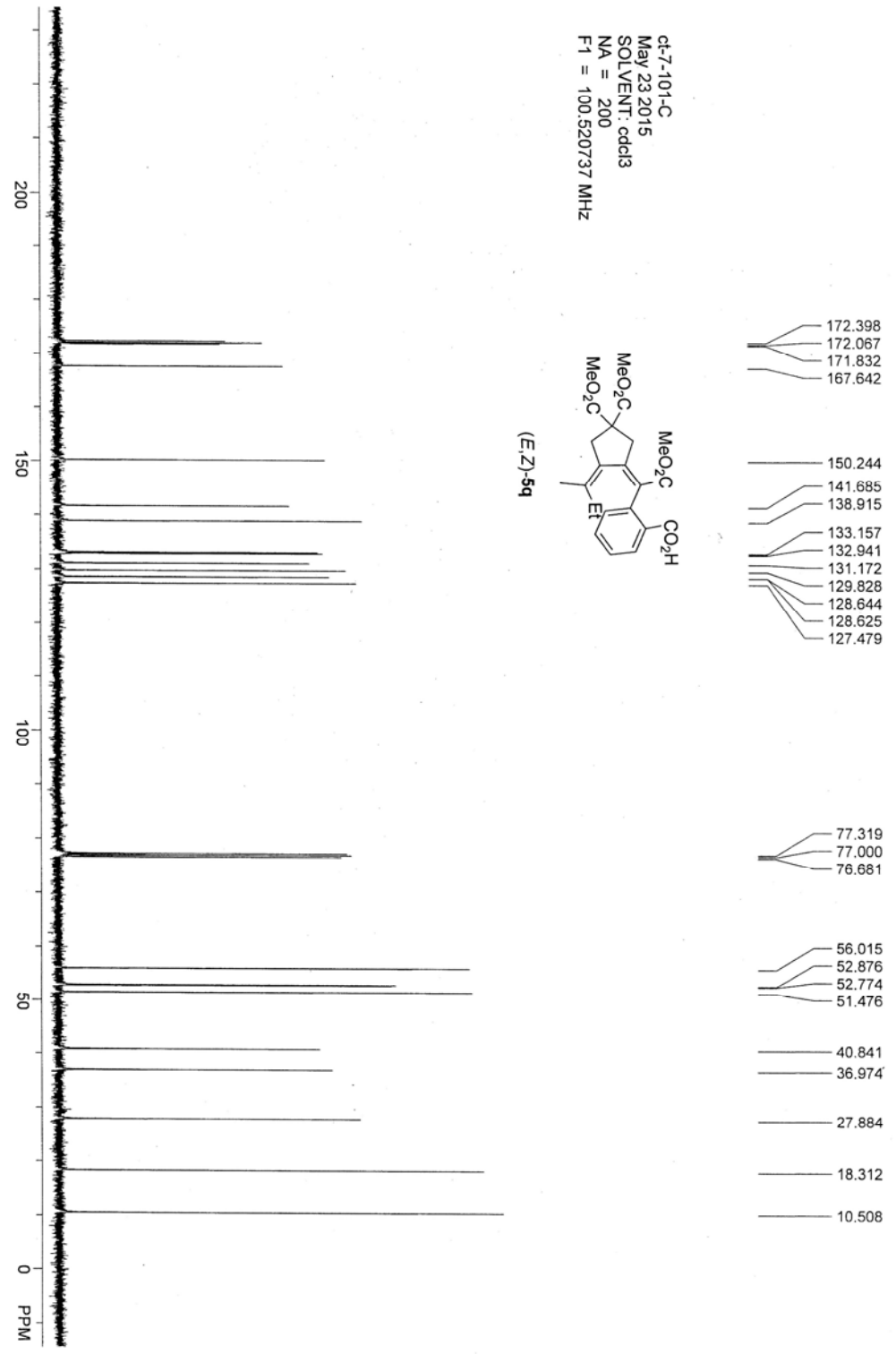

ct-6-139-H
Jan 16 2016
SOLVENT: d6-dmso
NA = 40
F1 = 399.724731 MHz
HO2C
CO2Me
Et
(Z,E)-4s
12.365
7.939
7.920
7.512
7.493
7.475
7.421
7.402
7.384
7.200
7.181
4.758
4.722
4.594
4.558
4.455
4.427
4.328
4.302
3.763
1.680
1.661
1.643
1.626
1.608
1.588
1.495
1.415
1.395
1.377
1.360
1.342
1.325
0.101
0.083
0.065
0.000
0.92
0.98
1.05
0.99
1.03
1.05
1.04
1.05
1.03
3.02
2.94
1.13
1.05
3.00
PPM

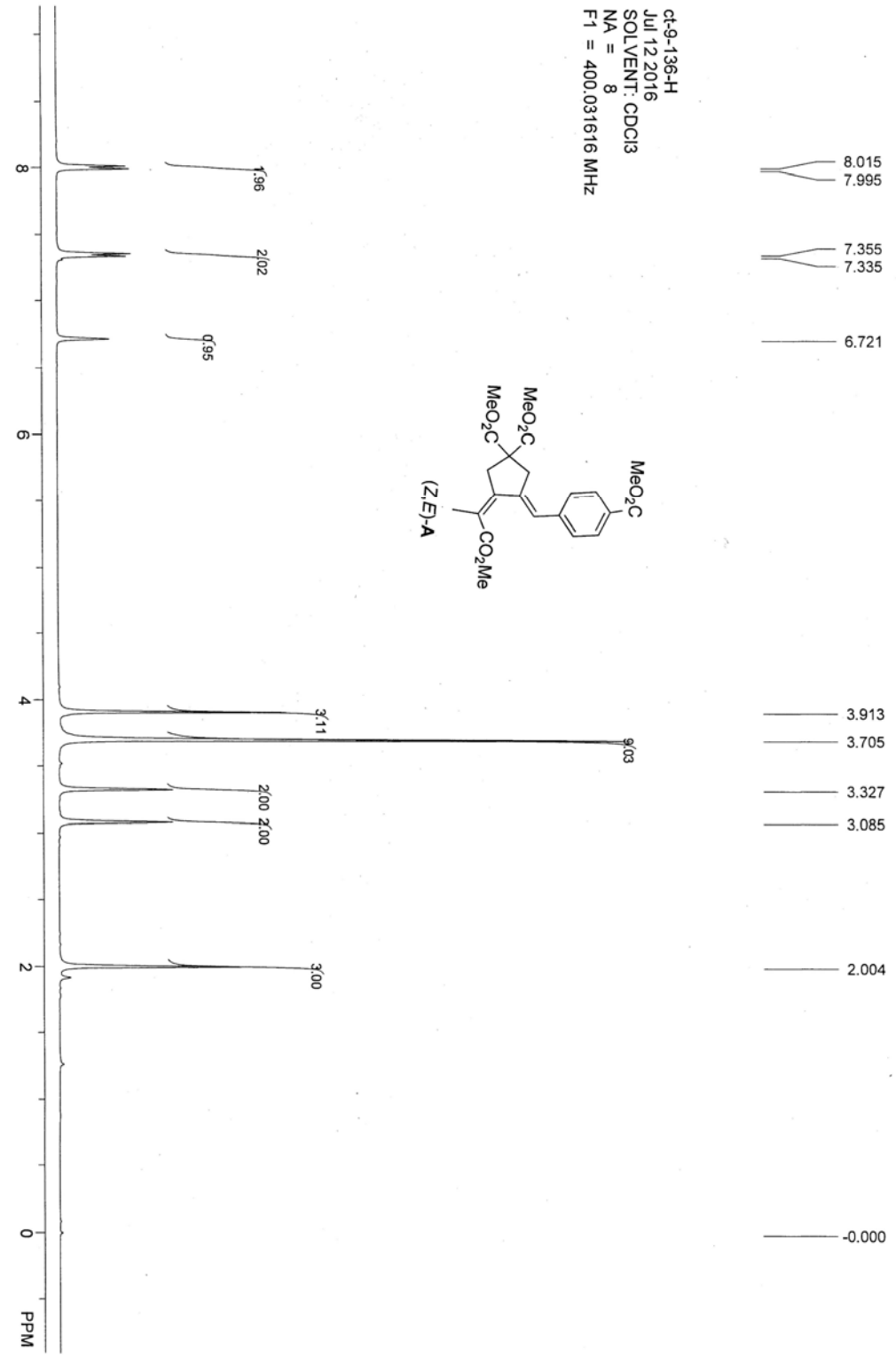

ct-6-139-C
Dec 5 2015
SOLVENT: cdcl3
NA = 200
F1 = 100.520760 MHz
(Z,E)-4s
Et
HO2C
CO2Me
172.339
167.186
150.771
140.355
140.049
132.567
132.414
130.647
129.969
129.465
127.896
126.976
77.321
77.000
76.686
72.497
69.183
52.074
28.338
19.053
10.192
200
150
100
50
0 PPM

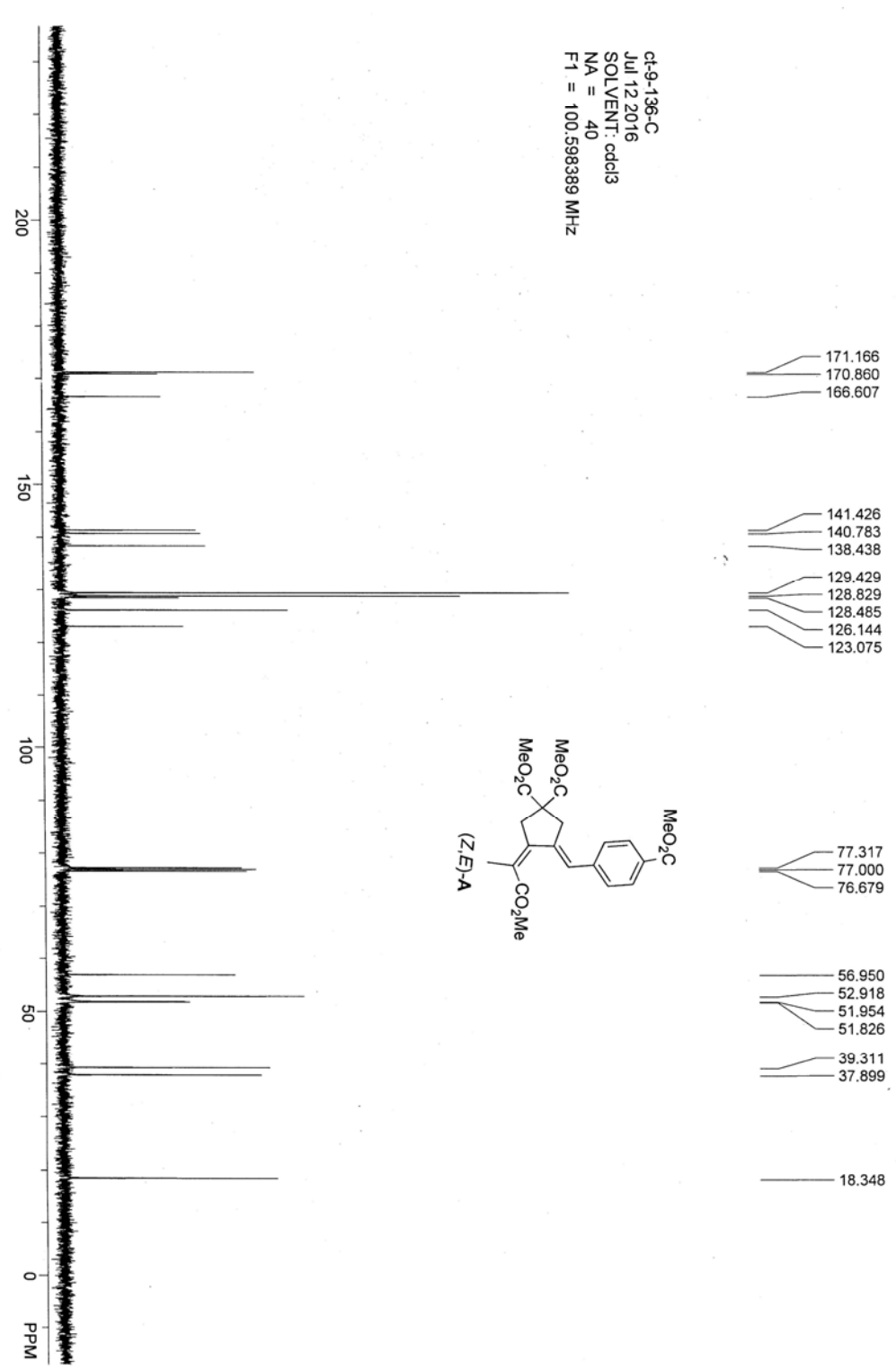

ct-7-59-H
Apr 12 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E)-2t
MeO2C
MeO2C
MeO2C
Me
S
CO2Me
7.371
7.358
6.807
6.795
3.820
3.743
3.682
3.457
2.985
1.609
1.012
-0.000
0.93
0.95
3.06
2.90
5.88
1.95
1.91
2.93
3.00
PPM

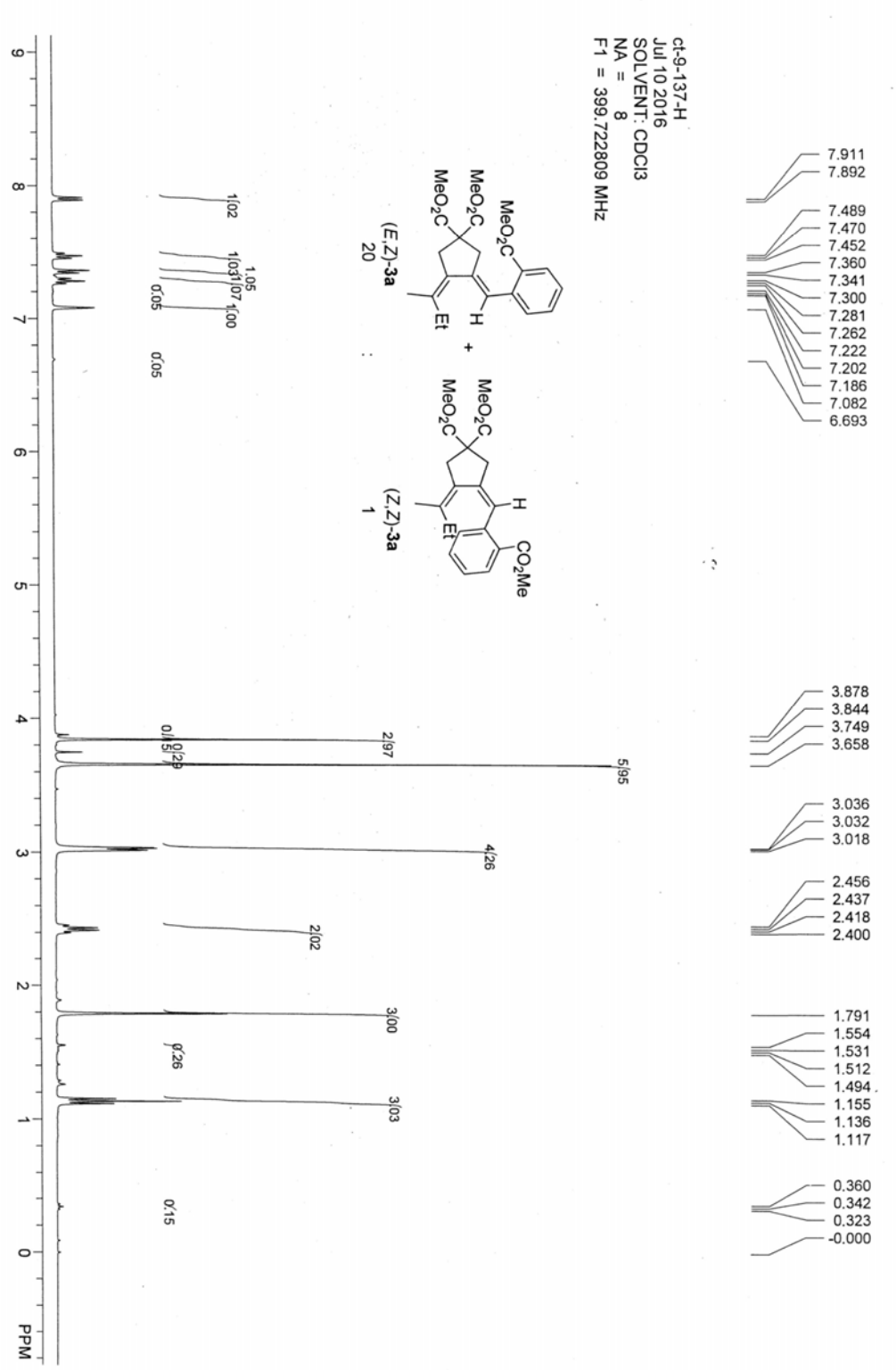

ct-7-59-C
Apr 12 2015
SOLVENT: cdcl3
NA = 200
F1 = 100.520737 MHz
(E)-2t
MeO2C
MeO2C
MeO2C
Me
S
CO2Me
171.712
167.400
162.231
151.793
145.508
135.830
131.586
130.243
129.248
128.208
123.062
77.319
77.000
76.681
55.988
52.709
51.775
51.548
40.768
36.768
22.239
22.140
200
150
100
50
0
PPM

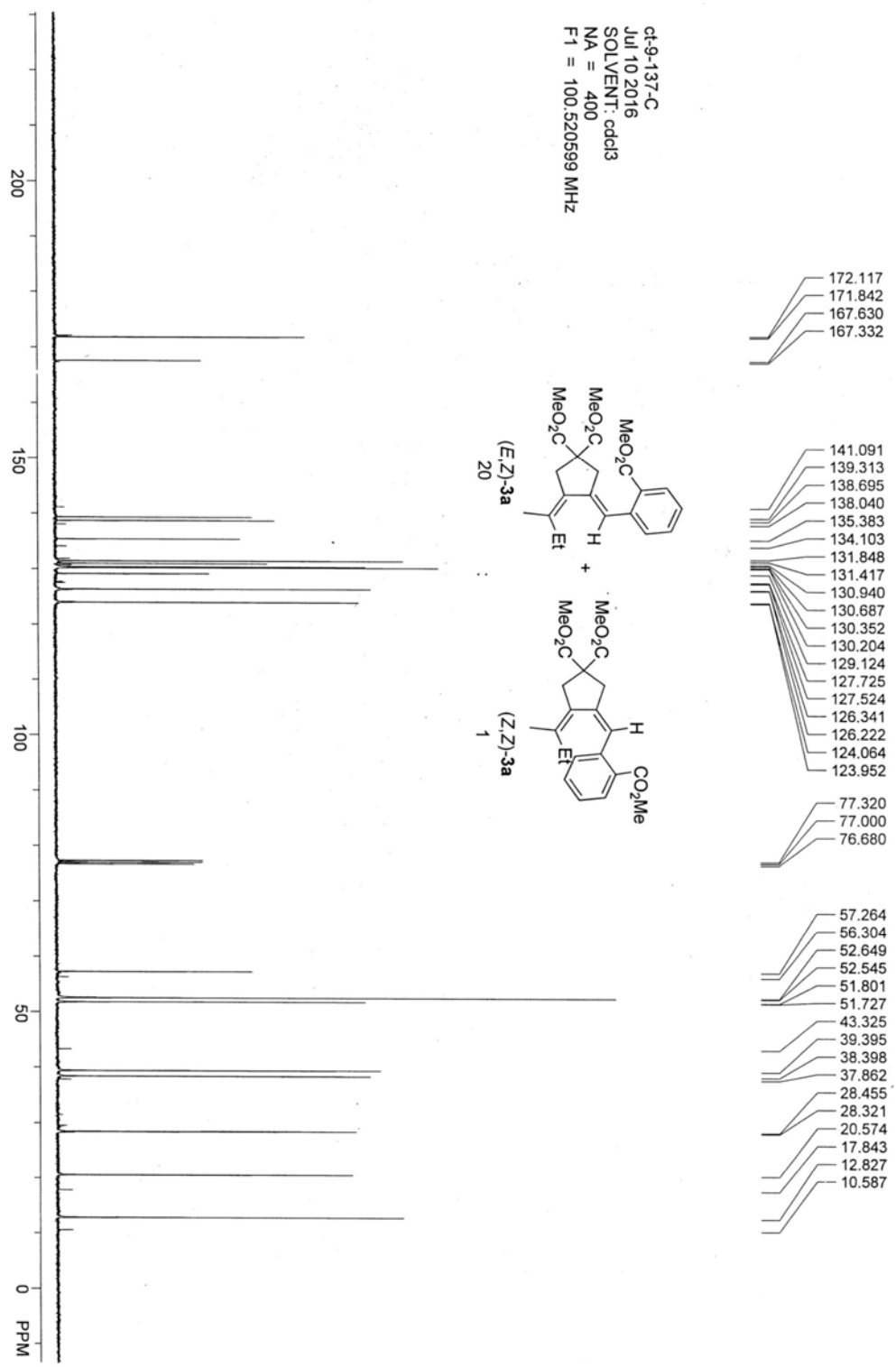

ct-7-101-H
May 23 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E,Z)-5q
MeO2C
MeO2C
MeO2C
Et
CO2H
10.466
8.125
8.106
7.461
7.442
7.424
7.359
7.339
7.321
7.169
7.150
3.761
3.754
3.637
3.610
3.567
3.485
3.442
3.089
3.051
2.960
2.921
1.769
1.751
1.733
1.716
1.697
1.678
1.517
1.370
1.353
1.334
1.317
1.299
1.280
0.197
0.179
0.160
-0.000
0.92
0.95
0.99
0.97
1.00
5.88
2.92
1.07
0.98
0.98
0.96
1.08
1.14
2.94
2.95
12
10
8
6
4
2
0 PPM


ct-7-101-C
May 23 2015
SOLVENT: cdcl3
NA = 200
F1 = 100.520737 MHz
(E,Z)-5q
MeO2C
MeO2C
MeO2C
Et
CO2H
172.398
172.067
171.832
167.642
150.244
141.685
138.915
133.157
132.941
131.172
129.828
128.644
128.625
127.479
77.319
77.000
76.681
56.015
52.876
52.774
51.476
40.841
36.974
27.884
18.312
10.508
200
150
100
50
0
PPM


ct-9-136-H
Jul 12 2016
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz
MeO2C
MeO2C
MeO2C
CO2Me
(Z,E)-A
8.015
7.995
7.355
7.335
6.721
3.913
3.705
3.327
3.085
2.004
-0.000
1.96
2.02
0.95
3.11
9.03
2.00
2.00
3.00
8
6
4
2
0
PPM


ct-9-136-C
Jul 12 2016
SOLVENT: cdcl3
NA = 40
F1 = 100.598389 MHz
171.166
170.860
166.607
141.426
140.783
138.438
129.429
128.829
128.485
126.144
123.075
77.317
77.000
76.679
56.950
52.918
51.954
51.826
39.311
37.899
18.348
200
150
100
50
0
PPM
MeO2C
MeO2C
MeO2C
CO2Me
(Z,E)-A


ct-9-137-H
Jul 10 2016
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz
(E,Z)-3a
20
(Z,Z)-3a
1
7.911
7.892
7.489
7.470
7.452
7.360
7.341
7.300
7.281
7.262
7.222
7.202
7.186
7.082
6.693
3.878
3.844
3.749
3.658
3.036
3.032
3.018
2.456
2.437
2.418
2.400
1.791
1.554
1.531
1.512
1.494
1.155
1.136
1.117
0.360
0.342
0.323
-0.000
PPM


ct-9-137-C
Jul 10 2016
SOLVENT: cdcl3
NA = 400
F1 = 100.520599 MHz
(E,Z)-3a
20
:
(Z,Z)-3a
1
MeO2C
MeO2C
Et
H
CO2Me
172.117
171.842
167.630
167.332
141.091
139.313
138.695
138.040
135.383
134.103
131.848
131.417
130.940
130.687
130.352
130.204
129.124
127.725
127.524
126.341
126.222
124.064
123.952
77.320
77.000
76.680
57.264
56.304
52.649
52.545
51.801
51.727
43.325
39.395
38.398
37.862
28.455
28.321
20.574
17.843
12.827
10.587
200
150
100
50
0
PPM

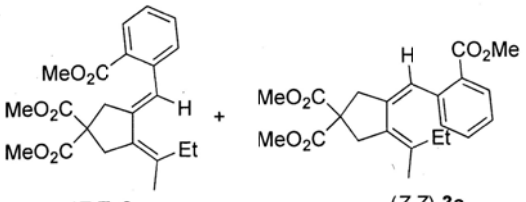
CT-8-88-NOESY

Sample Name:
CT-8-88-NOESY
Data Collected on:
OMC-NMR600-vnmrs600
Archive directory:
/home/omc/vnmrsys/data
Sample directory:
CT-8-88-NOESY_20151214_01
FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Dec 14 2015

Temp. 25.0 C / 298.1 K
Operator: omc

Relax. delay 1.500 sec
Acq. time 0.300 sec
Width 6097.6 Hz
2D Width 6097.6 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 599.7754542 MHz
DATA PROCESSING
Gauss apodization 0.088 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 4096 x 2048
Total time 1 hr, 18 min



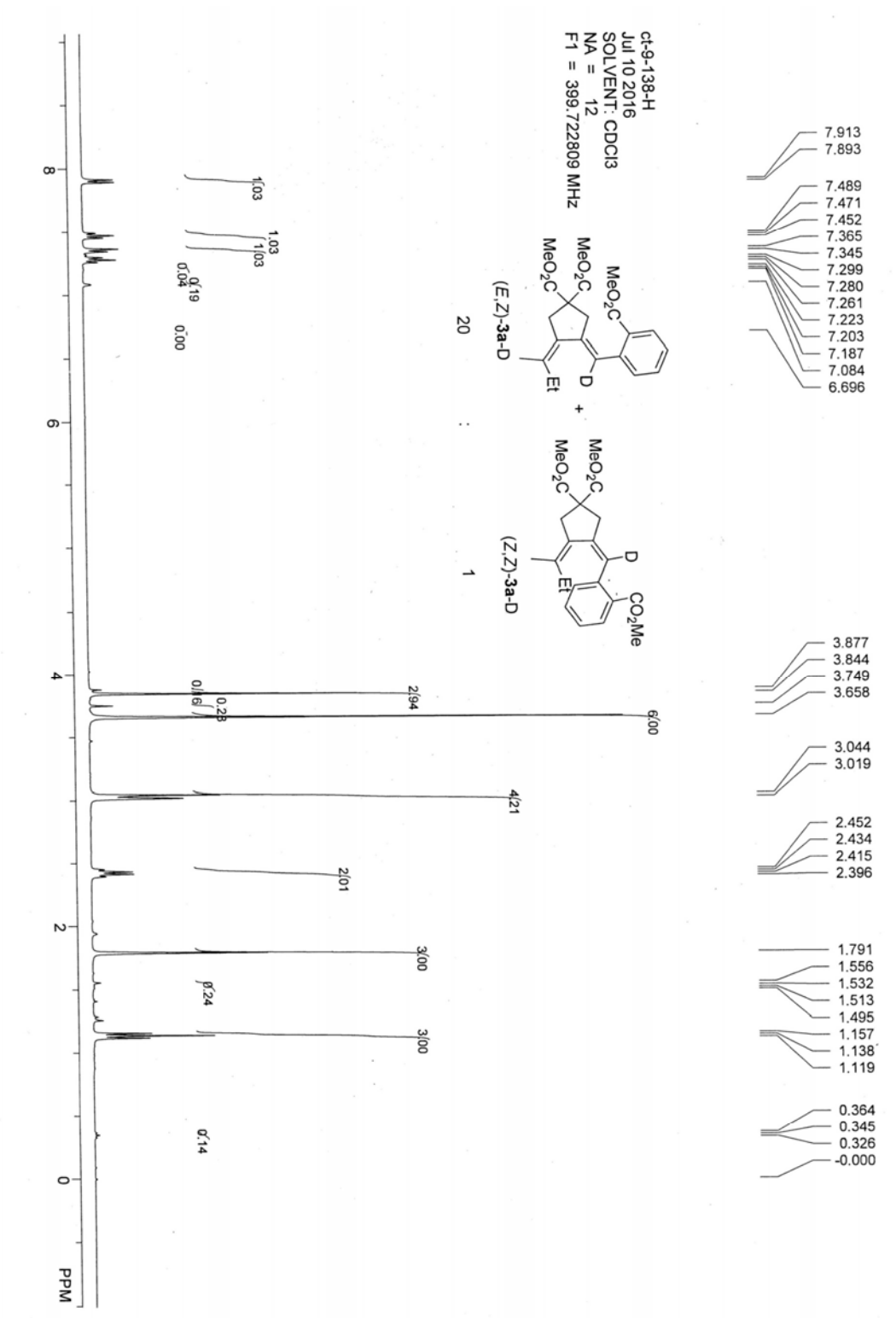
(*E*,*Z*)-**3a**

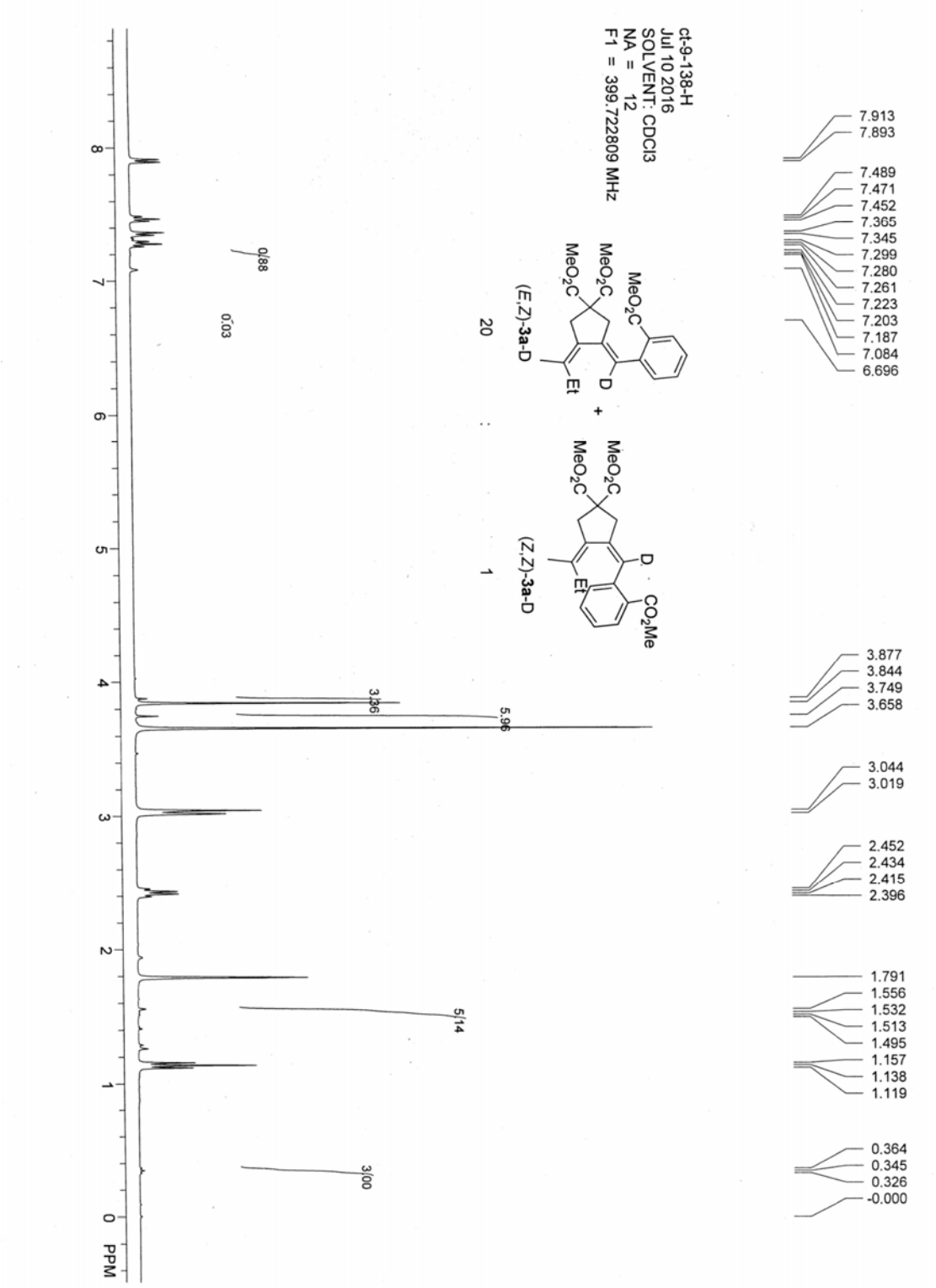
+

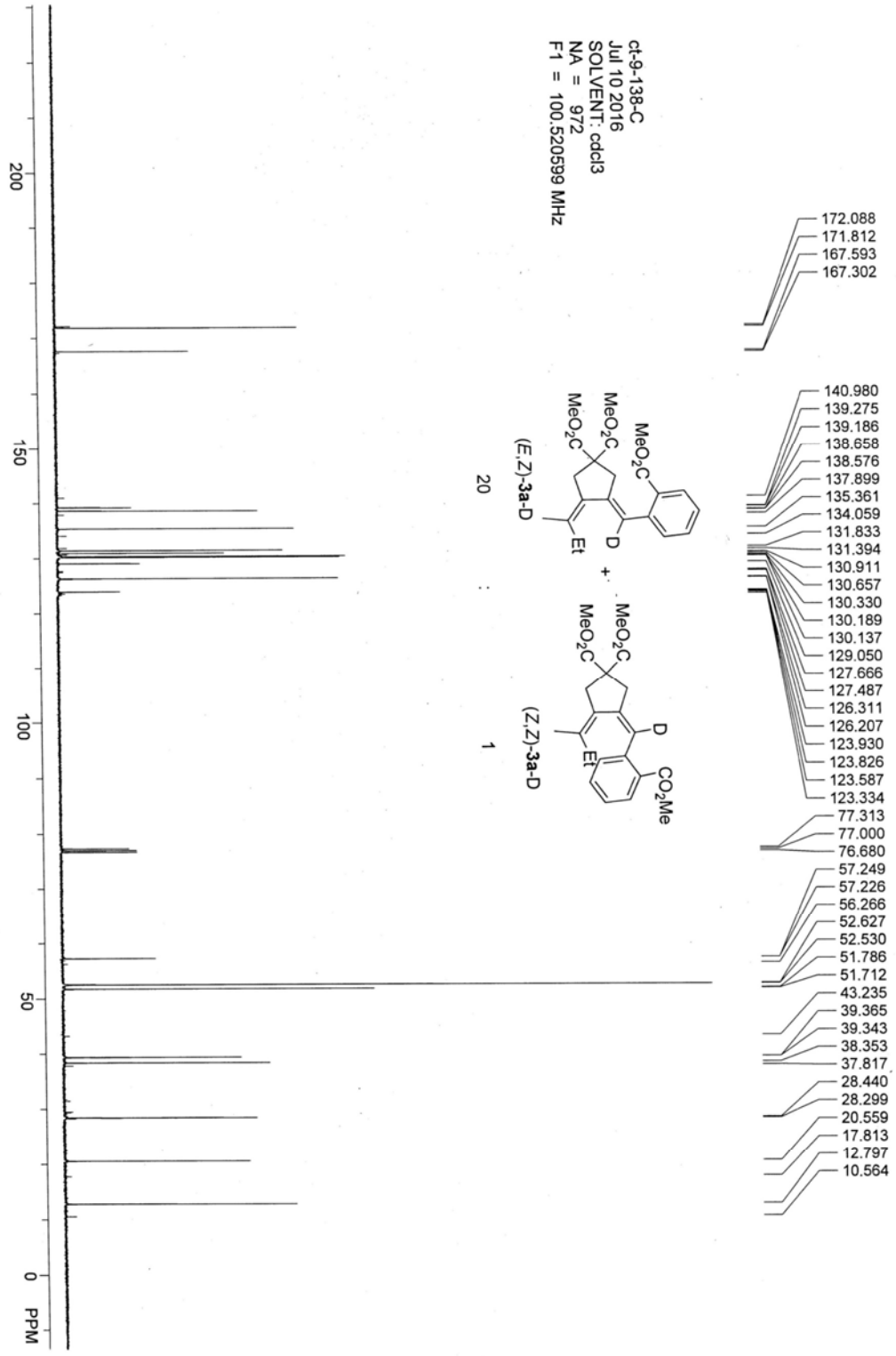
(*Z*,*Z*)-**3a**

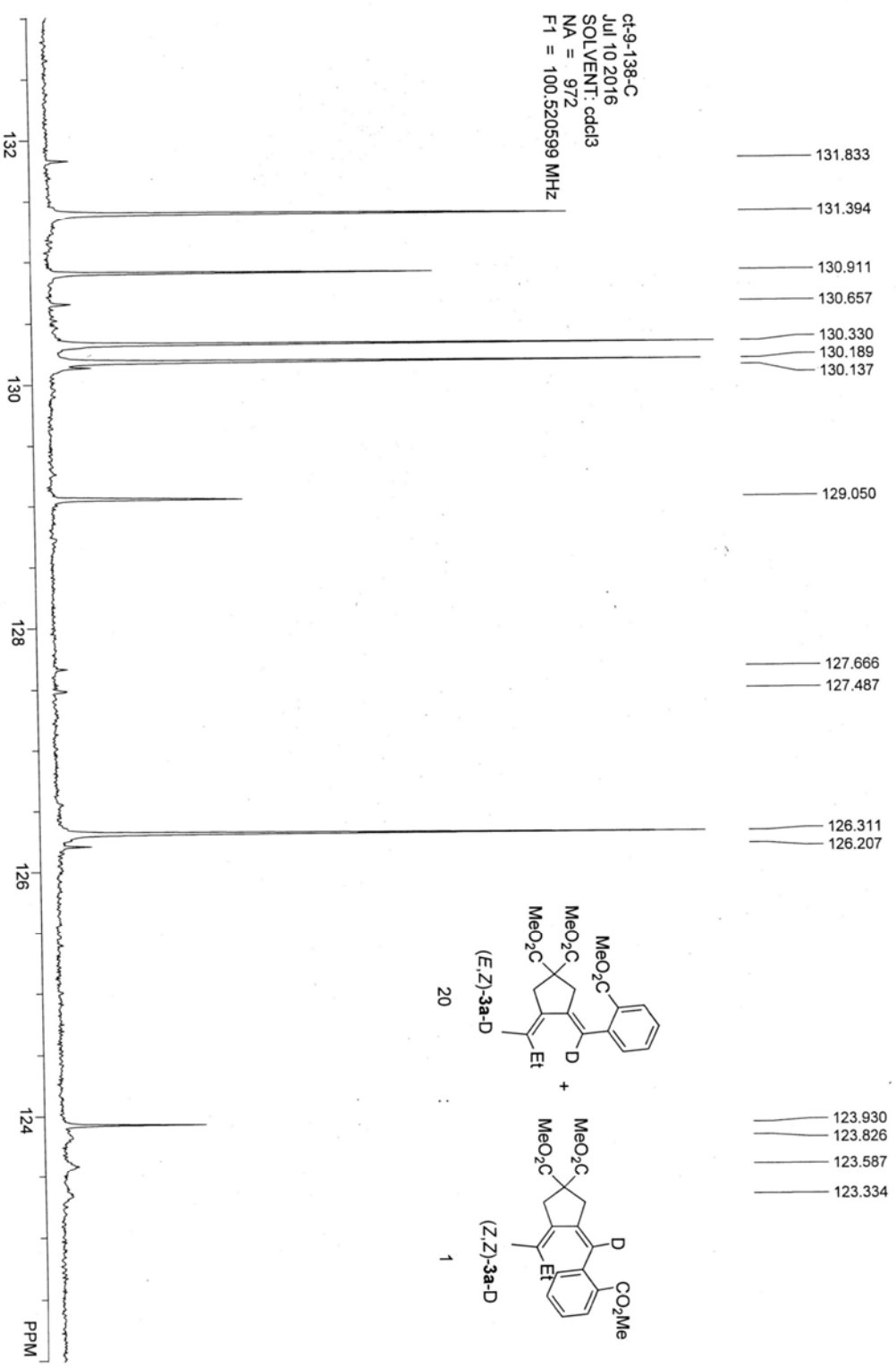
11 : 1

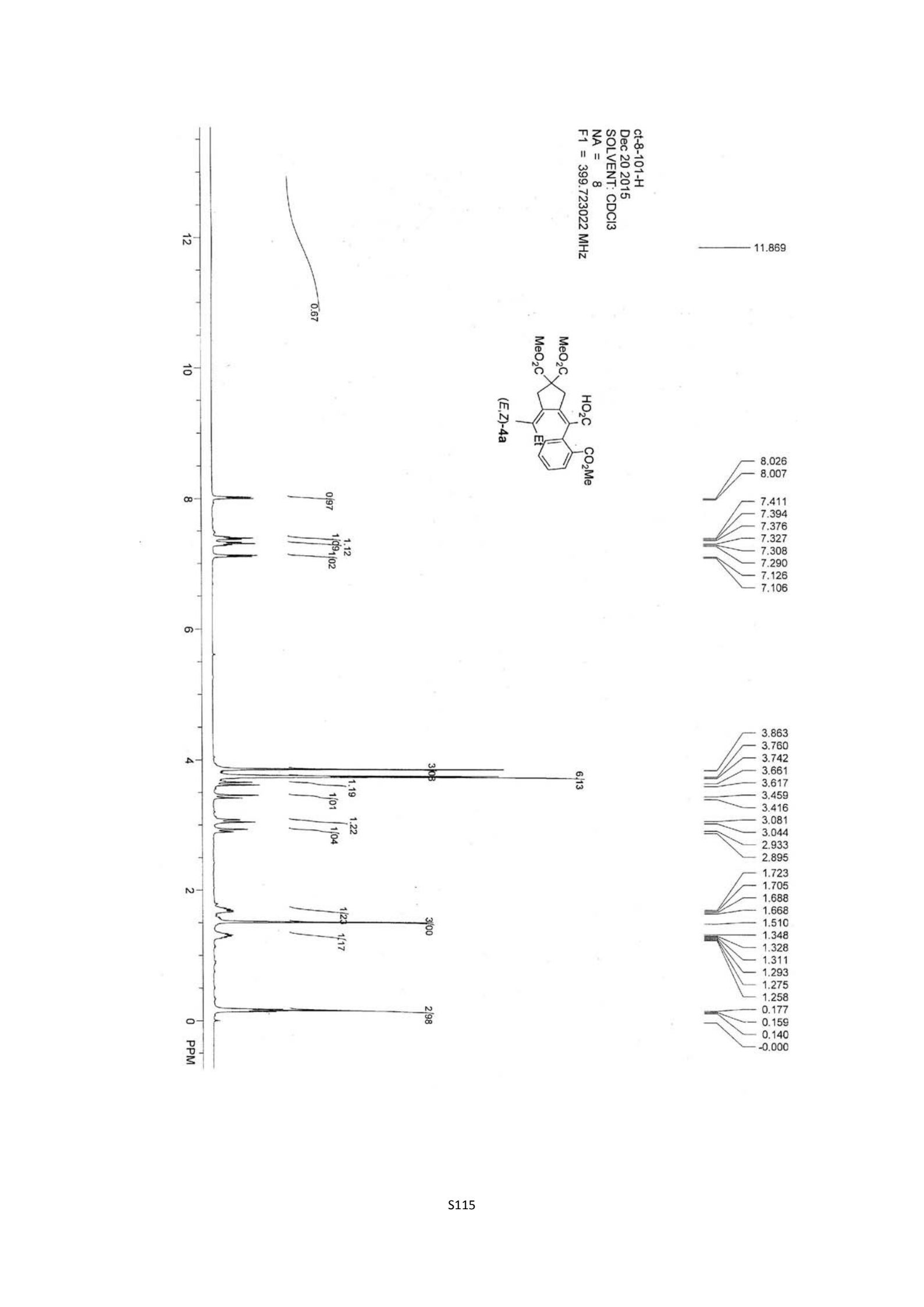
Plotname: --Not assigned--

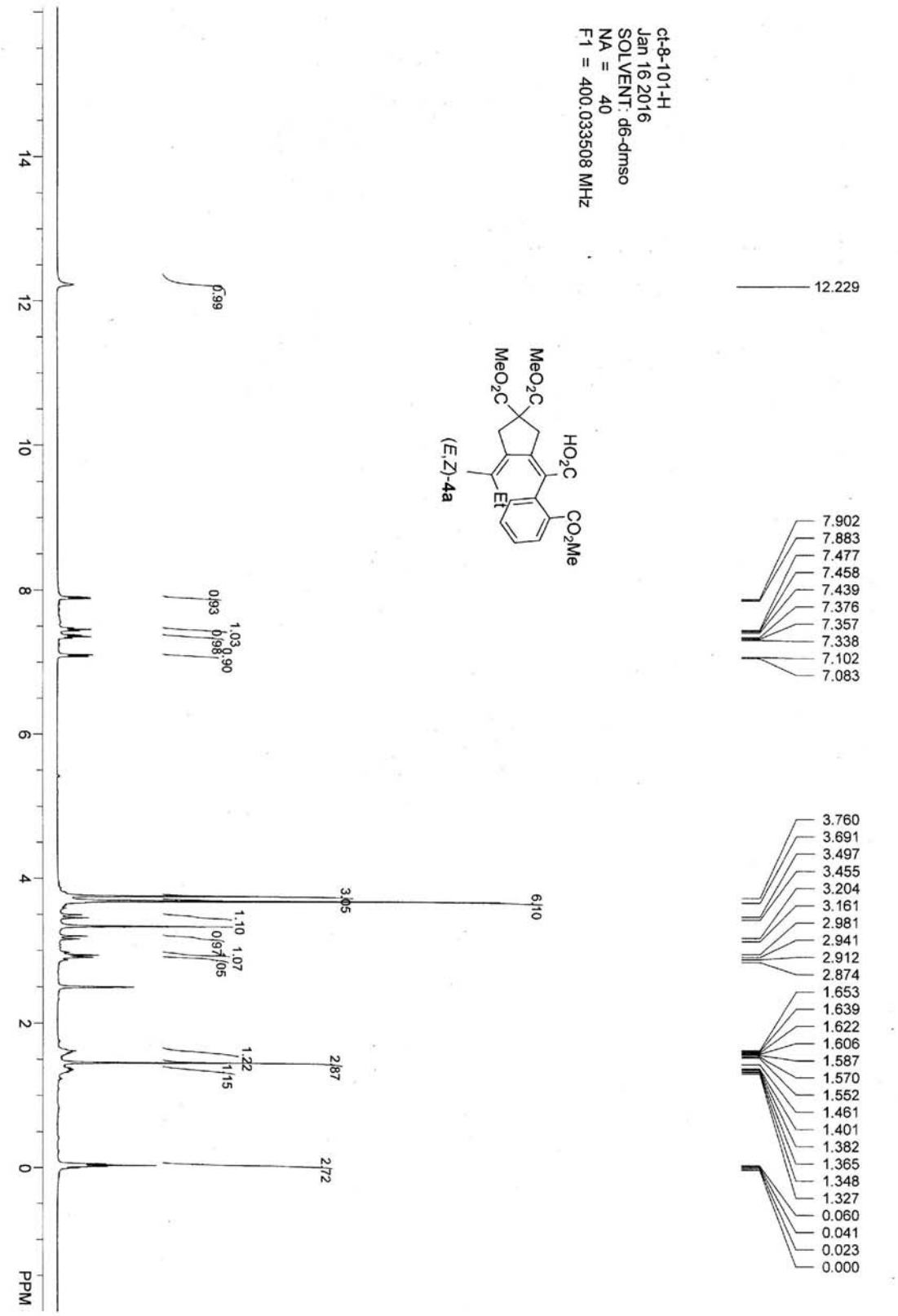

ct-9-138-H
Jul 10 2016
SOLVENT: CDCl3
NA = 12
F1 = 399.722809 MHz
(E,Z)-3a-D
20 : 1
(Z,Z)-3a-D
7.913
7.893
7.489
7.471
7.452
7.365
7.345
7.299
7.280
7.261
7.223
7.203
7.187
7.084
6.696
3.877
3.844
3.749
3.658
3.044
3.019
2.452
2.434
2.415
2.396
1.791
1.556
1.532
1.513
1.495
1.157
1.138
1.119
0.364
0.345
0.326
-0.000
PPM

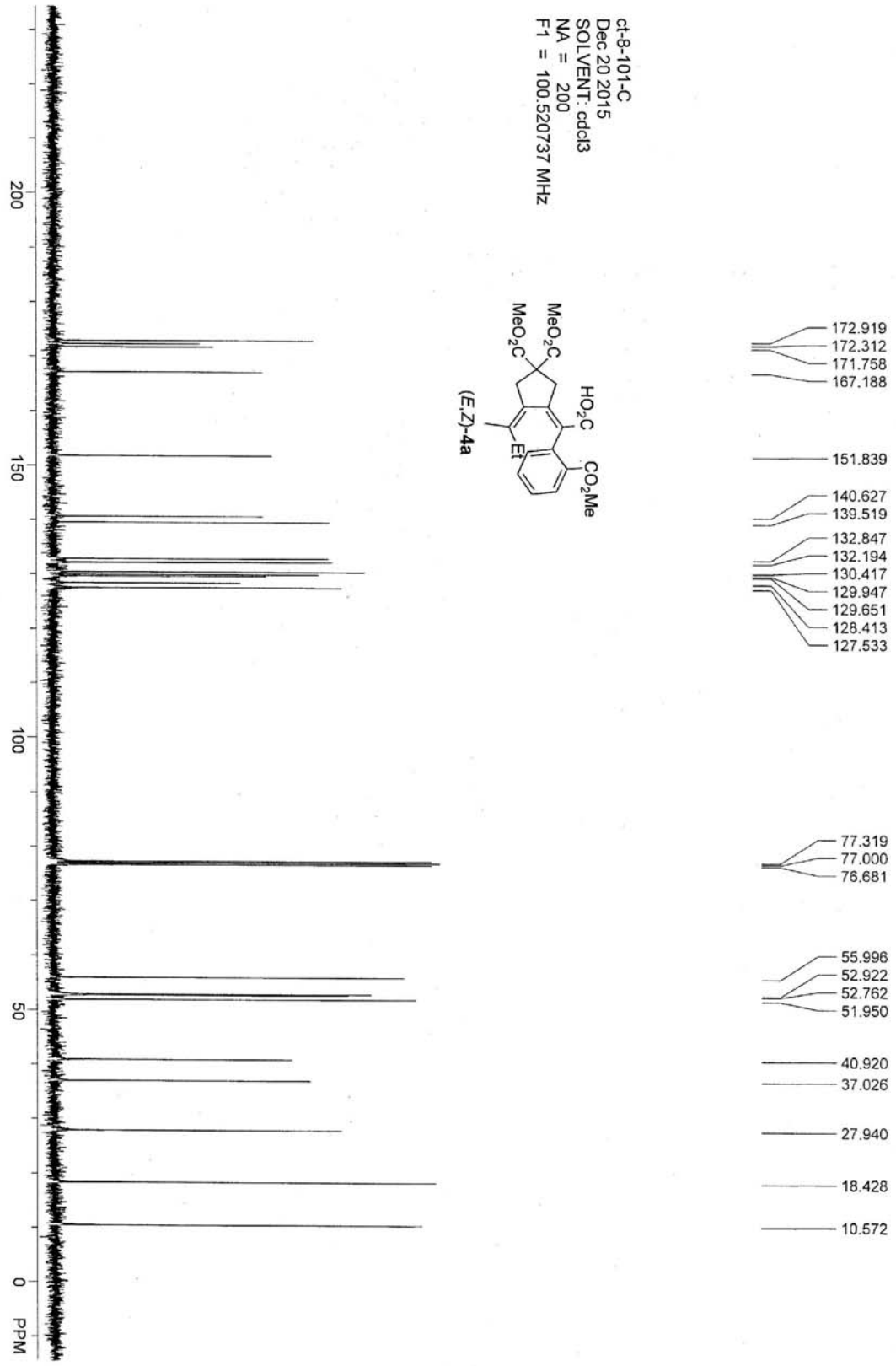

ct-9-138-H
Jul 10 2016
SOLVENT: CDCl3
NA = 12
F1 = 399.722809 MHz
(E,Z)-3a-D
20 : 1
(Z,Z)-3a-D
7.913
7.893
7.489
7.471
7.452
7.365
7.345
7.299
7.280
7.261
7.223
7.203
7.187
7.084
6.696
3.877
3.844
3.749
3.658
3.044
3.019
2.452
2.434
2.415
2.396
1.791
1.556
1.532
1.513
1.495
1.157
1.138
1.119
0.364
0.345
0.326
-0.000
0.88
0.03
3.36
5.96
5.14
3.00
PPM

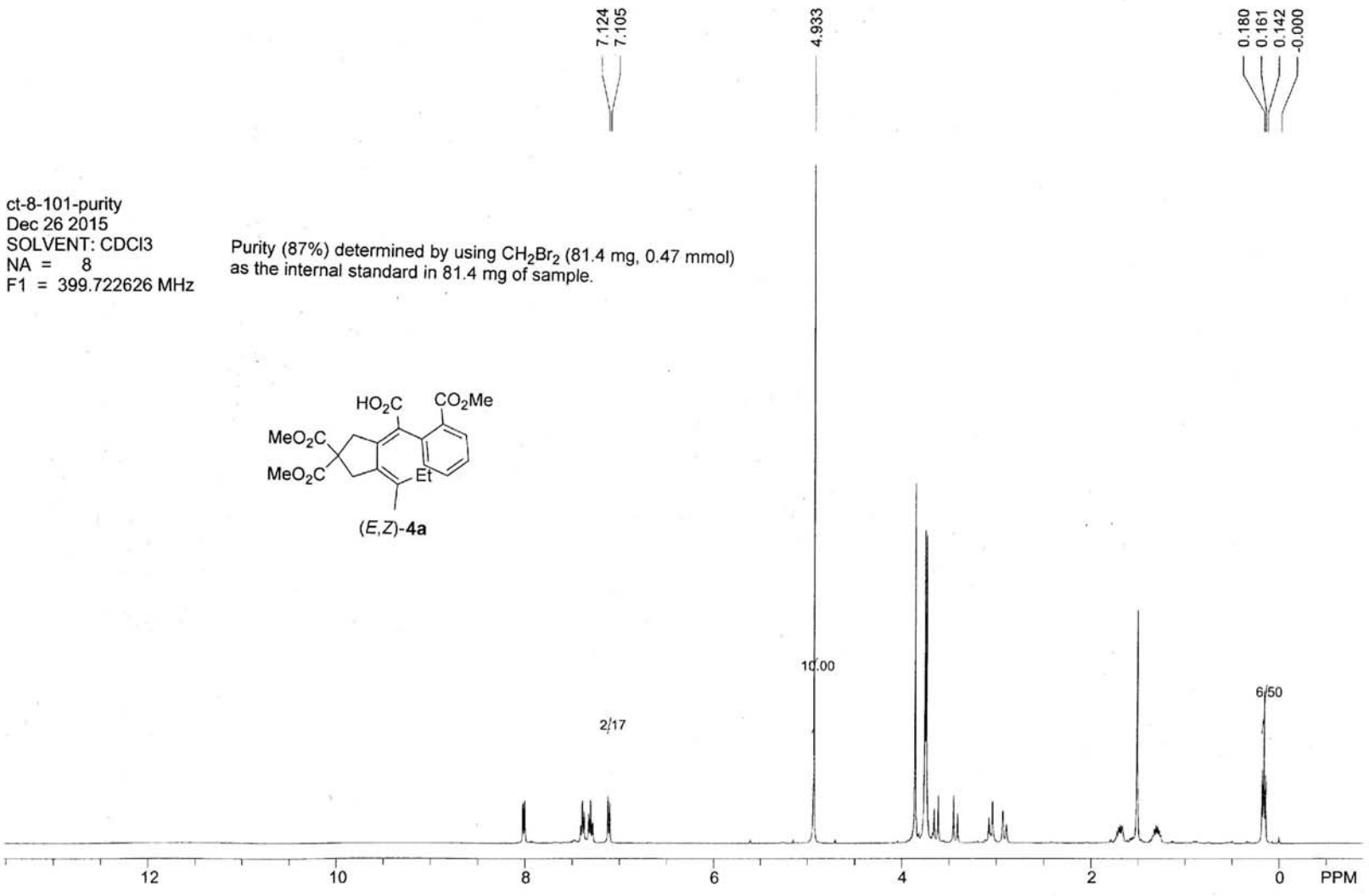

ct-9-138-C
Jul 10 2016
SOLVENT: cdcl3
NA = 972
F1 = 100.520599 MHz
(E,Z)-3a-D
20 : 1
(Z,Z)-3a-D
172.088
171.812
167.593
167.302
140.980
139.275
139.186
138.658
138.576
137.899
135.361
134.059
131.833
131.394
130.911
130.657
130.330
130.189
130.137
129.050
127.666
127.487
126.311
126.207
123.930
123.826
123.587
123.334
77.313
77.000
76.680
57.249
57.226
56.266
52.627
52.530
51.786
51.712
43.235
39.365
39.343
38.353
37.817
28.440
28.299
20.559
17.813
12.797
10.564
200
150
100
50
0
PPM


ct-9-138-C
Jul 10 2016
SOLVENT: cdcl3
NA = 972
F1 = 100.520599 MHz
131.833
131.394
130.911
130.657
130.330
130.189
130.137
129.050
127.666
127.487
126.311
126.207
123.930
123.826
123.587
123.334
132
130
128
126
124
PPM
20 : 1
(E,Z)-3a-D
(Z,Z)-3a-D
MeO2C
Et
D
CO2Me


ct-8-101-H
Dec 20 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.723022 MHz
(E,Z)-4a
11.869
8.026
8.007
7.411
7.394
7.376
7.327
7.308
7.290
7.126
7.106
3.863
3.760
3.742
3.661
3.617
3.459
3.416
3.081
3.044
2.933
2.895
1.723
1.705
1.688
1.668
1.510
1.348
1.328
1.311
1.293
1.275
1.258
0.177
0.159
0.140
-0.000
0.67
0.97
1.09
1.02
1.12
1.01
1.19
1.04
1.22
6.13
3.03
3.00
1.23
1.17
2.98
PPM


ct-8-101-H
Jan 16 2016
SOLVENT: d6-dmso
NA = 40
F1 = 400.033508 MHz
(E,Z)-4a
MeO2C
MeO2C
HO2C
Et
CO2Me
12.229
7.902
7.883
7.477
7.458
7.439
7.376
7.357
7.338
7.102
7.083
3.760
3.691
3.497
3.455
3.204
3.161
2.981
2.941
2.912
2.874
1.653
1.639
1.622
1.606
1.587
1.570
1.552
1.461
1.401
1.382
1.365
1.348
1.327
0.060
0.041
0.023
0.000
0.99
0.93
1.03
0.98
0.90
6.10
3.05
1.10
0.97
1.07
1.05
1.22
1.15
2.87
2.72
14
12
10
8
6
4
2
0
PPM


ct-8-101-C
Dec 20 2015
SOLVENT: cdcl3
NA = 200
F1 = 100.520737 MHz
MeO2C
MeO2C
HO2C
CO2Me
Et
(E,Z)-4a
172.919
172.312
171.758
167.188
151.839
140.627
139.519
132.847
132.194
130.417
129.947
129.651
128.413
127.533
77.319
77.000
76.681
55.996
52.922
52.762
51.950
40.920
37.026
27.940
18.428
10.572
200
150
100
50
0
PPM


7.124
7.105
4.933
0.180
0.161
0.142
-0.000
ct-8-101-purity
Dec 26 2015
SOLVENT: CDCl3
NA = 8
F1 = 399.722626 MHz
Purity (87%) determined by using CH_2Br_2 (81.4 mg, 0.47 mmol) as the internal standard in 81.4 mg of sample.
HO_2C
CO_2Me
MeO_2C
MeO_2C
Et
(E,Z)-4a
2.17
10.00
6.50
12
10
8
6
4
2
0
PPM