Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


**Supporting Information for**

# β-Lactam and Penicillin Substituted Mesoionic Metal Carbenes Complexes

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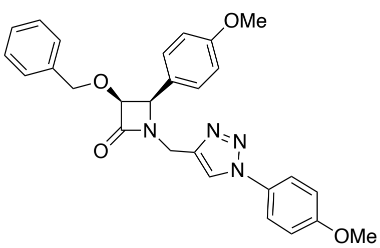
## General methods.

Unless noted otherwise, all manipulations were carried out under argon atmosphere using standard Schlenk techniques. DMF, toluene, $CH_2Cl_2$ and $CH_3CN$ were dried by passage through solvent purification columns containing activated alumina. Other solvents were HPLC grade and were used without purification. All reagents were obtained from commercial sources and used without additional purification, unless noted otherwise. Flash column chromatography was performed using silica gel 60 (Merck, n° 1.09385, 230-400 mesh). $^1H$ and $^{13}C$ NMR spectra were recorded at 400 or 500 MHz ($^1H$ NMR) and at 101 or 126 MHz ($^{13}C$ NMR) using $CDCl_3$ or Acetonitrile-$d_3$ as solvents with the residual solvent signal as internal reference ($CHCl_3$ 7.26 and 77.2 ppm), (Acetonitrile 1.94, and 118.26 and 1.32 ppm). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br (broad). The NMR peak assignments were based on the analysis of $^1H$–$^{13}C$ –HMBC and HSQC recorded spectra along with previously reported data for related compounds. High-resolution mass spectrometry (HRMS) by the ESI technique was performed with an Agilent 6500 accurate mass apparatus with a Q-TOF analyser. IR spectra were recorded on a Perkin-Elmer 681 spectrophotometer. Melting points were determined on a Koffler block.
Compounds **9**,[1] **10b**,[2] **10c**,[3] **11**,[4] and **18**[5] were prepared according to previously described procedures. Benzyloxyacetyl chloride **10a** and Penicillin G potassium salt were obtained from commercial sources and used without further purification.

## General procedure for the synthesis of triazoles.

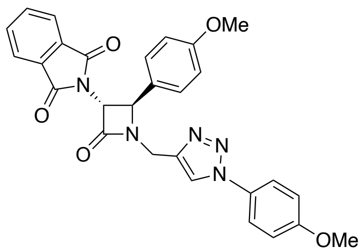
A mixture of organic azide (1.0 equiv), alkyne (1.2 equiv), sodium (L)-ascorbate (0.5 equiv) and $CuSO_4·5H_2O$ (0.25 equiv) in DMF was stirred under argon at rt until completion of the reaction (TLC analysis). The reaction was quenched with water at 0 °C and allowed to reach rt. The mixture was extracted with $CH_2Cl_2$ (x3). The organic layer was dried over $MgSO_4$, filtered, and the solvent removed under *vacuum*. The crude product was purified by column chromatography ($SiO_2$) to afford the pure triazoles ***cis*-12a**, ***cis*-12b**, ***trans*-12c** and **19**.

*Triazole* ***cis-12a***.




Following the general procedure, a mixture of *p*-anisyl azide **11** (75 mg, 0.50 mmol, 1.00 equiv), alkyne ***cis*-8a** (172 mg, 0.53 mmol, 1.10 equiv), sodium (L)-ascorbate (50 mg, 0.25 mmol, 0.50 equiv) and $CuSO_4·5H_2O$ (31 mg, 0.13 mmol, 0.25 equiv) in DMF (5 mL) was stirred under Ar at rt for 3 h. The crude obtained after workup was purified by $SiO_2$ chromatography (Hex/EtOAc 1:4) to yield ***cis*-12a** as a white solid (197 mg, 86%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H, $N_3C$=CH), 7.54 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 7.28 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 7.23 – 7.17 (m, 3H, Ph), 7.02 – 6.95 (m, 4H, 2H *p*-OMe-$C_6H_4$, 2H Ph), 6.89 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 4.85 (d, *J* = 4.3 Hz, 1H, β-lactam *cis*), 4.80 (d, *J* = 15.5 Hz, 1H, N-$CH_2$) 4.80 (d, *J* = 4.3 Hz, 1H, β-lactam *cis*), 4.29 (d, *J* = 11.3 Hz, 1H, O-$CH_2$), 4.21 (d, *J* = 15.5 Hz, 1H, N-$CH_2$), 4.19 (d, *J* = 11.3 Hz, 1H, O-$CH_2$), 3.85 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$), 3.80 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 167.0 (C, C=O), 160.1 (C, *p*-OMe-$C_6H_4$), 160.0 (C, *p*-OMe-$C_6H_4$), 142.6 (C, $N_3C$=CH), 136.5 (C, Ph), 130.4 (C, *p*-OMe-$C_6H_4$), 130.1 (2CH, *p*-OMe-$C_6H_4$), 128.3 (2CH, Ph), 128.3 (2CH, Ph), 128.0 (CH, Ph), 125.5 (C, *p*-OMe-$C_6H_4$), 122.2 (2CH, *p*-OMe-$C_6H_4$), 121.0 (CH, $N_3C$=CH), 114.9 (2CH, *p*-OMe-$C_6H_4$), 114.0 (2CH, *p*-OMe-$C_6H_4$), 83.8 (CH, β-lactam), 72.3 ($CH_2$, O-$CH_2$), 61.9 (CH, β-lactam), 55.7 ($CH_3$, *p*-OMe-$C_6H_4$), 55.4 ($CH_3$, *p*-OMe-$C_6H_4$), 35.4 ($CH_2$, N-$CH_2$). IR (KBr): $\nu_{max}$ 1759, 1611, 1518, 1455, 1304, 1253, 1176, 1045, 1033, 835, 738, 699. $cm^{-1}$. MS (ESI) *m/z* calculated for $C_{27}H_{27}N_4O_4$: 471.2027 $[M+H]^+$; found 471.2018. Mp: 137–139 $^oC$.

*Triazole* ***trans-12c***.



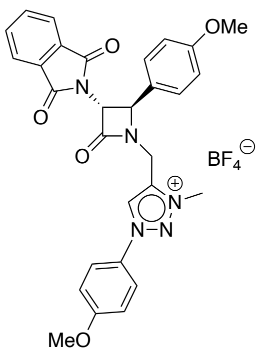

Following the general procedure, a mixture of *p*-anisyl azide **11** (120 mg, 0.8 mmol, 1.0 equiv), alkyne **8c** (317 mg, 0.9 mmol, 1.1 equiv), sodium (L)-ascorbate (78 mg, 0.4 mmol, 0.5 equiv) and $CuSO_4 \cdot 5H_2O$ (49 mg, 0.2 mmol, 0.3 equiv) in DMF (6 mL) was stirred under Ar at rt for 5 h. The crude obtained after workup was purified by $SiO_2$ chromatography (Hex/EtOAc 3:7) to yield ***trans*-12c** as a white solid (358 mg, 89%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H, $N_3C$=CH), 7.89 – 7.81 (m, 2H, Phth), 7.77 – 7.71 (m, 4H, 2H Phth+ 2H *p*-OMe-$C_6H_4$), 7.23 (d, *J* = 8.3 Hz, 2H, *p*-OMe-$C_6H_4$), 7.05 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 6.91 (d, *J* = 8.2 Hz, 2H, *p*-OMe-$C_6H_4$), 5.27 (d, *J* = 2.5 Hz, 1H, β-lactam *trans*), 5.04 (d, *J* = 16.1 Hz, 1H, N-$CH_2$), 4.89 (d, *J* = 2.3 Hz, 1H, β-lactam *trans*), 4.25 (d, *J* = 16.1 Hz, 1H, N-$CH_2$), 3.88 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$), 3.80 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 167.0 (2C, C=O, Phth), 165.0 (C, C=O, β-lactam), 160.5 (C, *p*-OMe-$C_6H_4$), 159.9 (C, *p*-OMe-$C_6H_4$), 142.8 (C, $N_3C$=CH), 134.6 (2CH, Phth), 131.8 (2C, Phth), 130.8 (C, *p*-OMe-$C_6H_4$), 128.2 (2CH, *p*-OMe-$C_6H_4$), 126.8 (C, *p*-OMe-$C_6H_4$), 123.9 (2CH, Phth), 122.2 (2CH, *p*-OMe-$C_6H_4$), 121.5 (CH, $N_3C$=CH), 114.9 (2CH, *p*-OMe-$C_6H_4$), 114.8 (2CH, *p*-OMe-$C_6H_4$), 62.6 (CH, β-lactam), 60.2 (CH, β-lactam), 55.8 ($CH_3$, *p*-OMe-$C_6H_4$), 55.5 ($CH_3$, *p*-OMe-$C_6H_4$), 36.6 ($CH_2$, N-$CH_2$). IR (KBr): $\nu_{max}$ 1767, 1720,1612, 1518, 1392, 1253, 1179, 1104, 1033, 834, 717, 530 $cm^{-1}$. MS (ESI) *m/z* calculated for $C_{28}H_{24}N_5O_5$: 510.1772 $[M+H]^+$; found 510.1761. Mp: 168–170 $^oC$.

**General procedure for the synthesis of triazolium salts**.

***Method A.*** A mixture of triazole (1.0 equiv) and Meerwein's salt (1.3 equiv) in $CH_2Cl_2$ was stirred under argon at rt until reaction completion (TLC analysis). The reaction was quenched with some drops of methanol. The solvent was removed under *vacuum* and the resulting residue was dissolved in the minimum amount of $CH_2Cl_2$ and precipitated with $Et_2O$. The solvents were decanted, and the solid was washed with $Et_2O$ (x3) and *vacuum*-dried to yield pure triazolium salts ***cis*-13b** and ***trans*-13c**.

***Method B.*** MeOTf (0.9 equiv) was added to a $CH_2Cl_2$ solution of triazole (1.0 equiv) at 0 ˚C. The mixture was stirred at 0 ˚C for 4h, until no evolution of the reaction was observed. The solvent was removed under *vacuum* and the resulting residue was dissolved in the minimum amount of $CH_2Cl_2$ and precipitated with $Et_2O$. The solvents were decanted and the solid was washed with $Et_2O$ (x3) and *vacuum*-dried to yield the pure triazolium salts ***cis*-13a** and **20**.

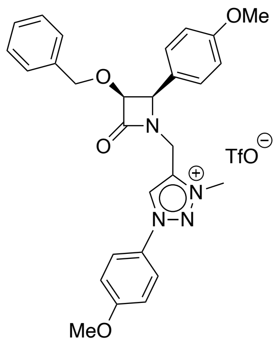
*Triazolium salt* ***trans-13c****.*




Following *Method A*, treatment of **12c** (120 mg, 0.2 mmol, 1.0 equiv) with $Me_3OBF_4$ (45 mg, 0.3 mmol, 1.3 equiv) in $CH_2Cl_2$ (8 mL) afforded pure ***trans*-13c** as a light pink solid (127 mg, 88%). $^1H$ NMR (400 MHz, Acetonitrile-$d_3$): δ 8.82 (s, 1H, $N_3C$=CH), 7.90 – 7.81 (m, 4H, Phth), 7.78 (d, *J* = 9.1 Hz, 2H, *p*-OMe-$C_6H_4$), 7.39 (d, *J* = 8.6 Hz, 2H, *p*-OMe-$C_6H_4$), 7.23 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 6.97 (d, *J* = 8.6 Hz, 2H, *p*-OMe-$C_6H_4$), 5.27 (d, *J* = 2.0 Hz, 1H, β-lactam *trans*), 5.10 – 4.99 (m, 2H, 1H β-lactam *trans* + 1H N-$CH_2$), 4.44 (d, *J* = 17.1 Hz, 1H, N-$CH_2$), 4.32 (s, 3H, $CH_3$, N-$CH_3$), 3.92 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$), 3.77 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$). $^{13}C$ NMR (101 MHz, Acetonitrile-$d_3$): δ 168.3 (2C, C=O, Phth), 165.8 (C, C=O, β-lactam), 163.3 (C, *p*-OMe-$C_6H_4$), 161.5(C, *p*-OMe-$C_6H_4$), 140.7 (C, $N_3C$=CH), 135.9 (2CH, Phth), 132.7 (2C, Phth), 129.7 (2CH, *p*-OMe-$C_6H_4$), 128.9 (C, *p*-OMe-$C_6H_4$), 128.5 (CH, $N_3C$=CH), 127.6 (C, *p*-OMe-$C_6H_4$), 124.5 (2CH, Phth), 124.1 (2CH, *p*-OMe-$C_6H_4$), 116.5 (2CH, *p*-OMe-$C_6H_4$), 115.5 (2CH, *p*-OMe-$C_6H_4$), 63.8 (CH, β-lactam), 61.4 (CH, β-lactam), 56.8 ($CH_3$, *p*-OMe-$C_6H_4$), 56.1 ($CH_3$, *p*-OMe-$C_6H_4$), 39.4 ($CH_3$, N-$CH_3$), 34.3 ($CH_2$, N-$CH_2$).

IR (KBr): $\nu_{max}$ 1770, 1718, 1516, 1392, 1258, 1179, 1057, 1027, 837, 719 $cm^{-1}$. MS (ESI) *m/z* calculated for $C_{29}H_{26}N_5O_5$: 524.1929 $[M]^+$; found 524.1929. Mp: 245–247 $^oC$.

*Triazolium salt **cis-13a**.*

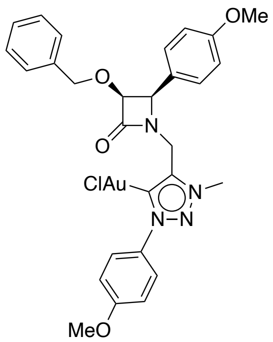



Following *Method B*, treatment of **12a** (277 mg, 0.6 mmol, 1.0 equiv) with MeOTf (80 µL, 0.7 mmol, 1.2 equiv) in $CH_2Cl_2$ (20 mL) afforded pure ***cis*-13a** as a white solid (367 mg, 98%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H, $N_3C$=CH), 7.62 (d, *J* = 9.1 Hz, 2H, *p*-OMe-$C_6H_4$), 7.26 (m, 5H, 3H Ph + 2H *p*-OMe-$C_6H_4$), 7.03 (d, *J* = 9.1 Hz, 2H, *p*-OMe-$C_6H_4$), 7.01 – 6.96 (m, 2H, Ph), 6.76 (d, *J* = 8.3 Hz, 2H, *p*-OMe-$C_6H_4$), 5.04 (d, *J* = 4.1 Hz, 1H, β-lactam *cis*), 5.01 (d, *J* = 4.1 Hz, 1H, β-lactam *cis*), 4.78 (d, *J* = 16.4 Hz, 1H, N-$CH_2$), 4.70 (d, *J* = 16.4 Hz, 1H, N-$CH_2$), 4.35 – 4.26 (m, 4H, 3H N-$CH_3$ + 1H O-$CH_2$), 4.15 (d, *J* = 11.1 Hz, 1H, O-$CH_2$), 3.88 (s, 3H, *p*-OMe-$C_6H_4$), 3.64 (s, 3H, *p*-OMe-$C_6H_4$). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 167.3 (C, C=O), 162.1 (C, *p*-OMe-$C_6H_4$), 160.0 (C, *p*-OMe-$C_6H_4$), 139.5 (C, $N_3C$=CH), 136.1 (C, Ph), 130.3 (2CH, *p*-OMe-$C_6H_4$), 128.3 (2CH, Ph), 128.2 (2CH, Ph), 128.2 (CH, Ph), 128.0 (CH, $N_3C$=CH), 127.4 (C, *p*-OMe-$C_6H_4$), 125.2 (C, *p*-OMe-$C_6H_4$), 122.8 (2CH, *p*-OMe-$C_6H_4$), 115.3 (2CH, *p*-OMe-$C_6H_4$), 113.8 (2CH, *p*-OMe-$C_6H_4$), 84.0 (CH, β-lactam), 72.6 ($CH_2$, O-$CH_2$), 62.4 (CH, β-lactam), 55.9 ($CH_3$, *p*-OMe-$C_6H_4$), 55.1 ($CH_3$, *p*-OMe-$C_6H_4$), 38.2 ($CH_3$, N-$CH_3$), 32.8 ($CH_2$, N-$CH_2$). IR (KBr): $\nu_{max}$ 3065, 2939, 1763, 1611, 1516, 1264, 1177, 1159, 1031, 837, 737, 701, 639, 518 cm$^{-1}$. MS (ESI) *m/z* calculated for $C_{28}H_{29}N_4O_4$: 485.2183 [M]$^+$; found 485.2178. Mp: 72–75 $^o$C.

**General procedure for the synthesis of Au-NHCs**.

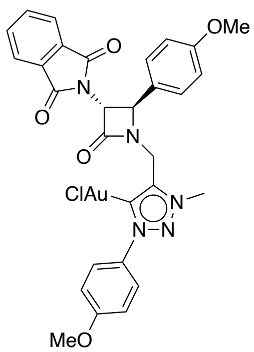
In a Schlenk flask charged with 4 Å molecular sieves, a mixture of triazolium salt (1.0 equiv), $NMe_4Cl$ (1.5 equiv) and $Ag_2O$ (0.8 equiv) was stirred at rt in the dark in a 1:10 $CH_3CN/CH_2Cl_2$ mixture until formation of the corresponding silver carbene ($^1$H NMR analysis). [AuCl($SMe_2$)] complex (1.0 equiv) was then added and the mixture was stirred at rt until the reaction was completed ($^1$H NMR analysis). The mixture was filtered through a pad of Celite and the volatiles were removed under *vacuum* to afford the corresponding carbene complexes ***cis*-14a**, ***cis*-14b** and ***trans*-14c**, which were purified through a short pad of $SiO_2$.

*Au(I) complex* ***cis-14a***.



Following the general procedure, a mixture of ***cis*-13a** (100 mg, 0.2 mmol, 1.0 equiv), $NMe_4Cl$ (26 mg, 0.2 mmol, 1.5 equiv) and $Ag_2O$ (28 mg, 0.1 mmol, 0.8 equiv) in 10:1 $CH_2Cl_2$: $CH_3CN$ (11 mL) was stirred under argon at rt overnight. [AuCl($SMe_2$)] (46 mg, 0.2 mmol, 1.0 equiv) was then added and the mixture was stirred for another 2h. The residue was purified ($SiO_2$, $CH_2Cl_2$/MeOH 98:2) to yield ***cis*-14a** as a white solid (67 mg, 59%). Suitable crystals for X-ray analysis were obtained from a $CHCl_3$/EtOAc/Hexane mixture of solvents. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 7.29 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 7.24 – 7.20 (m, 3H, Ph), 7.00 (dd, *J* = 6.6, 2.9 Hz, 2H, Ph), 6.95 (d, *J* = 9.1 Hz, 2H, *p*-OMe-$C_6H_4$), 6.82 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 5.00 (d, *J* = 4.4 Hz, 1H, β-lactam *cis*), 4.90 (d, *J* = 4.3 Hz, 1H, β-lactam *cis*), 4.49 (d, *J* = 15.9 Hz, 1H, N-$CH_2$), 4.43 (d, *J* = 15.9 Hz, 1H, N-$CH_2$), 4.29 – 4.24 (m, 4H, 3H N-$CH_3$ + 1H O-$CH_2$), 4.17 (d, *J* = 11.3 Hz, 1H, O-$CH_2$), 3.84 (s, 3H, *p*-OMe-$C_6H_4$), 3.75 (s, 3H, *p*-OMe-$C_6H_4$). $^{13}$C NMR (101 MHz, $CDCl_3$): δ 167.2 (C, C=O), 161.1 (C, *p*-OMe-$C_6H_4$), 160.2 (C, *p*-OMe-$C_6H_4$), 159.0 (C, $N_3C$=CAu), 141.6 (C, $N_3C$=CAu), 136.1 (C, Ph), 131.7 (C, *p*-OMe-$C_6H_4$), 130.8 (2CH, *p*-OMe-$C_6H_4$), 128.5 (2CH, Ph), 128.4 (2CH, Ph), 128.2 (CH, Ph), 125.3 (2CH, *p*-OMe-$C_6H_4$), 124.8 (C, *p*-OMe-$C_6H_4$), 114.6 (2CH, *p*-OMe-$C_6H_4$), 114.1 (2CH, *p*-OMe-$C_6H_4$), 83.9 (CH, β-lactam), 72.7 ($CH_2$, O-$CH_2$), 62.5 (CH, β-lactam), 55.8 ($CH_3$, *p*-OMe-$C_6H_4$), 55.4 ($CH_3$, *p*-OMe-$C_6H_4$), 37.5 ($CH_3$, N-$CH_3$), 34.6 ($CH_2$, N-$CH_2$). IR (KBr): $\nu_{max}$ 1757, 1610, 1513, 1252, 1175, 1029, 836 cm$^{-1}$. MS (ESI) *m/z* calculated for $C_{28}H_{28}AuN_4O_4$: 681.1776 $[M\text{-}Cl]^+$; found 681.1853. Mp: 119–122 $^o$C.

*Au(I) complex* ***trans-14c***.



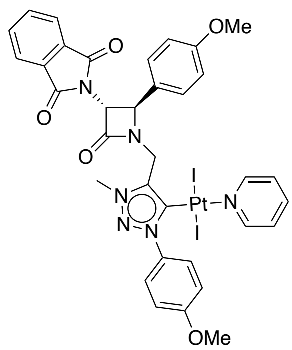
Following the general procedure, a mixture of **13c** (100 mg, 0.2 mmol, 1.0 equiv), $NMe_4Cl$ (27 mg, 0.2 mmol, 1.5 equiv) and $Ag_2O$ (29 mg, 0.1 mmol, 0.8 equiv) in 10:1 $CH_2Cl_2$:$CH_3CN$ (16.5 mL) was stirred under argon at rt overnight. [AuCl($SMe_2$)] (48 mg, 0.2 mmol, 1.0 equiv) was then added and the mixture was stirred for another 3 h. The residue was purified ($SiO_2$, $CH_2Cl_2$/MeOH 98:2) to yield ***trans*-13c** as a brownish white solid (69 mg, 57%).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 7.83 – 7.80 (m, 2H, Phth), 7.76 – 7.72 (m, 2H, Phth), 7.41 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 7.00 (dd, *J* = 8.9, 2.1 Hz, 4H, *p*-OMe-$C_6H_4$), 5.35 (d, *J* = 2.4 Hz, 1H, β-lactam *trans*), 4.90 (d, *J* = 2.4 Hz, 1H, β-lactam *trans*), 4.79 (d, *J* = 15.7 Hz, 1H, N-$CH_2$), 4.48 (s, 3H, $CH_3$, N-$CH_3$), 4.35 (d, *J* = 15.8 Hz, 1H, N-$CH_2$), 3.87 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$), 3.84 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$). **$^{13}$C NMR** (126 MHz, $CDCl_3$): δ 166.9 (2C, C=O, Phth), 165.4 (C, C=O, β-lactam), 161.1 (C, *p*-OMe-$C_6H_4$), 160.9 (C, *p*-OMe-$C_6H_4$), 158.8 (C, $N_3C$=**C**Au), 140.8 (C, $N_3$**C**=CAu), 134.7 (2CH, Phth), 132.0 (C, *p*-OMe-$C_6H_4$), 131.7 (2C, Phth), 129.1 (2CH, *p*-OMe-$C_6H_4$), 125.4 (2CH, *p*-OMe-$C_6H_4$), 125.2,(C, *p*-OMe-$C_6H_4$), 123.9 (2CH, Phth), 115.4 (2CH, *p*-OMe-$C_6H_4$), 114.7 (2CH, *p*-OMe-$C_6H_4$), 62.1 (CH, β-lactam), 60.3 (CH, β-lactam), 55.9 ($CH_3$, *p*-OMe-$C_6H_4$), 55.6 ($CH_3$, *p*-OMe-$C_6H_4$), 38.1 ($CH_3$, N-$CH_3$), 34.7 ($CH_2$, N-$CH_2$). **IR (KBr):** $\nu_{max}$ 1767, 1720, 1514, 1390, 1253, 1176, 1103, 1030, 836, 717 $cm^{-1}$. **MS** (ESI) *m/z* calculated for $C_{29}H_{25}AuN_5O_5$: 720.1516 $[M-Cl]^+$; found 720.1510. **Mp:** (dec.).

**General method for the synthesis of Pd/Pt-NHCs**.

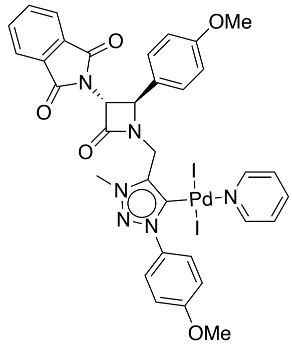
To a mixture of triazolium salt (1.0 equiv), potassium carbonate (1.1 equiv), $[K_2(PtCl_4)]$ or $PdCl_2$ (1.1 equiv) and potassium iodide (5.0 equiv), 5 mL of pyridine were added. The mixture was stirred under argon at 84 °C for 17-48 h. Pyridine was evaporated under vacuum and the residue was diluted with water and extracted with $CH_2Cl_2$. The organic layer was washed with water and brine, dried over anhydrous $Na_2SO_4$ and filtered. The solvent was removed under *vacuum* and the crude product was purified by column chromatography ($SiO_2$) to afford the pure carbenes ***cis*-15**, **16a**, **16b** and **22**.

*Complex **trans-16a**.*



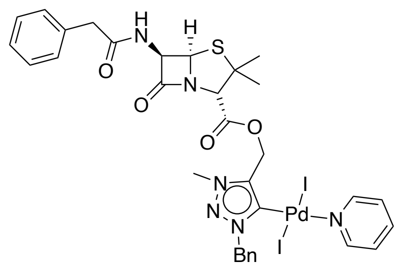
Following the general method, a mixture of triazolium salt ***trans*-13c** (150 mg, 0.2 mmol, 1.0 equiv), $K_2CO_3$ (38 mg, 0.3 mmol, 1.1 equiv), $[K_2(PtCl_4)]$ (112 mg, 0.3 mmol, 1.1 equiv) and KI (66 mg, 0.4 mmol, 5.0 equiv) was stirred in pyridine (5 mL) at 84°C for 48 h, yielding, after purification ($SiO_2$, Hex/EtOAc 2:3), pure ***trans-16a***(44 mg, 17%) as an orange solid. (47 mg of triazole ***trans*-12c** were also recovered during purification as previously described).[6] $^1$H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 8.17 (d, *J* = 5.0 Hz, 2H, Py), 7.87 – 7.82 (m, 2H, Phth), 7.76 – 7.73 (m, 2H, Phth), 7.58 (t, *J* = 7.7 Hz, 1H, Py), 7.53 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 7.13 – 7.08 (m, 2H, Py), 7.06 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 6.97 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 5.38 (d, *J* = 2.1 Hz, 1H, β-lactam *trans*), 5.22 (d, *J* = 15.9 Hz, 1H, N-$CH_2$), 5.13 (d, *J* = 2.2 Hz, 1H, β-lactam *trans*), 5.02 (d, *J* = 15.9 Hz, 1H, N-$CH_2$), 4.45 (s, 3H, $CH_3$, N-$CH_3$), 3.89 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$), 3.87 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 166.8 (2C, C=O, Phth), 165.5 (C, C=O, β-lactam), 160.4 (C, *p*-OMe-$C_6H_4$), 159.9 (C, *p*-OMe-$C_6H_4$), 153.6 (2CH, Py), 139.6 (C, $N_3C$=CPt), 137.1 (CH, Py), 134.6 (2CH, Phth), 133.0 (C, *p*-OMe-$C_6H_4$), 131.8 (2C, Phth), 129.0 (2CH, *p*-OMe-$C_6H_4$), 127.7 (C, *p*-OMe-$C_6H_4$), 127.3 (C, $N_3C$=CPt), 126.8 (2CH, *p*-OMe-$C_6H_4$), 124.6 (2CH, Py), 123.9 (2CH, Phth), 114.7 (2CH, *p*-OMe-$C_6H_4$), 113.7 (2CH, *p*-OMe-$C_6H_4$), 63.7 (CH, β-lactam), 60.9 (CH, β-lactam), 55.7 ($CH_3$, *p*-OMe-$C_6H_4$), 55.5 ($CH_3$, *p*-OMe-$C_6H_4$), 38.1 ($CH_3$, N-$CH_3$), 35.1 ($CH_2$, N-$CH_2$). IR (KBr): $\nu_{max}$ 1767, 1721, 1607, 1514, 1390, 1251, 1175, 834, 716 $cm^{-1}$. MS (ESI) *m/z* calculated for$C_{34}H_{31}I_2N_6O_5Pt$: 1052.0090 $[M+H]^+$; found 1052.010. Mp: 187–189 $^oC$.

*Complex* ***trans-16b***.



Following the general method, a mixture of triazolium salt ***trans*-13c** (100 mg, 0.2 mmol, 1.0 equiv), $K_2CO_3$ (45 mg, 0.3 mmol, 2.0 equiv), $PdCl_2$ (32 mg,0.2 mmol, 1.1 equiv) and KI (135 mg, 0.8 mmol, 5.0 equiv) was stirred in pyridine (4 mL) at 84 $^oC$ for 24 h, yielding, after purification ($SiO_2$, Hex/EtOAc 1:1), pure ***trans-16b*** (79 mg, 50 %) as an orange solid. (Again, a small amount of triazole ***trans*-12c** was observed in the $^1H$ NMR of the crude).[6] Suitable crystals for X-ray analysis were obtained from an EtOAc/Hexane mixture. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 9.0 Hz, 2H, *p*-OMe-$C_6H_4$), 8.10 (d, *J* = 4.8 Hz, 2H, Py), 7.80 – 7.74 (m, 2H, Phth), 7.69 – 7.64 (m, 2H, Phth), 7.56 – 7.50 (m, 1H, Py,), 7.48 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 7.06 – 7.03 (m, 2H, Py,), 7.01 (d, *J* = 8.9 Hz, 2H, *p*-OMe-$C_6H_4$), 6.89 (d, *J* = 8.7 Hz, 2H, *p*-OMe-$C_6H_4$), 5.33 (d, *J* = 2.1 Hz, 1H, β-lactam *trans*), 5.07 (d, *J* = 16.1 Hz, 1H, N-$CH_2$), 5.07 (d, *J* = 2.2 Hz, 1H, β-lactam *trans*), 4.98 (d, *J* = 16.1 Hz, 1H, N-$CH_2$), 4.36 (s, 3H, $CH_3$, N-$CH_3$), 3.82 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$), 3.78 (s, 3H, $CH_3$, *p*-OMe-$C_6H_4$). $^{13}C$ NMR (101 MHz, $CDCl_3$): δ 166.7 (2C, C=O, Phth), 165.4 (C, C=O, β-lactam), 160.6 (C, *p*-OMe-$C_6H_4$), 160.0 (C, *p*-OMe-$C_6H_4$), 153.3 (2CH, Py), 138.8 (C, $N_3C$=CPd), 137.3 (C, $N_3C$=CPd), 137.2 (CH, Py), 134.5 (2CH, Phth), 133.0 (C, *p*-OMe-$C_6H_4$), 131.7 (2C, Phth), 129.1 (2CH, *p*-OMe-$C_6H_4$), 127.2 (C, *p*-OMe-$C_6H_4$), 126.5 (2CH, *p*-OMe-$C_6H_4$), 124.0 (2CH, Py), 123.8 (2CH, Phth), 114.6 (2CH, *p*-OMe-$C_6H_4$), 113.9 (2CH, *p*-OMe-$C_6H_4$), 63.6 (CH, β-lactam), 61.1 (CH, β-lactam), 55.6 ($CH_3$, *p*-OMe-$C_6H_4$), 55.4 ($CH_3$, *p*-OMe-$C_6H_4$), 38.1 ($CH_3$, N-$CH_3$), 35.6 ($CH_2$, N-$CH_2$). IR (KBr): $\nu_{max}$ 1767, 1721, 1514, 1390, 1251, 1175, 834, 716 $cm^{-1}$. MS (ESI) *m/z* calculated for $C_{34}H_{31}N_6O_5I_2Pd$: 962.9487 $[M+H]^+$; found 962.9428. Mp: (dec.).

*Complex* **22**.



Following the general method, a mixture of triazolium salt **20** (150 mg, 0.2 mmol, 1.0 equiv), $K_2CO_3$ (62 mg, 0.5 mmol, 2.0 equiv), $PdCl_2$ (44 mg,0.3 mmol, 1.1 equiv) and KI (185 mg, 1.1 mmol, 5.0 equiv) was stirred in pyridine (2 mL) at 80 ˚C for 17 h, yielding, after purification ($SiO_2$, Hex/AcOEt 1:1), pure **23** (54 mg, 25 %) as an orange solid. $^1$H NMR (500 MHz, $CDCl_3$): δ 8.96 (dt, *J* = 5.0, 1.6 Hz, 2H, Py), 7.72 (tt, *J* = 7.7, 1.7 Hz, 1H, Py), 7.65 (dd, *J* = 7.5, 2.0 Hz, 2H, Py), 7.45 – 7.21 (m, 10H, 2Ph), 6.04 (d, *J* = 9.1 Hz, 1H, NH), 5.95 (s, 2H, N-$CH_2$), 5.67 – 5.60 (m, 2H, 1H β-lactam + 1H O-$CH_2$), 5.57 (d, *J* = 4.2 Hz, 1H, β-lactam), 5.50 (d, *J* = 13.5 Hz, 1H, O-$CH_2$), 4.49 (s, 1H, β-lactam), 4.05 (s, 3H, N-$CH_3$), 3.63 (s, 2H, Ph-$CH_2$), 1.56 (s, 3H, $CH_3$), 1.47 (s, 3H, $CH_3$). $^{13}$C NMR (126 MHz, $CDCl_3$): δ 173.5 (C, C=O, β-lactam), 170.4 (C, C=O, HN-C=O), 167.6 (C, C=O,O-C=O), 154.0 (2CH, Py), 139.9 (C, $N_3C$=**C**Pd), 137.9 (C, $N_3$**C**=CPd), 137.7 (CH, Py), 133.9 (C, Ph), 133.2 (C, Ph), 130.3 (2CH, Py), 129.7 (2CH, Ph), 129.3 (2CH, Ph), 129.2 (CH, Ph), 129.0 (2CH, Ph), 127.8 (CH, Ph), 124.6 (2CH, Ph), 70.4 (CH, β-lactam), 68.2 (CH, β-lactam), 65.0 (C, **C**$(CH_3)_2$), 60.1 ($CH_2$, N-$CH_2$), 58.9 (CH, β-lactam), 57.3 ($CH_2$, O-$CH_2$), 43.6 ($CH_2$, Ph-$CH_2$), 37.5 ($CH_3$, N-$CH_3$), 32.1 ($CH_3$), 27.6 ($CH_3$). IR (KBr): $\nu_{max}$ 1782, 1749, 1678, 1447, 1201, 1180, 1153, 695 $cm^{-1}$. HRMS (ESI) *m/z* calculated for $C_{27}H_{29}I_2N_5O_4PdS$: 879.906 $[M\text{-py} + H]^+$; found 879.915. Mp: 148–152 ˚C. $[\alpha]^{25}_D$ = + 14.01 (*c* 0.40, $CHCl_3$).

## **Catalysis experiments**.

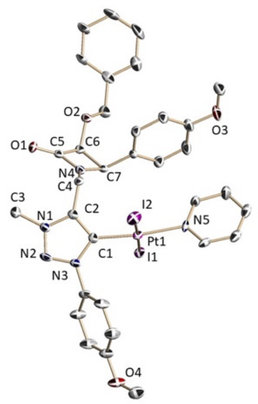
*General procedure for the cycloisomerisation of enyne* **23**.[7]

Gold carbene complex (0.006 mmol, 3 mol%) and Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBArF) (0.006 mmol, 3 mol%) were stirred under Ar in 2 mL of anhydrous $CH_2Cl_2$ for 15 min. A solution of enyne **23** (0.2 mmol, 1.0 equiv) in 2 mL of anhydrous $CH_2Cl_2$ was added in one portion to the resulting slurry. The reaction mixture was stirred at rt until completion of the reaction (TLC). The reaction crude was filtered through a short pad of Celite and $SiO_2$, the solvent was removed under *vacuum* and the residue was purified through a short pad of $SiO_2$.

*General procedure for hydrosilylation of alkynes*.[8]

To a solution of catalyst (5 mg, 0.005 mmol, 1 mol%) in toluene (3 mL), phenylacetylene (54 µL, 0.49 mmol, 1.0 equiv) and triethylsilane (86 µL, 0.54 mmol, 1.1 equiv) were quickly added via syringe. After stirring at 100°C for 14 h the reaction was stopped and allowed to reach rt. The crude mixture was filtered through a short pad of $SiO_2$ and the solvent was removed under *vacuum*. The resulting mixtures were analysed by $^1$H NMR spectroscopy.

### Crystallographic data for 15:




All data were collected at low temperature using oil-coated shock-cooled crystals at 120(2) K on a Bruker-AXS APEX II diffractometer with MoKa radiation (λ = 0.71073 Å). The structure was solved by direct[9] and all non hydrogen atoms were refined anisotropically using the least-squares method on $F^2$.[10]

Only one of three independent molecules present in the asymmetric unit is depicted as thermal ellipsoid plot at the 50% level. Hydrogen atoms and disorders of the pyridine ligand and of the benzyl group connected to O2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1-C1 1.974(7), Pt1-I1 2.599(1), Pt1-I2 2.596(1), Pt1-N5 2.133(15), I1-Pt1-I2 178.2(1), C1-Pt1-N5 172.4(6), C1-Pt1-I1 87.9(2), C1-Pt1-I2 90.3(2), I1-Pt1-N5 91.2(9), I2-Pt1-N5 90.6(9).

**15**: $C_{33}H_{33}I_2N_5O_4Pt$, Mr = 1012.53, crystal size = 0.40 x 0.40 x 0.10 mm$^3$, triclinic, space group $P\bar{1}$, *a* = 12.5954(5) Å, *b* = 20.4792(8) Å, *c* = 21.2634(9) Å, *α* = 91.735(2)°, *β* = 106.457(2)°, *γ* = 94.822(2)°, V = 5233.0(4) Å$^3$, Z = 6, 184964 reflections collected, 28040 unique reflections ($R_{int}$ = 0.0747), R1 = 0.0501, wR2 = 0.0930 [I>2σ(I)], R1 = 0.0954, wR2 = 0.1197 (all data), residual electron density = 4.102 e Å$^{-3}$.

CCDC 2110874 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## References

1 Muntaner, J. G.; Casarrubios, L.; Sierra, M. A. *Synthesis of new Bioorganometallic Ir-and Rh-Complexes Having ß-Lactam Containing Ligands. Org. Biomol. Chem.* **2014**, *12*, 286–297.

2 Evans, D. A.; Sjogren, B. E. *The Asymmetric Synthesis of β-Lactam Antibiotics - I. Application of Chiral Oxazolidones in The Staudinger Reaction. Tetrahedron Letters* **1985**, *26*, 3783–3786.

3 Usifoh, C. O.; Lambert, D. M.; Wouters, J.; Scriba, G. K. E. *Synthesis and Anticonvulsant Activity of N,N-Phthaloyl Derivatives of Central Nervous System Inhibitory Amino Acids*. *Archiv der Pharmazie* **2001**, *334*, 323–331.

4 Wilkening, I.; Signore, G. D.; Hackenberger, C. P. R. *Synthesis of Phosphonamidate Peptides by Staudinger Reactions of Silylated Phosphinic Acids and Esters*. *Chem. Commun.* **2011**, *47*, 349–351.

5 Alvarez, S. G.; Alvarez, M. T. *A Practical Procedure for The Synthesis of Alkyl Azides at Ambient Temperature in Dimethyl Sulfoxide in High Purity and Yield*. *Synthesis* **1997**, 413–414.

6 Maity, R.; Tichter, T.; van der Meer, M.; Sarkar, B. *C–H activation in $Ir^{III}$ and N-Demethylation in $Pt^{II}$ Complexes with Mesoionic Carbene Ligands: Examples of Monometallic, Homobimetallic and Heterobimetallic Complexes. Dalton Trans.*, **2015**, *44,* 18311–18315.

7 Frutos, M.; Avello, M. G.; Viso, A.; Fernández de la Pradilla, R.; de la Torre, M. C.; Sierra, M. A.; Gornitzka, H.; Hemmert, C. *Gold Sulfinyl Mesoionic Carbenes: Synthesis, Structure, and Catalytic Activity. Org. Lett.* **2016**, *18*, 3570–3573.

8 Hu, J. J.; Li, F.; Hor, T. S. A. *Novel Pt (II) Mono-and Biscarbene Complexes: Synthesis, Structural Characterization and Application in Hydrosilylation Catalysis. Organometallics* **2009**, *28*, 1212–1220.

9 Sheldrick, G. M*. Phase annealing in SHELX-90: direct methods for larger structures.* *Acta Crystallographica Section A* **1990**, *46*(6), 467-473.

10 Sheldrick, G. M. *Crystal structure refinement with SHELXL*. *Acta Crystallographica Section C: Structural Chemistry* **2015**, *71*(1), 3-8.

## $^{1}$H and $^{13}$C NMR Spectra

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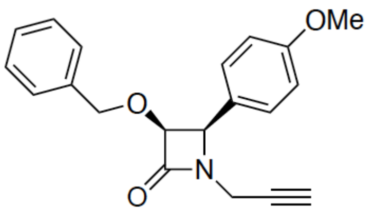


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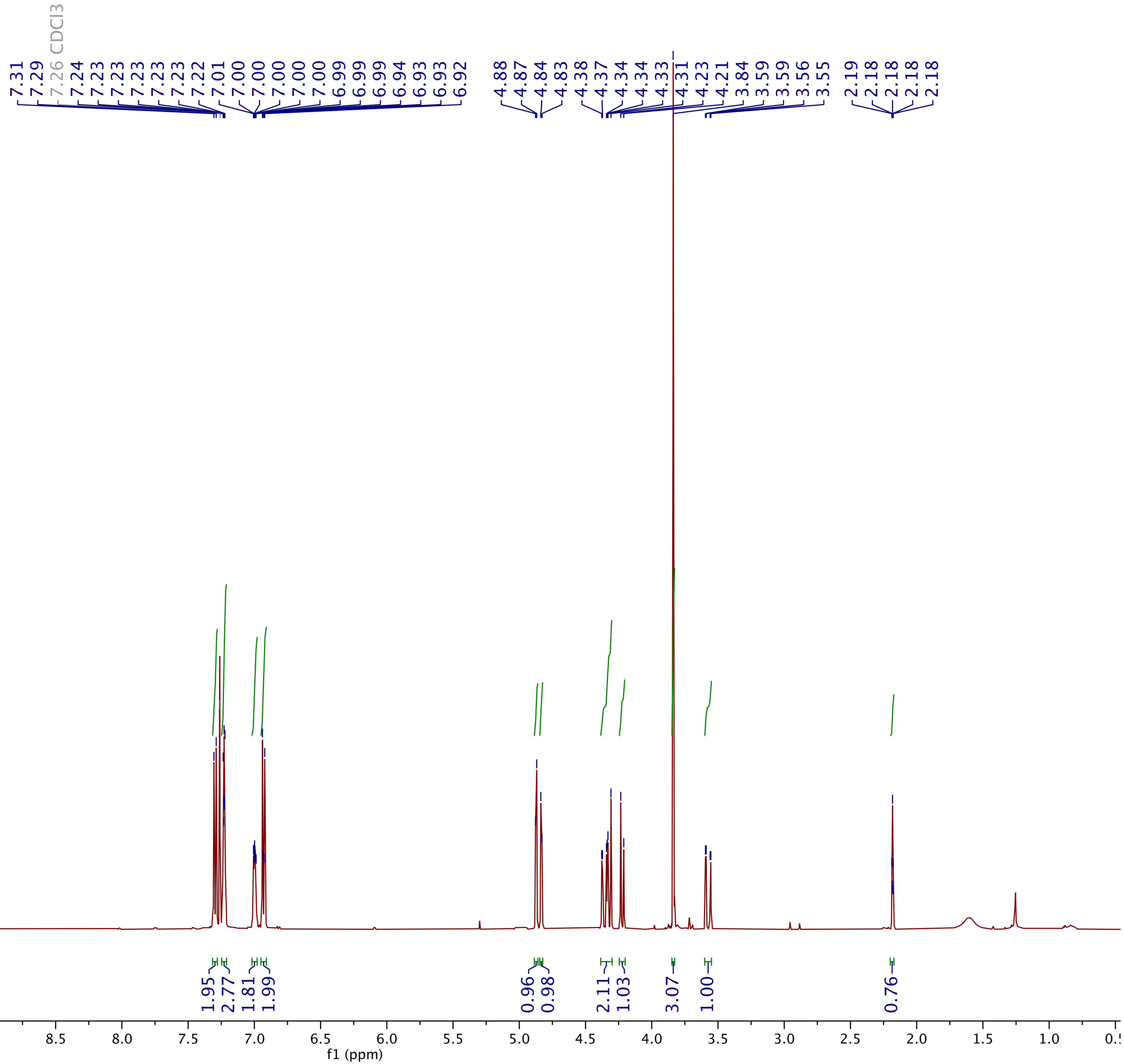

MGM-BJ13-13c
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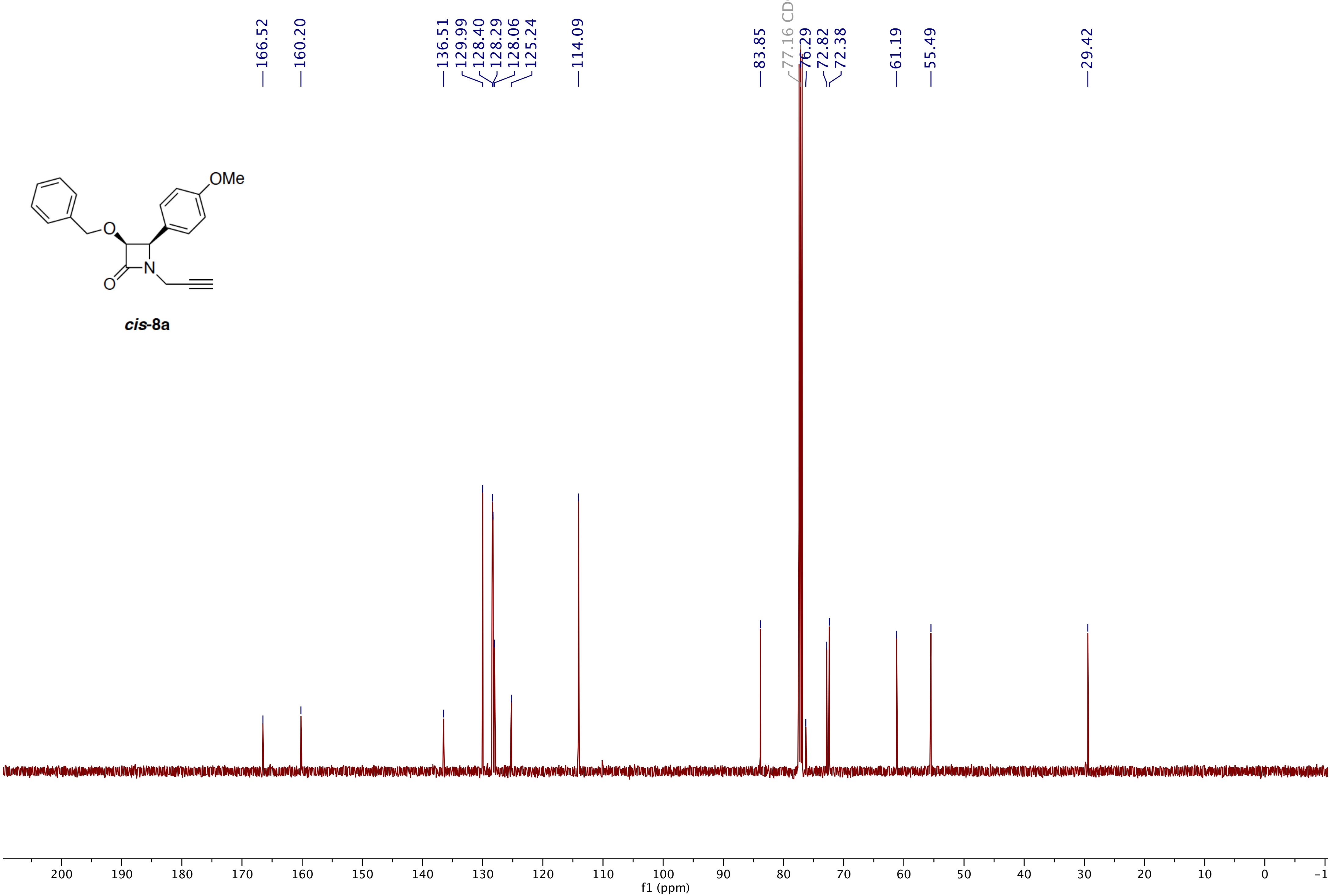
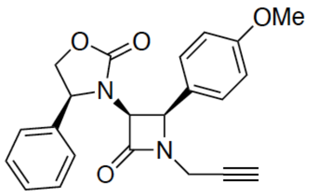
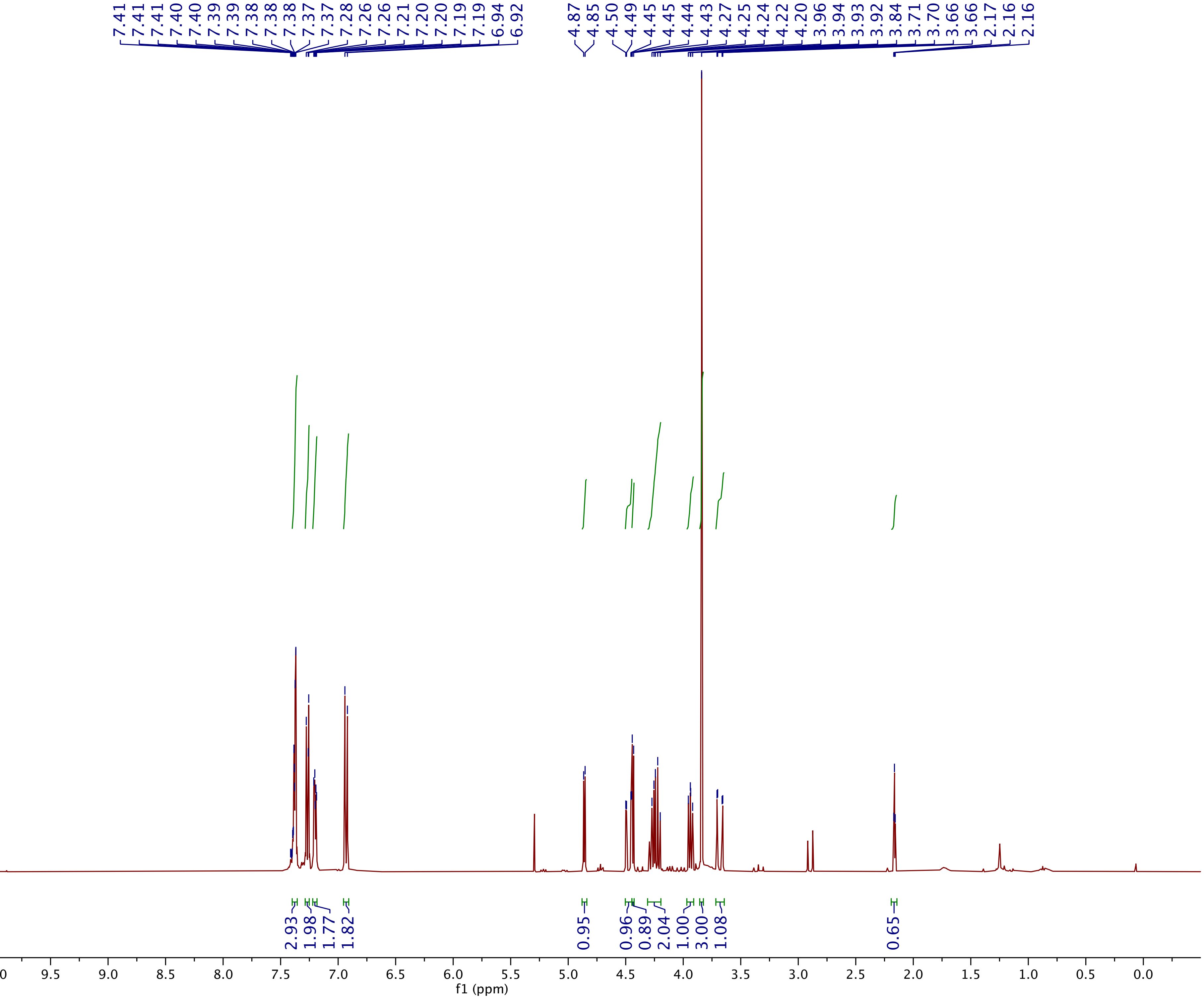



OMe
O
O
N
N
O

***cis*-8b**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7.41
7.41
7.40
7.40
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7.39
7.38
7.38
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7.37
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7.28
7.26
7.26
7.21
7.20
7.20
7.19
7.19
6.94
6.92
4.87
4.85
4.50
4.49
4.45
4.45
4.44
4.43
4.27
4.25
4.24
4.22
4.20
3.96
3.94
3.93
3.92
3.84
3.71
3.70
3.66
3.66
2.17
2.16
2.16
2.93
1.98
1.77
1.82
0.95
0.96
0.89
2.04
1.00
3.00
1.08
0.65
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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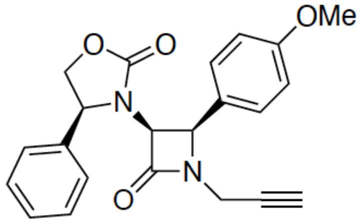
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

MGM921B
single pulse decoupled gated NOE

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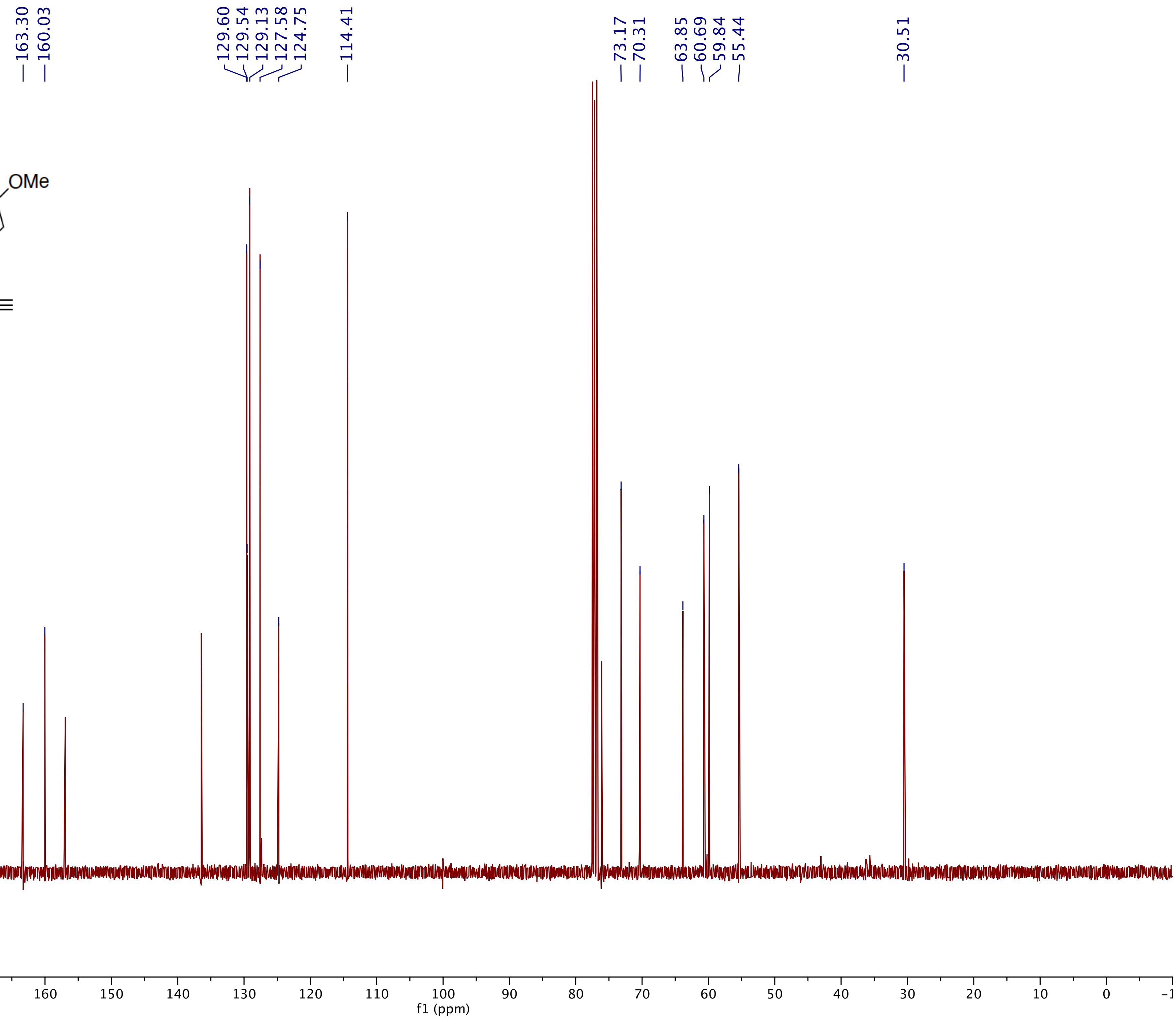

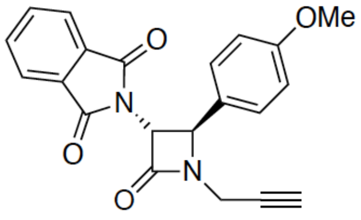
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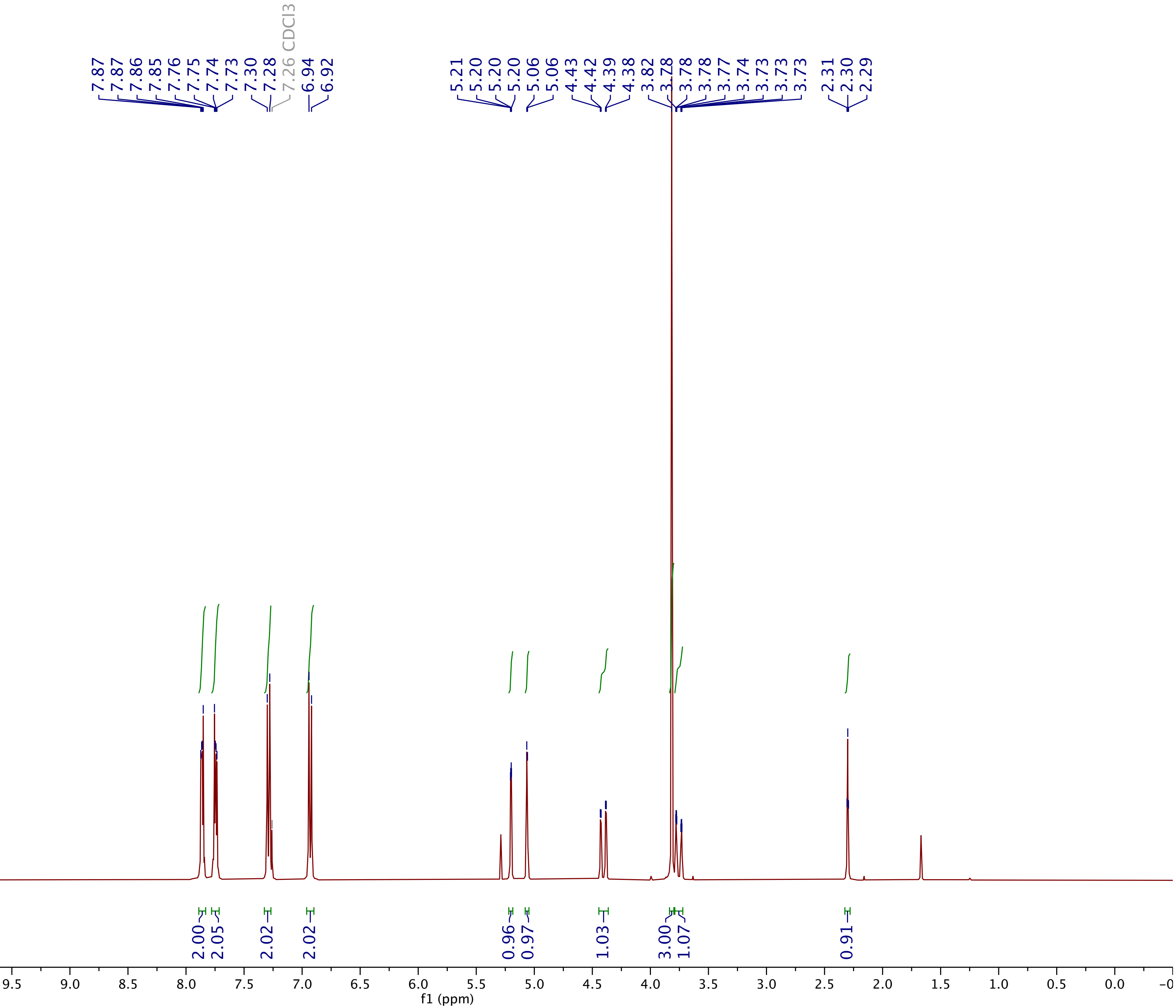
N
O

***trans*-8c**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6.92
5.21
5.20
5.20
5.20
5.06
5.06
4.43
4.42
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2.02
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3.5
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1.5
1.0
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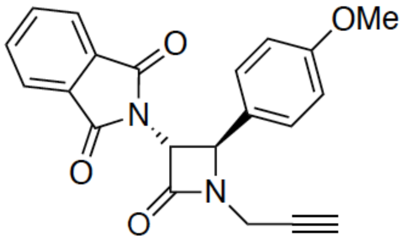
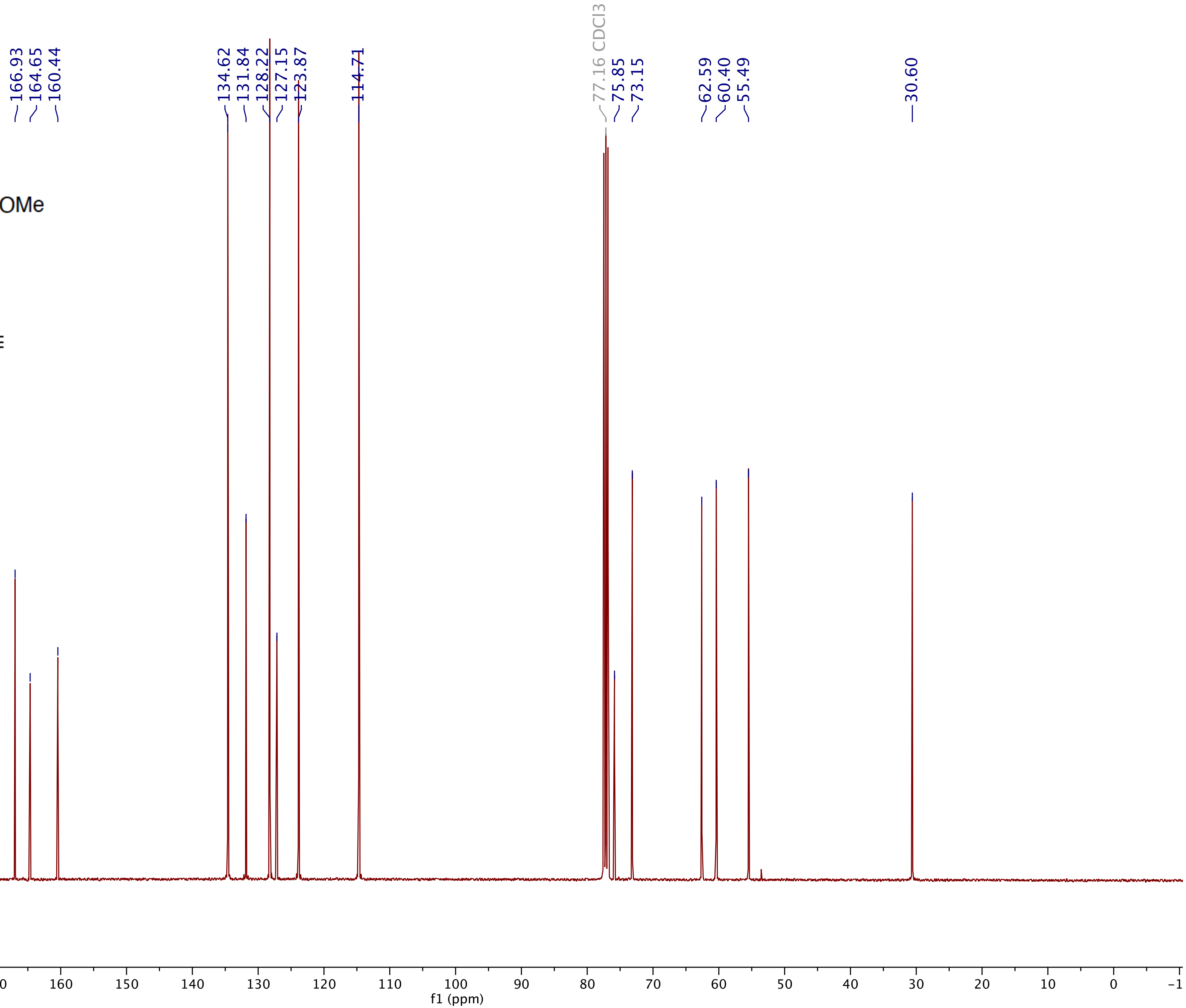
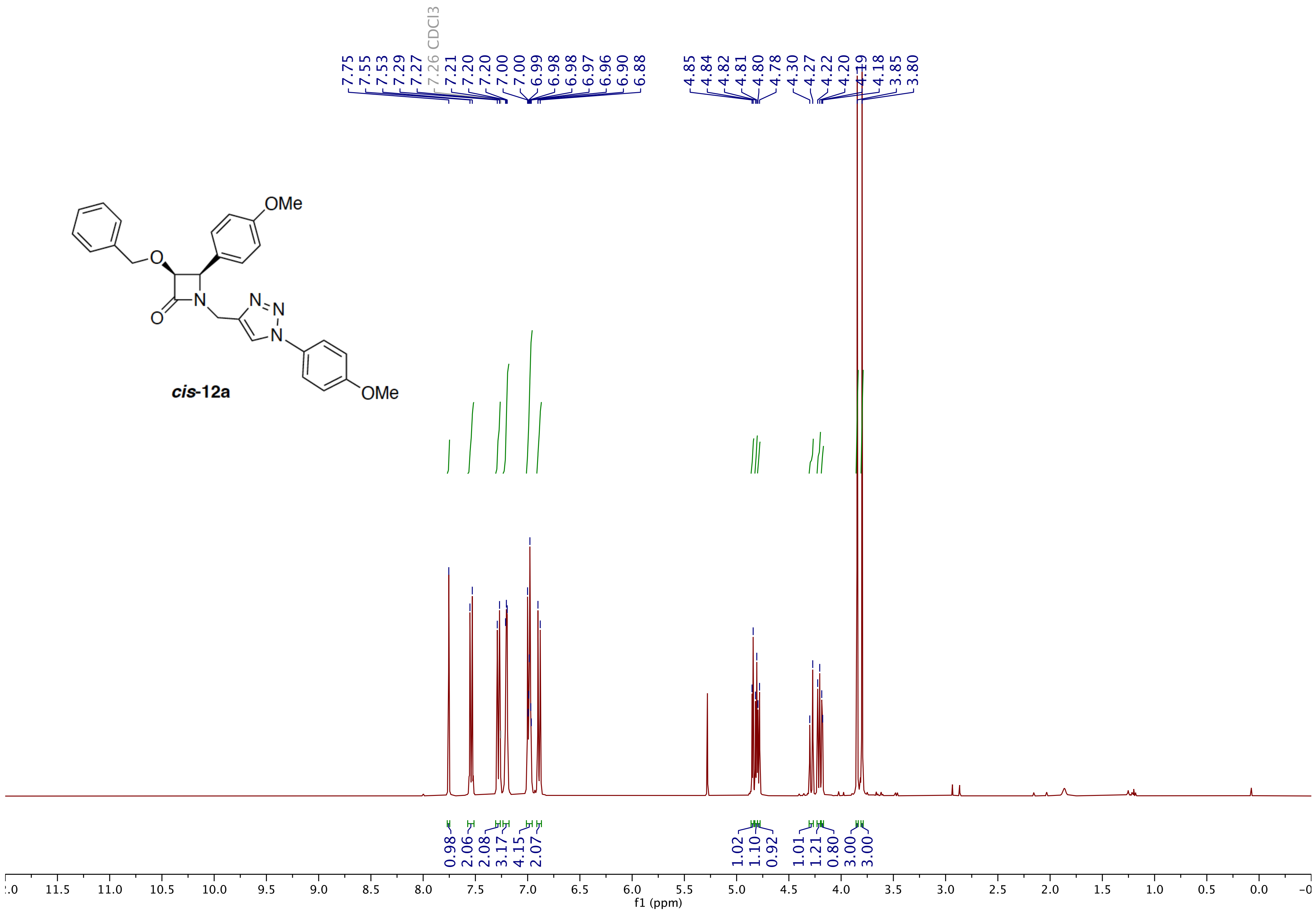
−0
f1 (ppm)

MGM–BJ11.14.fid




*trans*-8c

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3.85
3.80
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OMe
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2.08
3.17
4.15
2.07
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1.01
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5.0
4.5
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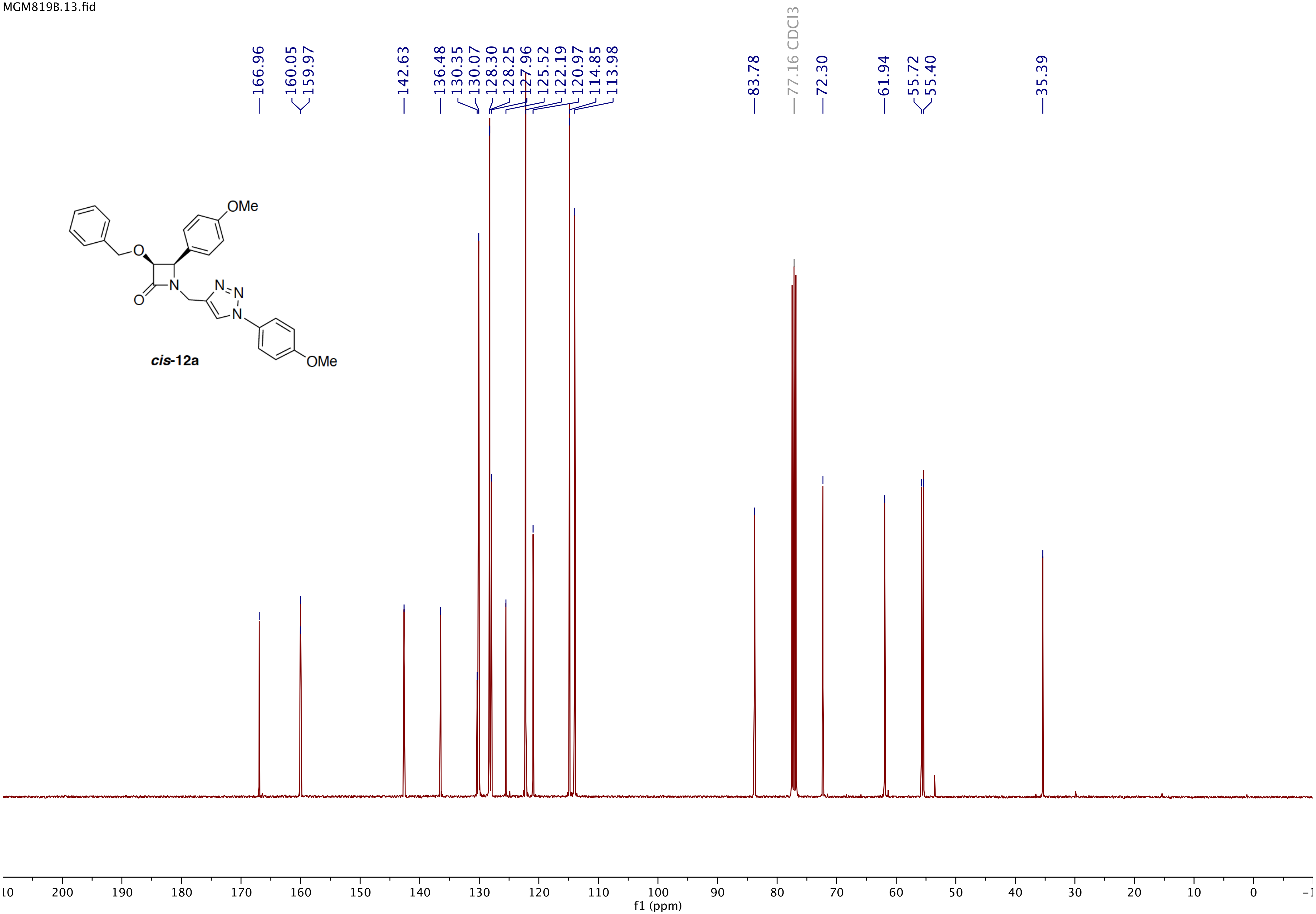
f1 (ppm)

***cis*-12a**



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113.98
83.78
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72.30
61.94
55.72
55.40
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N
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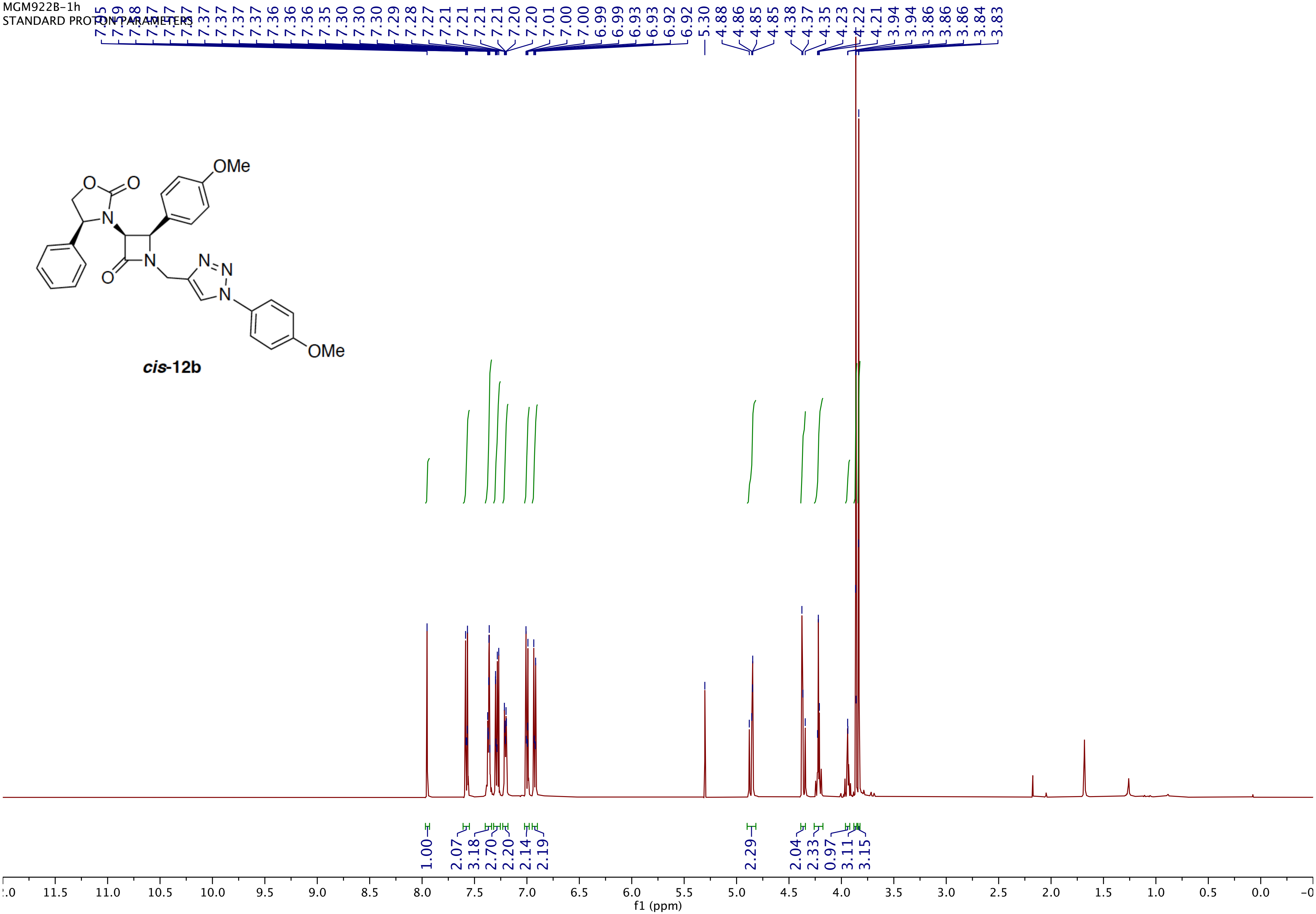
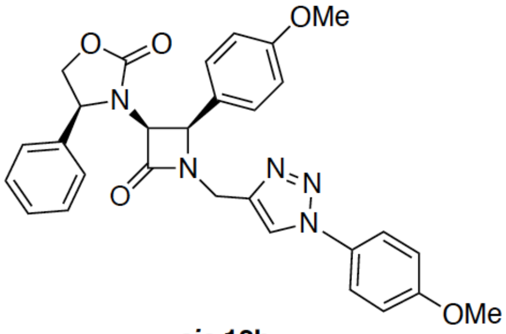
cis-12a
f1 (ppm)

MGM922B-1h
STANDARD PROTON PARAMETERS

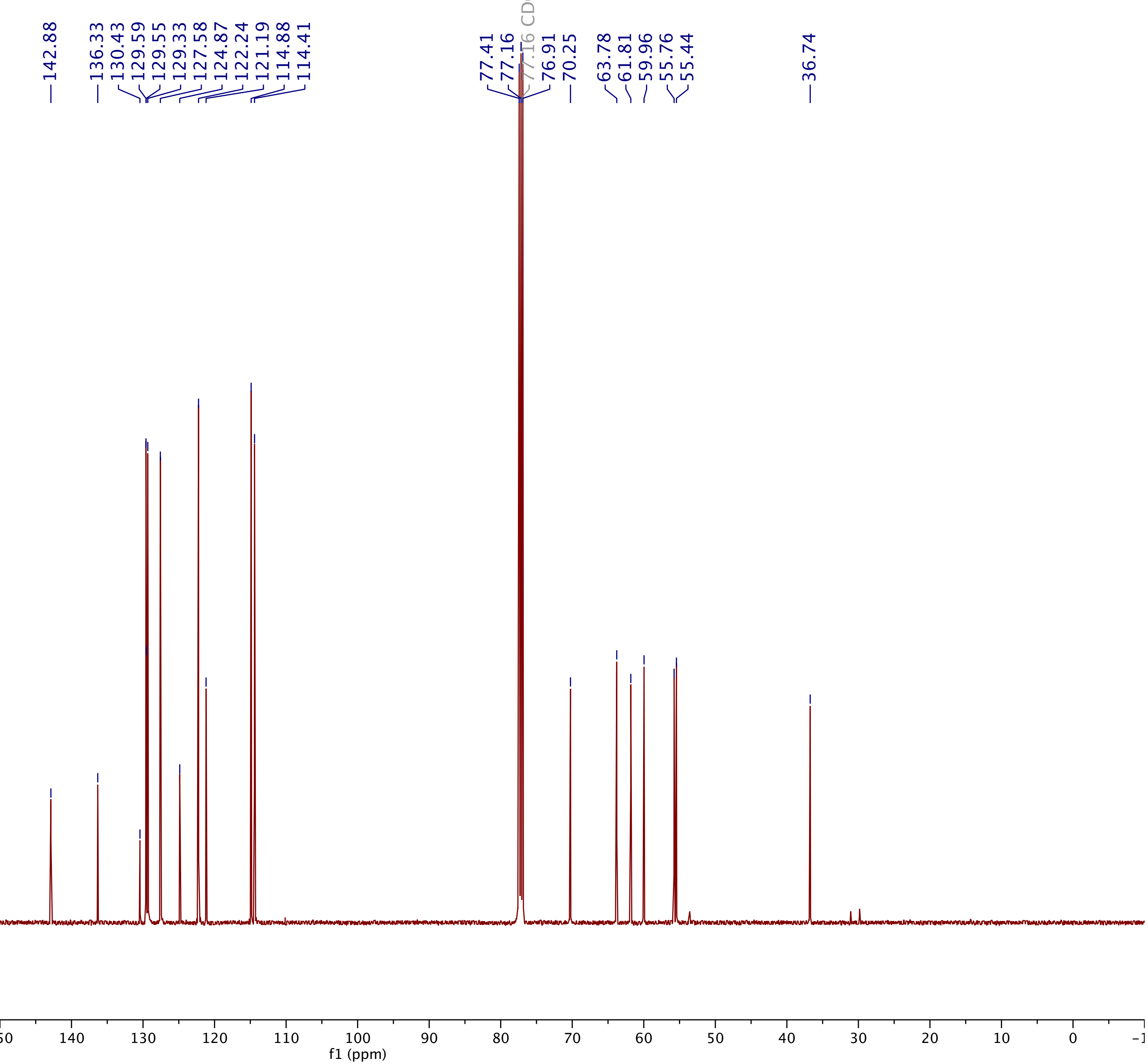


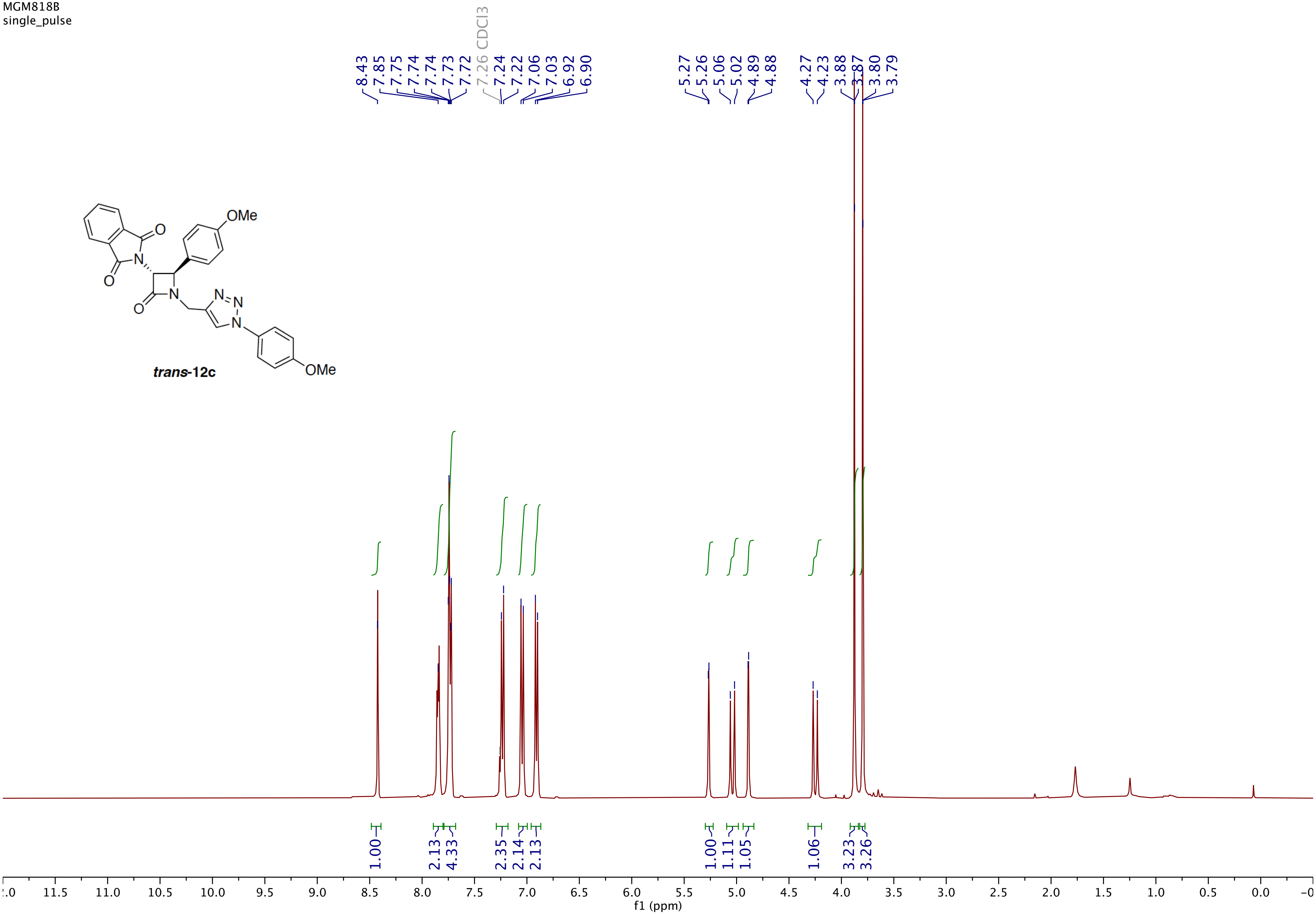

***cis*-12b**

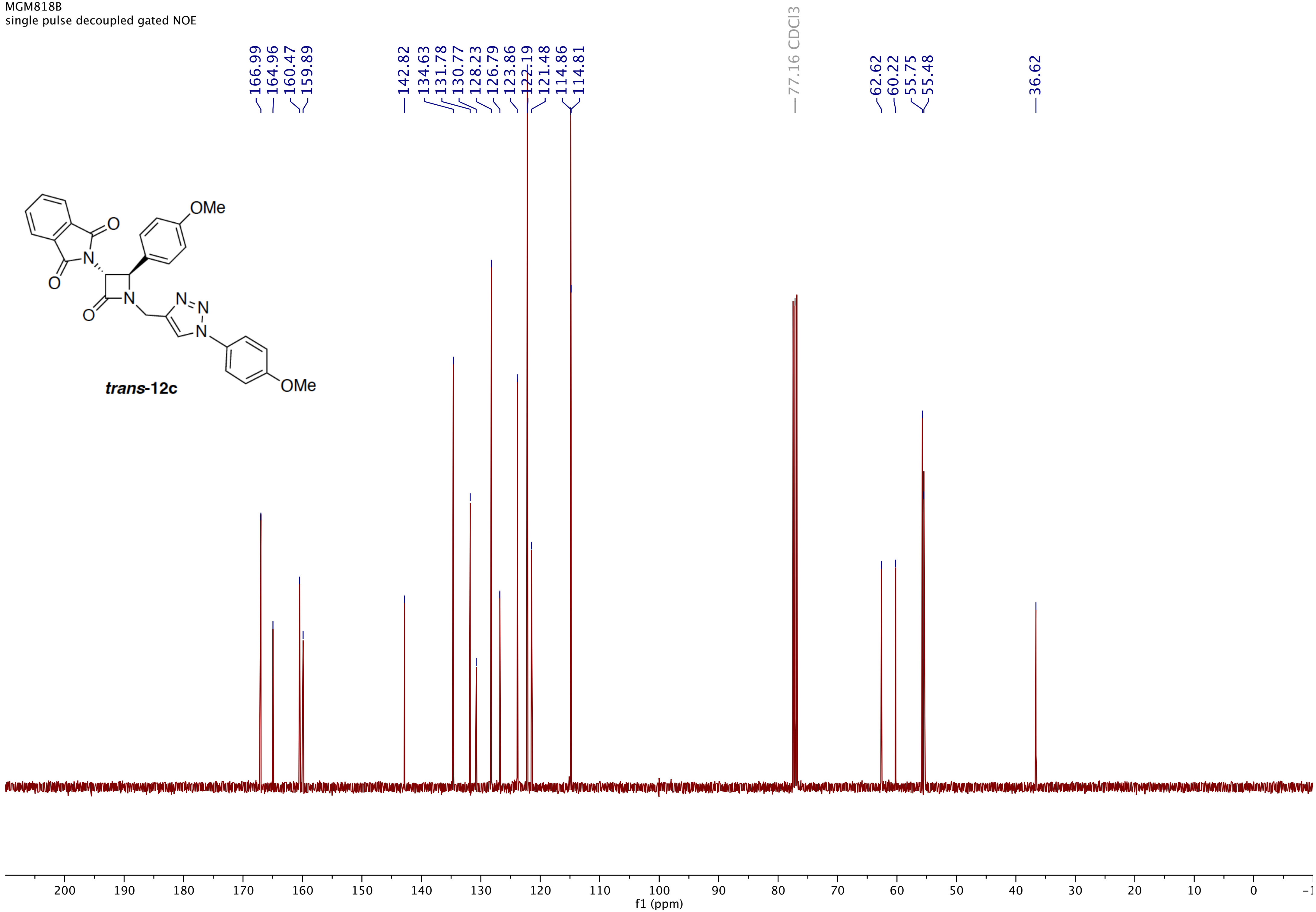
MGM922B-13c
STANDARD PROTON PARAMETERS

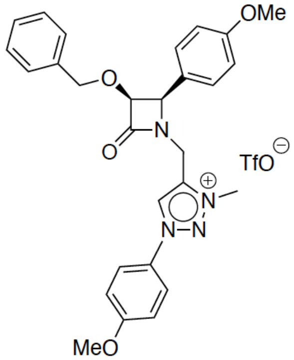


*cis*-12b

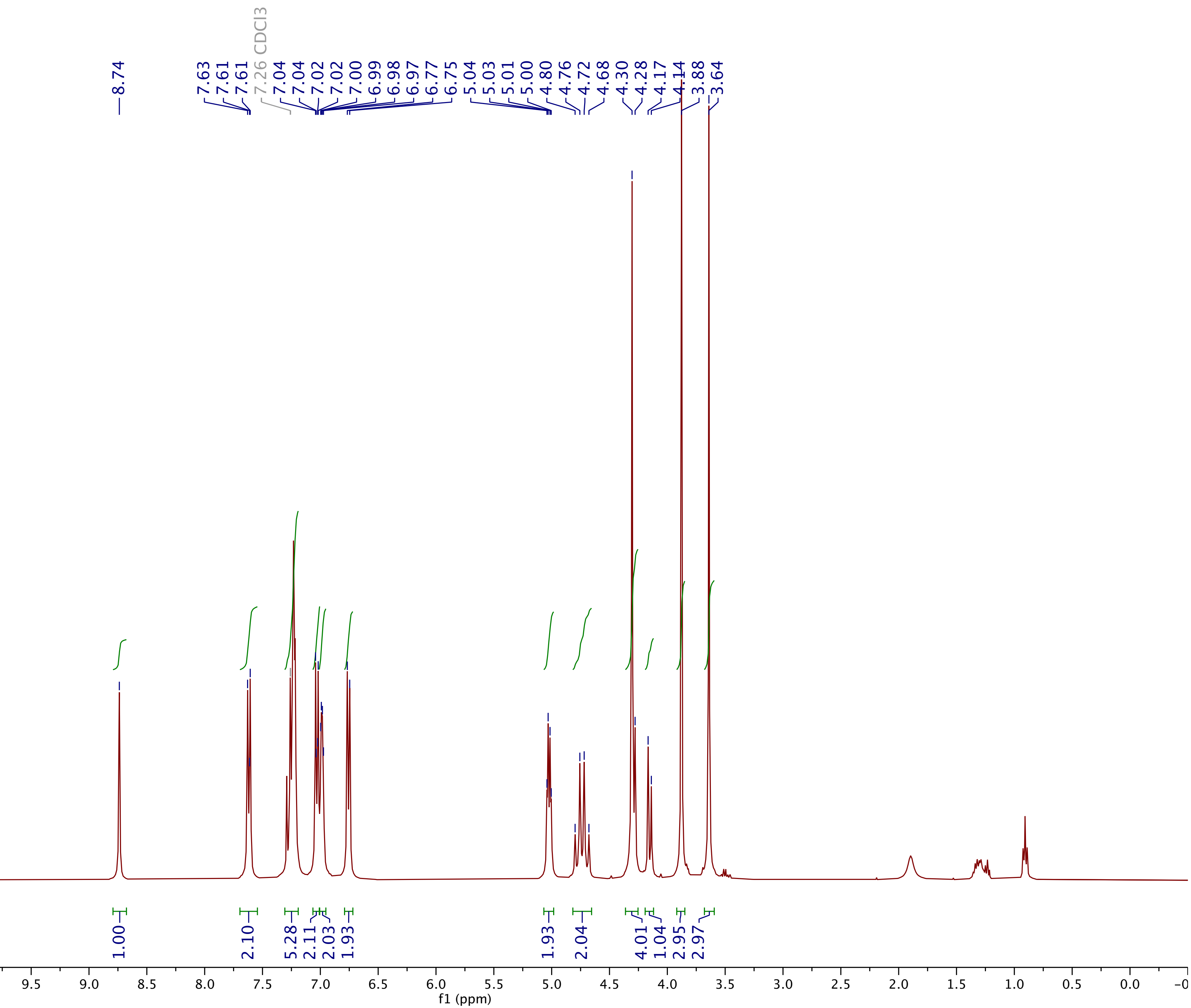



MGM818B
single_pulse
8.43
7.85
7.75
7.74
7.74
7.73
7.72
7.26 CDCl3
7.24
7.22
7.06
7.03
6.92
6.90
5.27
5.26
5.06
5.02
4.89
4.88
4.27
4.23
3.88
3.87
3.80
3.79
OMe
O
N
O
O
N
N
N
N
OMe
trans-12c
1.00
2.13
4.33
2.35
2.14
2.13
1.00
1.11
1.05
1.06
3.23
3.26
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

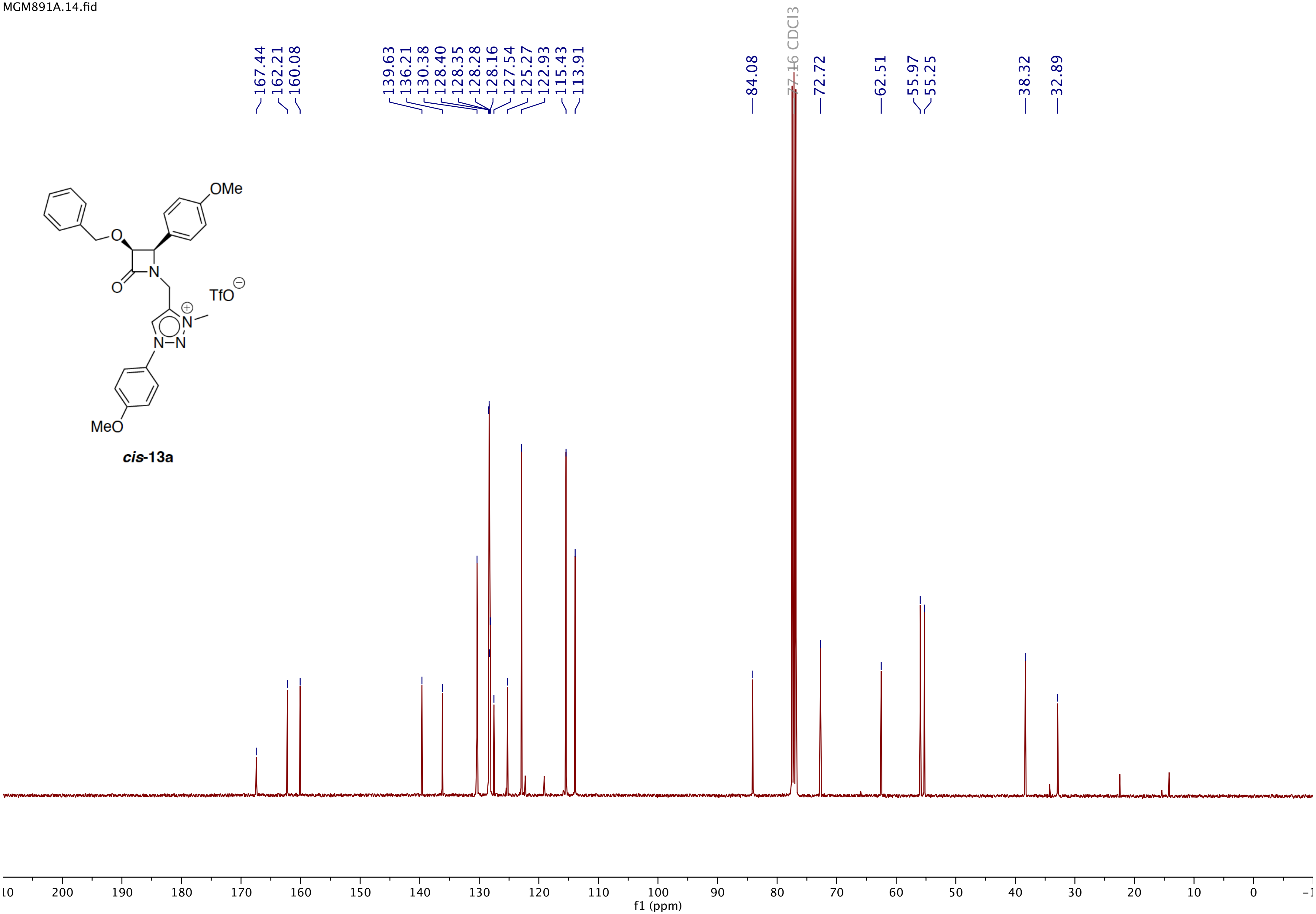

MGM818B
single pulse decoupled gated NOE
166.99
164.96
160.47
159.89
142.82
134.63
131.78
130.77
128.23
126.79
123.86
122.19
121.48
114.86
114.81
77.16 CDCl3
62.62
60.22
55.75
55.48
36.62
OMe
O
N
O
O
N
N
N
N
OMe
trans-12c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
O
O
N
TfO
N
N–N
MeO

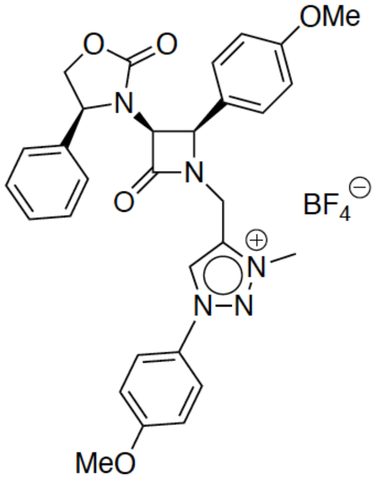
*cis*-**13a**


8.74
7.63
7.61
7.61
7.26 CDCl3
7.04
7.04
7.02
7.02
7.00
6.99
6.98
6.97
6.77
6.75
5.04
5.03
5.01
5.00
4.80
4.76
4.72
4.68
4.30
4.28
4.17
4.14
3.88
3.64
1.00
2.10
5.28
2.11
2.03
1.93
1.93
2.04
4.01
1.04
2.95
2.97
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0
f1 (ppm)

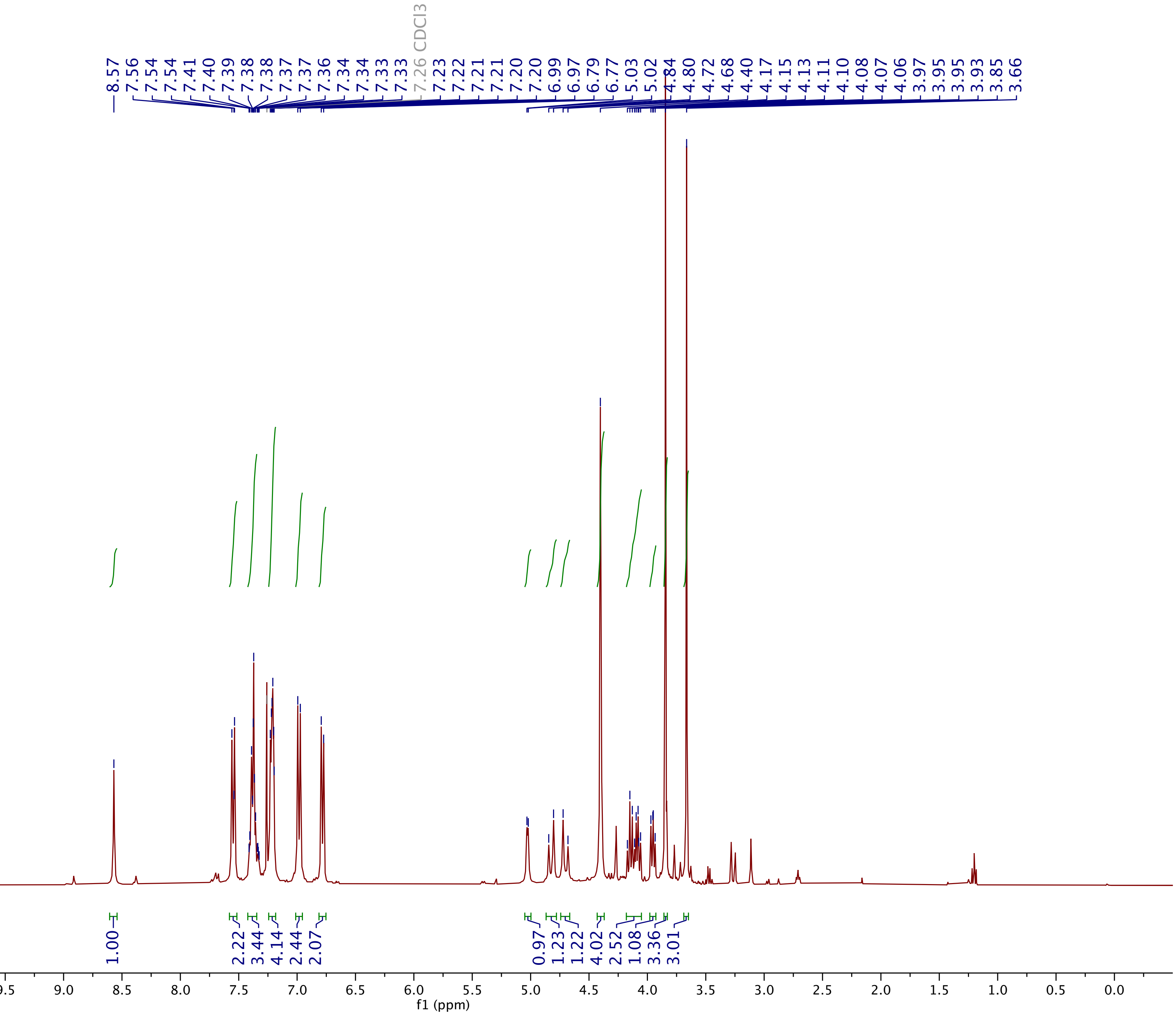
MGM891A.14.fid

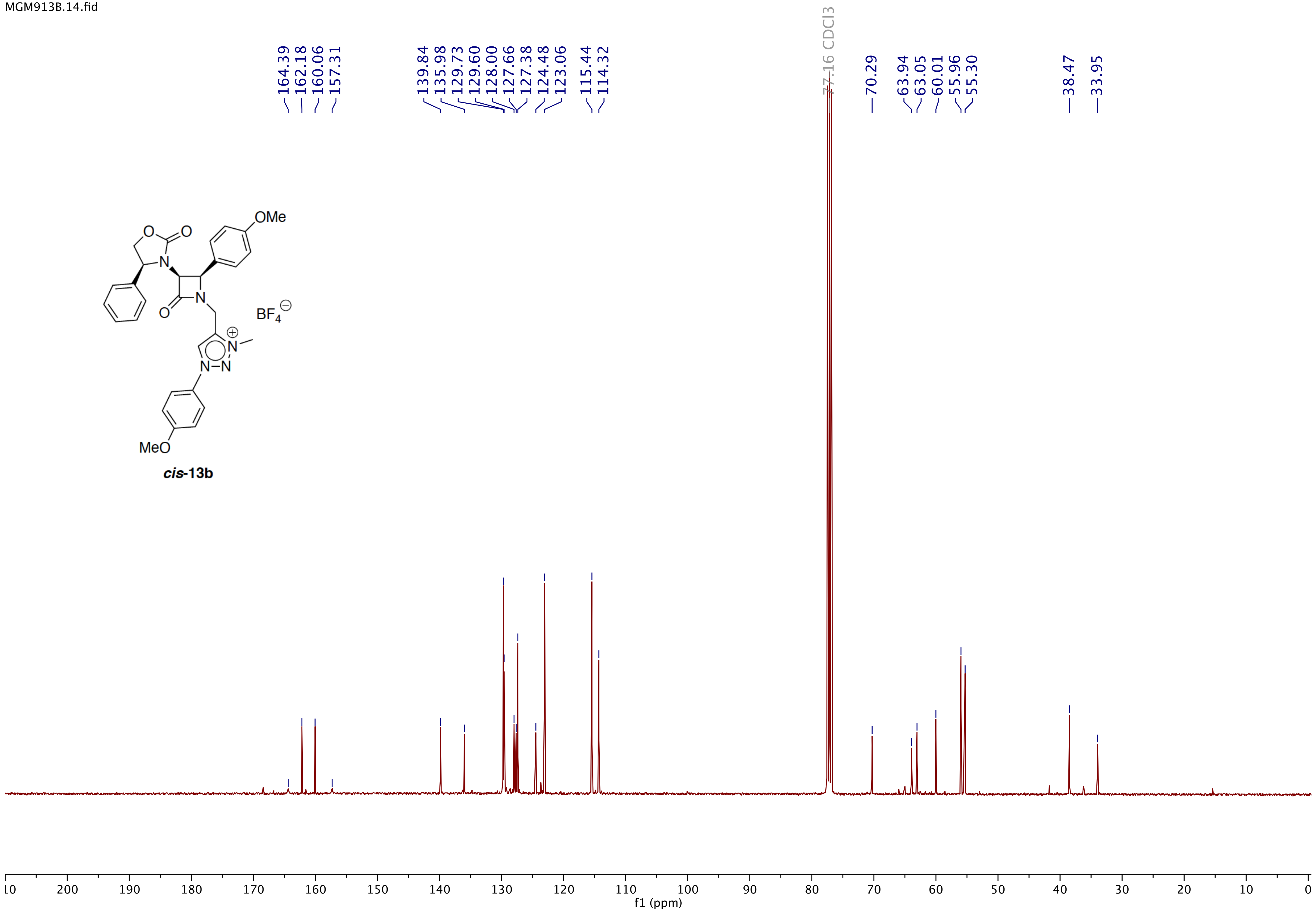



***cis*-13a**

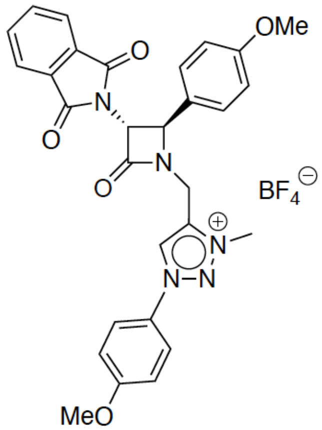

OMe
BF4
MeO

***cis*-13b**

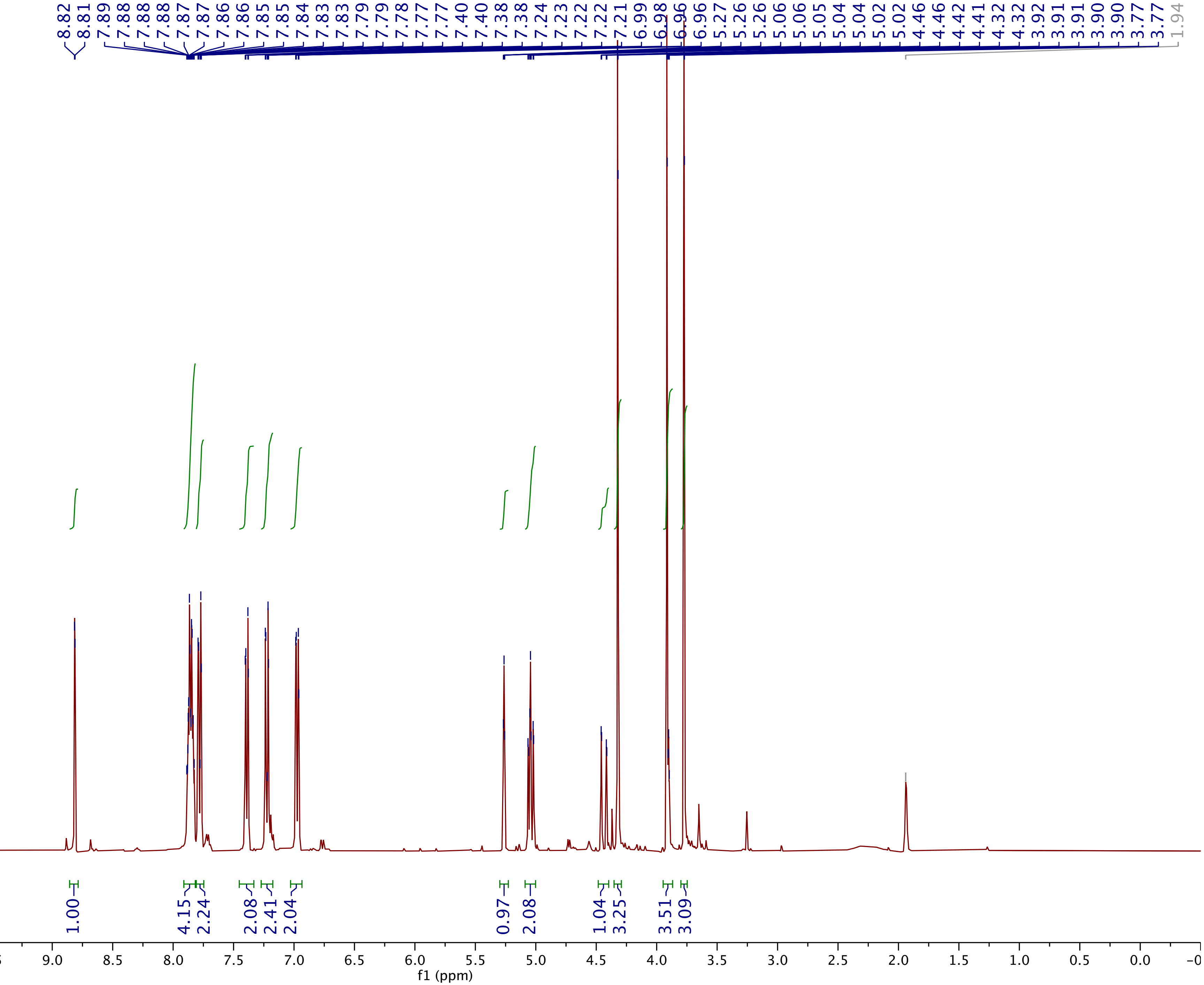

8.57
7.56
7.54
7.54
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.34
7.34
7.33
7.33
7.26 CDCl3
7.23
7.22
7.21
7.21
7.20
7.20
6.99
6.97
6.79
6.77
5.03
5.02
4.84
4.80
4.72
4.68
4.40
4.17
4.15
4.13
4.11
4.10
4.08
4.07
4.06
3.97
3.95
3.95
3.93
3.85
3.66
1.00
2.22
3.44
4.14
2.44
2.07
0.97
1.23
1.22
4.02
2.52
1.08
3.36
3.01
f1 (ppm)


MGM913B.14.fid
164.39
162.18
160.06
157.31
139.84
135.98
129.73
129.60
128.00
127.66
127.38
124.48
123.06
115.44
114.32
77.16 CDCl3
70.29
63.94
63.05
60.01
55.96
55.30
38.47
33.95
OMe
O
O
N
N
O
BF4
N
N–N
MeO
cis-13b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

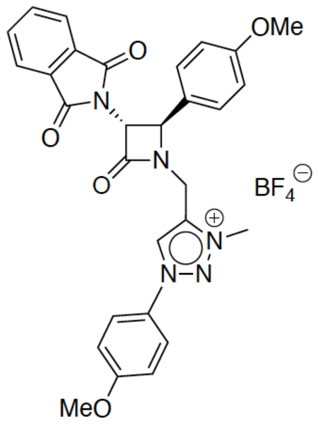
MGM820
single_pulse



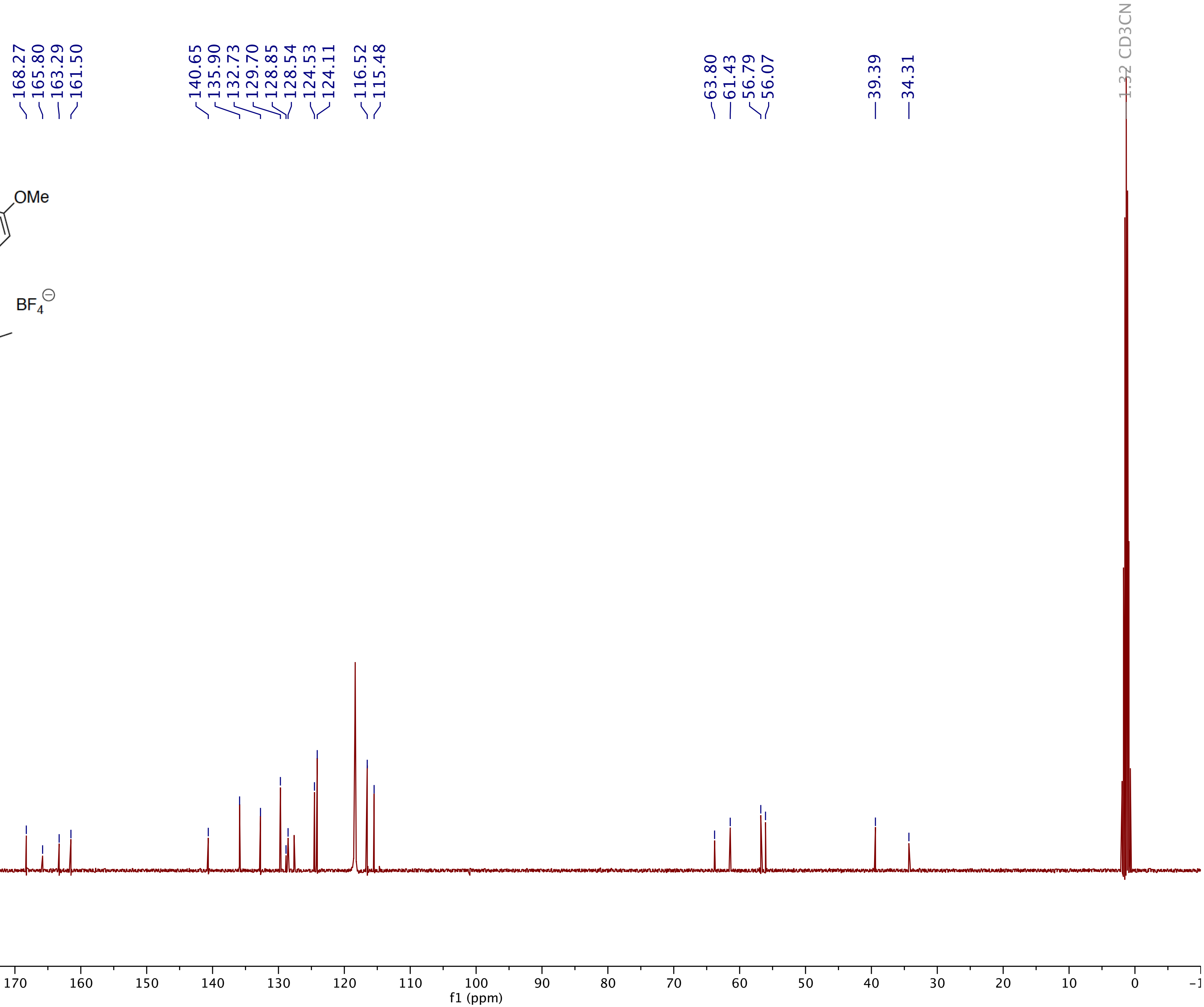

*trans*-13c

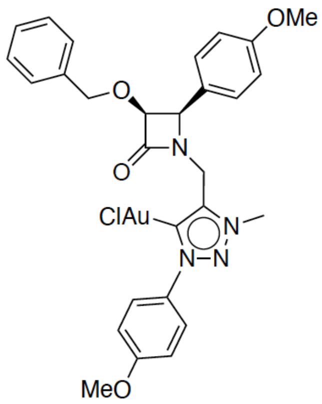


MGM820
single pulse decoupled gated NOE

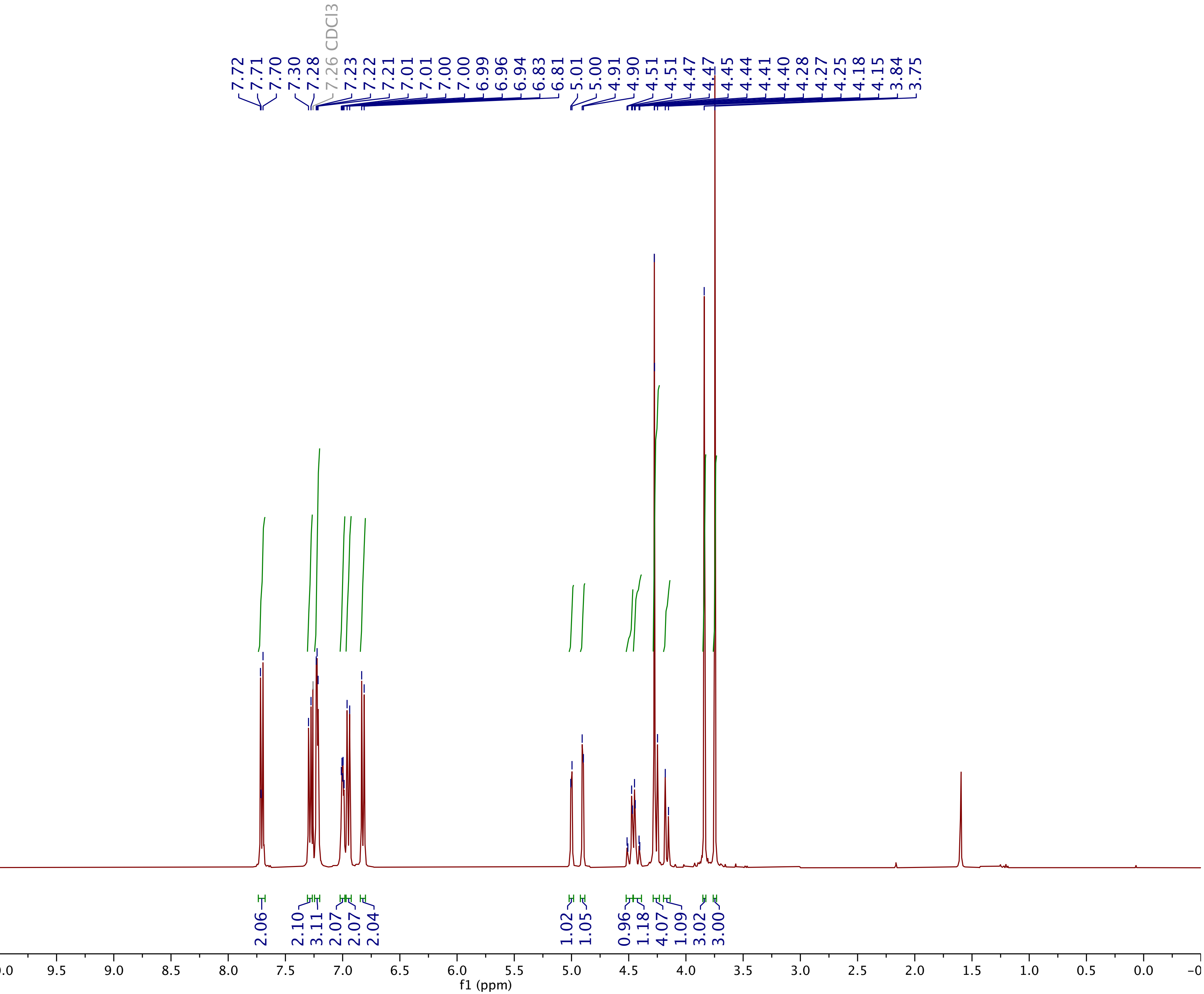


***trans*-13c**

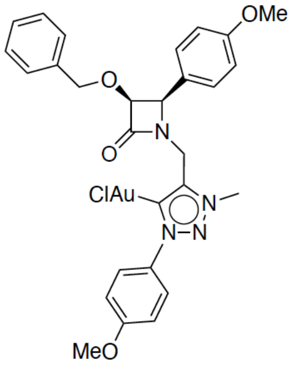



OMe
O
O
N
ClAu
N
N–N
MeO

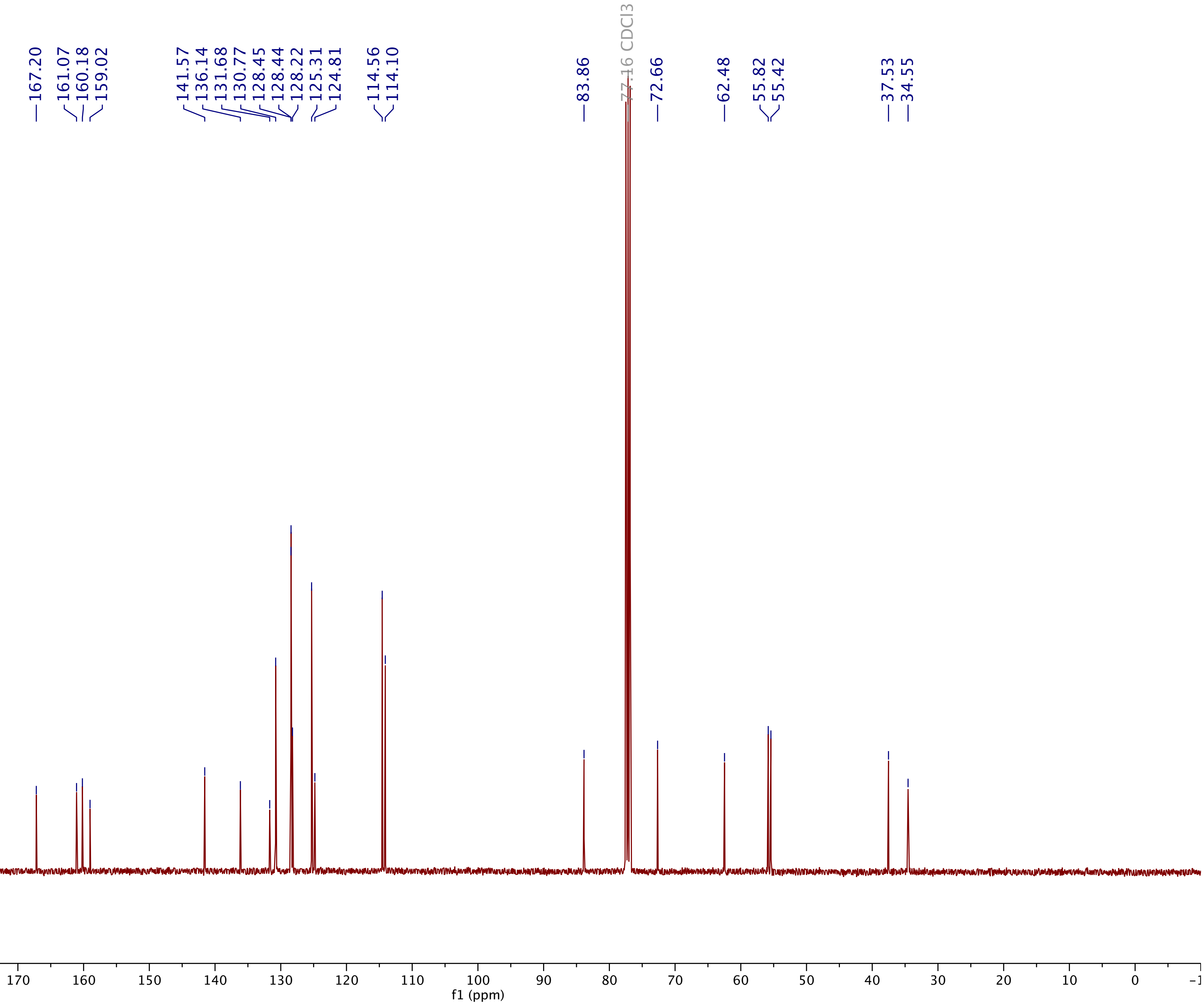
***cis*-14a**

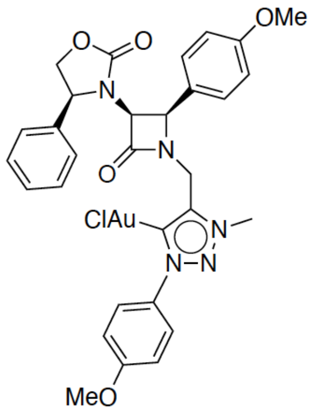

7.72
7.71
7.70
7.30
7.28
7.26 CDCl3
7.23
7.22
7.21
7.01
7.01
7.00
7.00
6.99
6.96
6.94
6.83
6.81
5.01
5.00
4.91
4.90
4.51
4.51
4.47
4.47
4.45
4.44
4.41
4.40
4.28
4.27
4.25
4.18
4.15
3.84
3.75
2.06
2.10
3.11
2.07
2.07
2.04
1.02
1.05
0.96
1.18
4.07
1.09
3.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0
f1 (ppm)

MGM871C.14.fid

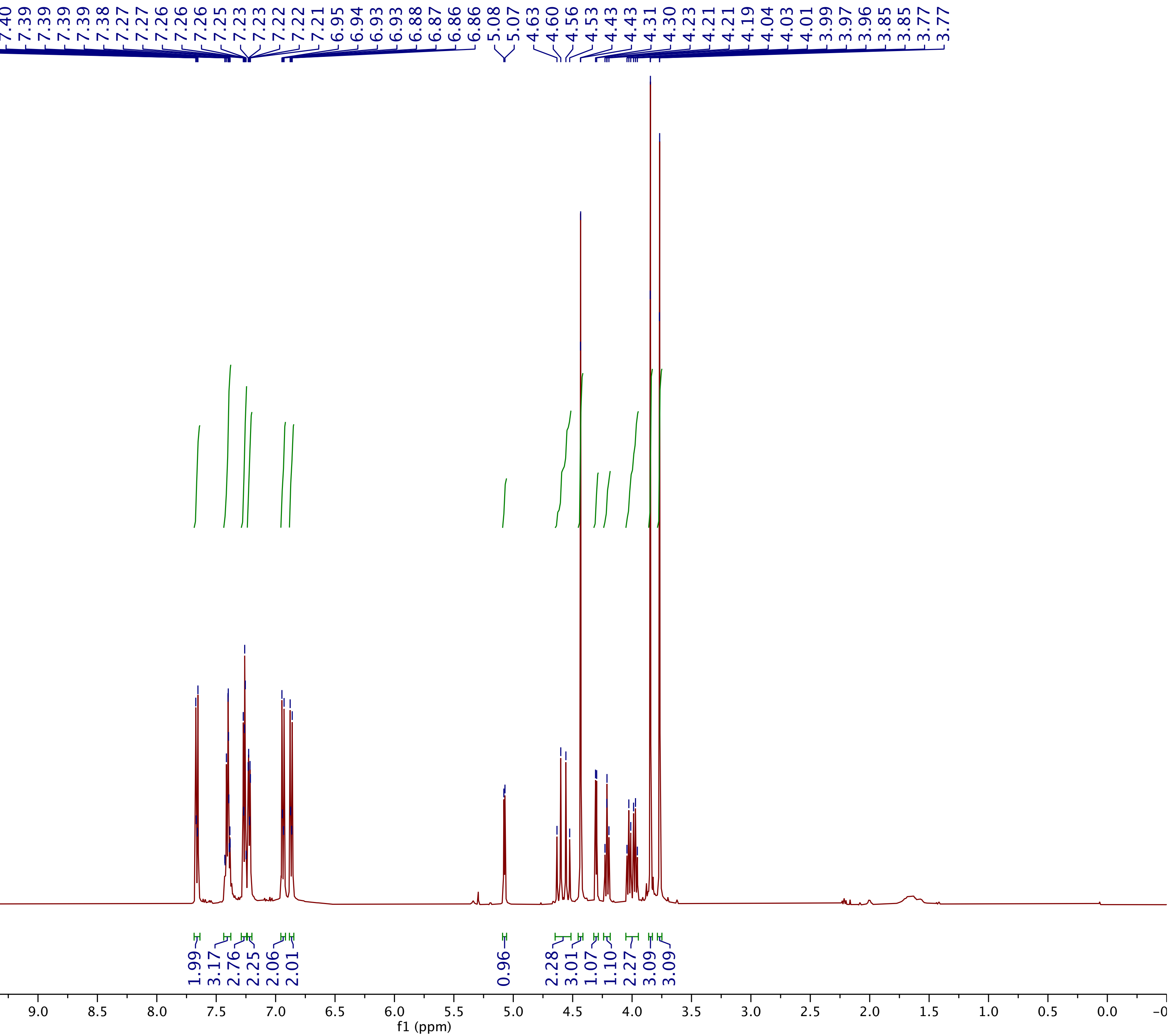


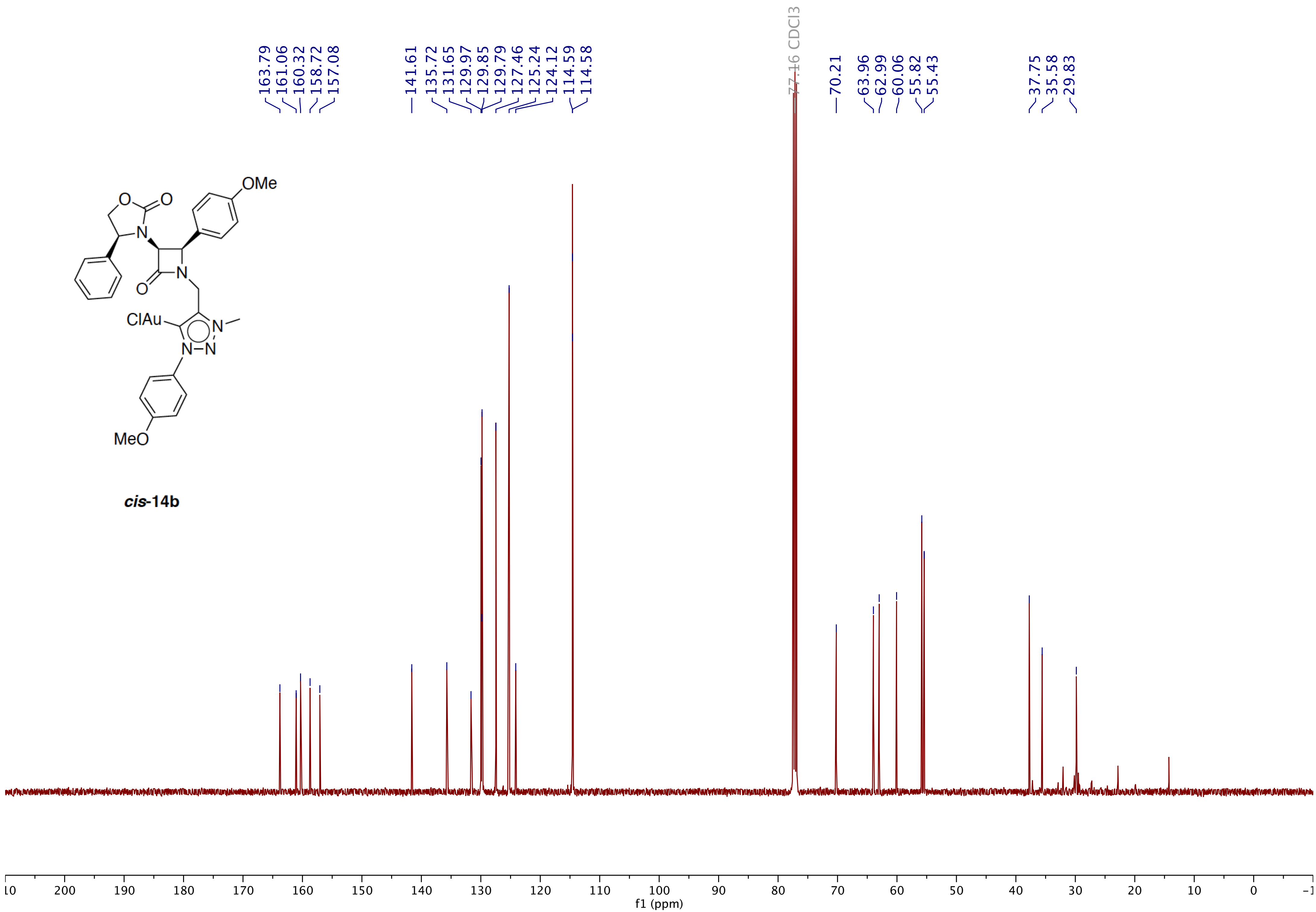
*cis*-**14a**



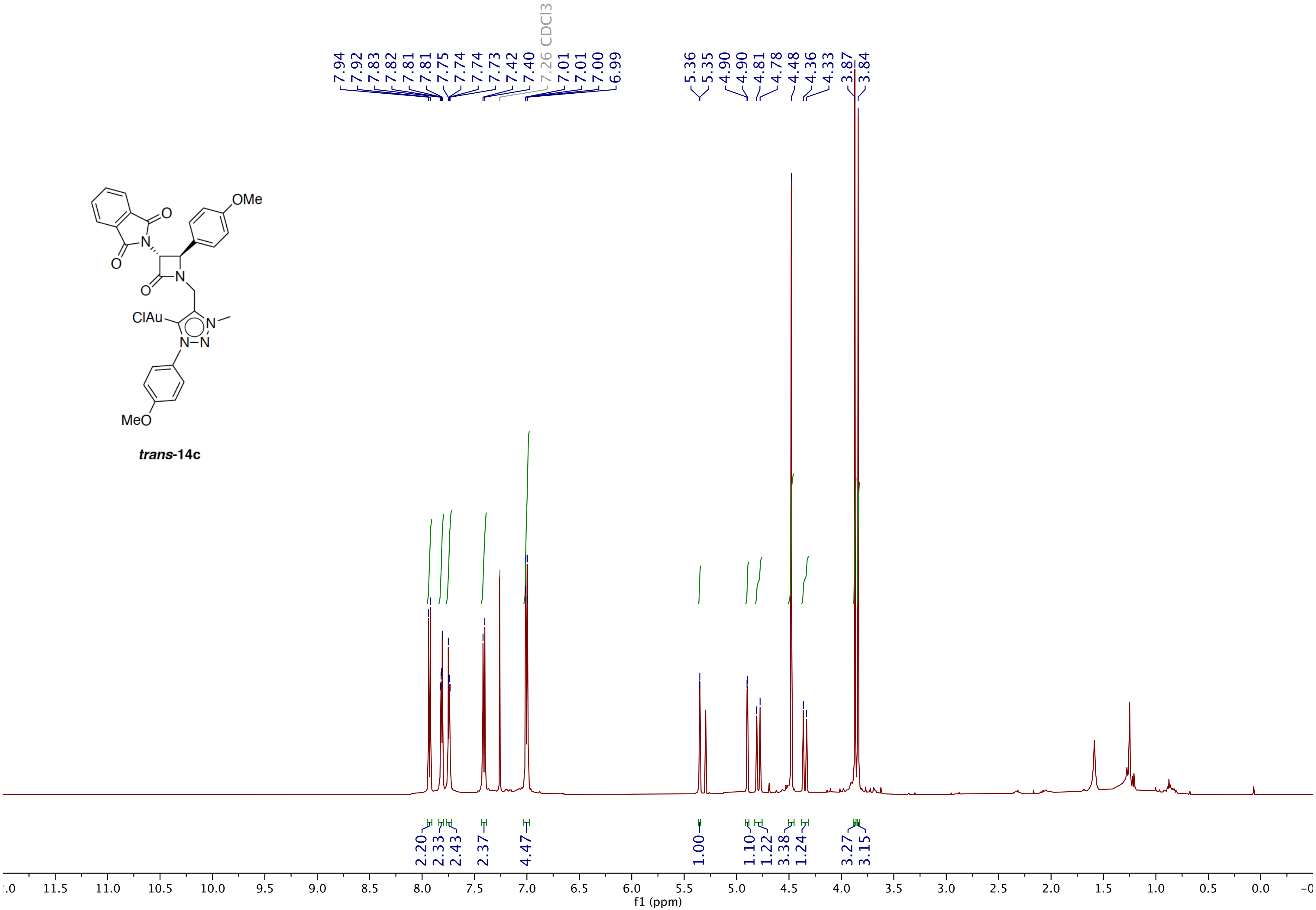

OMe
O
O
N
N
O
ClAu
N
N–N
MeO

***cis*-14b**


7.67
7.67
7.66
7.65
7.43
7.43
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.39
7.38
7.27
7.27
7.26
7.26
7.26
7.25
7.23
7.23
7.22
7.22
7.21
6.95
6.94
6.93
6.93
6.88
6.87
6.86
6.86
5.08
5.07
4.63
4.60
4.56
4.53
4.43
4.43
4.31
4.30
4.23
4.21
4.21
4.19
4.04
4.03
4.01
3.99
3.97
3.96
3.85
3.85
3.77
3.77
1.99
3.17
2.76
2.25
2.06
2.01
0.96
2.28
3.01
1.07
1.10
2.27
3.09
3.09
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

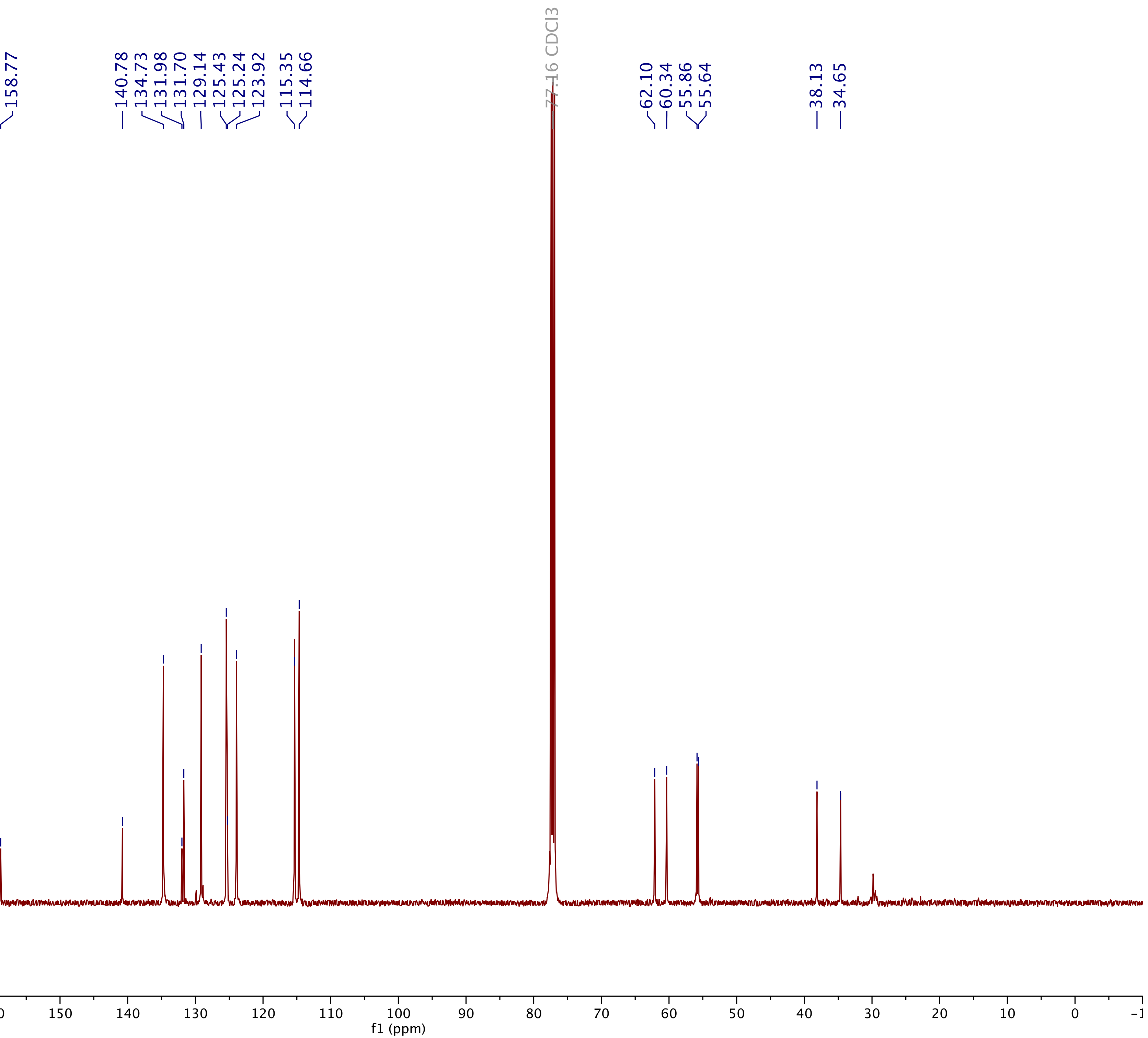

163.79
161.06
160.32
158.72
157.08
141.61
135.72
131.65
129.97
129.85
129.79
127.46
125.24
124.12
114.59
114.58
77.16 CDCl3
70.21
63.96
62.99
60.06
55.82
55.43
37.75
35.58
29.83
OMe
O
O
N
N
O
ClAu
N
N–N
MeO
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
–1
f1 (ppm)

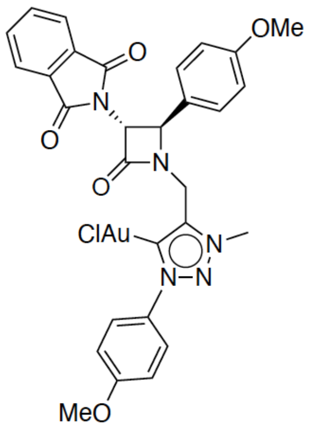
***cis*-14b**


7.94
7.92
7.83
7.82
7.81
7.81
7.75
7.74
7.74
7.73
7.42
7.40
7.26 CDCl3
7.01
7.01
7.00
6.99
5.36
5.35
4.90
4.90
4.81
4.78
4.48
4.36
4.33
3.87
3.84
OMe
O
N
ClAu
MeO
2.20
2.33
2.43
2.37
4.47
1.00
1.10
1.22
3.38
1.24
3.27
3.15
f1 (ppm)

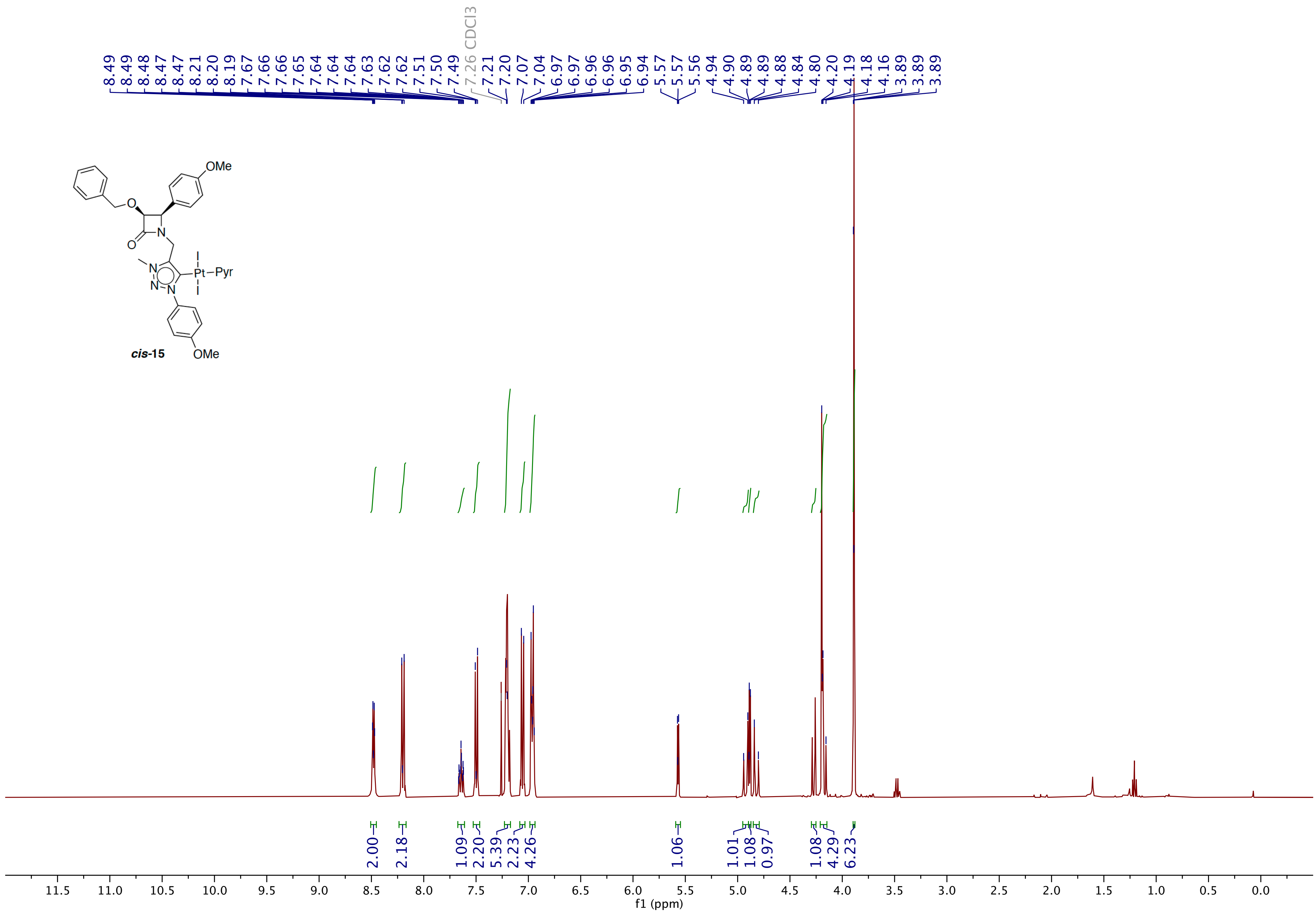
***trans*-14c**

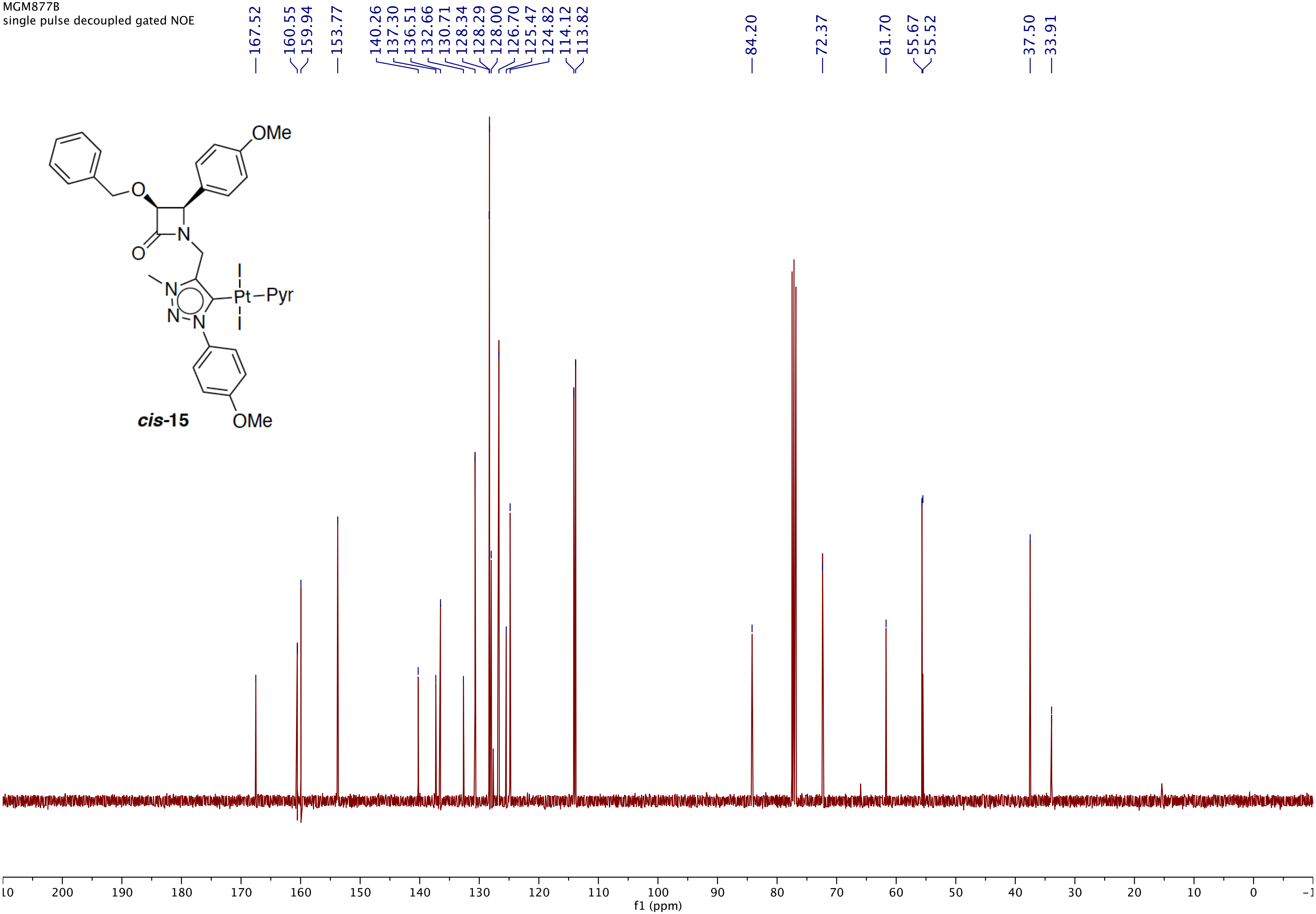
MGM822B-13c
STANDARD PROTON PARAMETERS
Selective band center: 5.42 (ppm); width: 9.8 (Hz)

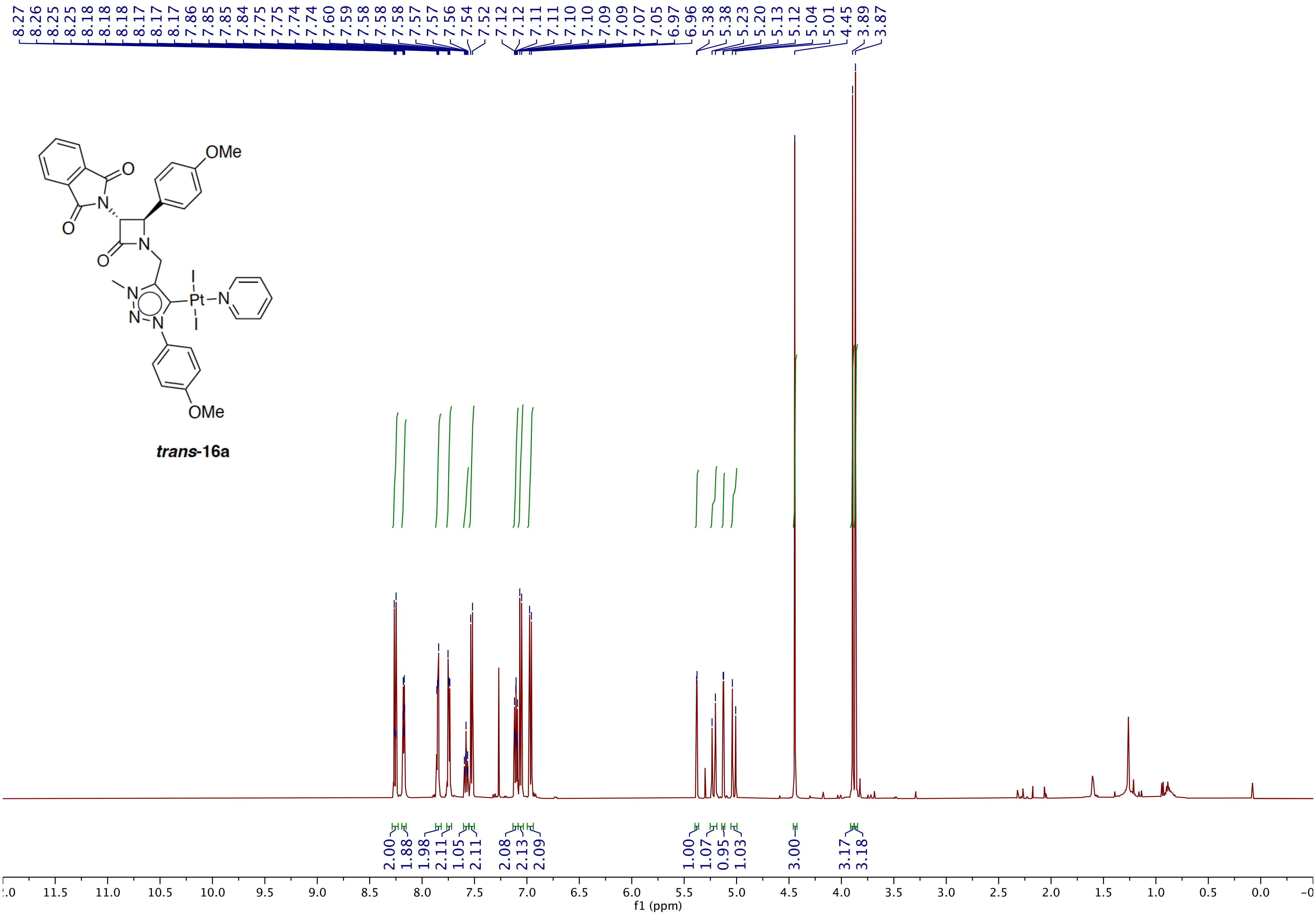



***trans*-14c**

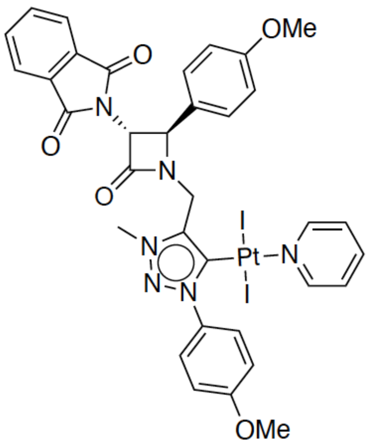

8.49 8.49 8.48 8.47 8.47 8.21 8.20 8.19 7.67 7.66 7.66 7.65 7.64 7.64 7.64 7.63 7.62 7.62 7.51 7.50 7.49 7.26 CDCl3 7.21 7.20 7.07 7.04 6.97 6.97 6.96 6.96 6.95 6.94 5.57 5.57 5.56 4.94 4.90 4.89 4.89 4.88 4.84 4.80 4.20 4.19 4.18 4.16 3.89 3.89 3.89
OMe
Pt–Pyr
OMe
cis-15
2.00 2.18 1.09 2.20 5.39 2.23 4.26 1.06 1.01 1.08 0.97 1.08 4.29 6.23
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


MGM877B
single pulse decoupled gated NOE
167.52
160.55
159.94
153.77
140.26
137.30
136.51
132.66
130.71
128.34
128.29
128.00
126.70
125.47
124.82
114.12
113.82
84.20
72.37
61.70
55.67
55.52
37.50
33.91
OMe
O
N
O
N
N
N
I
Pt
Pyr
I
OMe
cis-15
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

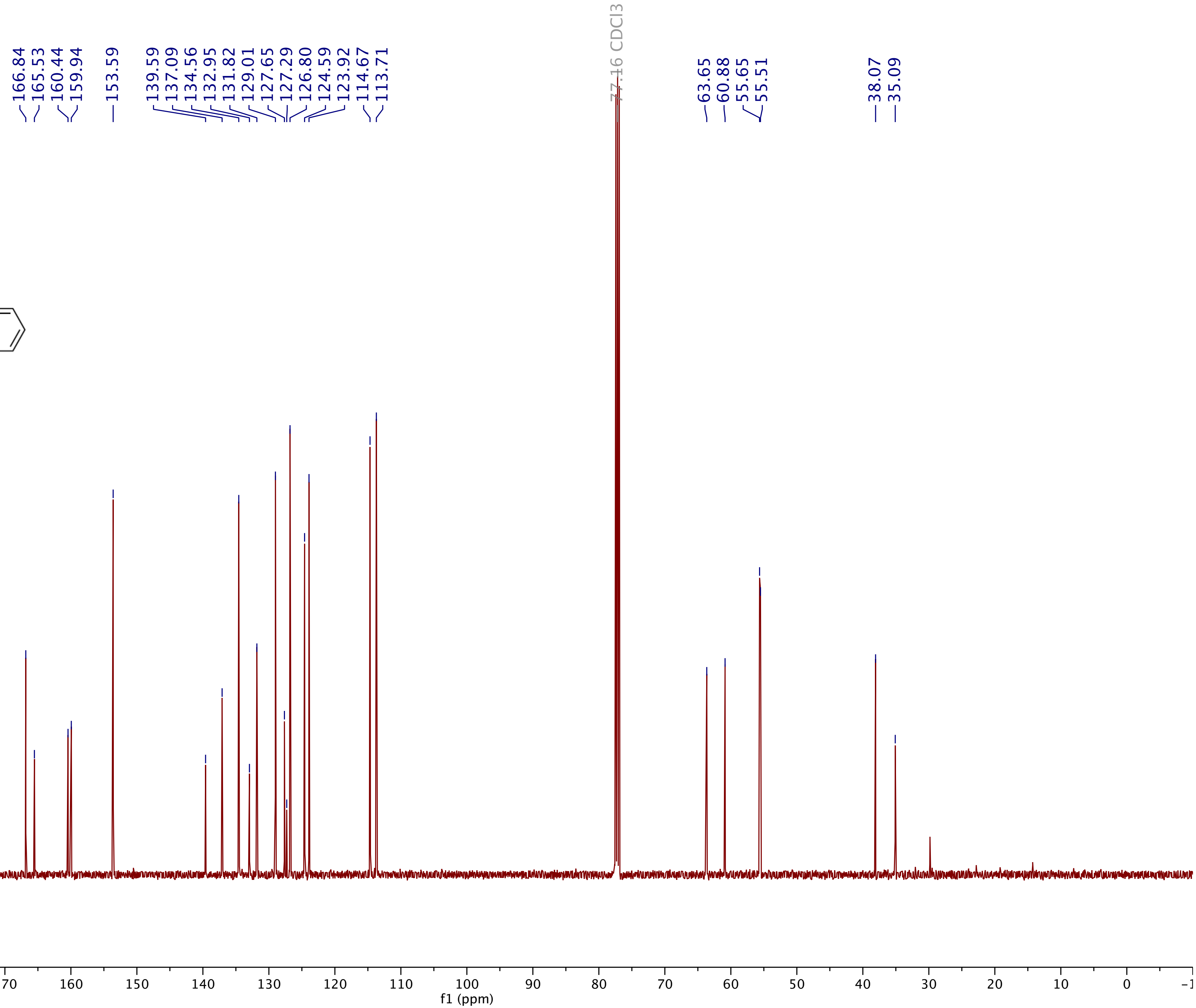


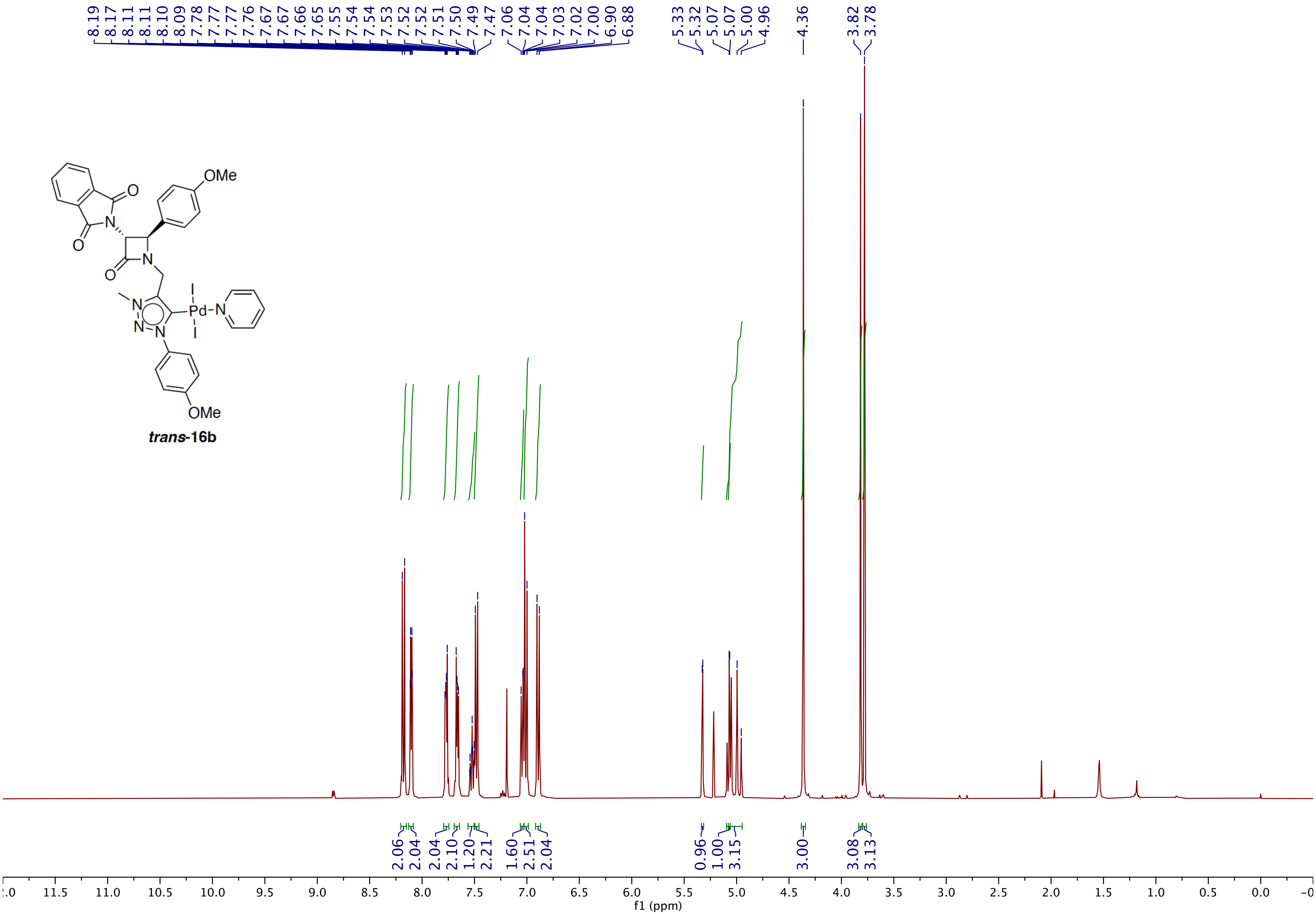
8.27 8.26 8.25 8.25 8.18 8.18 8.18 8.17 8.17 8.17 7.86 7.85 7.85 7.84 7.75 7.75 7.74 7.74 7.60 7.59 7.58 7.58 7.58 7.57 7.57 7.56 7.54 7.52 7.12 7.12 7.11 7.11 7.10 7.10 7.09 7.09 7.07 7.05 6.97 6.96 5.38 5.38 5.23 5.20 5.13 5.12 5.04 5.01 4.45 3.89 3.87
OMe
O
N
O
O
N
N
N
N
Pt
I
I
N
OMe
trans-16a
2.00 1.88 1.98 2.11 1.05 2.11 2.08 2.13 2.09 1.00 1.07 0.95 1.03 3.00 3.17 3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

MGM837CB-13c
STANDARD PROTON PARAMETERS

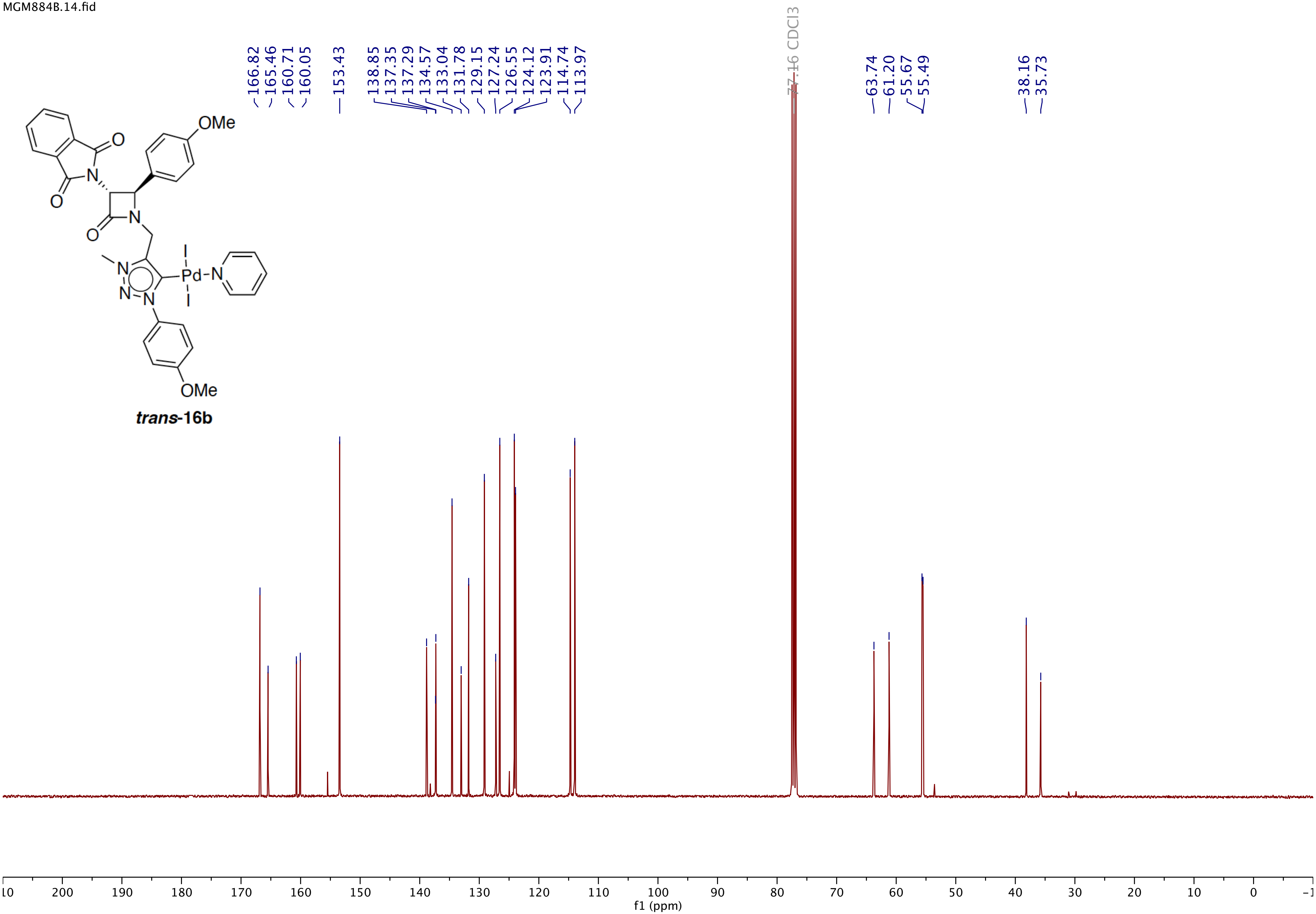


*trans*-16a

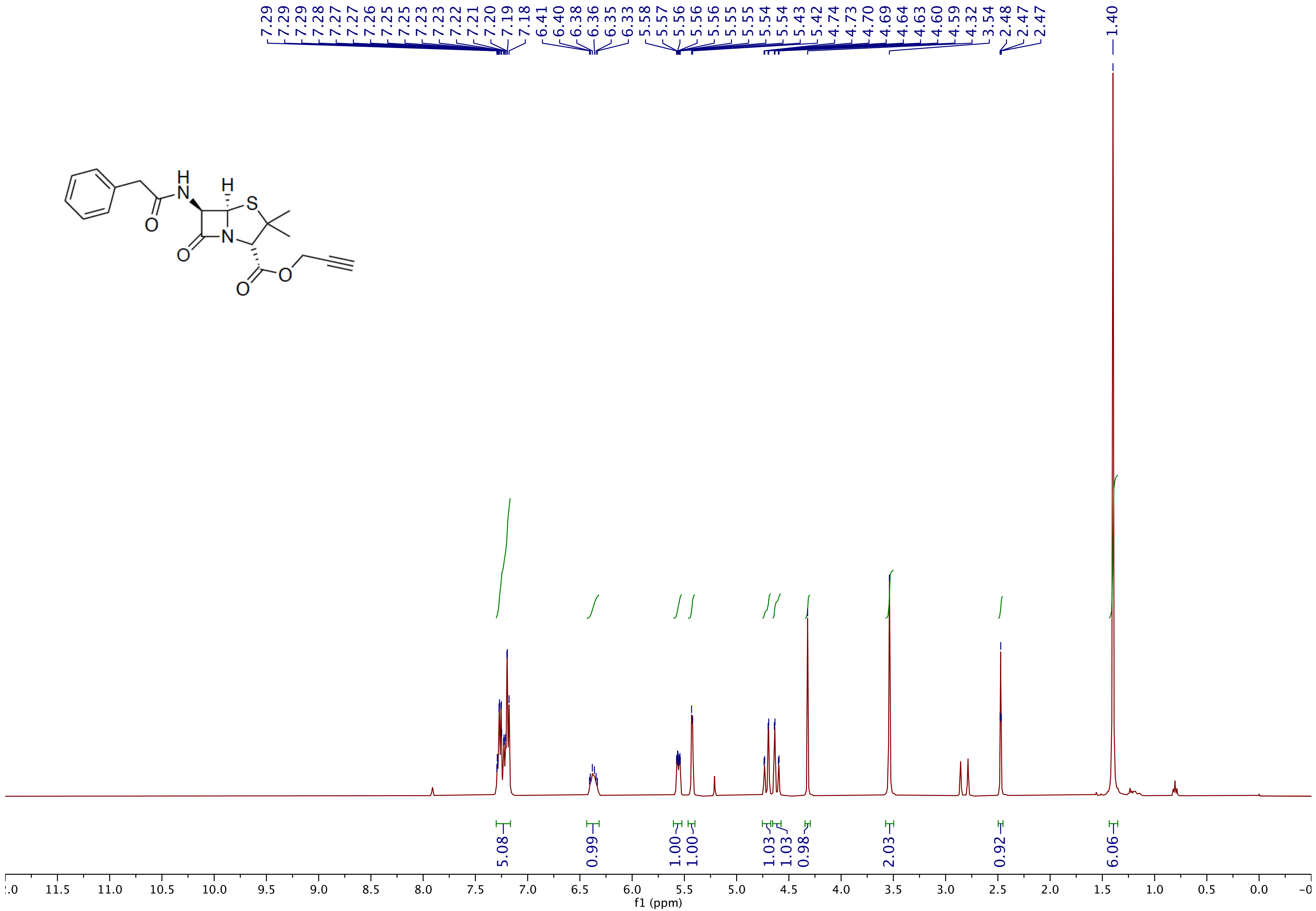


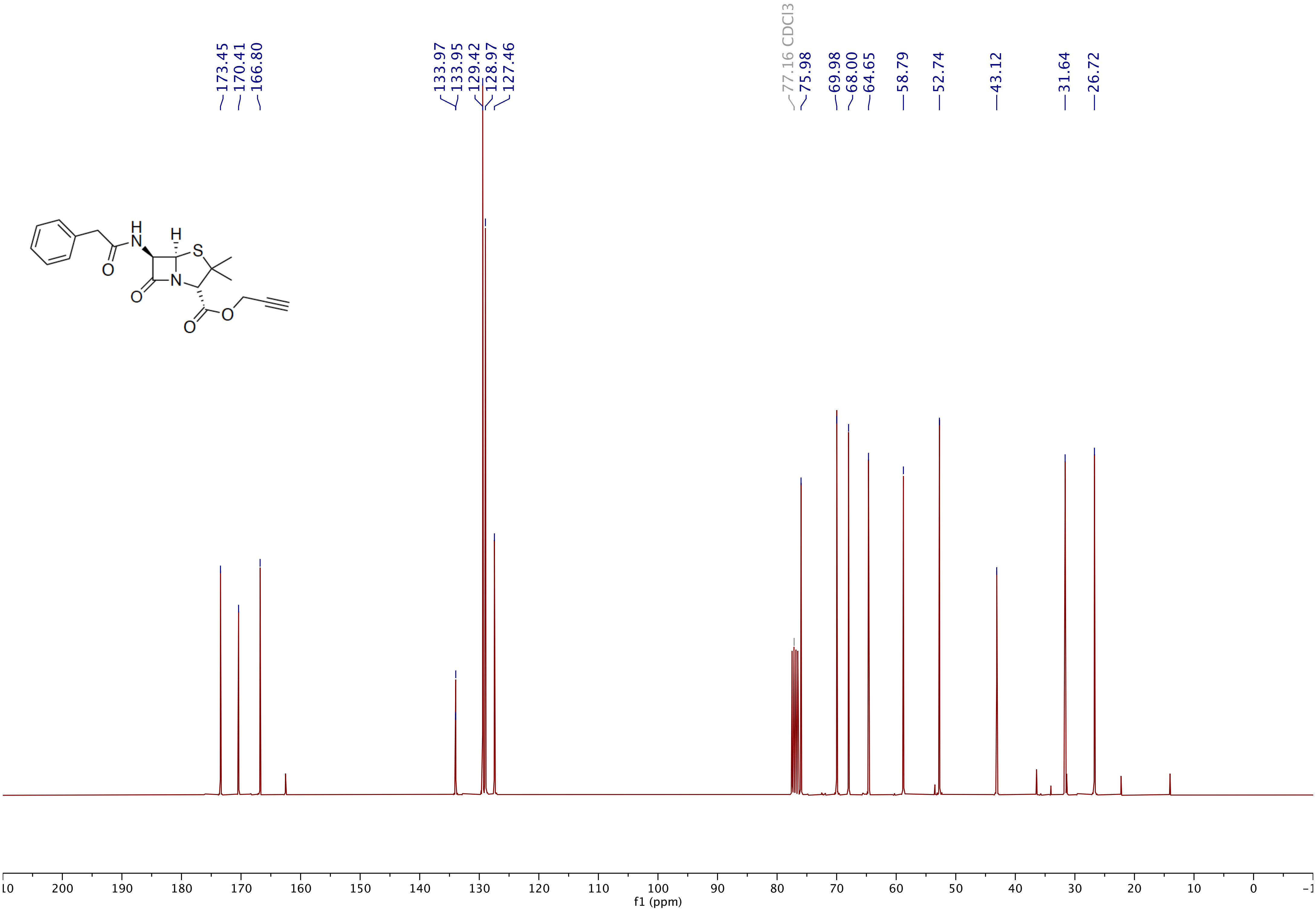

OMe
O
N
O
O
N
N
N
N
I
Pd
N
I
OMe
*trans*-16b
8.19 8.17 8.11 8.11 8.10 8.09 7.78 7.77 7.77 7.76 7.67 7.67 7.66 7.65 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.50 7.49 7.47 7.06 7.04 7.04 7.03 7.02 7.00 6.90 6.88
5.33 5.32 5.07 5.07 5.00 4.96
4.36
3.82 3.78
2.06 2.04 2.04 2.10 1.20 2.21 1.60 2.51 2.04
0.96 1.00 3.15
3.00
3.08 3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

MGM884B.14.fid

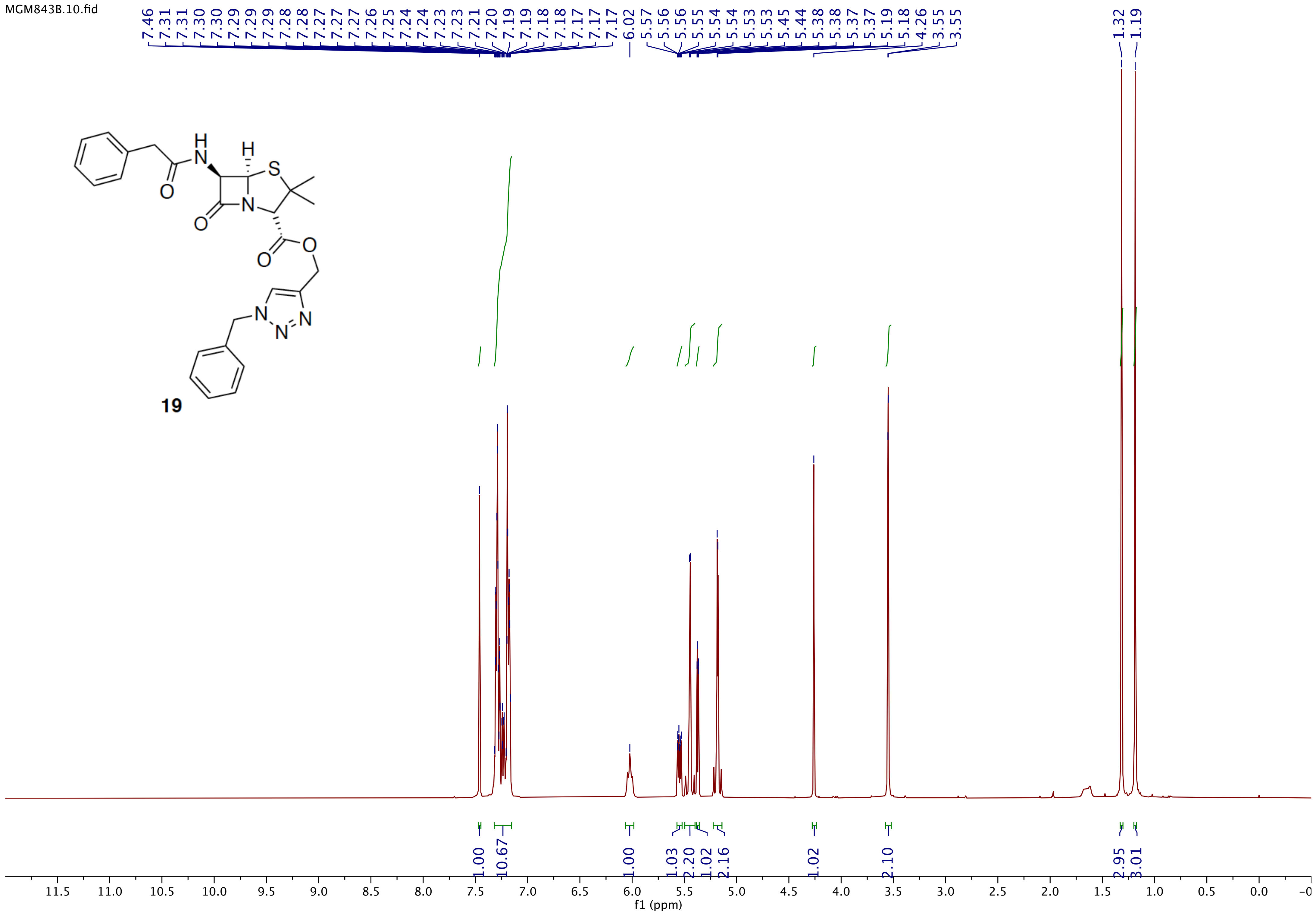



***trans*-16b**

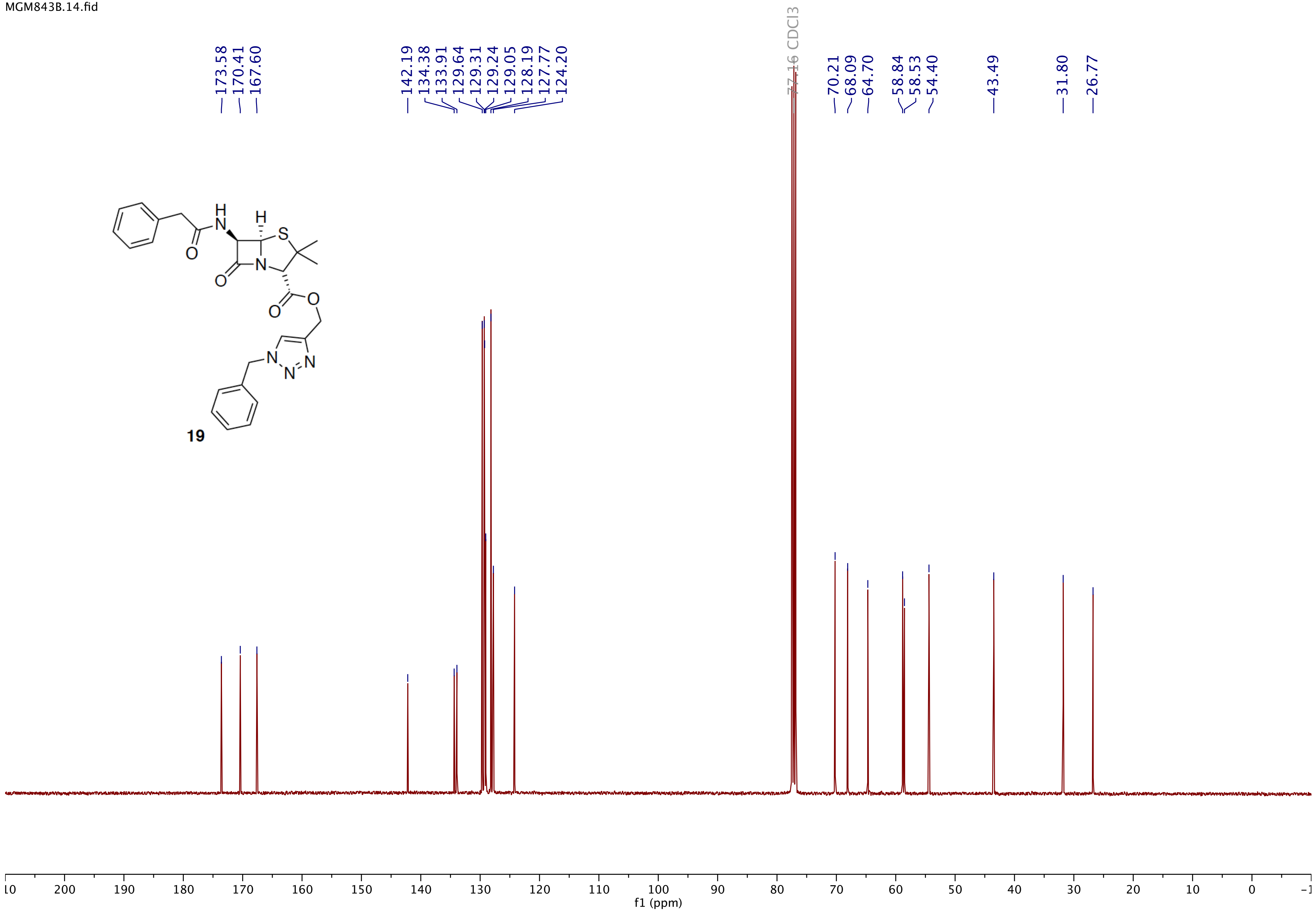

7.29 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.23 7.23 7.22 7.21 7.20 7.19 7.18 6.41 6.40 6.38 6.36 6.35 6.33 5.58 5.57 5.56 5.56 5.56 5.55 5.55 5.54 5.54 5.43 5.42 4.74 4.73 4.70 4.69 4.64 4.63 4.60 4.59 4.32 3.54 2.48 2.47 2.47 1.40
5.08
0.99
1.00
1.00
1.03
1.03
0.98
2.03
0.92
6.06
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



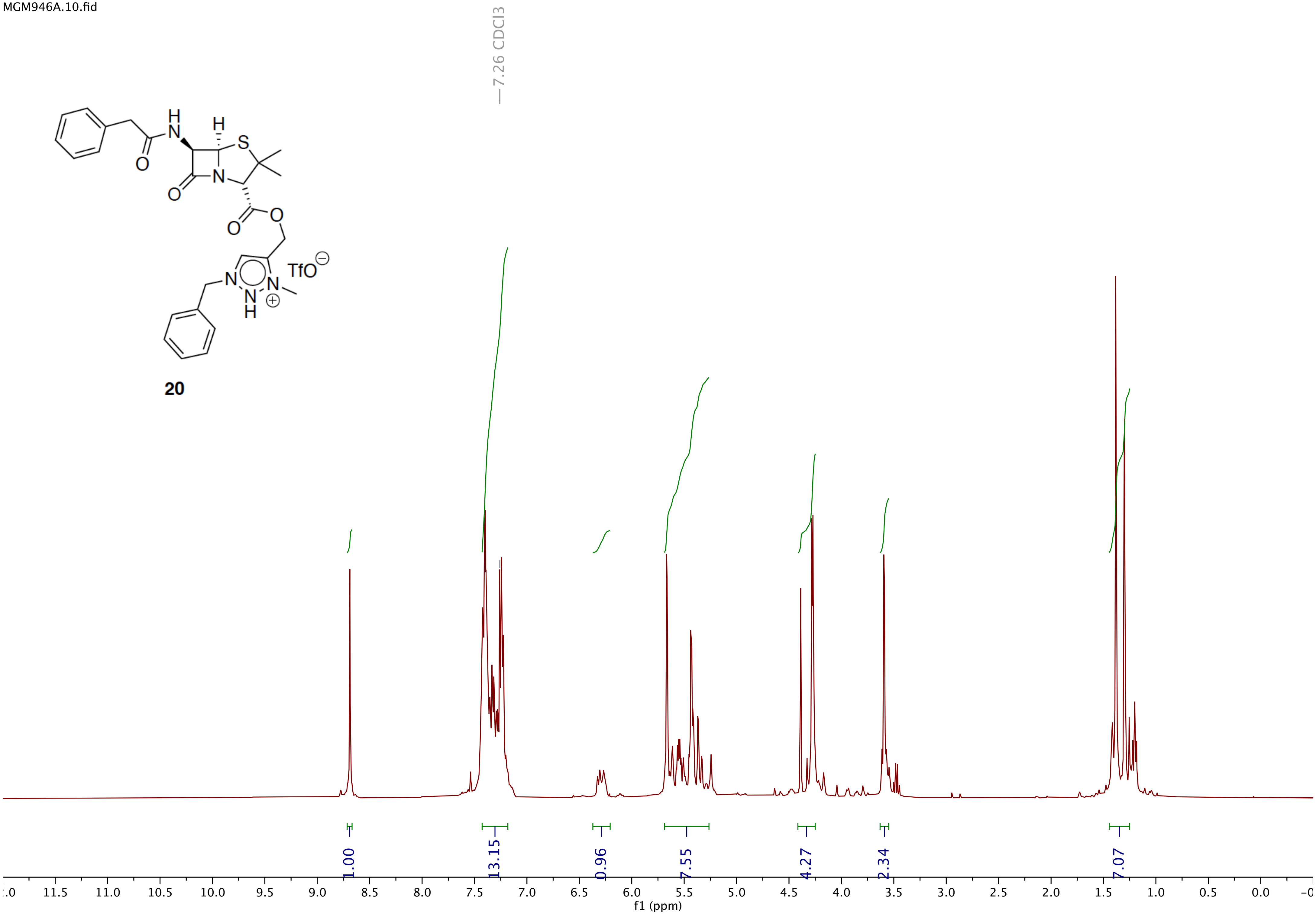
173.45
170.41
166.80
133.97
133.95
129.42
128.97
127.46
77.16 CDCl3
75.98
69.98
68.00
64.65
58.79
52.74
43.12
31.64
26.72
H
N
H
S
N
O
O
O
O
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

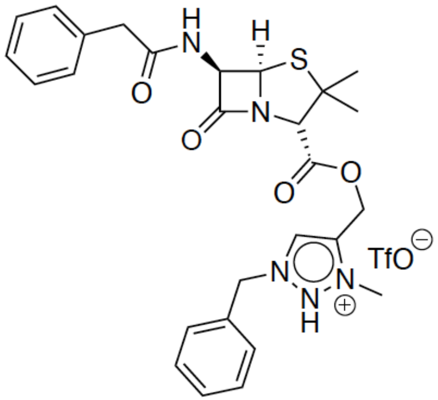


MGM843B.10.fid
7.46 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.25 7.24 7.24 7.23 7.23 7.21 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.17 6.02 5.57 5.56 5.56 5.55 5.54 5.54 5.53 5.53 5.45 5.44 5.38 5.38 5.37 5.37 5.19 5.18 4.26 3.55 3.55
1.32 1.19
H
N
H
S
O
N
O
O
O
N
N
N
19
1.00 10.67 1.00 1.03 2.20 1.02 2.16 1.02 2.10 2.95 3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0
f1 (ppm)

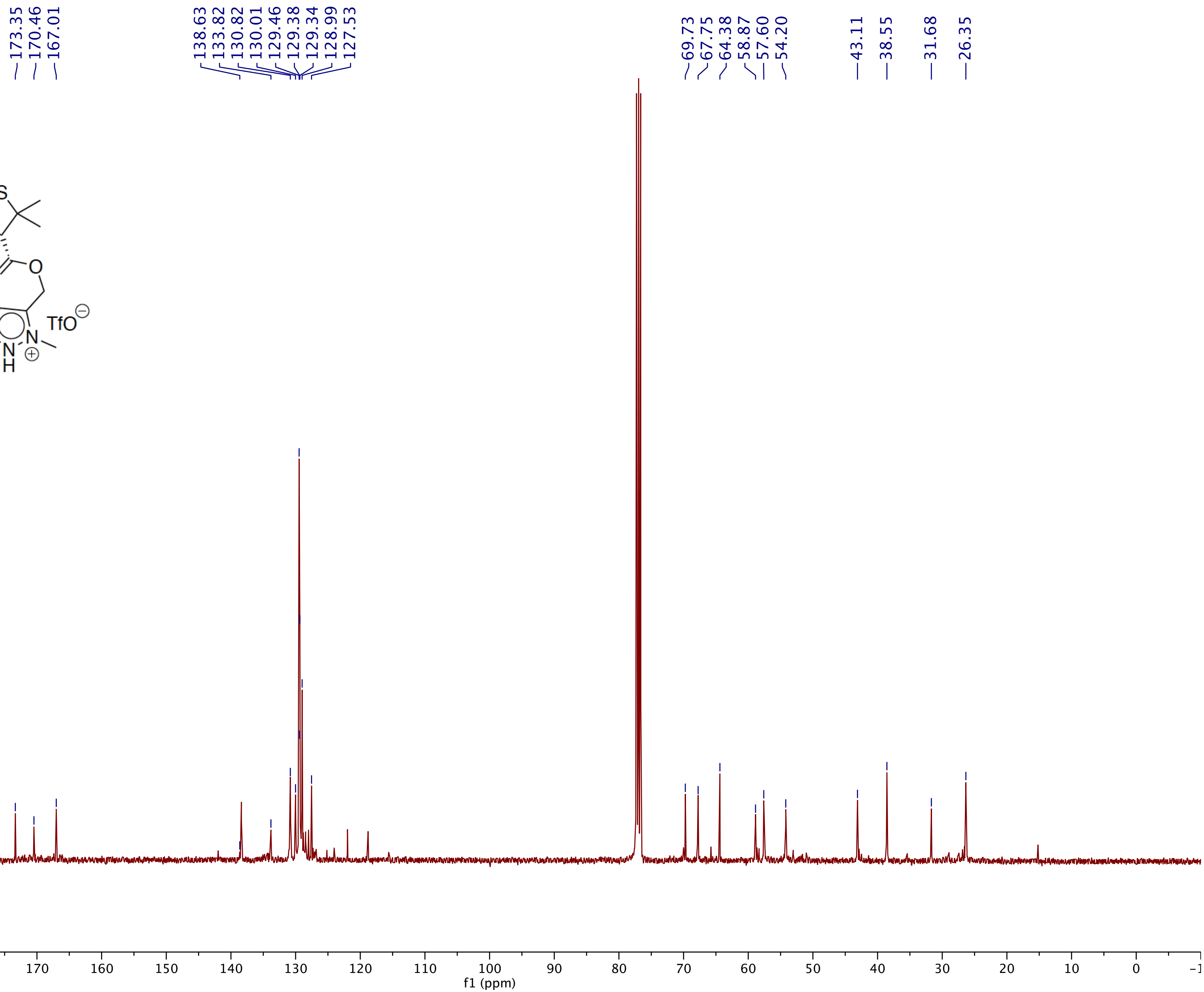

MGM843B.14.fid
173.58
170.41
167.60
142.19
134.38
133.91
129.64
129.31
129.24
129.05
128.19
127.77
124.20
77.16 CDCl3
70.21
68.09
64.70
58.84
58.53
54.40
43.49
31.80
26.77
19
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

MGM946A.10.fid




H
N
H
S
O
N
O
O
O
N
TfO
N
N
H

**20**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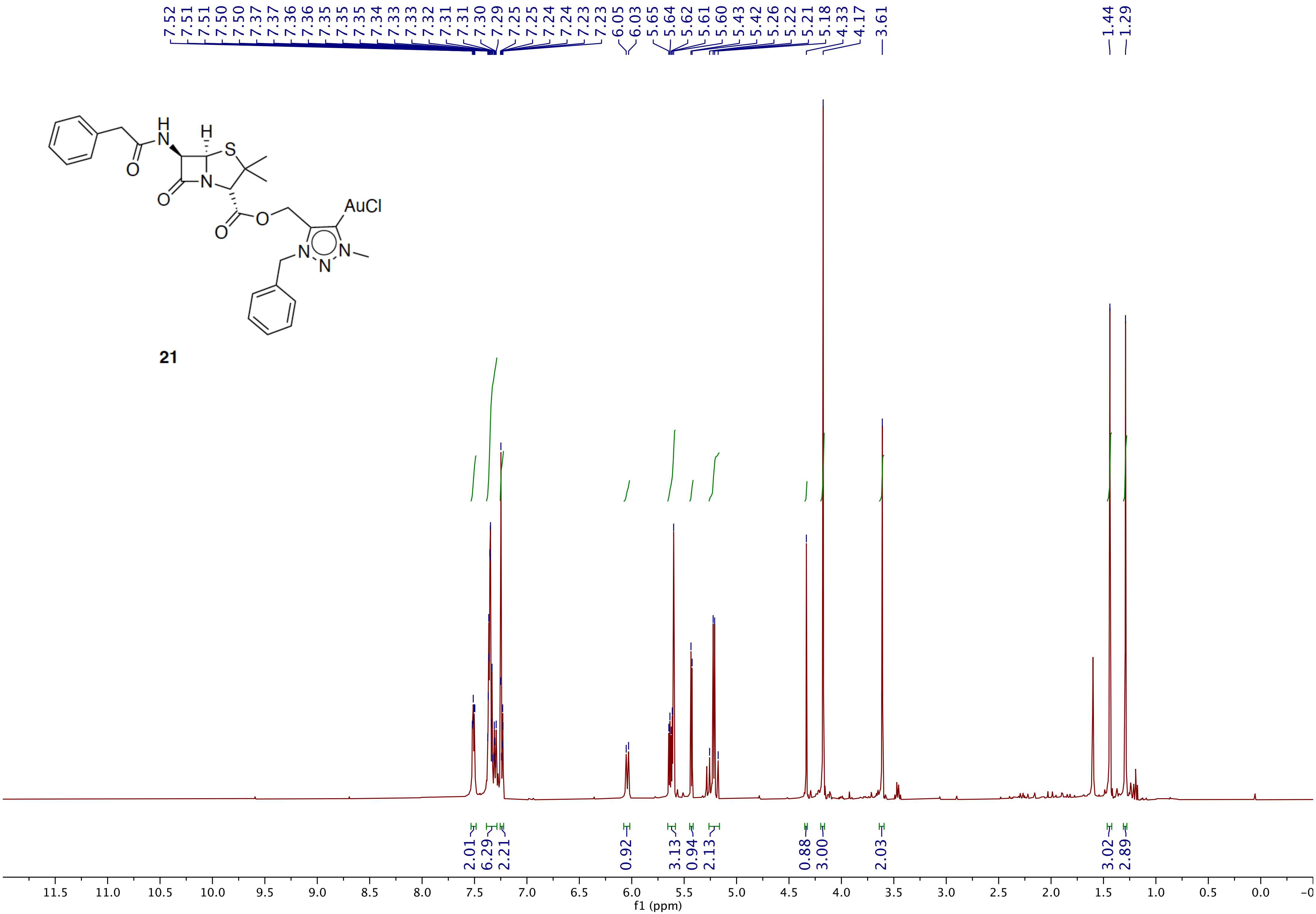
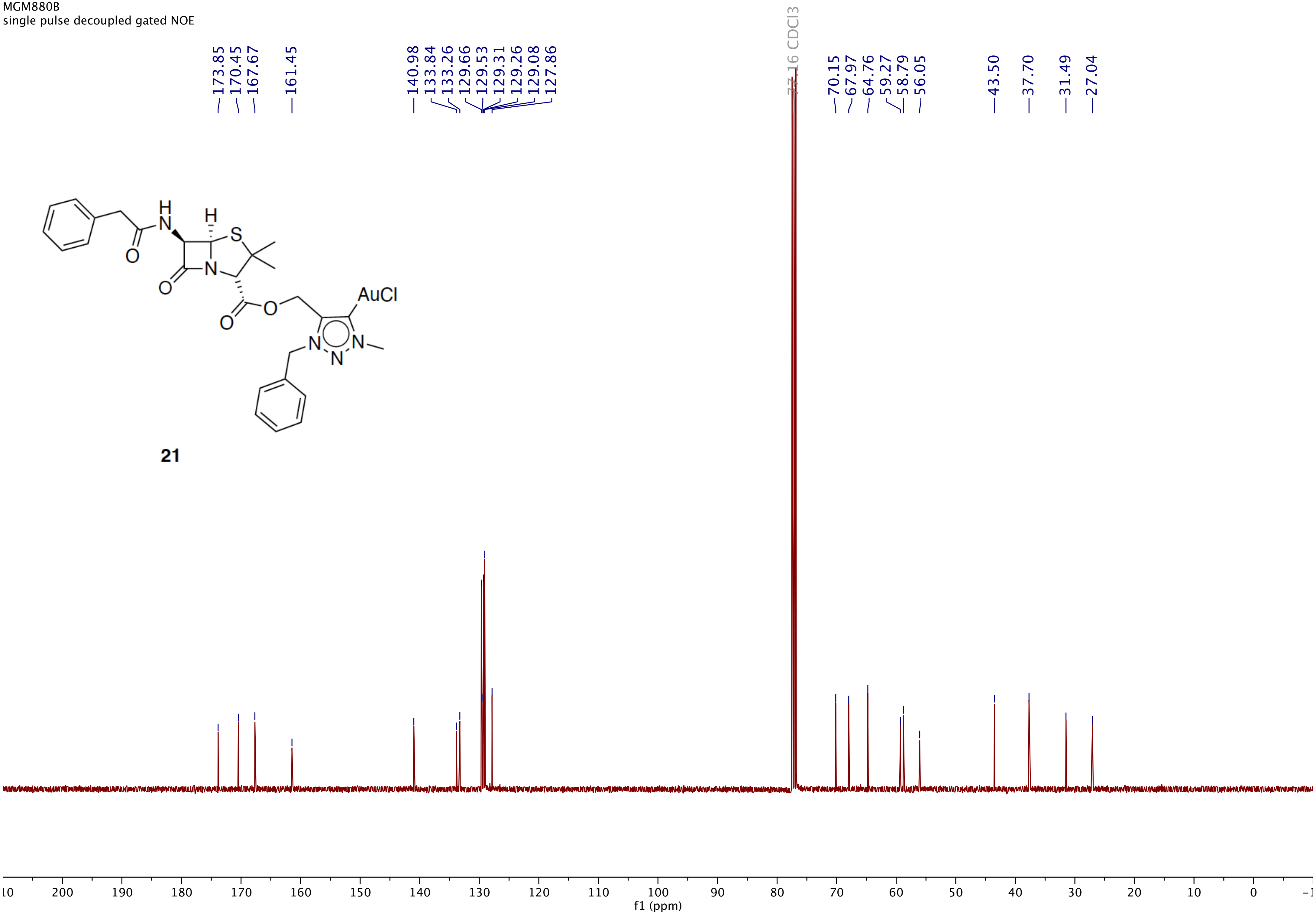
173.35
170.46
167.01
138.63
133.82
130.82
130.01
129.46
129.38
129.34
128.99
127.53
69.73
67.75
64.38
58.87
57.60
54.20
43.11
38.55
31.68
26.35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



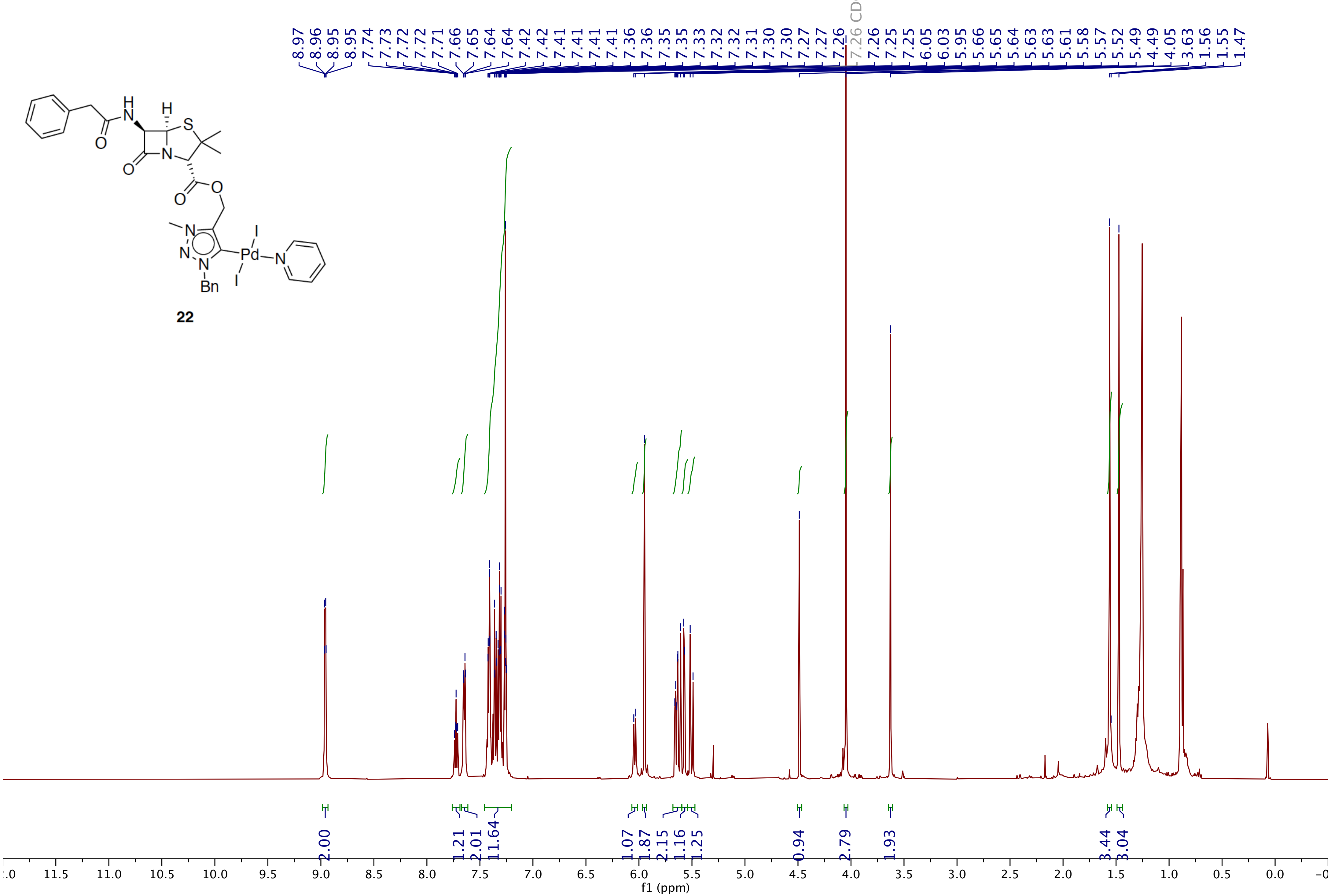
7.52
7.51
7.51
7.50
7.50
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.25
7.25
7.24
7.24
7.23
7.23
6.05
6.03
5.65
5.64
5.62
5.61
5.60
5.43
5.42
5.26
5.22
5.21
5.18
4.33
4.17
3.61
1.44
1.29
2.01
6.29
2.21
0.92
3.13
0.94
2.13
0.88
3.00
2.03
3.02
2.89
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


**21**

MGM880B
single pulse decoupled gated NOE

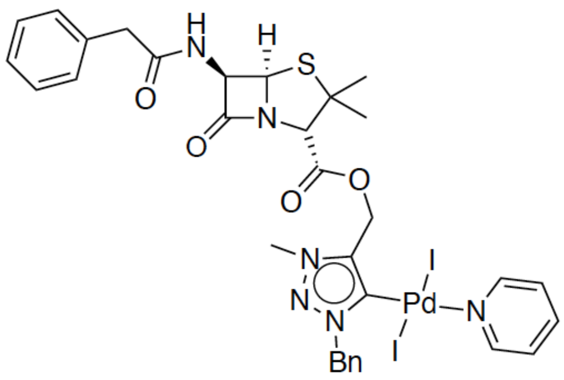


MGM947B-1h
STANDARD PROTON PARAMETERS



**22**

MGM947B-13c
STANDARD PROTON PARAMETERS



**22**