Supporting Material belonging to the manuscript entitled:

Desulfinylation of Ag (I) Sulfinyl Mesoionic Carbenes: Preparation of *C*-Unsubstituted Au (I)-1,2,3-Triazole Carbene Complexes

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General Methods

Unless noted otherwise, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. DMF and CH_3CN were dried by passage through solvent purification columns containing activated alumina. CH_2Cl_2 was stored on $CaCl_2$ for 24 h and dried through a distillation with CaH_2. Other solvents were HPLC grade and were used without further purification. All reagents were obtained from commercial sources and used without further purification, unless noted otherwise. Flash column chromatography was performed using silica gel (Merck, n° 9385, 230-400 mesh). ^1H and ^{13}C NMR spectra were recorded at 300, 400 or 500 MHz (^1H NMR) and at 100 or 125 MHz (^{13}C NMR) using $CDCl_3$ and DMSO-d_6 as solvents with the residual solvent signal as internal reference ($CDCl_3$, 7.26 and 77.2 ppm) and (DMSO-d_6, 2.50 and 39.5 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). 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. Optical rotations were measured on a Jasco P-2000 polarimeter using a sodium lamp. Melting points were determined on a Koffler block.

Alkynes [1] **9a**-**b** and azide [2] **10a** were prepared following a procedure previously described.

10b-**e** were prepared following a modified procedure previously reported: [3]

Amine (16 mmol, 1.00 equiv) was dissolved in THF (20 mL). Ice was then added followed by HCl 37% (3.5 mL). A solution of $NaNO_2$ (24.00 mmol, 1.50 equiv) in H_2O (10 mL) was added to the solution. The reaction was stirred at 0°C for 15 min. In case of acidic pH of the solution crude must be neutralized by $NaHCO_3$. NaN_3 (24 mmol, 1.50 equiv) dissolved in H_2O was added dropwise. The crude reaction was stirred for 1h. The mixture was extracted with Et_2O three times. The organic layer is washed with HCl 0.1M (three times), water (three times), dried over $MgSO_4$ and filtered. All the

[1] Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahasi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078.
[2] Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413.
[3] Wilkening, I.; del Signore, G.; Hackenberger, C. P. R. *Chem. Commun.* **2011**, 349.

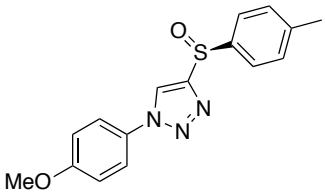
volatiles were removed under *vacuum* affording the corresponding azide, which was purified through a short pad of SiO_2.

1,2,3-Triazoles **11aa**, **11ab**, and their triazolium salts **8aa**, **8ab** and **17** were prepared following the same procedure as previously described.[4]

General procedure for the synthesis of 1,2,3-triazoles

A mixture of organic azide (1.20 equiv), alkyne (1.00 equiv), sodium (L)-ascorbate (0.50 equiv) and $CuSO_4 \cdot 5H_2O$ (0.25 equiv) in DMF was stirred under Ar 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 three times. The organic layer was dried over $MgSO_4$, filtered and the volatiles were removed under vacuum to afford the corresponding reaction products, which were purified through a short pad of SiO_2.

Synthesis of compound 11ba



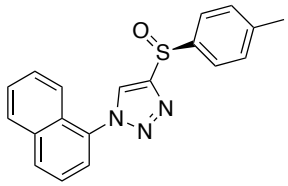
Following the general procedure a mixture of azide **10b** (623 mg, 4.17 mmol, 1.20 equiv), alkyne **9a** (571 mg, 3.48 mmol, 1.00 equiv), sodium (L)-ascorbate (344 mg, 1.74 mmol, 0.50 equiv) and $CuSO_4 \cdot 5H_2O$ (217 mg, 0.87 mmol, 0.25 equiv) in DMF (76 mL) was stirred under Ar at rt for 2 h. The resulting residue was purified (SiO_2, Hex/EtOAc 6:4) to yield **11ba** as a white solid (901 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H, N_3C=CH), 7.69 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 7.56 (d, J = 9.0 Hz, 2H, Ar *p*-$OMeC_6H_4$), 7.32 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 6.98 (d, J = 9.0 Hz, 2H, Ar *p*-$OMeC_6H_4$), 3.83 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.4 (C, Ar), 153.7 (C, N_3C=CH), 142.0 (C,

[4] Frutos, M.; Avello, M. G.; Viso, A.; Fernández de la Pradilla, R.; de la Torre, M. C.; Gornitzka, H.; Hemmet, C. *Org. Lett.* **2016**, *18*, 3570.

Ar), 140.0 (C, Ar), 130.2 (2CH, Ar), 129.7 (C, Ar), 124.8 (2CH, Ar), 122.4 (2CH, Ar), 122.2 (CH, N_3C=CH), 114.9 (2CH, Ar), 55.7 (OCH_3), 21.5 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3435, 3124, 1595, 1520, 1312, 1253, 1049, 1039, 826, 810, 631. $[\alpha]_D^{25}$ + 267.3 (*c* 0.9, $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{16}H_{16}N_3O_2S$: 314.0958 $[M+H]^+$, found: 314.0960. **m.p.** 94–97 °C.

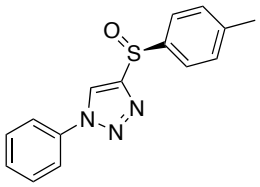
Synthesis of compound 11ca



Following the general procedure a mixture of azide **10c** (268 mg, 1.58 mmol, 1.30 equiv), alkyne **9a** (200 mg, 1.22 mmol, 1.00 equiv), sodium (L)-ascorbate (121 mg, 0.61 mmol, 0.50 equiv) and $CuSO_4 \cdot 5H_2O$ (76 mg, 0.30 mmol, 0.25 equiv) in DMF (27 mL) was stirred under Ar at rt for 3 h. The resulting residue was purified (SiO_2, Hex/EtOAc 6:4) to yield **11ca** as a white solid (252 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H, N_3C=CH), 8.02 (dd, *J* = 7.5 Hz, 2.0 Hz, 1H, Ar naph), 7.95 (br d, *J* = 8.0 Hz, 1H, Ar naph), 7.77 (d, *J* = 8.2 Hz, 2H, Ar *p*-tolyl), 7.55 (m, 5H, Ar), 7.37 (br d, *J* = 8.0 Hz, 0.6 Hz, 2H, Ar *p*-tolyl), 2.42 (s, 3H, CH_3 *p*-tolyl); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4 (C, N_3C=CH), 142.4 (C, Ar), 139.9 (C, Ar), 134.2 (C, Ar), 133.0 (C, Ar), 131.1 (2CH, Ar), 130.3 (2CH, Ar), 128.5 (CH, Ar), 128.3 (CH, Ar), 128.2 (C, Ar), 127.4 (CH, Ar), 126.5 (CH, N_3C=CH), 125.0 (CH, Ar), 124.9 (2CH, Ar), 123.8 (CH, Ar), 122.0 (CH, Ar), 21.6 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3435, 3104, 1490, 1085, 1054, 1033, 814, 796, 768, 521. $[\alpha]_D^{25}$ + 243.0 (*c* 0.8 $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{19}H_{16}N_3OS$: 334.1009 $[M+H]^+$, found: 334.1006. **m.p.** 97–100 °C.

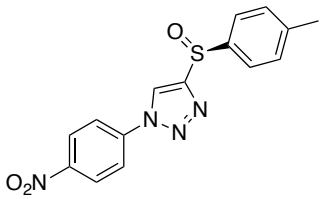
Synthesis of compound 11da



Following the general procedure a mixture of azide **10d** (430 mg, 3.61 mmol, 1.30 equiv), alkyne **9a** (456 mg, 2.78 mmol, 1.00 equiv), sodium (L)-ascorbate (275 mg, 1.38 mmol, 0.50 equiv) and $CuSO_4 \cdot 5H_2O$ (173 mg, 0.69 mmol, 0.25 equiv) in DMF (46 mL) was stirred under Ar at rt for 4 h. The resulting residue was purified (SiO_2, Hex/EtOAc 6:4) to yield **11da** as a white solid (449 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H, N_3C=CH), 7.70 (d, J = 8.1 Hz, 2H, Ar *p*-tolyl), 7.67 (m, 2H, Ar), 7.48 (m, 3H, Ar), 7.33 (d, J = 8.1 Hz, 2H, Ar *p*-tolyl), 2.39 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1 (C, N_3C=CH), 142.4 (C, Ar), 140.0 (C, Ar), 136.5 (C, Ar), 130.3 (2CH, Ar), 130.0 (2CH, Ar), 129.6 (CH, Ar), 124.8 (2CH, Ar), 122.1 (CH, N_3C=CH), 120.8 (2CH, Ar), 21.6 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3119, 1597, 1508, 1237, 1084, 1052, 1038, 811, 759, 686, 549, 511. $[\alpha]_D^{25}$ + 254.8 (*c* 0.8, $CHCl_3$). **HRMS (ESI)** *m*/*z* calculated for $C_{15}H_{14}N_3OS$: 284.0852 $[M+H]^+$, found: 284.0859. **m.p.** 116–119 °C.

Preparation of compound 11ea

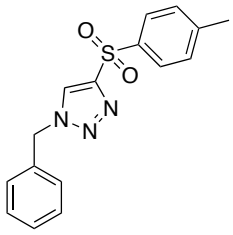


Following the general procedure a mixture of azide **10e** (513 mg, 3.16 mmol, 1.30 equiv), alkyne **9a** (400 mg, 2.43 mmol, 1.00 equiv), sodium (L)-ascorbate (241 mg, 1.22 mmol, 0.50 equiv) and $CuSO_4 \cdot 5H_2O$ (187 mg, 0.61 mmol, 0.25 equiv) in DMF (40

mL) was stirred under Ar at rt for 2 h 30. The resulting residue was purified (SiO_2, Hex/EtOAc 1:1) to yield **I11ae** as a white solid (513 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H, N_3C=CH), 8.41 (d, J = 9.1 Hz, 2H, Ar *p*-$NO_2C_6H_4$), 7.96 (d, J = 9.1 Hz, 2H, Ar *p*-$NO_2C_6H_4$), 7.72 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 7.36 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 2.41 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4 (C, N_3C=CH), 147.9 (C, Ar), 142.8 (C, Ar), 140.6 (C, Ar), 139.7 (C, Ar), 130.5 (2CH, Ar), 125.8 (2CH, Ar), 124.9 (2CH, Ar), 122.1 (CH, N_3C=CH), 121.0 (2CH, Ar), 21.7 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3145, 3101, 1598, 1532, 1505, 1344, 1235, 1082, 1055, 1032, 855, 573. **$[\alpha]_D^{25}$** + 252.2 (*c* 0.5 $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{15}H_{13}N_4O_3S$: 329.0703 $[M+H]^+$, found: 329.0710. **m.p.** 209–210 °C.

Synthesis of compound 16[5]



In a bottom flask, triazole **7aa** (90 mg, 0.30 mmol, 1.00 equiv) and mcpba (105 mg, 0.61 mmol, 2.00 equiv) were dissolved in $CHCl_3$ (5 mL) 1 h at rt. The reaction was quenched with $Na_2S_2O_3$ 0.5 M. The crude reaction was extracted twice with CH_2Cl_2. The organic layers were washed with NaOH 1.0 M and the combined aqueous phases were again extracted three times with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under vacuum to afford the corresponding reaction product **16** as a white solid (94 mg, quantitative). No further purifications were needed.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H, N_3C=CH), 8.22 (d, J = 8.1 Hz, 2H, Ar *p*-tolyl), 7.68 (br s, 3H, Ar), 7.61 (d, J = 8.1 Hz, 2H, Ar *p*-tolyl), 7.58 (br s, 2H, Ar), 5.81 (s, 2H, NCH_2), 2.69 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7 (C,

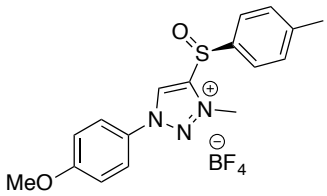
[5] Bolje, A.; Košmrlj, J. *Org. Lett.* **2013**, *15*, 5084.

N_3C=CH), 145.2 (C, Ar), 137.1 (C, Ar), 133.1 (C, Ar), 130.1 (2CH, Ar), 129.5 (3CH, Ar), 128.7 (2CH, Ar), 128.2 (2CH, Ar), 125.6 (CH, N_3C=CH), 55.0 (NCH_2), 21.8 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 2963, 2924, 1769, 1698, 1428, 1324, 1262, 1100, 802, 720, 598. **HRMS (ESI)** *m/z* calculated for $C_{16}H_{16}N_3O_2S$: 314.0958 $[M+H]^+$, found 314.0955. **m.p.** 140–143 °C.

General procedure for the synthesis of triazolium salts

Triazole (1.00 equiv) and Meerwein's salt (1.30 equiv per triazole) were stirred under Ar at rt in anh CH_2Cl_2 until completion of reaction (^{1}H NMR analysis). The reaction was quenched with methanol and filtered through a short pad of $NaHCO_3$. The solvent was removed under vacuum to afford the corresponding reaction product without further purification. In some cases, the product was washed with a mixture of CH_2Cl_2:pentane to remove the starting material traces.

Synthesis of compound 8ba

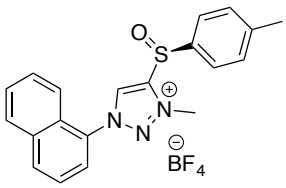


Following the general procedure a mixture of **11ba** (112 mg, 0.36 mmol, 1.00 equiv) and Me_3OBF_4 (69 mg, 0.46 mmol, 1.30 equiv) in CH_2Cl_2 (12 mL) was stirred under Ar at rt overnight. The reaction was quenched with methanol and filtered through a plug of $NaHCO_3$. The solvent was removed under vacuum to yield **8ba** as a white solid (139 mg, 93%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 1H, N_3C=CH), 7.91 (m, 4H, 2CH Ar *p*-$OMeC_6H_4$ + 2CH *p*-tolyl), 7.54 (d, J = 8.1 Hz, 2H, Ar *p*-tolyl), 7.25 (d, J = 9.1 Hz, 2H, Ar *p*-$OMeC_6H_4$), 4.37 (s, 3H, NCH_3), 3.87 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 161.7 (C, Ar), 146.4 (C, N_3C=CH), 144.0 (C, Ar), 136.5 (C, Ar), 130.8 (2CH, Ar), 129.3 (CH, N_3C=CH), 127.7 (C, Ar), 126.2 (2CH, Ar),

123.5 (2CH, Ar), 115.3 (2CH, Ar), 56.0 (OCH_3), 39.6 (NCH_3), 21.1 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3436, 3124, 2923, 1607, 1595, 1514, 1260, 1184, 1057, 836, 813, 520. $[\alpha]_D^{25}$ + 24.6 (*c* 0.5, $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{17}H_{18}N_3O_2S$: 328.1114 [M–BF_4]$^+$, found: 328.1127. **m.p.** 50–52 °C.

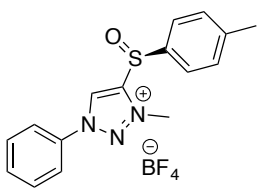
Synthesis of compound 8ca



Following the general procedure a mixture of **11ca** (430 mg, 1.29 mmol, 1.00 equiv) and Me_3OBF_4 (248 mg, 1.68 mmol, 1.30 equiv) in CH_2Cl_2 (40 mL) was stirred under Ar at rt overnight. The reaction was quenched with methanol and filtered through a plug of $NaHCO_3$. The solvent was removed under vacuum to yield **8ca** as a white solid (477 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H, Ar naph), 7.95 (m, 5H, Ar *p*-tolyl, N_3C=CH and Ar naph), 7.61 (m, 4H, Ar naph), 7.43 (d, *J* = 8.0 Hz, 2H, Ar *p*-tolyl), 4.68 (s, 3H, NCH_3), 2.41 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4 (C, N_3C=CH), 145.0 (C, Ar), 134.4 (C, Ar), 133.9 (C, Ar), 133.3 (CH, Ar), 131.8 (C, Ar), 131.2 (2CH, Ar), 130.6 (C, Ar), 129.7 (CH, Ar), 128.8 (CH, Ar), 128.1 (CH, Ar), 126.9 (CH, Ar), 125.9 (2CH, Ar), 125.7 (CH, Ar), 125.2 (CH, N_3C=CH), 120.6 (2CH, Ar), 40.2 (NCH_3), 21.8 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3436,3108, 3061, 1059, 807, 772, 519. $[\alpha]_D^{25}$ + 136.0 (*c* 0.5 $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{20}H_{18}N_3OS$: 348.1165 [M–BF_4]$^+$, found: 348.1165. **m.p.** 140–143 °C.

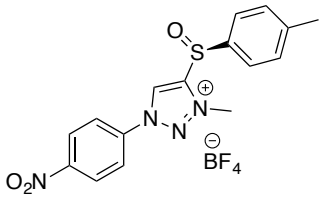
Synthesis of compound 8da



Following the general procedure a mixture of **11da** (91 mg, 0.32 mmol, 1.00 equiv) and Me_3OBF_4 (62 mg, 0.42 mmol, 1.30 equiv) in CH_2Cl_2 (10 mL) was stirred under Ar at rt overnight. The reaction was quenched with methanol and filtered through a plug of $NaHCO_3$. The solvent was removed under vacuum to yield **8da** as a white solid (123 mg, quantitative).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H, N_3C=CH), 7.84 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 7.79 (m, 2H, Ar), 7.54 (m, 3H, Ar), 7.42 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 4.45 (s, 3H, NCH_3), 2.41 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1 (C, N_3C=CH), 144.9 (C, Ar), 135.0 (C, Ar), 134.6 (C, Ar), 132.4 (CH, Ar), 131.3 (2CH, Ar), 130.5 (2CH, Ar), 128.9 (CH, N_3C=CH), 125.8 (2CH, Ar), 122.3 (2CH, Ar), 40.0 (NCH_3), 21.7 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3414, 3037, 1084, 1062, 817, 772, 521. $[\alpha]_D^{25}$ + 55.4 (*c* 0.7 $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{16}H_{16}N_3OS$: 298.1009 [M–BF_4]$^+$, found: 298.1018. **m.p.** 110–112 °C.

Synthesis of compound 8ea

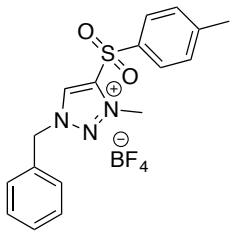


Following the general procedure a mixture of **11ea** (263 mg, 0.80 mmol, 1.00 equiv) and Me_3OBF_4 (154 mg, 1.04 mmol, 1.30 equiv) in CH_2Cl_2 (25 mL) was stirred under Ar at rt overnight. The reaction was quenched with methanol and filtered through a plug of $NaHCO_3$. The solvent was removed under vacuum to yield **8ea** as a white solid (210 mg, 76%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H, N_3C=CH), 8.58 (d, J = 9.1 Hz, 2H, Ar *p*-$NO_2C_6H_4$), 8.29 (d, J = 9.1 Hz, 2H, Ar *p*-$NO_2C_6H_4$), 7.91 (d, J = 8.3 Hz, 2H, Ar *p*-tolyl), 7.56 (d, J = 8.3 Hz, 2H, Ar *p*-tolyl), 4.46 (s, 3H, NCH_3), 2.44 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 149.1 (C, Ar), 147.1 (C, N_3C=CH), 144.1 (C, Ar), 138.6 (C, Ar), 136.3 (C, Ar), 130.8 (2CH, Ar), 130.5 (CH, N_3C=CH), 126.2 (2CH, Ar), 125.7 (2CH, Ar), 123.3 (2CH, Ar), 40.0 (NCH_3), 21.1 (CH_3, *p*-tolyl). **IR (KBr)**

$\nu_{máx}$ 3401, 3126, 1536, 1350, 1062, 856, 573. $[\alpha]_D^{25}$ + 67.5 (*c* 0.2, MeOH/$CHCl_3$ 4:1). **HRMS (ESI)** *m/z* calculated for $C_{16}H_{15}N_4O_3S$: 343.0859 $[M–BF_4]^+$, found: 343.0861. **m.p.** 209–211 °C.

Synthesis of compound $[16Me]^+BF_4^-$



Following the general procedure a mixture of **16** (70 mg, 0.22 mmol, 1.00 equiv) and Me_3OBF_4 (43 mg, 0.29 mmol, 1.30 equiv) in CH_2Cl_2 (7 mL) was stirred under Ar at rt overnight. The reaction was quenched with methanol and filtered through a plug of $NaHCO_3$. The solvent was removed under vacuum to yield $[16Me]^+BF_4^-$ as a white solid (91 mg, quantitative).

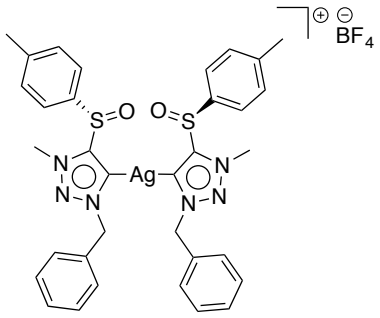
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 1H, N_3C=CH), 8.06 (d, *J* = 8.4 Hz, 2H, Ar *p*-tolyl), 7.60 (d, *J* = 8.4 Hz, 2H, Ar *p*-tolyl), 7.51 (m, 2H, Ar), 7.45 (m, 3H, Ar), 5.85 (s, 2H, NCH_2), 4.37 (s, 3H, NCH_3), 2.46 (s, 3H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.8 (C, Ar), 141.1 (C, N_3C=CH), 134.2 (CH, N_3C=CH), 133.7 (C, Ar), 132.0 (C, Ar), 130.9 (2CH, Ar), 129.4 (CH, Ar), 129.3 (2CH, Ar), 129.1 (2CH, Ar), 129.0 (2CH, Ar), 57.1 (NCH_2), 40.2 (NCH_3), 21.3 (CH_3, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3420, 1594, 1456, 1353, 1169, 1083, 813, 738, 690, 651, 597, 534. **HRMS (ESI)** *m/z* calculated for $C_{17}H_{18}N_3O_2S$: 328.1114 $[M–BF_4]^+$, found: 328.1123. **m.p.** 180–183 °C.

General procedure for the synthesis of silver carbenes

In a schlenk flask charged with 4 Å molecular sieves, a mixture of triazolium salt (1.00 equiv), NMe_4Cl (1.50 equiv) and Ag_2O (0.75 equiv) was stirred at rt in the

dark in anh CH_3CN:CH_2Cl_2 (1:10) until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the volatiles were removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite to separate the product form NMe_4Cl. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction products.

Synthesis of compound 7aa

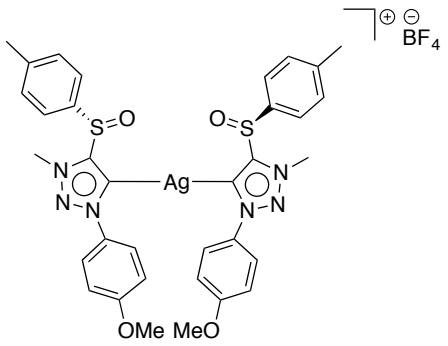


Following the general procedure a mixture of triazolium salt **8aa** (168 mg, 0.47 mmol, 1.00 equiv), NMe_4Cl (77 mg, 0.70 mmol, 1.50 equiv) and Ag_2O (81 mg, 0.35 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (26 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction product **7aa** as a brownish solid (170 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.3 Hz, 4H, Ar *p*-tolyl), 7.21 (m, 4H, Ar), 7.35 (m, 10H, 6H Ar and 4H Ar *p*-tolyl), 5.67 (d, J = 14.1 Hz, 2H, NCH_2), 5.62 (d, J = 14.1 Hz, 2H, NCH_2), 4.16 (s, 6H, NCH_3), 2.42 (s, 6H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4 (2C, N_3C=*C*Ag, observed in HMBC), 149.0 (2C, N_3*C*=CAg), 143.5 (2C, Ar), 136.7 (2C, Ar), 133.2 (2C, Ar), 130.9 (4CH, Ar), 129.6 (2CH, Ar), 129.4 (4CH, Ar), 128.9 (4CH, Ar), 124.7 (4CH, Ar), 60.6 ($2NCH_2$), 38.1 ($2NCH_3$), 21.7 ($2CH_3$, *p*-tolyl). **IR (KBr) $\nu_{máx}$** 3440, 3031, 2950, 1492, 1456, 1316, 1083, 1052, 811,

745, 708. **$[\alpha]_D^{25}$** – 40.6 (*c* 0.2, $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{34}H_{34}AgN_6O_2S_2$: 731.1228 $[M–BF_4]^+$, found: 731.1229. **m.p.** decomposes before melting.

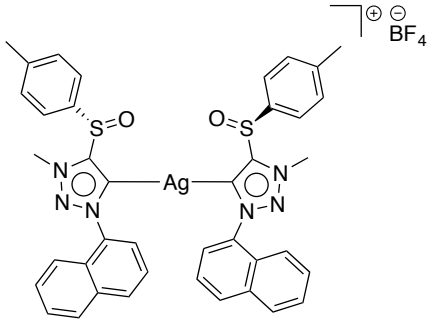
Synthesis of compound 7ba



Following the general procedure a mixture of triazolium salt **8ba** (150 mg, 0.46 mmol, 1.00 equiv), NMe_4Cl (75 mg, 0.69 mmol, 1.50 equiv) and Ag_2O (79 mg, 0.34 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (24 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2 to afford the corresponding reaction product **7ba** as a brownish solid (171 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 4H, Ar *p*-$OMeC_6H_4$), 7.62 (d, *J* = 8.2 Hz, 4H, Ar *p*-tolyl), 7.33 (d, *J* = 8.2 Hz, 4H, Ar *p*-tolyl), 6.92 (d, *J* = 9.0 Hz, 4H, Ar *p*-$OMeC_6H_4$), 4.24 (s, 6H, NCH_3), 3.77 (s, 6H, OCH_3), 2.34 (s, 6H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3 (2C, Ar), 149.8 (2C, N_3C=CAg), 143.1 (2C, Ar), 137.0 (2C, Ar), 132.6 (2C, Ar), 130.9 (4CH, Ar), 125.0 (4CH, Ar), 124.9 (4CH, Ar), 114.9 (4CH, Ar), 55.8 ($2OCH_3$), 38.2 ($2NCH_3$), 21.5 ($2CH_3$, *p*-tolyl), $C_{carbene}$ not observed. **IR (KBr) $\nu_{máx}$** 3456, 3050, 2957, 2841, 1606, 1512, 1258, 1084, 1055, 837, 813, 738, 612. **$[\alpha]_D^{25}$** – 157.2 (*c* 0.2 $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{34}H_{34}AgN_6O_4S_2$: 763.1127 $[M–BF_4]^+$, found: 763.1118. **m.p.** decomposes before melting.

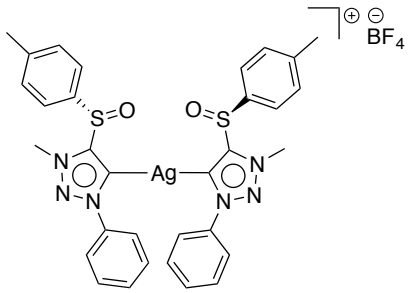
Synthesis of compound 7ca



Following the general procedure a mixture of triazolium salt **8ca** (186 mg, 0.43 mmol, 1.00 equiv), NMe_4Cl (70 mg, 0.64 mmol, 1.50) and Ag_2O (74 mg, 0.32 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (20 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction product **7ca** as a brownish solid (170 mg, 89 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H, Ar naph), 7.86 (d, J = 8.1 Hz, 2H, Ar naph), 7.63 (d, J = 7.3 Hz, 2H, Ar naph), 7.55 (m, 2H, Ar naph), 7.46 (m, 6H, Ar naph), 7.39 (d, J = 8.2 Hz, 4H, Ar *p*-tolyl), 7.29 (d, J = 8.2 Hz, 4H, Ar *p*-tolyl) 4.20 (s, 6H, NCH_3), 2.37 (s, 6H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9 (2C, N_3C=*C*Ag), 149.1 (2C, N_3*C*=CAg), 142.8 (2C, Ar), 136.5 (2C, Ar), 135.8 (2C, Ar), 134.0 (2C, Ar), 131.7 (2CH, Ar), 130.8 (4CH, Ar), 128.7 (2CH, Ar), 128.6 (2CH, Ar), 127.6 (2CH, Ar), 127.5 (2C, Ar), 125.2 (2CH, Ar), 125.0 (2CH, Ar), 124.7 (4CH, Ar), 121.6 (2CH, Ar), 38.3 ($2NCH_3$), 21.6 ($2CH_3$, *p*-tolyl). **IR (KBr)** $\nu_{máx}$ 3054, 2922, 1598, 1084, 1055, 806, 773. $[\alpha]_D^{25}$ – 119.3 (*c* 0.8 $CHCl_3$). **HRMS (ESI)** *m*/*z* calculated for $C_{40}H_{34}AgN_6O_2S_2$: 803.1230 $[M–BF_4]^+$, found: 803.1236. **m.p.** decomposes before melting.

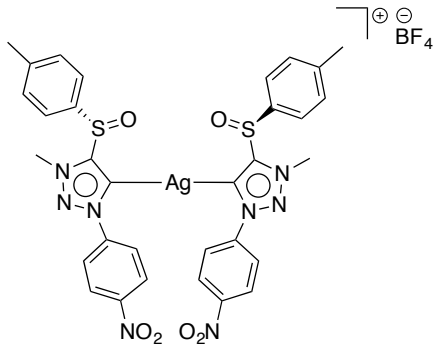
Synthesis of compound 7da



Following the general procedure a mixture of triazolium salt **8da** (153 mg, 0.40 mmol, 1.00 equiv), NMe_4Cl (65 mg, 0.59 mmol, 1.50 equiv) and Ag_2O (69 mg, 0.30 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (19 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction product **7da** as a brownish solid (139 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 4H, Ar), 7.67 (d, J = 8.3 Hz, 4H, Ar *p*-tolyl), 7.52 (m, 6H, Ar), 7.39 (d, J = 8.3 Hz, 4H, Ar *p*-tolyl), 4.29 (s, 6H, NCH_3), 2.42 (s, 6H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.4 (2C, N_3C=CAg), 143.4 (2C, Ar), 139.2 (2C, Ar), 136.9 (2C, Ar), 131.1 (2CH, Ar), 131.0 (4CH, Ar), 130.0 (4CH, Ar), 124.8 (4CH, Ar), 123.3 (4CH, Ar), 38.3 ($2NCH_3$), 21.7 ($2CH_3$, *p*-tolyl), $C_{carbene}$ not observed. **IR (KBr)** $\nu_{máx}$ 3467, 3045, 1594, 1493, 1325, 1084, 1054, 813, 766, 687. $[\alpha]_D^{25}$ – 140.9 (*c* 0.3 $CHCl_3$). **HRMS (ESI)** *m/z* calculated for $C_{32}H_{30}AgN_6O_2S_2$: 703.0915 $[M–BF_4]^+$, found: 703.0911. **m.p.** decomposes before melting.

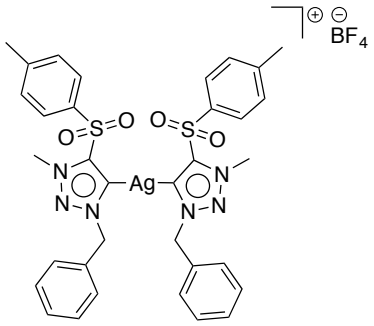
Synthesis of compound 7ea



Following the general procedure a mixture of triazolium salt **8ea** (107 mg, 0.25 mmol, 1.00 equiv), NMe_4Cl (41 mg, 0.38 mmol, 1.50 equiv) and Ag_2O (43 mg, 0.19 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (11 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction product **7ea** as a yellow solid (104 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 9.1 Hz, 4H, Ar *p*-$NO_2C_6H_4$), 8.30 (d, J = 9.1 Hz, 4H, Ar *p*-$NO_2C_6H_4$), 7.77 (d, J = 8.3 Hz, 4H, Ar *p*-tolyl), 7.38 (d, J = 8.3 Hz, 4H, Ar *p*-tolyl), 4.25 (s, 6H, NCH_3), 2.40 (s, 6H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2 (2C, N_3C=*C*Ag), 149.7 (2C, N_3*C*=CAg), 148.7 (2C, Ar), 143.5 (2C, Ar), 143.4 (2C, Ar), 136.7 (2C, Ar), 131.0 (4CH, Ar), 125.3 (2CH, Ar), 125.0 (4CH, Ar), 124.6 (4CH, Ar), 38.5 ($2NCH_3$), 21.6 ($2CH_3$, *p*-tolyl), $C_{carbene}$ not observed. **IR (KBr)** $\nu_{máx}$ 3435, 3050, 1595, 1530, 1493, 1345, 1081, 1050, 855, 812, 751, 543. **$[\alpha]_D^{25}$** – 141.0 (*c* 0.4 $CHCl_3$). **HRMS (ESI)** *m*/*z* calculated for $C_{32}H_{28}AgN_8O_6S_2$: 793.0617 $[M–BF_4]^+$, found: 793.0643. **m.p.** decomposes before melting.

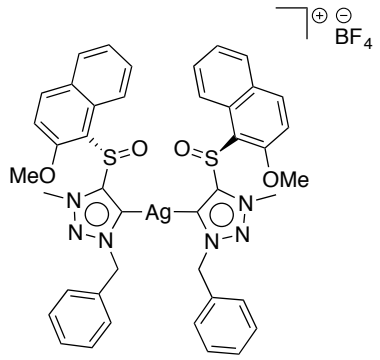
Synthesis of compound 15



Following the general procedure a mixture of triazolium salt **[16Me]$^{+}$BF$_4^{-}$** (40 mg, 0.10 mmol, 1.00 equiv), NMe_4Cl (16 mg, 0.14 mmol, 1.50 equiv) and Ag_2O (17 mg, 0.07 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (7 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction product **15** as a brownish solid (29 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 4H, Ar *p*-tolyl), 7.43 (m, 8H, Ar), 7.34 (m, 6H, 2H Ar and 4H Ar *p*-tolyl), 5.67 (s, 4H, NCH_2), 4.39 (s, 6H, NCH_3), 2.47 (s, 6H, CH_3 *p*-tolyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2 (2C, Ar), 147.7 (2C, N_3C=CAg), 134.8 (2C, Ar), 133.2 (2C, Ar), 131.1 (4CH, Ar), 129.6 (2CH, Ar), 129.4 (4CH, Ar), 129.1 (6CH, 4CH Ar and 2CH Ar), 129.0 (2CH, Ar), 60.9 ($2NCH_2$) 39.6 ($2NCH_3$), 22.1 ($2CH_3$, *p*-tolyl), $C_{carbene}$ not observed. **IR (KBr) $\nu_{máx}$** 3027, 2955, 2923, 1594, 1337, 1152, 1079, 814, 747, 687, 652, 599, 533. **HRMS (ESI)** *m/z* calculated for $C_{34}H_{34}AgN_6O_4S_2$: 763.1136 $[M–BF_4]^+$, found: 763.1127. **m.p.** decomposes before melting.

Synthesis of compound 7ab



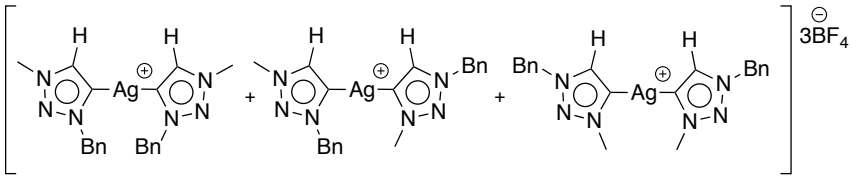
Following the general procedure a mixture of triazolium salt **8ab** (88 mg, 0.22 mmol, 1.00 equiv), NMe_4Cl (36 mg, 0.33 mmol, 1.50 equiv) and Ag_2O (38 mg, 0.17 mmol, 0.75 equiv) in CH_3CN:CH_2Cl_2 (12 mL) was stirred under Ar at rt overnight until the formation of the silver carbene (^{1}H NMR analysis). The reaction was filtered through a pad of Celite and the solvent was removed under vacuum. The solid was then redissolved in CH_2Cl_2 and filtered again through a pad of Celite. The residue was precipitated in a mixture of CH_2Cl_2:pentane to afford the corresponding reaction products **7ab** as a brownish solid (87 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.6 Hz, 2H, Ar 2-OCH_3naph), 8.14 (d, J = 9.1 Hz, 2H, Ar 2-OCH_3naph), 7.87 (d, J = 8.2 Hz, 2H, Ar 2-OCH_3naph), 7.52 (br s, 2H, Ar), 7.42 (t, J = 7.5 Hz, 4H, Ar), 7.30 (m, 10H, Ar), 5.40 (m, 4H, NCH_2), 4.53 (s, 6H, OCH_3), 4.03 (s, 6H, OCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8 (2C, Ar), 148.6 (2C, N_3C=CAg), 137.3 (2CH, Ar), 133.2 (2C, Ar), 131.3 (2C, Ar), 129.7 (2C, Ar), 129.6 (2CH, Ar) 129.3 (2CH, Ar), 129.2 (4CH, Ar), 129.1 (2CH, Ar), 128.6 (4CH, Ar), 125.0 (2CH, Ar), 122.3 (2CH, Ar), 119.3 (2C, Ar), 113.1 (2CH, Ar), 60.5 ($2NCH_2$), 57.0 (2-OCH_3naph), 38.7 ($2NCH_3$) $C_{carbene}$ not observed. **IR (KBr)** $\nu_{máx}$ 3435, 1620, 1507, 1275, 1252, 1059, 818, 746. $[\alpha]_D^{25}$ + 51.5 (c 1.0, $CHCl_3$). **HRMS (ESI)** m/z calculated for $C_{42}H_{38}AgN_6O_4S_2$: 863.1442 $[M–BF_4]^+$, found: 863.1471. **m.p.** decomposes before melting.

General procedure for the desulfinylation process

In a bottom flask, silver carbene was dissolved in CH_2Cl_2. Alcohol was then added dropwise and the reaction was stirred at rt. Once the sulfinate was formed, volatiles were removed under vacuum. The sulfinate was separated from the carbene mixture washing with CH_2Cl_2:pentane (twice).

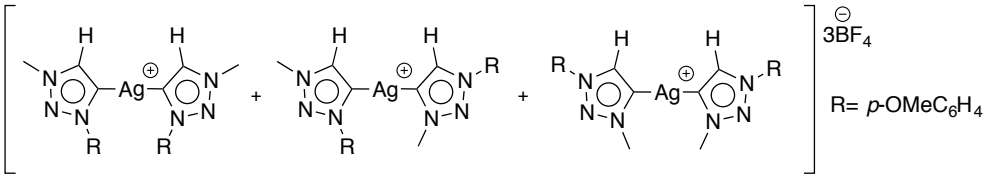
Synthesis of compound 12a



Following the general procedure silver carbene **7aa** (81 mg, 0.10 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (1 mL). MeOH was added dropwise. The solution started to become darker instantaneously. After 5 min of stirring at rt, the crude reaction was filtered through a pad of Celite. Volatiles were removed under vaccum yielding a brownish solid. To separate the sulfinate from the solid, the crude mixture was dissolved in the minimum volume of CH_2Cl_2 and precipitated in pentane. The mixture was stirred for 5 min. Solvents were separated from the solid, which was dried under vacuum affording silver carbenes **12a** as a brownish solid (36 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, Ar), 5.98 (s, NCH_2), 5.63 (s, NCH_2), 5.58 (s, NCH_2), 4.46 (s, NCH_2), 4.24 (s, NCH_3), 4.18 (s, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0 (C, N_3C=*C*Ag, observed in HMBC), 165.2 (C, N_3C=*C*Ag, observed in HMBC), 134.5 (C), 132.7 (C), 131.9 (C), 130.6 (CH), 129.8 (CH, Ar), 129.5 (CH, Ar), 129.4 (CH, Ar), 129.3 (2CH, Ar), 129.0 (CH, Ar), 128.9 (CH, Ar), 128.8 (2CH, Ar), 128.4 (2CH, Ar), 59.4 (NCH_2), 57.2 (NCH_2), 55.5 (NCH_2), 43.0 (NCH_3), 40.4 (NCH_3), 38.4 (NCH_3). **HRMS (ESI)** *m/z* calculated for $C_{20}H_{22}AgN_6$: 453.0951 $[M–BF_4]^+$, found: 453.0938. **m.p.** decomposes before melting.

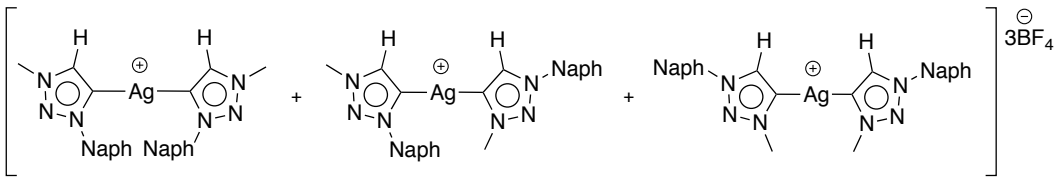
Synthesis of compound 12b



Following the general procedure silver carbene **7ba** (115 mg, 0.14 mmol, 1.00 equiv) was dissolved in of CH_2Cl_2 (3 mL). MeOH was added dropwise. The solution started to become darker instantaneously. After 5 min of stirring at rt, the crude reaction was filtered through a pad of Celite. Volatiles were removed under vaccum yielding a brownish solid. To separate the sulfinate from the solid, the crude mixture was dissolved in the minimum volume of CH_2Cl_2 and precipitated in pentane. The mixture was stirred for 5 min. Solvents were separated from the solid, which was dried under vacuum affording silver carbenes **12b** as a brownish solid (73 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, Ar), 7.94 (d, J = 9.0 Hz, Ar *p*-$OMeC_6H_4$), 7.88 (s, Ar), 7.78 (d, J = 9.0 Hz, Ar *p*-$OMeC_6H_4$), 7.64 (d, J = 9.0 Hz, Ar *p*-$OMeC_6H_4$), 7.06 (d, J = 9.0 Hz, Ar *p*-$OMeC_6H_4$), 6.98 (d, J = 9.0 Hz, Ar *p*-$OMeC_6H_4$), 4.57 (s, NCH_3), 4.31 (s, NCH_3), 4.28 (s, NCH_3), 3.88 (s, OCH_3), 3.86 (s, OCH_3), 3.85 (s, OCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7 (C, N_3C=*C*Ag), 162.2 (C, Ar), 161.5 (C, Ar), 161.0 (C, Ar), 136.6 (CH, Ar), 134.1 (CH, Ar), 133.2 (CH, Ar), 133.0 (CH, Ar), 129.2 (C, Ar), 128.6 (C, Ar), 124.7 (2CH, Ar), 123.0 (CH, Ar), 122.9 (CH, Ar), 115.6 (CH, Ar), 115.4 (2CH, Ar), 114.8 (2CH, Ar), 56.0 (NCH_2), 55.9 (NCH_2), 55.8 (OCH_3), 43.4 (NCH_3), 40.8 (NCH_3), 38.6 (NCH_3). **HRMS (ESI)** *m*/*z* calculated for $C_{20}H_{22}AgN_6O_2$: 485.0850 $[M–BF_4]^+$, found: 485.0883. **m.p.** decomposes before melting.

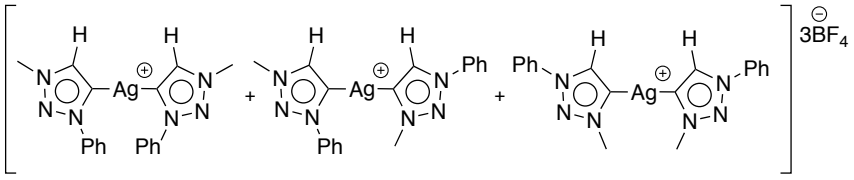
Synthesis of compound 12c



Following the general procedure silver carbene **7ca** (164 mg, 0.18 mmol, 1.00 equiv) was dissolved in of CH_2Cl_2 (3 mL). MeOH was added dropwise. The solution started to become darker instantaneously. After 5 min of stirring at rt, the crude reaction was filtered through a pad of Celite. Volatiles were removed under vaccum yielding a brownish solid. To separate the sulfinate from the solid, the crude mixture was dissolved in the minimum volume of CH_2Cl_2 and precipitated in pentane. The mixture was stirred for 5 min. Solvents were separated from the solid, which was dried under vacuum affording silver carbenes **12c** as a brownish solid (95 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, Ar), 8.60 (s, Ar), 8.10 (m, Ar), 7.91 (m, Ar), 7.59 (m, Ar), 4.58 (s, NCH_3), 4.34 (s, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.6 (C, Ar), 134.2 (C, Ar), 134.1 (C, Ar), 134.0 (C, Ar), 132.9 (CH, Ar), 132.8 (C, Ar), 132.6 (CH, Ar), 132.1 (CH, Ar), 131.9 (CH, Ar), 131.0 (CH, Ar), 129.5 (CH, Ar), 128.8 (CH, Ar), 128.7 (CH, Ar), 128.6 (CH, Ar), 128.4 (CH, Ar), 128.1 (CH, Ar), 128.0 (CH, Ar), 127.7 (CH, Ar), 127.6 (H, Ar), 127.3 (CH, Ar), 127.1 (C, Ar), 125.2 (CH, Ar), 125.1 (CH, Ar), 124.1 (CH, Ar), 121.2 (CH, Ar), 120.9 (CH, Ar), 43.2 (NCH_3), 41.1 (NCH_3), 38.8 (NCH_3). **HRMS (EI)** *m/z* calculated for $C_{26}H_{22}AgN_6$: 525.0951 [M–BF_4]$^+$, found: 525.0942. **m.p.** decomposes before melting.

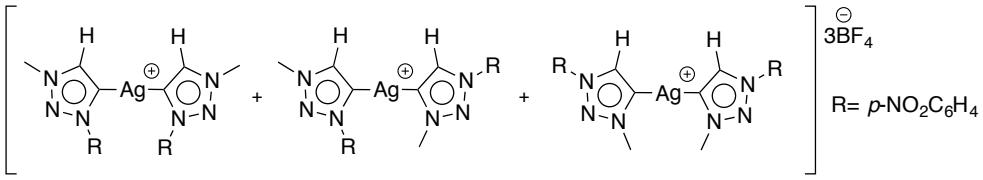
Synthesis of compound 12d



Following the general procedure silver carbene **7da** (139 mg, 0.18 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (4 mL). MeOH was added dropwise. The solution started to become darker instantaneously. After 5 min of stirring at rt, the crude reaction was filtered through a pad of Celite. Volatiles were removed under vaccum yielding a brownish solid. To separate the sulfinate from the solid, the crude mixture was dissolved in the minimum volume of CH_2Cl_2 and precipitated in pentane. The mixture was stirred for 5 min. Solvents were separated from the solid, which was dried under vacuum affording silver carbenes **12d** as a brownish solid (76 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, Ar), 7.51 (m, Ar), 4.64 (s, NCH_3), 4.38 (s, NCH_3), 4.37 (s, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3 (C, N_3C=*C*Ag, observed in HMBC), 140.0 (C, Ar), 135.4 (C, Ar), 131.8 (CH, Ar), 131.2 (CH, Ar), 130.7 (CH, Ar), 130.5 (CH, Ar), 130.2 (2CH, Ar), 130.0 (CH, Ar), 129.5 (2CH, Ar), 123.2 (2CH, Ar), 121.4 (2CH, Ar), 121.2 (2CH, Ar), 43.4 (NCH_3), 40.9 (NCH_3), 38.8 (NCH_3). **HRMS (ESI)** *m/z* calculated for $C_{18}H_{18}AgN_6$: 425.0638 $[M–BF_4]^+$, found: 425.0643. **m.p.** decomposes before melting.

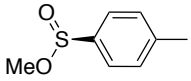
Synthesis of compound 12e



Following the general procedure silver carbene **7ea** (94 mg, 0.11 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (6 mL). MeOH was added dropwise. The solution started to become darker instantaneously. After 5 min of stirring at rt, the crude reaction was filtered through a pad of Celite. Volatiles were removed under vaccum yielding a brownish solid. To separate the sulfinate from the solid, the crude mixture was dissolved in the minimum volume of CH_2Cl_2 and precipitated in pentane. The mixture was stirred for 5 min. Solvents were separated from the solid, which was dried under vacuum affording silver carbenes **12e** as a brownish solid (34 mg, 53%).

Due to the insolubility and instability of the Ag-MICs **12e**, characterisation of the products could not be carried out. Reaction was confirmed to happen through the ^{1}H NMR spectrum analysis of the sulfinate formed.

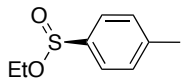
Synthesis of methyl (*R*)-4-methylbenzenesulfinate[6]



[6] J. L. Ruano, J. Alemán, M. B. Cid, A. Parra, *Org. Lett.* **2005**, *2*, 179.

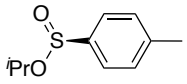
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 7.34 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 3.46 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3 *p*-tolyl).

Synthesis of ethyl (*R*)-4-methylbenzenesulfinate[7]



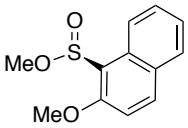
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 7.33 (m, 2H, Ar *p*-tolyl), 4.10 (dq, J = 10.0 Hz, 7.1 Hz, 1H, OCH_2CH_3), 3.72 (dq, J = 10.0 Hz, 7.1 Hz, 1H, OCH_2CH_3), 2.43 (s, 3H, CH_3 *p*-tolyl), 1.28 (t, J = 7.1 Hz, 1H, OCH_2CH_3).

Synthesis of isopropyl (*R*)-4-methylbenzenesulfinate[8]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 7.33 (d, J = 8.2 Hz, 2H, Ar *p*-tolyl), 4.60 (h, J = 6.2 Hz, 1H, CH), 2.42 (s, 3H, CH_3 *p*-tolyl), 1.38 (d, J = 6.2 Hz, 3H), 1.25 (d, J = 6.2 Hz, 3H).

Synthesis of methyl (*R*)-2-methoxynaphthalene-1-sulfinate[9]



^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09 (d, J = 8.6 Hz, 1H, Ar), 7.97 (d, J = 9.1 Hz, 1H, Ar), 7.80 (d, J = 8.6 Hz, 1H, Ar), 7.57 (ddd, J = 8.6 Hz, 6.9 Hz, 1.4 Hz, 1H, Ar), 7.42 (ddd, J = 8.1 Hz, 6.9 Hz, 1.1 Hz, 1H, Ar), 7.25 (d, J = 9.1 Hz, 2H, Ar), 4.01 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3).

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[7] T. Yoshino, S. Imori, H. Togo, *Tetrahedron* **2006**, *62*, 1309.
[8] M. Xia, Z.-C. Chen, *Synth. Commun.* **1997**, *27*, 1321.
[9] K. H. Bell, *Aust. J. Chem.* **1985**, *38*, 1209.

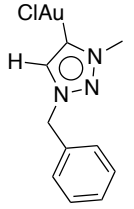
General procedure for the synthesis of gold carbenes

To a solution of Ag-MIC (1.00 equiv) in CH_2Cl_2, [AuCl(SMe_2)] (2.00 equiv) was added**.** The mixture was stirred at rt until the formation of the gold carbenes (TLC analysis). The crude reaction was filtered trough a Celite pad and volatiles were removed under vacuum. Both regioisomers were separated through a chromatography column.

Synthesis of compounds 13a-14a

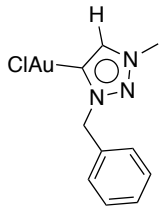
Following the general procedure, to a solution of Ag–MIC **12a** (36 mg, 0.07 mmol, 1.00 equiv) in CH_2Cl_2 (6 mL), [AuCl(SMe_2)] (39 mg, 0.13 mmol, 2.00 equiv) was added. The mixture was stirred at rt for 2 h. The reaction was filtered through a pad of Celite and the volatiles were removed under vacuum. The two regioisomers **13a-14a** were obtained as white solids in a mixture of 3:4. They were separated by a short pad of SiO_2 for their characterisation (53 mg, 98%).

13a



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H, N_3C=CH), 7.43 (m, 3H, Ar), 7.35 (m, 2H, Ar), 5.52 (s, NCH_2), 4.20 (s, 3H, NCH_3). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.6 (C, AuC=CH), 133.7 (CH, AuC=CH), 131.7 (C, Ar), 130.0 (CH, Ar), 129.7 (2CH, Ar), 128.9 (2CH, Ar), 56.4 (NCH_2), 42.2 (NCH_3). **IR (KBr) $\nu_{máx}$** 3106, 1497, 1458, 1276, 1094, 725, 694. **HRMS (ESI)** *m/z* calculated for $C_{10}H_{11}AuN_3$: 370.0613 $[M–Cl]^+$, found: 370.0610. **m.p.** decomposes before melting.

14a

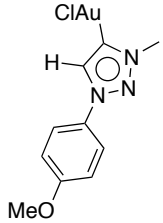


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H, N_3C=CH), 7.21 (m, 2H, Ar), 7.53 (m, 2H, Ar), 7.37 (m, 3H, Ar), 5.64 (s, NCH_2), 4.16 (s, 3H, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0 (C, AuC=CH), 134.9 (CH, AuC=CH), 133.7 (C, Ar), 129.3 (CH, Ar), 129.2 (2CH, Ar), 129.1 (2CH, Ar), 59.2 (NCH_2), 39.0 (NCH_3). **IR (KBr)** $\nu_{máx}$ 3413, 3105, 2320, 1496, 1456, 1431, 1331, 1319, 1160, 1093, 1073, 1040, 1030, 842, 735, 842, 735, 700, 658, 569. **HRMS (ESI)** *m/z* calculated for $C_{10}H_{11}AuN_3$: 370.0613 $[M–Cl]^+$, found: 370.0595. **m.p.** decomposes before melting.

Synthesis of compounds 13b-14b

Following the general procedure, to a solution of Ag-MIC **12b** (64 mg, 0.11 mmol, 1.00 equiv) in CH_2Cl_2 (6 mL), [AuCl(SMe_2)] (66 mg, 0.22 mmol, 2.00 equiv) was added. The mixture was stirred at rt for 2 h. The reaction was filtered through a pad of Celite and the volatiles were removed under vacuum. The two regioisomers **13b-14b** were obtained as 23hite solids in a mixture of 3:2. They were separated by a short pad of SiO_2 for their characterisation (66 mg, 71%).

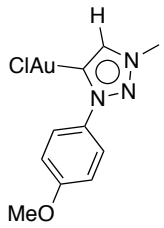
13b



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H, N_3C=CH), 7.63 (d, J = 9.0 Hz, 2H, Ar *p*-$OMeC_6H_4$), 7.08 (d, J = 9.0 Hz, 2H, Ar *p*-$OMeC_6H_4$), 4.31 (s, 3H, NCH_3), 3.90 (s, 3H, OCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.7 (C, Ar), 158.9 (C, N_3C=CAu), 131.5

(CH, CAu=CH), 128.5 (C, Ar), 122.8 (2CH, Ar), 115.5 (2CH, Ar), 56.0 (OCH_3), 42.4 (NCH_3). **IR (KBr) $\nu_{máx}$** 3107, 2958, 2924, 2853, 1716, 1641, 1611, 1592, 1519, 1496, 1464, 1378, 1316, 1263, 1214, 1173, 1166, 1099, 1032, 830, 819, 807, 720, 710, 654, 611, 553, 485. **HRMS (ESI)** *m/z* calculated for $C_{10}H_{11}AuN_3O$: 386.0562 $[M–Cl]^+$, found: 386.0562. **m.p.** decomposes before melting.

14b

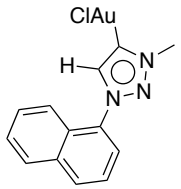


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.1 Hz, 2H, Ar *p*-$OMeC_6H_4$), 7.72 (s, 1H, N_3C=CH), 7.01 (d, J = 9.1 Hz, 2H, Ar *p*-$OMeC_6H_4$), 4.27 (s, 3H, NCH_3), 3.88 (s, 3H, OCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1 (C, Ar), 157.2 (C, N_3C=CAu), 135.0 (CH, CAu=CH), 132.1 (C, Ar), 125.4 (2CH, Ar), 114.7 (2CH, Ar), 55.9 (OCH_3), 39.0 (NCH_3). **IR (KBr) $\nu_{máx}$** 3146, 3117, 3100, 2958, 2924, 2853, 1723, 1606, 1592, 5119, 1463, 1414, 1378. 1333, 1304, 1255, 1171, 1114, 1093, 1059, 1027, 982, 833, 807, 752, 720, 610, 551, 518. **HRMS (ESI)** *m/z* calculated for $C_{10}H_{11}AuN_3O$: 386.0562 $[M–Cl]^+$, found: 386.0550. **m.p.** decomposes before melting.

Synthesis of compounds 13c-14c

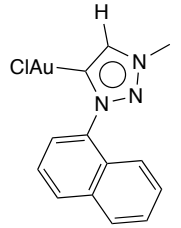
Following the general procedure, to a solution of Ag-MIC **12c** (223 mg, 0.36 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL), [$AuCl(SMe_2)$] (215 mg, 0.73 mmol, 2.00 equiv) was added. The mixture was stirred at rt for 2 h. The reaction was filtered through a pad of Celite and the volatiles were removed under vacuum. The two regioisomers **13c-14c** were obtained as white solids in a mixture of 5:4. They were separated by a short pad of SiO_2 for their characterisation (188 mg, 59%).

13c



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H, Ar napht), 8.03 (m, 1H, Ar napht), 7.91 (s, 1H, N_3CH=CAu), 7.66 (m, 4H, Ar napht), 7.53 (m, 1H, Ar napht), 4.42 (s, 3H, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6 (C, N_3CH=CAu), 136.2 (CH, N_3CH=CAu), 134.3 (C, Ar), 132.5 (CH, Ar), 131.8 (C, Ar), 129.1 (CH, Ar), 128.9 (CH, Ar), 128.0 (CH, Ar), 127.6 (C, Ar), 125.0 (CH, Ar), 124.2 (CH, Ar), 121.1 (CH, Ar), 42.7 (NCH_3). **IR (KBr) $\nu_{máx}$** 3098, 1513, 1411, 1271, 801, 769, 687. **HRMS (ESI)** *m*/*z* calculated for $C_{13}H_{11}AuN_3$: 406.0613 $[M–Cl]^+$, found: 406.0622. **m.p.** decomposes before melting.

14c



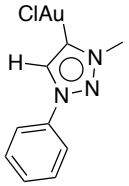
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.49 (s, 1H, N_3CH=CAu), 8.29 (d, J = 8.2 Hz, 1H, Ar napht), 8.16 (d, J = 8.2 Hz, 1H, Ar napht), 7.89 (br d, J = 7.3 Hz, 1H, Ar napht), 7.75 (t, J = 7.3 Hz, 1H, Ar napht), 7.69 (ddd, J = 8.2 Hz, 6.9 Hz, 1.3 Hz, 1H, Ar napht), 7.64 (td, J = 7.6 Hz, 6.9 Hz, 1.3 Hz, 1H, Ar napht), 7.41 (d, J = 8.4 Hz, 2H, Ar napht), 4.34 (s, 3H, NCH_3). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 158.6 (C, N_3CH=CAu), 135.5 (CH, N_3CH=CAu), 135.4 (C, Ar), 133.4 (C, Ar), 131.2 (CH, Ar), 128.4 (CH, Ar), 128.2 (CH, Ar), 128.1 (CH, Ar), 127.4 (CH, Ar), 125.4 (C, Ar), 125.3 (CH, Ar), 121.8 (CH, Ar), 39.0 (NCH_3). **IR (KBr) $\nu_{máx}$** 3430, 3114, 2923, 1501, 1330, 1078, 799, 771.

HRMS (ESI) *m/z* calculated for $C_{13}H_{11}AuN_3$: 406.0613 $[M–Cl]^+$, found: 406.0623. **m.p.** decomposes before melting.

Synthesis of compounds 13d-14d

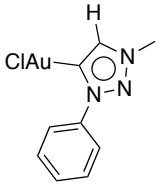
Following the general procedure, to a solution of Ag-MIC **12d** (77 mg, 0.15 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL), $[AuCl(SMe_2)]$ (89 mg, 0.30 mmol, 2.00 equiv) was added. The mixture was stirred at rt for 2 h. The reaction was filtered through a pad of Celite and the volatiles were removed under vacuum. The two regioisomers **13d-14d** were obtained as 26hite solids in a mixture of 4:3. They were separated by a short pad of SiO_2 for their characterisation (87 mg, 74%).

13d



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H, N_3C=CH), 7.74 (m, 2H, Ar), 7.62 (m, 3H, Ar), 4.34 (s, 3H, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2 (C, AuC=CH), 135.4 (C, Ar), 131.7 (CH, CH=CAu), 131.4 (CH, Ar), 130.5 (2CH, Ar), 121.4 (2CH, Ar), 42.6 (NCH_3). **IR (KBr)** $\nu_{máx}$ 3435, 3119, 2923, 1595, 1561, 1498, 1464. 1339, 1308, 1262, 1212, 1094, 1032, 982, 820, 760, 732, 682, 669. **HRMS (ESI)** *m/z* calculated for $C_7H_9AuN_3$: 356.0457 $[M–Cl]^+$, found: 356.0499. **m.p.** decomposes before melting.

14d



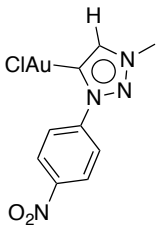
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 2H, Ar), 7.81 (s, 1H, N_3C=CH), 7.54 (m, 3H, Ar), 4.30 (s, 3H, NCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3 (C, AuC=CH),

139.0 (C, Ar), 135.4 (CH, CH=CAu), 130.6 (CH, Ar), 129.7 (2CH, Ar), 124.1 (2CH, Ar), 39.2 (NCH_3). **IR (KBr)** $\nu_{máx}$ 3424, 3111, 2922, 1595, 1494, 1456, 1333, 1317, 1261, 1216, 1173, 1072, 1008, 916, 835, 769, 689, 556. **HRMS (ESI)** *m/z* calculated for $C_7H_9AuN_3$: 356.0457 $[M–Cl]^+$, found: 356.0457. **m.p.** decomposes before melting.

Synthesis of compounds 13e-14e

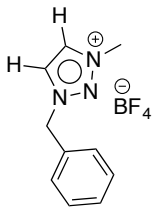
Following the general procedure, to a solution of Ag-MIC **12e** (34 mg, 0.06 mmol, 1.00 equiv) in CH_2Cl_2 (4 mL), [AuCl(SMe_2)] (33 mg, 0.11 mmol, 2.00 equiv) was added. The mixture was stirred at rt for 2 h. The reaction was filtered through a pad of Celite and the volatiles were removed under vacuum. Compound **14e** was obtained together with traces of the regioisomer **13e**, which could not be isolated. **14e** was purified by a short pad of SiO_2 for their characterisation (35 mg, 71%).

14e



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (d, J = 9.0 Hz, 2H, Ar *p*-$NO_2C_6H_4$), 8.43 (s, 1H, N_3C=CH), 8.30 (d, J = 9.0 Hz, 2H, Ar *p*-$NO_2C_6H_4$), 4.32 (s, 3H, NCH_3). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 155.8 (C, CH=CAu), 148.2 (C, Ar), 143.1 (C, Ar), 136.5 (CH, CAu=CH), 125.7 (2CH, Ar), 125.1 (2CH, Ar), 39.5 (NCH_3, overlaped with deuterated solvent). **IR (KBr)** $\nu_{máx}$ 3435, 3113, 2923, 1612, 1597, 1530, 1494, 1360, 1343, 1316, 1261, 1222, 1173, 1109, 1076, 1025, 1005, 857, 826, 755, 701, 689, 654, 499. **HRMS (ESI)** *m/z* calculated for $C_9H_8AuN_4O_2$: 401.0307 $[M–Cl]^+$, found: 401.0291. **m.p.** decomposes before melting.

Synthesis of compound 18[10]

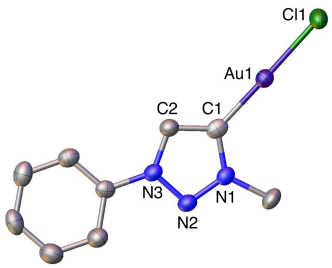


A mixture of **17** (92 mg, 0.20 mmol, 1.00 equiv) and Me_3OBF_4 (56 mg, 0.38 mmol, 1.50 equiv) in CH_2Cl_2 (20 mL) was stirred under Ar at rt overnight. The reaction was quenched with methanol (15 mL) and filtered through a plug of $NaHCO_3$. The solvent was removed under vacuum. The crude reaction was redissolved in CH_2Cl_2 and filtered through cotton to remove the $NaHCO_3$ dissolved by MeOH. The volatiles were removed under vacuum. The triazolium salt was separated from the methyl sulfinate washing with pentane. **18** was obtained as a white solid (52 mg, quantitative).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 2H, N_3CH=CH), 7.44 (m, 2H, Ar), 7.35 (m, 3H, Ar), 5.68 (s, 2H, NCH_2), 4.26 (s, 3H, NCH_3).

Crystal data for compound 13d:

Crystallization: Slow difussion of a concentrate solution of complex **13d** in dichloromethane into hexanes.



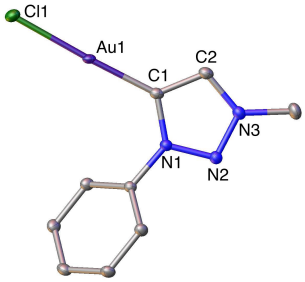
$C_9H_9AuClN_3$, Mr = 361.61, crystal dimensions 0.4 x 0.4 x 0.1 mm3, triclinic, P $\bar{1}$, a = 6.5022(3) Å, b = 7.7532(3) Å, c = 11.0346(6) Å, α = 77.138(3)°, β =

[10] For a complete characterisation of the triazolium salt **18** with iodide as contraion see: a) G. Boche, P. Andrews, K. Harms, M. Marsch, K. S. Rangappa, M. Schimeczek, C. Willeke, *J. Am. Chem. Soc.* **1996**, *118*, 4925; b) Y. Jeong, J.-S. Ryu, *J. Org. Chem.* **2010**, *75*, 4183.

82.169(3)°, γ = 83.193(2)°, cell volume = 535.02(4) Å3, Z = 2, ϱ_{calcd} = 2.431 Mg/m3, μ = 13.960 mm^{-1}, T = 173(2) K, $2\theta_{max}$ = 61.1°, 17088 reflections collected, 3185 independent, R_{int} = 0.1016, R1 = 0.0356 and wR2 = 0.0488 for I > 2σ(I), R1 = 0.0670 and wR2 = 0.0541 for all data, residual electron density = 1.345 eA^{-3}.

Crystal data for compound 14d:

Crystallization: Slow difussion of a concentrate solution of complex **14d** in dichloromethane into hexanes.

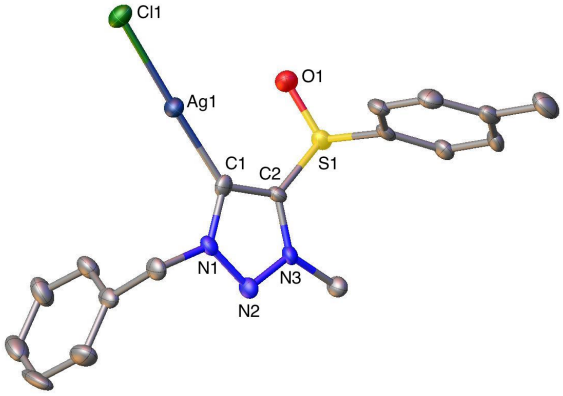


$C_9H_9AuClN_3$, Mr = 391.61, crystal dimensions 0.5 x 0.4 x 0.4 mm^3, monoclinic, $P2_1/n$, *a* = 11.668(2) Å, *b* = 7.578(1) Å, *c* = 12.803(2) Å, β = 115.593(4)°, cell volume = 1020.9(2) $Å^3$, Z = 4, ϱ_{calcd} = 2.548 Mg/m^3, μ = 14.633 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 90.8°, 82542 reflections collected, 8589 independent, R_{int} = 0.0435, R1 = 0.0175 and wR2 = 0.0396 for I > 2σ(I), R1 = 0.0280 and wR2 = 0.0442 for all data, residual electron density = 2.087 eA^{-3}.

Crystal data for Ag-monocarbene grown from 7aa[11]

Crystallization: Slow difussion of a concentrate solution of silver complex **7aa** in ethyl acetate into hexanes.

[11] Silver mono(carbene) could not be isolated in enough quantity for complete characterisation. Only X-ray diffraction and HRMS (ESI) (calculated for $C_{17}H_{17}AgN_3OS$: 418.01378 $[M–Cl]^+$, found: 418.0145) could be registered.



$C_{17}H_{17}AgClN_3OS$, Mr = 454.71, crystal dimensions 0.5 x 0.1 x 0.05 mm^3, monoclinic, $P2_1$, a = 10.565(2) Å, b = 6.892(1) Å, c = 12.256(2) Å, β = 95.573(5)°, cell volume = 888.1(2) $Å^3$, Z = 2, ϱ_{calcd} = 1.700 Mg/m^3, μ = 1.411 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 55.7°, 12999 reflections collected, 4199 independent, R_{int} = 0.0735, R1 = 0.0500 and wR2 = 0.1114 for I > 2σ(I), R1 = 0.0712 and wR2 = 0.1215 for all data, residual electron density = 1.779 eA^{-3}, absolute structure parameter x = –0.03(4).

Computational Details

Density functional theory (DFT) calculations were performed using the M06 density functional[12] with an ultrafine grid as implemented in Gaussian09.[13] This functional performs well for main-group chemistry and noncovalent interactions.[14] All intermediates and transition states were fully optimized in dichloromethane solution

[12] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

[13] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc.: Wallingford CT, **2009** Gaussian 09 (Revision D.01), Gaussian Inc., Wallingford CT, 2011.

[14] (a) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157; (b) Zhao, Y.; Truhlar, D. G. *Chem. Phys. Lett.* **2011**, *502*, 1.

(DCM, ε = 8.93) using the continuum method SMD[15] and 6-31G** basis set (**BS1**).[16] Final single-point calculations were performed with the 6-311++G** basis set (**BS2**).[17] Transition states were identified by having one imaginary frequency in the Hessian matrix. It was confirmed that transition states connect with the corresponding intermediates by means of application of the eigenvector of the imaginary frequency and subsequent optimization of the resulting structures. All energy values reported in the main text correspond to Gibbs energies in DCM in kcal mol^{-1}.

[15] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.
[16] (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257; (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
[17] (a) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. *J. Comput. Chem.* **1983**, *4*, 294; (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650; (c) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

Energies and XYZ coordinates for all species

$(MeOH)_2$
E(BS1) = -231.321766; G(BS1) = -231.247511; E(BS2) = -231.396522

C	1.738085	0.564517	-0.245263
H	1.367243	0.644867	-1.272176
H	2.835462	0.612167	-0.270720
H	1.364033	1.426491	0.324755
O	1.277323	-0.669159	0.274025
C	-1.727787	0.549130	0.249358
H	-2.814255	0.697577	0.214653
H	-1.434067	0.542077	1.312947
H	-1.265125	1.438362	-0.214942
O	-1.419398	-0.643624	-0.413281
H	-0.484979	-0.830408	-0.215839
H	1.506500	-0.710751	1.210801

$(MeOH)_3$
E(BS1) = -346.994886; G(BS1) = -346.872413; E(BS2) = -347.100223

C	1.795063	-1.735648	0.179629
H	2.580670	-1.804662	-0.579724
H	1.611062	-2.746978	0.569905
H	2.174844	-1.114171	1.004475
O	0.646855	-1.190455	-0.432323
C	1.197618	1.903864	0.334054
H	0.993995	2.949192	0.587451
H	1.075602	1.303819	1.251152
H	2.247059	1.829553	0.013942
O	0.302560	1.514843	-0.688183
H	0.539783	0.591160	-0.906056
C	-2.496593	-0.449952	-0.197784
H	-2.041432	-0.692176	-1.171221
H	-2.948287	-1.364109	0.200956
H	-3.300708	0.280367	-0.367498
O	-1.544894	0.015500	0.737777
H	-1.098858	0.780494	0.323529
H	-0.046426	-1.041174	0.239526

A
E(BS1) = -1255.630853; G(BS1) = -1255.398208; E(BS2) = -1255.868227

C	0.486318	0.317058	-0.383454
C	-0.455799	-0.174903	-1.283614
N	-1.224022	-0.890727	-0.400221
N	-0.872759	-0.856745	0.888195
N	0.196401	-0.110154	0.886451
C	-2.471256	-1.598251	-0.711367
H	-2.428618	-1.805051	-1.784216
H	-2.466044	-2.547173	-0.165215
C	0.911698	0.137261	2.130261
H	1.760712	-0.548600	2.206967
H	1.267046	1.170522	2.118798
H	0.222063	-0.026979	2.958959
C	-3.671285	-0.768451	-0.348942
C	-4.025922	0.328318	-1.137148
C	-4.411971	-1.059400	0.795543
C	-5.113872	1.119827	-0.786712
H	-3.436184	0.560171	-2.023800
C	-5.504728	-0.270234	1.144982
H	-4.127348	-1.910454	1.413588
C	-5.856432	0.819567	0.354075
H	-5.385731	1.972530	-1.405109
H	-6.080675	-0.506305	2.037190
H	-6.709968	1.436848	0.626003
S	1.817880	1.428017	-0.785015
C	3.191961	0.313728	-0.372030
C	3.333831	-0.896963	-1.045322
C	4.127667	0.750470	0.555131
C	4.433911	-1.696938	-0.756855
H	2.589738	-1.214950	-1.775344
C	5.224267	-0.061231	0.837217
H	3.982348	1.709275	1.049290
C	5.375913	-1.280286	0.183342
H	4.557082	-2.649028	-1.267750
H	5.962068	0.262615	1.567723
H	6.234922	-1.909913	0.403500
O	1.853671	2.535522	0.241005

TS-A
E(BS1) = -1602.643947; G(BS1) = -1602.269841; E(BS2) = -1602.980333

C	-1.367077	-0.787052	-0.174498
C	-0.235616	-0.703255	0.612557
N	0.453528	-1.869250	0.465200
N	-0.154232	-2.679532	-0.374368
N	-1.232265	-2.013130	-0.743369
C	1.748745	-2.292626	1.018920
H	1.749177	-2.040295	2.081340
H	1.760413	-3.382052	0.907169
C	-2.129361	-2.617436	-1.721823
H	-2.130493	-3.698467	-1.571706
H	-3.135576	-2.207881	-1.571248
H	-1.773999	-2.381296	-2.728692
C	2.905608	-1.641010	0.310593
C	4.007209	-1.220166	1.055745
C	2.910086	-1.478180	-1.075374
C	5.107998	-0.652777	0.421119
H	3.994702	-1.330262	2.138699
C	4.006744	-0.900917	-1.708048
H	2.050966	-1.796943	-1.665155
C	5.108775	-0.490333	-0.962080
H	5.963044	-0.328916	1.010222
H	3.999679	-0.771692	-2.788005
H	5.966037	-0.040365	-1.457836
S	0.187303	0.663135	1.720575
C	0.744253	1.776203	0.408643
C	-0.219218	2.576088	-0.197929
C	2.090015	1.832616	0.067423
C	0.185007	3.441034	-1.210990
H	-1.260154	2.524755	0.132923
C	2.477037	2.712337	-0.939041
H	2.814684	1.201409	0.581512
C	1.527276	3.507150	-1.578456
H	-0.549067	4.074233	-1.704160
H	3.524447	2.776969	-1.225535
H	1.838429	4.190982	-2.364877
O	1.384418	0.230754	2.520005
H	-2.381003	-0.034073	-0.435349
C	-3.037913	1.072085	-2.124098
H	-3.097145	2.167192	-2.256536
H	-3.682675	0.622025	-2.902381
H	-1.995302	0.783431	-2.379690
O	-3.388139	0.665506	-0.841867
C	-4.935781	-1.839135	0.445703
H	-5.506226	-2.768500	0.568608
H	-3.890326	-2.059263	0.735688
H	-5.332183	-1.111328	1.174321
O	-5.059623	-1.403862	-0.878161
H	-4.550490	-0.556097	-0.926732
C	-3.389817	1.366946	2.249445
H	-2.985932	1.771588	3.186837
H	-4.453541	1.128448	2.426234
H	-2.867777	0.410630	2.059372
O	-3.208219	2.305902	1.230167
H	-3.387074	1.823159	0.385523

B
E(BS1) = -1602.645855; G(BS1) = -1602.267220; E(BS2) = -1602.985914

C	1.661803	-1.063947	0.436058

C	0.618752	-0.861295	-0.438478
N	-0.159029	-1.974697	-0.319140
N	0.318827	-2.828455	0.564038
N	1.415358	-2.259793	1.009879
C	-1.467219	-2.280910	-0.909620
H	-1.421316	-1.988170	-1.961931
H	-1.565947	-3.369233	-0.837383
C	2.246130	-2.949690	1.988587
H	2.942736	-2.219677	2.405356
H	1.604205	-3.357443	2.770854
H	2.796893	-3.751683	1.492018
C	-2.587786	-1.567265	-0.200548
C	-3.785646	-1.380827	-0.892381
C	-2.478911	-1.122240	1.116721
C	-4.868825	-0.771770	-0.268978
H	-3.863719	-1.715062	-1.926384
C	-3.558510	-0.495990	1.733188
H	-1.546632	-1.246420	1.667811
C	-4.756555	-0.325491	1.045946
H	-5.799229	-0.634353	-0.815456
H	-3.460037	-0.139905	2.756379
H	-5.599579	0.160919	1.531435
S	0.366847	0.470149	-1.664755
C	-0.688112	1.500006	-0.575334
C	-0.193946	2.082252	0.589018
C	-1.991275	1.708428	-1.006377
C	-1.049242	2.870882	1.351661
H	0.850269	1.919724	0.856168
C	-2.832977	2.507686	-0.235835
H	-2.334254	1.240844	-1.927007
C	-2.364995	3.082705	0.942028
H	-0.681203	3.328486	2.267718
H	-3.858208	2.677599	-0.557861
H	-3.026256	3.704416	1.541630
O	-0.583560	-0.111902	-2.681081
H	2.523092	-0.461986	0.711961
C	2.695894	2.692713	-0.945290
H	3.712426	2.913813	-1.334840
H	2.452640	3.527238	-0.250565
H	2.012677	2.829443	-1.816216
O	2.582508	1.451028	-0.367988
C	2.959852	1.206795	2.778014
H	3.395276	1.003340	3.765440
H	2.758777	2.291341	2.726936
H	1.976749	0.695501	2.748728
O	3.838295	0.769708	1.783892
H	3.485607	1.146965	0.921722
C	4.608395	-0.974144	-1.272477
H	4.350125	-1.486805	-0.322680
H	5.094026	-1.723790	-1.912380
H	5.371988	-0.216519	-1.022027
O	3.507019	-0.444605	-1.940138
H	3.178193	0.328418	-1.399688

TS-B

E(BS1) = -1602.623169; G(BS1) = -1602.246251; E(BS2) = -1602.967497

C	-0.826722	2.256203	0.626812
C	-0.188649	1.455689	-0.288507
N	1.032284	2.028535	-0.460739
N	1.194577	3.100069	0.285753
N	0.066169	3.222564	0.943865
C	2.152745	1.561615	-1.280801
H	1.706935	1.065036	-2.151215
H	2.673352	2.462149	-1.623564
C	-0.120373	4.343772	1.858890
H	-0.462298	3.957627	2.820369
H	0.839654	4.847805	1.969475
H	-0.862393	5.026097	1.439345
C	3.073661	0.633810	-0.531101
C	4.069372	-0.010711	-1.268547
C	2.971813	0.399167	0.837918
C	4.954139	-0.879620	-0.642398
H	4.143725	0.170606	-2.340424
C	3.852357	-0.482478	1.460938
H	2.196394	0.885034	1.429424
C	4.845337	-1.120890	0.725973
H	5.726870	-1.375550	-1.225404
H	3.755923	-0.670886	2.528003
H	5.531699	-1.807486	1.216075
S	-0.923433	0.042949	-1.210798
C	-0.011810	-1.205293	-0.260119
C	-0.365973	-1.448286	1.063094
C	0.982384	-1.926694	-0.902366
C	0.321028	-2.429319	1.766951
H	-1.184098	-0.895926	1.521225
C	1.660097	-2.913218	-0.187196
H	1.215688	-1.715337	-1.944324
C	1.332667	-3.160438	1.141826
H	0.058131	-2.634255	2.802416
H	2.446544	-3.486185	-0.673428
H	1.862731	-3.932480	1.695134
O	-0.280920	0.075063	-2.569915
H	-1.822773	2.210494	1.049664
C	-3.261590	-2.813547	-0.125169
H	-4.100661	-3.046150	0.573448
H	-2.377331	-3.345303	0.303481
H	-3.505067	-3.367939	-1.059558
O	-3.055422	-1.472987	-0.305711
C	-3.674998	-0.411213	2.599953
H	-4.222359	-0.122591	3.509694
H	-3.221257	-1.401212	2.802542
H	-2.833189	0.308107	2.505268
O	-4.535926	-0.409920	1.513908
H	-4.000035	-0.793154	0.745341
C	-4.109089	1.236091	-1.533084
H	-3.204584	1.879845	-1.572864
H	-4.926904	1.830105	-1.970543
H	-4.348307	1.084060	-0.466024
O	-3.959785	0.039662	-2.226956
H	-3.644636	-0.640260	-1.561947

PhS(O)OMe

E(BS1) = -819.831342; G(BS1) = -819.730200; E(BS2) = -819.965609

S	-1.435362	-0.351238	-0.604612
C	0.322002	-0.164426	-0.274551
C	1.007414	0.878869	-0.887838
C	0.957965	-1.056396	0.584057
C	2.366102	1.038734	-0.624917
H	0.487589	1.556109	-1.565961
C	2.312970	-0.889257	0.839023
H	0.389110	-1.871316	1.028340
C	3.012774	0.156922	0.236166
H	2.919105	1.847586	-1.096177
H	2.829375	-1.575500	1.506209
H	4.074407	0.280897	0.437507
O	-1.740834	-1.789610	-0.415621
C	-1.967552	1.774601	0.775957
H	-0.948200	2.161699	0.911998
H	-2.380876	2.172266	-0.161841
H	-2.588986	2.117282	1.606725
O	-1.994888	0.351674	0.805571

C

E(BS1) = -551.453283; G(BS1) = -551.296229; E(BS2) = -551.591436

C	2.661403	-0.659491	-1.252674
C	1.485052	-1.258173	-0.799321
N	1.103377	-0.680828	0.373343
N	1.929010	0.268483	0.741880
N	2.835444	0.254280	-0.240464
C	-0.096333	-0.943204	1.170695
H	-0.203372	-2.029824	1.251181
H	0.106068	-0.540959	2.168600
C	3.942323	1.185327	-0.106619
H	4.679402	0.800731	0.605086
H	4.406981	1.293469	-1.087041
H	3.573081	2.152802	0.242681
C	-1.319136	-0.323849	0.551884

C	-2.351232	-1.127484	0.071538
C	-1.422329	1.065204	0.446294
C	-3.482130	-0.550321	-0.501544
H	-2.267546	-2.210980	0.149956
C	-2.547836	1.641318	-0.130079
H	-0.610736	1.691425	0.816548
C	-3.580955	0.833525	-0.603281
H	-4.284734	-1.184318	-0.871850
H	-2.622234	2.723706	-0.208537
H	-4.462696	1.285595	-1.052160
H	0.877999	-2.052303	-1.219139

TS-C

E(BS1) = -782.787531; G(BS1) = -782.538201; E(BS2) = -782.991607

C	1.913962	-0.532452	0.029051
C	0.774699	-0.254506	-0.695991
N	0.057764	-1.400764	-0.759645
N	0.641800	-2.393134	-0.127691
N	1.757801	-1.848797	0.334470
C	-1.287381	-1.574358	-1.325002
H	-1.234530	-1.324662	-2.389349
H	-1.522526	-2.637980	-1.222026
C	2.687111	-2.693637	1.068480
H	3.531786	-2.954667	0.426142
H	3.045803	-2.144298	1.940738
H	2.161629	-3.596967	1.381002
C	-2.260484	-0.692765	-0.595084
C	-2.760803	0.460111	-1.197413
C	-2.615013	-0.996360	0.721218
C	-3.618719	1.300974	-0.492613
H	-2.473421	0.698523	-2.220974
C	-3.468729	-0.155763	1.425182
H	-2.209628	-1.893228	1.190237
C	-3.971630	0.994123	0.817815
H	-4.008337	2.198512	-0.967365
H	-3.744007	-0.396520	2.449470
H	-4.639942	1.651527	1.369434
H	0.441874	0.687592	-1.118578
C	0.287410	2.659379	0.835827
H	-0.542851	3.359842	0.668400
H	0.783696	2.957589	1.774459
H	-0.168338	1.663818	1.013553
O	1.148479	2.684026	-0.262498
H	2.017432	2.295188	0.046405
C	4.169371	1.549549	-0.602541
H	3.989847	2.446484	-1.234033
H	3.998292	0.678162	-1.282878
H	5.258791	1.544839	-0.387327
O	3.386200	1.507966	0.525820
H	2.736676	0.343416	0.392607

D1

E(BS1) = -782.789037; G(BS1) = -782.537322; E(BS2) = -782.995597

C	1.888338	-0.592596	0.076620
C	0.771838	-0.250007	-0.646946
N	0.038075	-1.380926	-0.755091
N	0.597205	-2.407115	-0.153176
N	1.717188	-1.911620	0.340798
C	-1.301640	-1.516945	-1.347699
H	-1.224447	-1.239772	-2.403563
H	-1.550726	-2.579947	-1.277196
C	2.625901	-2.795590	1.056341
H	3.467017	-3.054415	0.408994
H	2.988674	-2.277403	1.945558
H	2.077407	-3.694535	1.339231
C	-2.275984	-0.642418	-0.611580
C	-2.754140	0.529761	-1.194319
C	-2.657748	-0.975384	0.689843
C	-3.620027	1.359310	-0.485885
H	-2.444844	0.791351	-2.205709
C	-3.518876	-0.145769	1.397598
H	-2.269364	-1.887362	1.143961
C	-4.001725	1.022289	0.808904
H	-3.993172	2.271645	-0.945341
H	-3.815737	-0.409468	2.410123
H	-4.676147	1.670888	1.363475
H	0.480700	0.723454	-1.030833
C	0.420695	2.651650	0.894336
H	-0.431839	3.327403	0.729727
H	0.951165	3.010118	1.794053
H	-0.009852	1.661710	1.157031
O	1.232575	2.621544	-0.234619
H	2.134643	2.243468	0.069757
C	4.168803	1.535556	-0.646249
H	3.965236	2.383765	-1.344416
H	3.981566	0.618467	-1.271676
H	5.273814	1.545630	-0.495095
O	3.449566	1.577563	0.509940
H	2.698881	0.120638	0.435837

D2

E(BS1) = -782.791098; G(BS1) = -782.540670; E(BS2) = -782.997740

C	-2.099363	-0.677975	-0.388542
C	-1.030134	-0.147264	0.292741
N	-0.357354	-1.237204	0.735867
N	-0.905242	-2.383422	0.381214
N	-1.968311	-2.024302	-0.303378
C	0.898342	-1.247373	1.502147
H	0.715586	-0.695628	2.429460
H	1.086543	-2.297134	1.747463
C	-2.860887	-3.048167	-0.825862
H	-3.711695	-3.169721	-0.151497
H	-3.208137	-2.738378	-1.812671
H	-2.302828	-3.982116	-0.897649
C	2.012848	-0.633284	0.706408
C	2.517762	0.618514	1.051431
C	2.519954	-1.301872	-0.410064
C	3.532659	1.195802	0.292458
H	2.103539	1.146269	1.909413
C	3.528152	-0.722810	-1.170991
H	2.114249	-2.277537	-0.679261
C	4.036728	0.526812	-0.818207
H	3.921843	2.173923	0.565967
H	3.921781	-1.245975	-2.039510
H	4.826828	0.979125	-1.413408
H	-0.744759	0.950496	0.461510
C	0.228361	2.542725	-0.854092
H	1.186913	3.098630	-0.725180
H	-0.250141	3.000827	-1.754552
H	0.547233	1.521120	-1.204039
O	-0.561150	2.531836	0.256202
H	-1.997262	2.387331	-0.311556
C	-3.732216	2.265735	0.525702
H	-3.638951	3.234901	1.048856
H	-3.499954	1.482339	1.275107
H	-4.792839	2.145395	0.260638
O	-2.947710	2.186910	-0.620526
H	-2.903974	-0.174413	-0.909193

TS-D

E(BS1) = -782.789814; G(BS1) = -782.541611; E(BS2) = -782.994044

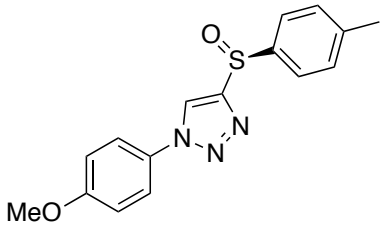
C	2.082603	0.692033	-0.394616
C	1.015510	0.130275	0.274390
N	0.345265	1.222177	0.727255
N	0.884841	2.383563	0.393873
N	1.950073	2.038547	-0.292780
C	-0.907603	1.221906	1.493671
H	-0.724773	0.665170	2.418178
H	-1.105065	2.268132	1.747836
C	2.840358	3.071958	-0.797628
H	3.678141	3.204211	-0.108763
H	3.210242	2.766531	-1.777706
H	2.275562	4.001068	-0.881210
C	-2.023215	0.607855	0.698861
C	-2.544937	-0.632954	1.058080
C	-2.518656	1.266380	-0.428826

C	-3.564519	-1.208407	0.303717
H	-2.140576	-1.153267	1.925336
C	-3.531261	0.689386	-1.185698
H	-2.099758	2.233098	-0.710128
C	-4.056800	-0.548908	-0.817930
H	-3.967055	-2.177634	0.589627
H	-3.915198	1.205516	-2.062814
H	-4.850608	-0.999441	-1.409608
H	0.734115	-1.091169	0.407904
C	-0.234773	-2.509176	-0.838168
H	-1.174908	-3.071514	-0.655376
H	0.255063	-3.016388	-1.698757
H	-0.561151	-1.514493	-1.233225
O	0.568837	-2.408907	0.271877
H	2.092641	-2.370647	-0.344529
C	3.805758	-2.260140	0.520051
H	3.713849	-3.218381	1.061162
H	3.555877	-1.460230	1.243186
H	4.865377	-2.136667	0.257769
O	3.034293	-2.213473	-0.641698
H	2.897154	0.213895	-0.924167

E

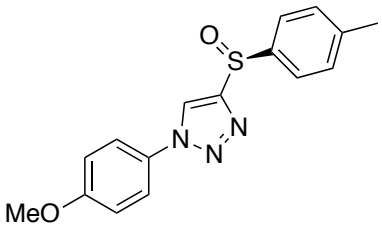
E(BS1) = -551.454096; G(BS1) = -551.296648; E(BS2) = -551.592176

C	2.701322	-0.921287	-0.746168
C	1.656216	-1.633251	-0.154977
N	1.121191	-0.623832	0.604395
N	1.697379	0.581028	0.532783
N	2.678070	0.369261	-0.309858
C	-0.090739	-0.710907	1.421851
H	-0.169747	-1.757289	1.729104
H	0.058627	-0.088734	2.310575
C	3.599649	1.449740	-0.614209
H	4.300178	1.586718	0.213868
H	4.148961	1.188799	-1.520545
H	3.034629	2.369982	-0.774906
C	-1.302963	-0.272850	0.648143
C	-1.921221	-1.155976	-0.238750
C	-1.790243	1.028235	0.770420
C	-3.018078	-0.745063	-0.988583
H	-1.528892	-2.167449	-0.340234
C	-2.889315	1.440707	0.021906
H	-1.301630	1.719048	1.457270
C	-3.504551	0.554134	-0.857662
H	-3.496598	-1.440121	-1.675240
H	-3.266114	2.455962	0.126062
H	-4.364713	0.874529	-1.441593
H	3.468347	-1.227533	-1.447438


O
S
N
N
N
MeO

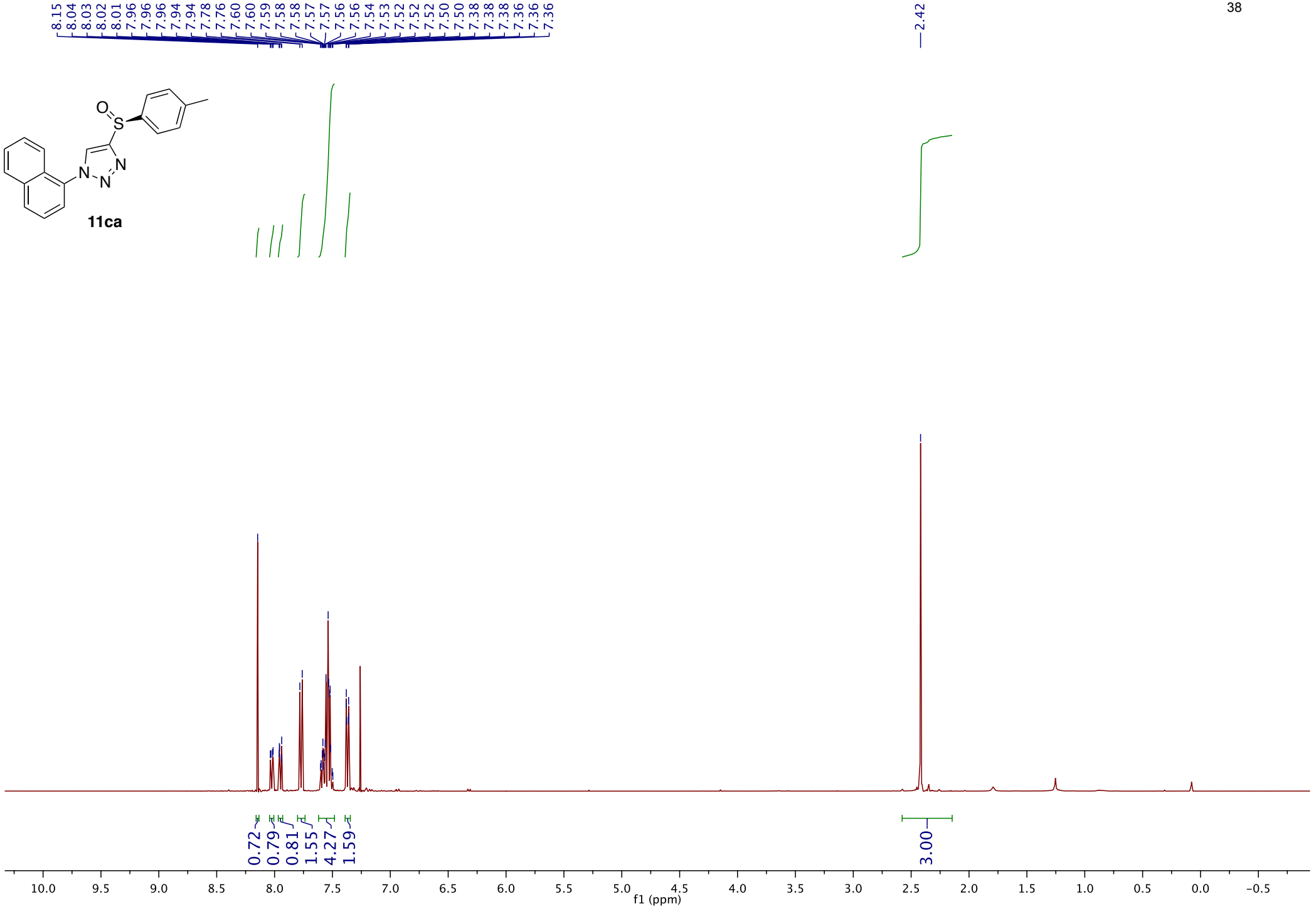
11ba

8.15
7.70
7.68
7.57
7.54
7.33
7.31
6.99
6.96
3.83
2.38
0.87
1.82
1.94
2.00
2.00
3.00
3.16
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
-0.5
f1 (ppm)


O
S
N
N
N
MeO

11ba

160.4
153.7
142.2
140.0
130.2
129.7
124.8
122.4
122.2
114.9
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
55.7
21.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.15
8.04
8.03
8.02
8.01
7.96
7.96
7.96
7.94
7.94
7.78
7.76
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7.60
7.59
7.58
7.58
7.57
7.57
7.56
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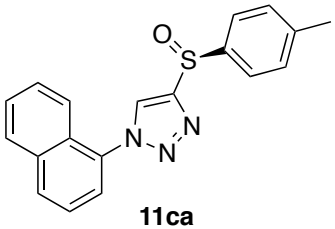
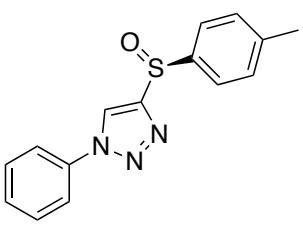
7.54
7.53
7.52
7.52
7.52
7.50
7.50
7.38
7.38
7.38
7.36
7.36
2.42
O
S
N
N
N
11ca
0.72
0.79
0.81
1.55
4.27
1.59
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)



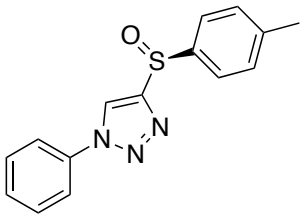
11ca

153.4
142.4
139.9
134.2
133.0
131.1
130.3
128.5
128.3
128.2
127.4
126.5
125.0
124.9
123.8
122.0
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
21.6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



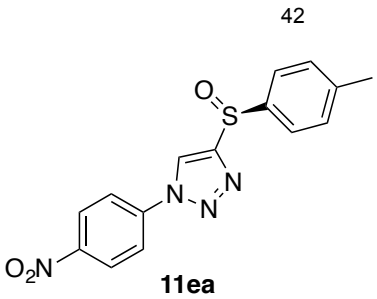
11da

8.25
7.71
7.69
7.69
7.69
7.68
7.66
7.66
7.65
7.53
7.52
7.51
7.49
7.47
7.46
7.45
7.43
7.34
7.32
2.39
0.86
1.82
2.02
2.82
1.88
3.01
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)



11da

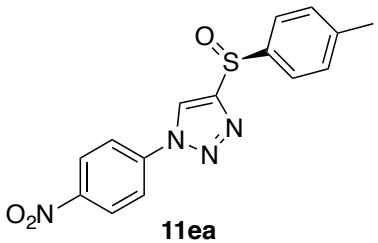
154.1
142.4
140.0
136.5
130.3
130.0
129.6
124.8
122.1
120.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
21.6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
S
N
N
N
O_2N

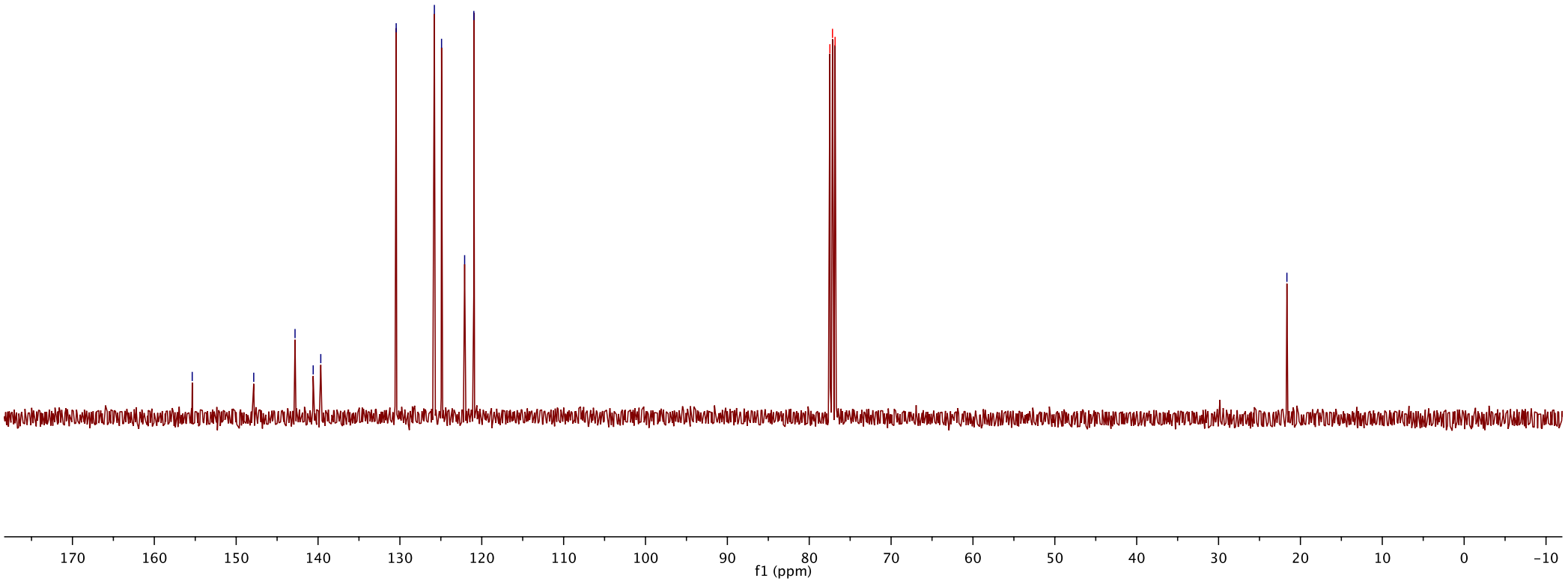
11ea

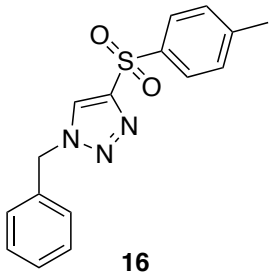
8.47
8.42
8.40
7.97
7.95
7.73
7.71
7.37
7.35
2.41
0.86
1.69
1.76
1.68
1.87
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

155.4
147.9
142.8
140.6
139.7
130.5
125.8
124.9
122.1
121.0
77.5
77.2
76.8
21.7



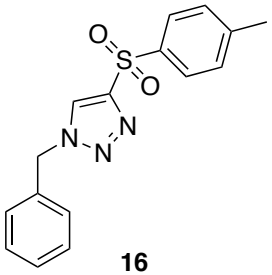
11ea





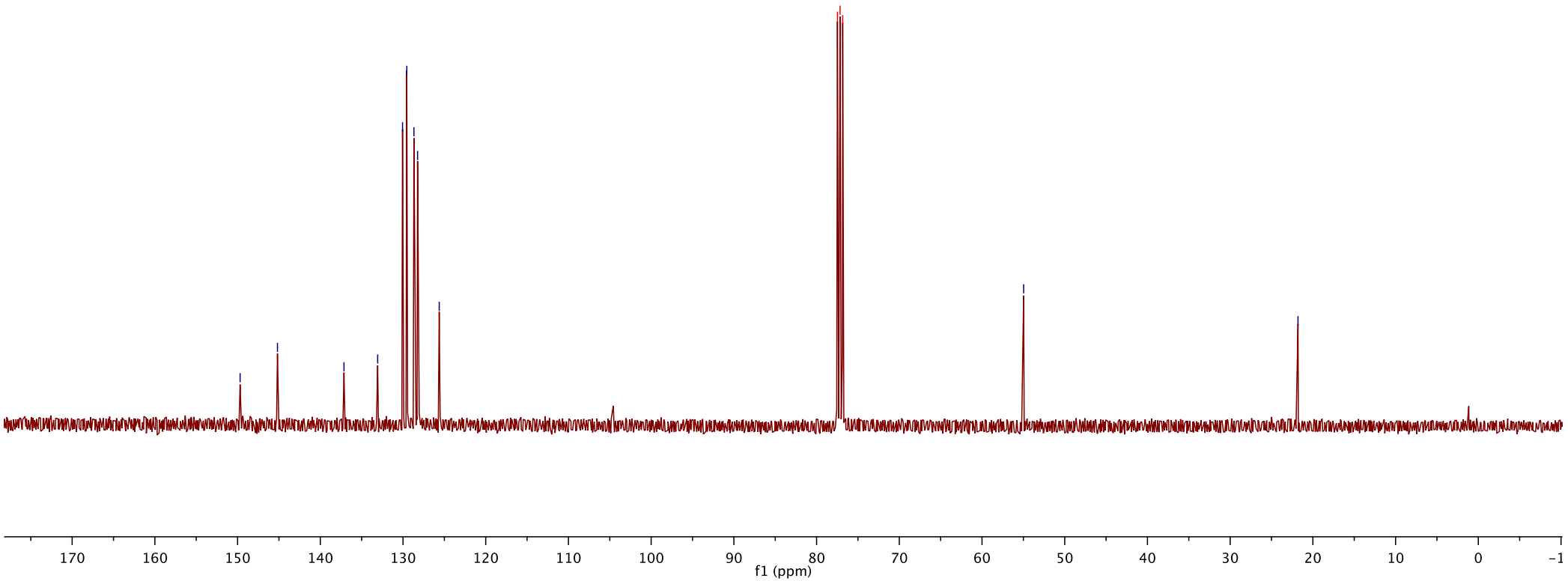
16

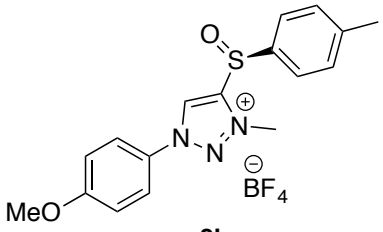
8.26
8.23
8.21
7.68
7.62
7.60
7.57
5.81
2.69
2.82
2.83
2.07
2.02
1.94
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



16

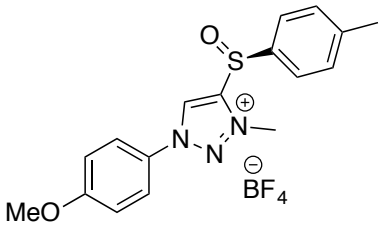
149.7
145.2
137.1
133.1
130.1
129.5
128.7
128.2
125.6
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
55.0
21.8




O
S
N
N
N
MeO
BF4

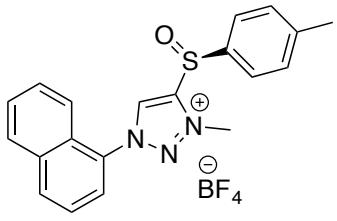
8ba

9.82
7.93
7.91
7.89
7.55
7.53
7.26
7.24
4.37
3.87
2.43
0.97
4.01
1.97
2.03
3.00
3.14
2.98
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
-0.5
f1 (ppm)


O
S
N
N
N
MeO
BF4

8ba

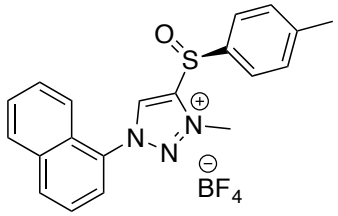
161.7
146.4
144.0
136.5
130.8
129.3
127.7
126.2
123.5
115.3
56.0
40.1 dmso
39.9 dmso
39.7 dmso
39.6
39.5 dmso
39.3 dmso
39.1 dmso
38.9 dmso
21.1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



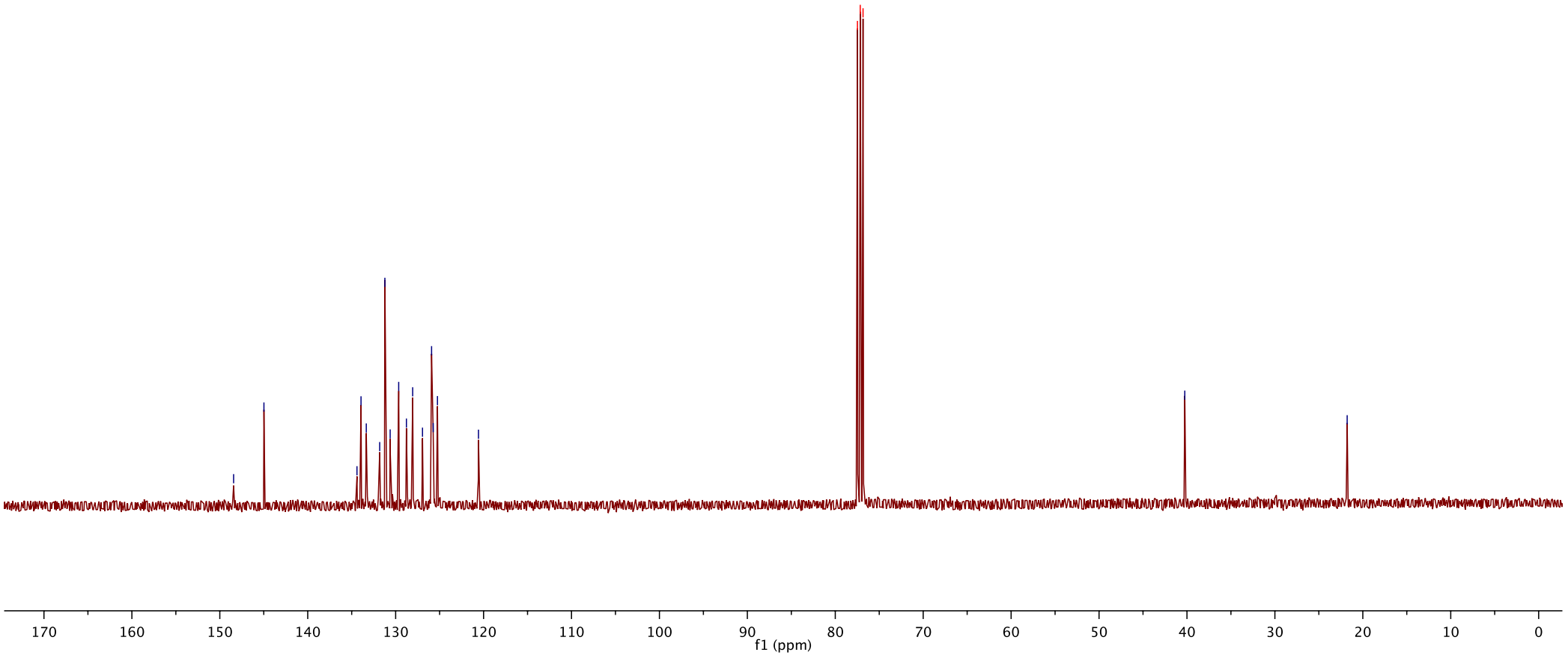
8ca

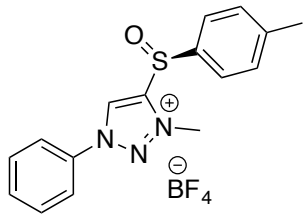
8.09
8.07
7.96
7.94
7.91
7.89
7.88
7.88
7.86
7.86
7.67
7.65
7.65
7.63
7.58
7.53
7.44
7.42
4.68
2.41
0.92
4.42
3.92
1.79
2.72
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

148.4
145.0
134.4
133.9
133.3
131.8
131.2
130.6
129.7
128.8
128.1
126.9
125.9
125.7
125.2
120.6
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
40.2
21.8



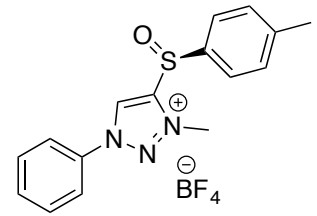
8ca





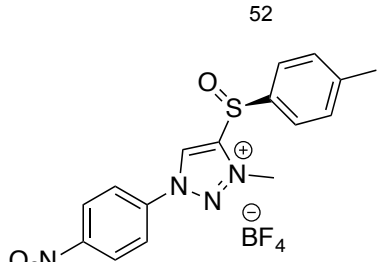
8da

8.63
7.85
7.83
7.80
7.80
7.78
7.78
7.58
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.51
7.50
7.49
7.49
7.43
7.41
4.45
2.41
0.91
2.01
1.92
3.06
1.88
2.88
3.00
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)



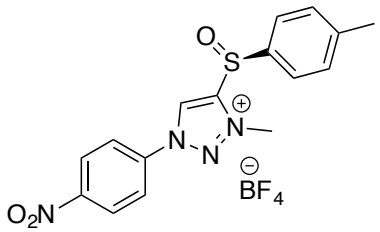
8da

147.1
144.9
135.0
134.6
132.4
131.3
130.5
128.9
125.8
122.3
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
40.0
21.7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



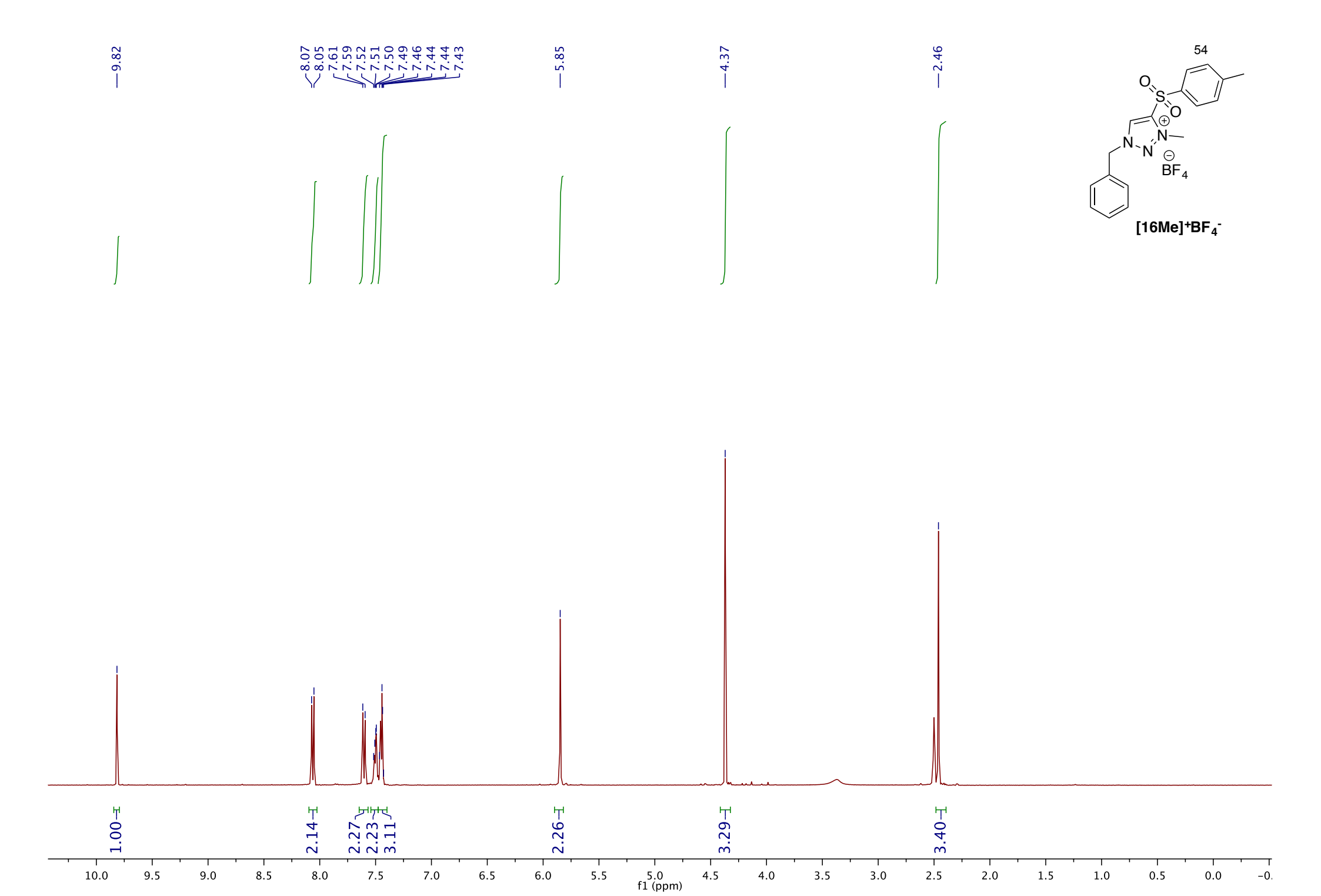
8ea

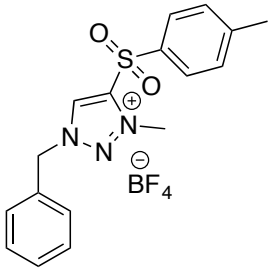
10.05
8.59
8.56
8.30
8.27
7.92
7.90
7.57
7.55
4.46
2.44
0.98
1.96
2.10
1.95
2.00
3.00
3.04
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



8ea

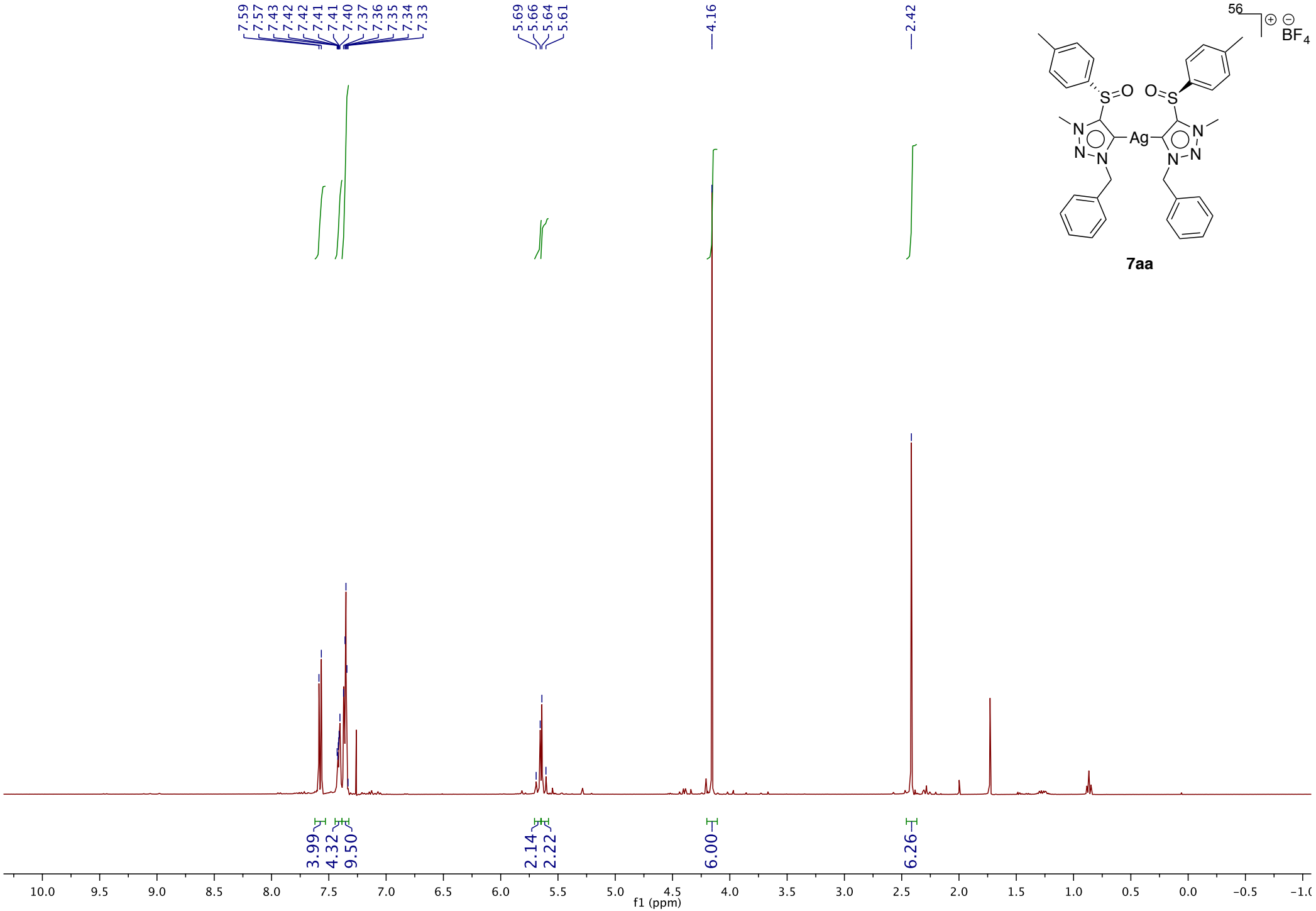
149.1
147.1
144.1
138.6
136.3
130.8
130.5
126.2
125.7
123.3
40.1 dmso
40.0
40.0 dmso
39.9 dmso
39.8 dmso
39.7 dmso
39.5 dmso
39.3 dmso
39.1 dmso
38.9 dmso
21.1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

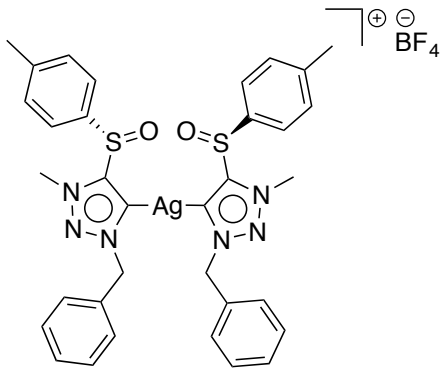

9.82
8.07
8.05
7.61
7.59
7.52
7.51
7.50
7.49
7.46
7.44
7.44
7.43
5.85
4.37
2.46
54
O
S
O
N
N
N
BF4
[16Me]+BF4-
1.00
2.14
2.27
2.23
3.11
2.26
3.29
3.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



[16Me]$^{+}$BF$_4^{-}$

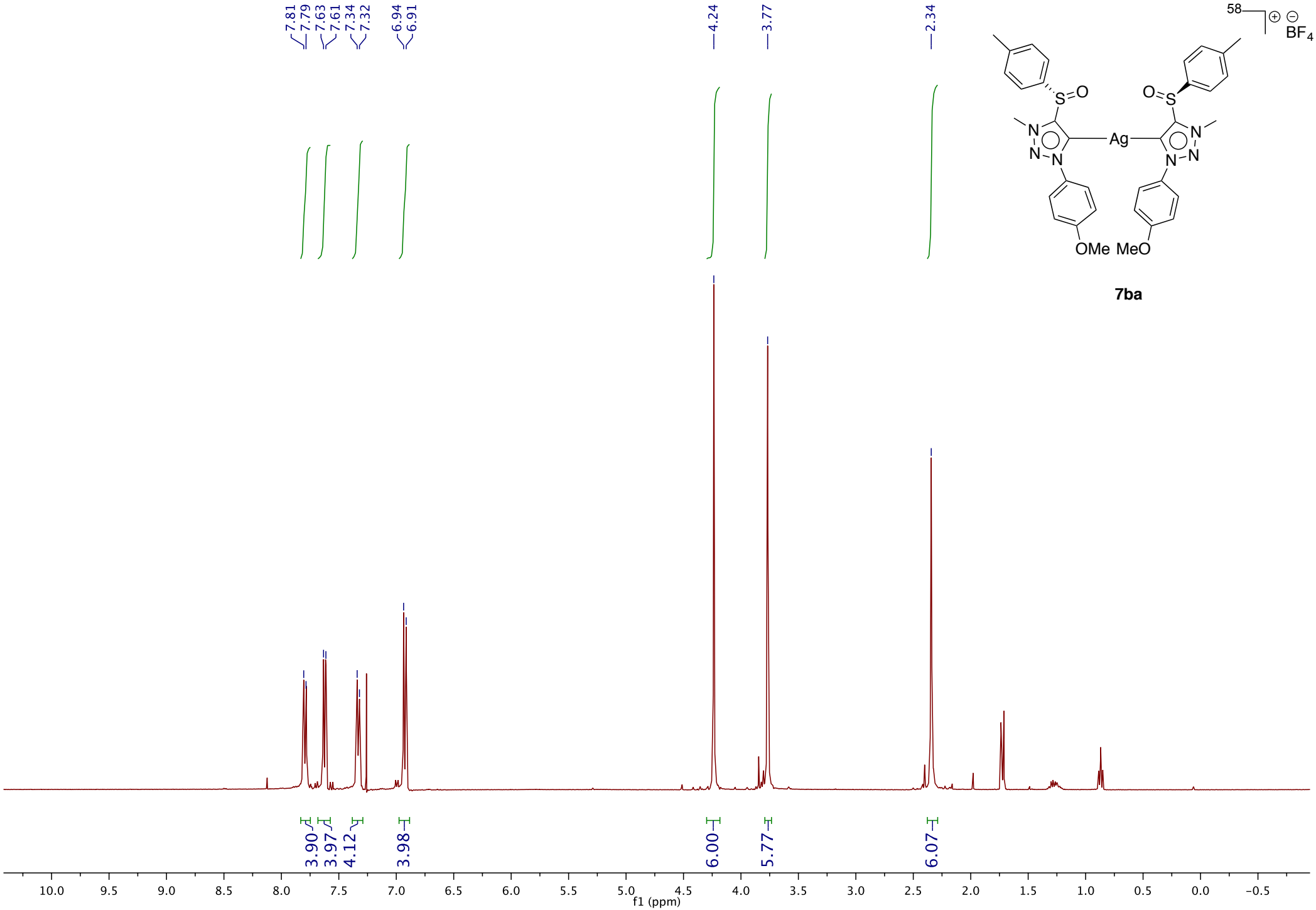
147.8
141.1
134.2
133.7
132.0
130.9
129.4
129.3
129.0
129.0
57.1
40.2
40.1 dmso
39.9 dmso
39.7 dmso
39.5 dmso
39.3 dmso
39.1 dmso
38.9 dmso
21.3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.59
7.57
7.43
7.42
7.42
7.41
7.41
7.40
7.37
7.36
7.35
7.34
7.33
5.69
5.66
5.64
5.61
4.16
2.42
56
BF4
Ag
7aa
3.99
4.32
9.50
2.14
2.22
6.00
6.26
f1 (ppm)

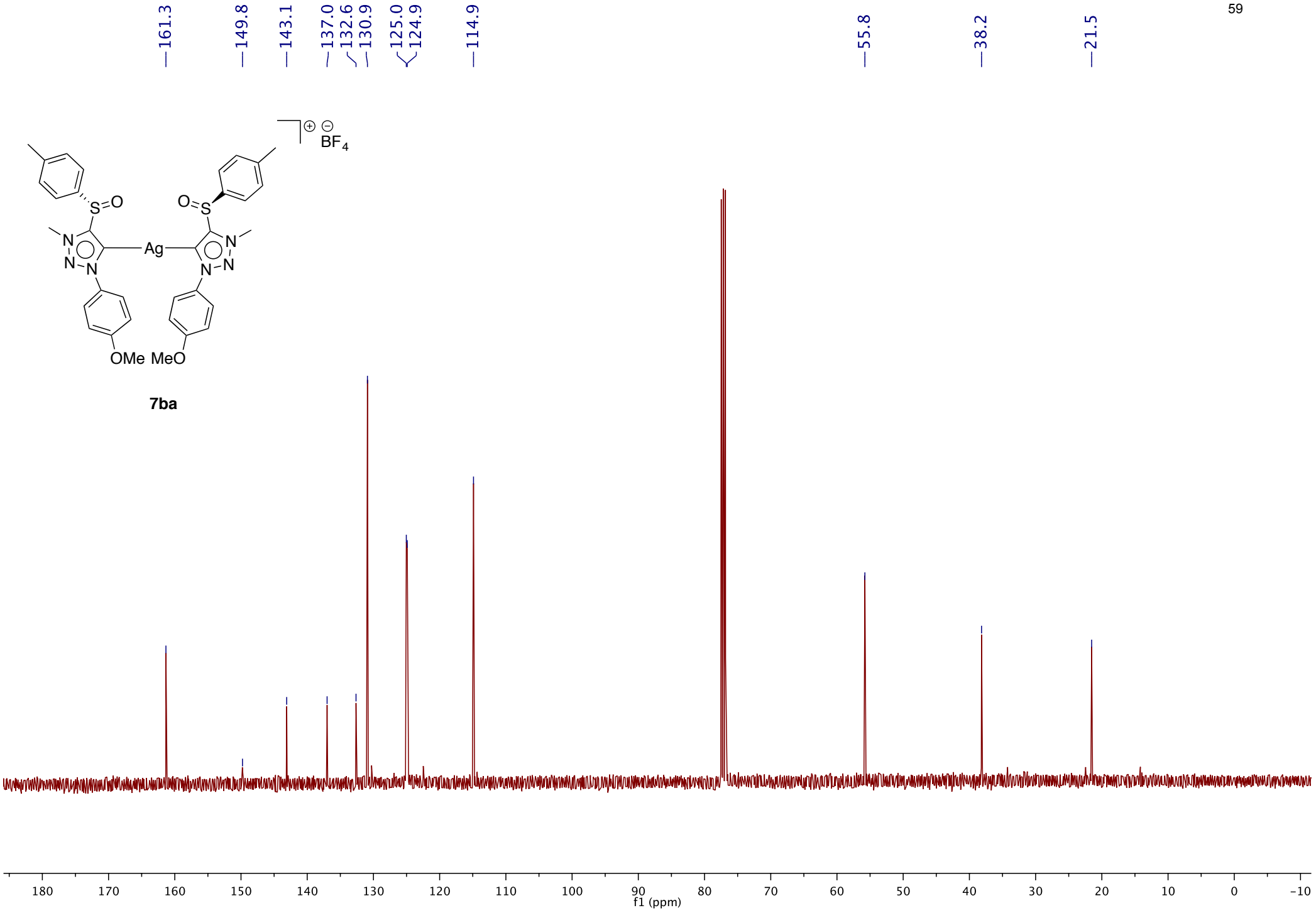

BF4
S
O
O
S
N
N
N
Ag
N
N
N

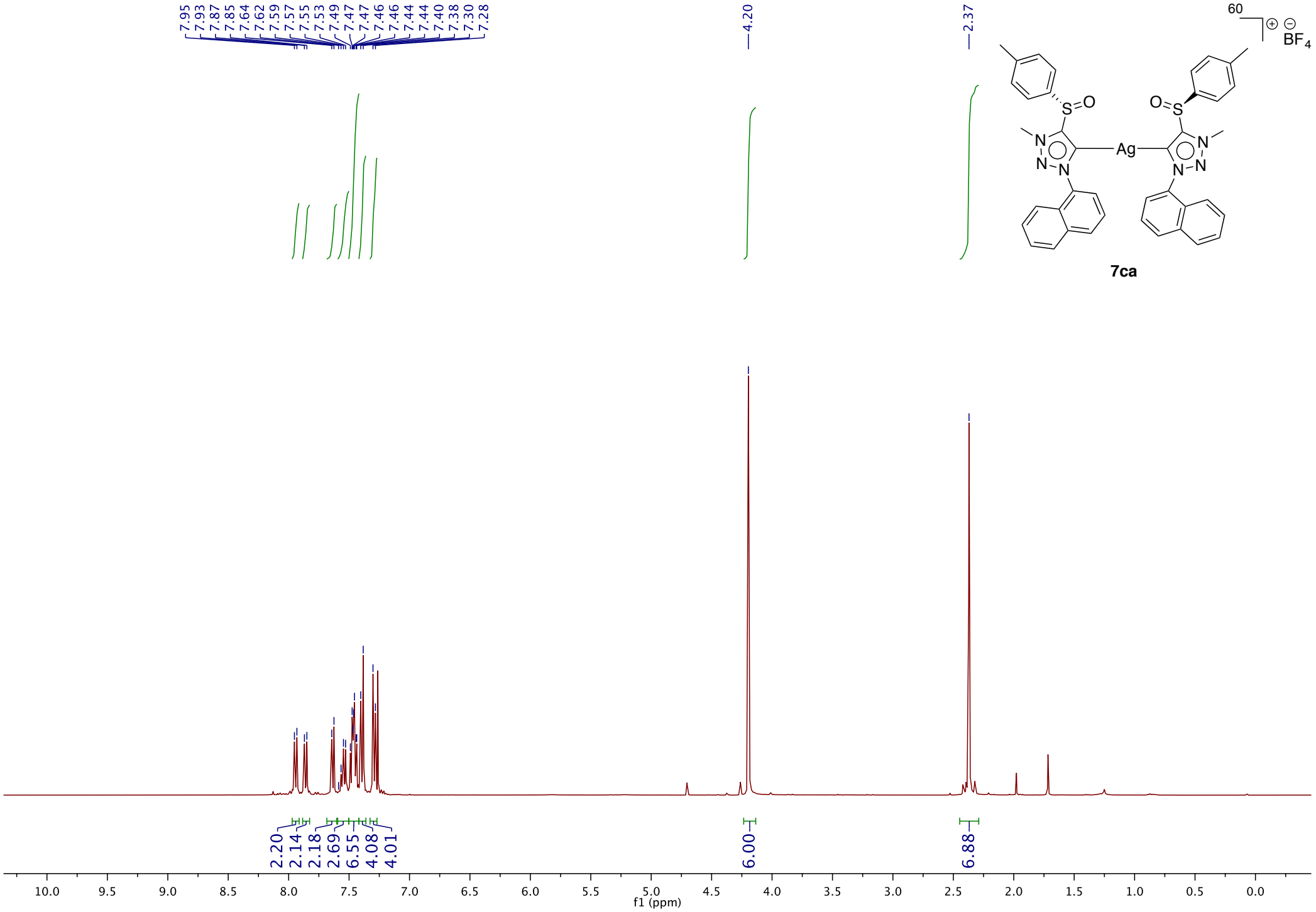
7aa

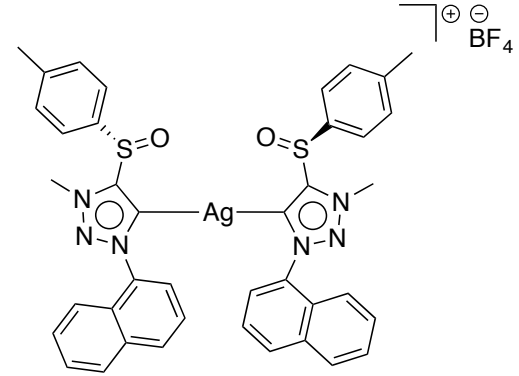
149.0
143.5
136.7
133.2
130.9
129.6
129.4
128.9
124.7
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
60.6
38.1
21.7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


7.81
7.79
7.63
7.61
7.34
7.32
6.94
6.91
4.24
3.77
2.34
3.90
3.97
4.12
3.98
6.00
5.77
6.07
f1 (ppm)
58
BF4
Ag
OMe
MeO

7ba

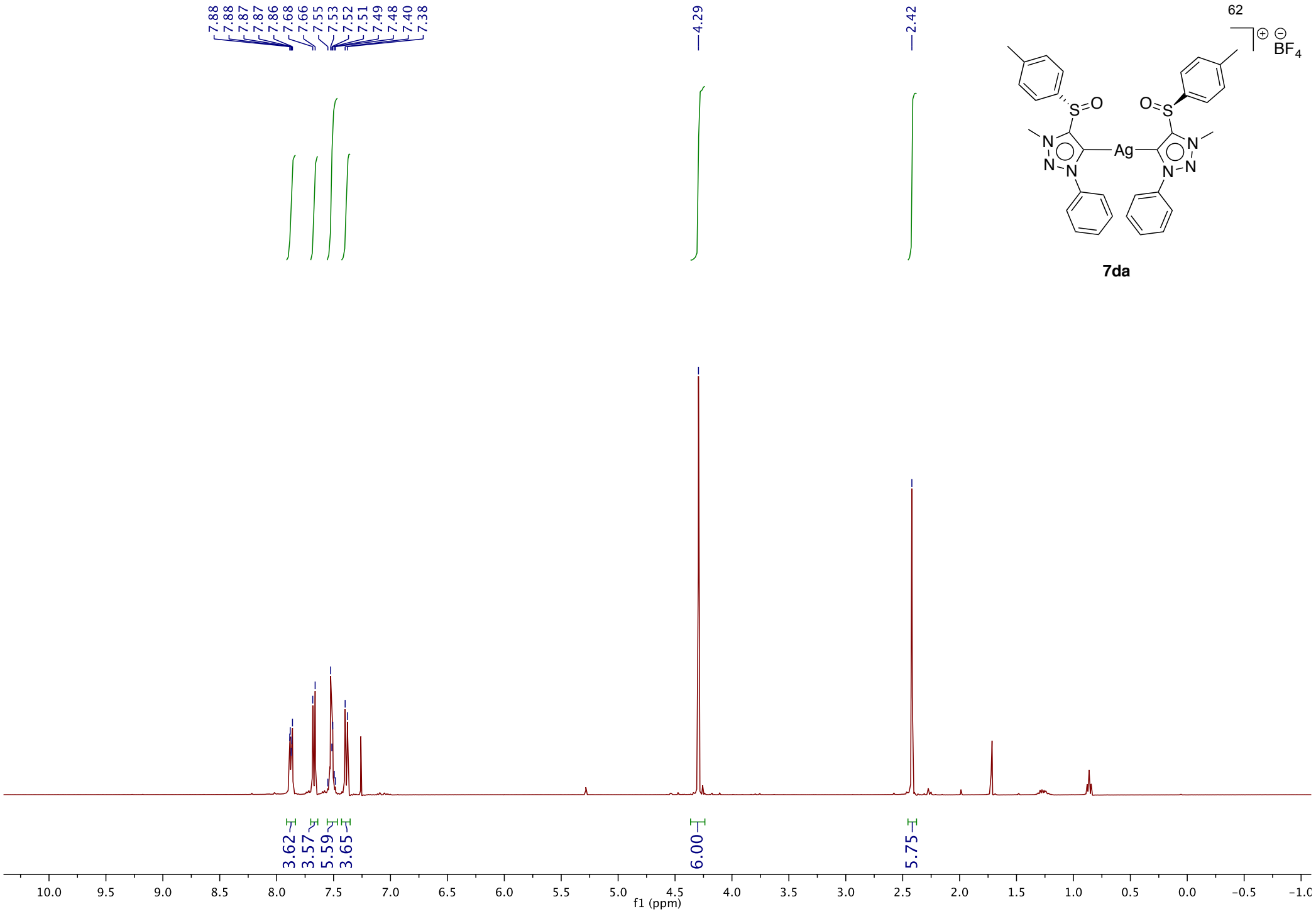

161.3
149.8
143.1
137.0
132.6
130.9
125.0
124.9
114.9
55.8
38.2
21.5
BF4
S=O
O=S
N
N
N
N
Ag
OMe
MeO
7ba
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

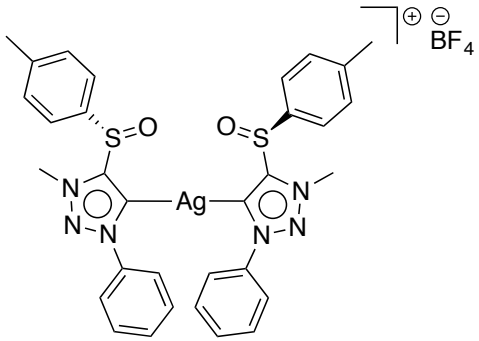

7.95
7.93
7.87
7.85
7.64
7.62
7.59
7.57
7.55
7.53
7.49
7.47
7.47
7.46
7.46
7.44
7.44
7.40
7.38
7.30
7.28
4.20
2.37
60
BF4
7ca
2.20
2.14
2.18
2.69
6.55
4.08
4.01
6.00
6.88
f1 (ppm)


BF4
S
O
Ag
N

7ca

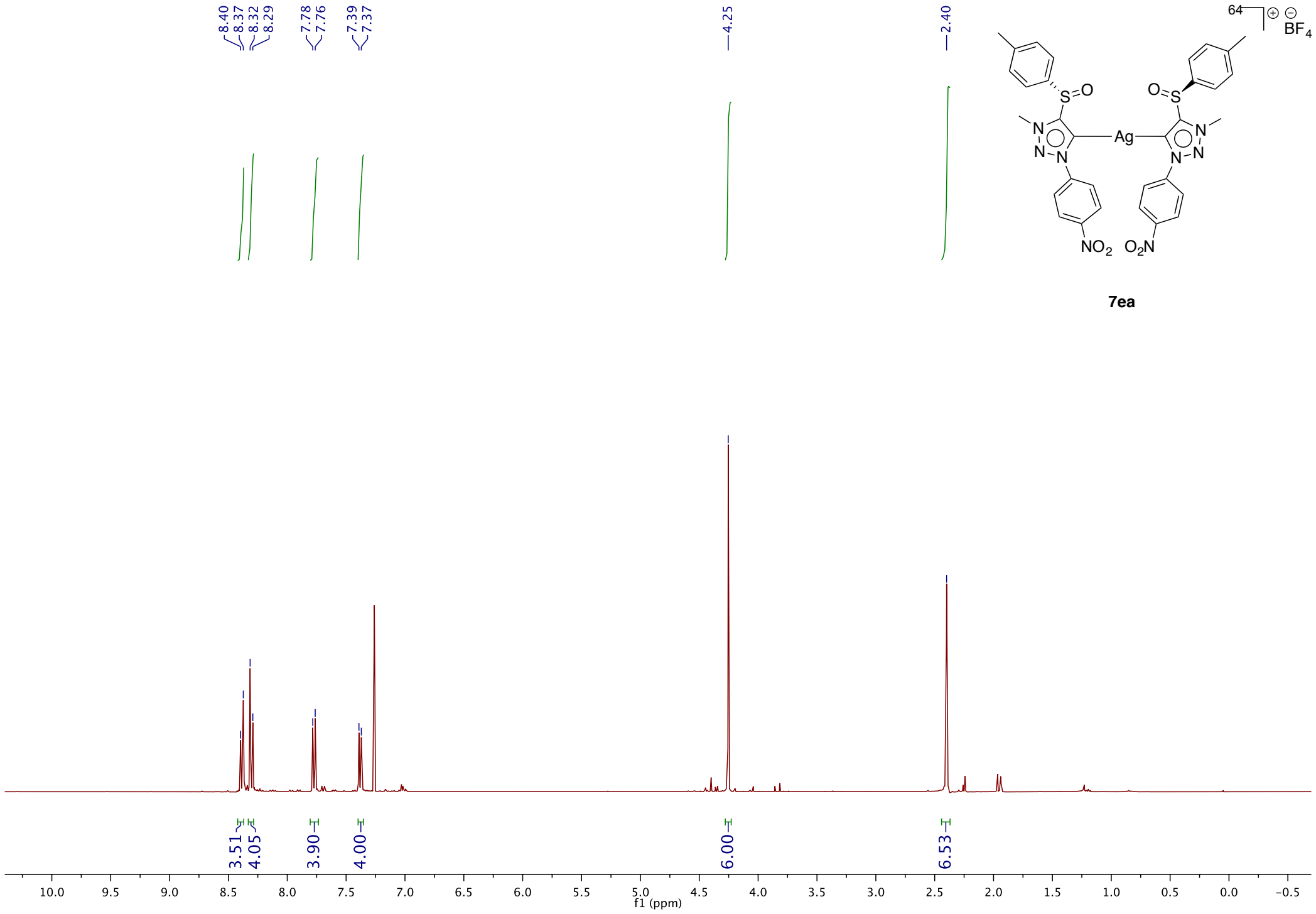
173.8
172.0
149.1
149.0
142.8
136.5
135.8
134.0
131.7
130.8
128.7
128.6
127.6
127.5
125.2
125.0
124.7
121.6
77.5 cdcl3
77.4 cdcl3
77.2 cdcl3
77.0 cdcl3
76.8 cdcl3
76.7 cdcl3
38.3
21.6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.88
7.88
7.87
7.87
7.86
7.68
7.66
7.55
7.53
7.52
7.51
7.49
7.48
7.40
7.38
4.29
2.42
62
BF4
S=O
O=S
N
N
N
Ag
7da
3.62
3.57
5.59
3.65
6.00
5.75
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
-0.5
-1.0
f1 (ppm)

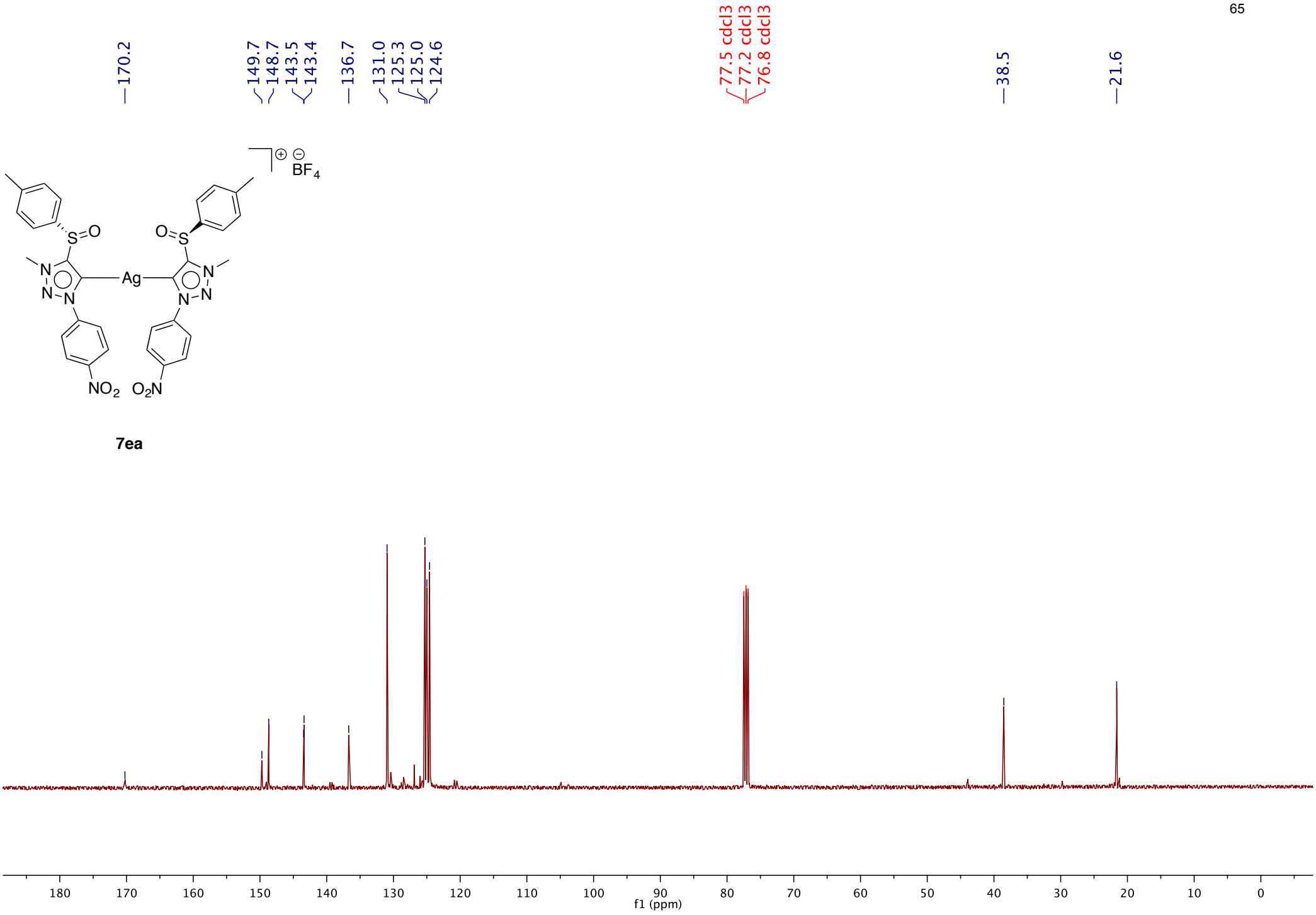

BF4
S
O
Ag
N

7da

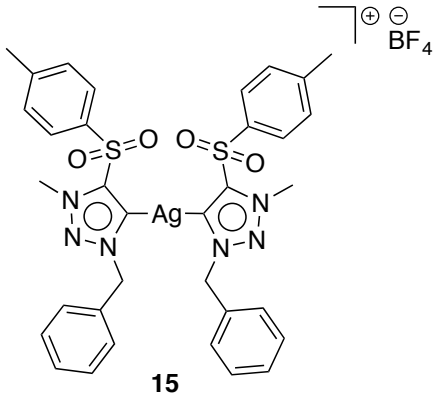
149.4
143.4
139.2
136.9
131.0
131.0
130.0
124.8
123.3
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
38.3
21.7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.40
8.37
8.32
8.29
7.78
7.76
7.39
7.37
4.25
2.40
64
BF4
S=O
O=S
N
N-N
Ag
NO2
O2N
3.51
4.05
3.90
4.00
6.00
6.53
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
-0.5
f1 (ppm)

7ea

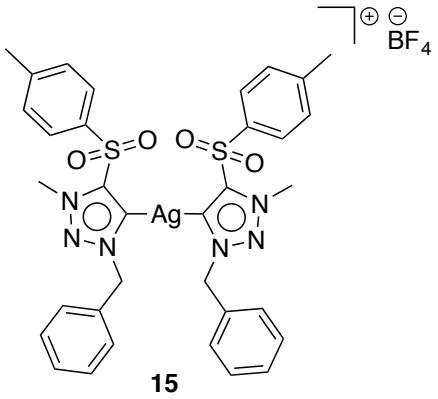

170.2
149.7
148.7
143.5
143.4
136.7
131.0
125.3
125.0
124.6
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
38.5
21.6
BF4
S=O
O=S
Ag
N
NO2
O2N
f1 (ppm)

7ea


BF4
O
S
O
N
N
N
Ag
N
N
N

15

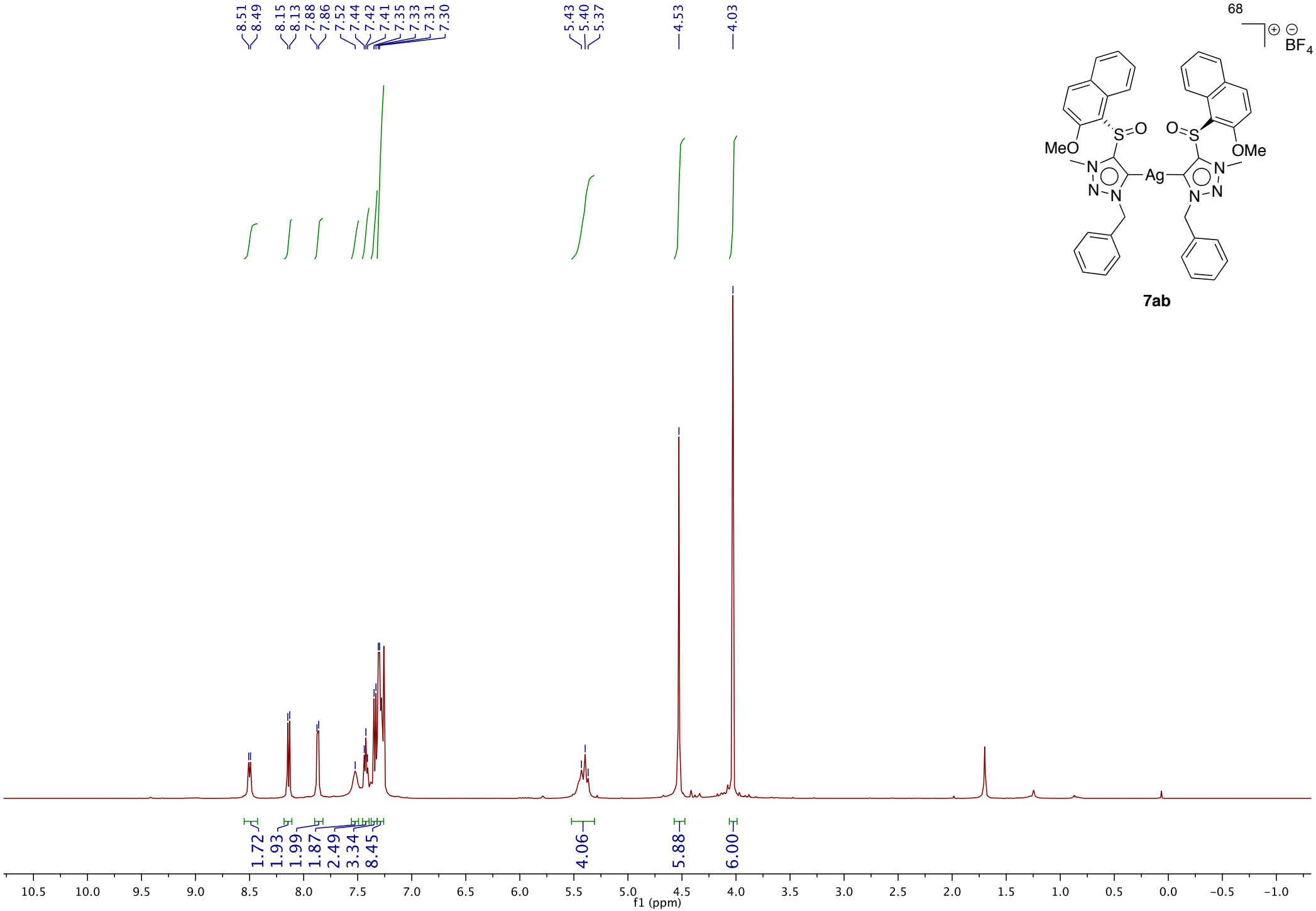
7.97
7.95
7.45
7.43
7.41
7.35
7.34
7.33
5.67
4.39
2.47
3.66
7.74
5.56
3.91
6.00
6.16
f1 (ppm)



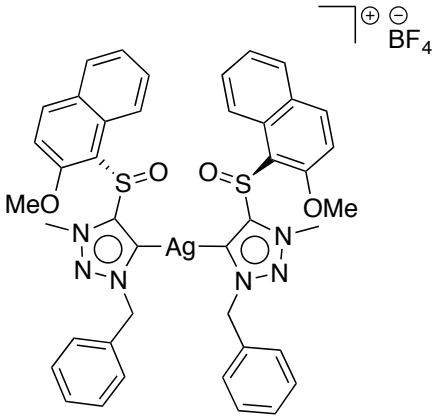
15

148.2
147.7
134.8
133.2
131.1
129.6
129.4
129.1
129.0
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
60.9
39.6
22.1

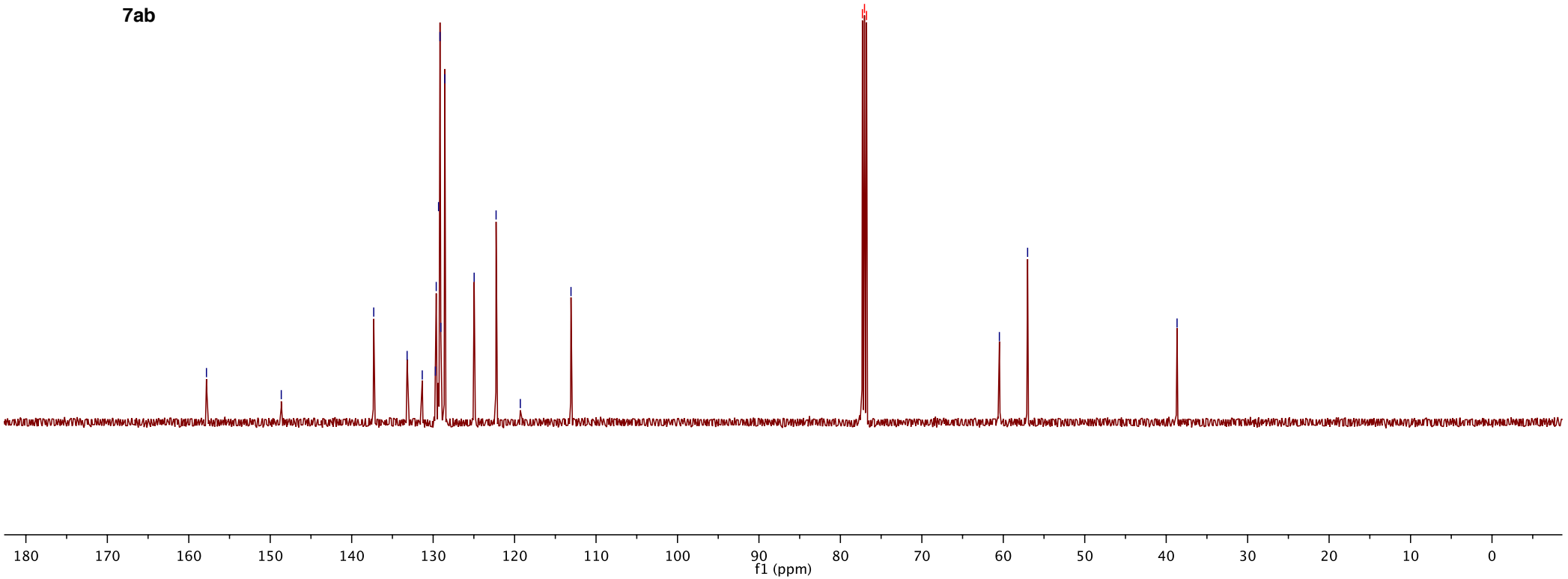
f1 (ppm)

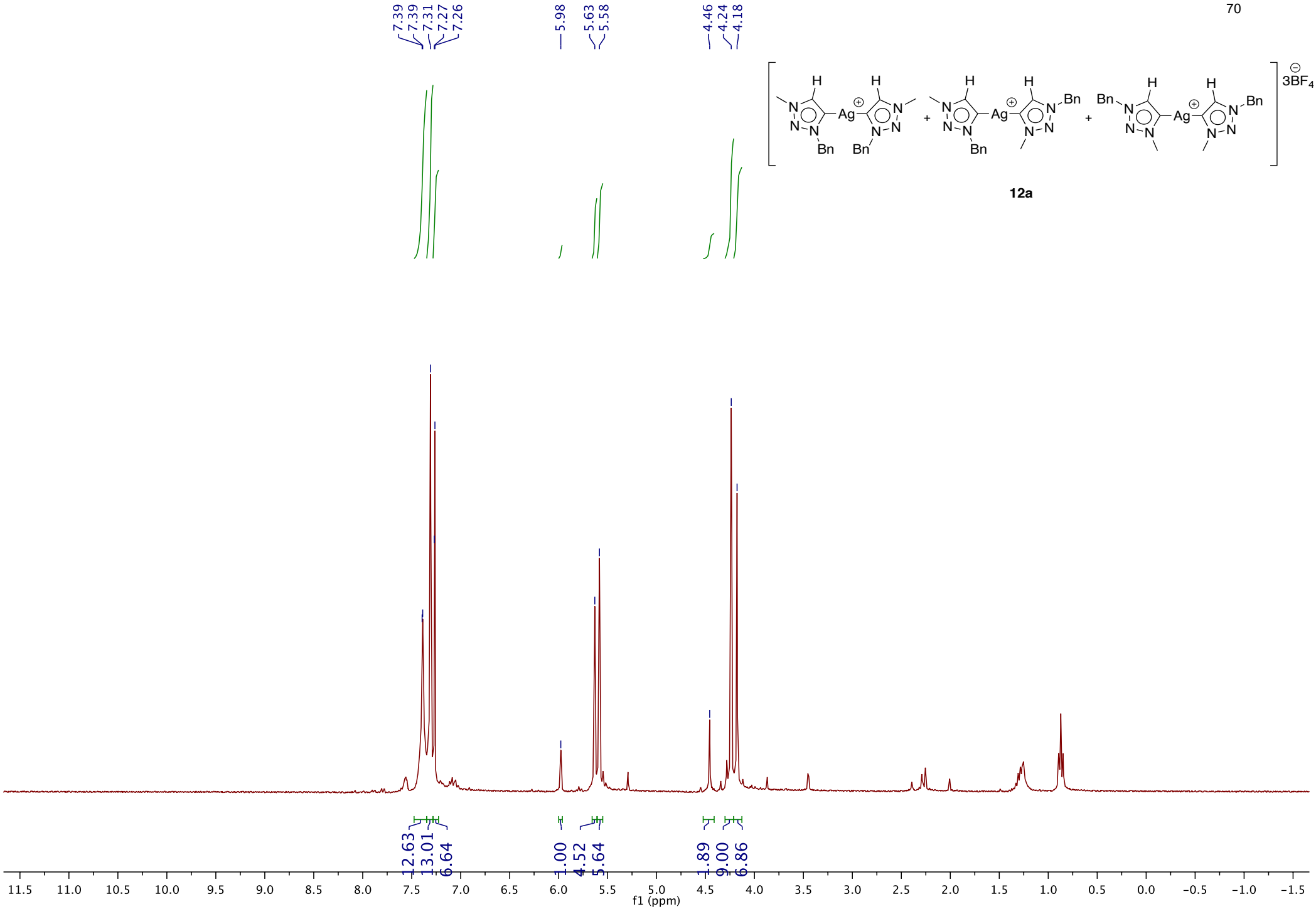

8.51
8.49
8.15
8.13
7.88
7.86
7.52
7.44
7.42
7.41
7.35
7.33
7.31
7.30
5.43
5.40
5.37
4.53
4.03
1.72
1.93
1.99
1.87
2.49
3.34
8.45
4.06
5.88
6.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
68
BF4
MeO
OMe
Ag
7ab

157.8
148.6
137.3
133.2
131.3
129.7
129.6
129.3
129.2
129.1
128.6
125.0
122.3
119.3
113.1
77.3 cdcl3
77.0 cdcl3
76.8 cdcl3
60.5
57.0
38.7

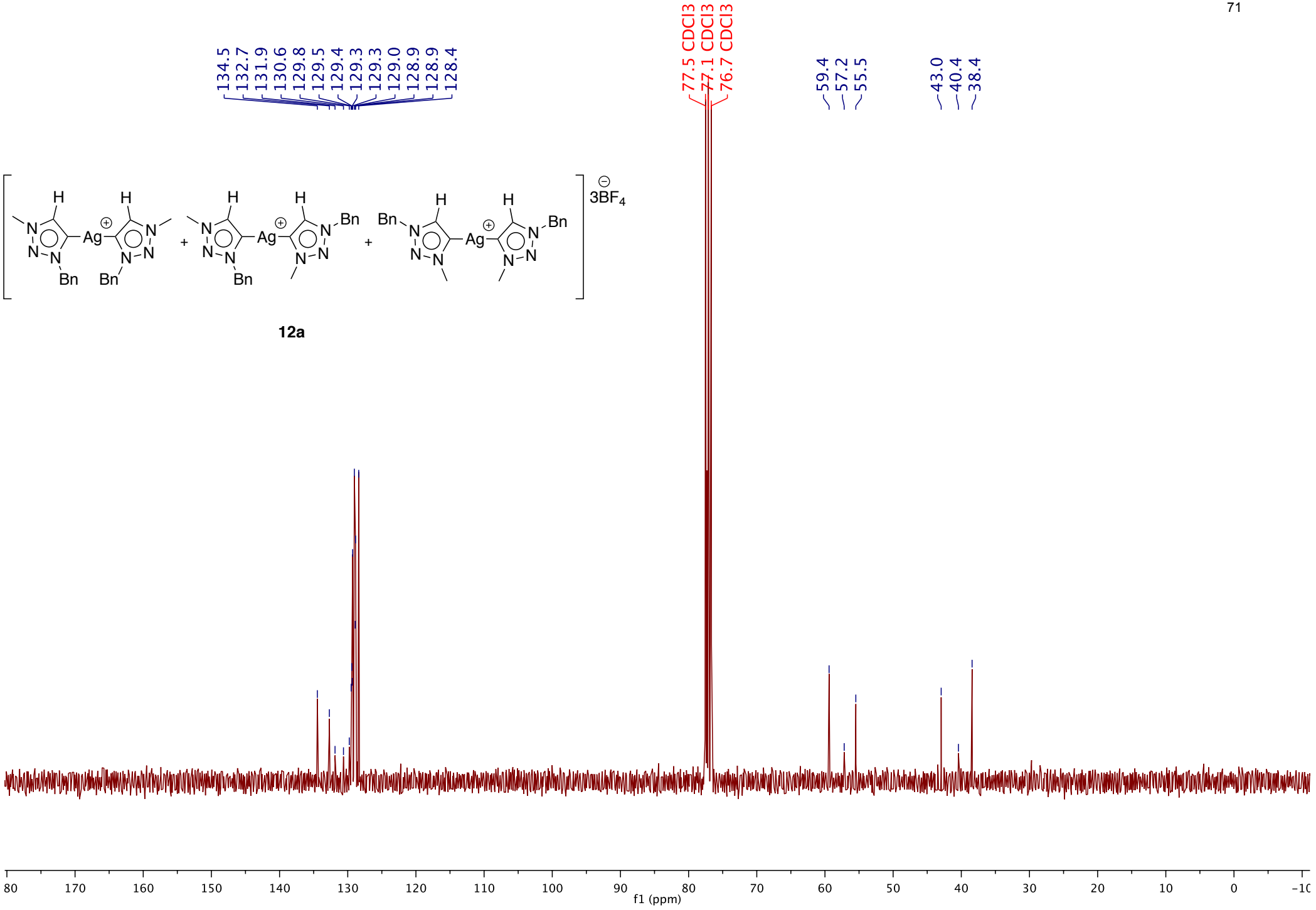


7ab

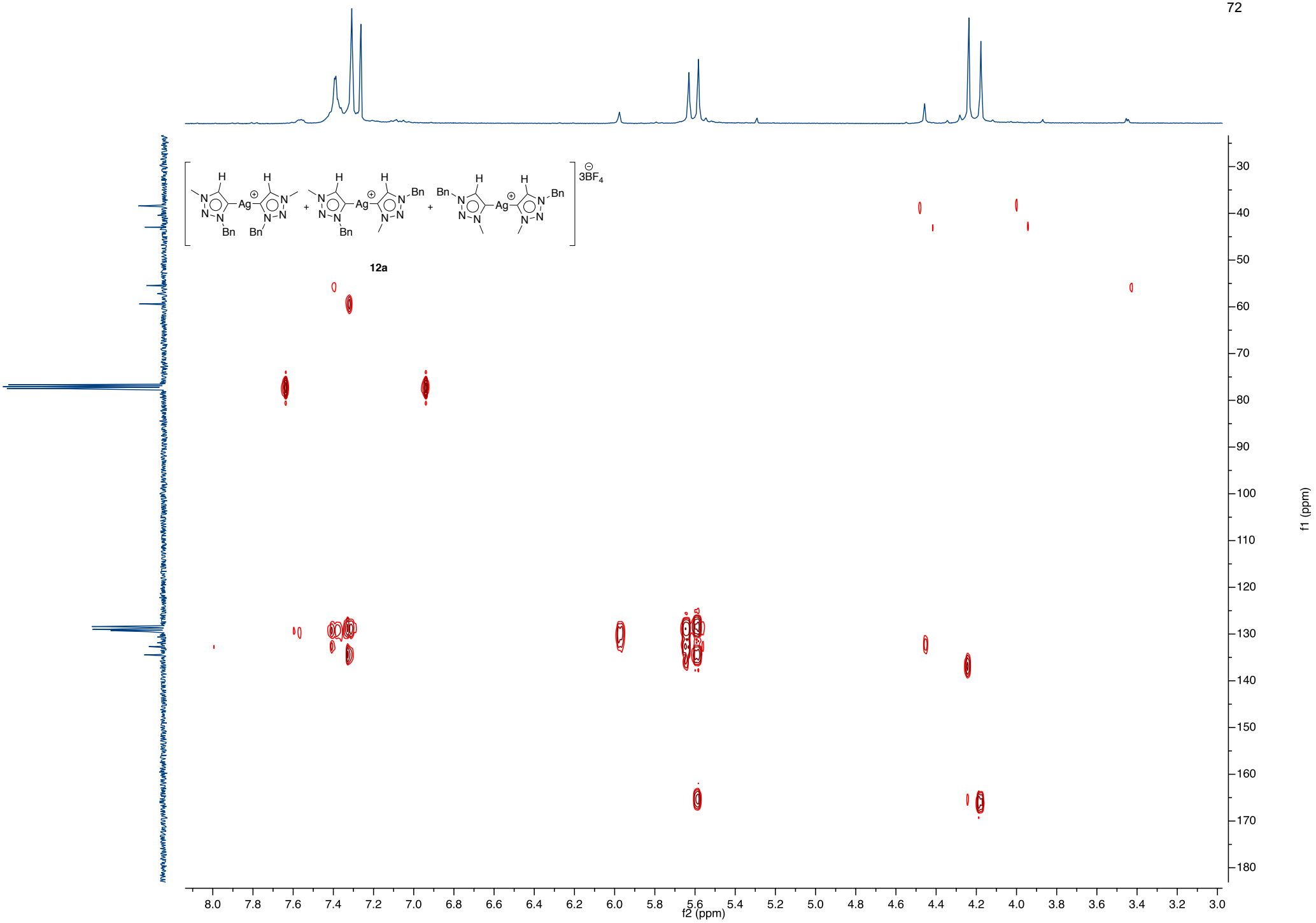


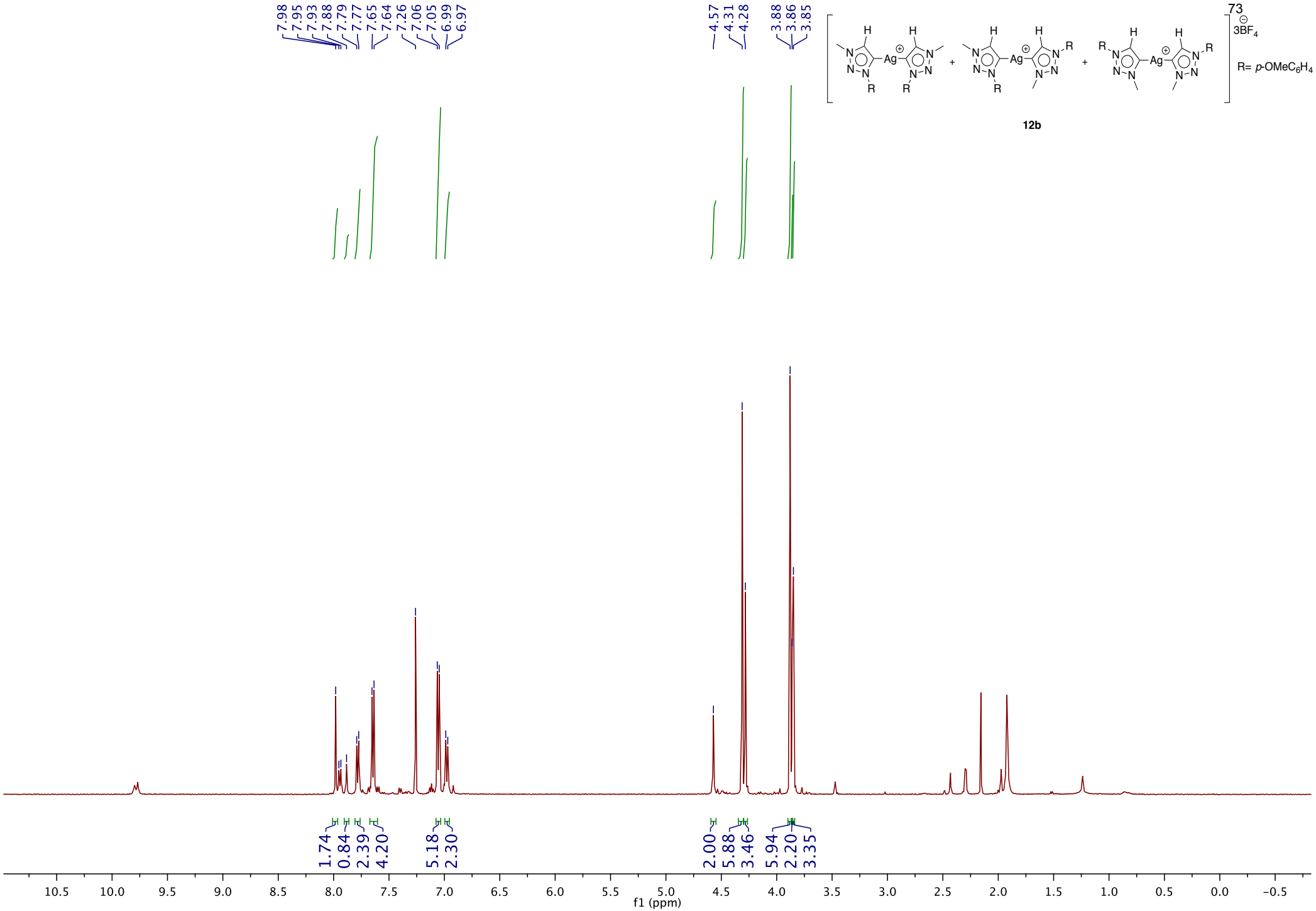

7.39
7.39
7.31
7.27
7.26
5.98
5.63
5.58
4.46
4.24
4.18
12.63
13.01
6.64
1.00
4.52
5.64
1.89
9.00
6.86
f1 (ppm)
3BF4

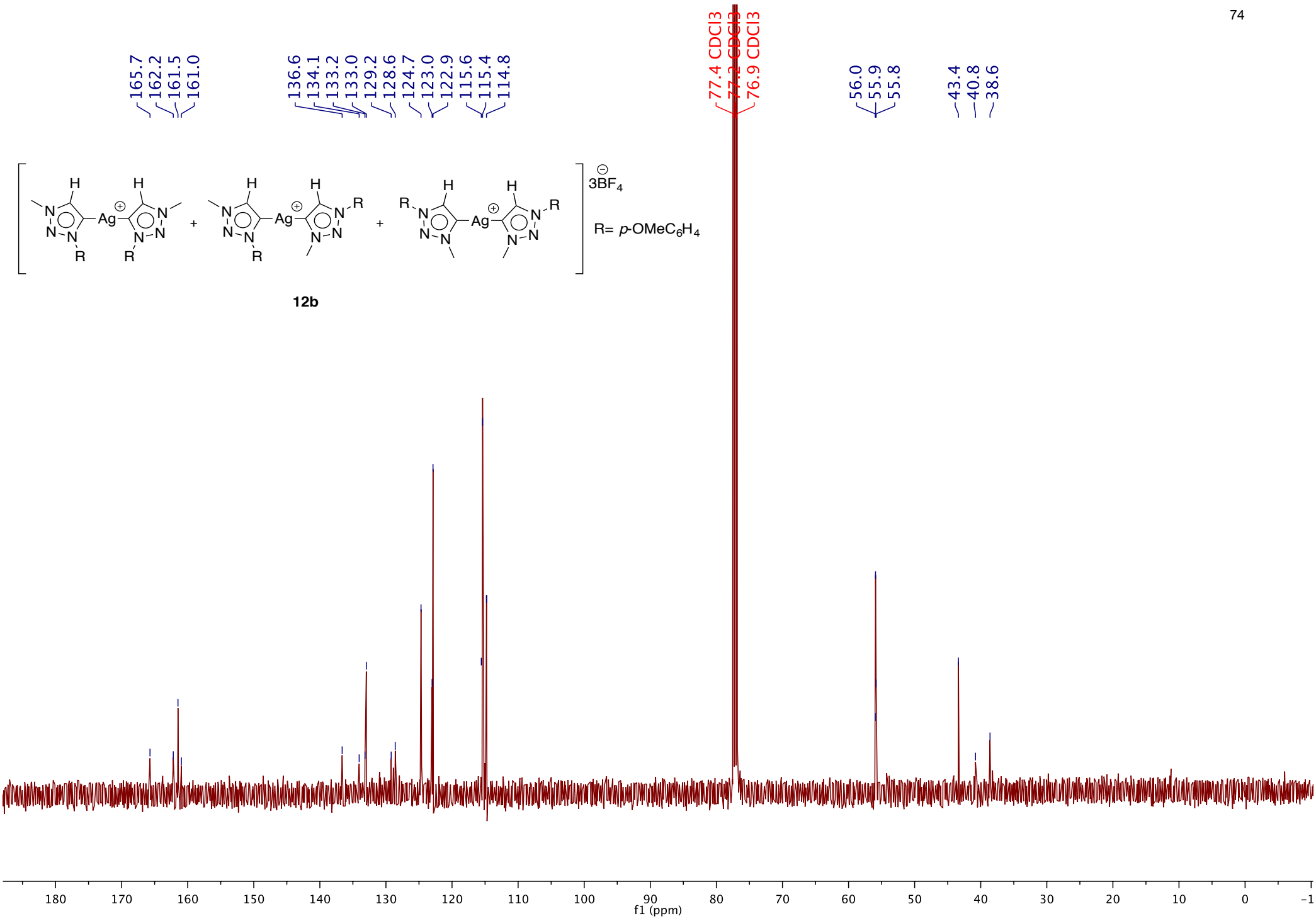
12a

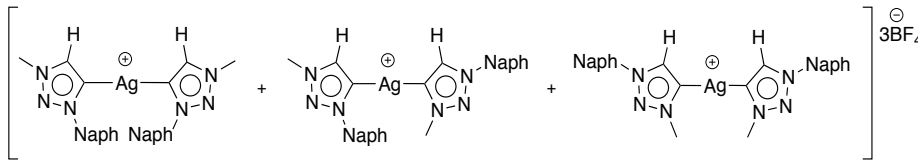

134.5
132.7
131.9
130.6
129.8
129.5
129.4
129.3
129.3
129.0
128.9
128.9
128.4
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
59.4
57.2
55.5
43.0
40.4
38.4
3BF4
f1 (ppm)

12a


12a
3BF4
f2 (ppm)
f1 (ppm)

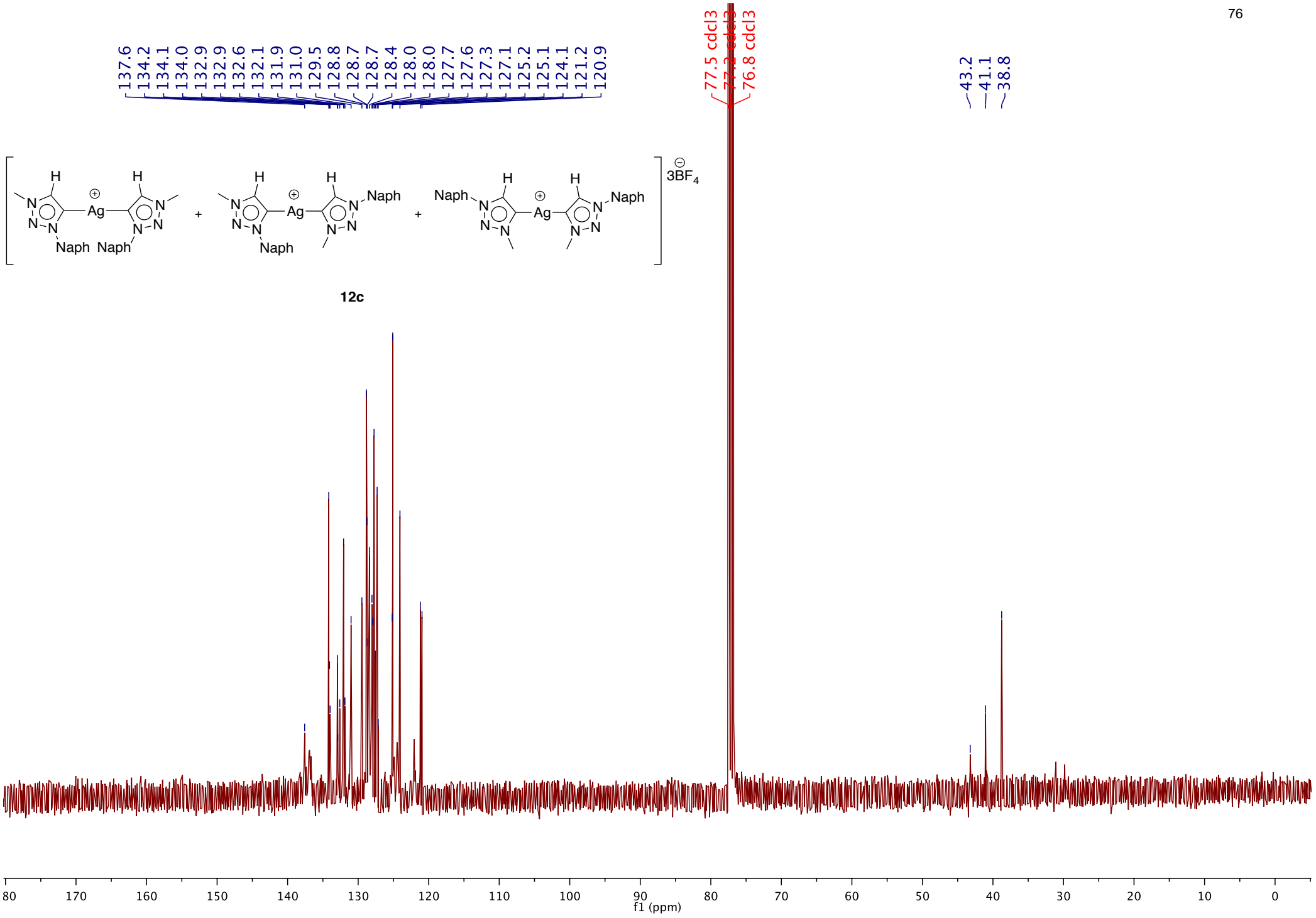

7.98
7.95
7.93
7.88
7.79
7.77
7.65
7.64
7.26
7.06
7.05
6.99
6.97
4.57
4.31
4.28
3.88
3.86
3.85
73
3BF4
R= p-OMeC6H4
12b
1.74
0.84
2.39
4.20
5.18
2.30
2.00
5.88
3.46
5.94
2.20
3.35
f1 (ppm)


165.7
162.2
161.5
161.0
136.6
134.1
133.2
133.0
129.2
128.6
124.7
123.0
122.9
115.6
115.4
114.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
56.0
55.9
55.8
43.4
40.8
38.6
3BF4
R= p-OMeC6H4
12b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

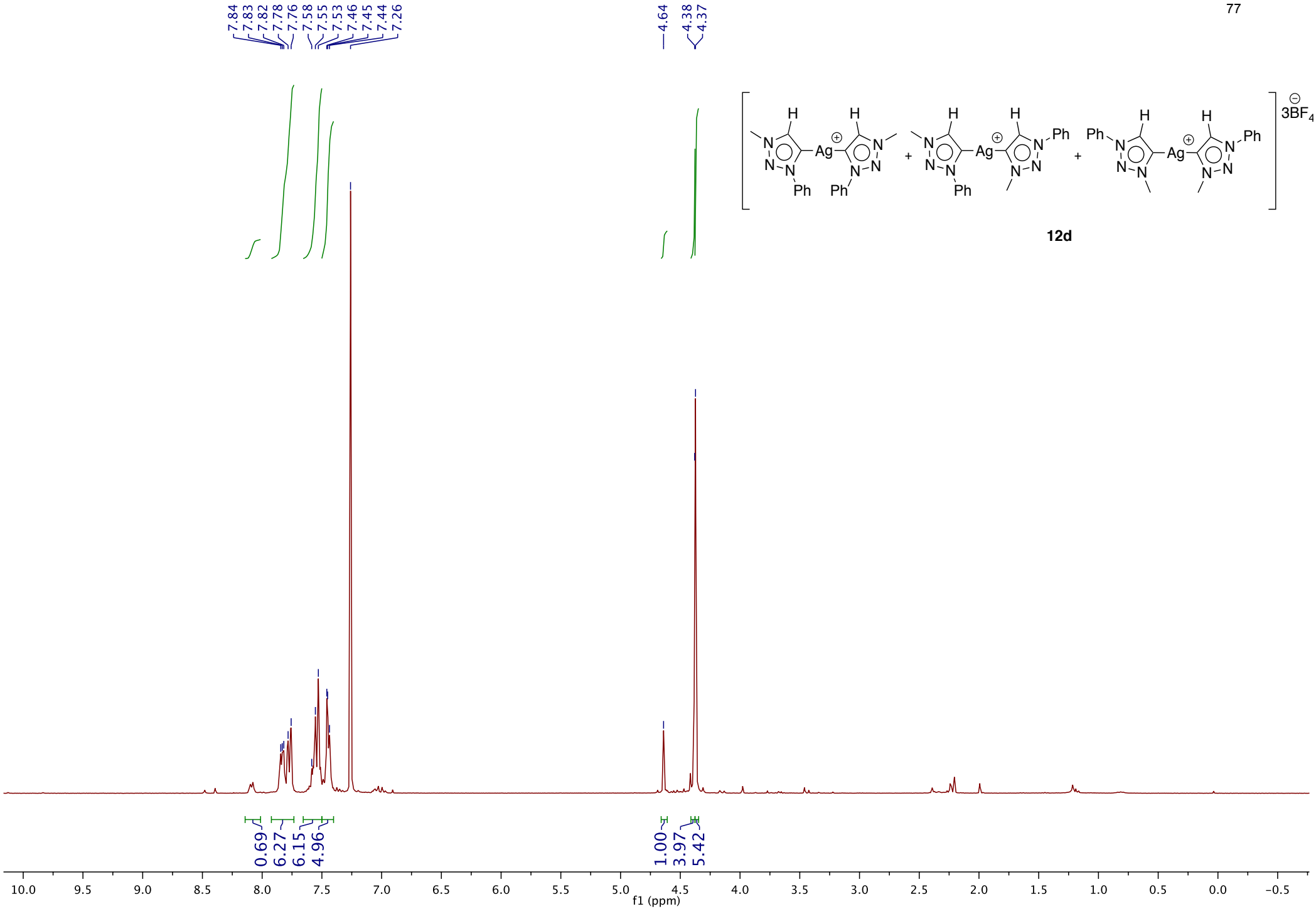

Naph
Naph
Naph
Naph
Naph
Ag
3BF4

12c

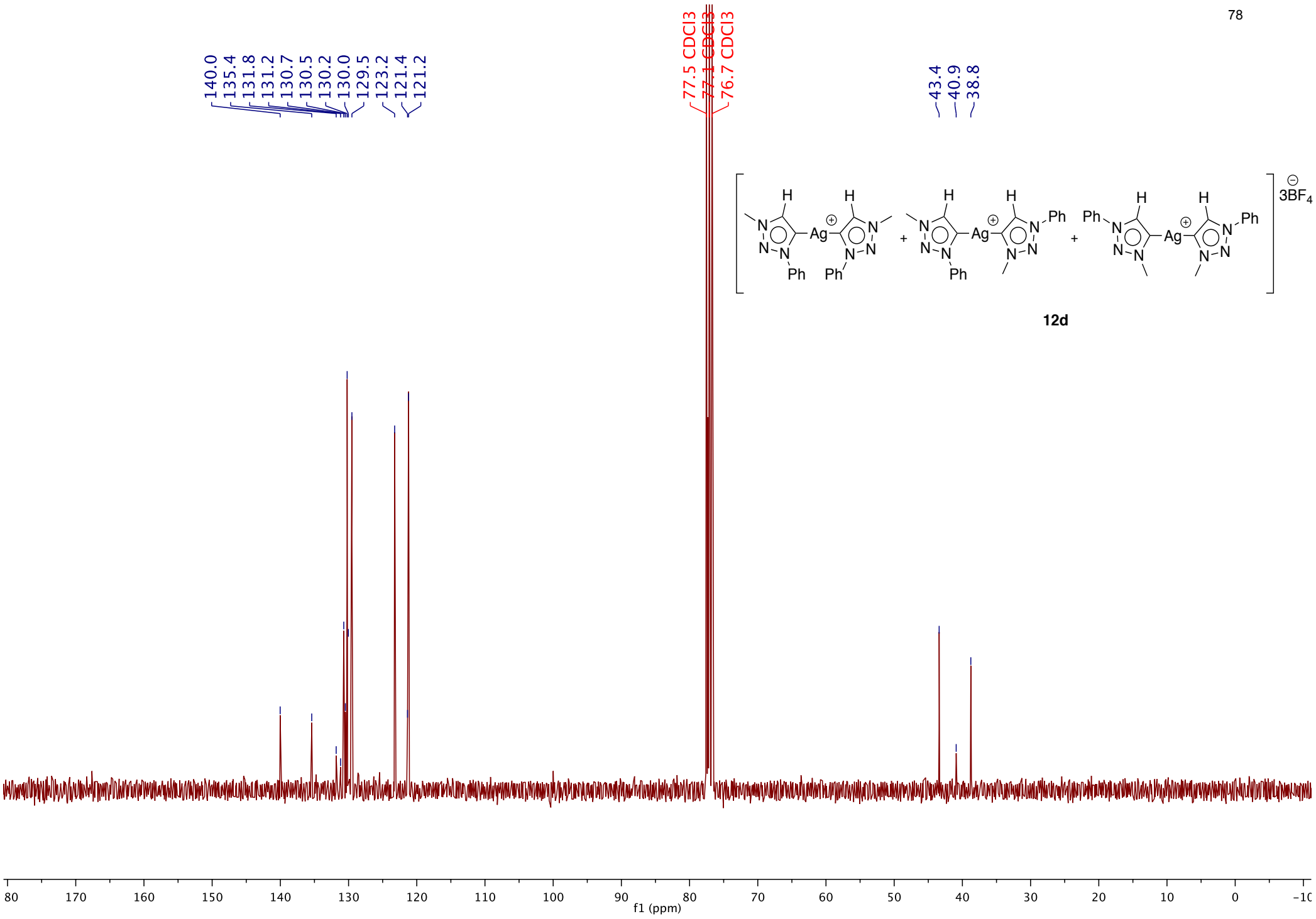
8.91
8.60
8.12
8.10
8.08
7.99
7.97
7.85
7.83
7.63
7.61
7.61
7.59
7.55
7.26
7.26
4.58
4.34
0.21
0.22
1.12
4.95
10.03
1.00
4.58
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

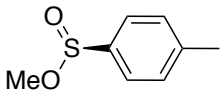

137.6
134.2
134.1
134.0
132.9
132.9
132.6
132.1
131.9
131.0
129.5
128.8
128.7
128.7
128.4
128.0
128.0
127.7
127.6
127.3
127.1
125.2
125.1
124.1
121.2
120.9
77.5 cdcl3
77.3 cdcl3
76.8 cdcl3
43.2
41.1
38.8
Naph
Ag
3BF4
f1 (ppm)

12c

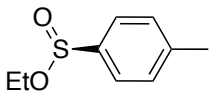

7.84
7.83
7.82
7.78
7.76
7.58
7.55
7.53
7.46
7.45
7.44
7.26
4.64
4.38
4.37
0.69
6.27
6.15
4.96
1.00
3.97
5.42
f1 (ppm)
3BF4

12d


140.0
135.4
131.8
131.2
130.7
130.5
130.2
130.0
129.5
123.2
121.4
121.2
77.5 CDCl3
77.1 CDCl3
76.7 CDCl3
43.4
40.9
38.8
3BF4
12d
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
S
MeO

7.60
7.58
7.35
7.33
3.46
2.43
1.80
1.89
3.00
3.18
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)



7.61 7.59 7.34 7.34 7.34 7.32 7.32 7.32

4.13 4.12 4.11 4.10 4.09 4.08 4.07 4.06 3.76 3.74 3.73 3.72 3.71 3.70 3.70 3.68

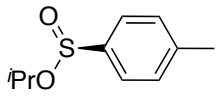
2.43

1.29 1.28 1.26

1.69 1.78 0.91 0.92 2.99 3.13

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 −0.5 −1

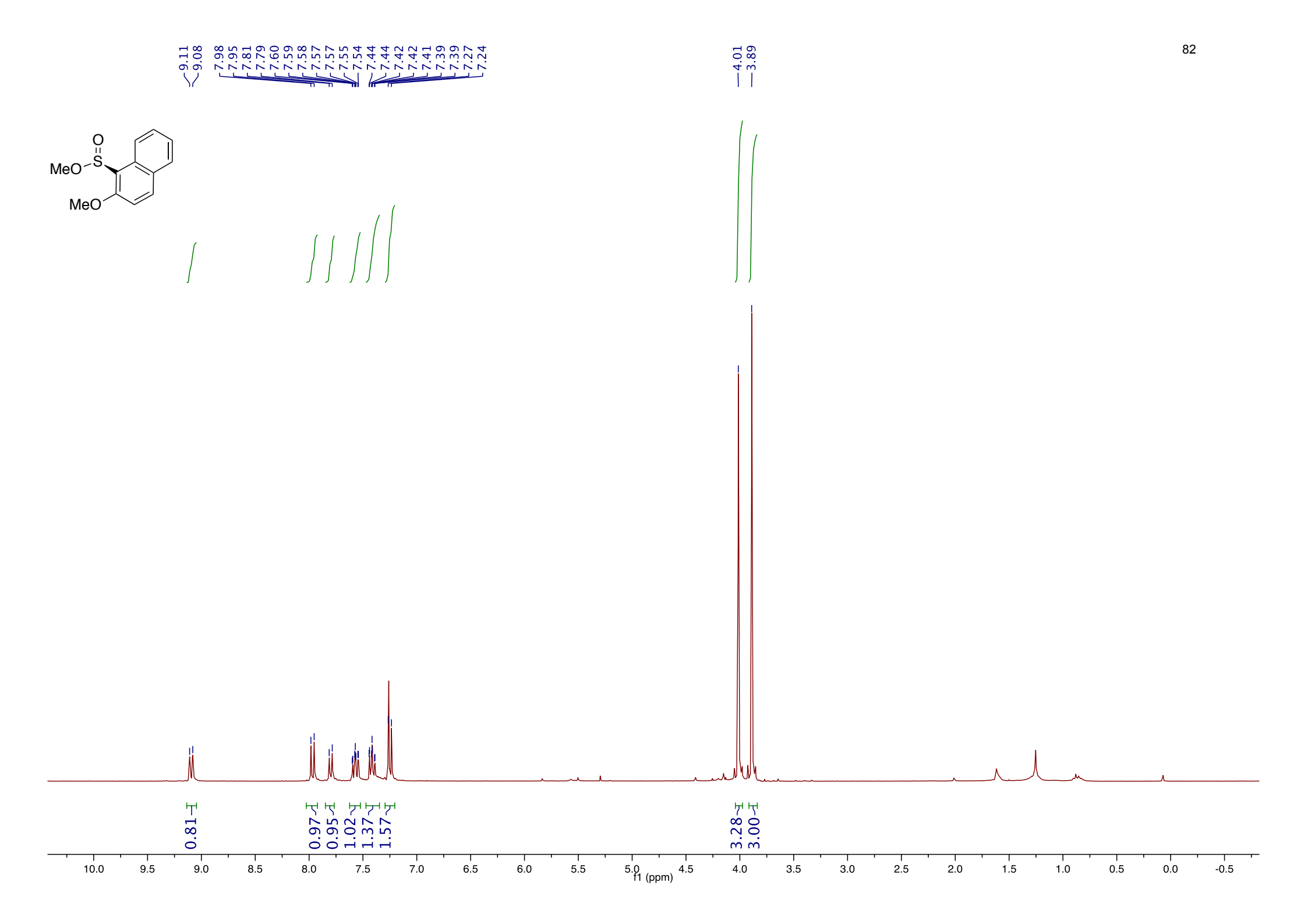
f1 (ppm)

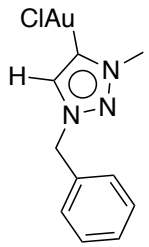


7.61
7.59
7.34
7.31
4.65
4.63
4.61
4.60
4.58
4.57
4.55
2.42
1.39
1.37
1.25
1.24

2.00
2.37
0.59
3.49
3.92
7.59

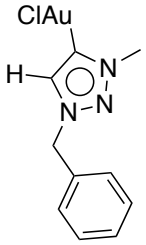
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


9.11
9.08
7.98
7.95
7.81
7.79
7.60
7.59
7.58
7.57
7.57
7.55
7.54
7.44
7.44
7.42
7.42
7.41
7.39
7.39
7.27
7.24
4.01
3.89
MeO
O
S
MeO
0.81
0.97
0.95
1.02
1.37
1.57
3.28
3.00
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
-0.5
f1 (ppm)


ClAu
H
N
N
N

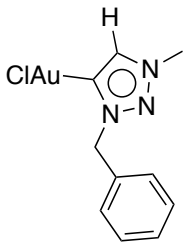
13a

7.61
7.45
7.44
7.43
7.43
7.42
7.36
7.36
7.36
7.35
7.35
7.34
5.52
4.20
0.48
2.71
1.85
2.16
3.00
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
-0.5
-1.
f1 (ppm)


ClAu
H
N
N
N

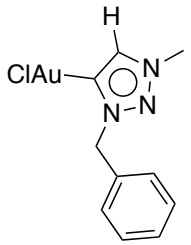
13a

158.6
133.7
131.7
130.0
129.7
128.9
77.4 cdcl3
77.2 cdcl3
76.9 cdcl3
56.4
42.2
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


H
ClAu
N
N
N

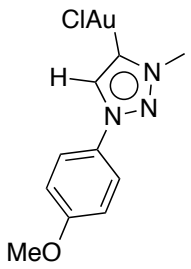
14a

7.60
7.54
7.53
7.53
7.52
7.51
7.39
7.38
7.37
7.36
7.35
7.35
5.64
4.16
0.46
1.73
2.62
2.06
3.00
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
-0.5
f1 (ppm)


H
ClAu
N
N
N

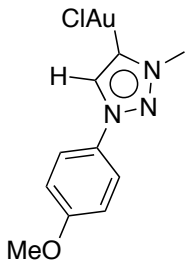
14a

158.0
134.9
133.7
129.3
129.2
129.1
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
59.2
39.0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

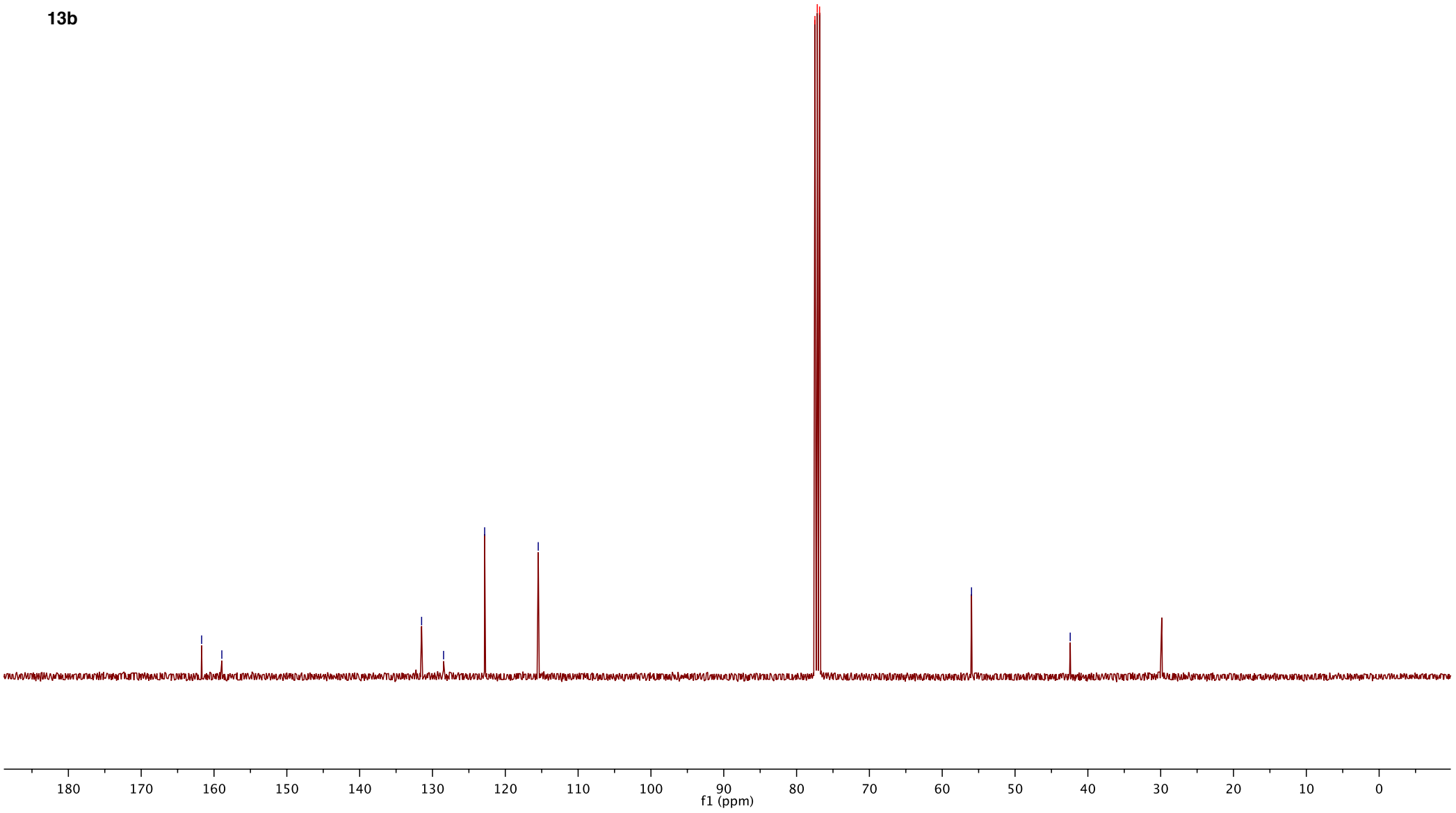

ClAu
H
N
N
N
MeO

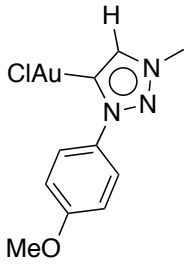
13b

7.91
7.64
7.62
7.09
7.07
4.31
3.90
0.83
1.96
2.09
3.00
3.26
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
-0.5
f1 (ppm)


ClAu
H
N
N
N
MeO

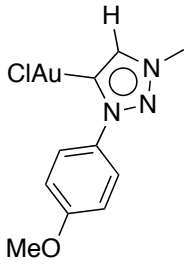
13b


161.7
158.9
131.5
128.5
122.8
115.5
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
56.0
42.4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
ClAu
N
N
N
MeO

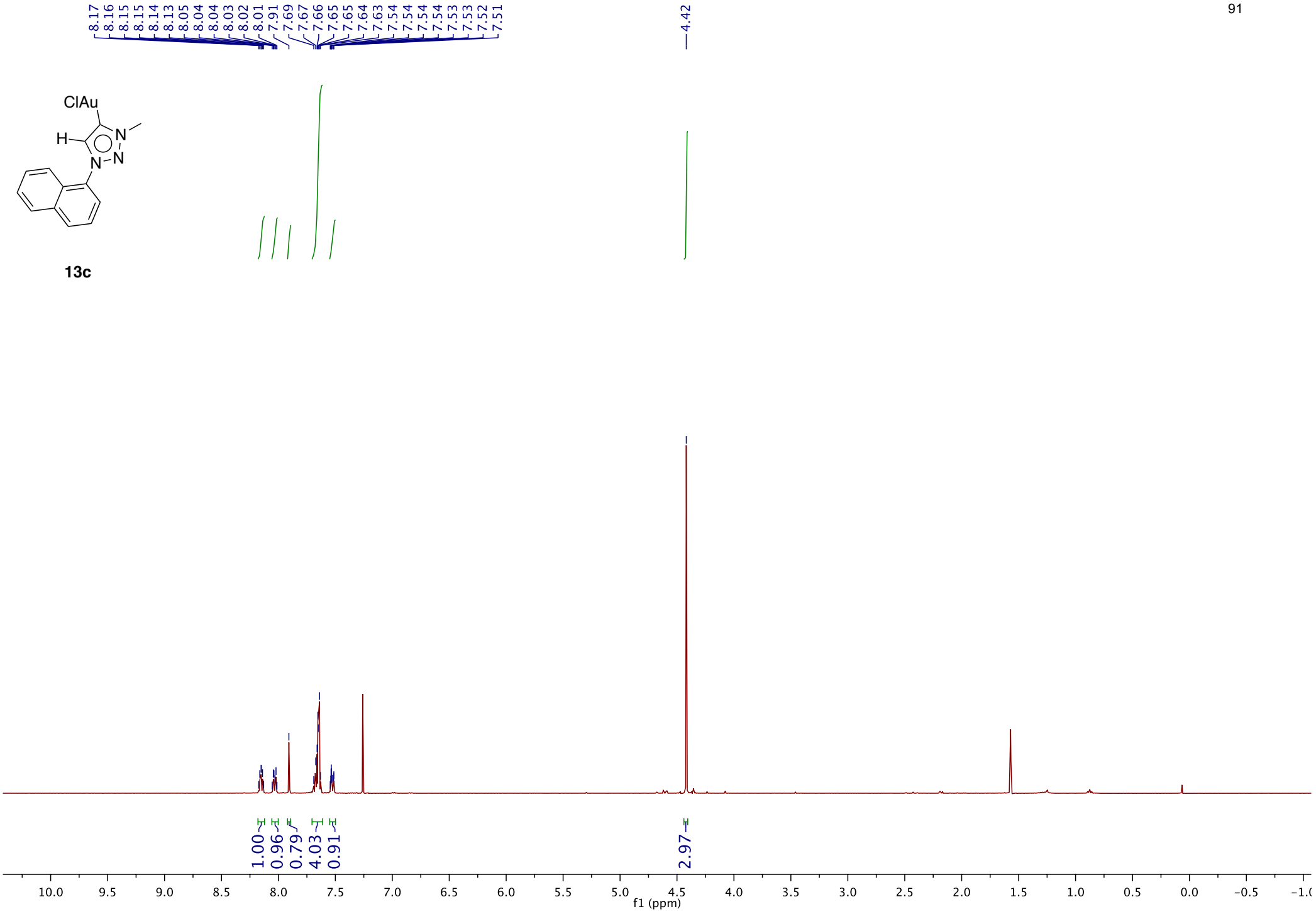
14b

7.95
7.93
7.72
7.02
7.00
4.27
3.88
1.84
0.82
1.95
3.00
3.03
f1 (ppm)

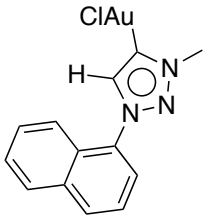

H
ClAu
N
N
N
MeO

14b

161.1
157.2
135.0
132.1
125.4
114.7
77.4 cdcl3
77.2 cdcl3
76.9 cdcl3
55.9
39.0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

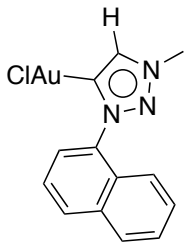

8.17
8.16
8.15
8.15
8.14
8.13
8.05
8.04
8.04
8.03
8.02
8.01
7.91
7.69
7.67
7.66
7.65
7.65
7.64
7.63
7.54
7.54
7.54
7.54
7.53
7.53
7.52
7.51
4.42
ClAu
H
N
N
N
1.00
0.96
0.79
4.03
0.91
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

13c


ClAu
H
N
N
N

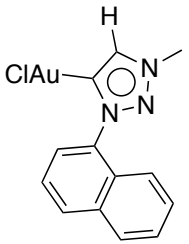
13c

158.6
136.2
134.3
132.5
131.8
129.1
128.9
128.0
127.6
125.0
124.2
121.1
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
42.7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
ClAu
N
N
N

14c

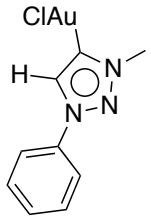
8.49
8.29
8.28
8.17
8.15
7.90
7.88
7.76
7.75
7.73
7.71
7.71
7.69
7.69
7.69
7.68
7.68
7.65
7.65
7.64
7.64
7.63
7.62
7.62
7.42
7.40
4.34
0.85
0.99
1.05
0.94
1.02
1.15
1.03
0.96
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



14c

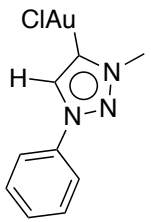
158.6
135.5
135.4
133.4
131.2
128.4
128.1
128.1
127.4
125.3
125.3
121.8
40.0 dmso
39.9 dmso
39.7 dmso
39.5 dmso
39.4 dmso
39.2 dmso
39.0
39.0 dmso

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

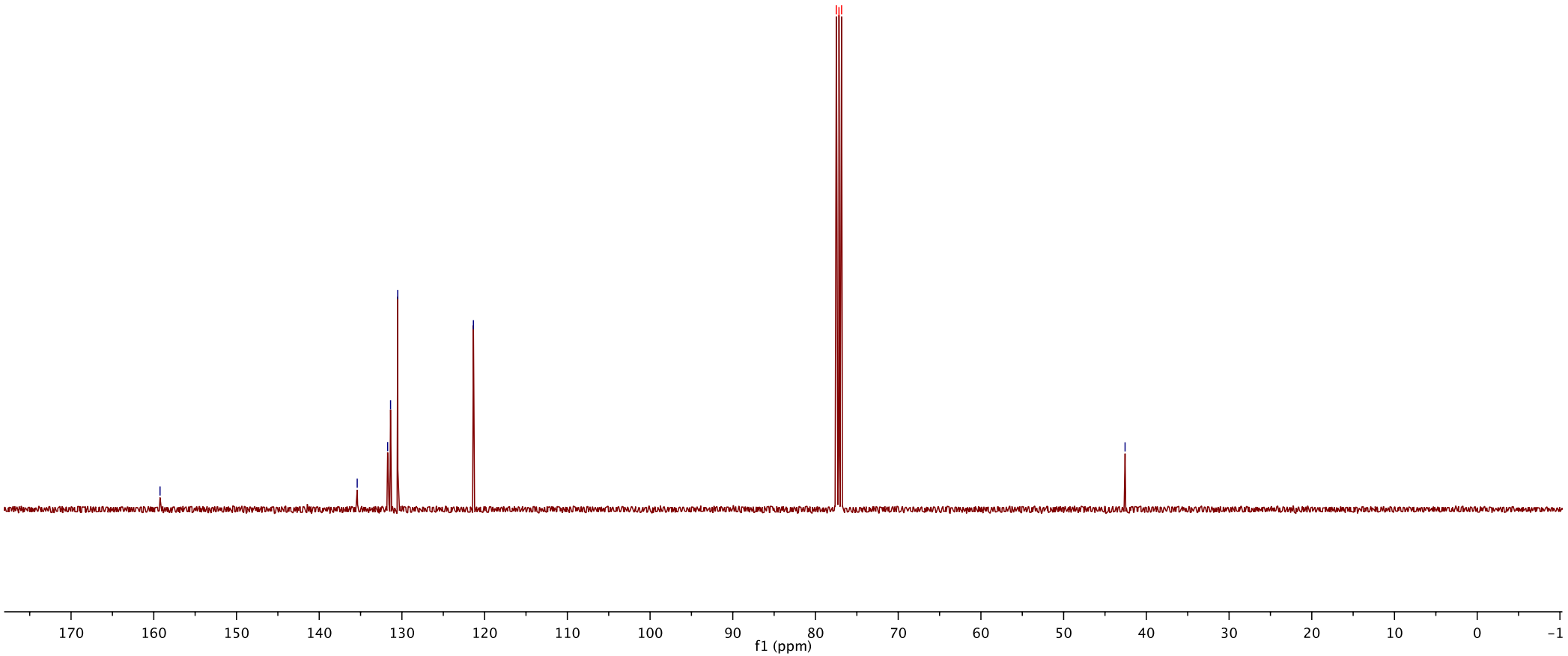

ClAu
H
N
N
N

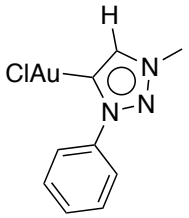
13d

8.08
7.77
7.76
7.76
7.75
7.75
7.75
7.74
7.74
7.73
7.73
7.72
7.65
7.65
7.64
7.63
7.62
7.62
7.62
7.61
7.61
7.60
7.60
7.59
4.34
0.54
1.90
2.85
3.00
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
-0.5
f1 (ppm)


ClAu
H
N
N
N

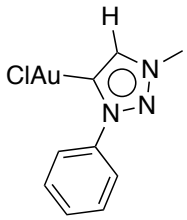
13d


159.2
135.4
131.7
131.4
130.5
121.4
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
42.6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


H
ClAu
N
N
N

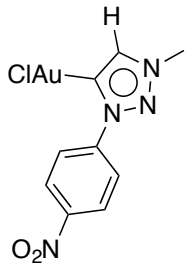
14d

8.04
8.03
8.03
8.02
8.01
7.81
7.56
7.55
7.55
7.54
7.53
7.52
7.51
4.30
1.73
0.58
2.77
3.00
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
-0.5
-1.0
f1 (ppm)


H
ClAu
N
N
N

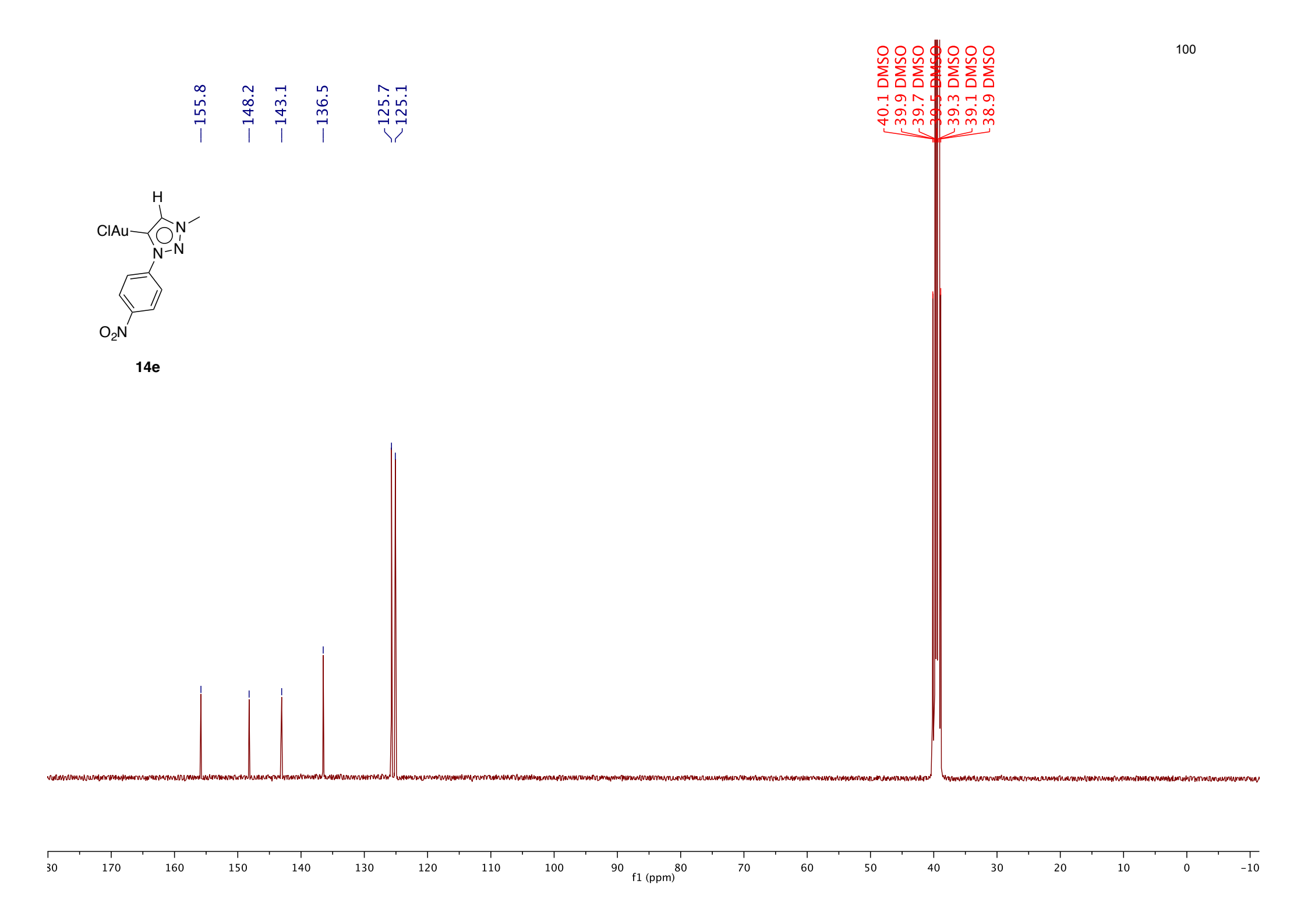
14d

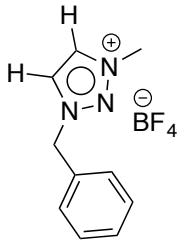
157.3
139.0
135.4
130.6
129.7
124.1
77.5 cdcl3
77.2 cdcl3
76.8 cdcl3
39.2
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
ClAu
N
N
N
O2N

14e

8.52
8.50
8.43
8.31
8.29
4.32
1.93
0.87
1.93
3.00
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
-0.5
f1 (ppm)


155.8
148.2
143.1
136.5
125.7
125.1
40.1 DMSO
39.9 DMSO
39.7 DMSO
39.5 DMSO
39.3 DMSO
39.1 DMSO
38.9 DMSO
100
H
ClAu
N
N
N
O_2N
14e
f1 (ppm)


H
H
N
N
N
BF4

18

8.45
7.45
7.42
7.36
7.34
5.68
4.26
2.02
1.95
2.85
2.03
3.00
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
-0.5
f1 (ppm)