Supporting Information for

Investigation into the Organobismuth Dismutation and Its Use for Rational Synthesis of Heteroleptic Triarylbismuthines, $Ar^1_2Ar^2Bi$

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1. General Comments on Experimental Section

All reactions were carried out under nitrogen atmosphere. All reagents and solvents were purchased from commercial suppliers. $BiCl_3$ and $ZnCl_2$ were purified by reflux with thionyl chloride, then dissolved in diethyl ether and filtered to remove impurities. *p*-Toluene-sulfonic acid monohydrate (*p*-$TsOH \cdot H_2O$) was purified by co-distillation in toluene. All other reagents were used as purchased without further purification. Solvents were purified through an alumina column solvent system and further dried with molecular sieves. Column chromatography was performed with 35-70 mesh silica gel using flash column techniques or Combiflash©.NextGen System. Varian Unity Inova 500 MHz was used for recording the ^1H and ^{13}C NMR spectra. Chemical shifts for ^1H and ^{13}C and were given in part per million (ppm), referenced internally according to the residual solvent resonances. Coupling constants were given in Hertz (Hz) and the following abbreviations were used: s, singlet; d, doublet; t, triplet; m, multiplet.

Diphenylbismuth chloride (Ph_2BiCl)[1], diphenylbismuth iodide (Ph_2BiI)[2] and dimesitylbismuth iodide **2b**[2] were prepared according to previously reported procedures.

^{13}C DEPT spectra are color coded and reported as follows: Blue: DEPT 135; Green: DEPT 90; Red: DEPT 45.

Instrumentation:

^1HNMR and ^{13}CNMR were collected on a Varian Unity Inova 500 MHz. EA samples were analyzed with a PerkinElmer 2400 Series II Analyzer at the University of Rochester by Bill Brennessel. HPLC chromatograms were collected on an Agilent 1200 series using a 25 minute 25:75 to 0:100 H_2O:Acetonitrile gradient on a Discovery® C18 25cm x 4mm, 5µm.

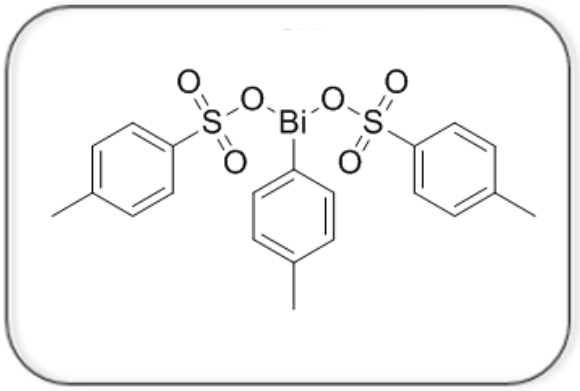
2. Experimental Details for the Synthesis of Organobismuths, 2 and 3

Diphenylbismuth tosylate (2a)

The synthetic protocol was modified from a previously reported procedure.[3] To a diethyl ether solution of triphenylbismuthane (20.0 g, 45.4 mmol) was added dropwise a solution of *p*-TsOH·H_2O (8.64 g, 45.4 mmol) in diethyl ether. The reaction mixture was allowed to stir for 5-6 hours, then filtered and the collected solid washed two times with diethyl ether to afford 20.8 g, 86% **2a**.

Phenylbismuth ditosylate (3a)

The protocol was modified from a previously reported procedure.[3] To a diethyl ether solution of triphenylbismuthane (1.0 g, 2.3 mmol in 10ml) was added dropwise a solution of *p*-TsOH·H_2O (0.91 g, 4.7 mmol). The reaction mixture was stirred at 90 °C for 3 hours, then cooled to room temperature, filtered, and the collected solid washed two times with diethyl ether (40ml) affording quantitatively phenylbismuth ditosylate (**3a**).



***p*-Tolylbismuth ditosylate (3b):** A solution of *p*-TsOH·H_2O (2.22 g, 11.7 mmol) was added slowly to a solution of tri(*p*-tolyl)bismuthane (2.77 g, 5.75 mmol) in diethyl ether. The reaction mixture stirred at 90 °C for 5 hours, then cooled to room temperature, filtered, and the collected solid washed two times with diethyl ether (25ml) affording the product (3.65g, 5.69 mmol) in 99% yield.

White Powder. **^{1}H NMR (d_6-DMSO):** δ 8.57 (d, *J* = 7.6 Hz, 2H, C_6H_4-CH_3, C*H*), 7.83 (d, *J* = 7.6 Hz, 2H, C_6H_4-CH_3, C*H*), 7.48 (d, *J* = 7.7 Hz, 4H, *Ar*SO_3Bi, C*H*), 7.11 (d, *J* = 7.7 Hz, 4H, *Ar*SO_3Bi, C*H*), 2.28 (overlapping singlets, 9H, C_6H_4-CH_3). **^{13}C NMR (d_6-DMSO):** δ 145.8, 138.2, 137.2, 136.8 (*Ar*-Bi, *C*H), 134.0 (*Ar*-Bi, *C*H), 132.7, 128.5 (*Ar*SO_3Bi, *C*H), 125.9 (*Ar*SO_3Bi, *C*H), 21.9 (C_6H_4-CH_3), 21.2 (C_6H_4-CH_3). **Anal. Calc. for $BiO_6C_{21}H_{21}S_2$:** C, 39.26; H, 3.29. Found**:** C, 38.87; H, 2.87.

3b did not pass EA in %H. EA was consistently low in %C and %H.

3. Experimental Details for the Preparation of Various Organometallic Reagents and their use in the Synthesis of Diphenyl(4-(dimethoxymethyl)phenyl)bismuthane (1a) in Table 1.

ArLi

4-bromobenzaldehyde dimethylacetal (260 mg, 1.12 mmol) was added to a Schlenk flask and dissolved in 5ml THF, then cooled to -78 ºC. A solution of *n*-butyllithium in hexanes (1.12 mmol, 0.7 ml) was added dropwise to the reaction solution and stirred at -78 ºC for 40 minutes. Then, diphenylbismuth tosylate (0.936 mmol) was added and the reaction mixture was allowed to warm to -10 ºC. The final concentration was kept to 0.075 M of the nucleophile in THF. The reaction was stirred for 1 hour and 40 minutes. Afterwards, the reaction mixture was allowed to warm to ambient temperature.

Work-up

Then, the reaction mixture was quenched with a saturated solution of $NaHCO_3$ in distilled water and diluted with EtOAc (15ml), upon which the two phases were separated. The aqueous phase was washed twice with EtOAc (10ml). The combined organic phases were washed twice with sat. $NaHCO_3$ (10ml) and twice with sat. brine solution (10ml). Finally, the organic phase was dried over $MgSO_4$, filtered through silica gel, and concentrated *in vacuo*. The crude reaction mixture was then purified by column chromatography using a 20:1 hexanes : ethyl acetate eluent.

$[Ar_2Cu]Li$

To a freshly prepared solution of 4-lithium benzaldehyde dimethyl acetal solution (2.25 mmol, 0.075 M) at -78 ºC was added CuI (1.12 mmol) and the solution was warmed to -40 ºC and stirred for 1 hour. To this organocuprate reagent was added diphenyl bismuth tosylate (0.936 mmol) and warmed to -10 ºC. The final concentration was kept to 0.075 M of the nucleophile in THF. The reaction was stirred for 1 hour and 40 minutes. Afterwards, the reaction was worked up as previously described.

ArMgBr

A modified preparation of Grignard reagent was utilized to prepare a stock solution of organomagnesium reagent. Magnesium turnings (7.9 g, 325 mmol) were added to a Schlenk bomb and to it was added 100ml THF. 4-Bromobenzaldehyde dimethylacetal (130 mmol) was dissolved in THF (50 ml) and added dropwise to the magnesium. The mixture was allowed to stir for 30 mins, then heated to 65 ºC for 4 hours.

A solution of organomagnesium reagent (1.12 mmol) was cooled to -10 ºC. To this solution was added diphenylbismuth tosylate (0.936 mmol) to give a final concentration of 0.075 M of the nucleophile in THF. The reaction was stirred for 1 hour and 40 minutes. Afterwards, the reaction was worked up as previously described.

$[Ar_2Cu]MgX$

A solution of Grignard reagent (2.25 mmol) was cooled to -40 ºC and to it was added CuI (1.12 mmol) and stirred for one hour. To this organocuprate reagent was added diphenylbismuth tosylate (0.936 mmol) to give a final concentration of 0.075 M of the nucleophile in THF. The reaction was warmed to -10 ºC and stirred for 1 hour and 40 minutes. Afterwards, the reaction was worked up the same as previously described.

[ArCuCN]MgX

A solution of organomagnesium reagent (1.12 mmol) was cooled to -40 ºC and to it was added CuCN (1.12 mmol) and stirred for one hour. To this organocuprate reagent was added diphenylbismuth tosylate (0.936 mmol) to give a final concentration of 0.075 M of the nucleophile in THF. The reaction was warmed to -10 ºC and stirred for 1 hour and 40 minutes. Afterwards, the reaction was worked up the same as previously described.

ArZnX

To a solution of Grignard reagent (1.12 mmol) was added anhydrous $ZnCl_2$ (153 mg, 1.12 mmol) dissolved in 5 ml THF. The reaction was stirred at room temperature for about 10 minutes, then cooled to -10 ºC. Next, diphenylbismuth tosylate (0.936 mmol) was added to the reaction mixture to give a final concentration of 0.075 M of the nucleophile in THF. The reaction was allowed to stir at -10 ºC for 1 hour and 40 minutes. Afterwards, the reaction was worked up the same as previously described.

4. Experimental Details for the Investigation of Dismutation

Investigation of Dismutation Initiated by 10mol% Additive (Scheme 2)

To a stirring THF (2mL) solution of diphenyl(4-methoxylphenyl)bismuthane **1b**, (100mg, 0.213 mmol), a THF (1mL) solution of 10mol% additive (0.0213 mmol) was added and stirred for one hour. After one hour, the mixture was filtered through Celite® and THF was removed *in vacuo* and the products were separated by Combiflash. The isolated yields are as follows ($Ph_2BiAnisyl$ (**1b**), Ph_3Bi (A), $Anisyl_2BiPh$ (B), $Anisyl_3Bi$ (C)):

Table S1: Recovery and Molar Ratio of Dismutation Side Products Initiated by 10 mol% Various Additives to diphenyl(4-methoxylphenyl)bismuthane 1b

Entry	Additive	1b (mg)	A (mg)	B (mg)	C (mg)	Recovery 1b%	1b:A:B:C (molar ratios)
1	PhMgBr	99	-	-	-	99	-
2	PhZnBr	98	-	-	-	98	-
3	$MgCl_2$	95	-	-	-	95	-
4	$ZnCl_2$	89	-	-	-	89	-
5	Ph_2BiCl	30	23	16	3	30	11.3: 9.2: 5.7: 1
6	Ph_2BiI	43	35	14	2.7	43	17.5: 15.1: 5.6: 1
7	Ph_2BiOTs	33	25	7	2	33	18.6: 15.1: 3.7: 1

Investigation of Dismutation Initiated by the Slow Addition of Electrophile into Nucleophile

To a stirring THF (2mL) solution of nucleophile, *p*-MeOC6H4ZnX (0.408 mmol), a THF (0.25 mL) solution of diphenylbismuth iodide (50mg; 0.102 mmol), was added four times in half hour intervals to give a final volume of 3ml and an equimolar ratio of electrophile to nucleophile. After the final addition and stirring for 30 minutes, the reaction was then quenched with sat. $NaHCO_3$ aqueous solution and extracted with ethyl acetate 2x 10ml. The combined organic phase was washed with sat. $NaHCO_3$ (2x 10ml), dried

over $MgSO_4$, and the solvent was removed *in vacuo*. Finally, the crude product was purified through a silica gel plug and the products were separated by Combiflash. The isolated yields were as follows: $Ph_2BiAnisyl$ (**1b**): 105mg (0.223 mmol, 55%); Ph_3Bi (A): 6mg (0.0136 mmol, 3%); $Anisyl_2BiPh$ (B): 8mg (0.0160 mmol, 4%).

Investigation of Dismutation Initiated by the Slow Addition of Nucleophile into Electrophile

To a stirring THF (2mL) solution of diphenylbismuth iodide (200mg; 0.408 mmol), a THF (0.25 mL) solution of nucleophile, *p*-MeOC6H4ZnX (0.102 mmol), was added four times in half hour intervals to give a final volume of 3ml and an equimolar ratio of electrophile to nucleophile. After the final addition and stirring for 30 minutes, the reaction was then quenched with sat. $NaHCO_3$ aqueous solution and extracted with ethyl acetate 2x 10ml. The combined organic phase was washed with sat. $NaHCO_3$ (2x 10ml), dried over $MgSO_4$, and the solvent was removed *in vacuo*. Finally, the crude product was purified through a silica gel plug and the products were separated by Combiflash. The isolated yields were as follows: $Ph_2BiAnisyl$ (**1b**): 60mg (0.128 mmol, 31%); Ph_3Bi (A): 42mg (0.0954 mmol, 23%); $Anisyl_2BiPh$ (B): 23mg (0.0460 mmol, 11%).

5. Experimental Details for the Synthesis of Heteroleptic Triarylbismuthanes (1)

General Procedure Utilizing Organozincs and Diarylbismuth Tosylate or Iodide (2) (Procedures A and B)

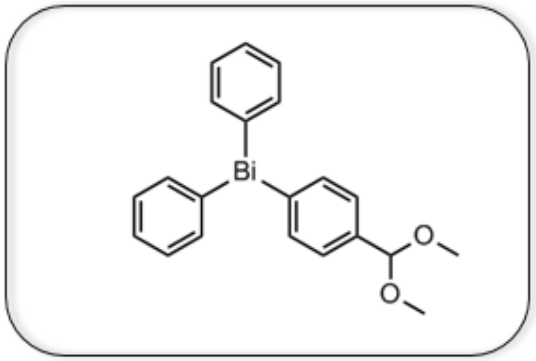
For compounds **1a**, **1c**, **1e**, **1f**, **1h**, organozinc reagent was prepared by the addition of anhydrous $ZnCl_2$ (153 mg, 1.12 mmol) dissolved in 5 ml THF to a solution of Grignard reagent (1.12 mmol). For compounds **1b**, **1g**, an organozinc reagent was prepared by Knochel's TurboGrignard procedure.[4] Compound **1d** was prepared utilizing Rieke procedures.[5]

The volume of solution of organozinc reagent (1.12 mmol) was adjusted to a final volume of 15ml by addition of dry THF. The reagent was stirred at room temperature for about 10 minutes, then cooled to -10 ^oC. After that, diarylbismuth tosylate (Procedure A) or iodide (Procedure B) **2** (0.936 mmol) was added at once to a stirred organozinc solution. The reaction mixture was stirred for 1 hour and 40 minutes and allowed to warm to room temperature. Then, the reaction was quenched by addition of a saturated solution of $NaHCO_3$ in distilled water and extracted with EtOAc (15ml). The aqueous phase was washed twice with EtOAc (10ml). The combined organic phases were washed twice with saturated $NaHCO_3$ (10ml) and twice with saturated brine solution (10ml). Finally, the organic phase was dried over $MgSO_4$, filtered through silica gel and concentrated *in vacuo* affording crude product. Further purification or recrystallization methods are described below for each compound.

General Procedure Utilizing Organozincs and Arylbismuth Ditosylates (3) (Procedure C)

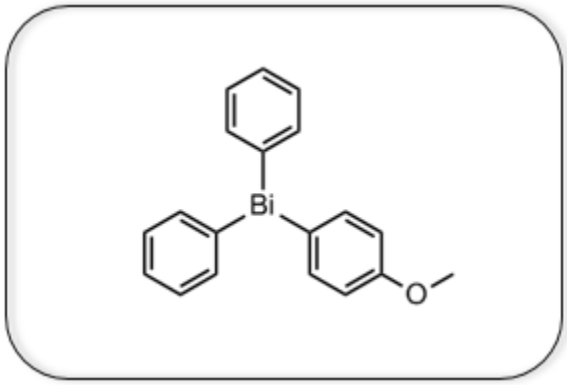
Regarding compounds **1i** and **1k**, an organozinc reagent was prepared by Knochel protocol.[4] For compounds **1j** and **1l**, organozinc reagent was prepared by the addition of anhydrous $ZnCl_2$ (293 mg, 2.15 mmol) dissolved in 5 ml THF to a solution of Grignard reagent (2.06 mmol).

The volume of the organozinc reagent (2.06 mmol) was adjusted by addition of THF to give a final volume of 15 ml, then subsequently cooled to -10 ºC and stirred. The monoarylbismuth ditosylate (0.936 mmol) was added at once to the stirred organozinc solution at -10 ºC and the reaction mixture was stirred for 1 hour and 40 minutes and then allowed to warm to room temperature. The work up is identical to **Procedure A**. Further purification or recrystallization methods are described below for each compound.



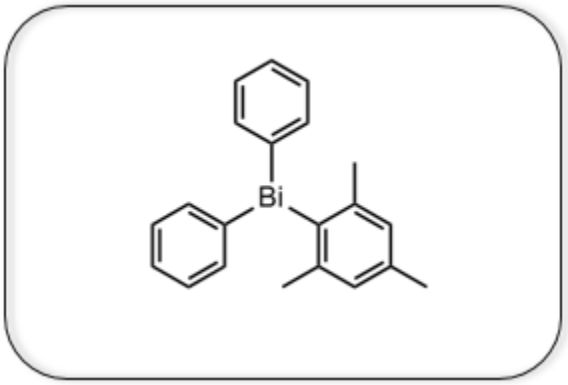
Diphenyl(4-dimethoxymethylphenyl)bismuthane (1a): Yield: 94 %. This compound was obtained according to **procedure A** from (4-benzaldehyde dimethyl acetal)magnesium(II) bromide (1.123 mmol) and diphenyl bismuth tosylate (0.5 g, 0.936 mmol). Purified by chromatography and eluted with a gradient mixture of solvents (hexane/ethyl acetate 100/0 to 20/80).

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.78-7.75 (m, 6H, C_6H_5), 7.48 (d, J = 7.9 Hz, 2H, C_6H_4-$CH(OCH_3)_2$), 7.40 (m, 4H, Ar), 7.35-7.32 (m, 2H, C_6H_5), 5.37 (s, 1H, C_6H_4-$CH(OCH_3)_2$, 3.35 (s, 6H, C_6H_4-$CH(OCH_3)_2$). **^{13}C NMR ($CDCl_3$):** δ 155.4, 155.0, 137.5, 137.5 (Ar, *C*H), 137.4 (C_6H_5, *C*H), 130.5 (Ar, *C*H), 128.7 (C_6H_4-$CH(OCH_3)_2$, *C*H), 127.7 (C_6H_5, *C*H), 103.3 (C_6H_4-*C*$H(OCH_3)_2$, 52.8 (C_6H_4-$CH(OCH_3)_2$). **Anal. Calc. for $BiO_2C_{21}H_{21}$:** C, 49.04; H, 4.12. Found**:** C, 48.76; H, 3.96.



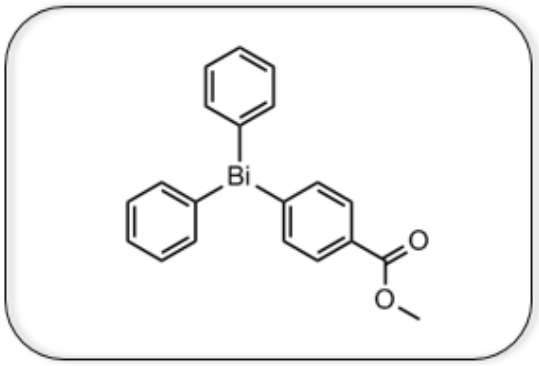
Diphenyl(4-methoxylphenyl)bismuthane (1b): Yield: 99%. This compound was obtained according to **procedure A** from (4-methoxyphenyl)magnesium(II) bromide (1.123 mmol) and diphenylbismuth tosylate (0.5 g, 0.936 mmol). Purified by chromatography and eluted with a gradient mixture of solvents (hexane/ethyl acetate 100/0 to 95/5.

Yellowish oil. **^{1}H NMR ($CDCl_3$):** δ 7.77 (d, J = 7.0 Hz, 4H, C_6H_5), 7.68 (d, J = 8.5 Hz, 2H, C_6H_4-OCH_3), 7.42 (d, J = 7.0 Hz, 4H, C_6H_5), 7.36-7.33 (m, 2H, C_6H_5), 6.96 (d, J = 8.5 Hz, 2H, C_6H_4-OCH_3), 3.81 (s, 3H, C_6H_4-OCH_3). **^{13}C NMR ($CDCl_3$):** δ 159.3, 154.8, 145.7, 138.8 (C_6H_4-OCH_3, *C*H), 137.4 (Ph, *C*H), 130.4 (Ph, *C*H), 127.6 (Ph, *C*H), 116.4 (C_6H_4-OCH_3, *C*H), 55.0 (C_6H_4-OCH_3). **Anal. Calc. for $BiOC_{19}H_{17}$:** C, 48.52; H, 3.64. Found**:** C, 48.65; H, 3.68.



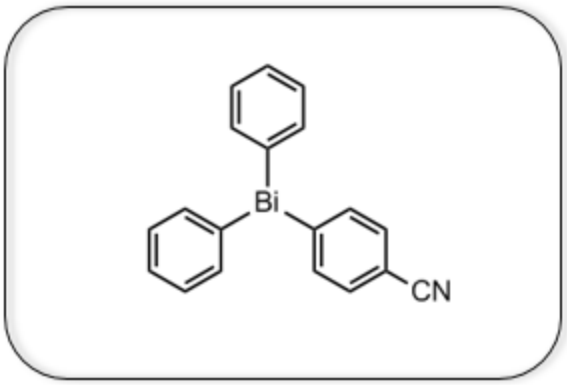
Diphenyl(2-mesityl)bismuthane (1c): Yield: 97%. This compound was obtained according to **procedure A** from (mesityl)magnesium(II) bromide (1.123 mmol) and diphenyl bismuth tosylate (0.5 g, 0.936 mmol). Recrystallized from cold hexanes.

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.86 (d, J = 6.5 Hz, 4H, C_6H_5), 7.40-7.37 (m, 4H, C_6H_5), 7.32-7.29 (m, 2H, C_6H_5), 7.04 (s, 2H, C_6H_2), 2.31 (s, 3H, C_6H_2-pCH_3), 2.26 (s, 6H, C_6H_2-oCH_3). **^{13}C NMR ($CDCl_3$):** δ 157.4, 152.1, 146.2, 138.2, 137.5 (Ph, *C*H), 130.2 (Ph, *C*H), 129.3 (C_6H_2, *C*H), 127.4 (Ph, *C*H), 28.5 (C_6H_2-o*C*H_3), 21.1 (C_6H_2-p*C*H_3). **Anal. Calc. for $BiC_{21}H_{21}$:** C, 52.29; H, 4.39. Found**:** C, 52.19; H, 4.29.



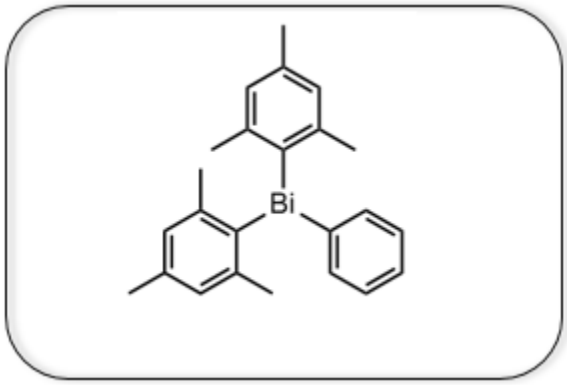
Diphenyl(4-methoxycarbonylphenyl)bismuthane (1d): Yield: 83%. This compound was obtained according to **procedure A** from (4-methoxycarbonylphenyl)zinc(II) halide (1.123 mmol) and diphenylbismuth tosylate (0.5 g, 0.936 mmol). Recrystallized from cold hexanes.

White solid. **^{1}H NMR ($CDCl_3$):** δ 8.02 (d, J = 8.1 Hz, 2H, C_6H_4-COOMe), 7.84 (d, J = 8.1 Hz, 2H, C_6H_4-COOMe), 7.74 (d, J = 6.6, Hz, 4H, C_6H_5), 7.43-7.40 (m, 4H, C_6H_5), 7.36-7.32 (m, 2H, C_6H_5), 3.91 (s, 3H, C_6H_4-COOCH_3). **^{13}C NMR ($CDCl_3$):** δ 167.3, 161.6, 155.3, 137.6 (C_6H_4-COOMe, *C*H), 137.5 (Ph, *C*H), 131.0 (C_6H_4-COOMe, *C*H), 130.6 (Ph, *C*H), 129.4, 127.9 (Ph, *C*H), 52.1 (C_6H_4-COO*C*H_3). **Anal. Calc. for $BiO_2C_{20}H_{17}$:** C, 48.20; H, 3.44. Found**:** C, 48.60; H, 3.26.



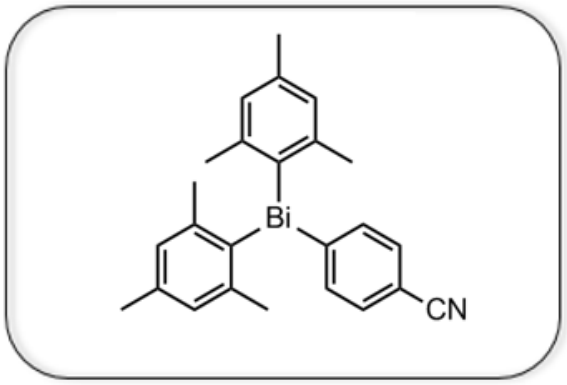
Diphenyl(4-cyanophenyl)bismuthane (1e): Yield: 84%. This compound was obtained according to **procedure A** from (4-cyanophenyl)zinc(II) halide (1.123 mmol) and diphenylbismuth tosylate (0.5 g, 0.936 mmol). Purified by column chromatography and eluted with a gradient mixture of solvents (hexane/ethyl acetate 100/0 to 25/75.

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.87 (d, *J* = 8.1 Hz, 2H, C_6H_4CN), 7.73 (d, *J* = 6.6 Hz, 4H, C_6H_5), 7.60 (d, *J* = 8.1 Hz, 2H, C_6H_4CN), 7.44 (t, *J* = 7.3 Hz, 4H, C_6H_5), 7.37 (m, 2H, C_6H_5). **^{13}C NMR ($CDCl_3$):** δ 161.5, 155.7, 138.1 (C_6H_4CN, *C*H), 137.4 (Ph, *C*H), 133.2 (C_6H_4CN, *C*H), 130.8 (Ph, *C*H), 128.1 (Ph, *C*H), 119.1, 111.3. **Anal. Calc. for $BiNC_{19}H_{14}$:** C, 49.04; H, 3.03; N, 3.01. Found**:** C, 49.14; H, 2.96; N, 2.93.



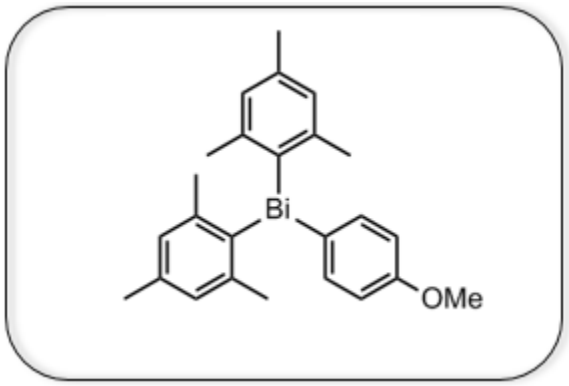
Dimesitylphenylbismuthane (1f): Yield: 94%. This compound was obtained according to **procedure B** from phenylmagnesium(II) bromide (1.123 mmol) and dimesitylbismuth iodide (0.537 g, 0.936 mmol mmol). Recrystallized from hexanes.

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.96 (d, *J* = 6.4 Hz, 2H, C_6H_5), 7.35-7.32 (m, 2H, C_6H_5), 7.28 (d, *J* = 7.2 Hz, 1H, C_6H_5), 7.00 (s, 4H, C_6H_2), 2.29 (overlapping singlets, 18H, C_6H_2-CH_3). **^{13}C NMR ($CDCl_3$):** δ 155.9, 150.6, 145.5, 138.7 (Ph, *C*H), 137.4, 129.8 (Ph, *C*H), 129.2 (C_6H_2, *C*H), 127.1 (Ph, *C*H), 27.9 (C_6H_2-CH_3), 21.0 (C_6H_2-CH_3). **Anal. Calc. for $BiC_{24}H_{27}$:** C, 54.96; H, 5.19. Found**:** C, 54.94; H, 4.80.



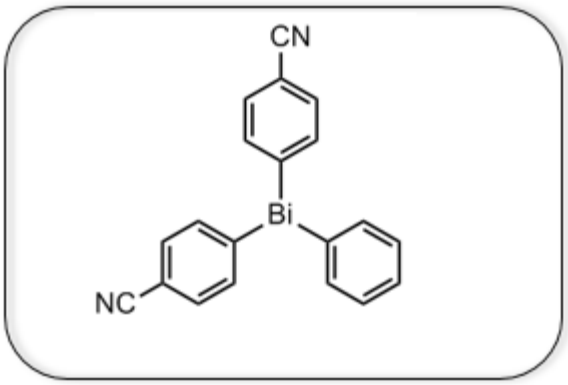
Dimesityl(4-cyanophenyl)bismuthane (1g): Yield: 92 %. This compound was obtained according to **procedure B** from (4-cyanophenyl)zinc(II) halide (1.123 mmol) and dimesitylbismuth iodide (0.537 g, 0.936 mmol). Recrystallized from hot ethanol.

White solid. **^{1}H NMR ($CDCl_3$):** δ 8.03 (d, *J* = 8.0 Hz, 2H, C_6H_4CN), 7.51 (d, *J* = 8.0 Hz, 2H, C_6H_4CN), 7.01 (s, 4H, C_6H_2), 2.27 (s, 6H, C_6H_2-*p*CH_3), 2.22 (s, 12H, C_6H_2-*o*CH_3). **^{13}C NMR ($CDCl_3$):** δ 156.9, 156.6, 145.3, 139.3 (C_6H_4CN, *C*H), 138.0, 132.5 (C_6H_4CN, *C*H), 129.6 (C_6H_2, *C*H), 119.2, 110.7, 27.8 (C_6H_2-*o*CH_3), 21.0 (C_6H_2-*p*CH_3). **Anal. Calc. for $BiC_{25}H_{26}N$:** C, 54.65; H, 4.77; N, 2.35. Found**:** C, 54.83; H, 4.88; N, 2.40.



Dimesityl(4-methoxyphenylbismuthane (1h): Yield: 94%. This compound was obtained according to **procedure B** from (4-methoxyphenyl) magnesium(II) bromide (1.123 mmol) and dimesitylbismuth iodide (0.537 g, 0.936 mmol). Recrystallized from cold hexanes.

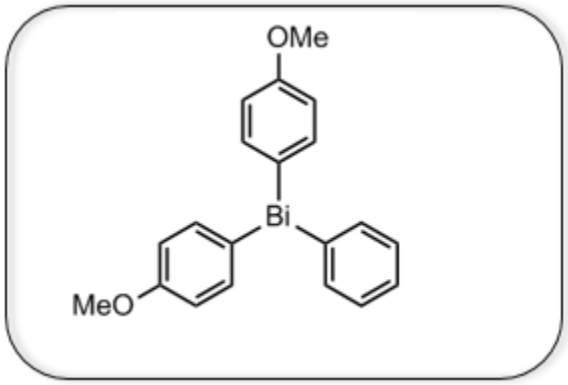
White solid. **^{1}H NMR ($CDCl_3$):** δ 7.82 (d, *J* = 8.5 Hz, 2H, C_6H_4-OCH_3), 6.98 (s, 4H, C_6H_2), 6.87 (d, *J* = 8.5 Hz, 2H, C_6H_4-OCH_3), 3.79 (s, 3H, C_6H_4-O*C*H_3), 2.27 (overlapping singlets, 18H, C_6H_2-*C*H_3). **^{13}C NMR ($CDCl_3$):** δ 158.9, 155.5, 145.5, 140.6, 139.9 (C_6H_4-OCH_3, *C*H), 137.4, 129.1 (C_6H_2, *C*H), 115.8 (C_6H_4-OCH_3, *C*H), 54.9 (C_6H_4-O*C*H_3), 27.8 (C_6H_2-*C*H_3), 21.0 (C_6H_2-*C*H_3). **Anal. Calc. for $BiOC_{25}H_{29}$**: C, 54.15; H, 5.27. Found**:** C, 54.10; H, 5.15.



Di(4-cyanophenyl)phenylbismuthane (1i): Yield: 87%. This compound was obtained according to **procedure C** from (4-cyanophenyl)zinc(II) halide (2.06 mmol) and phenylbismuth ditosylate (0.587 g, 0.936 mmol). Recrystallized from toluene/hexanes.

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.84 (d, *J* = 8.0 Hz, 4H, C_6H_4CN), 7.69 (d, *J* = 6.5 Hz, 2H, C_6H_5), 7.64 (d, *J* = 8.0 Hz, 4H, C_6H_4CN), 7.49-7.46 (m, 2H, C_6H_5), 7.43 – 7.37, (m, 1H, C_6H_5). **^{13}C NMR ($CDCl_3$):** δ 161.8, 156.3, 138.0 (C_6H_4CN, *C*H), 137.3 (Ph, *C*H), 133.5 (C_6H_4CN, *C*H), 131.2 (Ph, *C*H), 128.6 (Ph, *C*H), 118.8, 111.9. **Anal. Calc. for $BiN_2C_{20}H_{13}$**: C, 48.99; H, 2.67; N, 5.71. Found**:** C, 49.15; H, 2.62; N, 5.87.

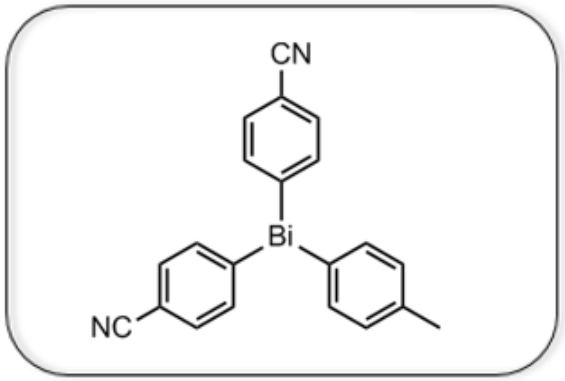
The synthesis of this compound was attempted through **procedure A** utilizing phenyl magnesium bromide and bis(4-cyanophenyl)bismuth tosylate. The yield for this reaction was only 45%, as the corresponding tosylate was not obtained in analytical purity.



Di(4-methoxyphenyl)phenylbismuthane (1j): Yield: 91%. This compound was obtained according to **procedure C** from (4-methoxyphenyl)magnesium(II) bromide (2.06 mmol) and phenylbismuth ditosylate (0.587 g, 0.936 mmol). Purified by column chromatography and eluted with a gradient mixture of solvents (hexane/ethyl acetate 100/0 to 25/75.

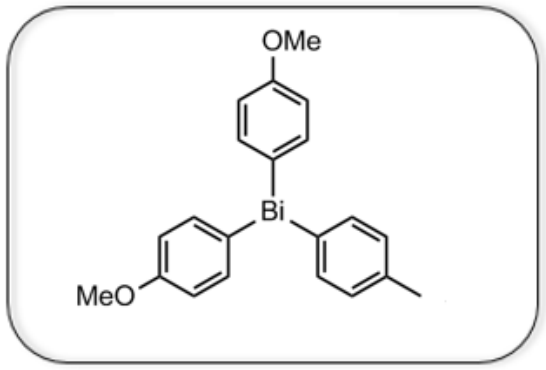
White solid. **^{1}H NMR ($CDCl_3$):** δ 7.74 (d, *J* = 7.5, 2H, C_6H_5), 7.64 (d, *J* = 8.6, 4H, C_6H_4-OCH_3), 7.40-7.37 (m, *J* = 7.5, 2H, C_6H_5), 7.34-7.31, (m, 1H, C_6H_5), 6.94, (d, *J* = 8.6, 4H, C_6H_4-OCH_3), 3.80 (s, 6H, C_6H_4-O*C*H_3). **^{13}C NMR ($CDCl_3$):** 159.3, 154.6, 145.3, 138.8 (C_6H_4-OCH_3, *C*H), 137.4 (Ph, *C*H), 130.3 (Ph, *C*H), 127.6 (Ph, *C*H), 116.3 (C_6H_4-OCH_3, *C*H), 55.0 (C_6H_4-O*C*H_3). **Anal. Calc. for $BiO_2C_{20}H_{19}$**: C, 48.01; H, 3.83. Found**:** C, 48.24; H, 3.66.

The synthesis of this compound was attempted through **procedure A** utilizing phenyl magnesium bromide and bis(4-methoxyphenyl)bismuth tosylate. The yield for this reaction was 87%, however the corresponding tosylate was not obtained in analytical purity.



Di(4-cyanophenyl)(*p*-tolyl)bismuthane (1k): Yield: 87%. This compound was obtained according to **procedure C** from (4-cyanophenyl)zinc(II) iodide (2.06 mmol) and (*p*-tolyl)bismuth ditosylate (0.547 g, 0.936 mmol). Purified by column chromatography and eluted with a gradient mixture of solvents (hexane/ethyl acetate 100/0 to 25/75.

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.84 (d, *J* = 8.2 Hz, 4H, C_6H_4CN), 7.63 (d, *J* = 8.2 Hz, 4H, C_6H_4CN), 7.57 (d, *J* = 7.8 Hz, 2H, C_6H_4-*p*CH_3), 7.29 (d, *J* = 7.8 Hz, 2H, C_6H_4-*p*CH_3), 2.35 (s, 3H, C_6H_4-CH_3). **^{13}C NMR ($CDCl_3$):** δ 161.6, 152.8, 138.6, 138.0 (C_6H_4CN, *C*H), 137.3 (C_6H_4-*p*CH_3, *C*H), 133.5 (C_6H_4CN, *C*H), 132.0 (C_6H_4-*p*CH_3, *C*H), 118.8, 111.7, 21.5 (C_6H_4-*p*CH_3). **Anal. Calc. for $BiN_2C_{21}H_{15}$**: C, 50.01; H, 3.00; N, 5.55. Found**:** C, 50.01; H, 2.87; N, 5.46.

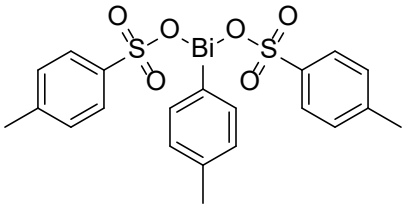


Di(4-methoxyphenyl)(*p*-tolyl)bismuthane (1l): Yield: 52 %. This compound was obtained according to **procedure C** from (4-methoxyphenyl)magnesium(II) bromide (2.06 mmol) and (*p*-tolyl) bismuth ditosylate (0.547 g, 0.936 mmol). Purified by column chromatography and eluted with a gradient mixture of solvents (hexane/ethyl acetate 100/0 to 20/80.

White solid. **^{1}H NMR ($CDCl_3$):** δ 7.65-7.61 (m, 6H, Ar), 7.20 (d, *J* = 7.5 Hz, 2H, C_6H_4-*p*CH_3), 6.93 (d, *J* = 8.4 Hz, 4H, C_6H_4-OCH_3), 3.80 (s, 6H, C_6H_4-OCH_3), 2.34 (s, 3H, C_6H_4-CH_3). **^{13}C NMR ($CDCl_3$):** δ 159.2, 150.9, 145.1, 138.7 (C_6H_4-OCH_3, *C*H), 137.4 (C_6H_4-*p*CH_3, *C*H), 137.3, 131.2 (C_6H_4-*p*CH_3, *C*H), 116.3 (C_6H_4-OCH_3, *C*H), 55.0 (C_6H_4-OCH_3), 21.5 (C_6H_4-CH_3). **Anal. Calc. for $BiO_2C_{21}H_{21}$:** C, 49.04; H, 4.12. Found**:** C, 49.06; H, 3.90

6. EA Report and NMR Spectra for 3b

NMR Spectra and EA Report of Compound 3b



Chemical Formula: $BiO_6C_{21}H_{21}S_2$

Molecular Weight: 642.49

Elemental Analysis: C: 39.26; Bi: 32.53; H: 3.29; O: 14.94; S: 9.98

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	8/2/2019 5:06:03PM
User ID	Administrator
Comments	TLG 2-67 [Hyvl]

DATE & TIME	8/2/2019 11:53:35 AM	P_ID	EA LAB
SAMPLE ID	19483	USER ID	Administrator
WEIGHT (mg)	2.376	MODE	CHN

CARBON	38.872%
HYDROGEN	2.867%
NITROGEN	0.040%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S1. EA Report of **3b**

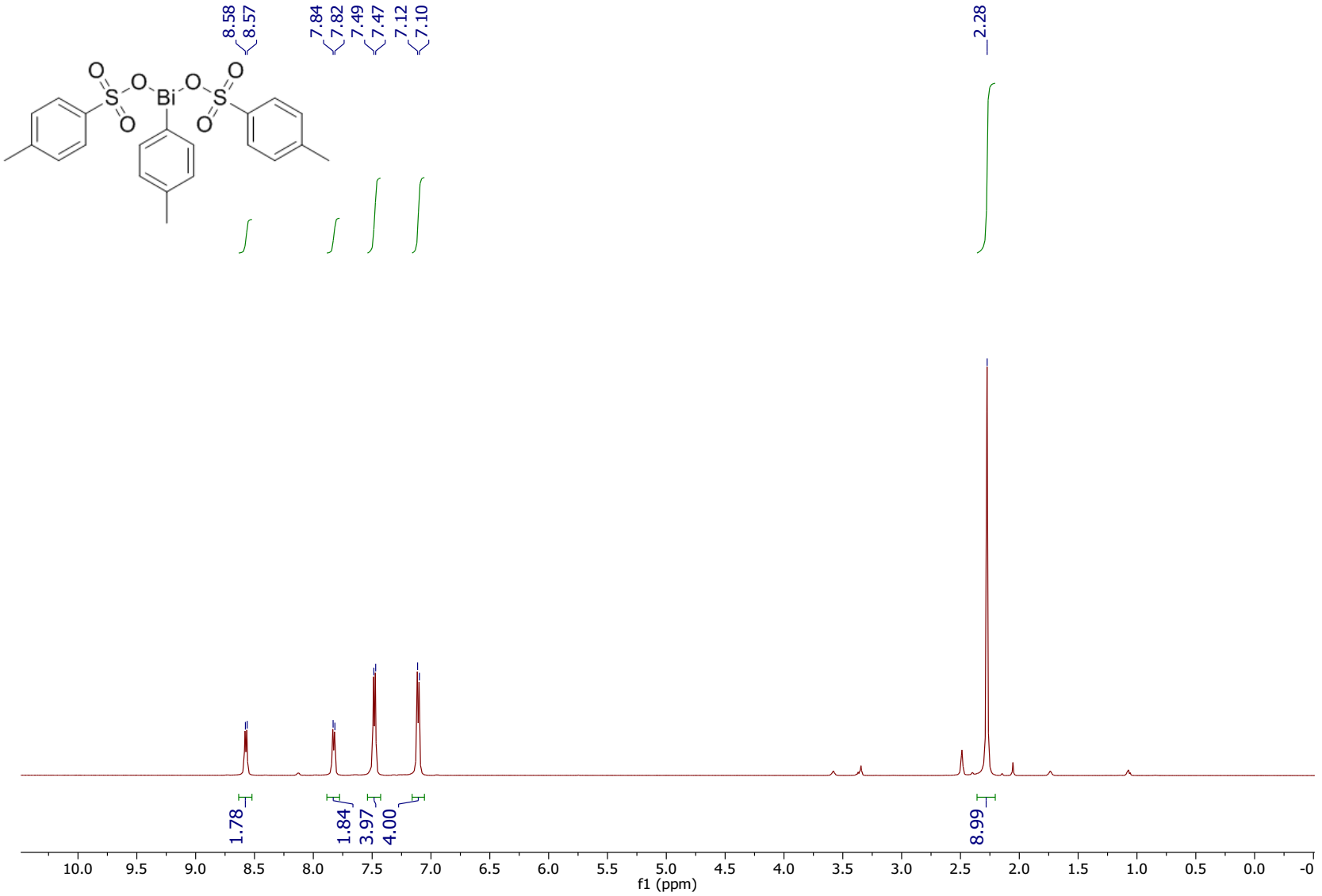


Figure S2. [1]HNMR of **3b** in d_6-DMSO

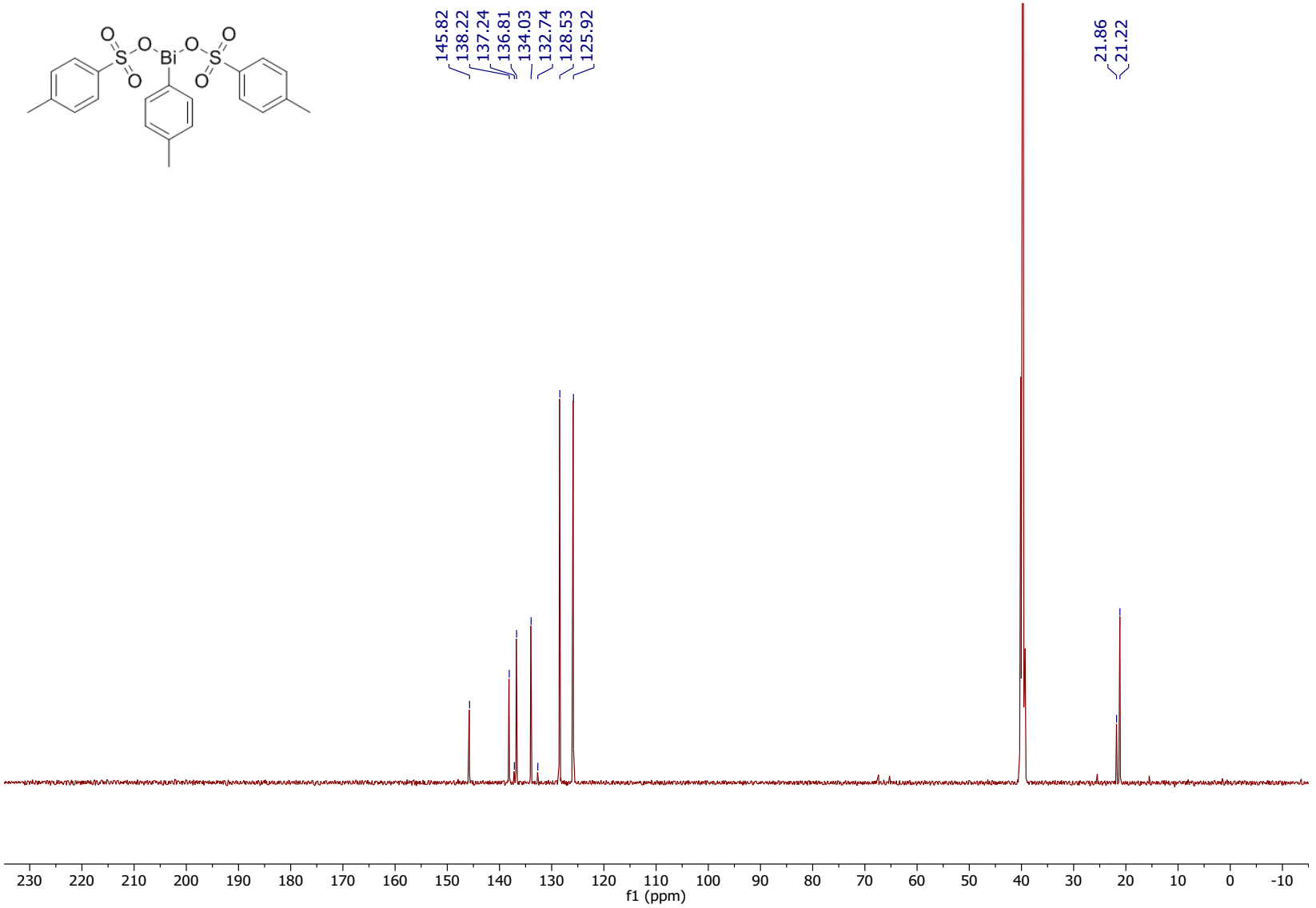


Figure S3. ^{13}C {H} NMR of **3b** in d_6-DMSO

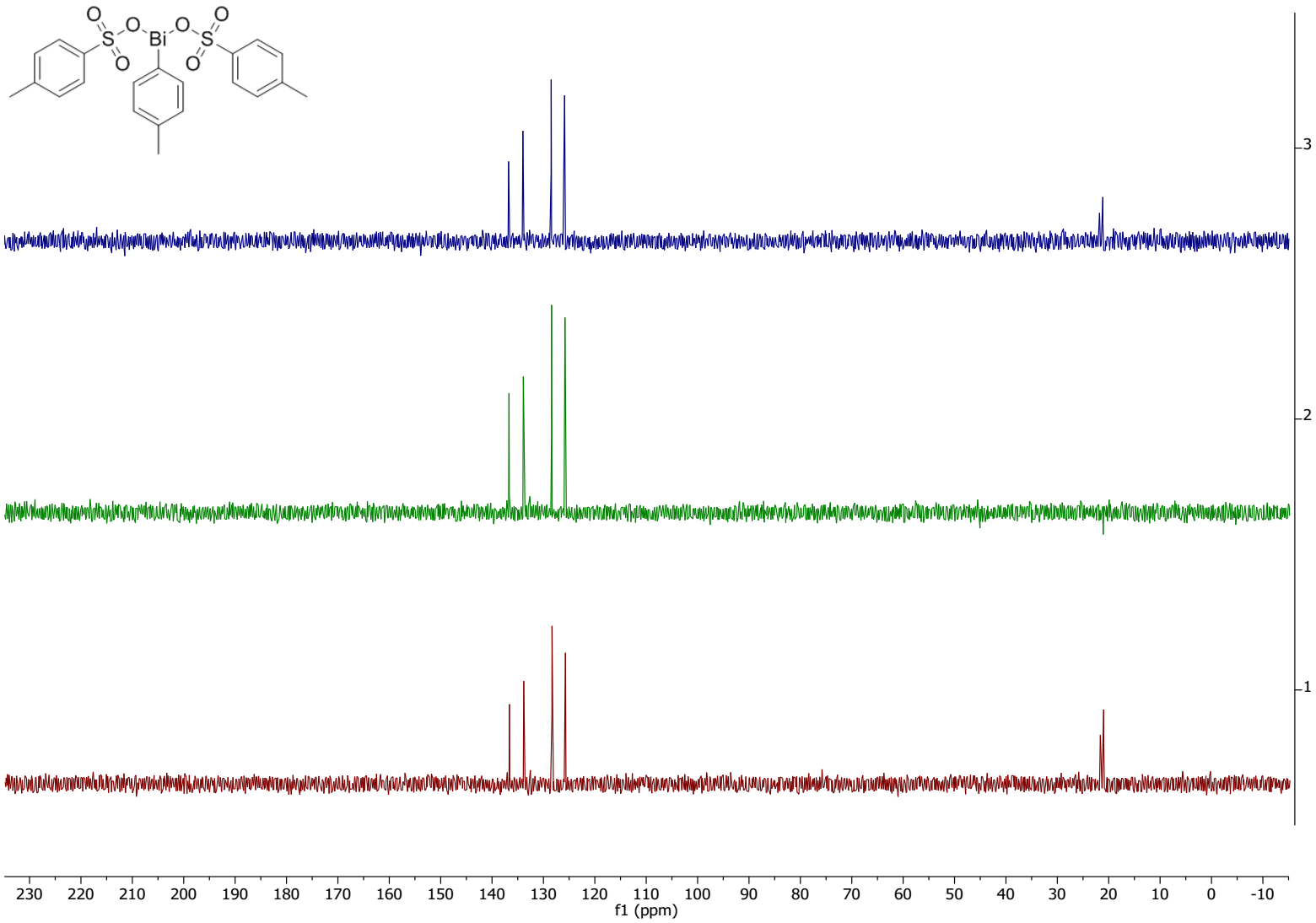


Figure S4. ^{13}C NMR DEPT of **3b** in d_6-DMSO

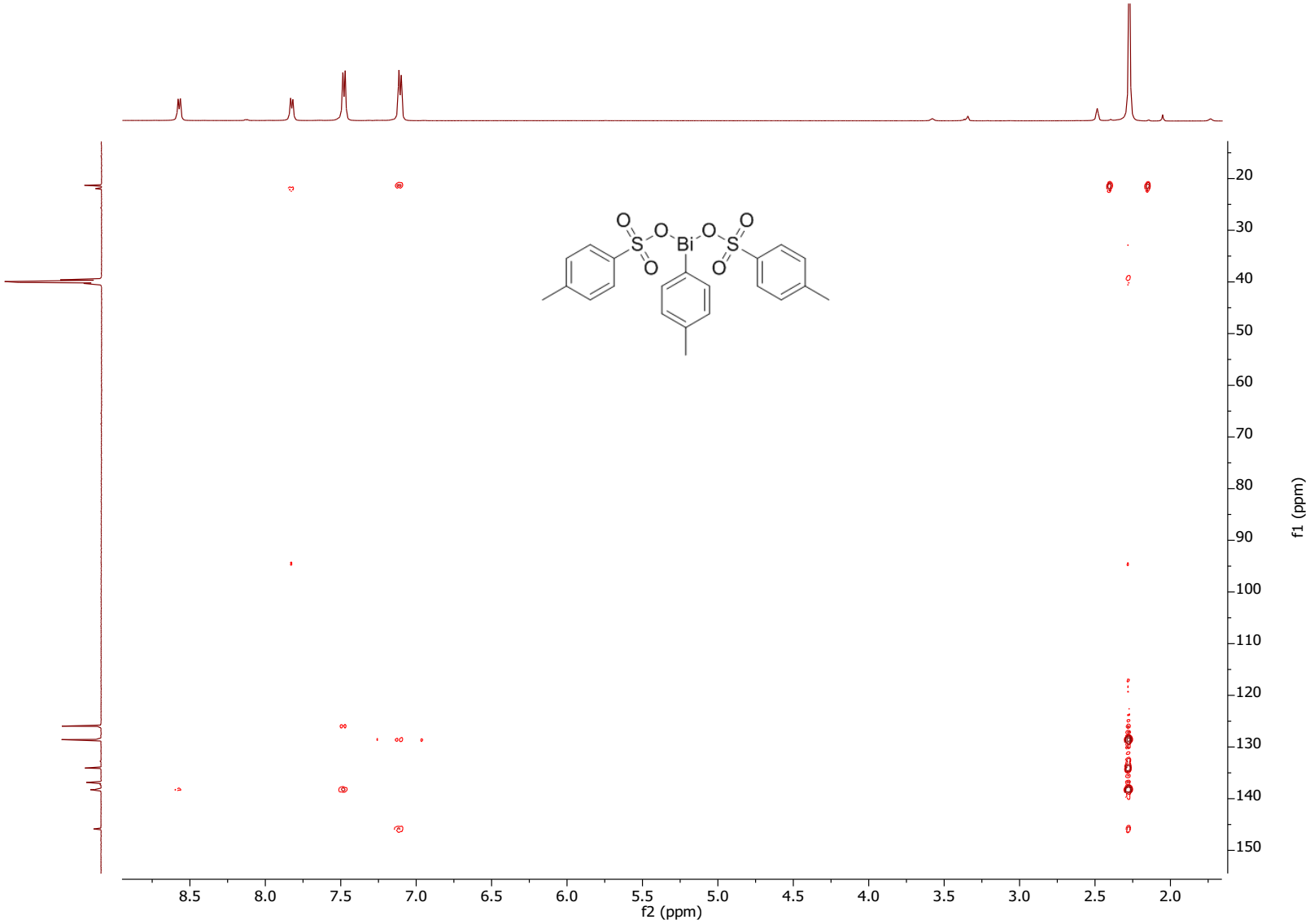
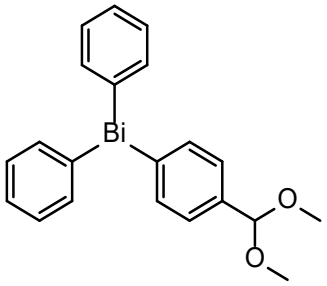


Figure S5. 2D HSQC of **3b** in d_6-DMSO

7. EA Report and NMR Spectra for Compounds 1

NMR Spectra and EA Report of Compound 1a



Chemical Formula: $BiO_2C_{21}H_{21}$
Molecular Weight: 514.38
Elemental Analysis: C: 49.04; Bi: 40.63; H: 4.12; O: 6.22

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/10/2019 2:28:53PM
User ID	Administrator
Comments	TLG_1_65 [Hyvl]

DATE & TIME	5/10/2019 12:20:59 PM	P_ID	EA LAB
SAMPLE ID	19284	USER ID	Administrator
WEIGHT (mg)	2.283	MODE	CHN

CARBON	48.763%
HYDROGEN	3.960%
NITROGEN	-.096%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S6. EA Report of **1a**

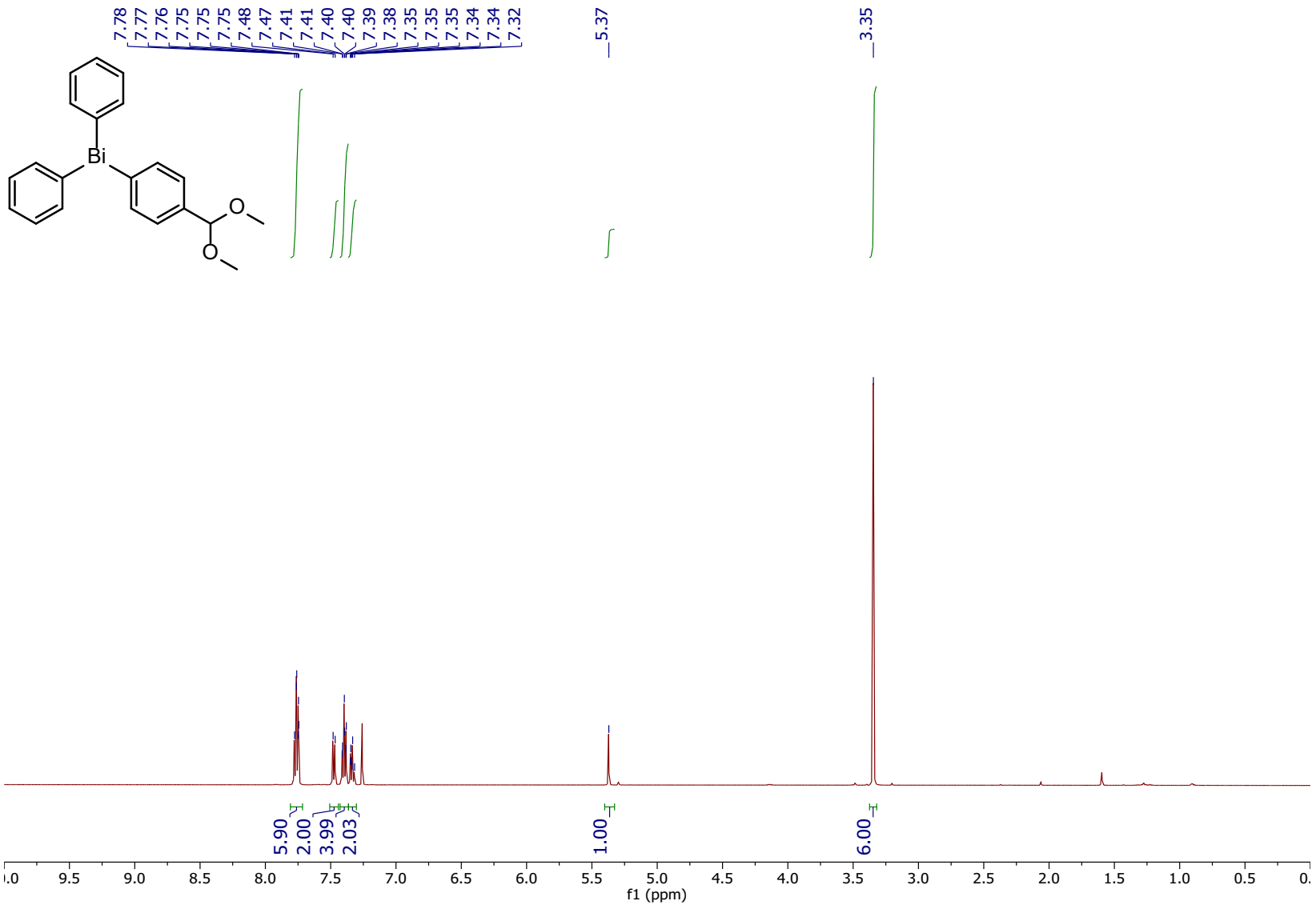


Figure S7. ^{1}HNMR of **1a** in $CDCl_3$

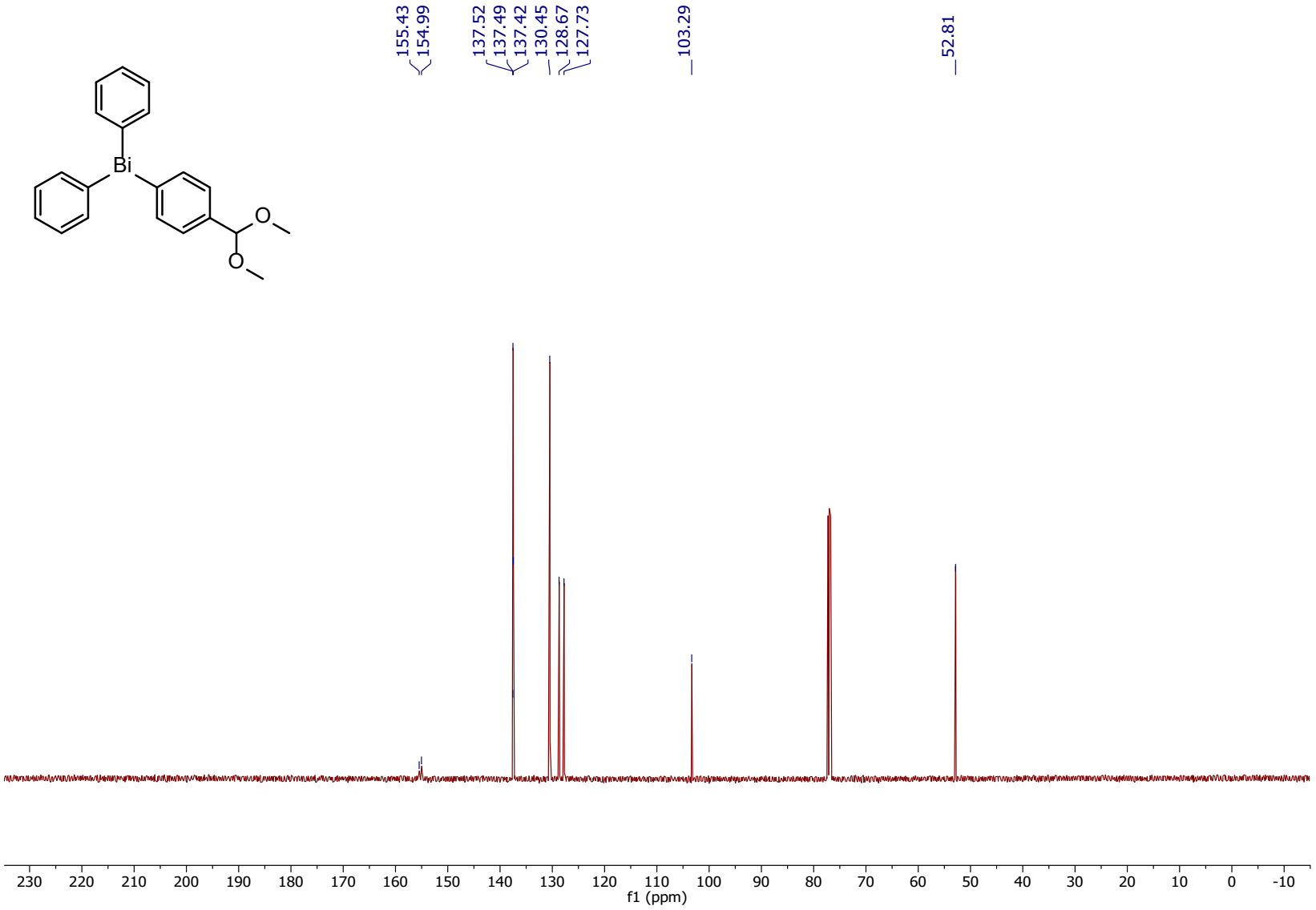


Figure S8. ^{13}C {^{1}H} NMR of **1a** in $CDCl_3$

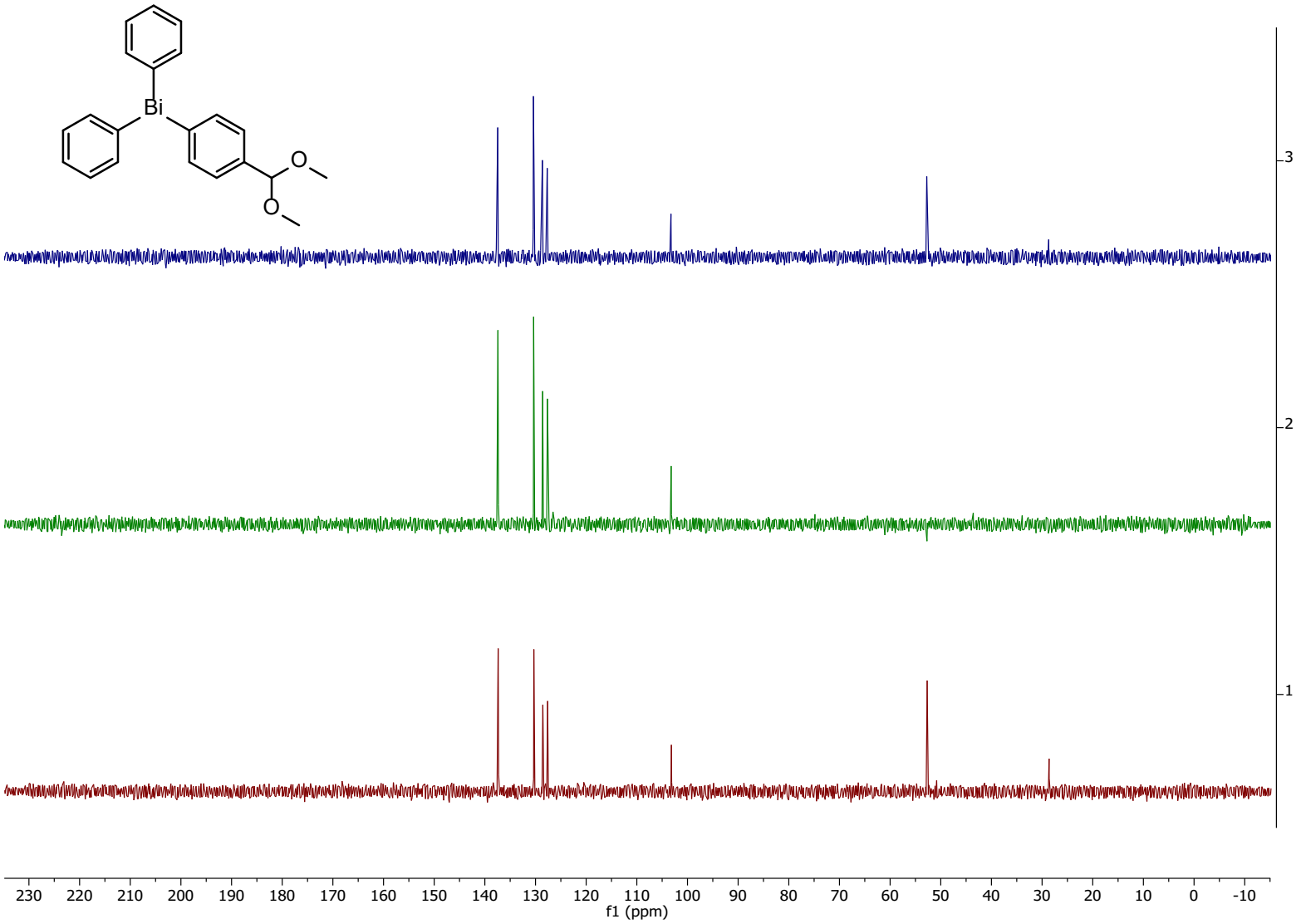


Figure S9. ^{13}C DEPT of **1a** in $CDCl_3$

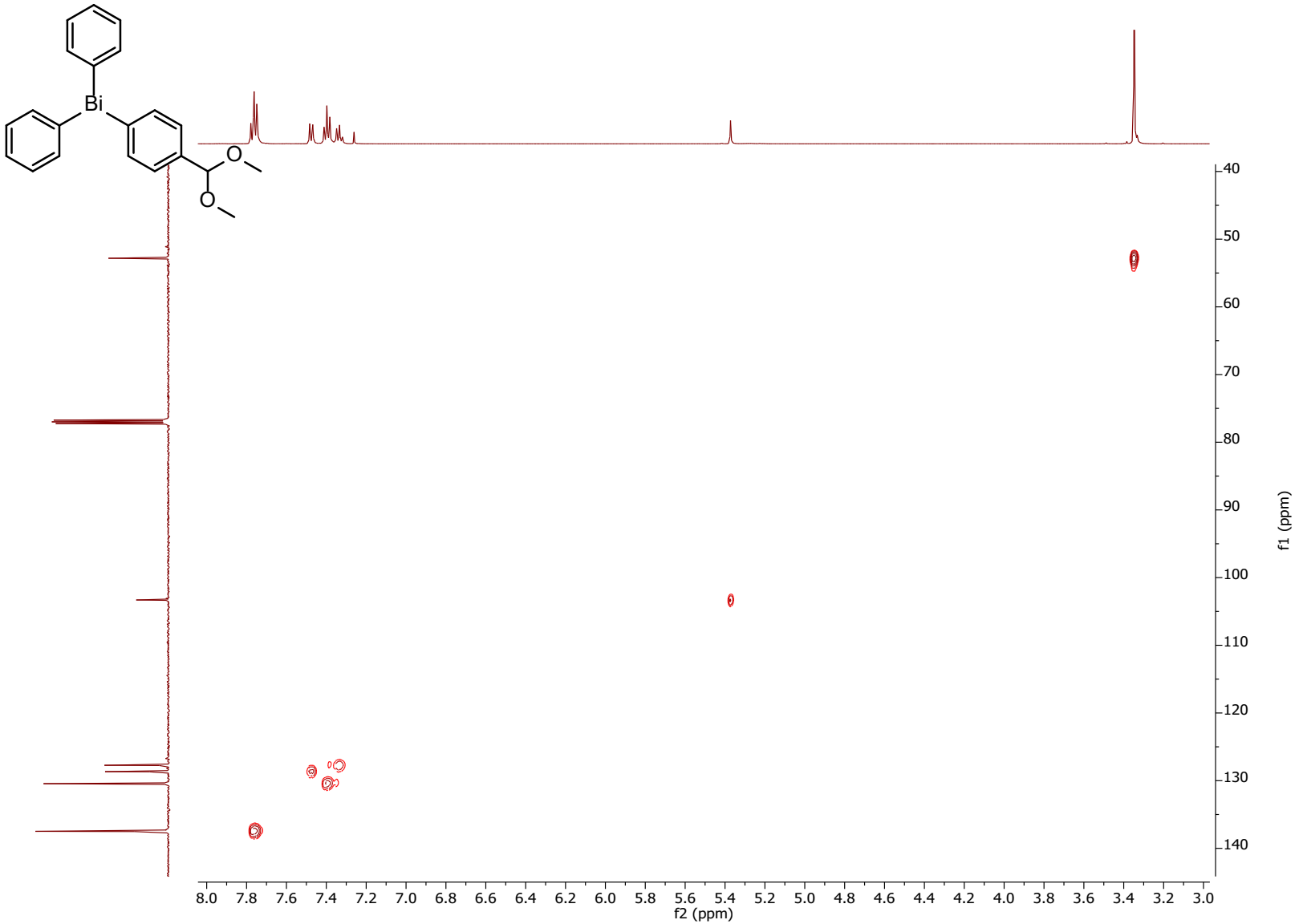
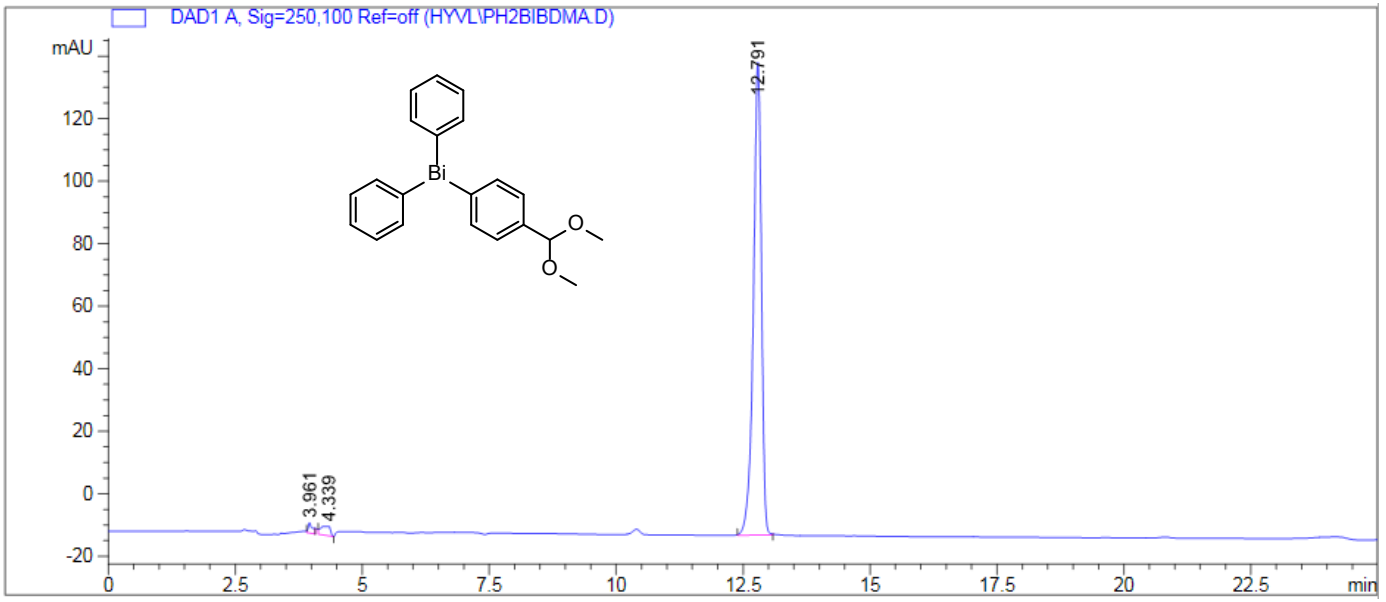


Figure S10. 2D HSQC of **1a** in $CDCl_3$

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Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
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   2   4.339 BV    0.1627   38.95380    3.05713   2.2664
   3  12.791 BB    0.1660 1660.45557  151.28766  96.6086
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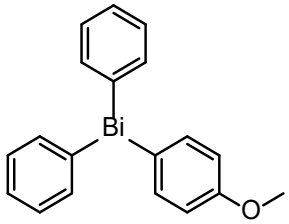
Figure S11. HPLC Chromatogram of **1a**

NMR Spectra and EA Report of Compound 1b



Chemical Formula: $BiOC_{19}H_{17}$
Molecular Weight: 490.36
Elemental Analysis: C: 48.52; Bi: 44.43; H: 3.64; O: 3.40

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/10/2019 2:34:38PM
User ID	Administrator
Comments	TLG_1_146 [Hyvl]

DATE & TIME	5/10/2019 1:54:48 PM	P_ID	EA LAB
SAMPLE ID	19295	USER ID	Administrator
WEIGHT (mg)	2.538	MODE	CHN

CARBON	48.645%
HYDROGEN	3.680%
NITROGEN	-.012%

Special Handling

The sample was combusted in a tin capsule that was crimp-sealed with a die apparatus.

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Figure S12. EA report for **1b**

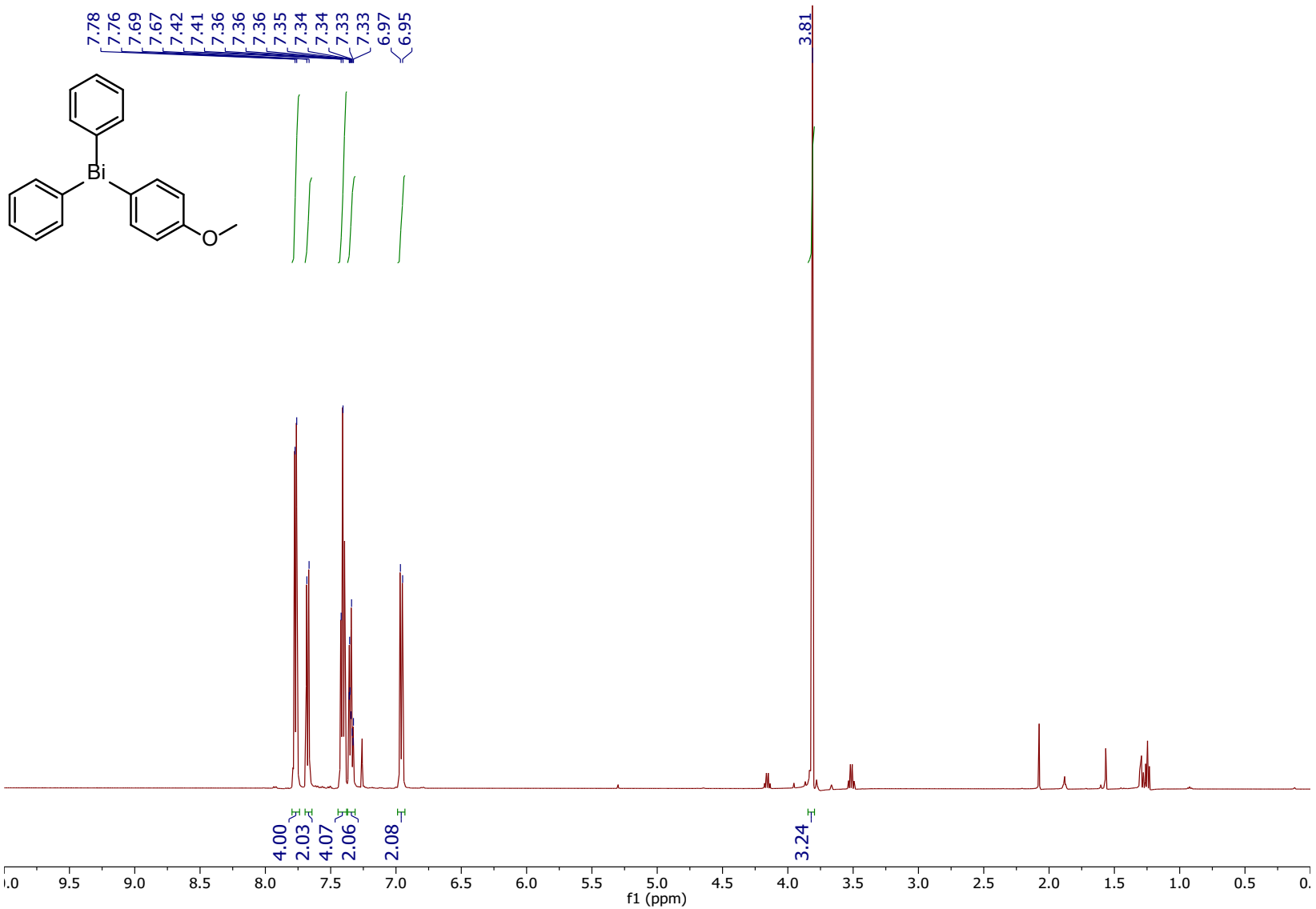


Figure S13. ^{1}H NMR of **1b** in $CDCl_3$

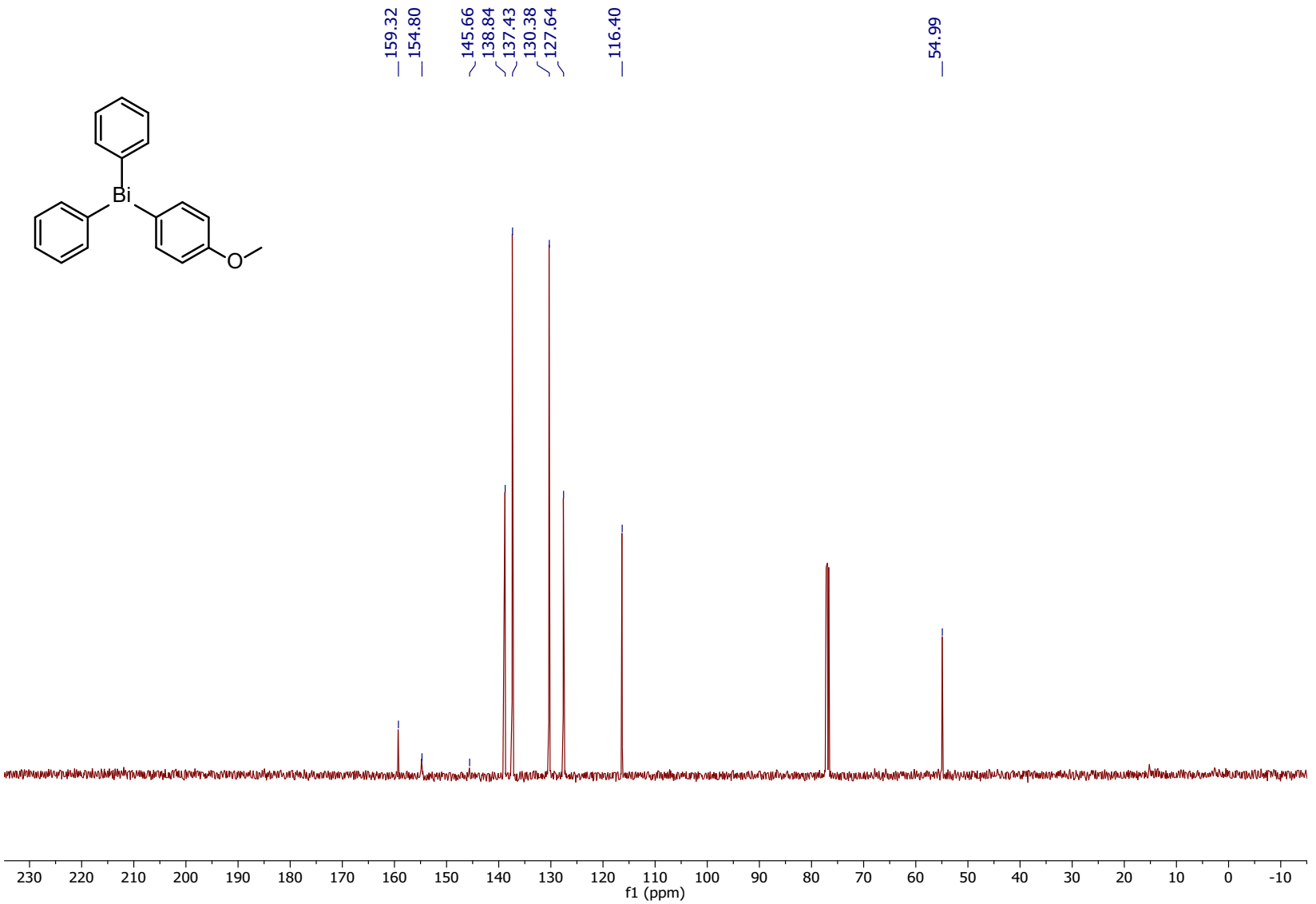


Figure S14. ^{13}C $\{^{1}H\}$ NMR of **1b** in $CDCl_3$

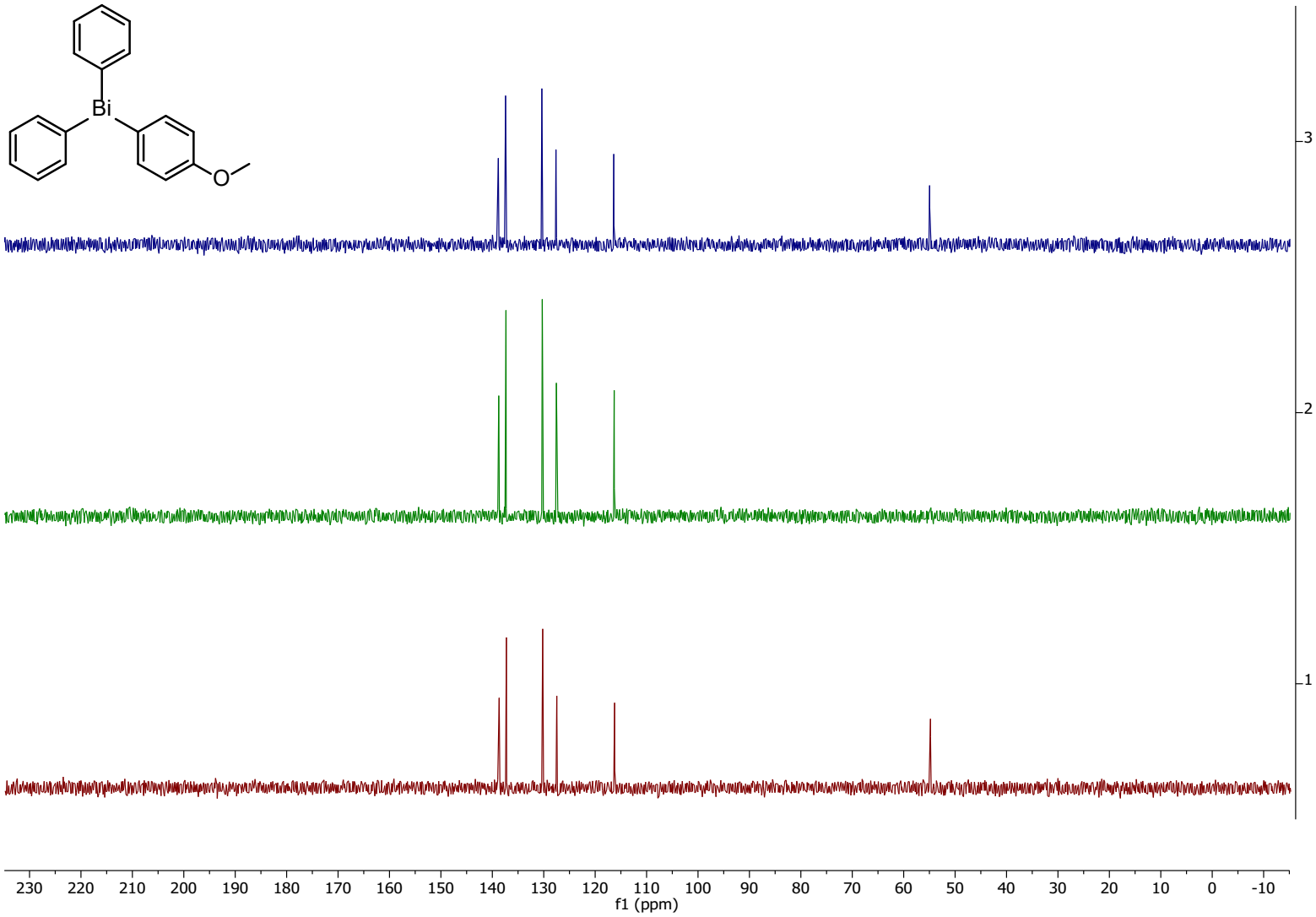


Figure S15. ^{13}C DEPT of **1b** in $CDCl_3$

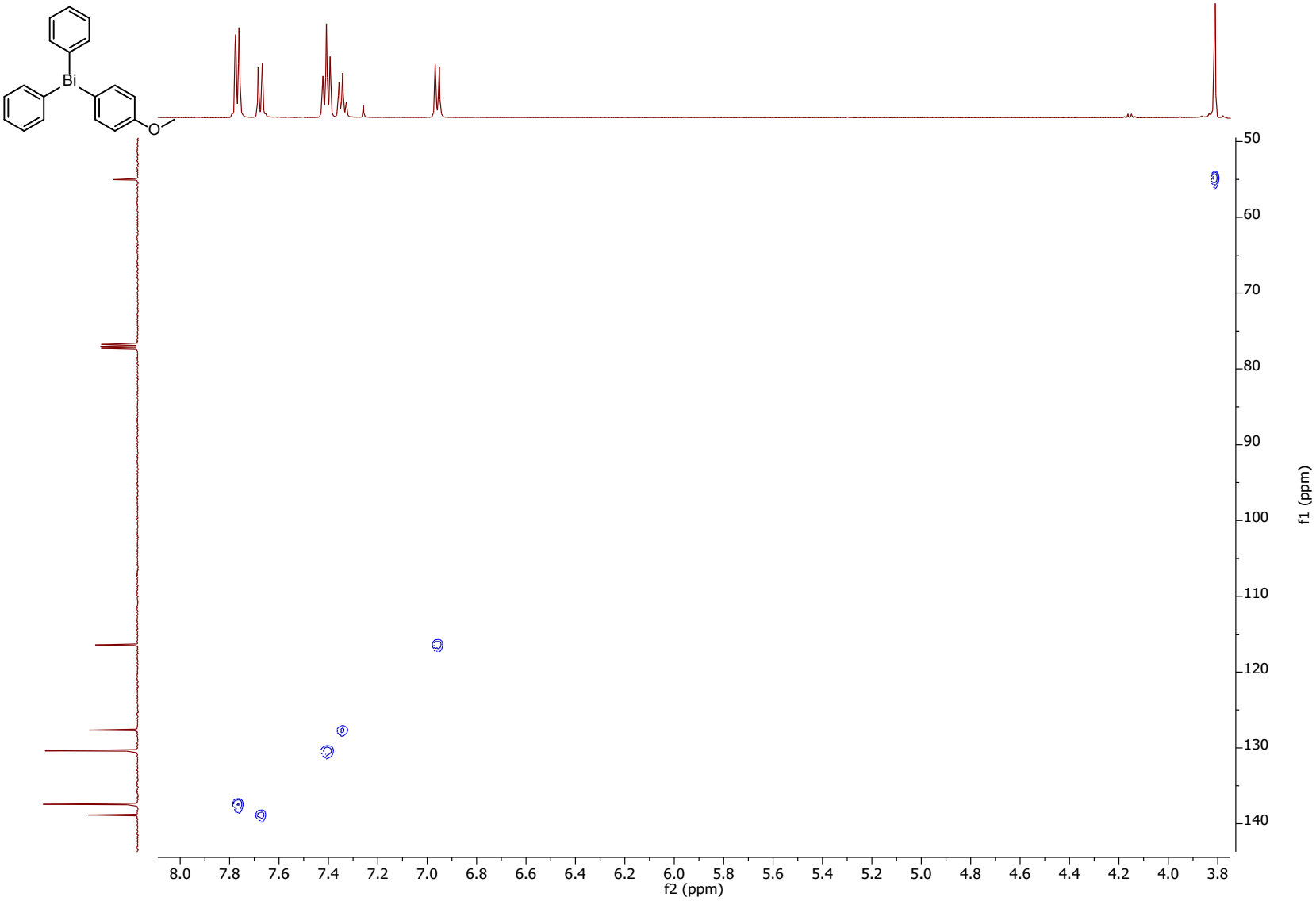
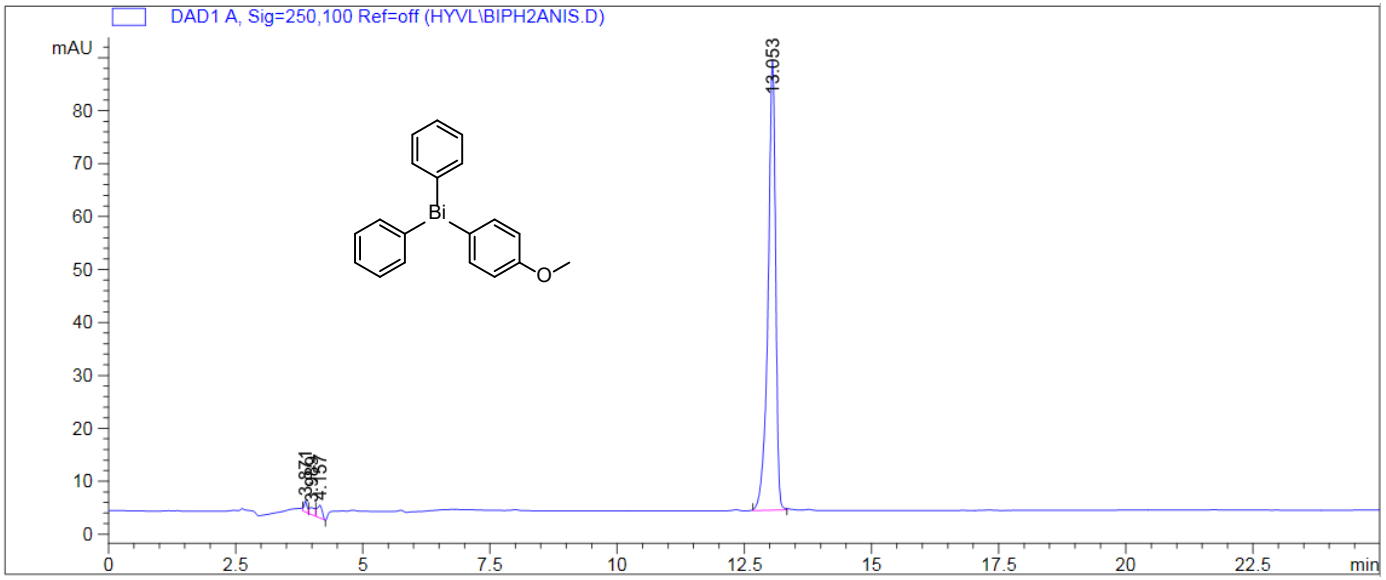


Figure S16. 2D HSQC of **1b** in $CDCl_3$

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=====================================================================
                        Area Percent Report
=====================================================================

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Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
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   1   3.871 BV    0.0615    8.75000    2.06416   0.9597
   2   3.989 VV    0.1130   11.17959    1.31753   1.2261
   3   4.157 VV    0.1015   15.79875    2.37831   1.7327
   4  13.053 BB    0.1543  876.05383   84.94643  96.0815
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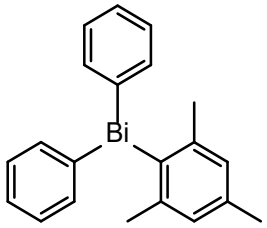
Figure S17. HPLC Chromatogram of **1b**

NMR Spectra and EA Report of Compound 1c



Chemical Formula: $BiC_{21}H_{21}$

Molecular Weight: 482.38

Elemental Analysis: C: 52.29; Bi: 43.32; H: 4.39

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/10/2019 2:29:39PM
User ID	Administrator
Comments	TLG_1_155 [Hyvl]

DATE & TIME	5/10/2019 11:35:29 AM	P_ID	EA LAB
SAMPLE ID	19286	USER ID	Administrator
WEIGHT (mg)	2.213	MODE	CHN

CARBON	52.194%
HYDROGEN	4.291%
NITROGEN	-.057%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S18. EA report for **1c**

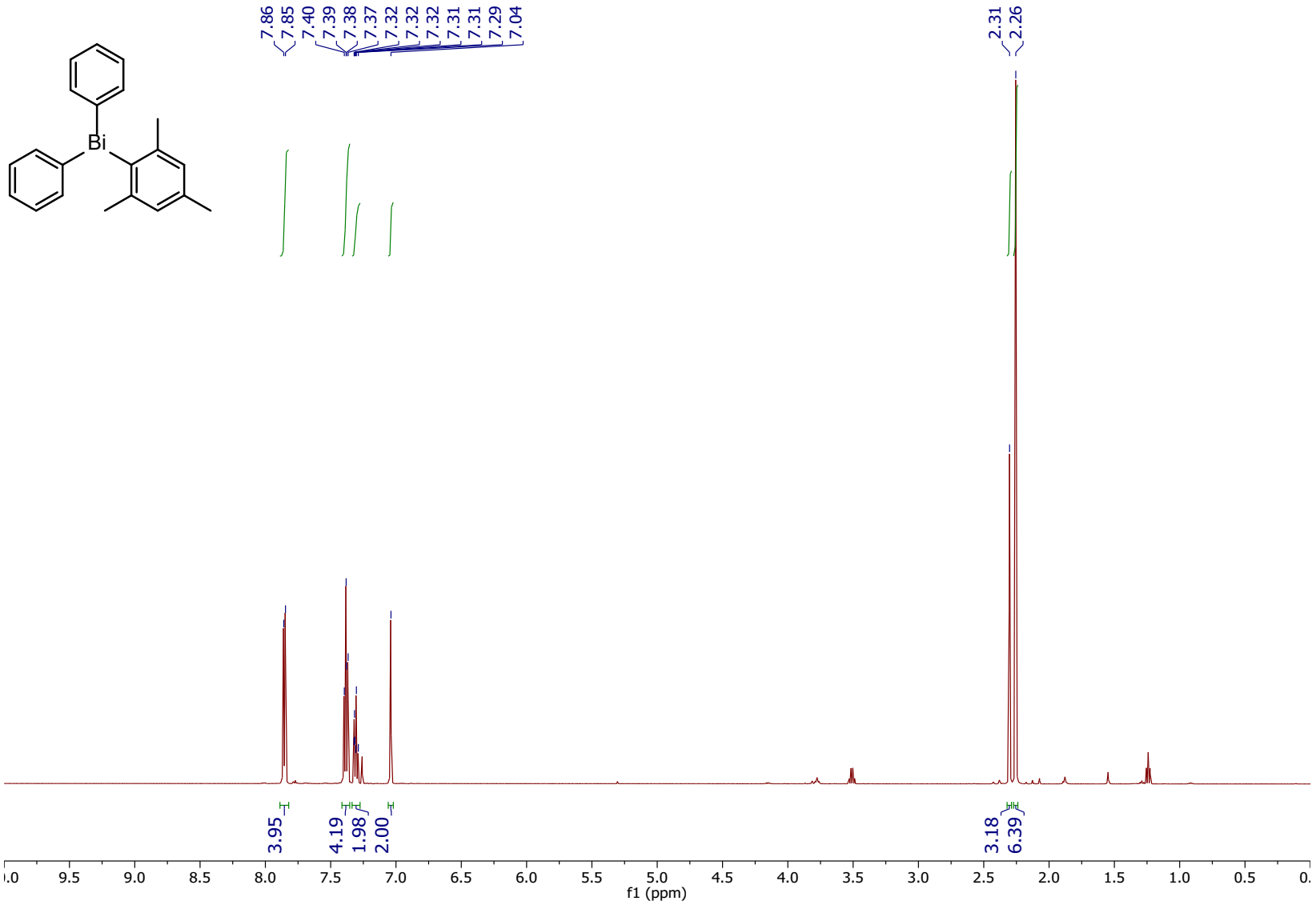


Figure S19. ^{1}H NMR of **1c** $CDCl_3$

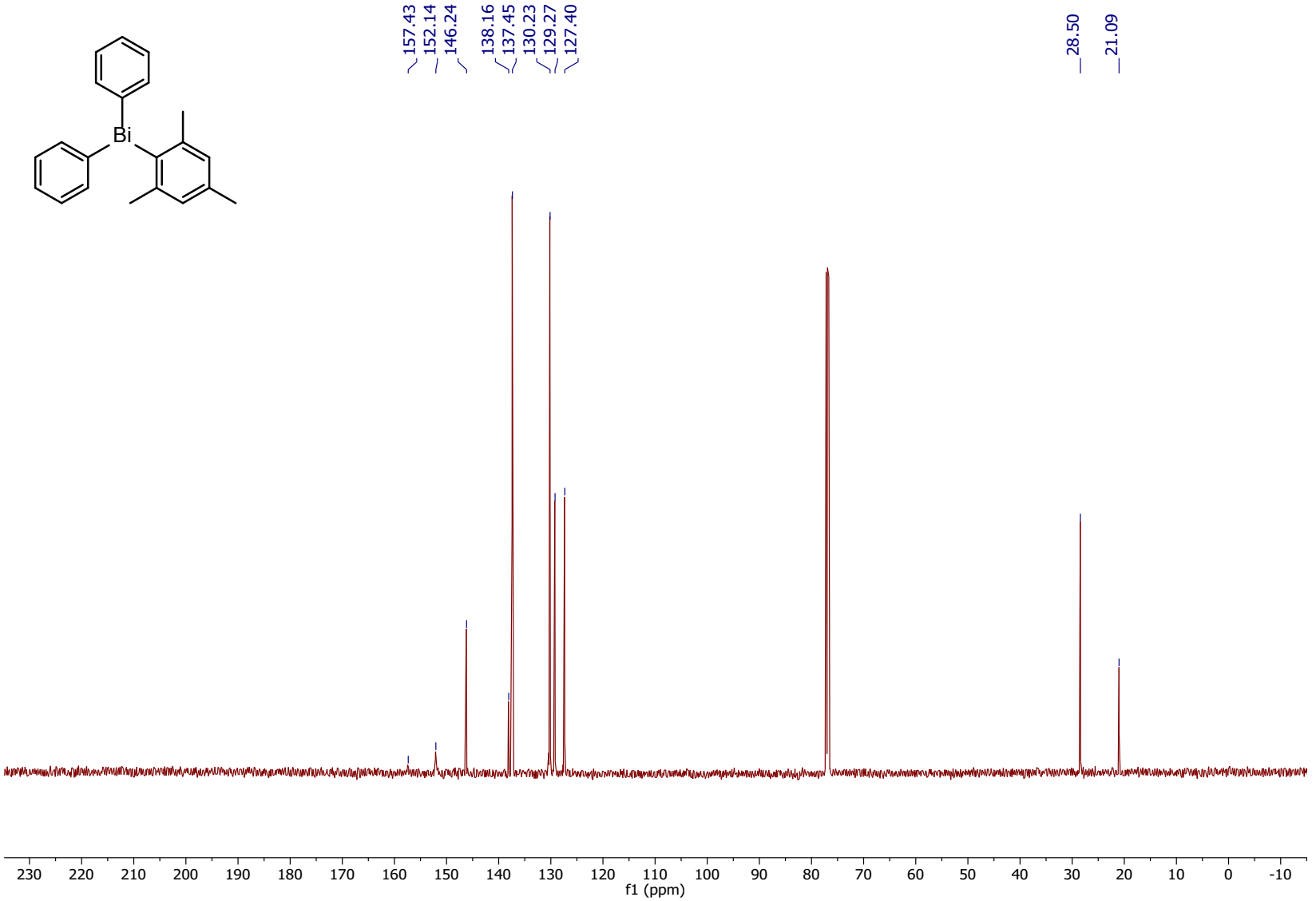


Figure S20. ^{13}C $\{^{1}H\}$ NMR of **1c** in $CDCl_3$

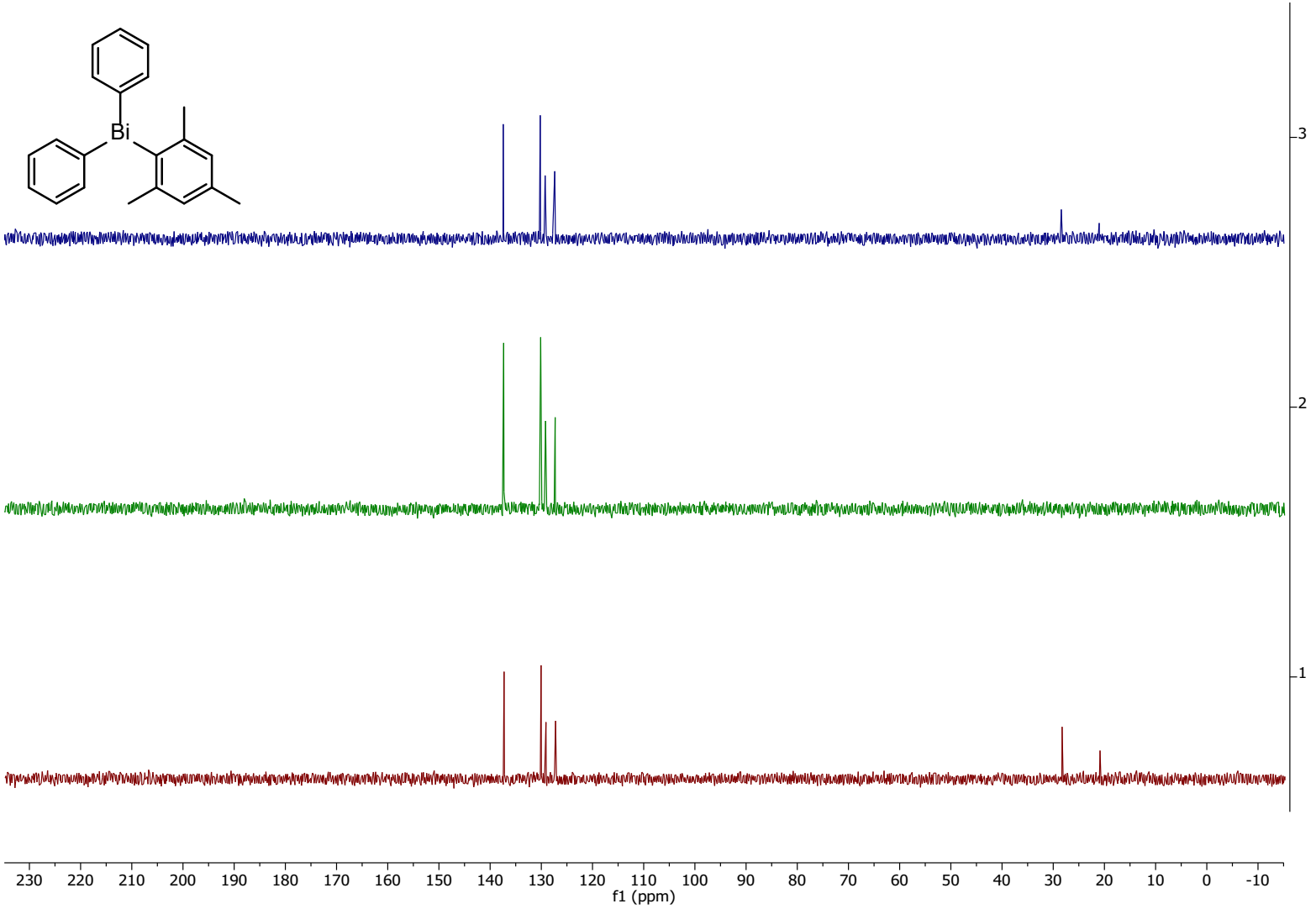


Figure S21. ^{13}C DEPT of **1c** in $CDCl_3$

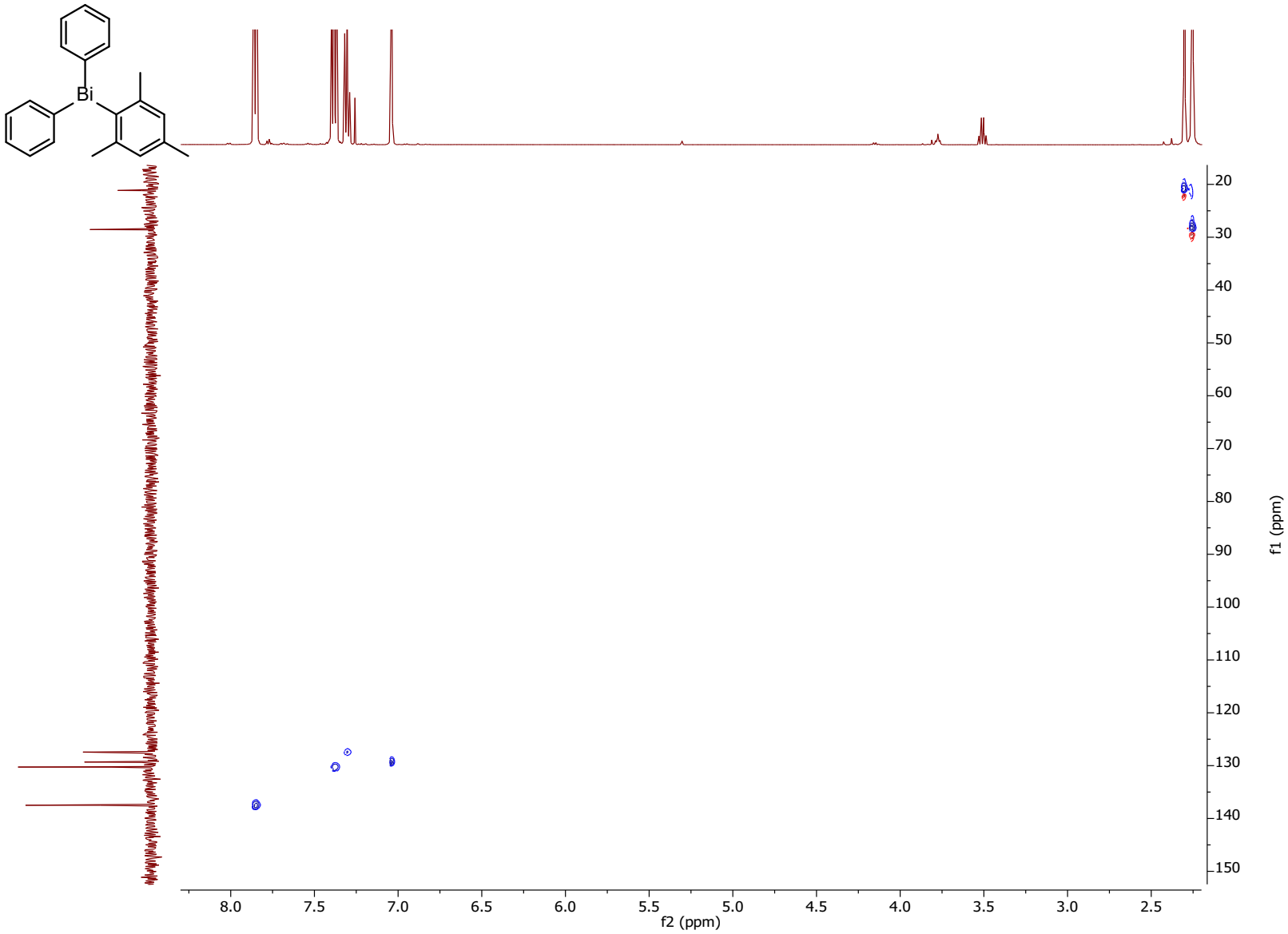
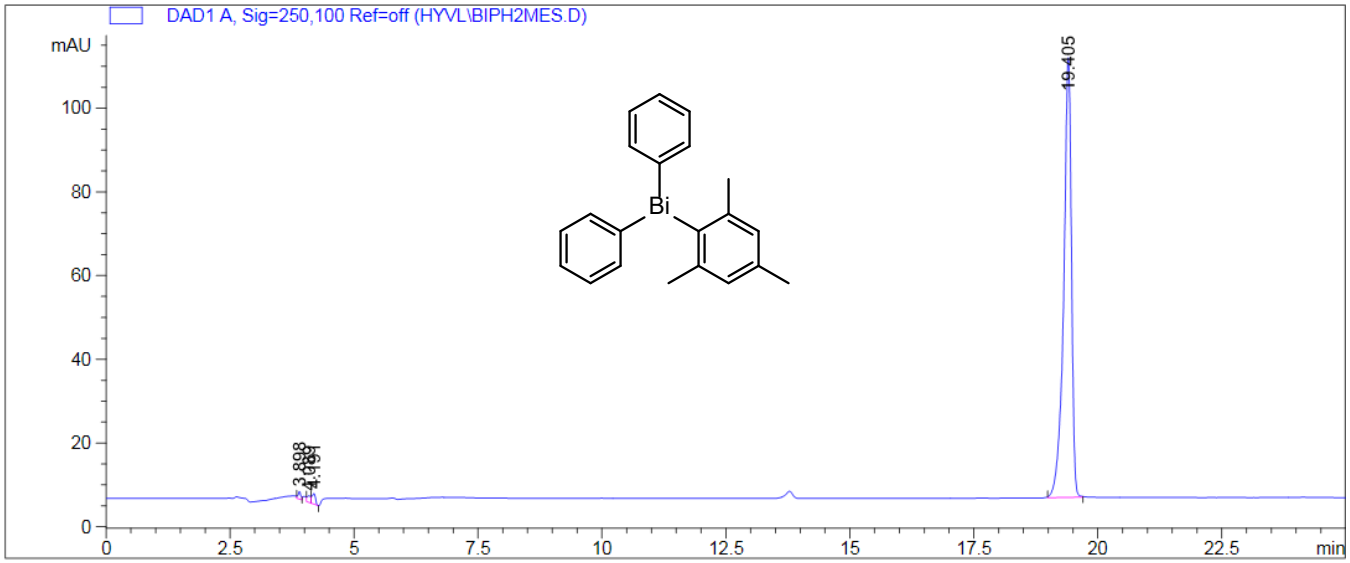


Figure S22. 2D HSQC of **1c** in $CDCl_3$

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                        Area Percent Report
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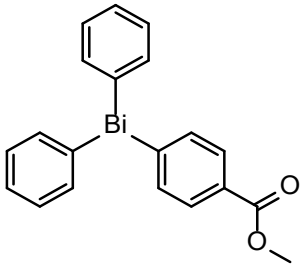
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.898 BV    0.0569    6.90854    1.79331   0.5888
   2   4.089 VV    0.0740    8.17104    1.58943   0.6964
   3   4.191 VV    0.0726   12.11588    2.49681   1.0325
   4  19.405 BB    0.1612 1146.20776  105.09236  97.6823
```

Figure S23. HPLC Chromatogram of **1c**

NMR Spectra and EA Report of Compound 1d



Chemical Formula: $BiO_2C_{20}H_{17}$
Molecular Weight: 498.33
Elemental Analysis: C: 48.20; Bi: 41.94; H: 3.44; O: 6.42

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	10/25/2019 6:17:04PM
User ID	Administrator
Comments	TLG_1_151_B [Hyvl]

DATE & TIME	10/25/2019 2:48:46 PM	P_ID	EA LAB
SAMPLE ID	19596	USER ID	Administrator
WEIGHT (mg)	2.188	MODE	CHN

CARBON	48.597%
HYDROGEN	3.260%
NITROGEN	0.0%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Figure S24. EA report for **1d**

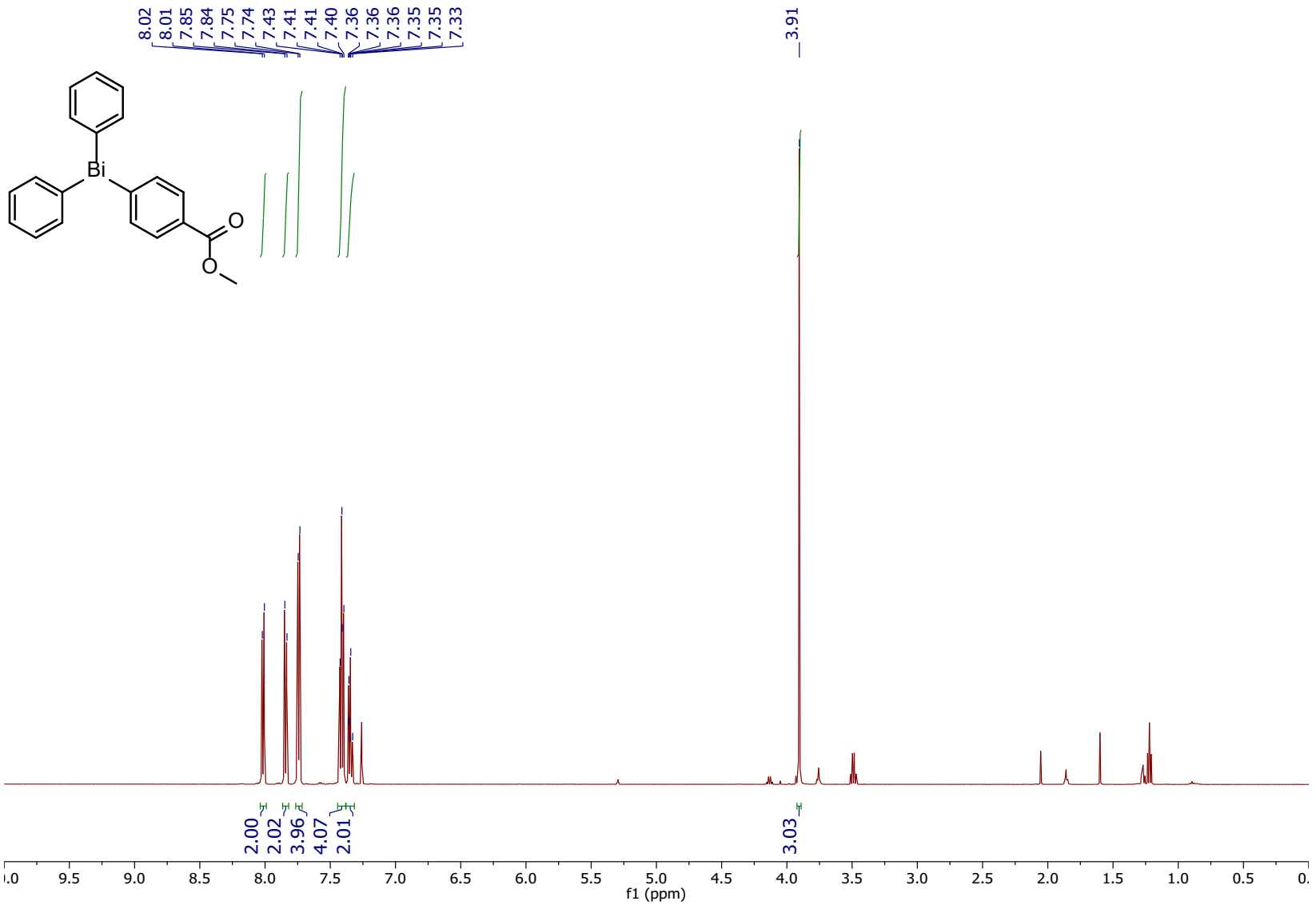


Figure S25. ^{1}H NMR of **1d** in $CDCl_3$

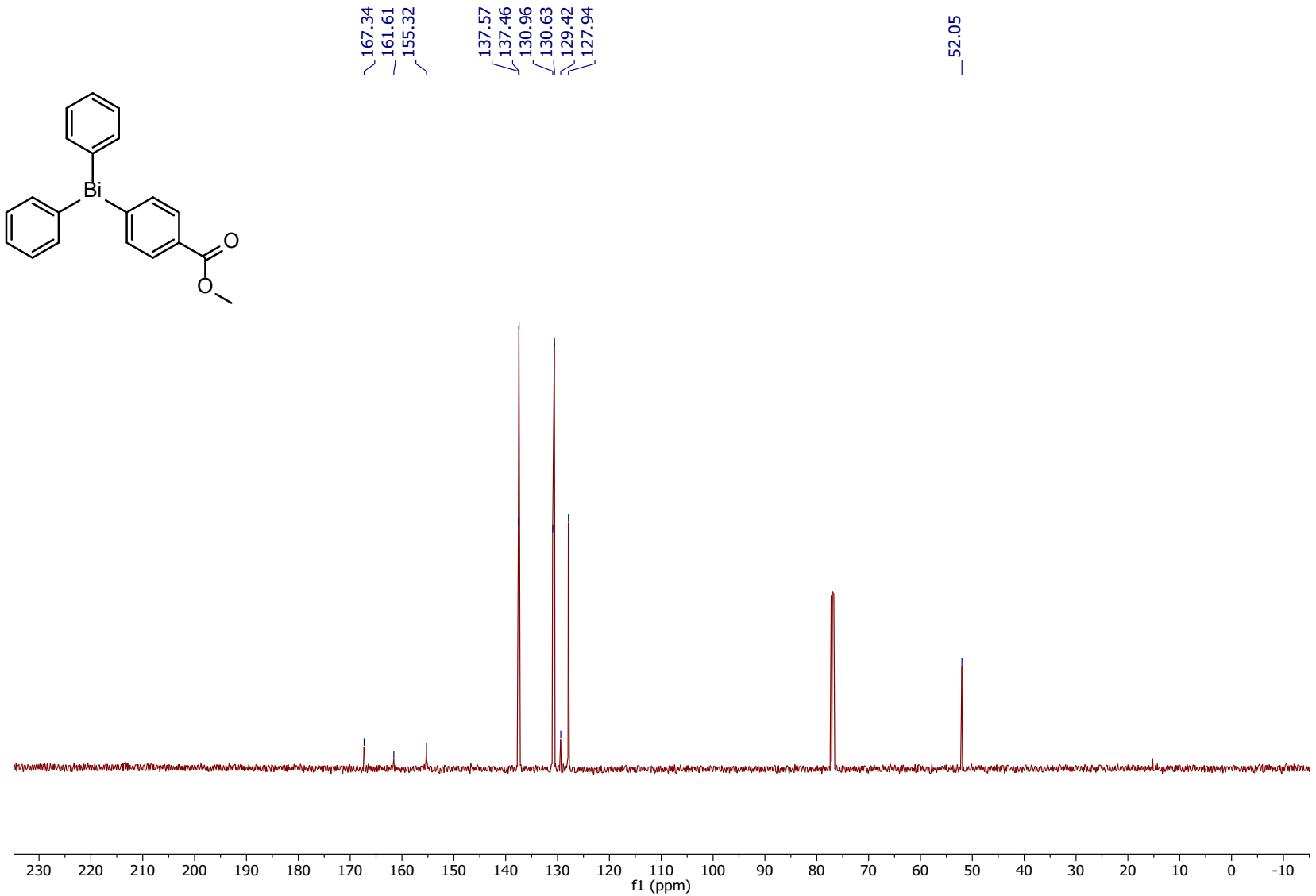


Figure S26. ^{13}C $\{^{1}H\}$ NMR of **1d** in $CDCl_3$

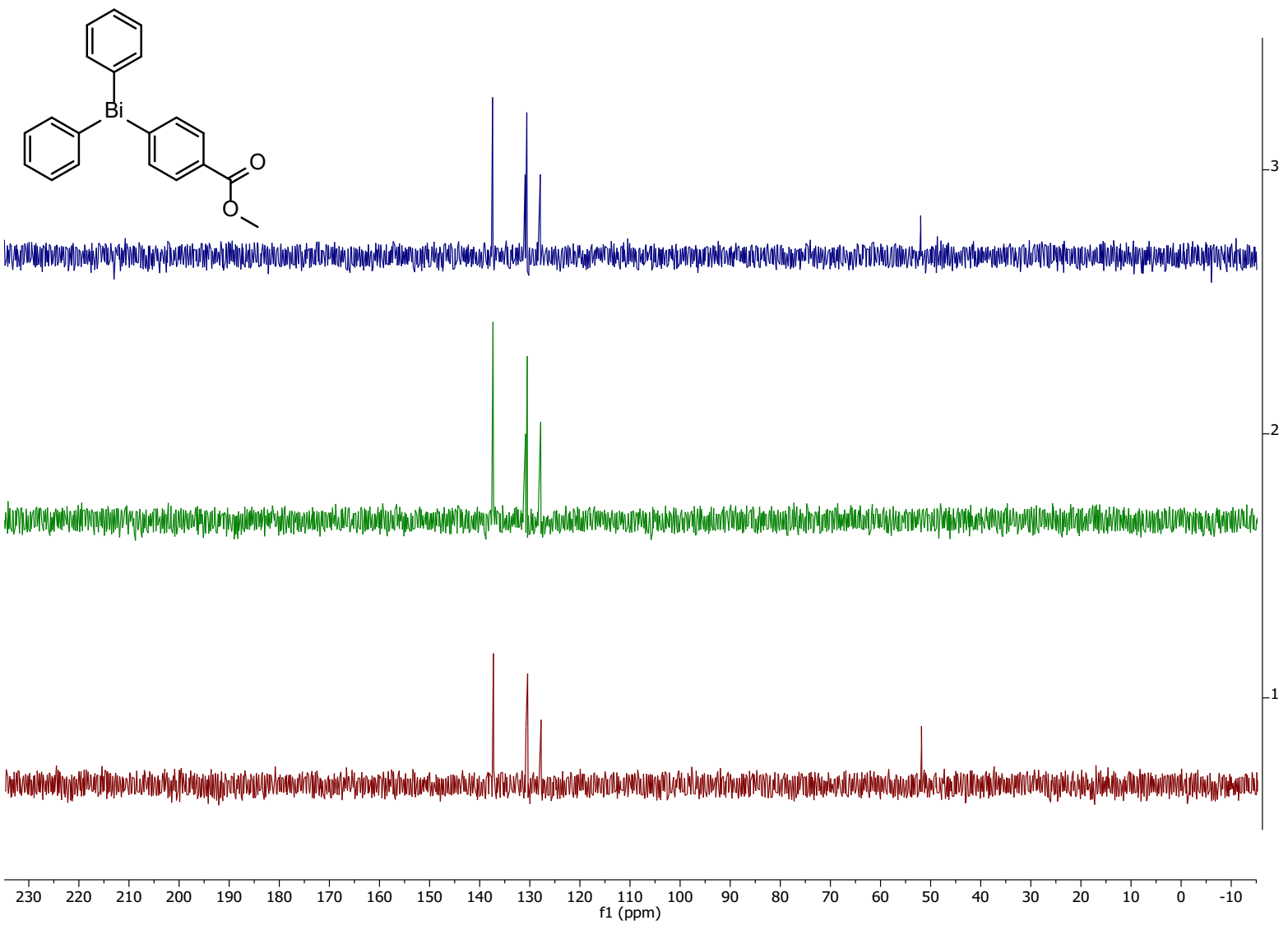


Figure S27. ^{13}C DEPT of **1d** in $CDCl_3$

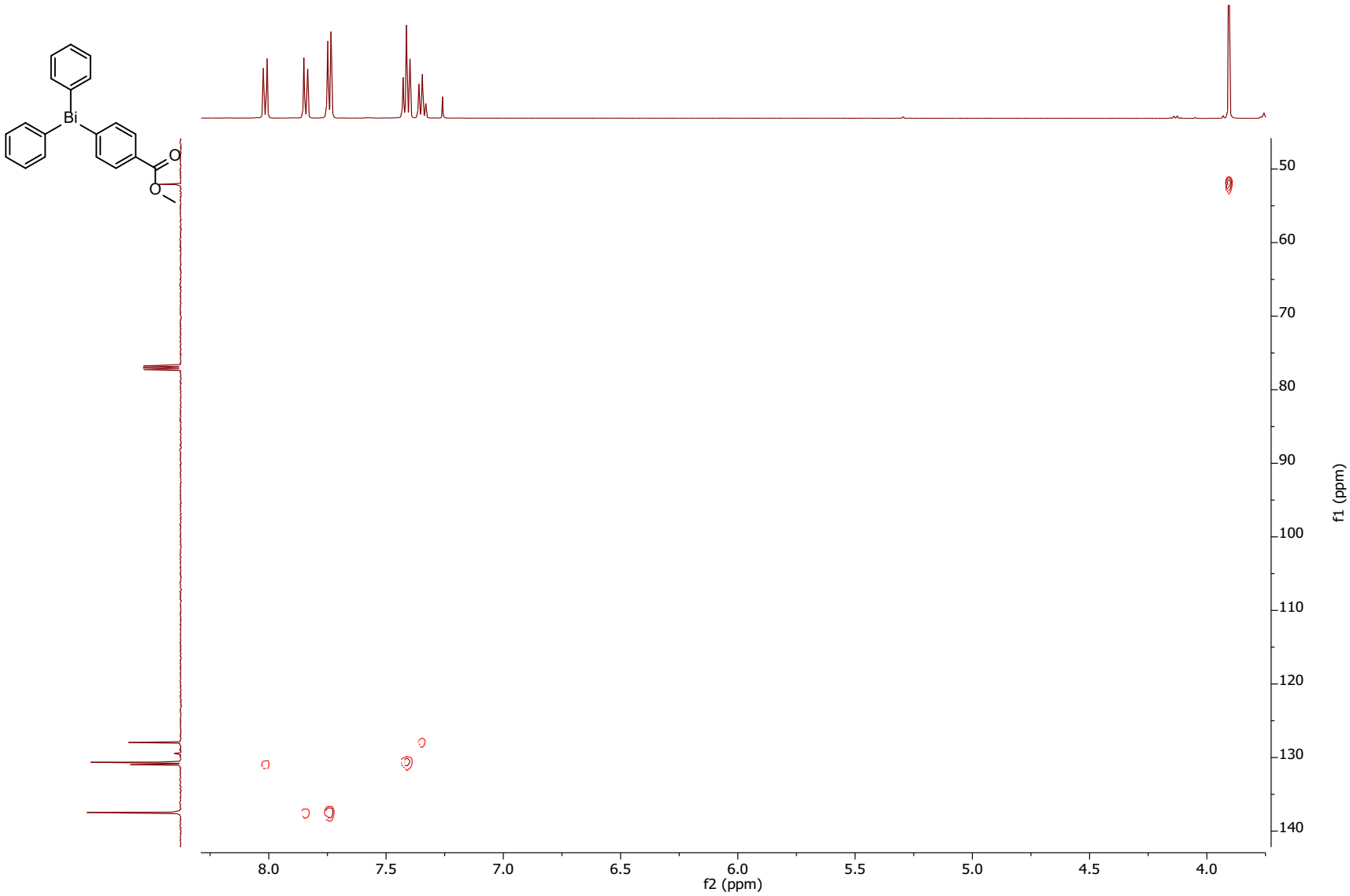
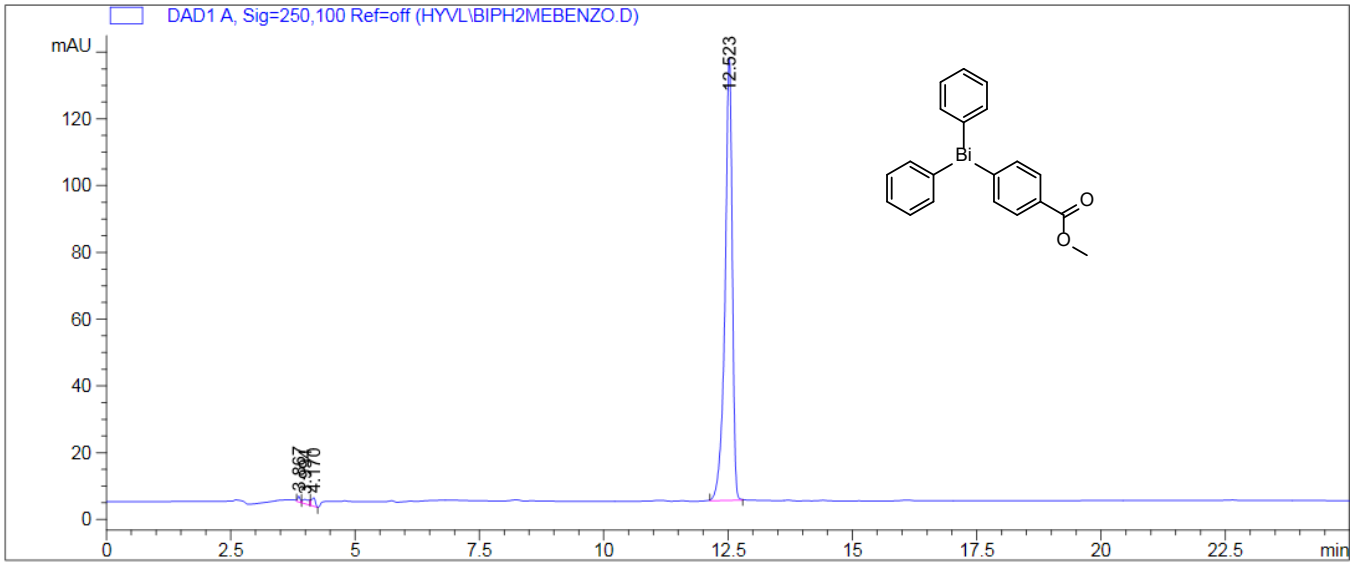


Figure S28. 2D HSQC of **1d** in $CDCl_3$

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                        Area Percent Report
=====================================================================

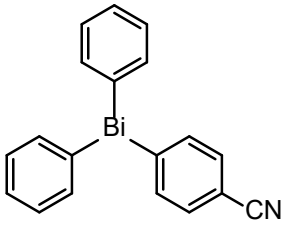
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.867 BV    0.0574    6.39290    1.71725   0.4643
   2   3.994 VB    0.1184   12.02068    1.34342   0.8730
   3   4.170 BV    0.0775   13.59000    2.57776   0.9870
   4  12.523 BB    0.1522 1344.91504  132.69420  97.6757
```

Figure S29. HPLC Chromatogram of **1d**

NMR Spectra and EA Report of Compound 1e



Chemical Formula: $BiNC_{19}H_{14}$
Molecular Weight: 465.31
Elemental Analysis: C: 49.04; Bi: 44.91; H: 3.03; N: 3.01

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/10/2019 2:29:53PM
User ID	Administrator
Comments	TLG_1_158 [Hyvl]

DATE & TIME	5/10/2019 11:40:34 AM	P_ID	EA LAB
SAMPLE ID	19287	USER ID	Administrator
WEIGHT (mg)	2.221	MODE	CHN

CARBON	49.139%
HYDROGEN	2.959%
NITROGEN	2.929%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S30. EA report for **1e**

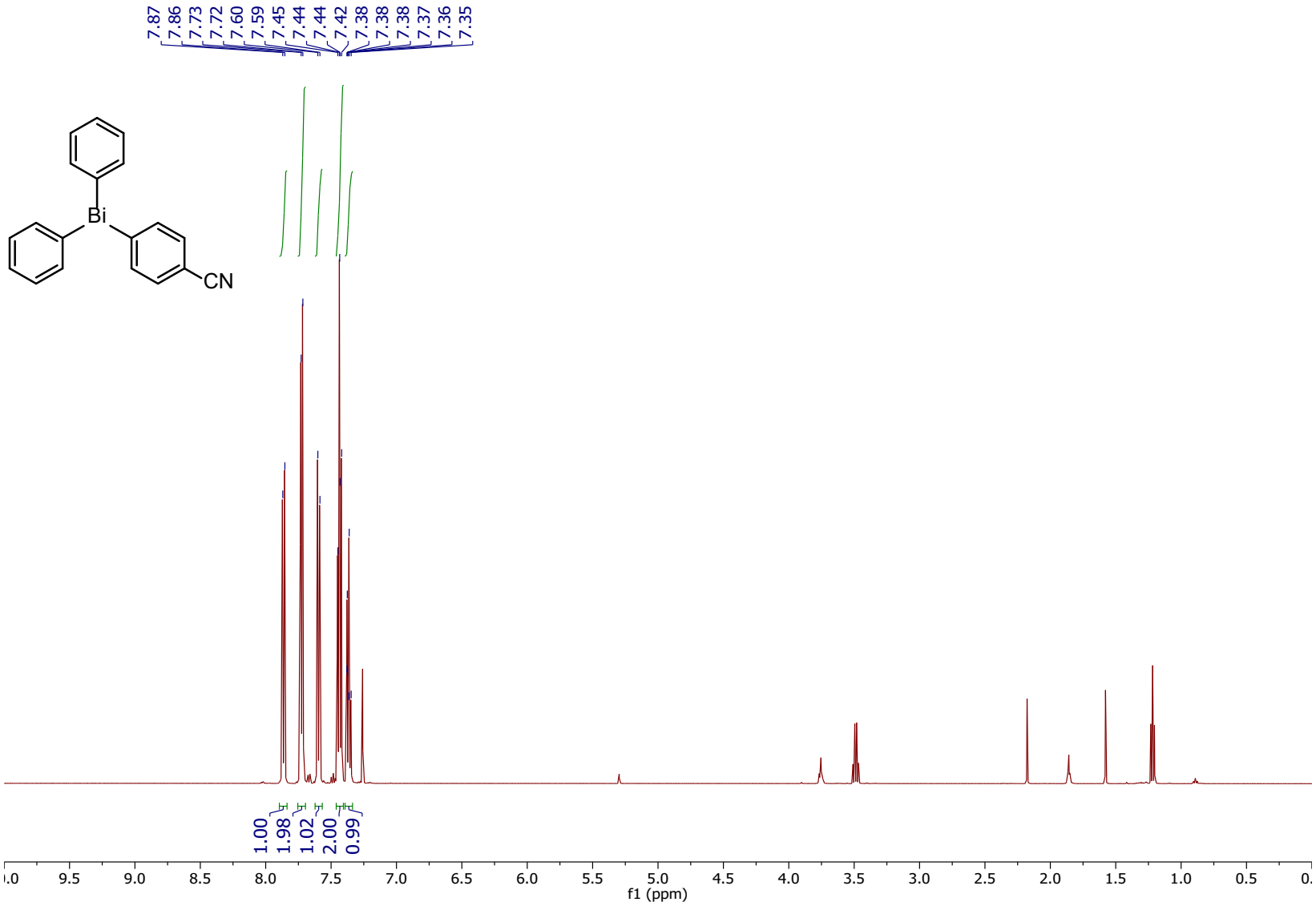


Figure S31. ^{1}H NMR of **1e** in $CDCl_3$

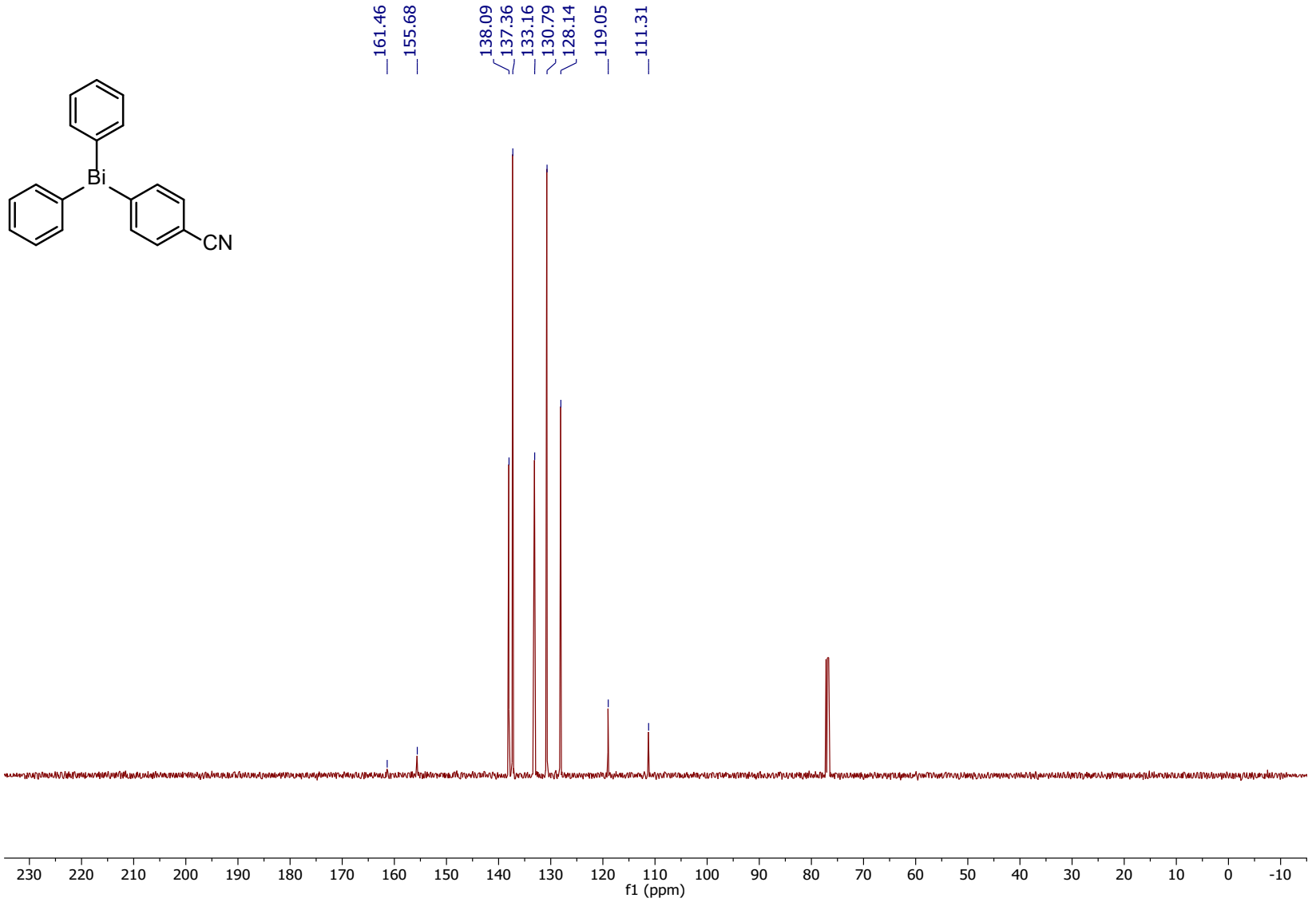


Figure S32. ^{13}C {^{1}H} NMR of **1e** in $CDCl_3$

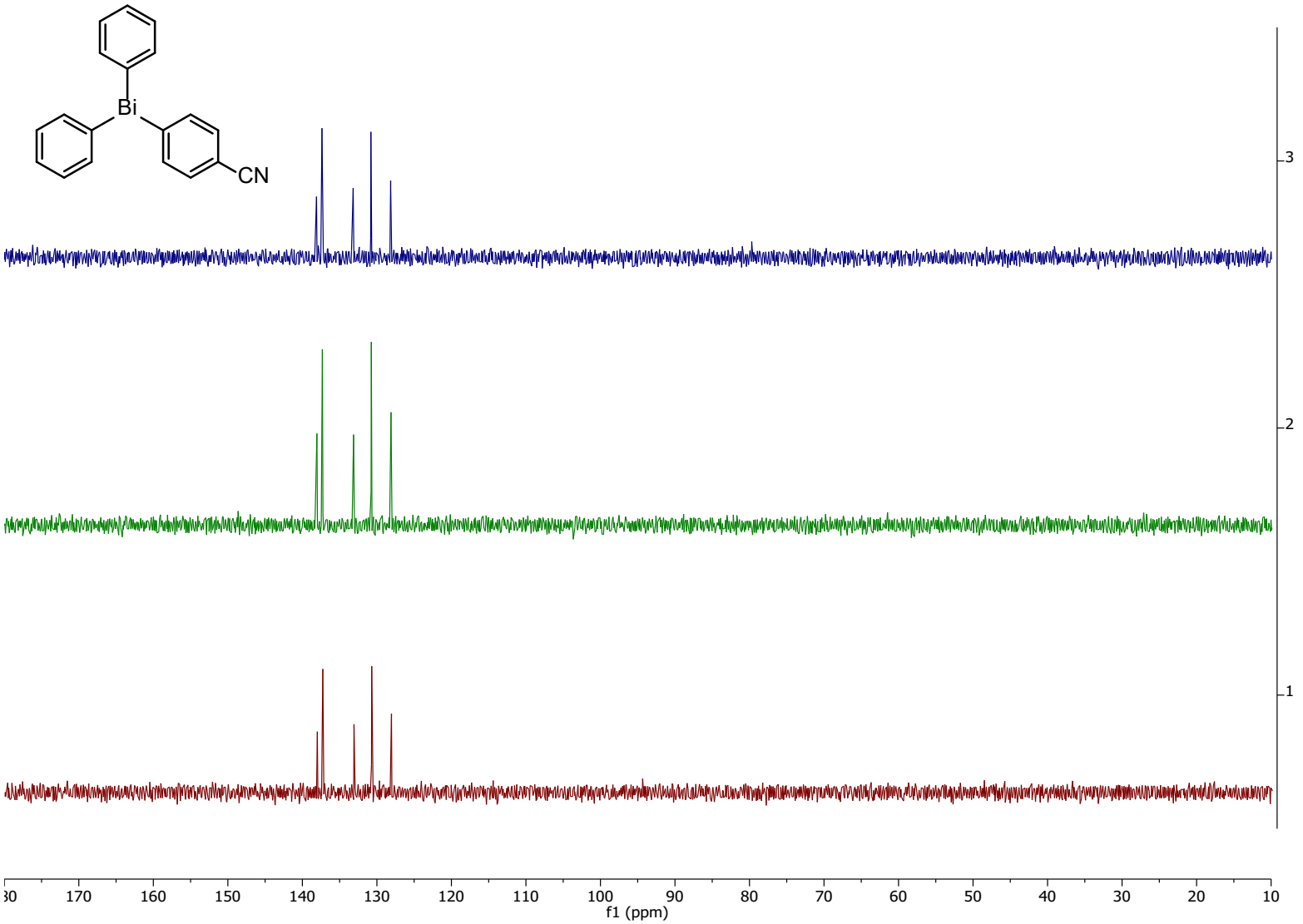


Figure S33. ^{13}C DEPT of **1e** in $CDCl_3$

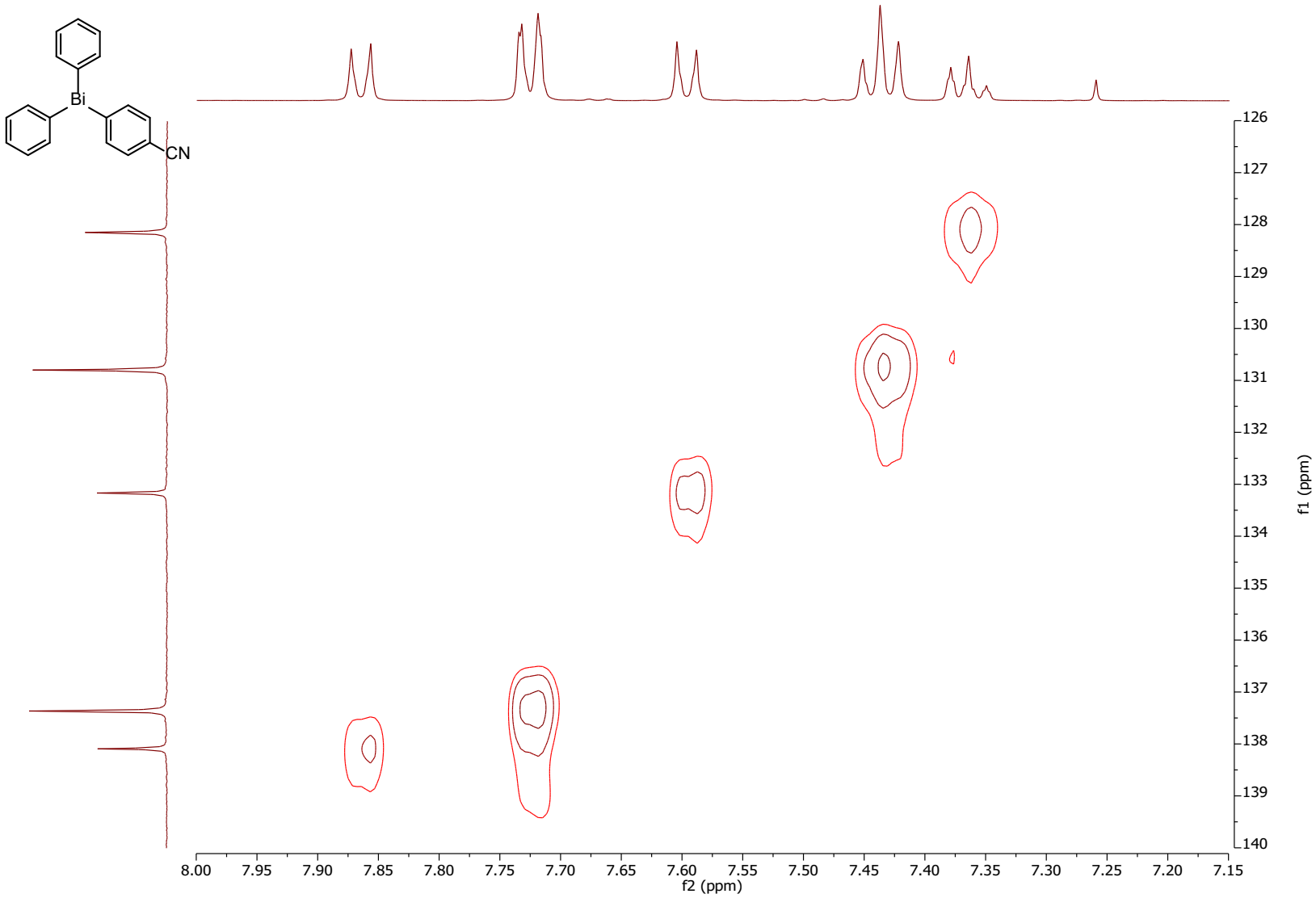
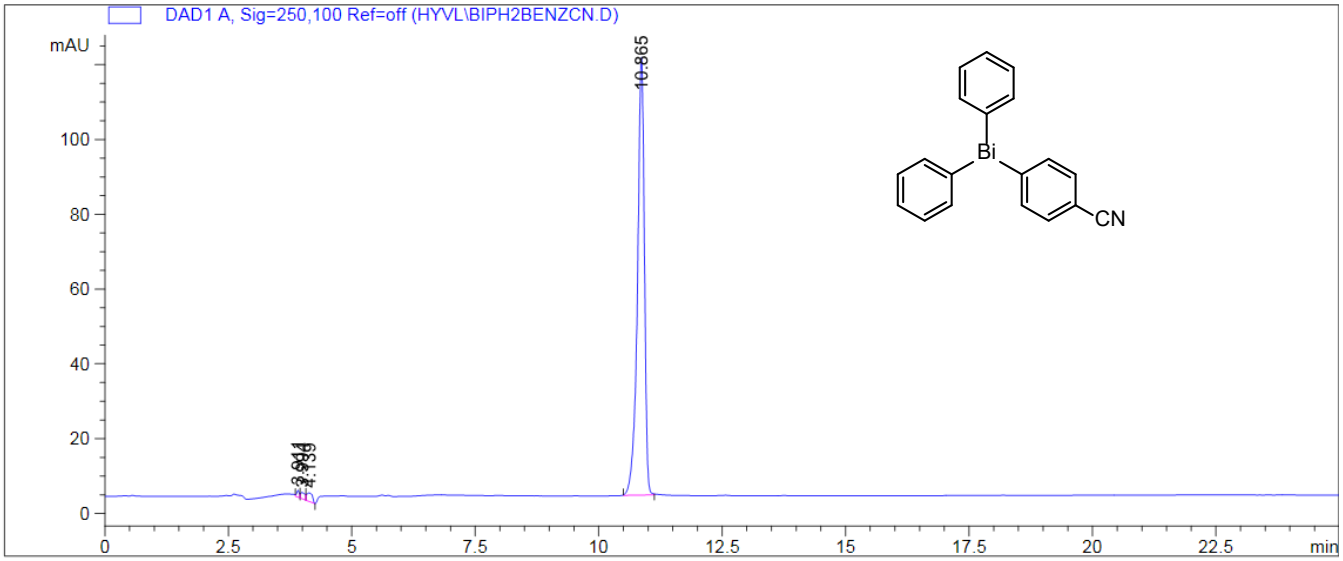


Figure S34. 2D HSQC of **1e** in $CDCl_3$

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                        Area Percent Report
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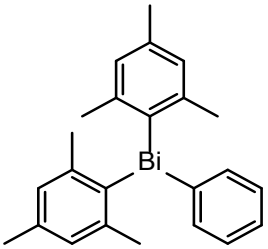
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.911 BV    0.0556    6.93817    1.85545   0.5882
   2   3.994 VV    0.0904   10.98717    1.67865   0.9315
   3   4.139 VV    0.1026   17.91453    2.30757   1.5188
   4  10.865 BB    0.1480 1143.66382  117.06699  96.9614
```

Figure S35. HPLC Chromatogram of **1e**

NMR Spectra and EA Report of Compound 1f



Chemical Formula: $BiC_{24}H_{27}$

Molecular Weight: 524.46

Elemental Analysis: C: 54.96; Bi: 39.85; H: 5.19

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/31/2019 4:52:06PM
User ID	Administrator
Comments	TLG_1_165 [Hyvl]

DATE & TIME	5/31/2019 2:35:37 PM	P_ID	EA LAB
SAMPLE ID	19330	USER ID	Administrator
WEIGHT (mg)	2.268	MODE	CHN

CARBON	54.939%
HYDROGEN	4.798%
NITROGEN	-.131%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S36. EA report for **1f**

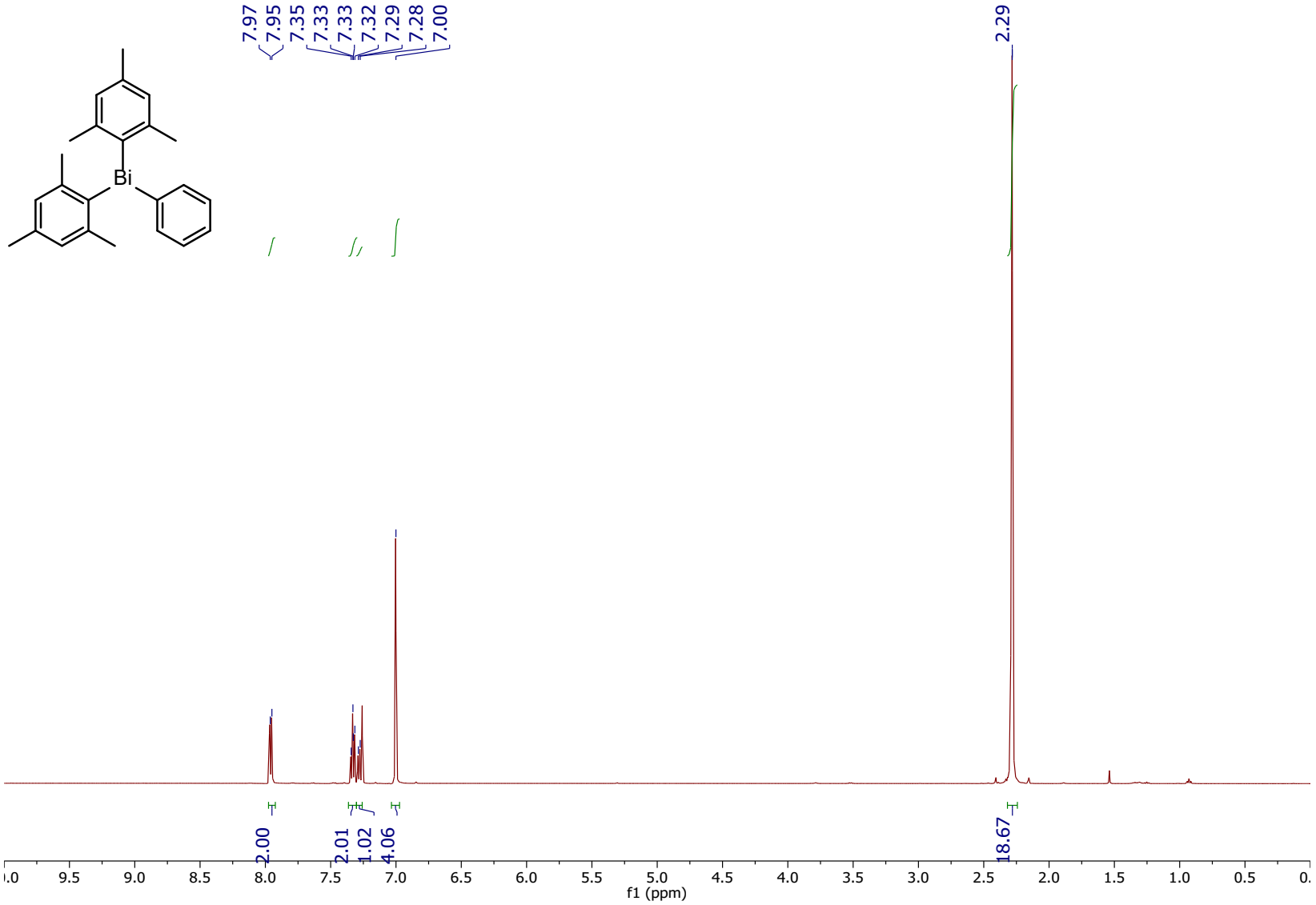


Figure S37. ^{1}H NMR of **1f** in $CDCl_3$

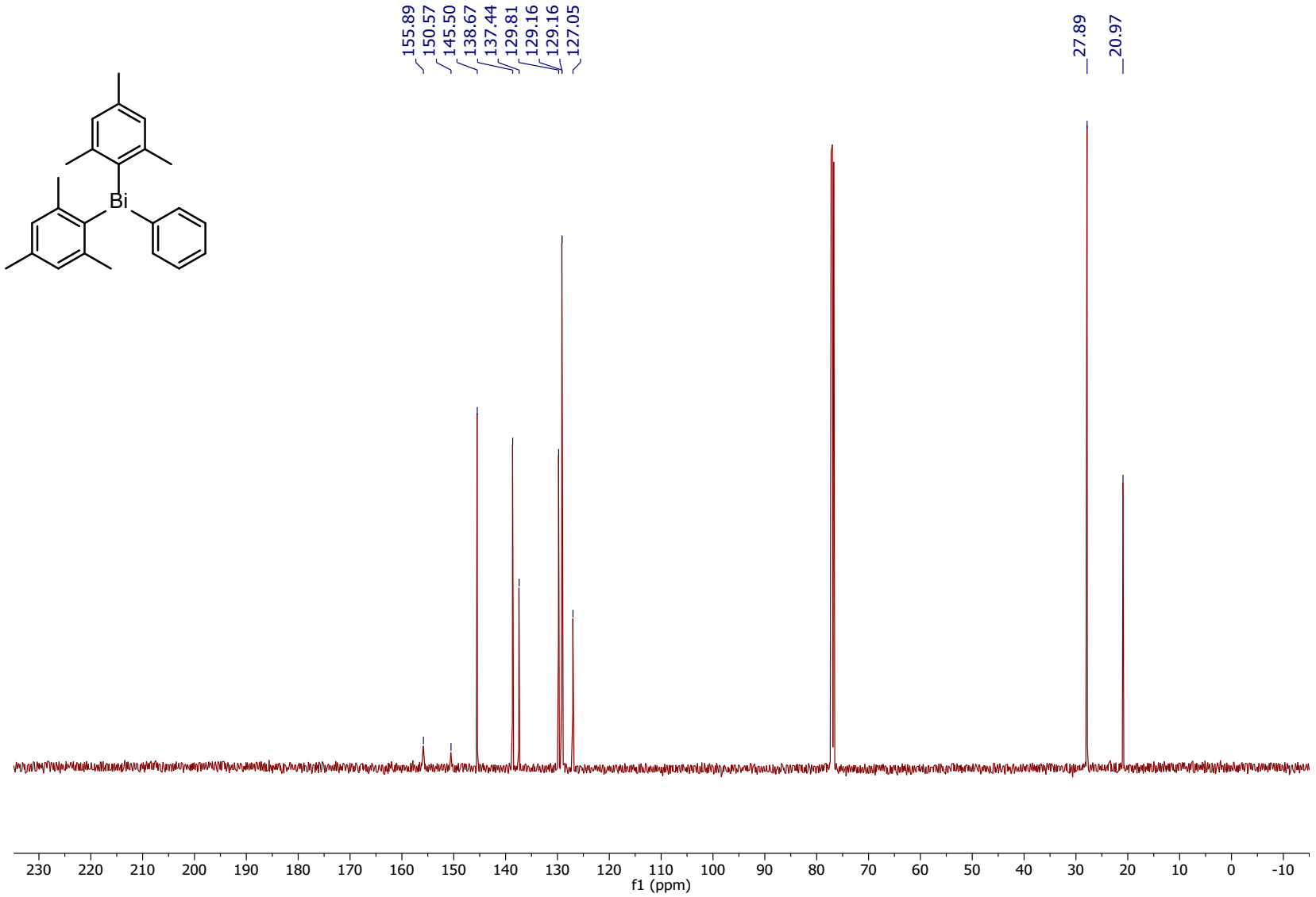


Figure S38. ^{13}C $\{^{1}H\}$ NMR of **1f** in $CDCl_3$

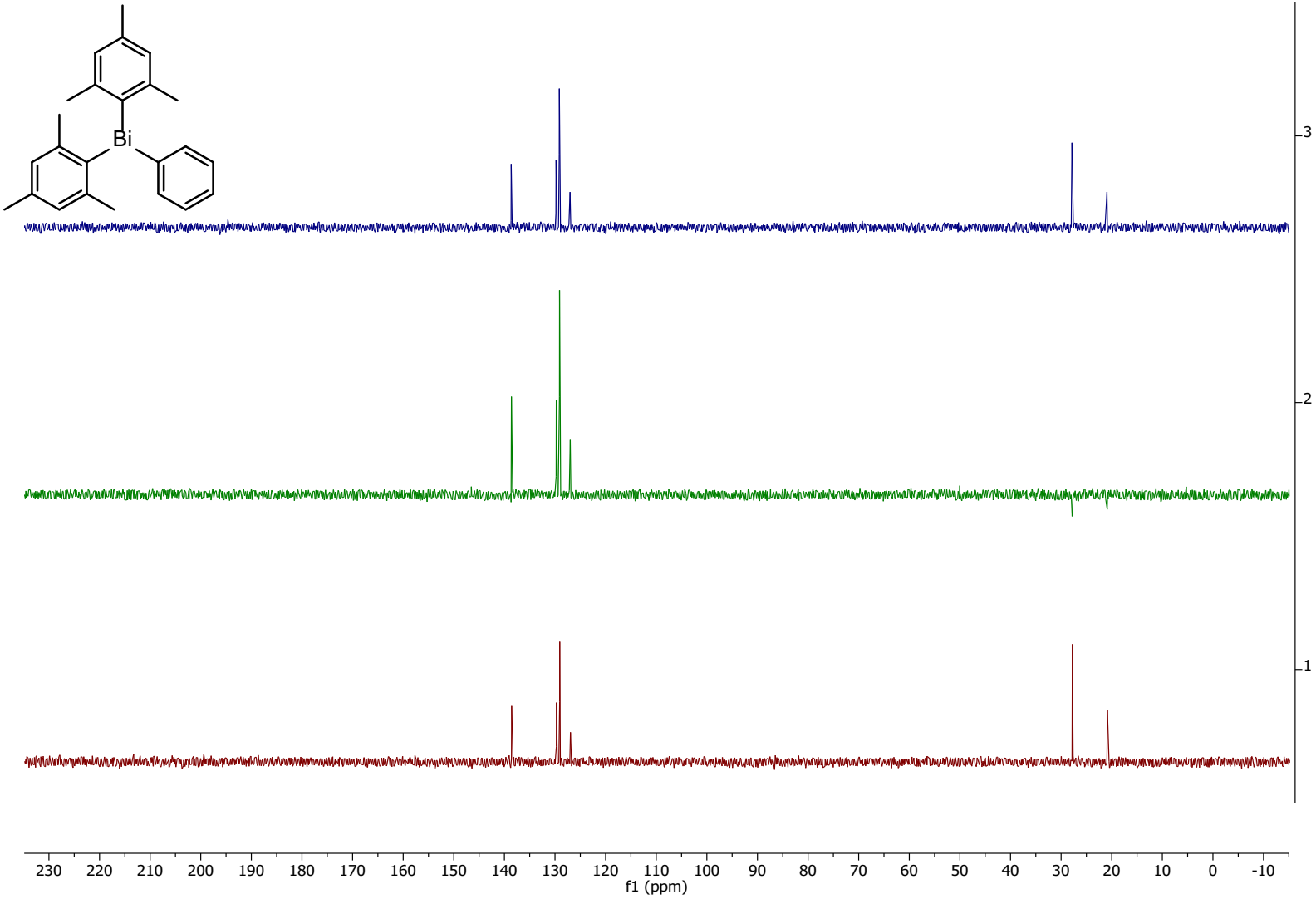


Figure S39. ^{13}C DEPT of **1f** in $CDCl_3$

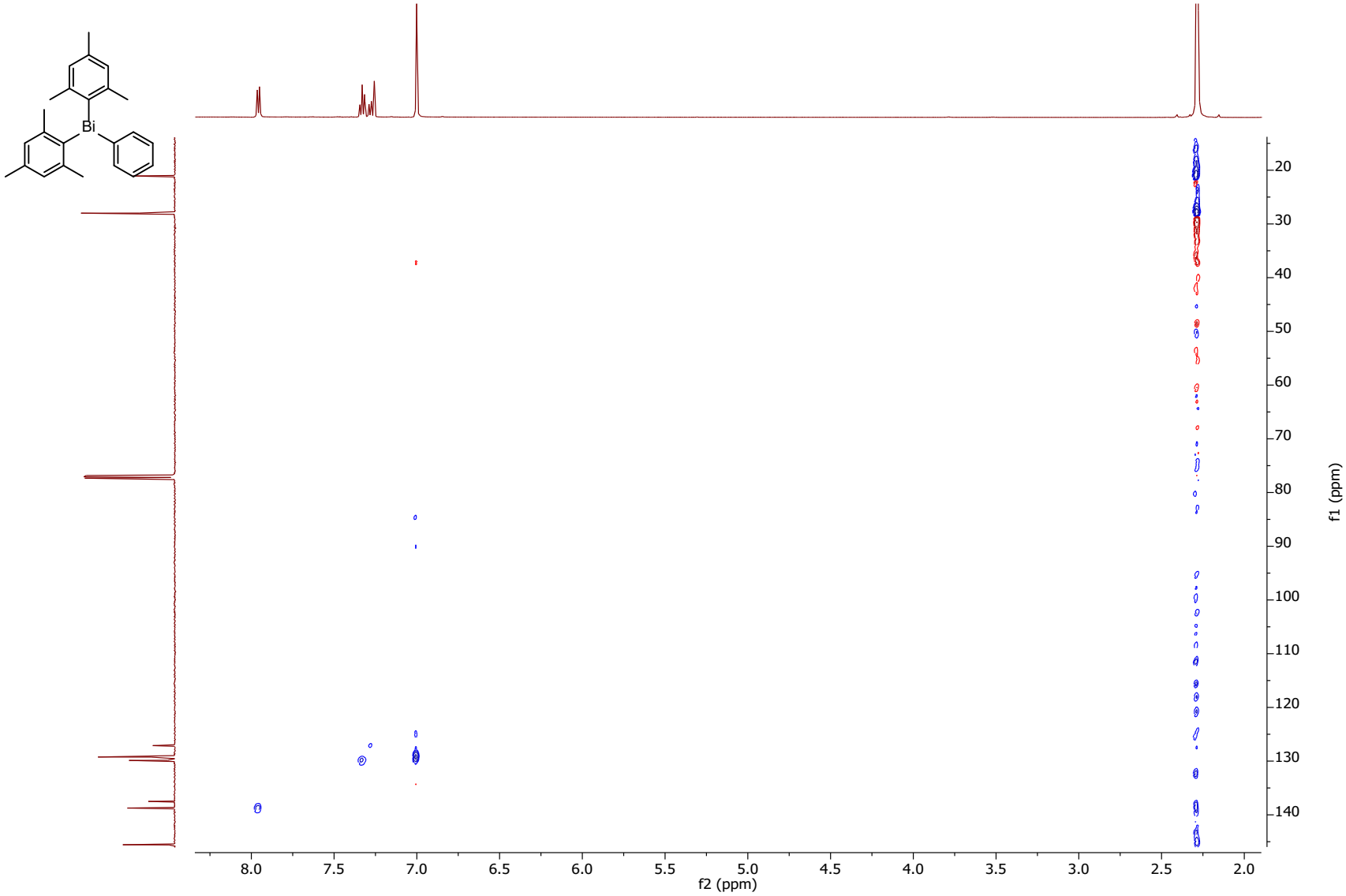
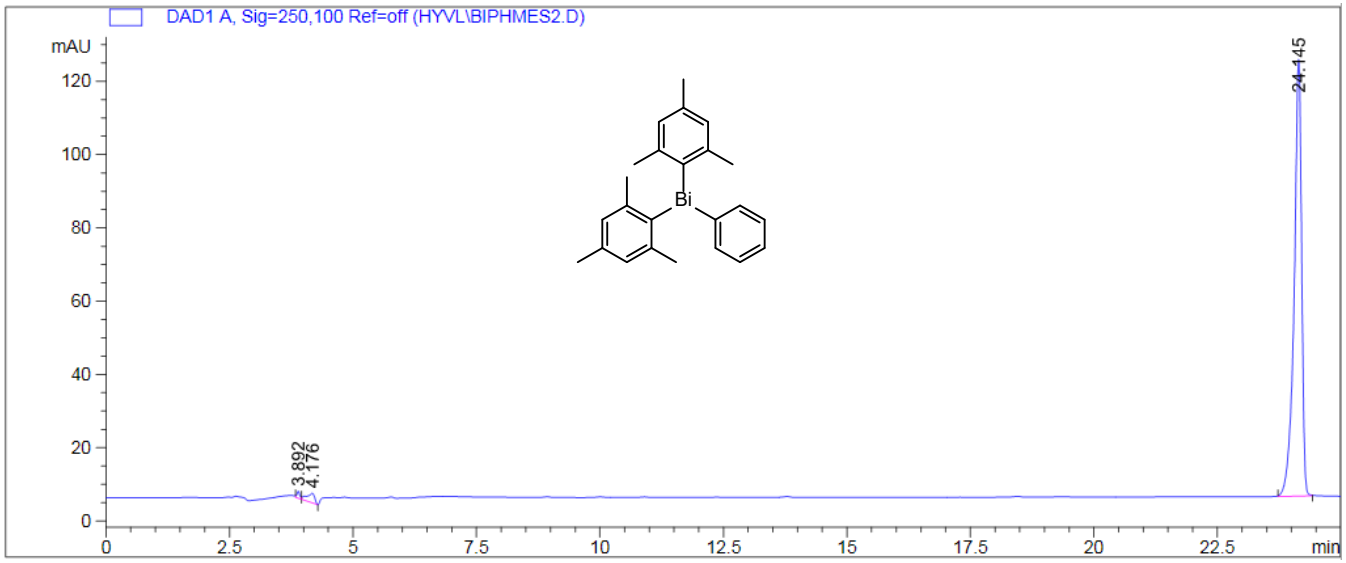


Figure S40. 2D HSQC of **1f** in $CDCl_3$

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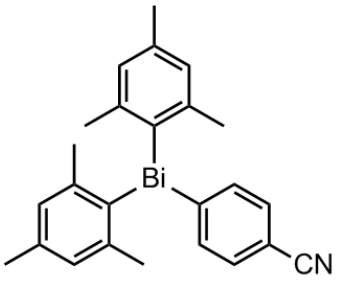
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.892 BV    0.0598    7.99999    1.95155   0.6197
   2   4.176 VV    0.1464   27.91670    2.66161   2.1623
   3  24.145 BB    0.1568 1255.12268  119.23830  97.2180
```

Figure S41. HPLC Chromatogram of **1f**

NMR Spectra and EA Report of Compound 1g



Chemical Formula: $BiC_{25}H_{26}N$
Molecular Weight: 549.47
Elemental Analysis: C: 54.65; Bi: 38.03; H: 4.77; N:2.35

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	8/10/2019 5:09:37PM
User ID	Administrator
Comments	TLG 2_80 [Hyvl]

DATE & TIME	8/10/2019 5:07:12 PM	P_ID	EA LAB
SAMPLE ID	19515	USER ID	Administrator
WEIGHT (mg)	2.061	MODE	CHN

CARBON	54.826%
HYDROGEN	4.880%
NITROGEN	2.395%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S42. EA report for **1g**

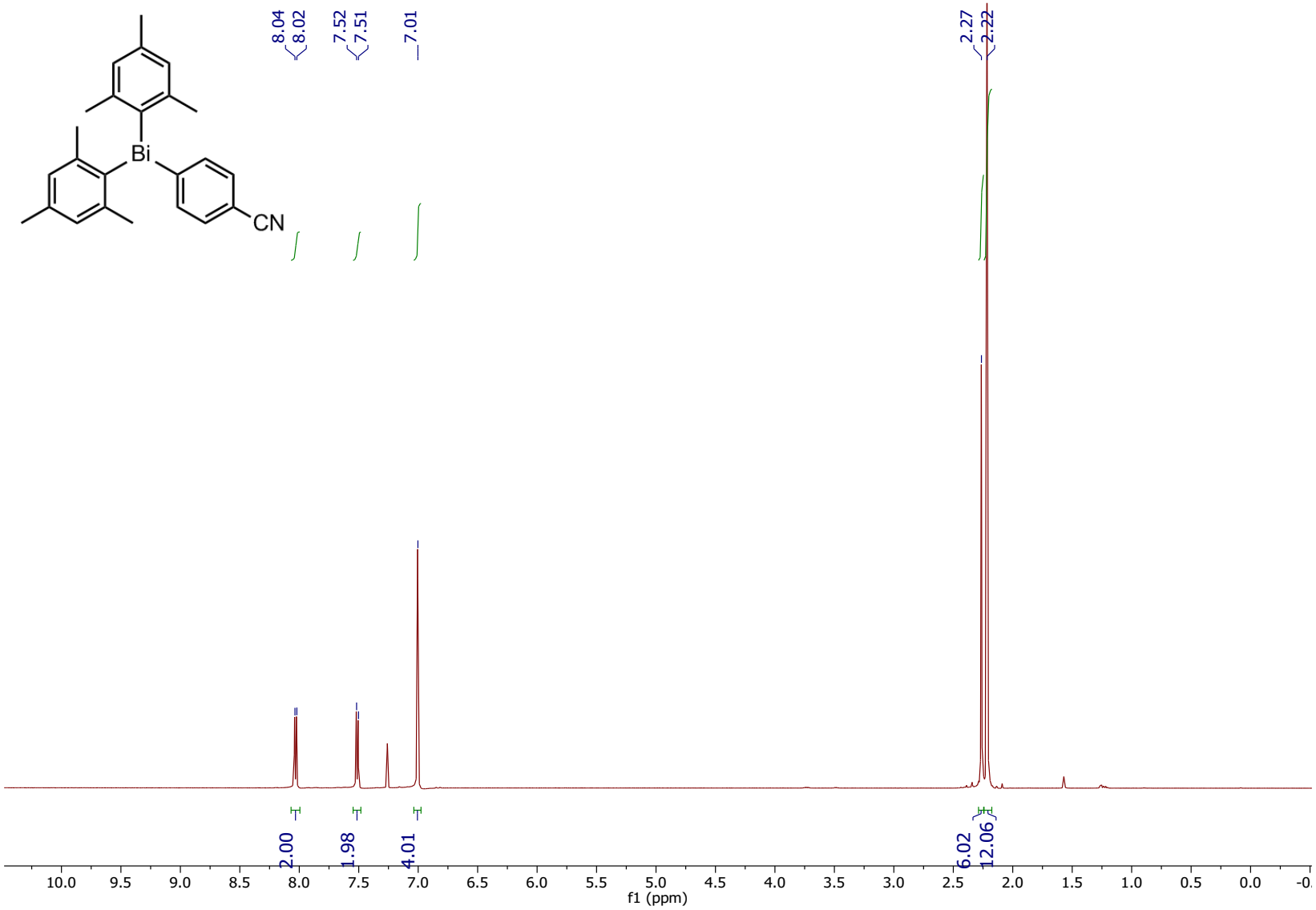


Figure S43. ^{1}H NMR of **1g** in $CDCl_3$

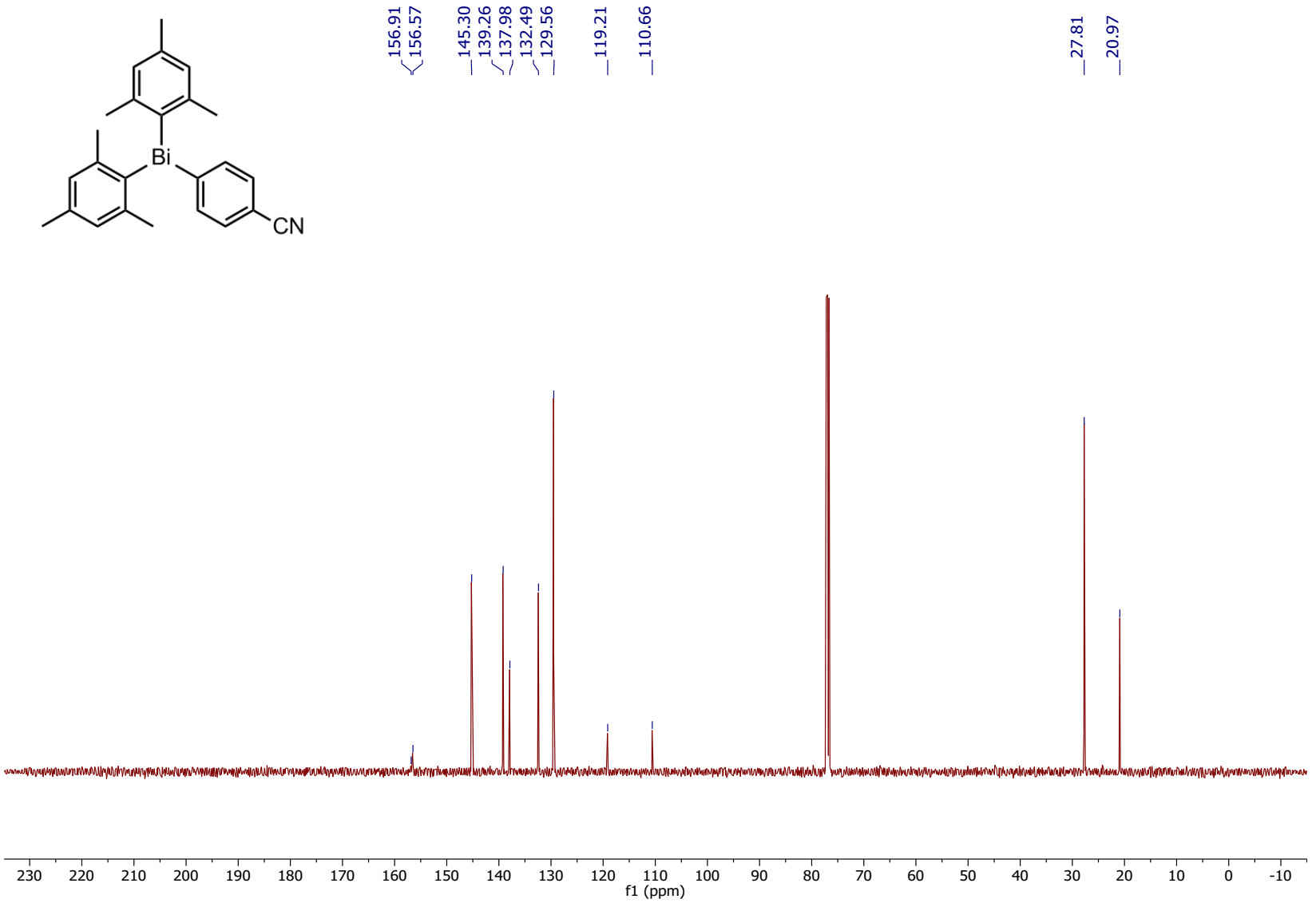


Figure S44. ^{13}C $\{^{1}H\}$ NMR of **1g** in $CDCl_3$

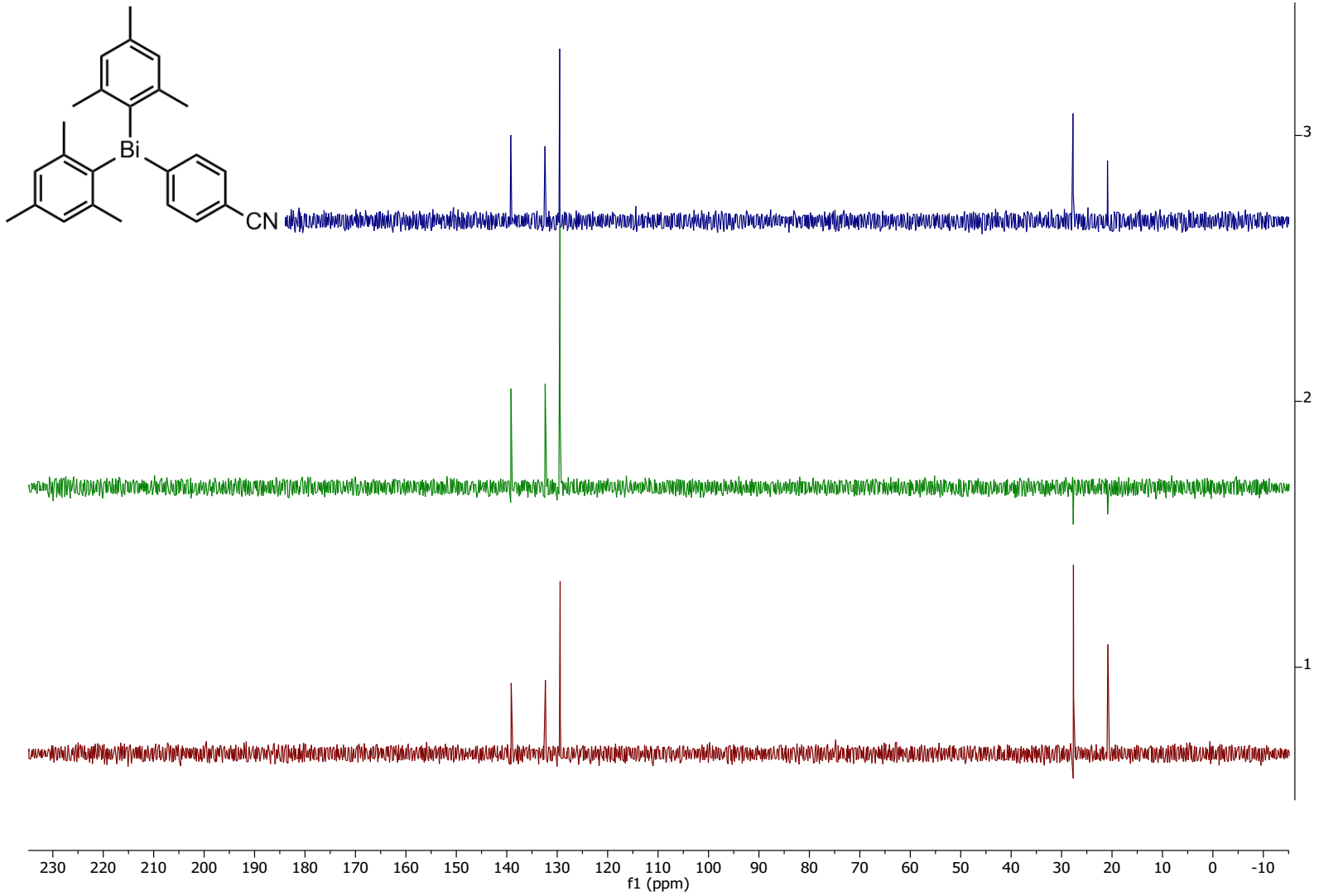


Figure S45. ^{13}C DEPT of **1g** in $CDCl_3$

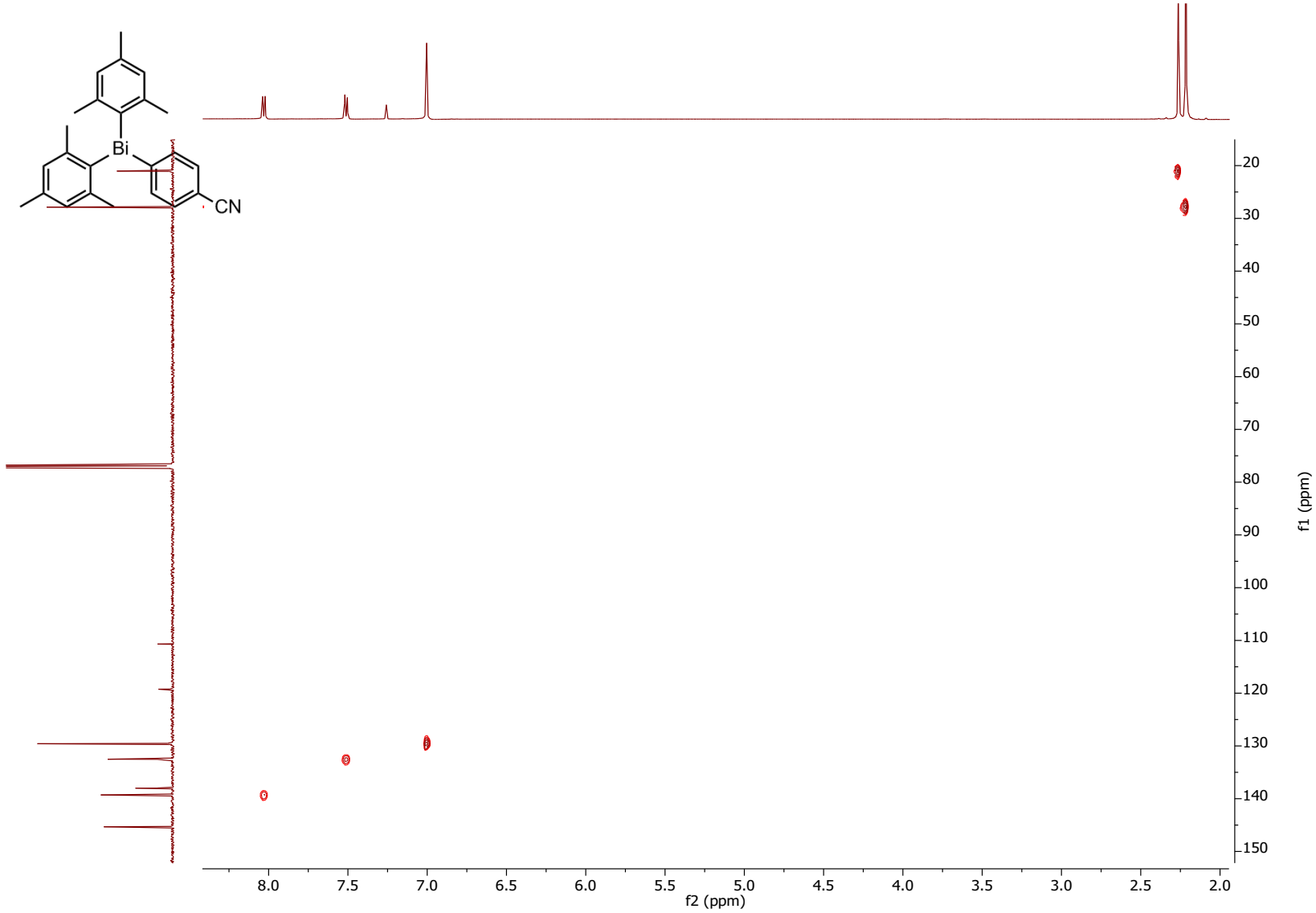
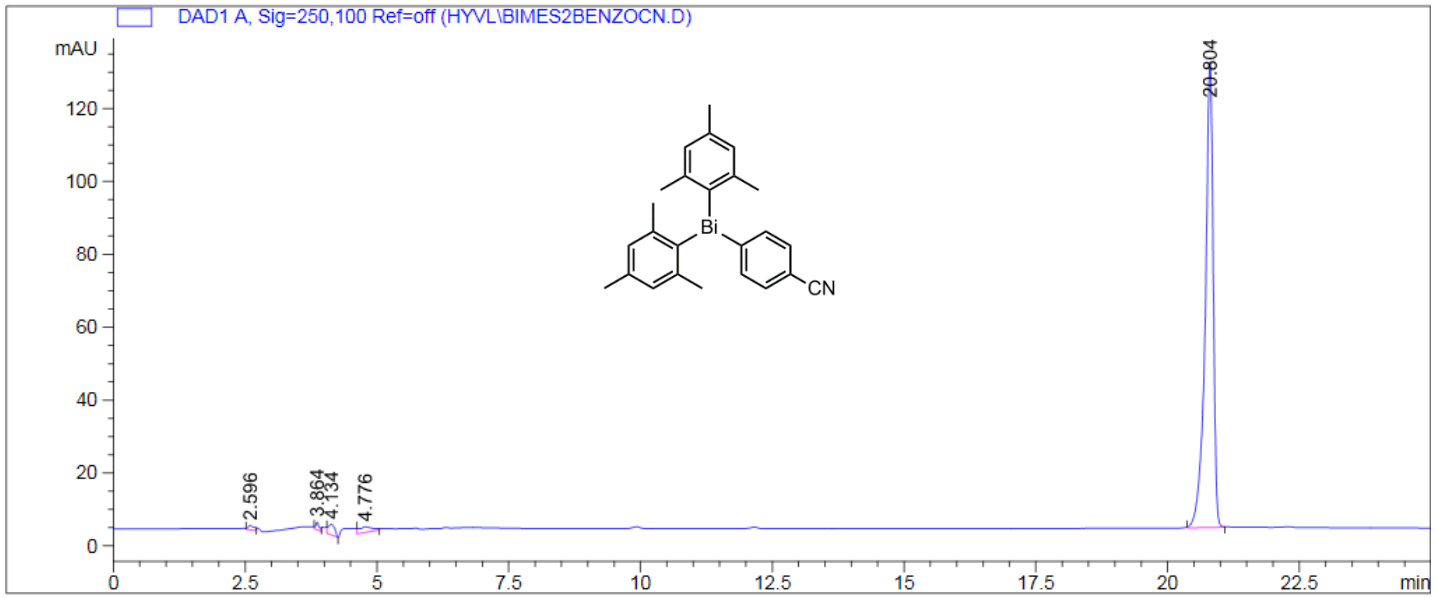


Figure S46. 2D HSQC of **1g** in $CDCl_3$

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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   2.596 BB    0.1066    9.04404    1.16519   0.6390
   2   3.864 BB    0.0664    9.94713    2.13506   0.7029
   3   4.134 BV    0.1346   24.92050    2.94877   1.7609
   4   4.776 BB    0.2193   27.37470    1.60261   1.9343
   5  20.804 BB    0.1566 1343.94800  127.86018  94.9629
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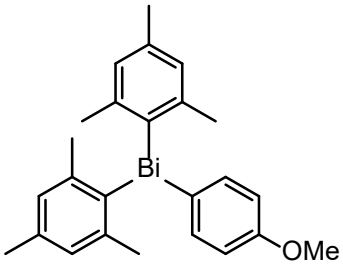
Figure S47. HPLC Chromatogram of **1g**

NMR Spectra and EA Report of Compound 1h



Chemical Formula: $BiOC_{25}H_{29}$
Molecular Weight: 554.49
Elemental Analysis: C: 54.15; Bi: 37.69; H: 5.27; O: 2.89

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	11/1/2019 6:03:25PM
User ID	Administrator
Comments	TLG_2_131A [Hyvl]

DATE & TIME	11/1/2019 3:14:38 PM	P_ID	EA LAB
SAMPLE ID	19617	USER ID	Administrator
WEIGHT (mg)	2.155	MODE	CHN

CARBON	54.098%
HYDROGEN	5.153%
NITROGEN	-.008%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S48. EA report for **1h**

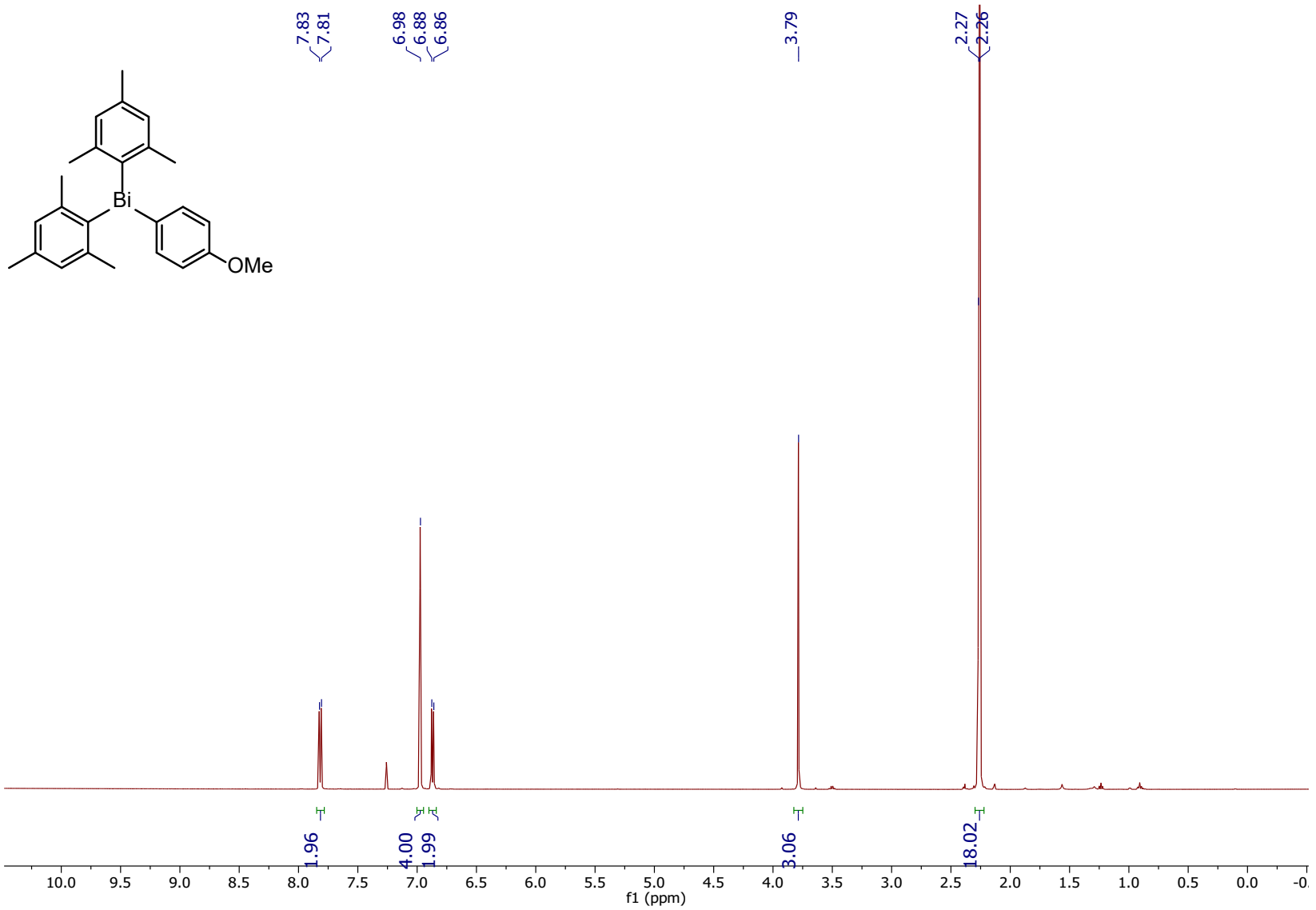


Figure S49. ^{1}H NMR of **1h** in $CDCl_3$

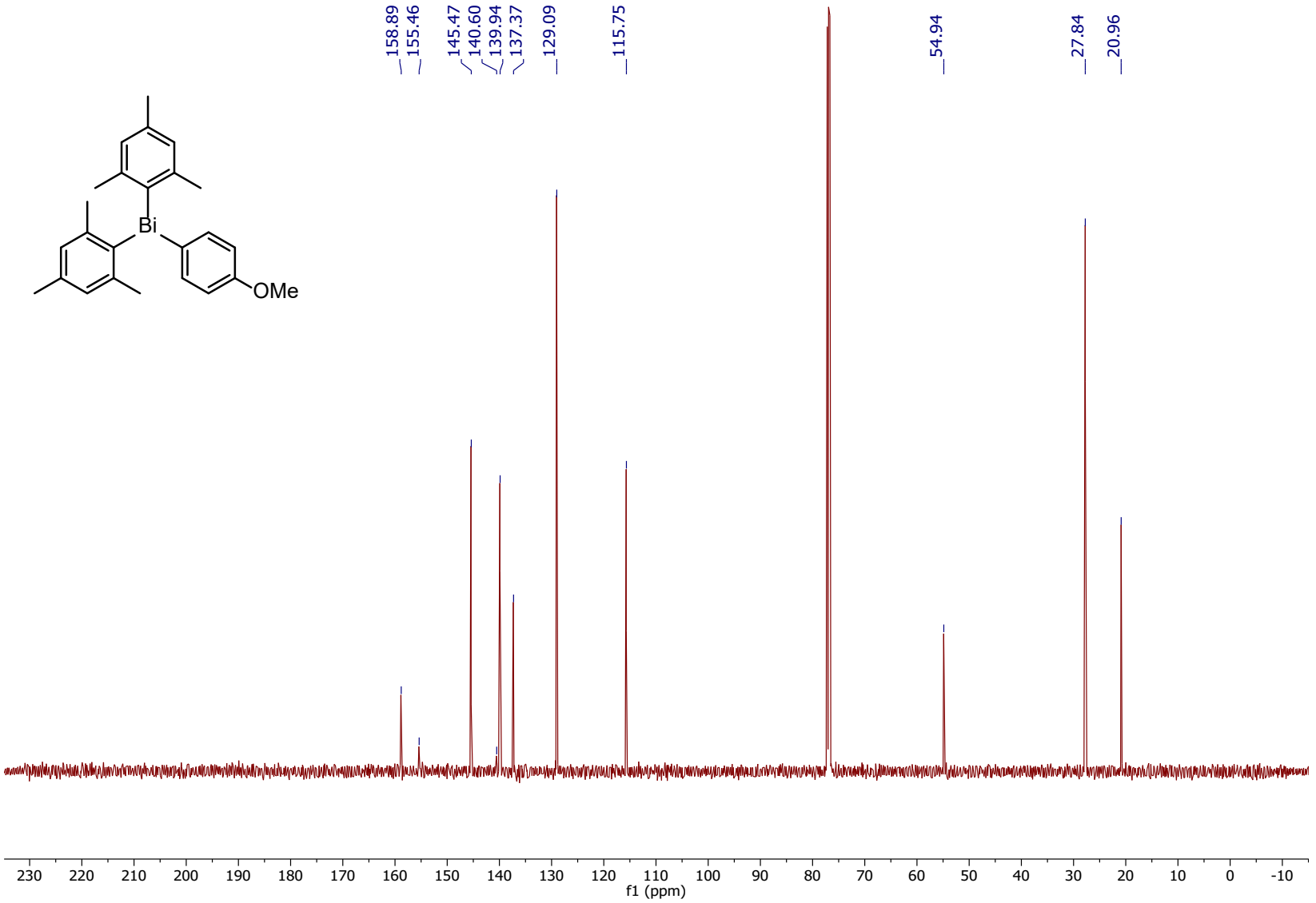


Figure S50. ^{13}C $\{^{1}H\}$ NMR of **1h** in $CDCl_3$

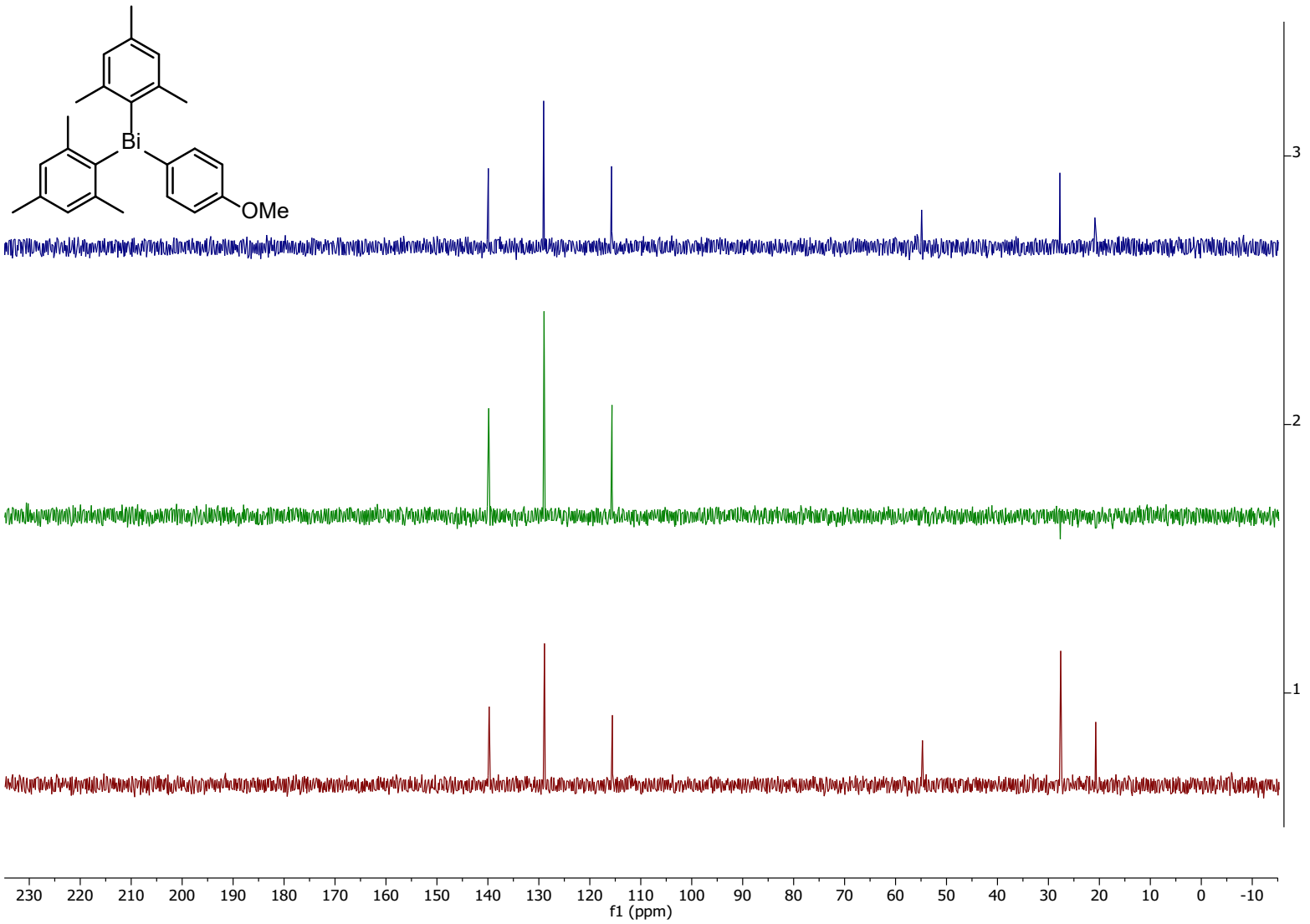


Figure S51. ^{13}C DEPT of **1h** in $CDCl_3$

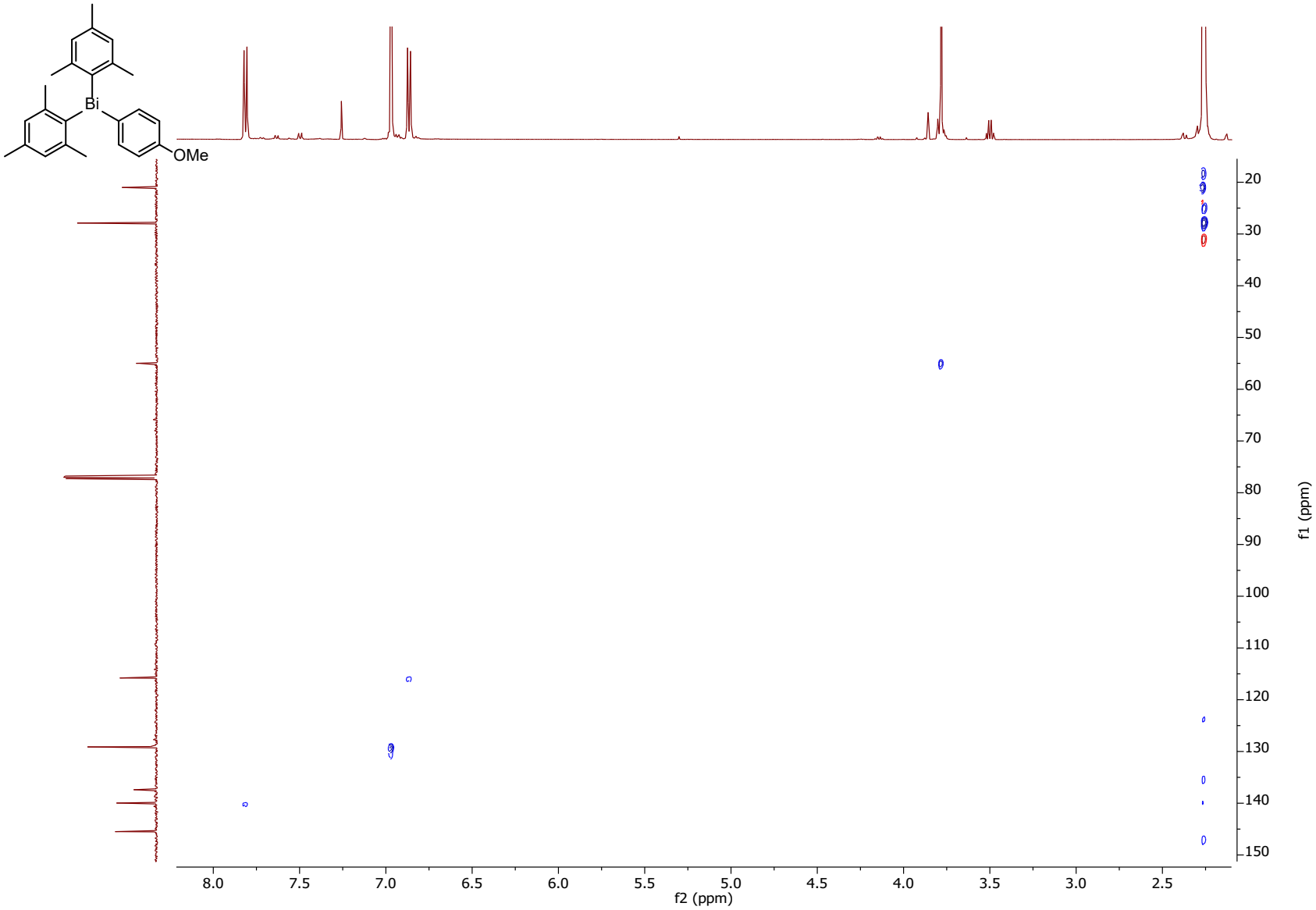


Figure S52. 2D HSQC of **1h** in $CDCl_3$

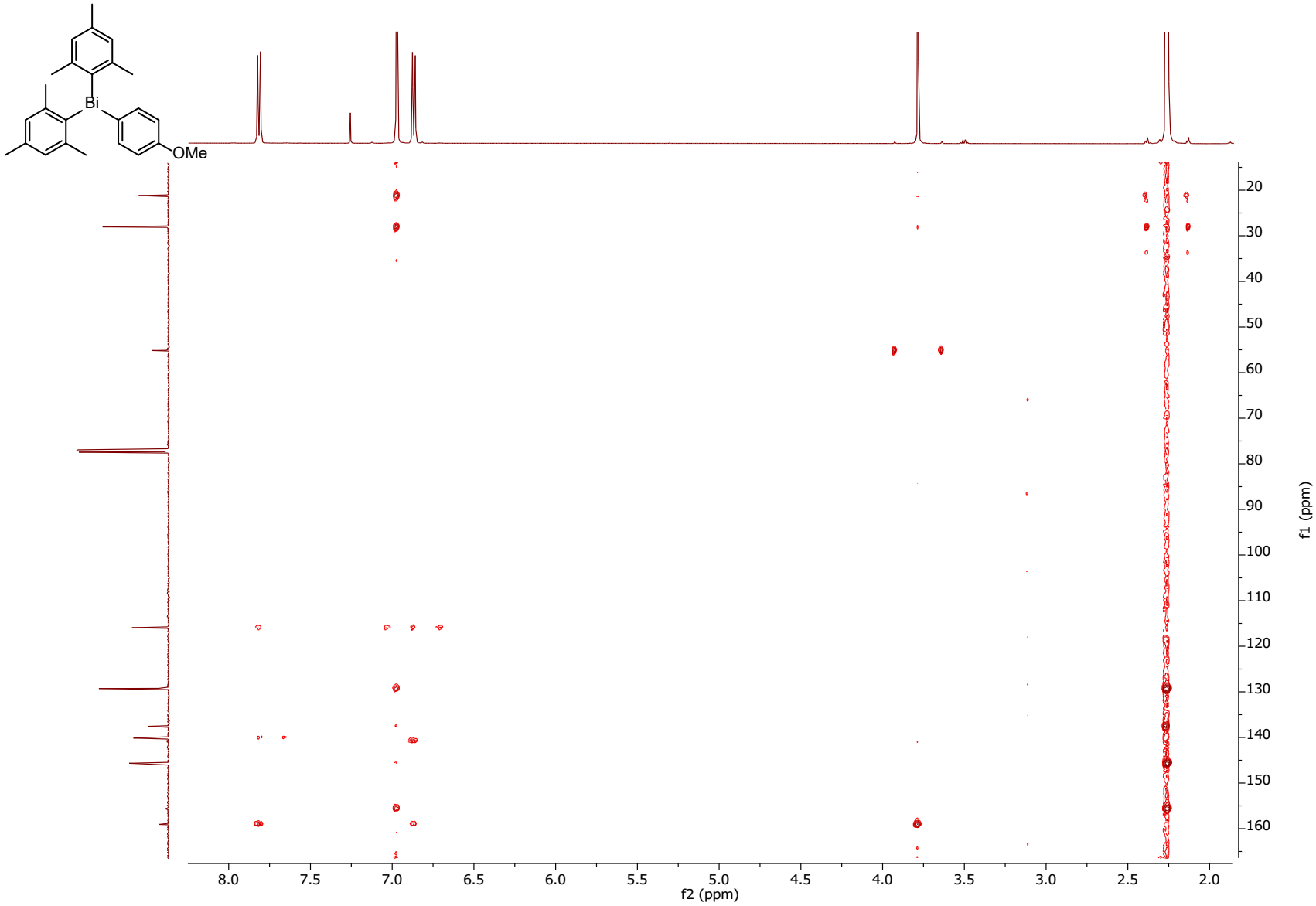
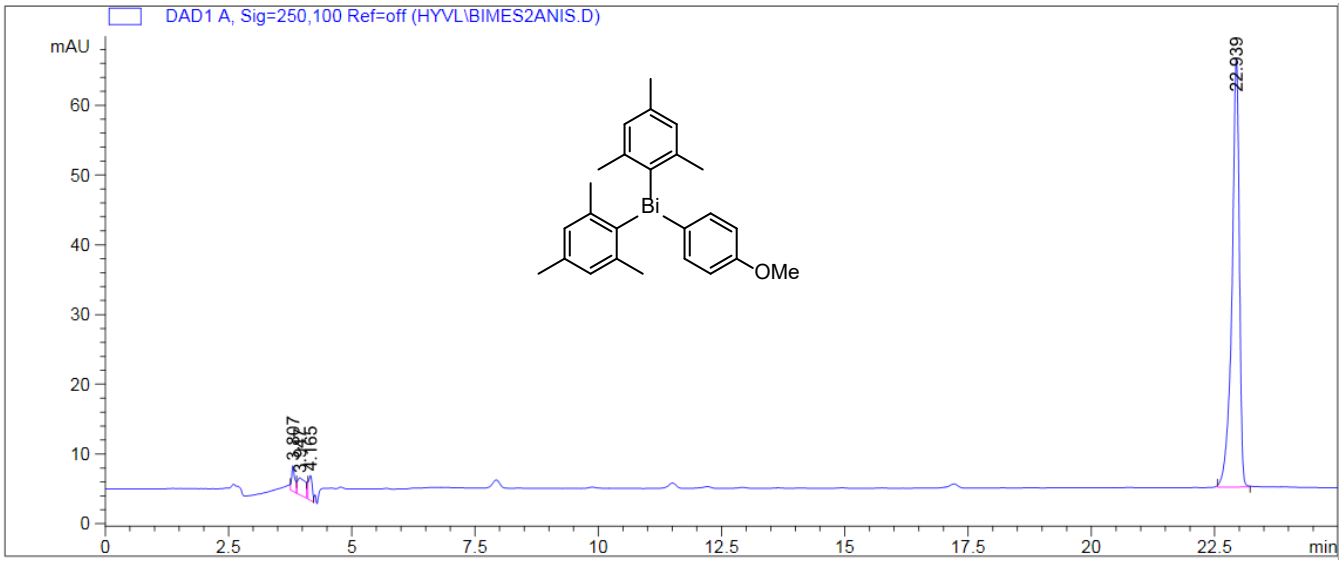


Figure S53. 2D HMBC of **1h** in $CDCl_3$



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Area Percent Report

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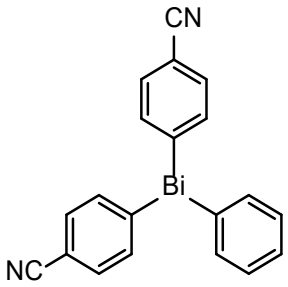
Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 20.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.807	BV	0.0653	16.86088	3.68864	2.4013
2	3.947	VB	0.1545	27.97085	2.42597	3.9836
3	4.165	BV	0.0754	18.10877	3.55799	2.5791
4	22.939	BB	0.1554	639.20490	61.44005	91.0360

Figure S54. HPLC Chromatogram of **1h**

NMR Spectra and EA Report of Compound 1i



Chemical Formula: $BiN_2C_{20}H_{13}$

Molecular Weight: 490.32

Elemental Analysis: C: 48.99; Bi: 42.62; H: 2.67; N: 5.71

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/31/2019 4:52:39PM
User ID	Administrator
Comments	TLG_2_16 [Hyvl]

DATE & TIME	5/31/2019 2:58:32 PM	P_ID	EA LAB
SAMPLE ID	19332	USER ID	Administrator
WEIGHT (mg)	2.214	MODE	CHN

CARBON	49.146%
HYDROGEN	2.616%
NITROGEN	5.870%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S55. EA report for **1i**

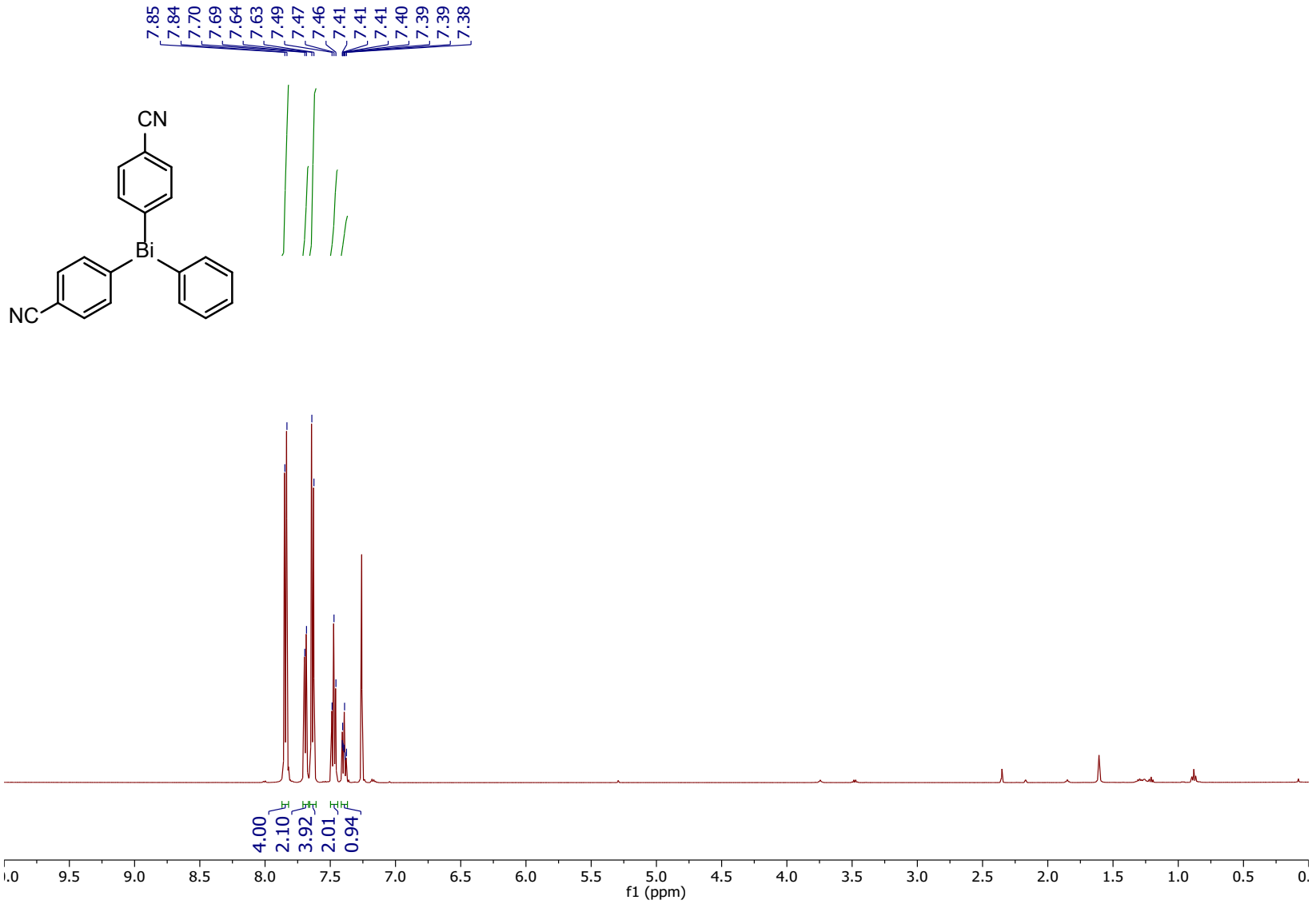


Figure S56. ^{1}H NMR of **1i** in $CDCl_3$

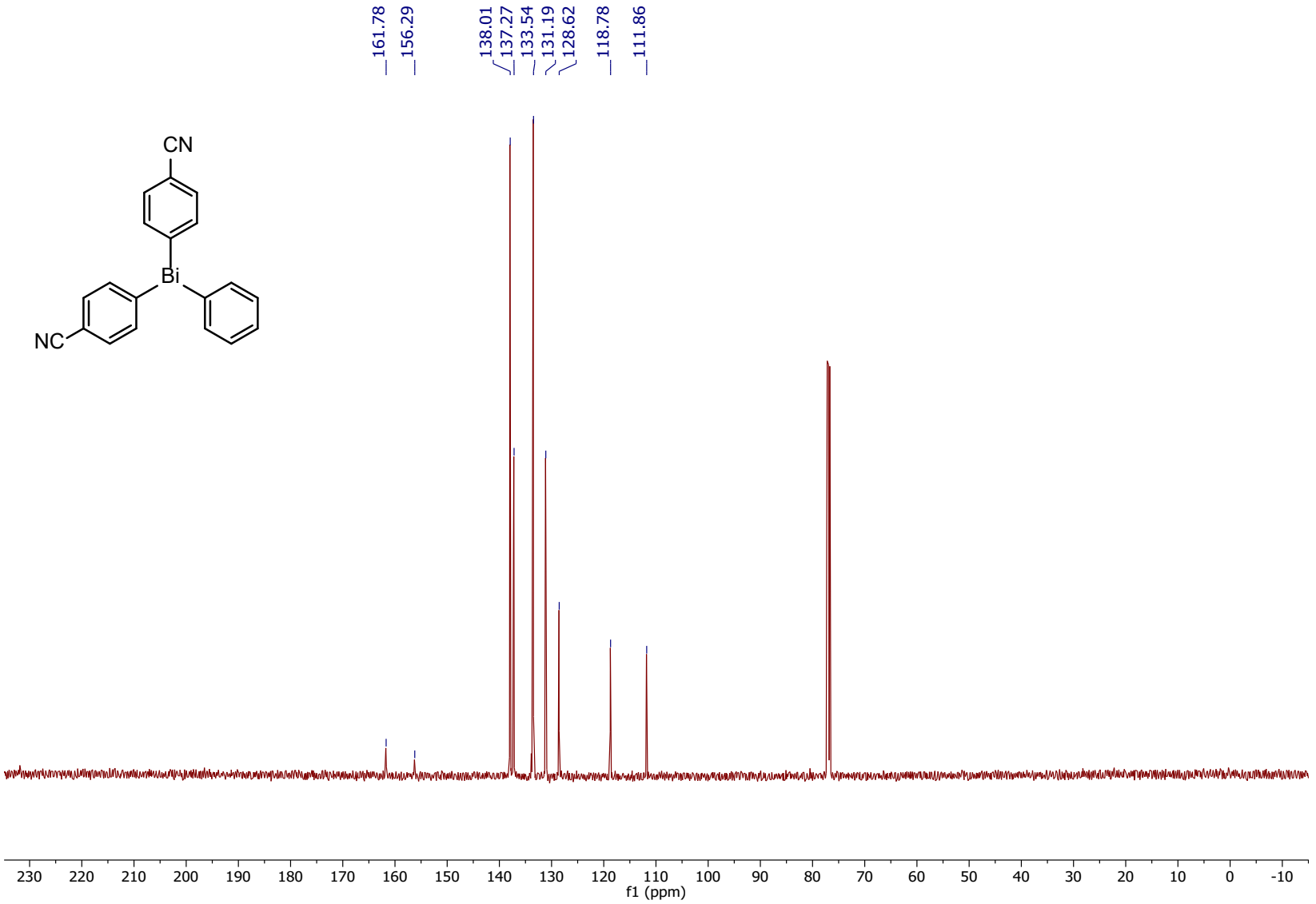


Figure S57. ^{13}C $\{^{1}H\}$ NMR of **1i** in $CDCl_3$

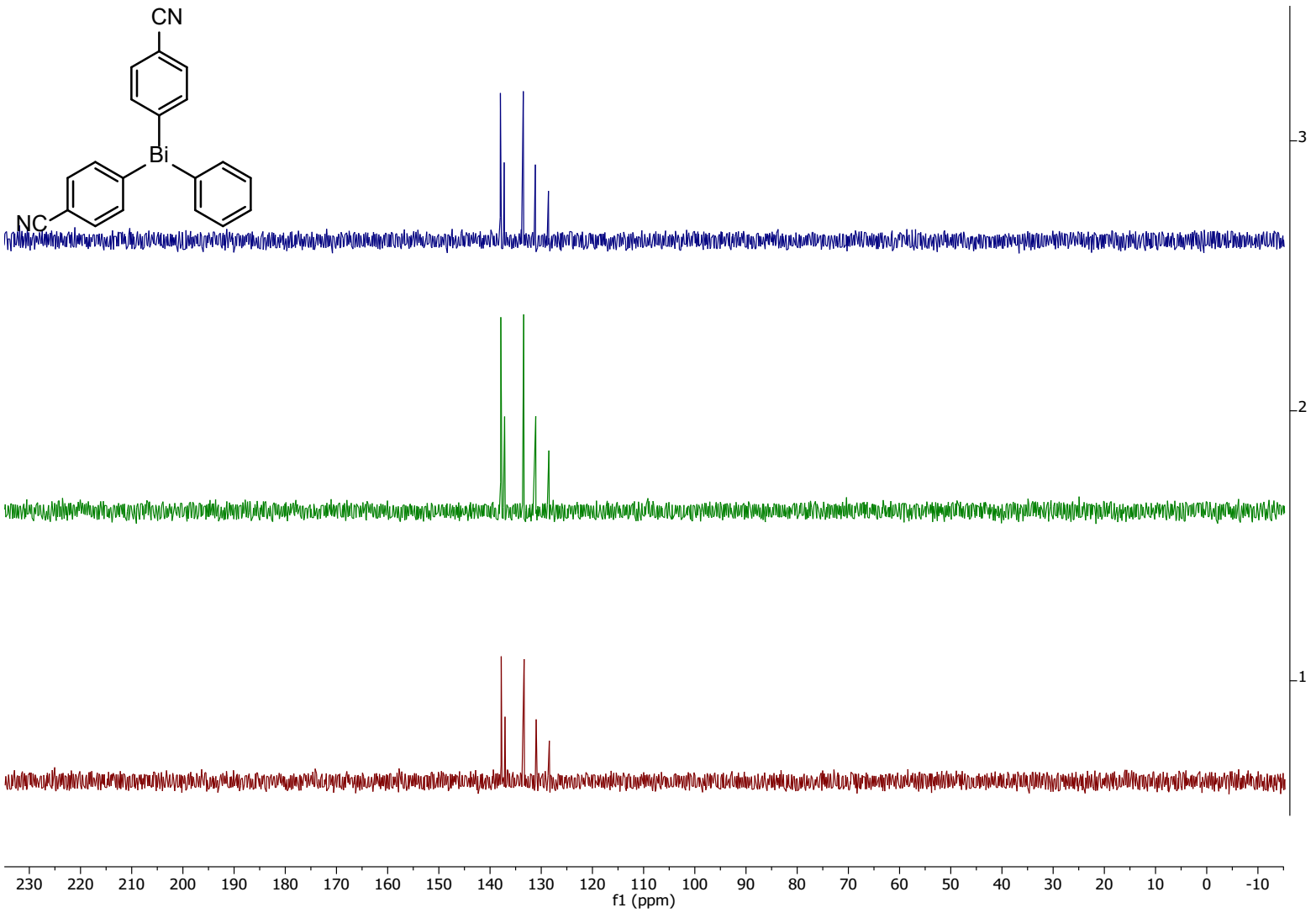


Figure S58. ^{13}C DEPT of **1i** in $CDCl_3$

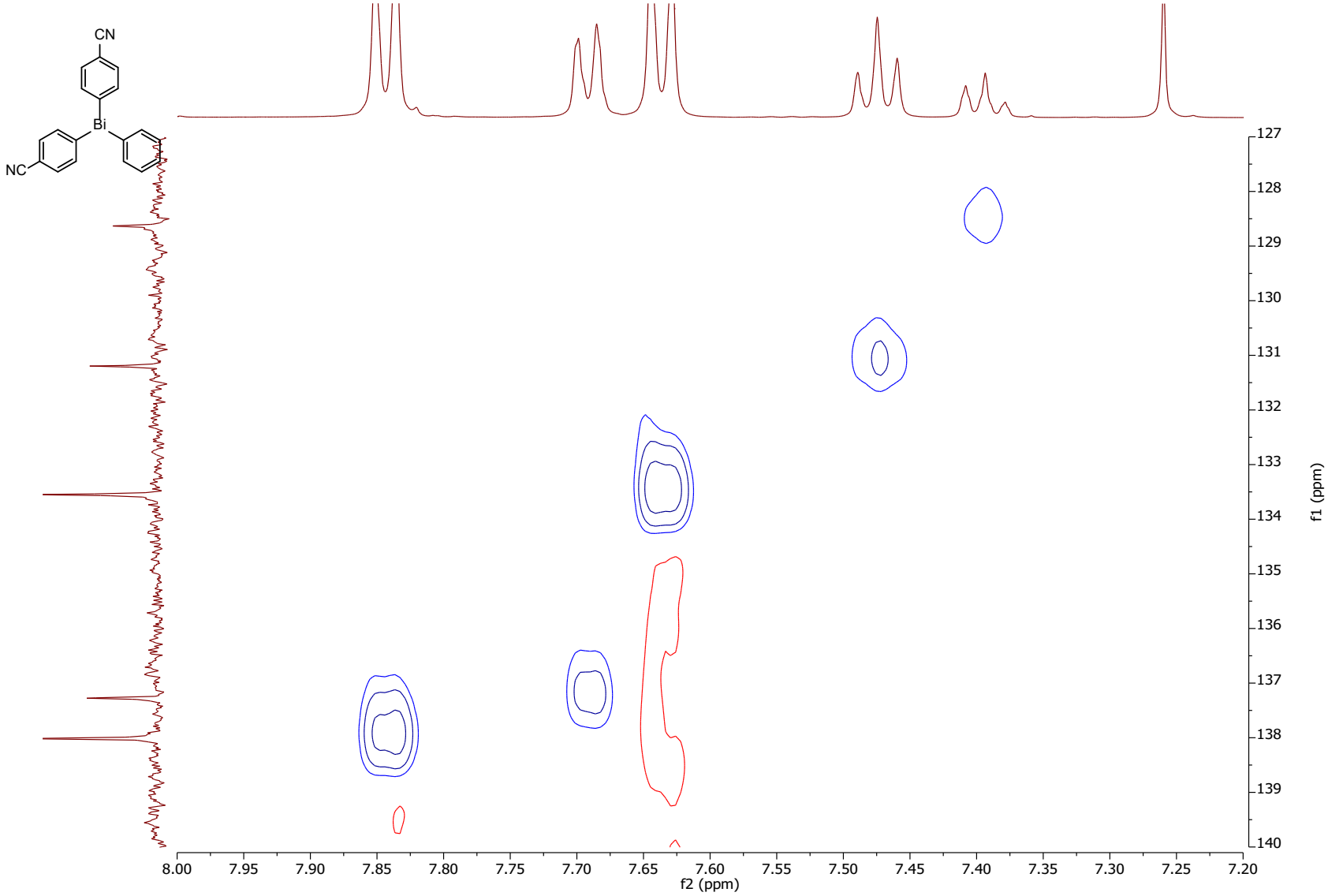
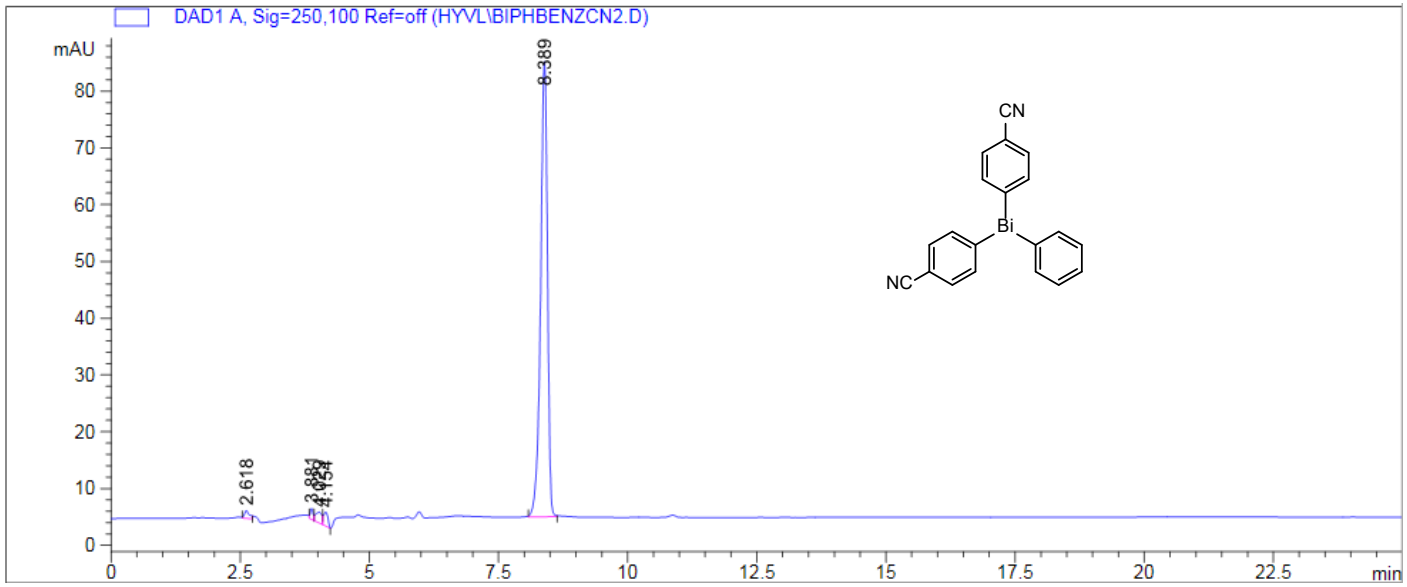


Figure S59. 2D HSQC of **1i** in $CDCl_3$

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                    Area Percent Report
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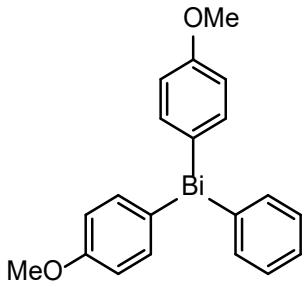
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   2.618 BB    0.0923    9.03760    1.38157   1.1502
   2   3.881 BV    0.0581    7.41773    1.96129   0.9440
   3   4.029 VV    0.1099   15.81809    1.92457   2.0131
   4   4.154 VV    0.0928   14.38671    2.43910   1.8310
   5   8.389 BB    0.1415  739.08337   80.22154  94.0617
```

Figure S60. HPLC Chromatogram of **1i**

NMR Spectra and EA Report of Compound 1j



Chemical Formula: $BiO_2C_{20}H_{19}$

Molecular Weight: 500.35

Elemental Analysis: C: 48.01; Bi: 41.77; H: 3.83; O: 6.40

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	5/10/2019 2:30:14PM
User ID	Administrator
Comments	TLG_1_161 [Hyvl]

DATE & TIME	5/10/2019 11:45:40 AM	P_ID	EA LAB
SAMPLE ID	19288	USER ID	Administrator
WEIGHT (mg)	2.087	MODE	CHN

CARBON	48.237%
HYDROGEN	3.656%
NITROGEN	-.008%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S61. EA report for **1j**

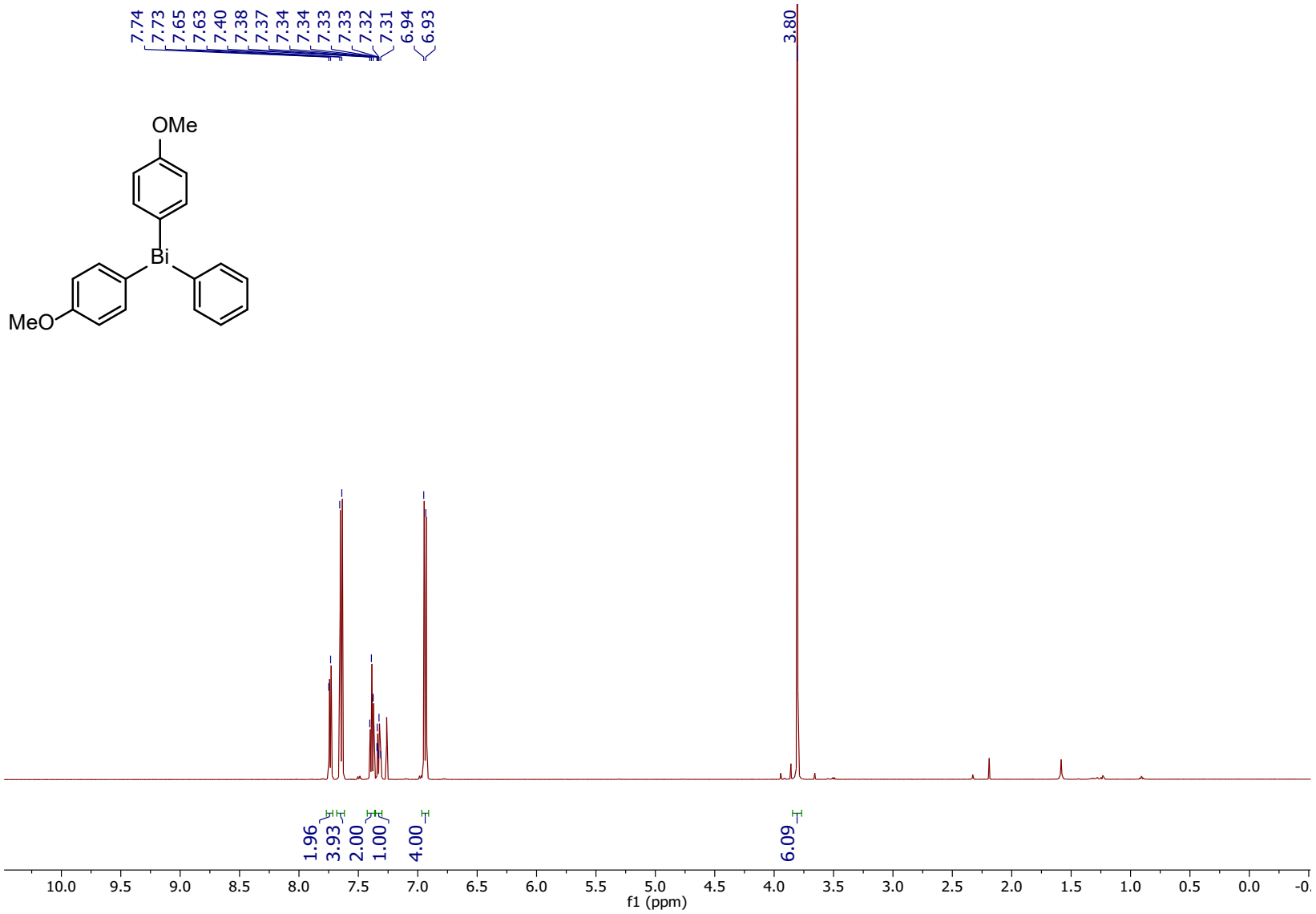


Figure S62. ^{1}H NMR of **1j** in $CDCl_3$

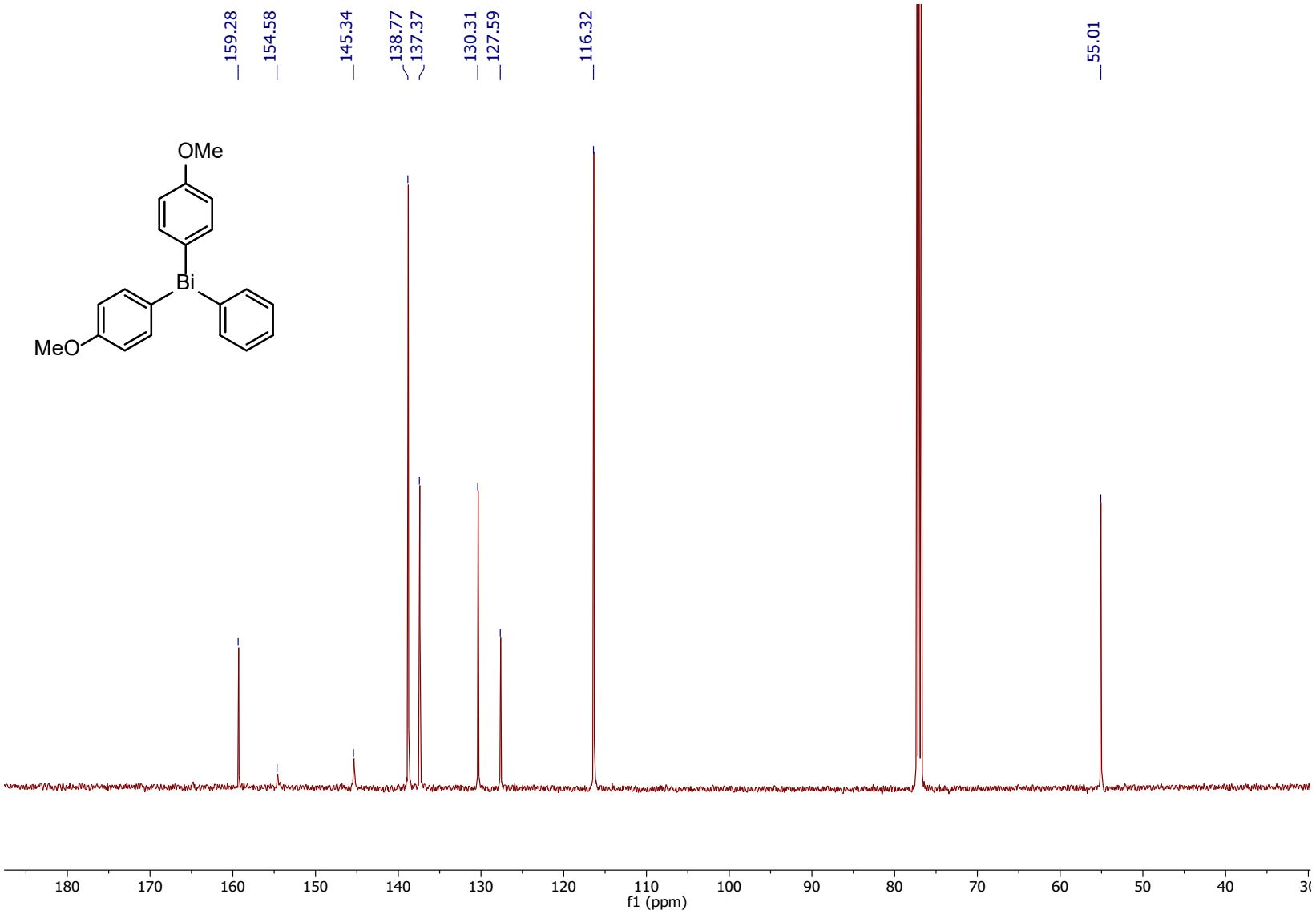


Figure S63. ^{13}C $\{^{1}H\}$ NMR of **1j** in $CDCl_3$

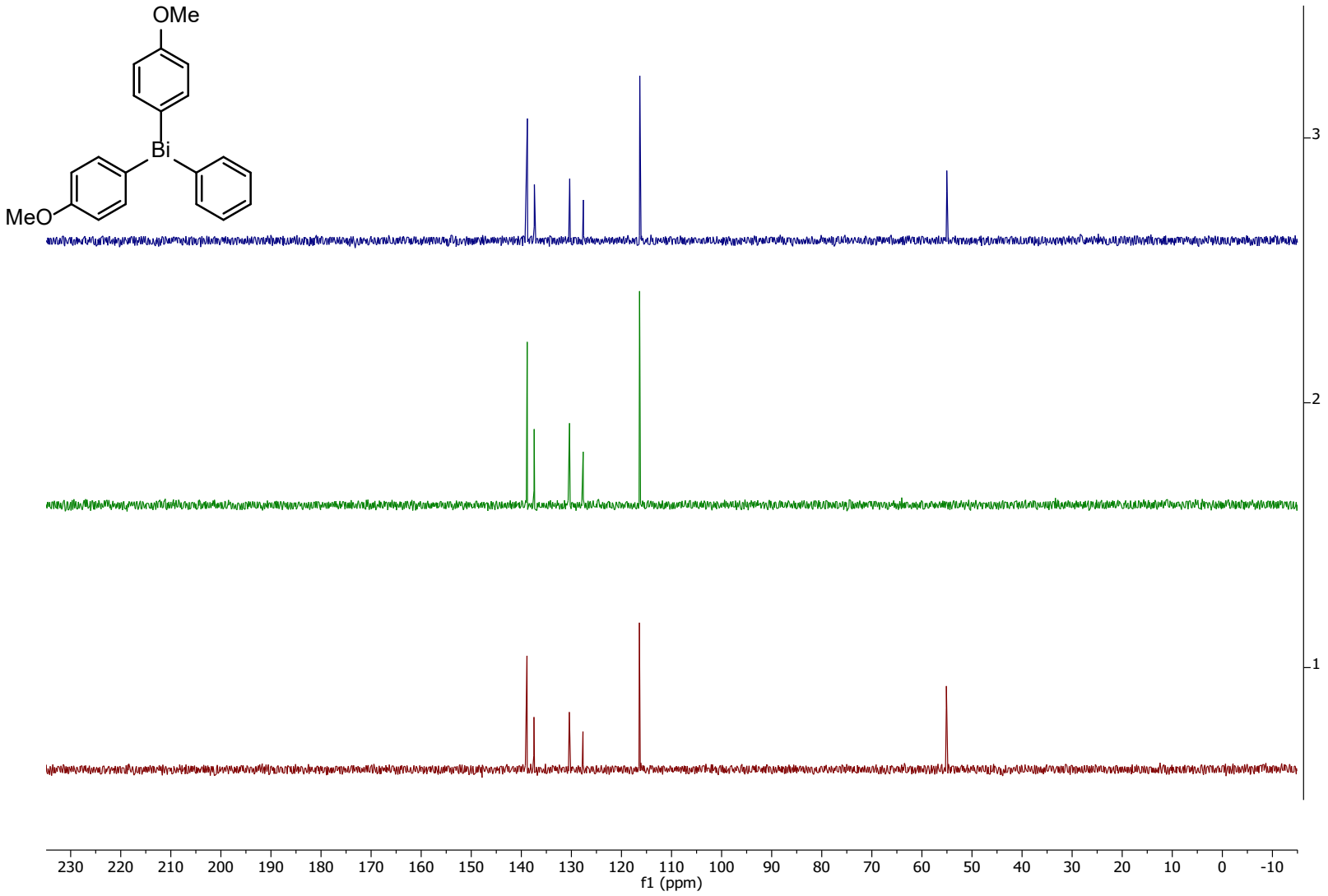


Figure S64. ^{13}C DEPT of **1j** in $CDCl_3$

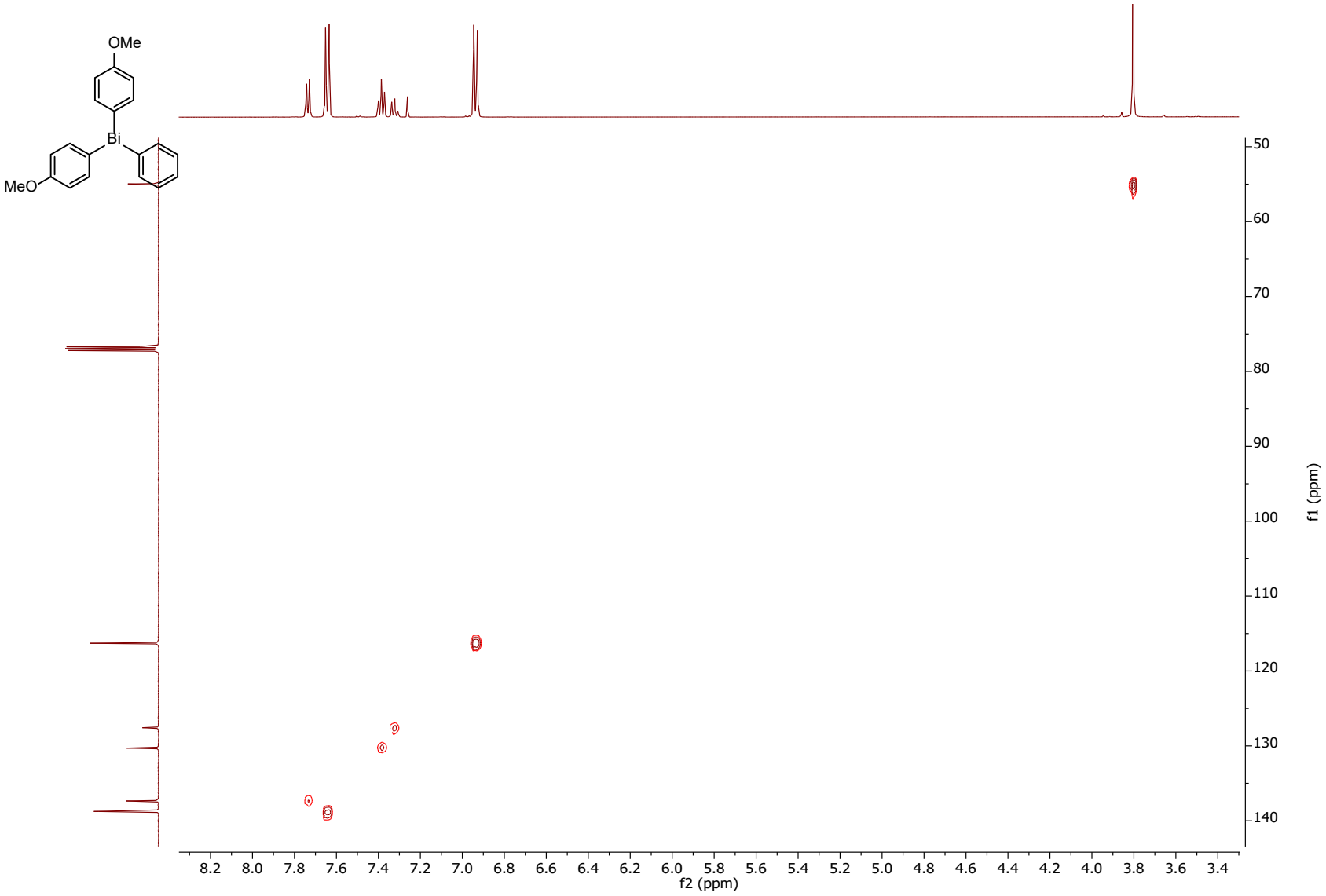
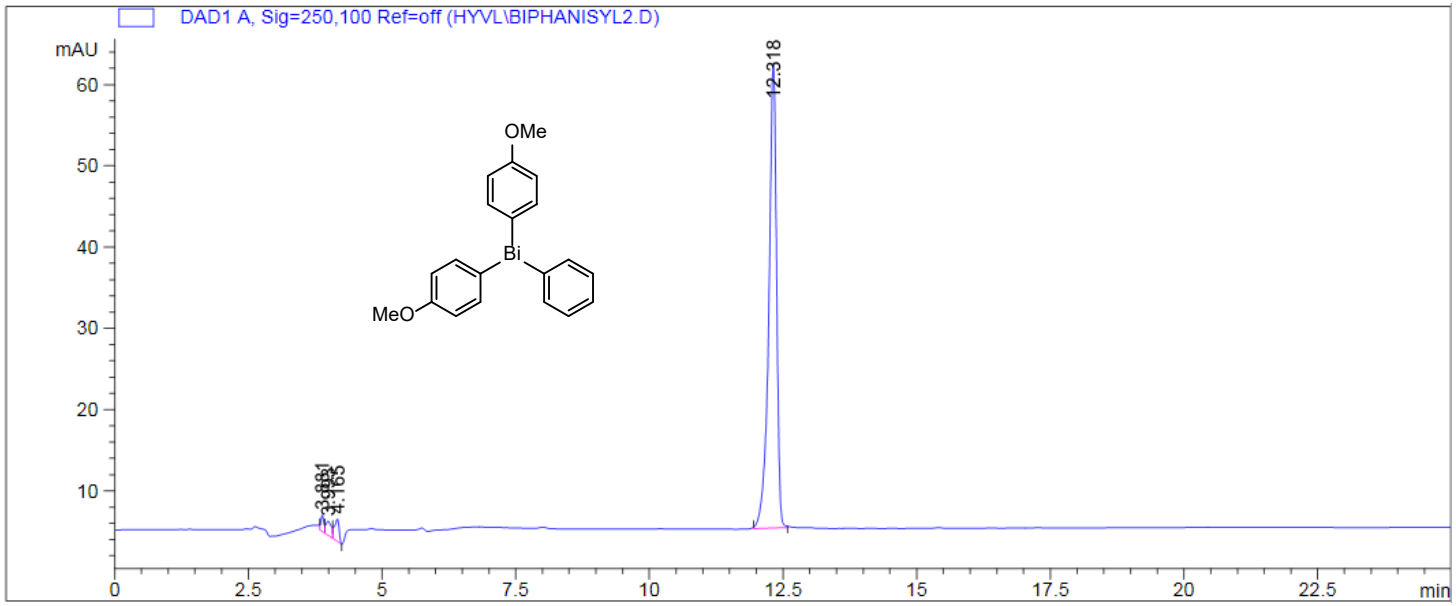


Figure S65. 2D HSQC of **1j** in $CDCl_3$

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================================================================================
                              Area Percent Report
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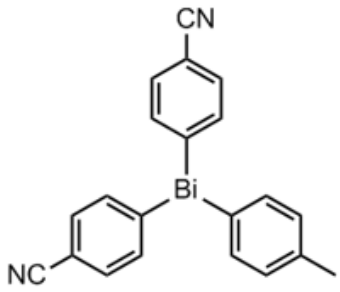
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.881 BV    0.0568    7.76358    2.02089   1.2641
   2   3.993 VV    0.1062   13.08445    1.73126   2.1304
   3   4.165 VV    0.0849   15.91393    2.77373   2.5911
   4  12.318 BB    0.1516  577.41180   57.26262  94.0144
```

Figure S66. HPLC Chromatogram of **1j**

NMR Spectra and EA Report of Compound 1k



Chemical Formula: $BiN_2C_{21}H_{15}$

Molecular Weight: 504.35

Elemental Analysis: C: 50.01; Bi: 41.44; H: 3.00; N: 5.55

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	10/25/2019 6:17:32PM
User ID	Administrator
Comments	TLG_2_114B [Hyvl]

DATE & TIME	10/25/2019 3:06:16 PM	P_ID	EA LAB
SAMPLE ID	19598	USER ID	Administrator
WEIGHT (mg)	2.160	MODE	CHN

CARBON	50.008%
HYDROGEN	2.868%
NITROGEN	5.464%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Figure S67. EA report for **1k**

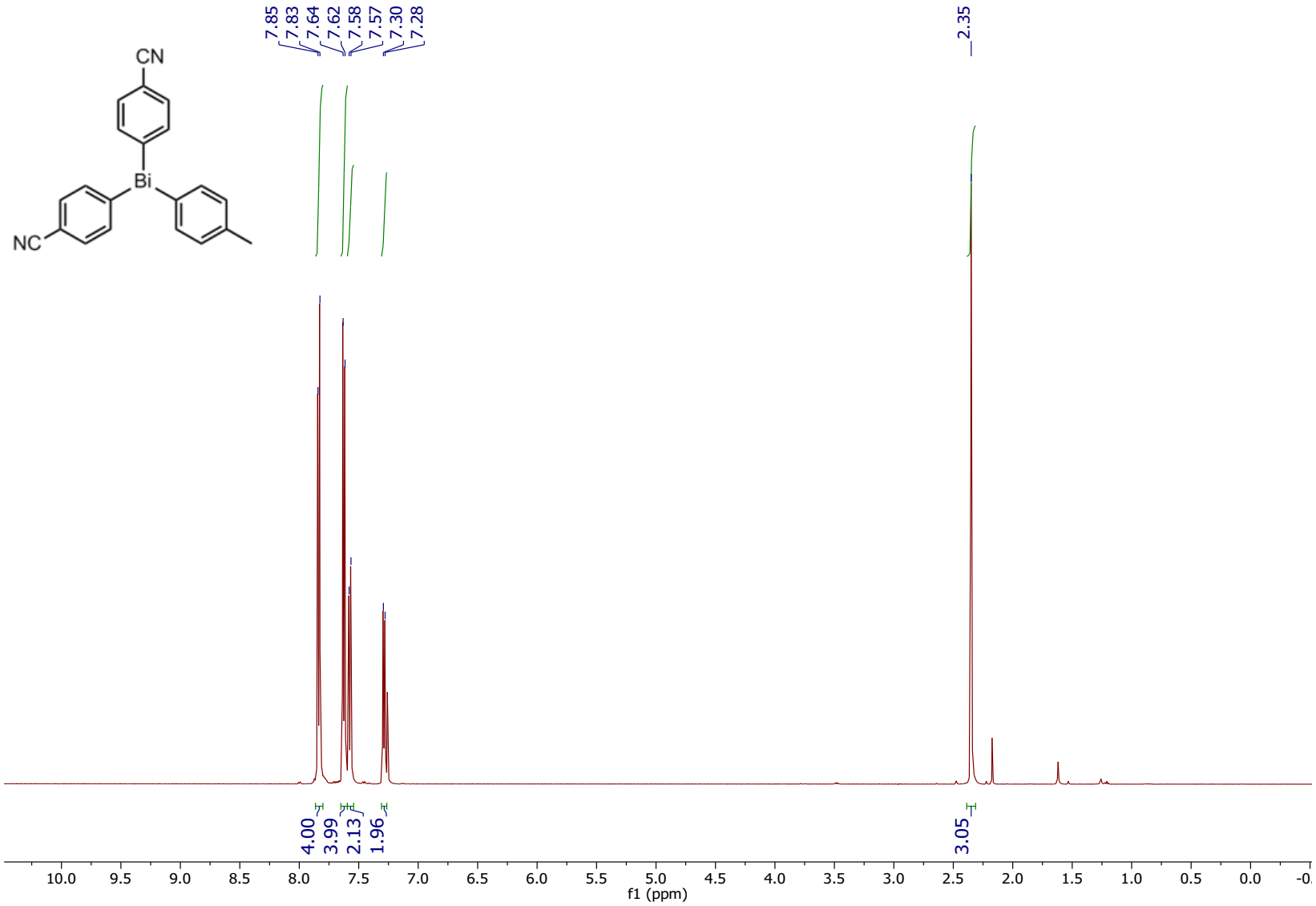


Figure S68. ^{1}H NMR of **1k** in $CDCl_3$

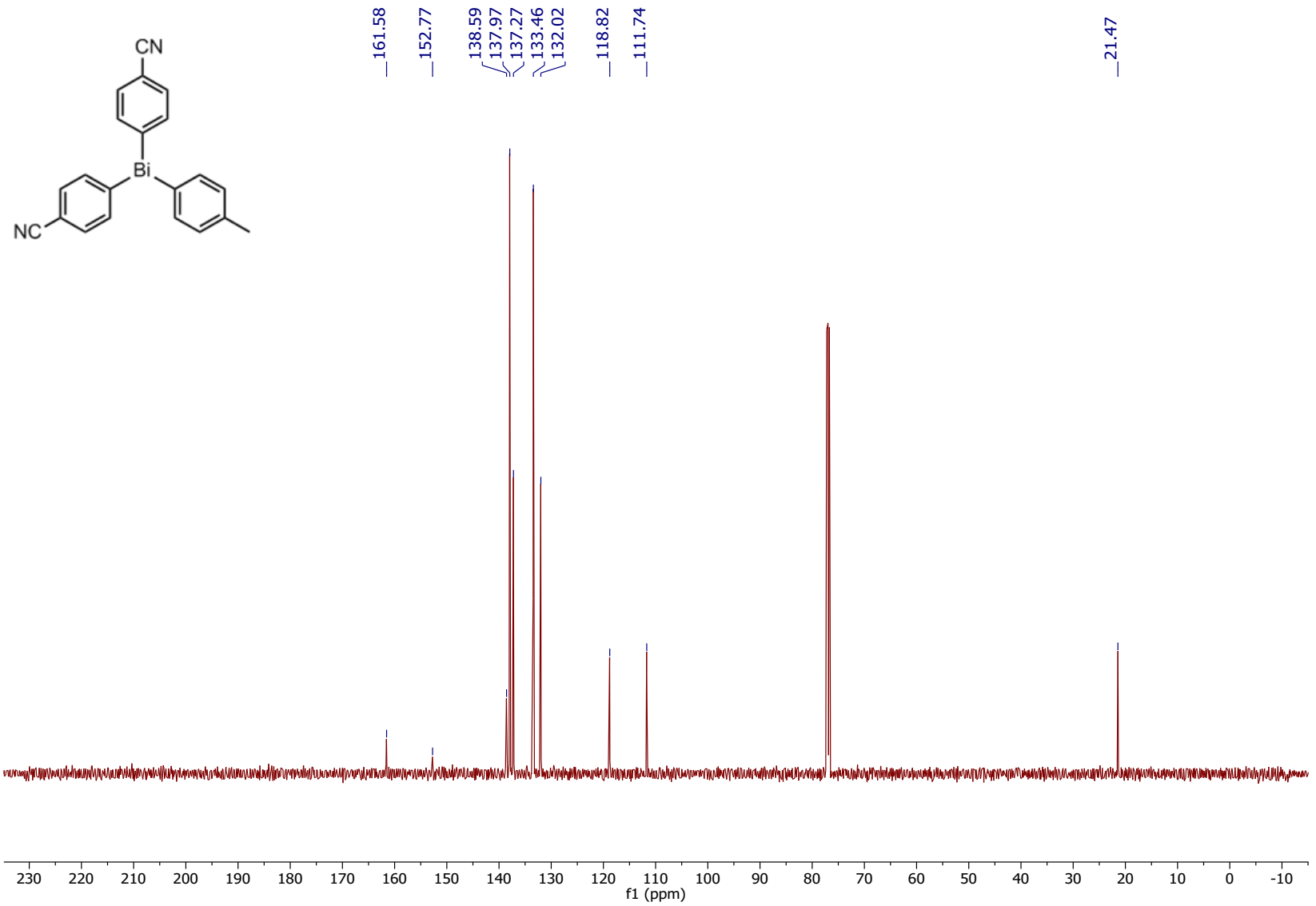


Figure S69. ^{13}C {^{1}H} NMR of **1k** in $CDCl_3$

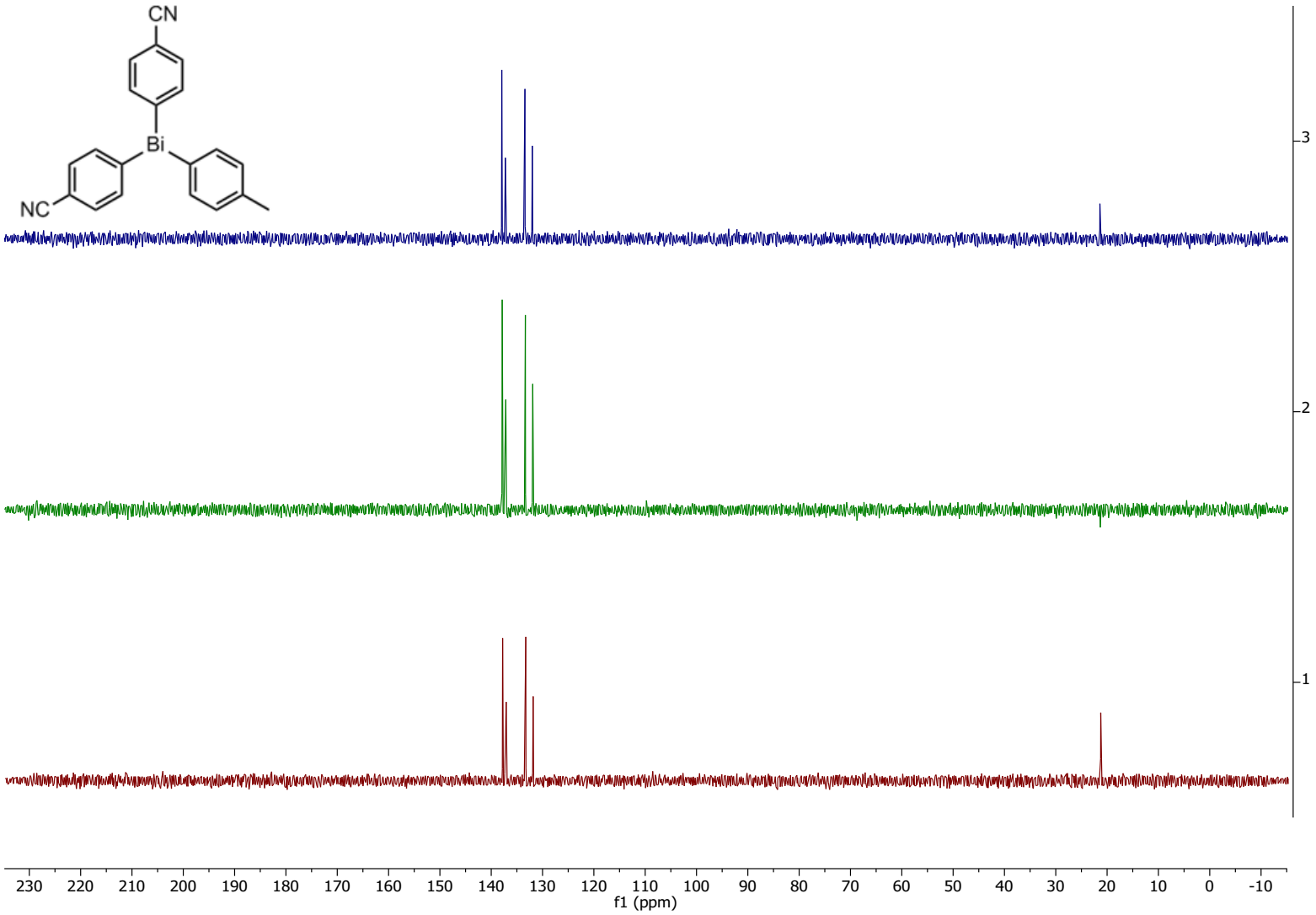


Figure S70. ^{13}C DEPT of **1k** in $CDCl_3$

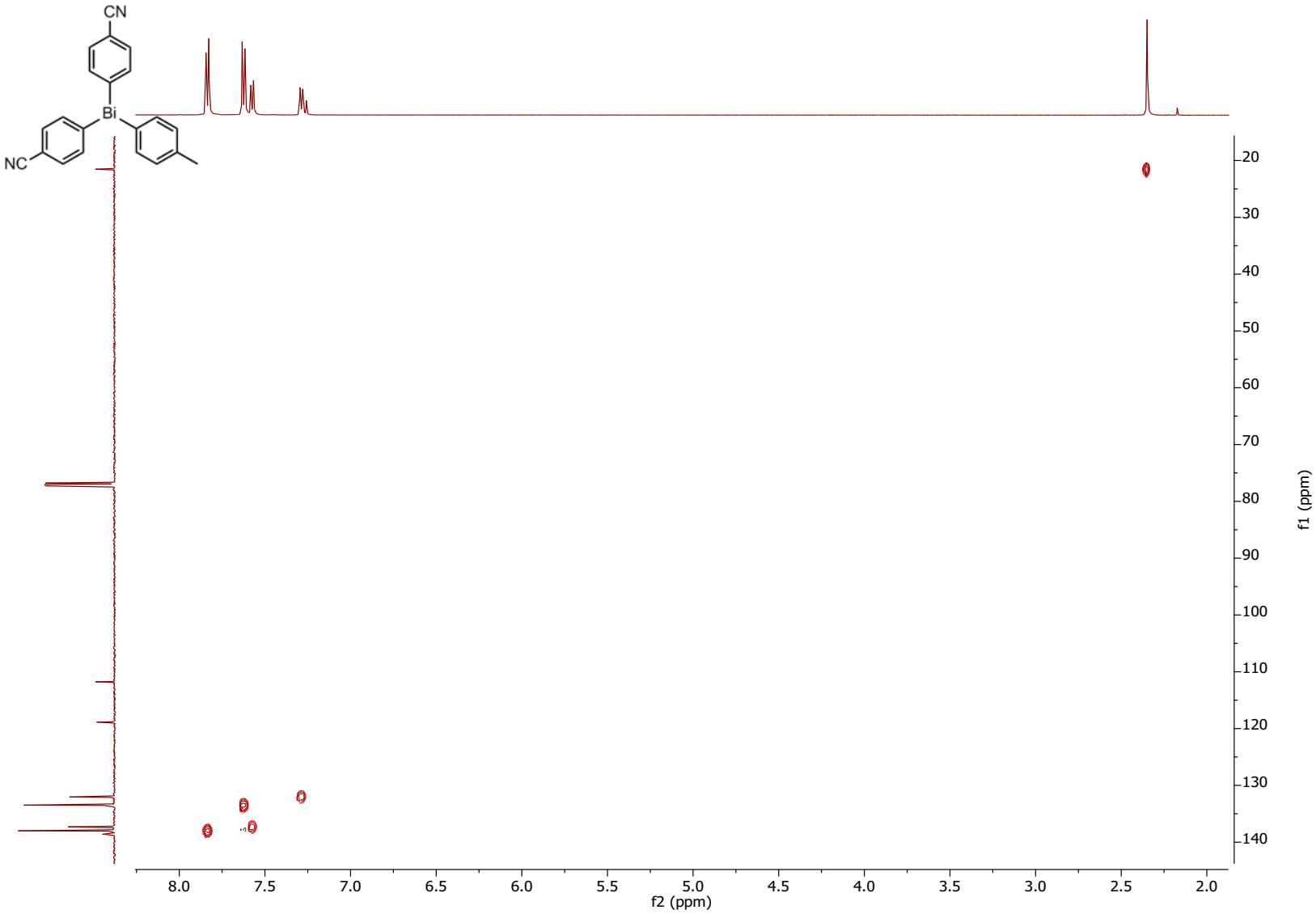
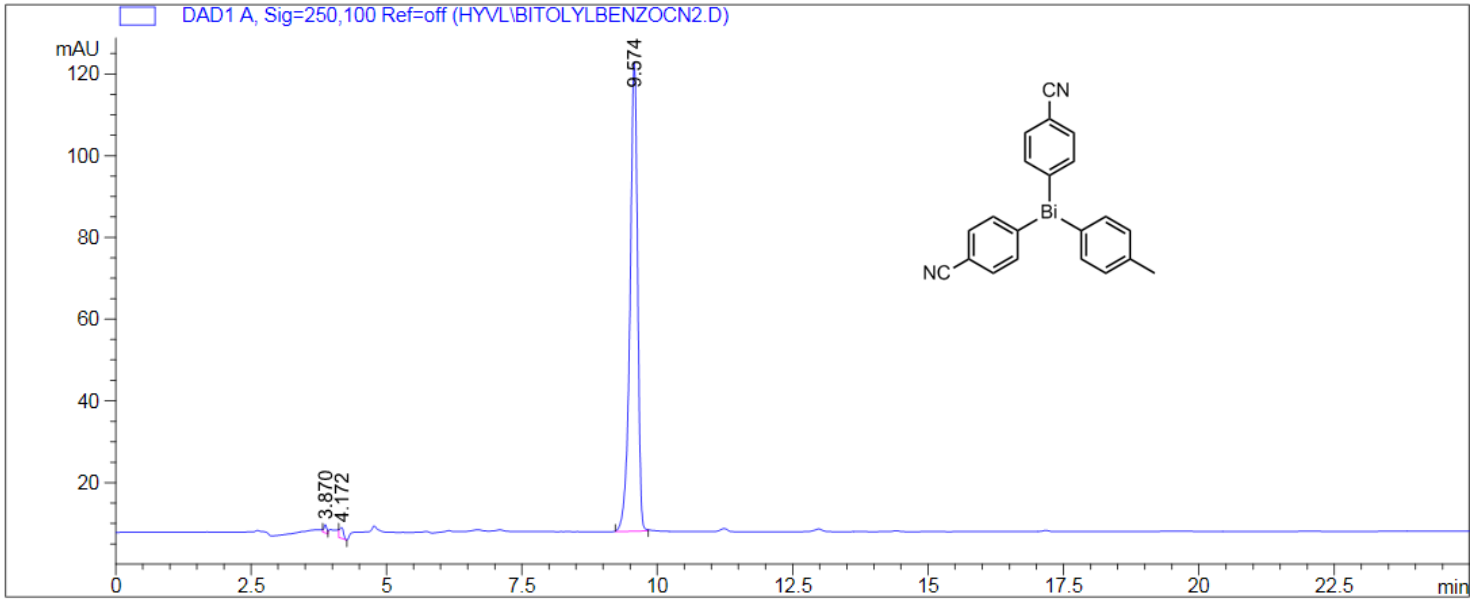


Figure S71. 2D HSQC of **1k** in $CDCl_3$

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                        Area Percent Report
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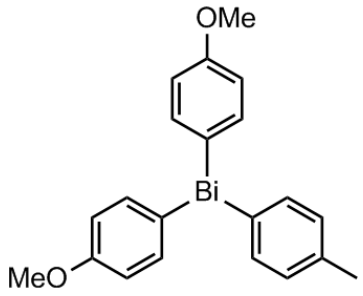
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   3.870 BV    0.0561    7.54989    1.99554   0.6639
   2   4.172 BV    0.0763   13.27818    2.65567   1.1676
   3   9.574 BB    0.1493 1116.35815  114.92860  98.1685
```

Figure S72. HPLC Chromatogram of **1k**

NMR Spectra and EA Report of Compound 1l



Chemical Formula: $BiO_2C_{21}H_{21}$

Molecular Weight: 514.38

Elemental Analysis: C: 49.04; Bi: 40.63; H: 4.12; O: 6.22

CENTC Elemental Analysis Facility
University of Rochester
Rochester, NY 14627 USA
Email: ealab@chem.rochester.edu

Date of report	8/2/2019 5:06:28PM
User ID	Administrator
Comments	TLG 2-69 [Hyvl]

DATE & TIME	8/2/2019 12:06:17 PM	P_ID	EA LAB
SAMPLE ID	19485	USER ID	Administrator
WEIGHT (mg)	2.159	MODE	CHN

CARBON	49.059%
HYDROGEN	3.900%
NITROGEN	0.022%

Acknowledgment

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456.

Instrumentation

Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer.

Figure S73. EA report for **1l**

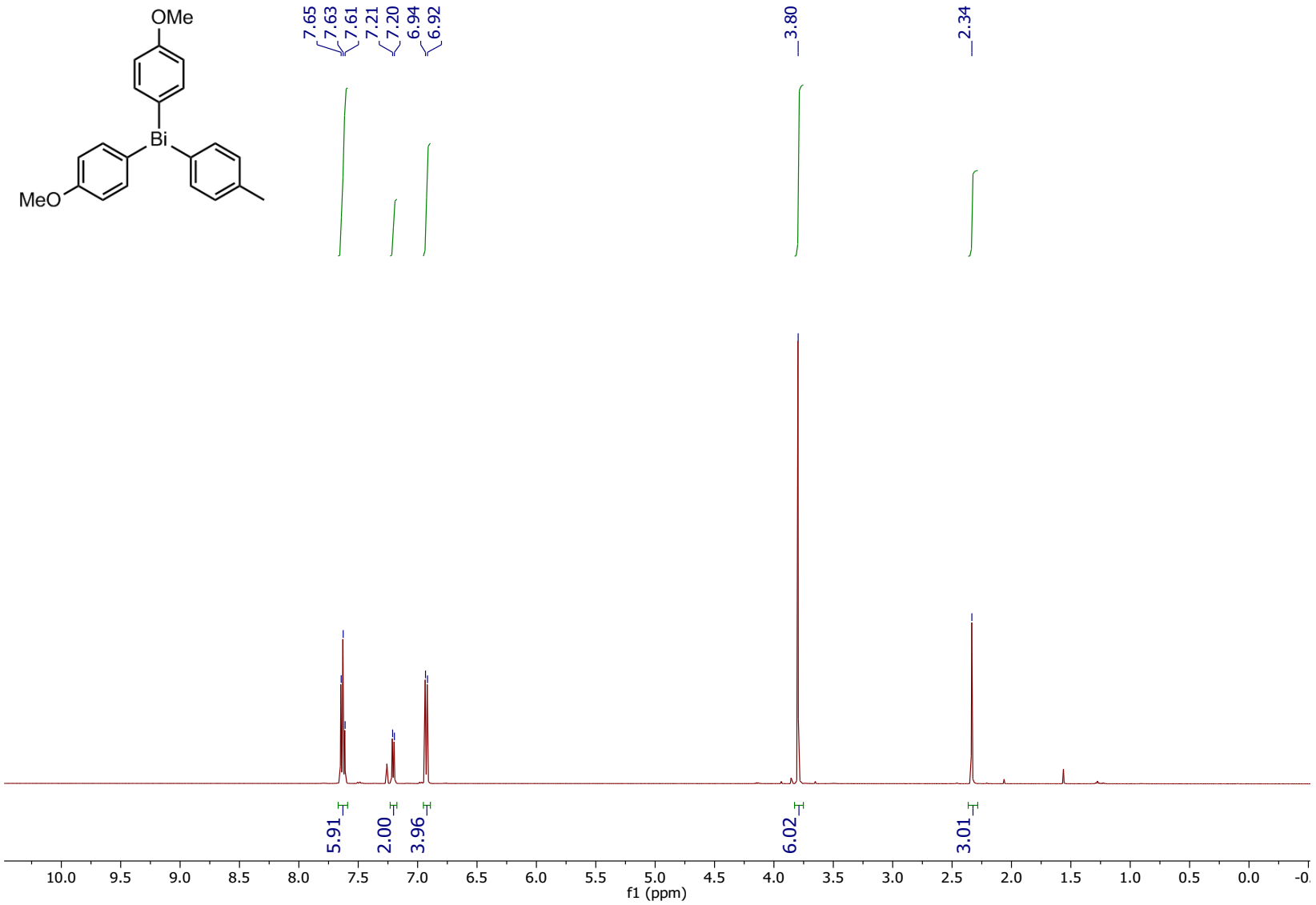


Figure S74. ^{1}H NMR of **1l** in $CDCl_3$

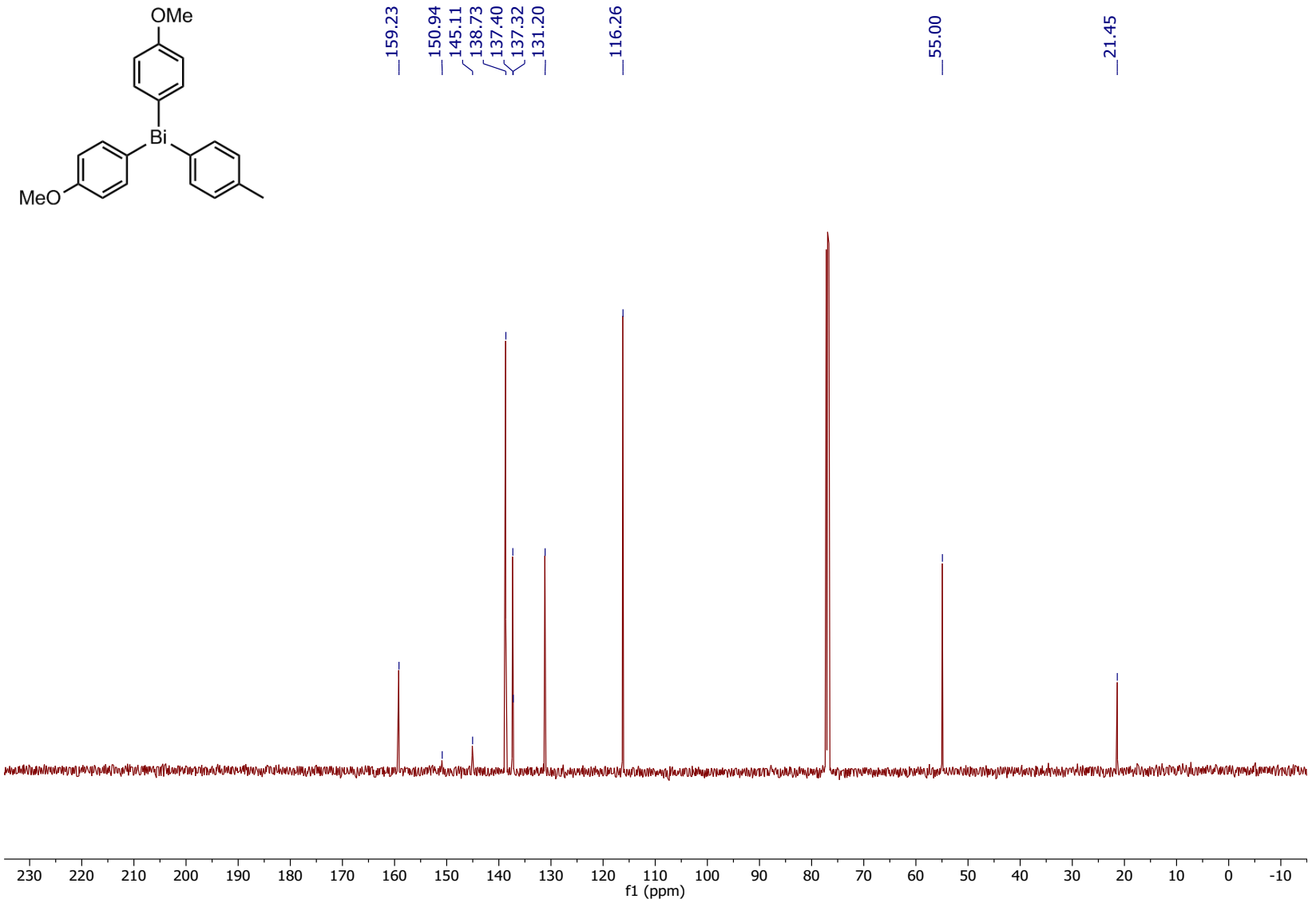


Figure S75. ^{13}C $\{^{1}H\}$ NMR of **1l** in $CDCl_3$

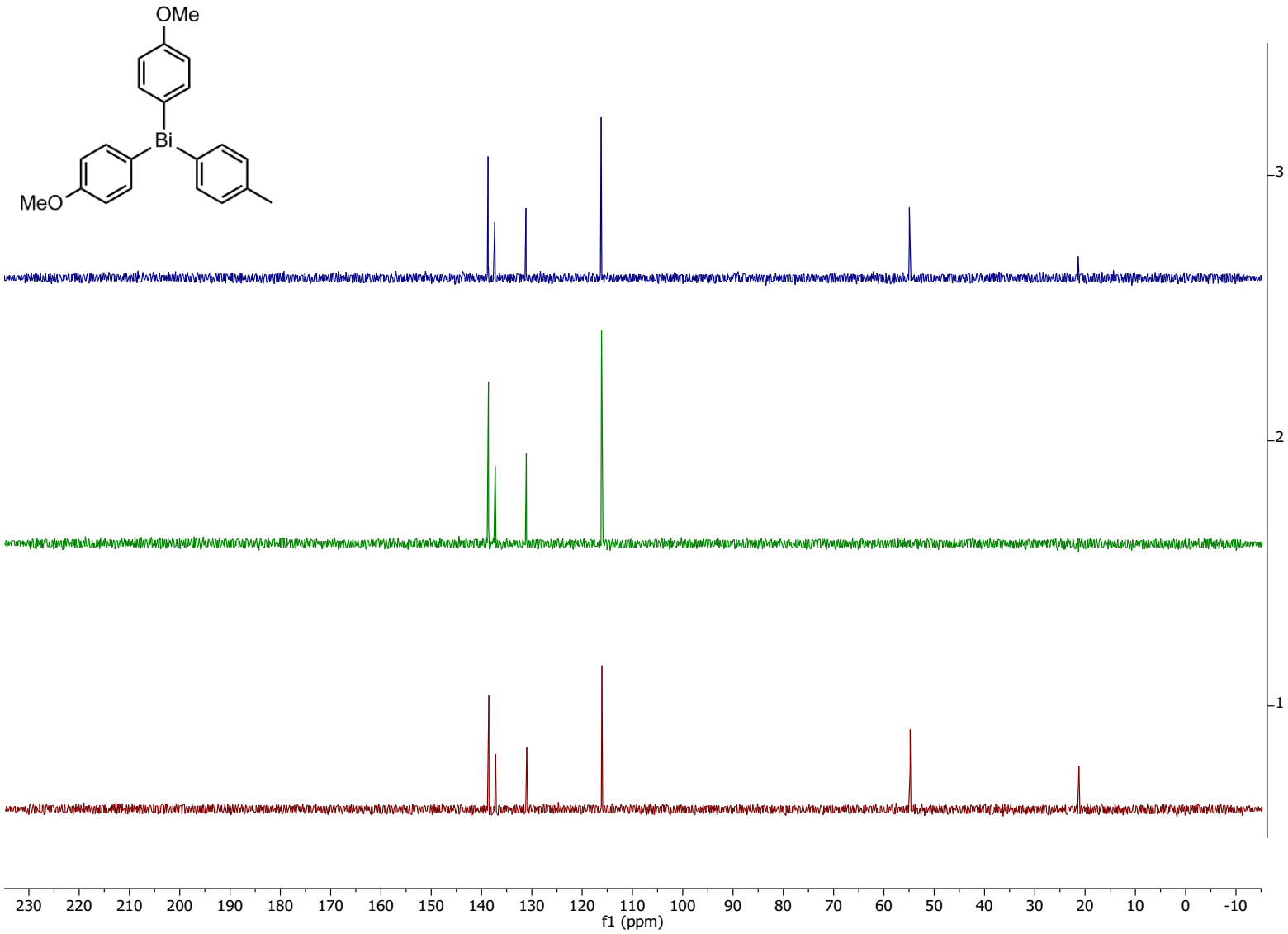


Figure S76. ^{13}C DEPT of **1l** in $CDCl_3$

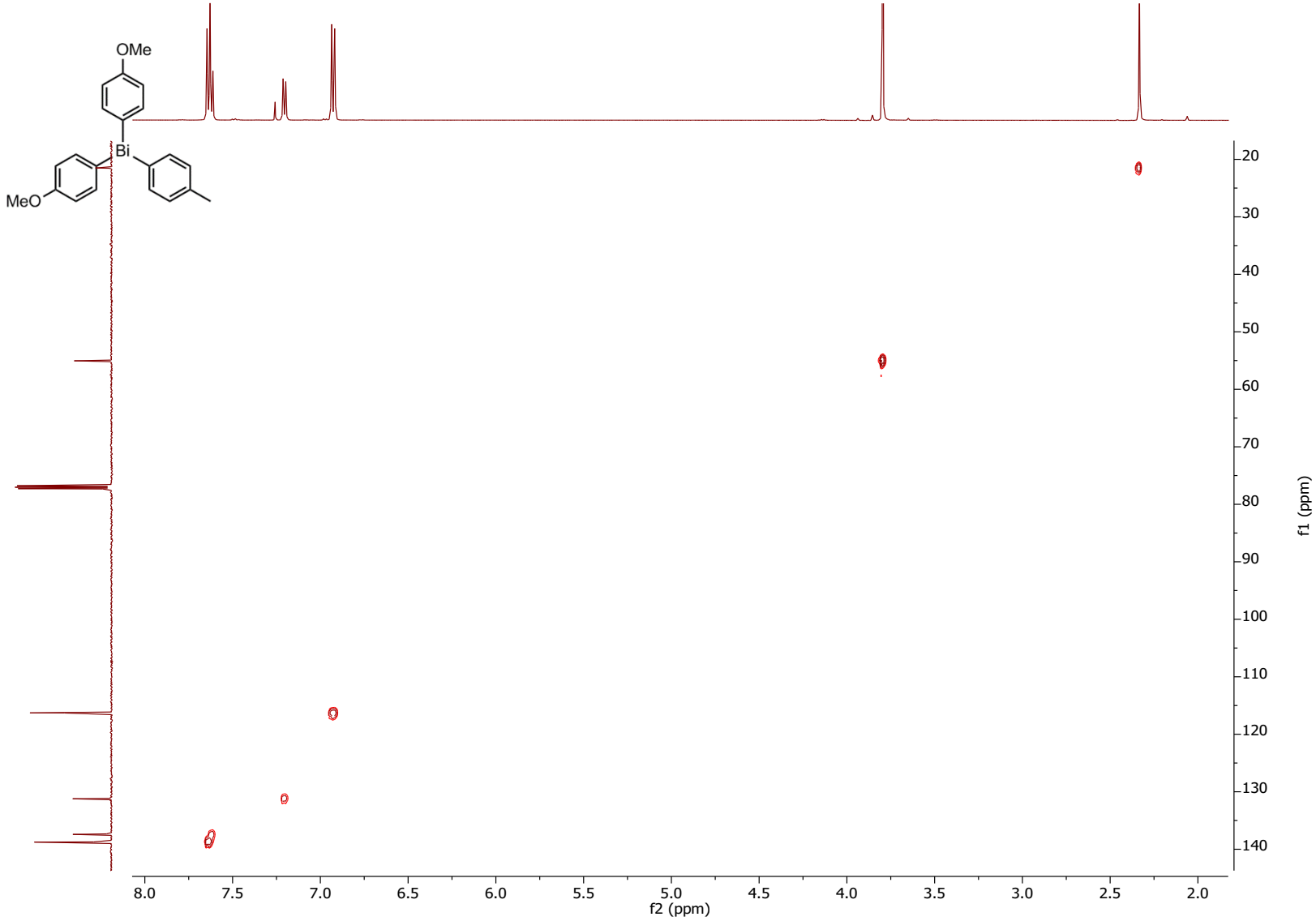
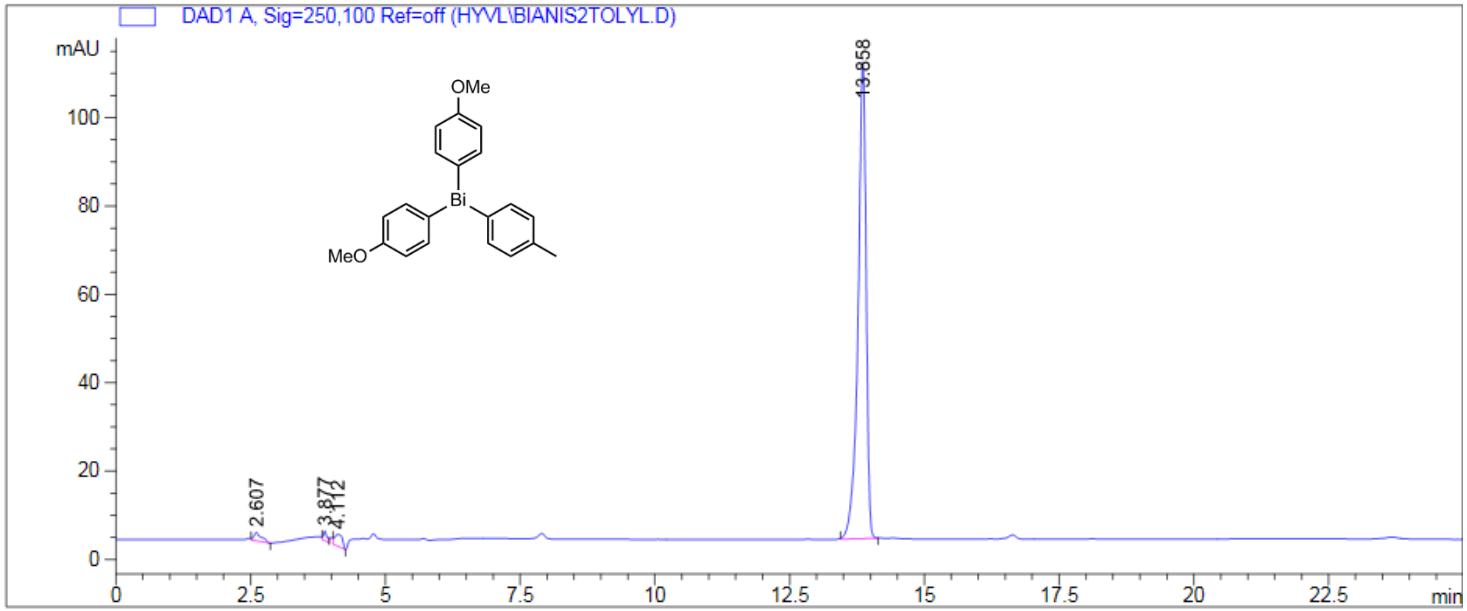


Figure S77. 2D HSQC of **1l** in $CDCl_3$

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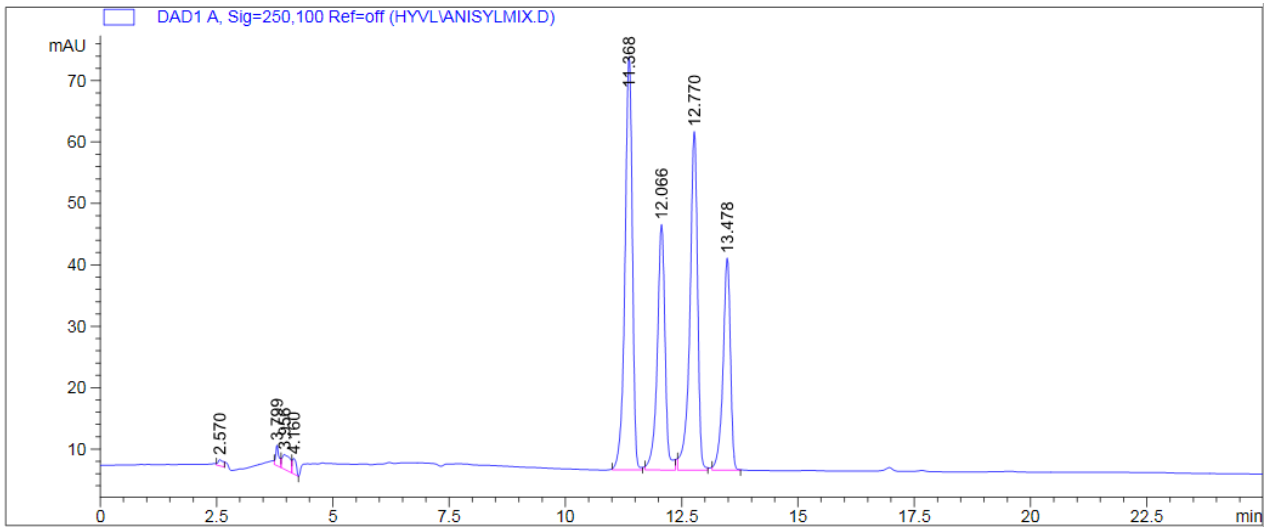
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   2.607 BB    0.1297   18.27940    1.90881   1.5462
   2   3.877 BB    0.0663   10.20038    2.19351   0.8628
   3   4.112 BV    0.1322   26.66670    2.67689   2.2556
   4  13.858 BB    0.1559 1127.08960  107.88406  95.3354
```

Figure S78. HPLC Chromatogram of **1l**

8. HPLC Chromatogram of 1:1:1:1 mixture of tri(4-methoxyphenyl)bismuthane, di(4-methoxyphenyl)phenylbismuthane (1j), diphenyl(4-methoxyphenyl)bismuthane (1b), and triphenylbismuthane used for monitoring of dismutation process in Scheme 2

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=====================================================================
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=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :     20.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,100 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   2.570 BB    0.1068    8.09482    1.01729   0.3526
   2   3.799 BB    0.0699   16.51229    3.32625   0.7192
   3   3.956 BV    0.1584   29.92288    2.41699   1.3034
   4   4.160 VV    0.0948   15.17814    2.49984   0.6611
   5  11.368 BB    0.1688  743.04004   67.29839  32.3655
   6  12.066 BB    0.1757  465.49442   40.02096  20.2761
   7  12.770 BB    0.1724  635.85394   55.19699  27.6967
   8  13.478 BB    0.1669  381.67932   34.55448  16.6253
```

Figure S79. HPLC Chromatogram of 1:1:1:1 mixture of tri(4-methoxyphenyl)bismuthane, di(4-methoxyphenyl)phenylbismuthane (**1j**), diphenyl(4-methoxyphenyl)bismuthane (**1b**) and triphenylbismuthane

9. Crystal Structure Data for Compound Di(4-cyanophenyl)(*p*-tolyl)bismuthane 1k

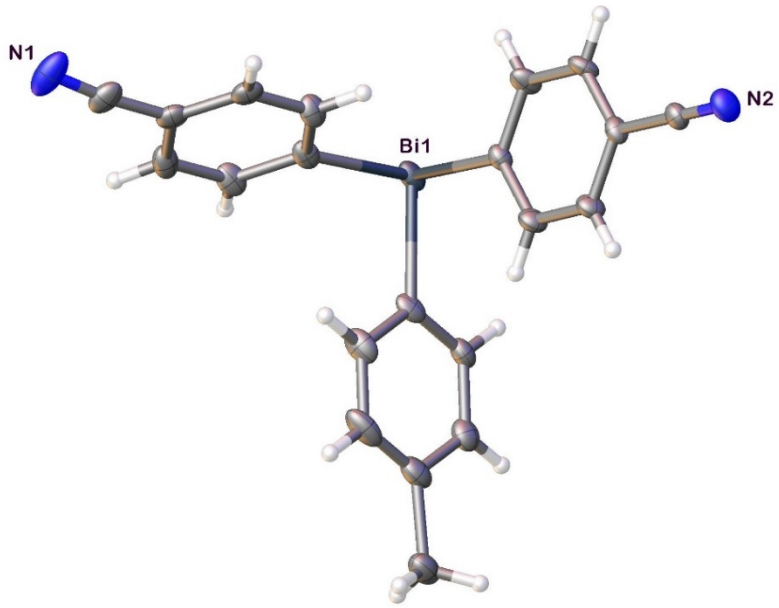

Figure S80. Solved Crystal Structure of Di(4-cyanophenyl)(*p*-tolyl)bismuthane **1k**

Table S2. **Crystal data and structure refinement for hyvl12_0m_a.**

Identification code	TLG 2-46	
Empirical formula	C21 H15 Bi N2	
Formula weight	504.33	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1718(10) Å	α= 105.132(4)°.
	b = 9.9011(14) Å	β= 105.299(4)°.
	c = 12.3098(15) Å	γ = 90.697(4)°.
Volume	923.9(2) Å^3	
Z	2	
Density (calculated)	1.813 Mg/m^3	
Absorption coefficient	9.545 mm^{-1}	
F(000)	476	
Crystal size	0.31 x 0.29 x 0.27 mm^3	
Theta range for data collection	1.783 to 26.425°.	
Index ranges	-10<=h<=8, -12<=k<=12, -15<=l<=15	
Reflections collected	13782	
Independent reflections	3786 [R(int) = 0.0308]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.432 and 0.284	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3786 / 21 / 222	
Goodness-of-fit on F^2	1.380	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0659	
R indices (all data)	R1 = 0.0383, wR2 = 0.0666	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.984 and -3.027 e.Å^{-3}	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for hyvl12_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Bi(1)	2066(1)	5487(1)	1371(1)	21(1)
C(1)	3382(8)	6758(6)	521(5)	23(1)
C(2)	5152(8)	6989(6)	841(5)	26(1)
C(17)	-478(8)	6996(6)	2734(5)	24(1)
C(16)	696(7)	7274(6)	2172(5)	24(1)
N(2)	9359(7)	6381(6)	6917(5)	31(1)
C(4)	5047(8)	8148(6)	-664(5)	25(1)
C(6)	2444(8)	7239(6)	-407(5)	27(1)
C(12)	6918(7)	6137(6)	5031(5)	19(1)
C(5)	3264(9)	7942(6)	-979(5)	29(2)
C(18)	-1325(8)	8077(7)	3265(5)	28(1)
C(10)	5570(8)	4975(6)	3017(5)	24(1)
C(13)	5642(7)	7051(6)	5030(5)	23(1)
C(9)	4269(7)	5869(6)	3010(5)	19(1)
C(11)	6890(7)	5098(6)	4018(5)	22(1)
C(14)	4314(7)	6917(6)	4023(5)	23(1)
C(20)	183(9)	9731(7)	2681(6)	37(2)
C(3)	5975(8)	7683(6)	270(5)	25(1)
C(22)	-1790(40)	10510(30)	3690(20)	36(3)
C(21)	1023(8)	8648(7)	2147(6)	30(2)
C(7)	5710(40)	8730(30)	-1320(20)	30(3)
C(15)	8284(7)	6276(6)	6083(5)	21(1)
C(19)	-999(8)	9444(7)	3238(6)	30(2)
N(3)	-2459(19)	11445(13)	4066(12)	50(3)
N(1)	6341(17)	9108(13)	-1924(10)	44(3)
C(8)	6080(40)	8900(30)	-1330(30)	30(3)
C(23)	-2000(40)	10670(30)	3920(20)	36(3)

Table S4. Bond lengths [Å] and angles [°] for hyvl12_0m_a.

Bi(1)-C(1)	2.255(6)
Bi(1)-C(16)	2.253(6)
Bi(1)-C(9)	2.263(5)
C(1)-C(2)	1.394(8)
C(1)-C(6)	1.397(8)
C(2)-H(2)	0.9500
C(2)-C(3)	1.381(9)
C(17)-H(17)	0.9500
C(17)-C(16)	1.384(9)
C(17)-C(18)	1.394(9)
C(16)-C(21)	1.393(8)
N(2)-C(15)	1.142(7)
C(4)-C(5)	1.403(9)
C(4)-C(3)	1.391(9)
C(4)-C(7)	1.324(14)
C(4)-C(8)	1.612(16)
C(6)-H(6)	0.9500
C(6)-C(5)	1.386(9)
C(12)-C(13)	1.389(8)
C(12)-C(11)	1.388(8)
C(12)-C(15)	1.443(7)
C(5)-H(5)	0.9500
C(18)-H(18)	0.9500
C(18)-C(19)	1.387(9)
C(10)-H(10)	0.9500
C(10)-C(9)	1.392(8)
C(10)-C(11)	1.384(8)
C(13)-H(13)	0.9500
C(13)-C(14)	1.390(8)
C(9)-C(14)	1.390(8)
C(11)-H(11)	0.9500
C(14)-H(14)	0.9500
C(20)-H(20)	0.9500
C(20)-C(21)	1.393(10)

C(20)-C(19)	1.388(10)
C(3)-H(3)	0.9500
C(22)-C(19)	1.321(14)
C(22)-N(3)	1.135(11)
C(21)-H(21)	0.9500
C(7)-N(1)	1.137(11)
C(19)-C(23)	1.643(17)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

C(1)-Bi(1)-C(9)	94.1(2)
C(16)-Bi(1)-C(1)	95.0(2)
C(16)-Bi(1)-C(9)	93.3(2)
C(2)-C(1)-Bi(1)	121.2(4)
C(2)-C(1)-C(6)	118.2(6)
C(6)-C(1)-Bi(1)	120.4(4)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-C(1)	121.6(6)
C(3)-C(2)-H(2)	119.2
C(16)-C(17)-H(17)	119.8
C(16)-C(17)-C(18)	120.4(6)
C(18)-C(17)-H(17)	119.8
C(17)-C(16)-Bi(1)	118.5(4)
C(17)-C(16)-C(21)	119.2(6)
C(21)-C(16)-Bi(1)	122.3(5)
C(5)-C(4)-C(8)	123.4(12)
C(3)-C(4)-C(5)	118.4(6)
C(3)-C(4)-C(8)	118.1(12)
C(7)-C(4)-C(5)	116.2(15)
C(7)-C(4)-C(3)	125.3(15)
C(1)-C(6)-H(6)	119.8
C(5)-C(6)-C(1)	120.4(6)

C(5)-C(6)-H(6)	119.8
C(13)-C(12)-C(15)	119.9(5)
C(11)-C(12)-C(13)	120.1(5)
C(11)-C(12)-C(15)	120.0(5)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-C(4)	120.9(6)
C(6)-C(5)-H(5)	119.5
C(17)-C(18)-H(18)	119.8
C(19)-C(18)-C(17)	120.3(6)
C(19)-C(18)-H(18)	119.8
C(9)-C(10)-H(10)	119.4
C(11)-C(10)-H(10)	119.4
C(11)-C(10)-C(9)	121.1(5)
C(12)-C(13)-H(13)	119.8
C(12)-C(13)-C(14)	120.3(6)
C(14)-C(13)-H(13)	119.8
C(10)-C(9)-Bi(1)	118.6(4)
C(14)-C(9)-Bi(1)	122.0(4)
C(14)-C(9)-C(10)	119.3(5)
C(12)-C(11)-H(11)	120.3
C(10)-C(11)-C(12)	119.3(5)
C(10)-C(11)-H(11)	120.3
C(13)-C(14)-H(14)	120.1
C(9)-C(14)-C(13)	119.8(5)
C(9)-C(14)-H(14)	120.1
C(21)-C(20)-H(20)	120.0
C(19)-C(20)-H(20)	120.0
C(19)-C(20)-C(21)	120.0(6)
C(2)-C(3)-C(4)	120.4(6)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
N(3)-C(22)-C(19)	178(3)
C(16)-C(21)-C(20)	120.5(7)
C(16)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
N(1)-C(7)-C(4)	174(3)

N(2)-C(15)-C(12)	179.6(7)
C(18)-C(19)-C(20)	119.6(6)
C(18)-C(19)-C(23)	117.7(13)
C(20)-C(19)-C(23)	122.7(13)
C(22)-C(19)-C(18)	123.5(16)
C(22)-C(19)-C(20)	116.9(16)
C(4)-C(8)-H(8A)	109.5
C(4)-C(8)-H(8B)	109.5
C(4)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(19)-C(23)-H(23A)	109.5
C(19)-C(23)-H(23B)	109.5
C(19)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for hyvl12_0m_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Bi(1)	18(1)	16(1)	23(1)	5(1)	-5(1)	-3(1)
C(1)	28(3)	14(3)	18(3)	0(2)	-2(2)	-1(2)
C(2)	25(3)	24(3)	20(3)	5(3)	-4(3)	-3(3)
C(17)	25(3)	19(3)	25(3)	10(3)	0(3)	3(2)
C(16)	16(3)	21(3)	26(3)	6(3)	-6(2)	1(2)
N(2)	28(3)	31(3)	29(3)	10(2)	-1(2)	3(2)
C(4)	28(2)	19(2)	22(2)	-4(2)	9(2)	1(2)
C(6)	24(3)	22(3)	24(3)	2(3)	-7(3)	-4(3)
C(12)	13(3)	22(3)	22(3)	10(2)	1(2)	0(2)
C(5)	42(4)	22(3)	18(3)	4(3)	0(3)	0(3)
C(18)	23(3)	33(4)	28(3)	13(3)	0(3)	3(3)
C(10)	26(3)	13(3)	25(3)	-1(2)	-1(3)	1(2)
C(13)	18(2)	25(2)	26(2)	7(2)	3(2)	7(2)
C(9)	18(3)	17(3)	21(3)	7(2)	1(2)	1(2)
C(11)	19(3)	14(3)	31(3)	5(2)	3(2)	6(2)
C(14)	18(2)	25(2)	26(2)	7(2)	3(2)	7(2)
C(20)	37(4)	18(3)	46(4)	10(3)	-8(3)	0(3)
C(3)	28(2)	19(2)	22(2)	-4(2)	9(2)	1(2)
C(22)	49(7)	28(5)	28(8)	6(5)	4(5)	13(3)
C(21)	23(3)	22(3)	44(4)	14(3)	1(3)	-5(3)
C(7)	38(9)	24(6)	23(3)	-5(4)	12(5)	-7(6)
C(15)	22(3)	18(3)	23(3)	9(2)	4(3)	2(2)
C(19)	29(4)	24(3)	31(3)	9(3)	-3(3)	6(3)
N(3)	70(9)	31(6)	48(8)	7(6)	20(7)	19(6)
N(1)	60(8)	38(7)	26(6)	-7(5)	18(5)	-24(6)
C(8)	38(9)	24(6)	23(3)	-5(4)	12(5)	-7(6)
C(23)	49(7)	28(5)	28(8)	6(5)	4(5)	13(3)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for hyvl12_0m_a.

	x	y	z	U(eq)
H(2)	5808	6662	1467	31
H(17)	-707	6063	2758	29
H(6)	1237	7083	-649	32
H(5)	2609	8289	-1593	35
H(18)	-2129	7876	3648	34
H(10)	5552	4267	2322	29
H(13)	5678	7772	5720	28
H(11)	7767	4478	4013	27
H(14)	3438	7539	4027	28
H(20)	419	10667	2665	45
H(3)	7181	7843	517	29
H(21)	1826	8849	1763	36
H(8A)	7224	9246	-814	45
H(8B)	5476	9683	-1533	45
H(8C)	6169	8215	-2044	45
H(23A)	-3173	10637	3431	54
H(23B)	-1413	11594	4052	54
H(23C)	-2017	10517	4667	54

10. References

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