Supplementary Information

Lipshutz-type Bis(amido)argentates for Directed *ortho* Argentation

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Table of Contents

1. General

Instrumentation.

NMR spectra of organics were obtained on a Bruker Avance III HD 500 spectrometer or a Bruker Ascend 400 spectrometer. NMR data of lithium argentates were collected on a Bruker Avance III HD 500 MHz Smart Probe FT NMR spectrometer (500.200 MHz for 1H, 125.775 MHz for 13C, 194.397 for 7Li) at 298 K and using deuterated solvent stored over sodium wire or molecular sieves (3 Å). Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard. ^{13}C NMR spectra were referenced to $CDCl_3$ or C_6D_6. For ^{7}Li, an external reference was used (1 M LiCl in D_2O). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, brs = broad singlet, brd = broad doublet, brq = broad quartet and br = broad peak. Automated medium pressure liquid chromatography (MPLC) system (YAMAZEN Parallel Frac FR-260, PUMP 580D, prep UV-10VW) and recycling gel permeation chromatography (GPC) system (JAI LC-9201 HPLC with JAIGEL 1H, JAI LC-5060 HPLC with JAIGEL 2HR or JAI LC-9210 II HPLC with JAIGEL 2HR, mobile phase: $CHCl_3$) were used for purification of products. IR spectra were obtained on a JASCO FT/IR-4700 spectrophotometer or (for air-sensitive argentates) as a nujol mull using NaCl plates on a Bruker Alpha spectrophotometer. Melting points were determined with an SRS MPA 100 OptiMelt automated melting point system, a Yanaco micro melting point apparatus or a Griffin melting point apparatus and were uncorrected. Compositions were established for C, H and N with a Perkin Elmer 240 elemental analyser. EI-MS spectra were obtained by GC-MS using either an Agilent 7890A/5975C or 7890B/5977A spectrometers. HRMS spectra were measured by ESI-MS using a Bruker micrOTOF-II spectrometer.

Materials.

Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., LLC., Kishida Chemical Co., Ltd. and other commercial suppliers. ^{n}BuLi in ^{n}hexane were obtained from Kanto Chemical Co., Inc. Anhydrous THF was purchased from Kanto Chemical Co., Inc. Chemicals were of reagent grade and used as received, except for TMP-argentate syntheses for X-ray analysis where solvents were freshly distilled from Na/K amalgam (toluene) or Na (THF, hexane). Air- and moisture-sensitive manipulations were performed with standard Schlenk techniques under argon atmosphere. Normal-phase column chromatography was performed with silica gel 60 (230–400 mesh) from Merck and thin-layer chromatography was carried out on 0.25 mm Merck silica gel plates (60 F_{254}). Preparative thin-layer chromatography (PTLC) was performed with 0.5 mm Merck silica gel plates (60 F_{254}).

2. Experimental Details

2.1. Preparation of Argentates

The protocols below were scaled up on demand ranging from 0.12 mmol to 1.2 mmol.

Preparation of TMPLi in THF (0.24 mmol scale)*

To a solution of 2,2,6,6-tetramethylpiperidine (40.5 μL, 0.24 mmol) in 0.24 mL of anhydrous THF was added ^{n}BuLi (1.54 M ^{n}hexane solution, 156 μL, 0.24 mmol) at –78 °C under Ar. The mixture was stirred for 15–30 min at 0 °C to give a slightly yellow solution of TMPLi (lithium 2,2,6,6-tetramethylpiperidide) in THF.

* When 1,4-dioxane was employed as a solvent, ^{n}BuLi was added to solid state TMPH in 1,4-dioxane at –78 °C. The mixture gradually transformed into a deep red solution with a small amount of precipitate upon warming to room temperature. This was stirred for 15 min to give TMPLi in dioxane.

* When benzene was employed as a solvent, ^{n}BuLi was added to a solid mixture of TMPH and benzene at –78 °C. The mixture gradually gave a ayellowish viscous solution upon warming to 0 °C, which was stirred for 30 min to give TMPLi in benzene.

General Procedure for Preparation of mono-TMP silvers (TMP)Ag(X)Li in THF (0.12 mmol scale)

To a suspension of silver source (0.12 mmol) in 0.24 mL of anhydrous THF was added the solution of TMPLi in THF (0.12 mmol) *via* cannula at –78 °C under Ar. The mixture was stirred at 0 °C for 15–30 min to give a solution of (TMP)Ag(X)Li in THF.

1. (TMP)Ag(NO_3)Li: $AgNO_3$ (20.8 mg, 0.12 mmol) was used.
2. (TMP)Ag(CN)Li: AgCN (16.1 mg, 0.12 mmol) was used.

General Procedure for Preparation of bis-TMP argentate $(TMP)_2Ag(X)Li_2$ in THF (0.12 mmol scale)

To a suspension of silver source (0.12 mmol) in 0.12 mL of anhydrous THF was added the solution of TMPLi in THF (0.24 mmol) *via* cannula at –78 °C under Ar. The mixture was stirred at 0 °C for 15–30 min to give a solution of $(TMP)_2Ag(X)Li_2$ in THF.*

3. $(TMP)_2Ag(NO_3)Li_2$: $AgNO_3$ (20.5 mg, 0.12 mmol) was used.
4. $(TMP)_2Ag(1/2{\bullet}CO_3)Li_2$: Ag_2CO_3 (16.5 mg, 0.06 mmol) was used.
5. $(TMP)_2Ag(OTf)Li_2$: AgOTf (30.9 mg, 0.12 mmol) was used.
6. $(TMP)_2Ag(CN)Li_2$: AgCN (16.3 mg, 0.12 mmol) was used.

* When 1,4-dioxane was employed as a solvent, TMPLi in 1,4-dioxane was added to the solid mixture of AgCN and 1,4-dioxane at –78 °C. The mixture gradually formed a dark brown solution with a small amount of precipitate upon warming to room temperature and was stirred for 15 min to give $(TMP)_2Ag(CN)Li_2$ in 1,4-dioxane.

* When benzene was employed as a solvent, TMPLi in benzene was added to the solid AgCN in benzene at –78 °C. The mixture gradually turned to be the black solution upon warming to 0 °C and was stirred for 30 min to give $(TMP)_2Ag(CN)Li_2$ in benzene.

Preparation of $(Cy_2N)_2Ag(CN)Li_2$ in THF (0.12 mmol scale)

To a solution of dicyclohexylamine (47.8 μL, 0.24 mmol) in 0.24 mL of anhydrous THF was added ^{n}BuLi (1.54 M ^{n}hexane solution, 156 μL, 0.24 mmol) at –78 °C under Ar. The mixture was stirred for 30 min at 0 °C to give a solution of Cy_2NLi (lithium dicyclohexylamide) in THF. To a suspension of silver cyanide (16.2 mg, 0.12 mmol) in 1.2 mL of anhydrous THF was added the solution of Cy_2NLi in THF (0.24 mmol) *via* cannula at –78 °C under Ar, and the reaction mixture was stirred at 0 °C for 30 min to give a brown suspension of $(Cy_2N)_2Ag(CN)Li_2$ in THF.

Preparation of $(^{i}Pr_2N)_2Ag(CN)Li_2$ in THF (0.12 mmol scale)

To a solution of diisopropylamine (33.9 μL, 0.24 mmol) in 0.24 mL of anhydrous THF was added ^{n}BuLi (1.54 M ^{n}hexane solution, 156 μL, 0.24 mmol) at –78 °C under Ar. The mixture was stirred for 30 min at 0 °C to give the solution of $^{i}Pr_2NLi$ (lithium diisopropylamide) in THF. To a suspension of silver cyanide (16.2 mg, 0.12 mmol) in 1.2 mL of anhydrous THF was added the solution of $^{i}Pr_2NLi$ in THF (0.24 mmol) *via* cannula at –78 °C under Ar, and the reaction mixture was stirred at 0 °C for 30 min to give a yellowish brown solution of $(^{i}Pr_2N)_2Ag(CN)Li_2$ in THF.

Preparation of $(HMDS)_2Ag(CN)Li_2$ in THF (0.12 mmol scale)

To a suspension of silver cyanide (16.2 mg, 0.12 mmol) in 0.24 mL of anhydrous THF was added HMDSLi (1.0 M THF solution, 240 μL, 0.24 mmol) at –78 °C under Ar. The mixture was stirred at 0 °C for 30 min to give a yellow solution of $(HMDS)_2Ag(CN)Li_2$ in THF.

Preparation of $Me(TMP)Ag(CN)Li_2$ in THF (0.12 mmol scale)

To a suspension of silver cyanide (16.3 mg, 0.12 mmol) in 0.24 mL of anhydrous THF was added MeLi (1.00 M diethylether solution, 120 μL, 0.12 mmol) at –78 °C under Ar. The mixture was stirred at 0 °C for 30 min to give a solution of $MeAg(CN)Li$ in THF. To the solution was added the TMPLi solution (0.12 mmol) at –78 °C, and the reaction mixture was stirred at 0 °C for 30 min to give a dark brown solution of $Me(TMP)Ag(CN)Li_2$ in THF.

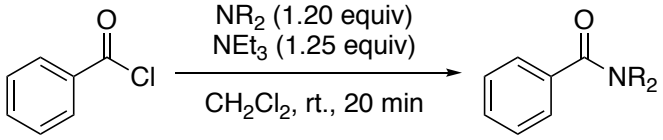
Preparation of $(TMP)_2Cu(CN)Li_2$ in THF (0.24 mmol scale)

To a suspension of copper cyanide (21.5 mg, 0.24 mmol) in 0.24 mL of anhydrous THF was added the solution of TMPLi in THF (0.48 mmol) *via* cannula at –78 °C under Ar. The mixture was stirred at 0 °C for 15–30 min to give the slightly yellow solution of $(TMP)_2Cu(CN)Li_2$ in THF.

2.2. Preparation of Substrates

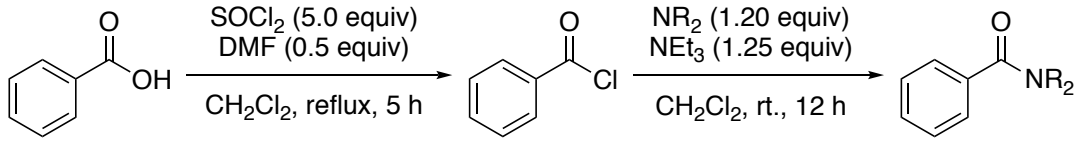
Benzamides were prepared from the corresponding acyl chlorides or acids following General Procedure A or B.

General Procedure A



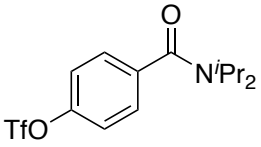
To a solution of amine (12 mmol) and NEt_3 (1.8 mL, 12.5 mmol) in 20 mL of CH_2Cl_2 was added acyl chloride (10 mmol) in one portion at room temperature leading the mixture to self-reflux. The reaction mixture was stirred for 20 min at room temperature and then diluted with CH_2Cl_2. The solution was transferred to a separation funnel and was washed with 1M HCl aq (3 × 20 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the corresponding benzamide substrates. All the substrates were used after recrystallization.

General Procedure B



Thionyl chloride (4.02 g, 33.8 mmol) was added to a solution of carboxylic acid (6.8 mmol) and DMF (8 mL, 3.3 mmol) in 34 mL of CH_2Cl_2 at room temperature. The mixture was heated under reflux for 5 h, and then the excess thionyl chloride and CH_2Cl_2 were removed *in vacuo*. The resultant acyl chloride was dissolved in dry CH_2Cl_2 and cooled to 0 °C, then amine (8.1 mmol) was added. After 5 min, NEt_3 (1.2 mL, 8.5 mmol) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The mixture was diluted with CH_2Cl_2 and washed with 3 M HCl aq. (2 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude residue by flash column chromatography on silica gel afforded the corresponding benzamide substrates. All the substrates were used after recrystallization.

4-(Diisopropylcarbamoyl)phenyl trifluoromethanesulfonate (1p)

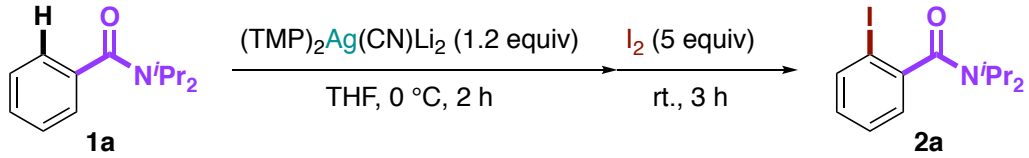


Trifluoromethanesulfonic anhydride (2.3 mL, 8.6 mmol) was added in 3 portions to the vigorously stirred suspension of 4-hydroxy-*N*,*N*-diisopropylbenzamide (1.59 g, 7.2 mmol, synthesized following General Procedure B) in a mixture of CH_2Cl_2 (30 mL) and 30% aq. K_3PO_4 (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was washed with water 3 times, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/4) as an eluent to give the titled compound **1p** as a white solid in 43% yield (1.103 g). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.35 (brd, 12H), 3.58 (brs, 1H), 3.72 (brs, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.8, 46.4 (brs), 51.2 (brs), 118.9 (CF_3, q, *J* = 321 Hz), 121.8, 128.0, 139.3, 149.5, 169.1. **^{19}F NMR (376 MHz, $CDCl_3$):** δ –72.9. **FTIR (ATR):** 2975, 1618, 1423, 1346, 1120, 1138, 888, 603 cm^{-1}. **mp:** 107.9 °C (recrystallized from hexane). **Anal.:** Calcd for $C_{14}H_{18}F_3NO_4S$: C, 47.59; H, 5.13; N, 3.96. Found: C, 47.78; H, 5.20; N, 4.00. **HRMS (pos. ESI):** *m/z*: calcd for $C_{14}H_{18}F_3NNaO_4S$ $[M+Na]^+$ 376.0801, found 376.0810.

2.3. *ortho* Iodination of Aromatics (Table 2)

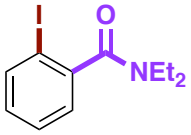
General Procedure:
Unless otherwise noted, the reactions were performed on 0.5 mmol scale.

2-Iodo-*N*,*N*-diisopropylbenzamide (2a)



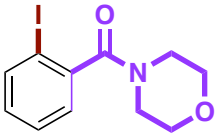
N,*N*-Diisopropylbenzamide **1a** (102.7 mg, 0.5 mmol) and dry THF (0.5 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.6 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 h at 0 °C. To the mixture was added iodine (634.5 mg, 2.5 mmol) at –78 °C, then stirred for 3 h at room temperature. The reaction was quenched with aqueous NH_4Cl (5 mL) and aqueous $Na_2S_2O_3$ (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/4) as an eluent to give the titled compound **2a** as a white solid in 92% yield (141.8 mg). ^{1}H NMR spectrum was in agreement with the reference.[1] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.07 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.57 (d, *J* = 6.9 Hz, 3H), 1.60 (d, *J* = 6.9 Hz, 3H), 3.52 (sep, *J* = 6.9 Hz, 1H), 3.58 (sep, *J* = 6.7 Hz, 1H), 7.03 (dd, *J* = 7.6, 8.1 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{13}H_{18}INNaO$ $[M+Na]^+$ 354.0325, found 354.0341.

***N*,*N*-diethyl-2-iodobenzamide (2b)**



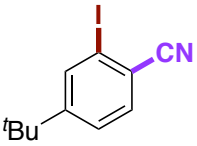
Following the **General Procedure** (purification: AcOEt/hexane = 1/3), the titled compound was obtained as a pale yellow oil in 98% yield (146.0 mg). ^{1}H NMR spectrum was in agreement with the reference.[2] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.07 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 3.12 (q, *J* = 7.1 Hz, 1H), 3.15 (q, *J* = 7.1 Hz, 1H), 3.29 (brq, *J* = 7.1 Hz, 1H), 3.87 (brq, *J* = 7.1 Hz, 1H), 7.06 (ddd, *J* = 1.7, 7.6, 7.7 Hz, 1H), 7.21 (dd, *J* = 1.7, 7.6 Hz, 1H), 7.38 (ddd, *J* = 1.7, 7.6, 7.6 Hz, 1H), 7.82 (dd, *J* = 1.7, 7.7 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{11}H_{14}INNaO$ $[M+Na]^+$ 326.0012, found 326.0016.

(2-Iodophenyl)(morpholino)methanone (2c)



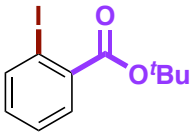
Following the **General Procedure** (purification: AcOEt/hexane = 1/3), the titled compound was obtained as a brown solid in 48% yield (81.9 mg, 6% starting material **1a** was included). ^{1}H NMR spectrum was in agreement with the reference.[3] **^{1}H NMR (400 MHz, CDCl$_3$):** δ 3.15-3.21 (m, 1H), 3.26-3.32 (m, 1H), 3.56-3.62 (m, 1H), 3.75-3.90 (m, 5H), 7.09 (ddd, *J* = 1.5, 7.6, 7.7 Hz, 1H), 7.20 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.40 (ddd, *J* = 1.0, 7.6, 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{11}H_{12}INNaO_2$ $[M+Na]^+$ 339.9805, found 339.9816.

4-(*tert*-butyl)-2-iodobenzonitrile (2d)



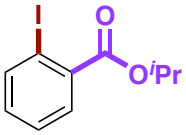
Following the **General Procedure** (purification: AcOEt/hexane = 1/60), the titled compound was obtained as a white solid in 95% yield (135.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.31 (s, 9H), 7.45 (dd, *J* = 1.7, 8.1 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 1.7 Hz, 1H). **^{13}C NMR (125 MHz, CDCl$_3$):** δ 31.0, 35.4, 98.7, 117.8, 119.7, 125.8, 134.0, 136.9, 158.2. **FTIR (ATR):** 2963, 2225, 1589, 1478, 1380, 1256, 1035, 831, 670, 609 cm^{-1}. **mp:** 30.0 °C (recrystallized from hexane). **Anal.:** Calcd for $C_{11}H_{12}IN$: C, 46.34; H, 4.24; N, 4.91. Found: C, 46.15; H, 4.22; N, 4.84. **HRMS (pos. ESI):** *m/z*: calcd for $C_{11}H_{12}INNa$ $[M+Na]^+$ 307.9907, found 307.9908.

***tert*-Butyl 2-iodobenzoate (2e)**



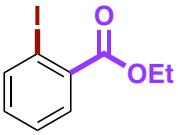
Following the **General Procedure** (purification: AcOEt/hexane = 1/50 followed by distillation with Kugelrohr), the titled compound was obtained as a colorless oil in 92% yield (139.3 mg). ^{1}H NMR spectrum was in agreement with the reference.[4] **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.62 (s, 9H), 7.10 (ddd, *J* = 1.7, 7.6, 7.8 Hz, 1H), 7.37 (ddd, *J* = 1.0, 7.6, 7.8 Hz, 1H), 7.68 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.94 (dd, *J* = 1.0, 7.8 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{11}H_{13}INaO_2$ $[M+Na]^+$ 326.9852, found 326.9862.

Isopropyl 2-iodobenzoate (2f)



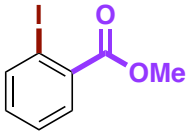
Following the **General Procedure** (purification: AcOEt/hexane = 1/50), the titled compound was obtained as a colorless oil in 90% yield (130.0 mg). ^{1}H NMR spectrum was in agreement with the reference.[5] **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.40 (d, *J* = 6.4 Hz, 6H), 5.28 (sep, *J* = 6.4 Hz, 2H), 7.13 (dd, *J* = 7.6, 7.7 Hz, 1H), 7.39 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{10}H_{11}INaO_2$ $[M+Na]^+$ 312.9696, found 312.9698.

Ethyl 2-iodobenzoate (2g)



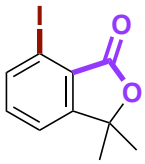
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/50), the titled compound was obtained as a colorless oil in 93% yield (130.5 mg). ^{1}H NMR spectrum was in agreement with the reference.[6] **^{1}H NMR (400 MHz, CDCl$_3$):** δ 1.42 (t, *J* = 7.2 Hz, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 7.15 (ddd, *J* = 1.7, 7.6, 7.8 Hz, 1H), 7.40 (ddd, *J* = 1.2, 7.6, 7.8 Hz, 1H), 7.79 (dd, *J* = 1.7, 7.8 Hz, 1H), 7.99 (dd, *J* = 1.2, 7.8 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_9H_9INaO_2$ $[M+Na]^+$ 298.9539, found 298.9536.

Methyl 2-iodobenzoate (2h)



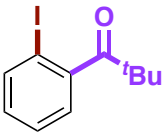
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/50), the titled compound was obtained as a pale yellow oil in 86% yield (112.9 mg). ^{1}H was in agreement with the reference.[7] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.94 (s, 3H), 7.15 (ddd, *J* = 1.7, 7.6, 7.7 Hz, 1H), 7.40 (ddd, *J* = 1.2, 7.6, 7.7 Hz, 1H), 7.80 (dd, *J* = 1.7, 7.7 Hz, 1H), 8.00 (dd, *J* = 1.2, 7.7 Hz, 1H). **EI-MS (% relative intensity):** *m/z*: 262 (M+, 78), 231 (100), 203 (31), 127 (29), 76 (30).

7-Iodo-3,3-dimethylisobenzofuran-1(3*H*)-one (2i)



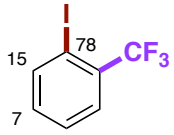
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/4), the titled compound was obtained as a white solid in 99% yield (146.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.65 (s, 6H), 7.33 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 27.4, 83.1, 92.4, 120.7, 126.5, 135.0, 140.5, 157.2, 167.9. **FTIR (ATR):** 2978, 1753, 1591, 1451, 1234, 1037, 689 cm^{-1}. **mp:** 139.1 °C (recrystallized from hexane). **Anal.:** Calcd for $C_{10}H_9IO_2$: C, 41.69; H, 3.15. Found: C, 41.66; H, 3.34. **HRMS (pos. ESI):** *m/z*: calcd for $C_{10}H_9INaO_2$ $[M+Na]^+$ 310.9539, found 310.9552.

1-(2-iodophenyl)-2,2-dimethylpropan-1-one (2j)



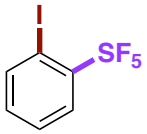
Following the **General Procedure** (0.2 mmol scale; purification: AcOEt/hexane = 0/100 → 1/20; 96% NMR yield determined by ^{1}H NMR spectroscopy using mesitylene), the titled compound was obtained as a colorless oil in 85% yield (48.8 mg). ^{1}H NMR spectroscopy was in agreement with the literature.[8] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.31 (s, 9H), 7.07 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H) **HRMS (pos. ESI):** *m/z*: calcd for $C_{11}H_{13}INaO$ $[M+Na]^+$ 310.9903, found 310.9909.

Iodo α,α,α -trifluorotoluene (*ortho* : *meta* : *para* = 78 : 15 : 7) (2k)



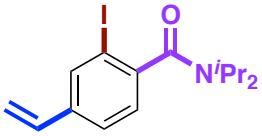
Following the **General Procedure** (0.2 mmol scale; careful evaporation due to high volatility of the products), the titled compound was obtained as a brown oil. The argentation proceeded at *ortho*, *meta* and *para* position in 43%, 8% and 4% yield, respectively, determined by ^{1}H NMR using mesitylene (8.2 mg) as an internal standard (mesitylene : *ortho* : *meta* : *para* = 1 : 0.42 : 0.08 : 0.04). ^{1}H NMR spectrum was in agreement with the reference.[9] 2-Iodo α,α,α-trifluorotoluene **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.20 (dd, *J* = 7.6, 7.9 Hz, 1H), 7.45 (dd, *J* = 7.6, 7.9 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 8.04 (d, *J* = 7.9 Hz, 1H). 3-iodo α,α,α-trifluorotoluene **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.23 (dd, *J* = 7.6, 7.9 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.96 (s, 1H). 4-iodo α,α,α-trifluorotoluene **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H). **EI-MS (% relative intensity, All isomers are separately detected): Peak (A):** *m/z*: 272 (M+, 36), 145 (100), 127 (32). **Peak (B):** 272 (M+, 100), 253 (14), 145 (65), 127 (15). **Peak (C):** 272 (M+, 100), 253 (5), 145 (50), 127 (18).

Pentafluoro(2-iodophenyl)-λ⁶-sulfane (2l)



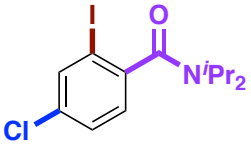
Following the **General Procedure** (careful evaporation due to high volatility of the product), the titled compound was obtained as a brown oil. The titled compound was obtained in 14% yield determined by ^{1}H NMR using mesitylene (19.1 mg) as an internal standard (mesitylene : **2k** = 1 : 0.14). ^{1}H NMR spectrum was in agreement with the reference.[10] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.13 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.45 (m, 1H), 7.82 (dd, *J* = 1.5, 8.6 Hz, 1H), 8.15 (d, *J* = 7.3 Hz, 1H). **EI-MS (% relative intensity):** *m/z*: 330 (M+, 100), 203 (21), 127 (55), 89 (51), 76 (34).

2-Iodo-*N*,*N*-diisopropyl-4-vinylbenzamide (2m)



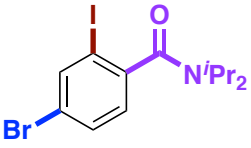
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/8), the titled compound was obtained as a white solid in 86% yield (154.0 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.07 (d, *J* = 6.7 Hz, 3H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.56 (d, *J* = 6.7 Hz, 3H), 1.59 (d, *J* = 6.7 Hz, 3H), 3.51 (sep, *J* = 6.7 Hz, 1H), 3.60 (sep, *J* = 6.7 Hz, 1H), 5.31 (d, *J* = 11.0 Hz, 1H), 5.75 (d, *J* = 17.7 Hz, 1H), 6.61 (dd, *J* = 11.0, 17.7 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.85 (d, *J* = 1.5 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.2, 20.7, 20.8, 20.9, 46.1, 51.4, 92.7, 115.9, 126.0, 126.1, 134.9, 137.1, 139.1, 143.5, 169.8. **FTIR (ATR):** 2968, 1631, 1437, 1336 cm^{-1}. **mp:** 118.4 °C (recrystallized from hexane). **Anal.:** Calcd for $C_{15}H_{20}INO + 1/8{\cdot}H_2O$: C, 50.12; H, 5.68; N, 3.90. Found: C, 50.11; H, 5.56; N, 3.90. **HRMS (pos. ESI):** *m/z*: calcd for $C_{15}H_{20}INNaO$ $[M+Na]^+$ 380.0482, found 380.0496.

4-Chloro-2-iodo-*N*,*N*-diisopropylbenzamide (2n)



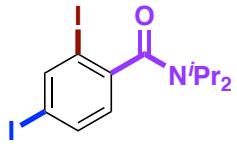
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/6), the titled compound was obtained as a white solid in 95% yield (173.1 mg, 3% of 3-iodo isomer included). ^{1}H NMR spectrum was in agreement with the reference.[2] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.07 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.55 (d, *J* = 6.9 Hz, 3H), 1.59 (d, *J* = 6.9 Hz, 3H), 3.52 (sep, *J* = 6.9 Hz, 1H), 3.55 (sep, *J* = 6.9 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 7.34 (dd, *J* = 2.0, 8.1 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{13}H_{17}ClINNaO$ $[M+Na]^+$ 387.9936, found 387.9941.

4-Bromo-2-iodo-*N*,*N*-diisopropylbenzamide (2o)



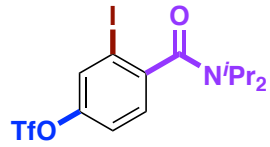
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/8), the titled compound was obtained as a white solid in 98% yield (201.3 mg, 3% of 3-iodo isomer included). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.07 (d, *J* = 6.7 Hz, 3H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.55 (d, *J* = 6.7 Hz, 3H), 1.59 (d, *J* = 6.7 Hz, 3H), 3.51 (sep, *J* = 6.7 Hz, 1H), 3.55 (sep, *J* = 6.7 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 7.49 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.98 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.2, 20.8, 20.9 (overlapped), 46.3, 51.4, 93.0, 122.3, 127.0, 131.6, 141.5, 143.3, 169.1. **FTIR (ATR):** 2929, 1631, 1435, 1335, 1020, 820 cm^{-1}. **mp:** 104.8 °C (26 : 1 mixture with isomer; recrystallized from hexane). **Anal.:** Calcd for $C_{13}H_{17}BrINO$: C, 38.07; H, 4.18; N, 3.42. Found: C, 38.16; H, 4.24; N, 3.46. **HRMS (pos. ESI):** *m/z*: calcd for $C_{13}H_{17}BrINNaO$ $[M+Na]^+$ 431.9430, found 431.9434.

2,4-Diiodo-*N*,*N*-diisopropylbenzamide (2p)



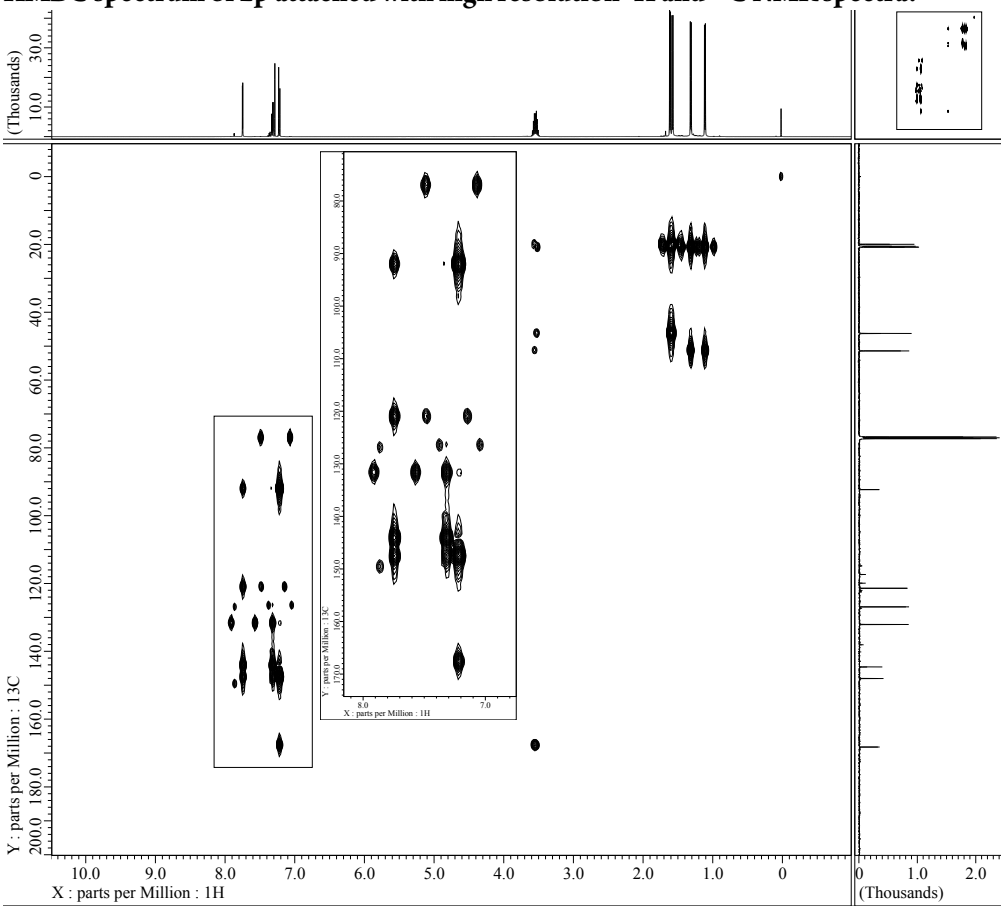
Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/8), the titled compound was obtained as a pale yellow solid in 97% yield (220.8 mg). ^{1}H NMR spectrum was in agreement with the reference.[1] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.07 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.55 (d, *J* = 6.9 Hz, 3H), 1.58 (d, *J* = 6.9 Hz, 3H), 3.51 (sep, *J* = 6.9 Hz, 1H), 3.55 (sep, *J* = 6.9 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 7.68 (dd, *J* = 1.5, 8.1 Hz, 1H), 8.17 (d, *J* = 1.5 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{13}H_{17}I_2NNaO$ $[M+Na]^+$ 479.9292, found 479.9297.

4-(Diisopropylcarbamoyl)-3-iodophenyl trifluoromethanesulfonate (2q)

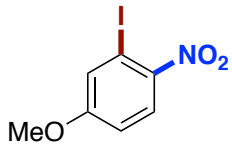


Following the **General Procedure** (argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/10), the titled compound was obtained as a pale yellow oil in 43% yield (108.9 mg, the yield was determined after subtraction of 15% of CH_2Cl_2.; 6% of 2-iodo isomer included). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.09 (d, *J* = 6.9 Hz, 3H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.56 (d, *J* = 6.9 Hz, 3H), 1.59 (d, *J* = 6.9 Hz, 3H), 3.51 (sep, *J* = 6.9 Hz, 1H), 3.54 (sep, *J* = 6.9 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.30 (dd, *J* = 2.5, 8.3 Hz, 1H), 7.73 (d, *J* = 2.5 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.1, 20.7, 20.9, 21.0, 46.4, 51.5, 92.4, 118.8 (CF_3, q, *J* = 320 Hz), 121.5, 127.0, 132.2, 144.7, 148.2, 168.3. **^{19}F NMR (376 MHz, $CDCl_3$):** δ –72.7. Metalated position (*ortho* to amide group) was determined by HMBC, which shows only one correlation between ^{13}C(CON^{i}Pr$_2$) and ^{1}H(aromatic). **FTIR (ATR):** 2976, 1632, 1426, 1209, 1138, 895, 729, 607 cm^{-1}. **HRMS (pos. ESI):** *m/z*: calcd for $C_{14}H_{17}F_3INNaO_4S$ $[M+Na]^+$ 501.9767, found 501.9783.

HMBC spectrum of 2p attached with high resolution ^{1}H and ^{13}C NMR spectra:

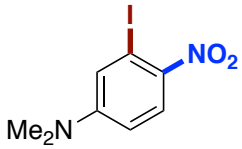


2-Iodo-4-methoxy-1-nitrobenzene (2r)



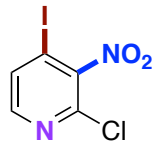
Following the **General Procedure** (0.2 mmol scale; argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 0/100 → 1/3), the titled compound was obtained as a yellow solid in 80% yield (44.6 mg). ^{1}H NMR spectrum was in agreement with the reference.[11] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.89 (s, 3H), 6.95 (dd, *J* = 2.7, 9.1 Hz, 1H), 7.54 (d, *J* = 2.7 Hz, 1H), 8.00 (d, *J* = 9.1 Hz, 1H). **EI-MS (% relative intensity):** *m/z*: 279 (M+, 100), 263 (5), 249 (60), 233 (8).

3-Iodo-*N,N*-dimethyl-4-nitroaniline (2s)



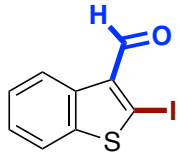
Following the **General Procedure** (0.2 mmol scale; argentation reaction was performed at –40 °C.; purification: PTLC with CH_2Cl_2/hexane = 2/1), the titled compound was obtained as a yellow solid in 81% yield (47.6 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 3.08 (s, 6H), 6.60 (dd, *J* = 2.8, 9.5 Hz, 1H), 7.22 (d, *J* = 2.8 Hz, 1H), 8.05 (d, *J* = 9.5 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 40.3, 90.1, 110.5, 142.0, 128.1, 139.7, 153.2. **FTIR (ATR):** 1594, 1547, 1297, 1271, 1011, 829, 741 cm^{-1}. **mp:** 122.7 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_8H_9IN_2O_2$: C, 32.90; H, 3.11; N, 9.59. Found: C, 32.82; H, 3.17; N, 9.49. **HRMS (pos. ESI):** *m/z*: calcd for $C_8H_9IN_2NaO$_ $[M+Na]^+$ 314.9601, found 314.9600.

2-Chloro-4-iodo-3-nitropyridine (2t)



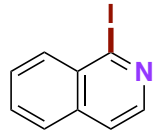
Following the **General Procedure** (0.2 mmol scale; argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 0/100 → 1/4), the titled compound was obtained as a white solid in 90% yield (51.3 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 5.2 Hz, 1H), 8.13 (d, *J* = 5.2 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 98.6, 134.0, 141.8, 150.1, 150.9. **FTIR (ATR):** 1550, 1535, 1352, 777 cm^{-1}. **mp:** 126.0 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_5H_2ClIN_2O_2$: C, 21.11; H, 0.71; N, 9.85. Found: C, 21.18; H, 0.95; N, 9.74. **EI-MS (% relative intensity):** *m/z*: 284 (M+, 100), 238 (84), 127 (52).

2-Iodobenzo[*b*]thiophene-3-carbaldehyde (2u)



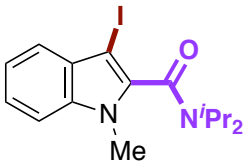
Following the **General Procedure** (0.2 mmol scale; argentation reaction was performed at –40 °C.; purification: AcOEt/hexane = 1/19 → 3/17), the titled compound was obtained as a slightly yellow solid in 87% yield (50.1 mg). ^{1}H NMR spectrum was in agreement with the reference.[12] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (m, 2H), 7.76 (d, *J* = 7.1 Hz, 1H), 8.74 (d, *J* = 7.6 Hz, 1H), 10.0 (s, 1H). **EI-MS (% relative intensity):** *m/z*: 288 (M+, 100), 259 (9), 160 (23), 132 (41).

1-Iodoisoquinoline (2v)



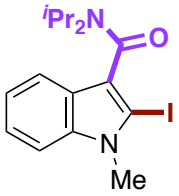
Following the **General Procedure** (purification: AcOEt/hexane = 1/20), the titled compound was obtained as a yellow solid in 81% yield (59.8 mg). ^{1}H NMR spectrum was in agreement with the reference.[13] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 (d, *J* = 5.6 Hz, 1H), 7.67-7.76 (m, 3H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 5.6 Hz, 1H). **HRMS (pos. ESI):** *m/z*: calcd for C_9H_7IN $[M+H]^+$ 255.9618, found 255.9616.

3-Iodo-*N*,*N*-diisopropyl-1-methyl-1*H*-indole-2-carboxamide (2w)



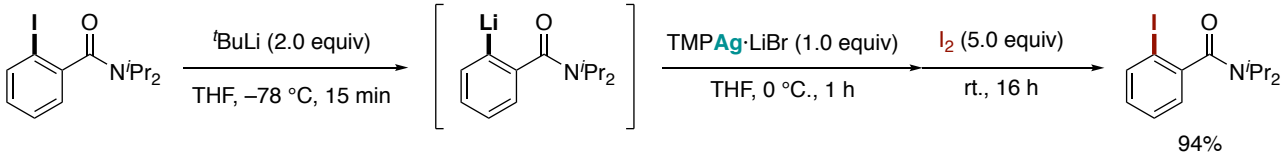
Following the **General Procedure** (0.2 mmol scale; purification: AcOEt/hexane = 1/10), the titled compound was obtained as a white solid in 79% yield (60.8 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.11 (d, *J* = 6.9 Hz, 3H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.63 (d, *J* = 6.9 Hz, 3H), 1.67 (d, *J* = 6.6 Hz, 3H), 3.59 (sep, *J* = 6.6 Hz, 1H), 3.76 (s, 3H), 3.79 (sep, *J* = 6.9 Hz, 1H), 7.20-7.24 (m, 1H), 7.28-7.33 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.3, 20.7, 21.4, 21.6, 31.6, 46.5, 51.8, 54.2, 109.9, 121.0, 121.6, 123.3, 129.7, 136.6, 137.9, 162.9. **FTIR (ATR):** 2970, 1633, 1307, 741 cm^{-1}. **mp:** 143.3 °C (decomp. started at 100 °C; recrystallized from hexane). **Anal.:** Calcd for $C_{16}H_{21}IN_2O$ + 1/23·H_2O: C, 50.34; H, 5.61; N, 7.22. Found: C, 50.35; H, 5.57; N, 7.20. **HRMS (pos. ESI):** *m/z*: calcd for $C_{16}H_{21}IN_2NaO$ $[M+Na]^+$ 407.0591, found 407.0595.

2-Iodo-*N*,*N*-diisopropyl-1-methyl-1*H*-indole-3-carboxamide (2x)



Following the **General Procedure** (purification: AcOEt/hexane = 1/3), the titled compound was obtained as a pale yellow solid in 99% yield (190.2 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.27-1.53 (brd, 12H), 3.62-3.90 (br, 2H), 3.77 (brs, 2H), 3.77 (s, 3H), 7.08 (dd, *J* = 7.6, 8.2 Hz, 1H), 7.17 (dd, *J* = 7.6, 7.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 21.3, 34.2, 46.2 (brs), 51.3 (brs), 84.0, 109.9, 118.7, 120.4, 121.5, 122.6, 126.6, 137.8, 166.4. **FTIR (ATR):** 2968, 1613, 1459, 1366, 1304, 737 cm^{-1}. **mp:** 211.1 °C (decomp. started at 100 °C; recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{16}H_{21}IN_2O$ + 1/4·H_2O: C, 49.43; H, 5.57; N, 7.21. Found: C, 49.49; H, 5.45; N, 7.16. **HRMS (pos. ESI):** *m/z*: calcd for $C_{16}H_{21}IN_2NaO$ $[M+Na]^+$ 407.0591, found 407.0610.

Scheme S1. Control Experiment on the Effect of LiCN in Iodination Step



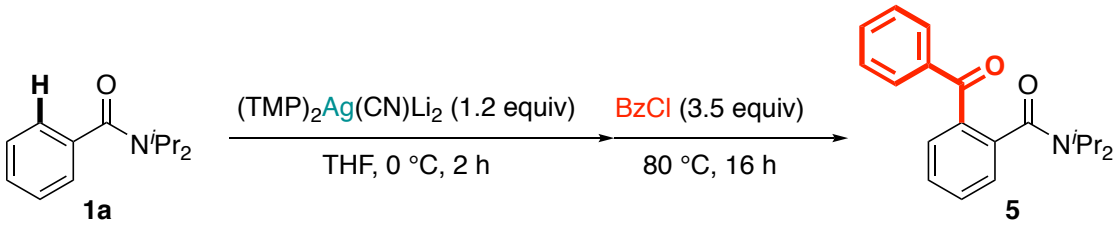
NMR Yield based on mesitylene as an internal standard.

Procedure for Scheme S1[14]:

To a suspension of silver bromide (37.6 mg, 0.2 mmol) in dry THF (0.4 mL) in a heat gun-dried brown Schlenck tube was added TMPLi in THF (0.2 mmol) *via* cannula at –78 °C under Ar. The mixture was covered with aluminum foil to exclude light and stirred at room temperature for 30 min during which time the block-shaped solid of silver bromide disappeared (= mixture **A**). Meanwhile, to a solution of 2-Iodo-*N*,*N*-diisopropylbenzamide (66.2 mg, 0.2 mmol) in dry THF (2.0 mL) was added ^{t}BuLi (1.48M ^{n}pentane solution, 270 μL, 0.2 mmol) at –78 °C, and the resulting suspension was stirred for 15 min at the same temperature (= mixture **B**). Following the completion of halogen-metal exchange (confirmed by ESI-MS), mixture **B** was added to the mixture **A** *via* cannula at –78 °C, and the resultant mixture was stirred for 1 h at 0 °C. Iodine (253.8 mg, 1.0 mmol) was added and the mixture was stirred for 16 h at room temperature. The aluminum foil was removed after the addition of iodine. The reaction was quenched with aqueous NH_4Cl (5 mL) and aqueous $Na_2S_2O_3$ (5 mL) followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Yields were determined by NMR spectroscopy using mesitylene as an internal standard.

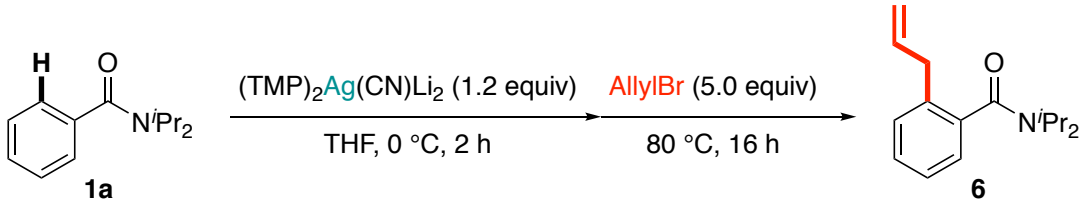
2.4. Reactions of Arylargentate with Electrophiles (Scheme 1)

2-Benzoyl-*N,N*-diisopropylbenzamide (5)



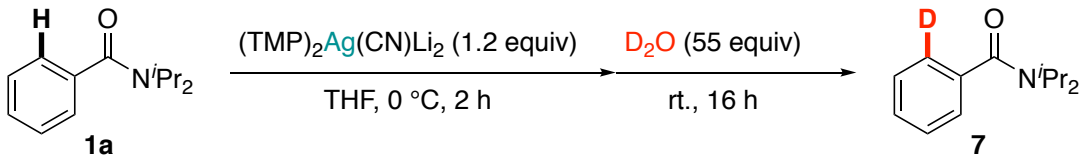
N,N-Diisopropylbenzamide **1a** (102.8 mg, 0.5 mmol) and dry THF (0.5 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.6 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 h at 0 °C. To the mixture was added benzoyl chloride (203.8 μL, 1.75 mmol) at –78 °C, then the Schlenk tube was immersed in pre-heated 80 °C oil bath and stirred for 16 h. The reaction was cooled to room temperature and quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/1) and PTLC using AcOEt/CH_2Cl_2 (1/6) to give the titled compound **5** as a pale pink solid in 82% yield (127.7 mg). ^{1}H NMR spectrum was in agreement with the reference.[1] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.20 (d, *J* = 6.6 Hz, 6H), 1.43 (d, *J* = 6.6 Hz, 6H), 3.45 (sep, *J* = 6.6 Hz, 1H), 3.84 (d, *J* = 6.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.37-7.58 (m, 6H), 7.80-7.82 (m, 2H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{20}H_{23}NNaO_2$ $[M+Na]^+$ 332.1621, found 332.1621.

2-Allyl-*N,N*-diisopropylbenzamide (6)



N,N-Diisopropylbenzamide **1a** (102.6 mg, 0.5 mmol) and dry THF (0.5 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.6 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 h at 0 °C. To the mixture was added allyl bromide (213 μL, 2.5 mmol) at –78 °C, then the Schlenk tube was immersed in pre-heated 80 °C oil bath and stirred for 16 h. The reaction was cooled to room temperature and quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Desired product **6** was obtained in 88% yield determined by ^{1}H NMR using mesitylene (20.8 mg) as an internal standard. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/7) and GPC to give the titled compound **6** as a white solid in 56% yield (68.1 mg). ^{1}H NMR spectra was in agreement with the reference.[1] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.10 (d, *J* = 6.6 Hz, 6H), 1.57 (d, *J* = 6.6 Hz, 6H), 3.42 (d, *J* = 6.6 Hz, 2H), 3.50 (sep, *J* = 6.6 Hz, 1H), 3.68 (sep, *J* = 6.6 Hz, 1H), 5.07-5.12 (m, 2H), 5.96 (ddt, *J* = 6.6, 10.0, 16.8 Hz 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.18-7.30 (m, 3H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{16}H_{23}NNaO$ $[M+Na]^+$ 268.1672, found 268.1677.

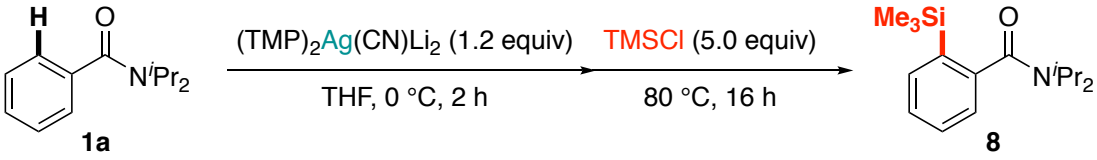
2-Deuterio-*N,N*-diisopropylbenzamide (7)



1a **7**

N,N-Diisopropylbenzamide **1a** (102.6 mg, 0.5 mmol) and dry THF (0.5 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.6 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 h at 0 °C. To the mixture was added D_2O (500 μL, 27.7 mmol), then the mixture was stirred for 16 h at room temperature. The reaction was quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/3) to give the titled compound **7** as a white solid in 96% yield (99.4 mg, D/H = 97/3). ^{1}H NMR spectrum was in agreement with the reference.[1] **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.16-1.52 (brd, 12H), 3.52-3.83 (brd, 2H), 7.30-7.32 (m, 1H), 7.36-7.38 (m 3H). **EI-MS (% relative intensity):** *m/z*: 206 (M+, 9), 191 (4), 163 (20), 106 (100), 78 (24).

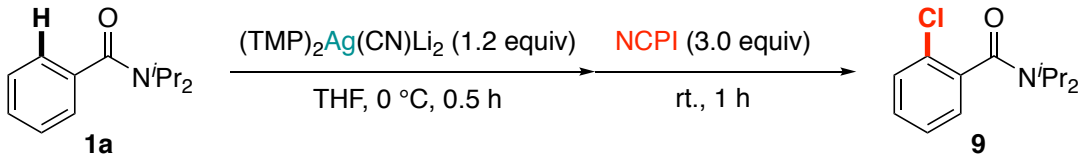
***N,N*-Diisopropyl-2-(trimethylsilyl)benzamide (8)**



1a **8**

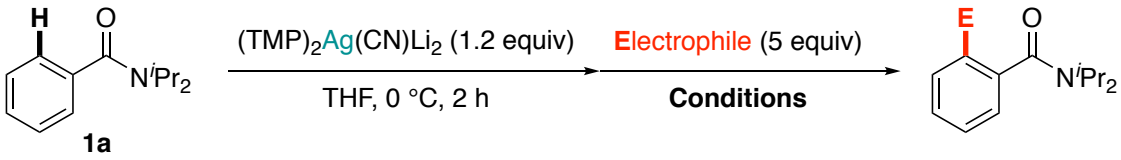
N,N-Diisopropylbenzamide **1a** (102.6 mg, 0.5 mmol) and dry THF (0.5 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.6 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 h at 0 °C. To the mixtutre was added chlorotrimethylsilane (316 μL, 2.5 mmol), then the Schlenk tube was immersed in pre-heated 80 °C oil bath and stirred for 16 h. The reaction was cooled to the room temperature and quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/10) to give the titled compound **9** as a white solid in 62% yield (85.5 mg). ^{1}H NMR spectrum was in agreement with the reference.[1] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 0.32 (s, 9H), 1.15 (d, *J* = 5.9 Hz, 6H), 1.56 (d, *J* = 5.6 Hz, 6H), 3.46-3.53 (brq, 1H), 3.77-3.84 (brq, 1H), 7.14-7.16 (m, 1H), 7.29-7.34 (m, 2H), 7.58-7.61 (m, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{16}H_{27}NNaOSi$ $[M+Na]^+$ 300.1754, found 300.1765.

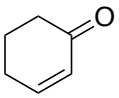
2-Chloro-*N,N*-diisopropylbenzamide (9)



N,N-Diisopropylbenzamide **1a** (41.1 mg, 0.20 mmol) and dry THF (0.2 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.24 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 0.5 h at 0 °C. To the mixture was added *N*-chlorophthalimide (109.0 mg, 0.60 mmol), then the mixture was stirred for 1 h at room temperature. The reaction was quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (3 mL × 3). The combined AcOEt layer was concentrated under reduced pressure and dissolved in Et_2O. The Et_2O solution was washed with 1M NaOH aq. (3 mL × 3) and brine (3 mL × 1), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/9 → 1/4) to give the titled compound **9** as a white solid in 92% yield (45.9 mg, 4% of **1a** included). ^{1}H NMR spectrum was in agreement with the reference.[15] **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.07 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H), 1.57 (d, *J* = 6.9 Hz, 3H), 1.58 (d, *J* = 6.9 Hz, 3H), 3.53 (sep, *J* = 6.7 Hz, 1H), 3.61 (sep, *J* = 6.7 Hz, 1H), 7.18-7.22 (m, 1H), 7.25-7.30 (m, 2H), 7.36-7.40 (m, 1H). **HRMS (pos. ESI):** *m/z*: calcd for $C_{13}H_{18}ClNNaO$ $[M+Na]^+$ 262.0969, found 262.0973.

Table S1. Electrophiles Unreactive to Arylargentate



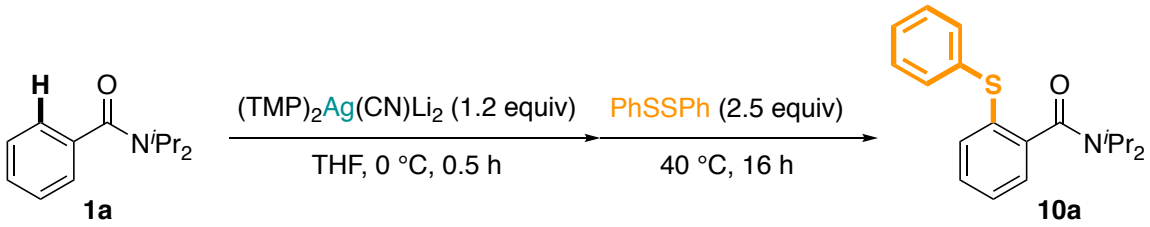
Entry	Electrophile	Conditions	NMR Yield
1	BnBr	80°C, 16 h	14%[a]
2	MeI	80°C, 16 h	trace
3	PhCHO	rt., 16 h	ND
4		80°C, 16 h	ND

NMR Yields based on mesitylene as an internal standard. [a] Isolated yield.

2.5. Chalcogen Installation *via* DoAg (Table 3)

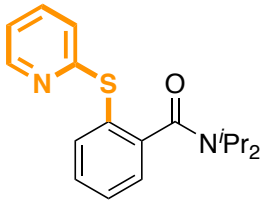
General Procedure:
The reactions were performed on 0.2 mmol scale.

_N,N_-Diisopropyl-2-(phenylthio)benzamide (10a)



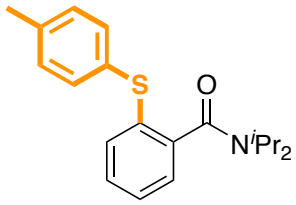
N,N-Diisopropylbenzamide **1a** (41.1 mg, 0.2 mmol) and dry THF (0.2 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.24 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 0.5 h at 0 °C. To the mixture was added diphenyldisulfide (109.2 mg, 0.5 mmol) at –78 °C, then the sealed Schlenk tube was immersed in pre-heated 40 °C oil bath and stirred for 16 h. The reaction was quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/6) to give the titled compound **10a** as a colorless oil in 99% yield (63.6 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.09 (d, *J* = 6.7 Hz, 3H), 1.17 (d, *J* = 6.7 Hz, 3H), 1.57-1.58 (brd, 6H), 3.51 (sep, *J* = 6.7 Hz, 1H), 3.71 (sep, *J* = 6.7 Hz, 1H), 7.17 (m, 5H), 7.27-7.31 (m, 2H), 7.35-7.39 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.4, 20.8, 20.9, 21.0, 46.1, 51.2, 125.8, 127.2, 127.4, 128.9, 129.3, 131.8, 132.1, 132.8, 135.3, 140.6, 168.9. **FTIR (ATR):** 2969, 1629, 1438, 1337, 1032, 739 cm^{-1}. **mp:** 86.4 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{23}NOS$: C, 72.80; H, 7.40; N, 4.47. Found: C, 72.69; H, 7.35; N, 4.42. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{23}NNaOS$ $[M+Na]^+$ 336.1393, found 336.1395.

_N,N_-Diisopropyl-2-(pyridin-2-ylthio)benzamide (10b)



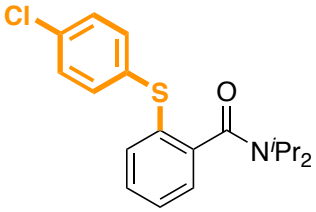
Following the **General Procedure** (purification: AcOEt/hexane = 1/10 → 1/3), the titled compound was obtained as a colorless oil in 99% yield (62.8 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.04 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.49 (d, *J* = 6.7 Hz, 3H), 1.53 (d, *J* = 6.7 Hz, 3H), 3.47 (sep, *J* = 6.7 Hz, 1H), 3.65 (sep, *J* = 6.7 Hz, 1H), 6.96-6.99 (m, 2H), 7.29 (dd, *J* = 1.5, 7.3 Hz, 1H), 7.38 (ddd, *J* = 1.5, 7.3, 7.5 Hz, 1H), 7.42-7,47 (m, 2H), 7.61 (dd, *J* = 1.2, 7.5 Hz, 1H), 8.37 (dd, *J* = 1.5, 5.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.2, 20.4, 20.7, 20.9, 46.0, 51.1, 120.1, 122.2, 126.3, 127.3, 129.2, 129.7, 136.8, 136.9, 144.1, 149.3, 160.9, 168.5. **FTIR (ATR):** 2968, 1627, 1338, 1119, 1032, 752, 723 cm^{-1}. **mp:** 117.5 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{18}H_{22}N_2OS$: C, 68.75; H, 7.05; N, 8.91. Found: C, 68.73; H, 7.10; N, 8.85. **HRMS (pos. ESI):** *m/z*: calcd for $C_{18}H_{22}N_2NaOS$ $[M+Na]^+$ 337.1345, found 337.1360.

_N,N_-Diisopropyl-2-(_p_-tolylthio)benzamide (10c)



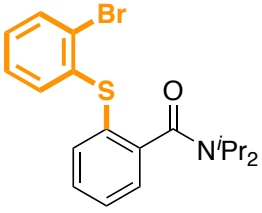
Following the **General Procedure** (sulfide formation was run at room temperature.; purification: AcOEt/hexane = 1/10 → 3/17), the titled compound was obtained as a white solid in 95% yield (61.9 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.09 (d, *J* = 6.7 Hz, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.58 (d, *J* = 6.7 Hz, 3H), 1.59 (d, *J* = 6.7 Hz, 3H), 2.34 (s, 3H), 3.52 (sep, *J* = 6.7 Hz, 1H), 3.72 (sep, *J* = 6.7 Hz, 1H), 7.06-7.08 (m, 1H), 7.12-7.20 (m, 5H), 7.32 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.4, 20.9, 21.3, 46.0, 51.2, 125.6, 126.5, 128.7, 130.2, 130.7, 130.9, 132.9, 134.1, 137.9, 139.6, 169.0. **FTIR (ATR):** 2970, 1629, 1337, 1033, 730 cm^{-1}. **mp:** 106.3 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{20}H_{25}NOS$: C, 73.35; H, 7.69; N, 4.28. Found: C, 73.11; H, 7.62; N, 4.23. **HRMS (pos. ESI):** *m/z*: calcd for $C_{20}H_{25}N_2NaOS$ $[M+Na]^+$ 350.1549, found 350.1554.

2-((4-Chlorophenyl)thio)-_N,N_-diisopropylbenzamide (10d)



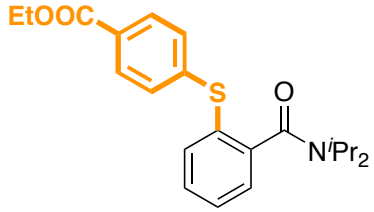
Following the **General Procedure** (sulfide formation was run at room temperature.; purification: AcOEt/hexane = 1/10 → 1/4 and GPC), the titled compound was obtained as a colorless oil in 81% yield (56.4 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.09 (d, *J* = 6.7 Hz, 3H), 1.16 (d, *J* = 6.7 Hz, 3H), 1.56 (d, *J* = 6.7 Hz, 6H), 3.51 (sep, *J* = 6.7 Hz, 1H), 3.67 (sep, *J* = 6.7 Hz, 1H), 7.19-7.30 (m, 8H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.4, 20.8 (overlapped), 20.9, 46.1, 51.2, 126.0, 127.9, 129.1, 129.5, 131.8, 132.6, 132.7, 133.3, 134.3, 141.3, 168.7. **FTIR (ATR):** 2971, 1628, 1474, 1338, 1092, 733 cm^{-1}. **mp:** 93.5 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{22}ClNOS$: C, 65.60; H, 6.37; N, 4.03. Found: C, 65.44; H, 6.40; N, 3.98. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{22}ClNNaOS$ $[M+Na]^+$ 370.1003, found 370.1017.

2-((2-Bromophenyl)thio)-_N,N_-diisopropylbenzamide (10e)



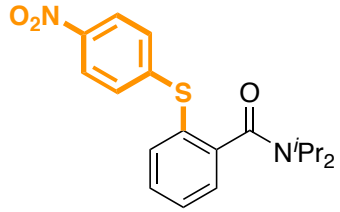
Following the **General Procedure** (purification: AcOEt/hexane = 7/93 → 1/4), the titled compound was obtained as a pale yellow oil in 99% yield (78.5 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.08 (d, *J* = 6.7 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.53 (d, *J* = 6.7 Hz, 3H), 1.54 (d, *J* = 6.7 Hz, 3H), 3.49 (sep, *J* = 6.7 Hz, 1H), 3.67 (sep, *J* = 6.7 Hz, 1H), 7.03 (ddd, *J* = 1.8, 7.3, 7.9 Hz, 1H), 7.07 (dd, *J* = 1.8, 7.9 Hz, 1H), 7.17 (ddd, *J* = 1.2, 7.3, 7.9 Hz, 1H), 7.26 (ddd, *J* = 0.9, 1.2, 7.3 Hz, 1H), 7.29-7.32 (m, 2H), 7.32-7.38 (m, 1H), 7.54 (dd, *J* = 1.2, 7.9 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.3, 20.7, 20.8, 21.0, 46.1, 51.2, 123.6, 126.4, 127.7, 128.0, 128.7, 129.2, 129.8, 131.1, 133.1, 134.2, 137.7, 142.5, 168.5. **FTIR (ATR):** 2969, 1630, 1444, 1338, 1018, 747 cm^{-1}. **mp:** 69.4 °C (decomp.; recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{22}BrNOS$: C, 58.16; H, 5.65; N, 3.57. Found: C, 58.09; H, 5.67; N, 3.51. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{22}BrNNaOS$ $[M+Na]^+$ 414.0498, found 414.0504.

Ethyl 4-((2-(diisopropylcarbamoyl)phenyl)thio)benzoate (10f)



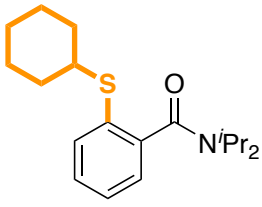
Following the **General Procedure** (sulfide formation was run at room temperature.; purification: AcOEt/hexane = 1/10 → 1/4 and PTLC with AcOEt/hexane = 1/4), the titled compound was obtained as a pale yellow solid in 93% yield (71.5 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.06 (d, *J* = 6.7 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.52 (d, *J* = 6.7 Hz, 3H), 1.54(d, *J* = 6.7 Hz, 3H), 3.49 (sep, *J* = 6.7 Hz, 1H), 3.65 (sep, *J* = 6.7 Hz, 1H), 4.34 (q, *J* = 7.0 Hz, 2H), 7.25-7.27 (m, 3H), 7.32 (ddd, *J* = 1.5, 7.3, 7.6 Hz, 1H), 7.37 (ddd, *J* = 1.2, 7.3, 7.6 Hz, 1H), 7.41 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 14.5, 20.4, 20.7, 20.8, 20.9, 46.1, 51.2, 61.1, 126.3, 128.3, 128.4, 129.0, 129.2, 129.3, 130.2, 135.0, 142.9, 143.5, 166.3, 168.5. **FTIR (ATR):** 2975, 1713, 1631, 1338, 1270, 1105, 761 cm^{-1}. **mp:** 92.7 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{22}H_{27}NO_3S$ + 1/4·H_2O: C, 67.75; H, 7.11; N, 3.59. Found: C, 67.79; H, 7.06; N, 3.54. **HRMS (pos. ESI):** *m/z*: calcd for $C_{22}H_{27}NNaO_3S$ $[M+Na]^+$ 408.1604, found 408.1613.

***N,N*-Diisopropyl-2-((4-nitrophenyl)thio)benzamide (10g)**



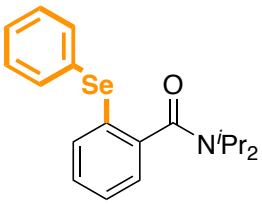
Following the **General Procedure** (sulfide formation was run at room temperature.; purification: AcOEt/hexane = 1/10 → 1/4 and GPC), the titled compound was obtained as a pale yellow solid in 86% yield (61.4 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.08 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1,47 (d, *J* = 6.7 Hz, 3H), 1.53 (d, *J* = 6.7 Hz, 3H), 3.49 (sep, *J* = 6.7 Hz, 1H), 3.61 (sep, *J* = 6.7 Hz, 1H), 7.23 (d, *J* = 9.2 Hz, 2H), 7.32 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.41 (ddd, *J* = 1.5, 7.6, 7.6 Hz, 1H), 7.48 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.54 (dd, *J* = 1.2, 7.6 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.3, 20.6, 20.7, 20.9, 46.1, 51.2, 124.1, 126.6, 127.0, 127.4, 129.6, 130.3, 136.5, 144.2, 145.6, 147.8, 168.1. **FTIR (ATR):** 2971, 1630, 1512, 1335, 852, 741 cm^{-1}. **mp:** 158.0 °C (decomp.; recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{22}N_2O_3S$ + 1/3·H_2O: C, 63.03; H, 6.24; N, 7.74. Found: C, 63.10; H, 6.23; N, 7.74. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{22}N_2NaO_3S$ $[M+Na]^+$ 381.1243, found 381.1252.

2-(Cyclohexylthio)-*N,N*-diisopropylbenzamide (10h)



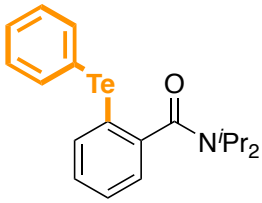
Following the **General Procedure** (sulfide formation was run at room temperature.; purification: AcOEt/hexane = 1/10 → 1/5), the titled compound was obtained as a colorless oil in 54% yield (34.7 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.03 (d, *J* = 6.7 Hz, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.21-1.41 (m, 6H), 1.56 (d, *J* = 6.7 Hz, 3H), 1.59 (d, *J* = 6.7 Hz, 3H), 1.71-1.77 (m, 2H), 1.91-1.98 (m, 2H), 3.21-3.26 (m, 1H), 3.50 (sep, *J* = 6.7 Hz, 1H), 3.56 (sep, *J* = 6.7 Hz, 1H), 7.13-7.15 (m, 1H), 7.22-7.27 (m, 2H), 7.42-7.46 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.1, 20.6, 20.7, 20.8, 25.8 (2C, overlaped), 26.1, 33.0, 33.7, 45.7, 47.1, 50.9, 125.7, 127.3, 128.1, 131.1, 133.7, 142.7, 169.1. **FTIR (ATR):** 2927, 1629, 1439, 1337, 1032, 769 cm^{-1}. **mp:** 47.6 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{29}NOS$: C, 71.43; H, 9.15; N, 4.38. Found: C, 71.68; H, 9.24; N, 4.56. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{29}NNaOS$ $[M+Na]^+$ 342.1862, found 342.1861.

***N,N*-Diisopropyl-2-(phenylselanyl)benzamide (10i)**



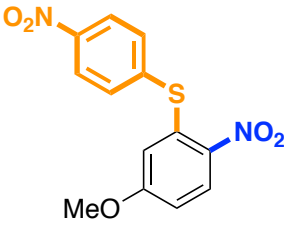
Following the **General Procedure** (selenide formation was run at 80 °C.; purification: AcOEt/hexane = 1/9 → 1/4), the titled compound was obtained as a pale yellow solid in 95% yield (56.2 mg, the yield was determined after subtraction of 5% of CH_2Cl_2). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.14 (brs, 6H), 1.59 (brs, 6H), 3.53 (brs, 1H), 3.75 (brs, 1H), 7.13-7.17 (m, 2H), 7.21-7.30 (m, 5H), 7.50-7.54 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.7, 20.9, 46.1, 51.3, 125.5, 127.2, 127.8, 129.0, 129.2, 129.5, 130.7, 133.6, 134.1, 141.3, 169.5. **FTIR (ATR):** 2968, 1627, 1437, 1336, 1031, 734, 691 cm^{-1}. **mp:** 85.6 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{23}NOSe$: C, 63.33; H, 6.43; N, 3.89. Found: C, 63.08; H, 6.48; N, 3.94. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{23}NNaOSe$ $[M+Na]^+$ 384.0837, found 384.0844.

***N,N*-Diisopropyl-2-(phenyltellanyl)benzamide (10j)**



Following the **General Procedure** (telluride formation was run at 80 °C.; purification: AcOEt/hexane = 1/49 → 1/4), the titled compound was obtained as a pale yellow oil in 97% yield (83.4 mg, the yield was determined after subtraction of 25% of AcOEt, which remained after high vaccum for 16 h.; AcOEt could be removed by iterative azeotropic evaporation with hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 1.38 (br, 12H), 3.74 (br, 2H), 7.05 (ddd, *J* = 1.8, 7.0, 7.6 Hz, 1H), 7.14-7.20 (m, 2H), 7.25 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.35 (ddd, *J* = 1.2, 6.7, 7.3 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 7.3 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.9, 46.4 (brs), 51.2(brs), 115.4, 116.8, 125.2, 126.7, 128.4, 129.2, 129.6, 136.8, 139.9, 142.9, 171.3. **FTIR (ATR):** 2967, 1614, 1434, 1337, 1017, 731, 691 cm^{-1}. **Anal.:** Calcd for $C_{19}H_{23}NOTe$ + 1/3·H_2O: C, 54.99; H, 5.75; N, 3.38. Found: C, 54.84; H, 5.58; N, 3.33. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{23}NNaOTe$ $[M+Na]^+$ 434.0734, found 434.0740.

(5-Methoxy-2-nitrophenyl)(4-nitrophenyl)sulfane (10k)

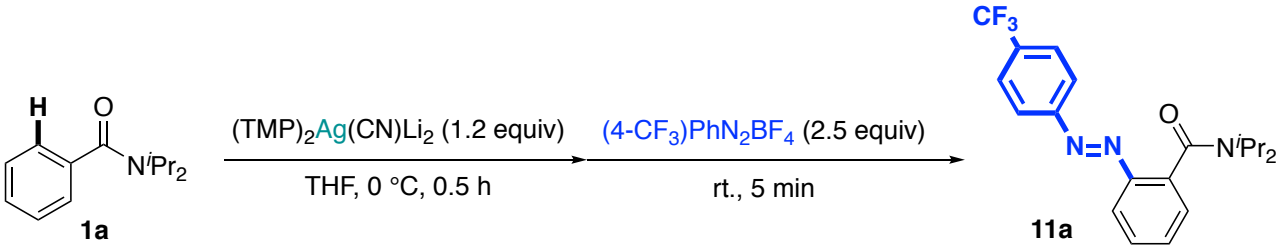


Following the **General Procedure** (argentation reaction was performed at –40 °C for 2 h; purification: AcOEt/hexane = 0/100 → 25/75), the titled compound was obtained as a yellow solid in 89% yield (54.4 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 3.72 (s, 3H), 6.36 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 2.8, 9.2 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 2H), 8.28 (d, *J* = 9.2 Hz, 1H), 8.30 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 56.0, 111.5, 114.3, 125.0, 128.6, 135.6, 138.9, 139.6, 140.8, 148.5, 163.6. **FTIR (ATR):** 3095, 2919, 2849, 1574, 1519, 1335, 1243, 1044, 852 cm^{-1}. **mp:** 158.1 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{13}H_{10}N_2O_5S$ + 1/3·H_2O: C, 50.00; H, 3.44; N, 8.97. Found: C, 49.92; H, 3.38; N, 8.91. **EI-MS (% relative intensity):** *m/z*: 306 (M+, 22), 259 (18), 196 (100), 181 (92), 153 (49).

2.6. Azo Synthesis *via* DoAg (Table 3)

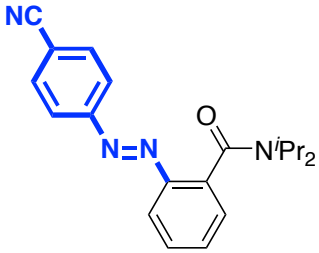
General Procedure:
The reactions were performed on 0.2 mmol scale.

(*E*)-*N*,*N*-Diisopropyl-2-((4-(trifluoromethyl)phenyl)diazenyl)benzamide (11a)



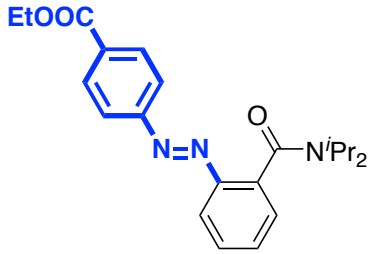
N,*N*-Diisopropylbenzamide **1a** (41.1 mg, 0.2 mmol) and dry THF (0.2 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.24 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 0.5 h at 0 °C. The mixture was transferred to a heat gun-dried Schlenk tube containing 4-(trifluoromethyl)benzenediazonium tetrafluoroborate (130.0 mg, 0.5 mmol, pre-dried for 1 h under high vacuum). Azo formation (mixture of *cis*- and *trans*-forms) completed within 5 min with a vigorous stirring at room temperature. The Schlenk tube was immersed in a pre-heated 80 °C oil bath and stirred for 16 h in order to obtain the *trans*-form. The reaction was cooled to the room temperature and quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt/hexane (1/10 → 1/4) and PTLC using AcOEt/hexane (1/4) to give the titled compound **11a** as an orange solid in 68% yield (51.5 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 0.94 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.63 (d, *J* = 6.7 Hz, 3H), 1.64 (d, *J* = 6.7 Hz, 3H), 3.54 (sep, *J* = 6.7 Hz, 1H), 3.73 (sep, *J* = 6.7 Hz, 1H), 7,41 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.47 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.54 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.2, 20.6, 20.8, 21.0, 46.1, 51.2, 116.6, 123.4, 124.0 (CF_3, q, *J* = 272 Hz), 126.4 (C_{Ar}–C_{Ar}–CF_3, q, *J* = 4 Hz), 126.6, 129.0, 132.4, 132.6 (C_{Ar}–CF_3, q, *J* = 35 Hz), 139.7, 147.9, 154.3, 168.8. **^{19}F NMR (470 MHz, $CDCl_3$):** δ –62.6. **FTIR (ATR):** 2970, 1632, 1440, 1319, 1125, 1063, 850, 764 cm^{-1}. **mp:** 158.7 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{20}H_{22}F_3N_3O$: C, 63.65; H, 5.88; N, 11.13. Found: C, 63.34; H, 5.98; N, 11.10. **HRMS (pos. ESI):** *m/z*: calcd for $C_{20}H_{22}F_3N_3NaO$ $[M+Na]^+$ 400.1607, found 400.1620.

(*E*)-2-((4-Cyanophenyl)diazenyl)-*N*,*N*-diisopropylbenzamide (11b)



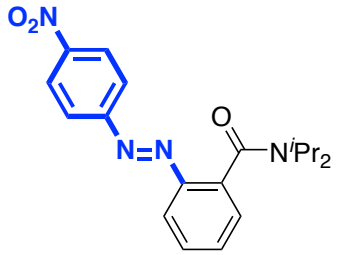
Following the **General Procedure** (purification: AcOEt/hexane = 7/93 → 1/4), the titled compound was obtained as a brown solid in 74% yield (49.8 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 0.93 (d, *J* = 6.7 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.62 (d, *J* = 6.7 Hz, 3H), 1.62 (d, *J* = 6.7 Hz, 3H), 3.54 (sep, *J* = 6.7 Hz, 1H), 3.72 (sep, *J* = 6.7 Hz, 1H), 7.41 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.47 (ddd, *J* = 1.2, 7.6, 8.2 Hz, 1H), 7.55 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.84 (dd, *J* = 1.2, 8.2 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.3, 20.6, 20.8, 20.9, 46.1, 51.2, 114.4, 116.7, 118.5, 123.7, 126.7, 129.1, 132.8, 133.4, 139.9, 147.9, 154.4, 168.6. **FTIR (ATR):** 2970, 2227, 1630, 1441, 1339, 848, 768, 734, 565 cm^{-1}. **mp:** 159.3 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{20}H_{22}N_4O + H_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.23; H, 6.37; N, 15.82. **HRMS (pos. ESI):** *m/z*: calcd for $C_{20}H_{22}N_4NaO$ $[M+Na]^+$ 357.1686, found 357.1690.

Ethyl (*E*)-4-((2-(diisopropylcarbamoyl)phenyl)diazenyl)benzoate (11c)



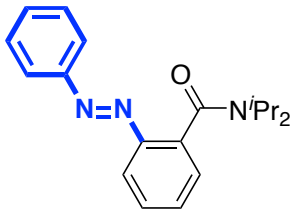
Following the **General Procedure** (purification: AcOEt/hexane = 7/93 → 1/4), the titled compound was obtained as a brown solid in 69% yield (53.0 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 0.93 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.63 (d, *J* = 6.7 Hz, 3H), 1.64 (d, *J* = 6.7 Hz, 3H), 3.54 (sep, *J* = 6.7 Hz, 1H), 3.72 (sep, *J* = 6.7 Hz, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 7.41 (dd, *J* = 1.5, 7.3 Hz, 1H), 7.47 (ddd, *J* = 1.5, 7.3, 7.9 Hz, 1H), 7.53 (ddd, *J* = 1.2, 7.3, 7.3 Hz, 1H), 7.84 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 2H), 8.17 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 14.5, 20.2, 20.5, 20.9, 21.0, 46.1, 51.1, 61.4, 116.5, 123.1, 126.6, 129.0, 130.7, 132.3, 132.6, 139.7, 148.0, 155.0, 166.1, 168.8. **FTIR (ATR):** 2971, 1714, 1626, 1442, 1339, 1269, 769 cm^{-1}. **mp:** 149.5 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{22}H_{27}N_3O_3$: C, 69.27; H, 7.13; N, 11.02. Found: C, 68.96; H, 7.09; N, 10.88. **HRMS (pos. ESI):** *m/z*: calcd for $C_{22}H_{27}N_3NaO_3$ $[M+Na]^+$ 404.1945, found 404.1953.

(*E*)-*N*,*N*-Diisopropyl-2-((4-nitrophenyl)diazenyl)benzamide (11d)



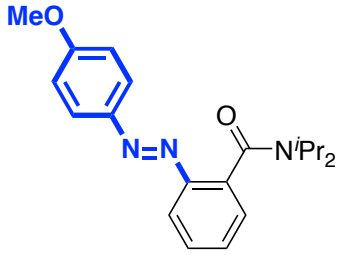
Following the **General Procedure** (purification: AcOEt/hexane = 7/93 → 1/4), the titled compound was obtained as a red solid in 72% yield (51.0 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 0.94 (d, *J* = 6.7 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.63 (d, *J* = 6.7 Hz, 3H) 1.64 (d, *J* = 6.7 Hz, 3H), 3.55 (sep, *J* = 6.7 Hz, 1H), 3.73 (sep, *J* = 6.7 Hz, 1H), 7.43 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.49 (ddd, *J* = 1.2, 7.6, 7.9 Hz, 1H), 7.57 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.86 (dd, *J* = 1.2, 7.9 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 2H), 8.37 (d, *J* = 9.2 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 20.3, 20.6, 20.8, 20.9, 46.1, 51.2, 116.6, 123.8, 124.9, 126.7, 129.1, 133.1, 140.1, 147.9, 149.0, 155.6, 168.6. **FTIR (ATR):** 2969, 1629, 1526, 1440,1339, 858, 765 cm^{-1}. **mp:** 153.6 °C (decomp.; recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{22}N_4O_3$ + 1/10·hexane + 1/5·H_2O: C, 64.21; H, 6.54; N, 15.28. Found: C, 64.14; H, 6.37; N, 15.39. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{22}N_4NaO_3$ $[M+Na]^+$ 377.1584, found 377.1591.

(*E*)-*N*,*N*-Diisopropyl-2-(phenyldiazenyl)benzamide (11e)



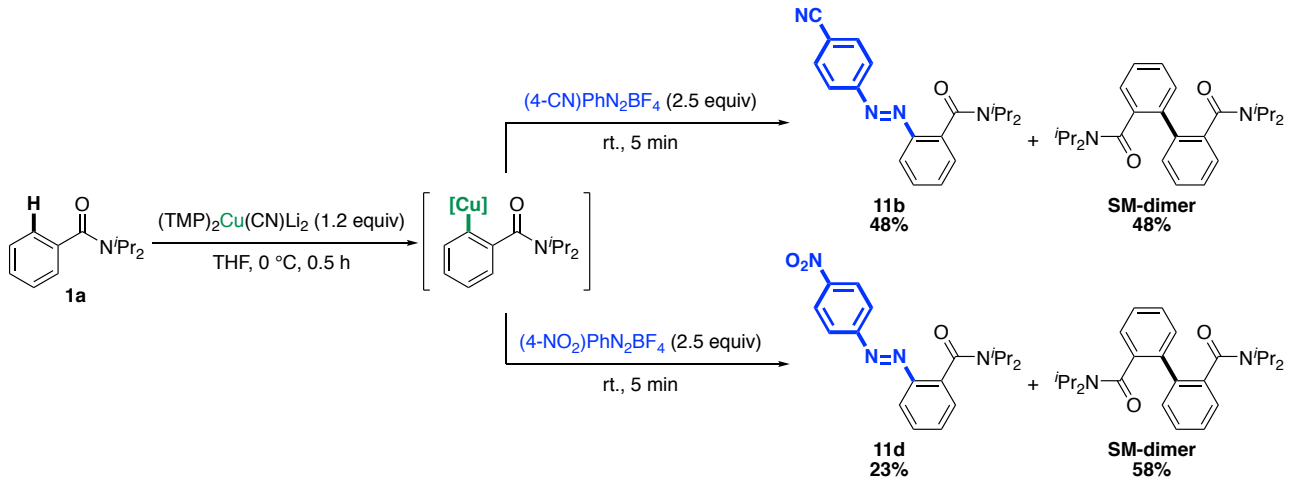
Following the **General Procedure** (purification: AcOEt/hexane = 1/10 → 1/4), the titled compound was obtained as an orange solid in 52% yield (32.3 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 0.94 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 1.62 (d, *J* = 6.7 Hz, 3H), 1.64 (d, *J* = 6.7 Hz, 3H), 3.53 (sep, *J* = 6.7 Hz, 1H), 3.73 (sep, *J* = 6.7 Hz, 1H), 7.39 (dd, *J* = 1.2, 7.0 Hz, 1H), 7.43-7.51 (m, 5H), 7.82 (dd, *J* = 1.2, 7.9 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.2, 20.5, 20.9, 21.0, 46.0, 51.1, 116.5, 123.4, 126.5, 128.9, 129.2, 131.4, 131.6, 139.1, 148.1, 152.6, 169.1. **FTIR (ATR):** 2968, 1631, 1440, 1338, 776, 688 cm^{-1}. **mp:** 111.9 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{19}H_{23}N_3O$ + 1/16·hexane + 1/8·H_2O: C, 73.40; H, 7.67; N, 13.25. Found: C, 73.35; H, 8.00; N, 13.54. **HRMS (pos. ESI):** *m/z*: calcd for $C_{19}H_{23}N_3NaO$ $[M+Na]^+$ 332.1733, found 332.1748.

(*E*)-*N*,*N*-Diisopropyl-2-((4-methoxyphenyl)diazenyl)benzamide (11f)



Following the **General Procedure** (purification: AcOEt/hexane = 7/93 → 1/4 and PTLC with AcOEt/hexane = 1/3), the titled compound was obtained as an orange solid in 34% yield (23.2 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 0.93 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.62 (d, *J* = 6.7 Hz, 3H), 1.65 (d, *J* = 6.7 Hz, 3H), 3.52 (sep, *J* = 6.7 Hz, 1H), 3.71 (sep, *J* = 6.7 Hz, 1H), 3.88 (s, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.36-7.38 (m, 1H), 7.41-7.46 (m, 2H), 7.77-7.80 (m, 1H), 7.90 (d, *J* = 8.9 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ 20.1, 20.6, 20.9, 21.0, 45.9, 51.1, 55.7, 114.3, 116.4, 125.3, 126.5, 128.9, 130.9, 138.7, 147.1, 148.2, 162.4, 169.3. **FTIR (ATR):** 2967, 1627, 1599, 1501, 1441, 1338, 1251, 1142, 1029, 839, 729, 549 cm^{-1}. **mp:** 124.8 °C (recrystallized from $CHCl_3$/hexane). **Anal.:** Calcd for $C_{20}H_{25}N_3O_2$ + 1/10·H_2O: C, 70.40; H, 7.44; N, 12.31. Found: C, 70.39; H, 7.44; N, 12.23. **HRMS (pos. ESI):** *m/z*: calcd for $C_{20}H_{25}N_3NaO_2$ $[M+Na]^+$ 362.1839, found 362.1850.

Scheme S2. Reactions of Arylcuprate and Diazonium Tetrafluoroborates

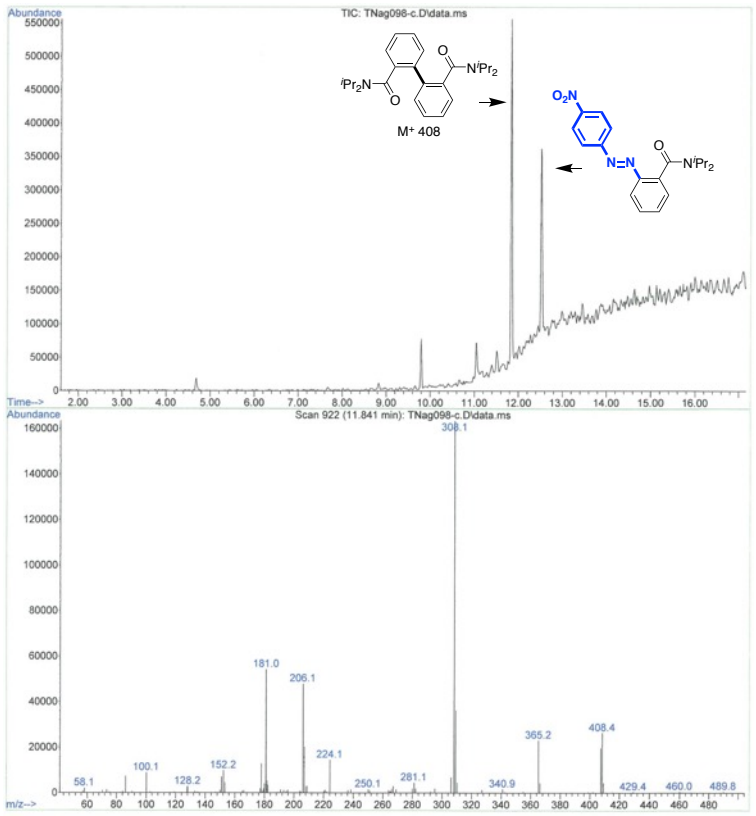


NMR yields based on mesitylene as an internal standard. Azo compounds were isomerized to their *trans* form at 80 °C for 16 h.

General Procedure for Scheme S2:

N,N-Diisopropylbenzamide **1a** (41.1 mg, 0.2 mmol) and dry THF (0.2 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Cu(CN)Li_2$ (0.24 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 h at 0 °C. The mixture was transferred to a heat gun-dried Schlenk tube containing diazonium tetrafluoroborate (0.5 mmol, pre-dried for 1 h under high vacuum). Azo formation (mixture of *cis*- and *trans*-forms) completed within 5 min with a vigorous stirring at room temperature. The Schlenk tube was immersed in a pre-heated 80 °C oil bath and stirred for 16 h in order to obtain the *trans*-form. The reaction was cooled to the room temperature and quenched with aqueous NH_4Cl (5 mL), followed by extraction with AcOEt (10 mL × 3). The combined AcOEt layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. NMR yields were determined using mesitylene as an internal standard (The yield of SM-dimer was calculated based on the reference).[1]

GC-MS chart of the reaction:



3. Crystal and Computational Details

3.1. General crystallographic details

For X-ray data, samples of cyanoargentate $(TMP)_2Ag(CN)Li_2(THF)$ (**3**(THF), Fig. S1) and argentate $(TMP)_2AgLi$ (Fig. S2) were transported to a microscope in a bath of anti-freeze, which was pre-chilled to –27 °C. Crystals were transferred quickly using a spatula to a drop of perfluoropolyether oil on a microscope slide. A stream of cold nitrogen (~ 0 °C) was passed over the slide whilst a suitable crystal was selected. Samples of two kinds of arylargentates (Fig. S3 and S4) were manipulated in a glove box at room temperature. The crystal was transferred to a pin fitted with a MicroLoop™ and attached quickly to the goniometer head. Data for cyanoargentate $(TMP)_2Ag(CN)Li_2(THF)$ and argentate $(TMP)_2AgLi$ were collected on a Bruker D8 Quest diffractometer (Cu-K_α, λ = 1.54184 Å) and data for two kinds of arylargentates (Fig. S3 and S4) were collected on a Rigaku XtaLAB Synergy-S (Cu-K_α, λ = 1.54184 Å). Structures were solved with the program SHELXT[1] with refinement, based on F^2, by full-matrix least squares refinement[2]. Non-hydrogen atoms were refined anisotropically (for disorder, standard restraints and constraints were applied, as appropriate) and a riding model, with idealized geometry was employed for H-atoms. Data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1919739, 1919740, 1957572 and 1960037. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

3.2. Synthesis and Characterization of TMP-Argentates (Fig. 2)

• **Cyanoargentate $(TMP)_2Ag(CN)Li_2(THF)$ (3(THF))**

To a solution of TMPH (0.34 mL, 2 mmol) in toluene (4 mL) at –78 °C was added ^{n}BuLi (1.25 mL, 2 mmol). The solution was warmed to room temperature whereupon it was transferred to a slurry of AgCN (0.13 g, 1 mmol) in toluene (2 mL) at –78 °C. The suspension was warmed to 0 °C and stirred for 10 min, and then stirred at room temperature for a further 10 min. During this time, the solution darkened. After no further darkening occurred, the solvent was removed *in vacuo* and THF (3 mL) was added. This was subsequently removed *in vacuo* and the residue digested in hexane (6 mL) and toluene (6 mL). Filtration gave an orange-yellow solution, which was concentrated until precipitation occurred. The precipitate was dissolved with gentle warming and the solution was stored at 5 °C for 24 h, after which time a crop of block-like crystals formed. **Yield:** 13% wrt. AgCN (65 mg). **^{1}H NMR (500 MHz, 298 K, C_6D_6):** δ 1.06 (s, 1.5H, TMPH-Me), 1.31 (br, m, 4H, THF), 1.46 (br, s, 16H, TMP-Me + TMP-3,5)*, 1.53 (s, 1.5H, unidentified), 1.61–1.64 (br, 2H, TMP-4), 1.67 (s, 12H, TMP-Me), 1.81 (m, 4H, TMP-3,5), 2.01 (m, 2H, TMP-4), 3.54 (m, 4H, THF). *Integration and COSY suggest one set of TMP-3,5 hydrogens lie beneath the broad TMP-Me resonance at δ 1.46 ppm. **^{13}C NMR (125 MHz, 298 K, C_6D_6):** δ 18.4 (TMPH-4), 19.7 (TMP-4), 24.9 (THF), 31.6 (TMPH-Me), 35.2 (TMP-Me), 38.2 (TMPH-3,5), 38.4 (TMP-Me), 39.8 (br, TMP-3,5), 49.1 (TMPH-2,6), 54.1 (d, $^2J_{Ag\text{-}C}$ = 3 Hz, TMP-2,6), 68.2 (THF), 168.2 (CN). **^{7}Li NMR (194 MHz, 298 K, C_6D_6):** δ 0.29 (s, 1Li, CA), 1.09 (s, 0.07Li, A). CA = cyanoargentate, A = argentate. **IR (nujol)** $\bar{\nu}$ (CN) = 2150 (br, w), 2102 (s). **m.p.**: 115 °C (decomp.). **Anal.:** Calcd for $C_{23}H_{44}AgLi_2N_3O$: C, 55.21; H, 8.86; N, 8.40. Found: C, 54.49; H, 8.57; N, 8.43. **X-ray:** $C_{46}H_{88}Ag_2Li_4N_6O_2$, M = 1000.72, triclinic, space group $P\bar{1}$, a = 8.3861(3), b = 11.5994(4), c = 14.0500(5) Å, α = 86.881(2), β = 79.282(2), γ = 83.876(2) °, V = 1334.35(8) Å^3, Z = 1, ρ_{calcd} = 1.245 g cm^{-3}, Cu-K_α radiation, λ = 1.54184 Å, μ = 6.615 mm^{-1}, T = 180(2) K. 14620 data (4655 unique, R_{int} = 0.0325, θ < 66.637 °) were collected. $wR2$ = $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.0673, conventional R = 0.0272 on F values of 4220 reflections with $F^2 > 2\sigma(F^2)$, S = 1.077, 307 parameters. Residual electron density extrema ±0.486 eÅ^{-3}.

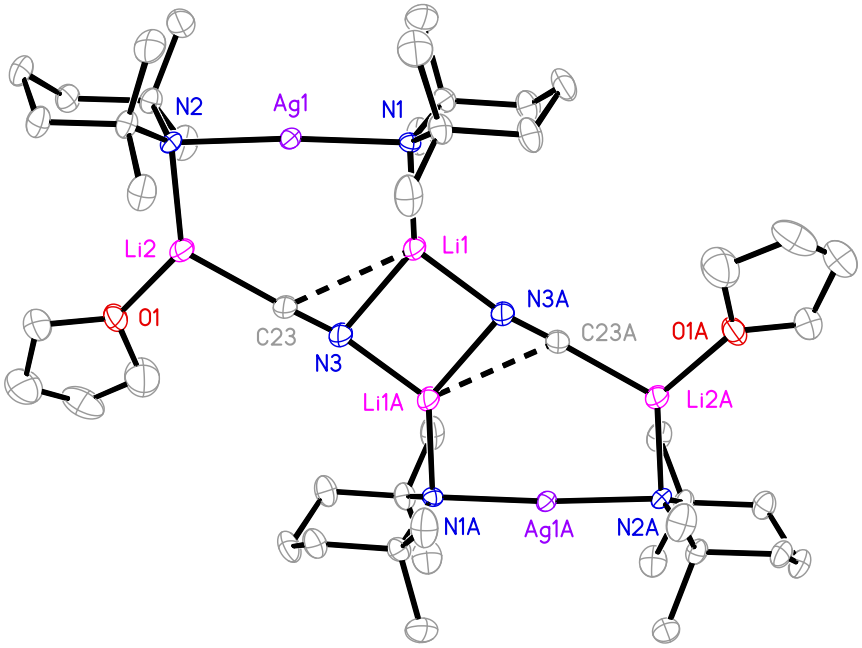


Fig. S1. Molecular structure of the dimer of **3**(THF) at 30% probability

N3–Li1	2.125(6)	C23–N3	1.140(4)
N3A–Li1	2.014(6)	N1–Ag1–N2	176.01(8)
Ag1–N1	2.134(2)	N3–Li1–N3A	92.7(2)
Ag1–N2	2.147(2)	N3A–Li1–N1	129.2(3)
N1–Li1	1.957(5)	C23–Li2–N2	123.9(3)
N2–Li2	1.976(5)	Li1–N1–Ag1	93.96(17)
C23–Li2	2.139(6)	Li2–N2–Ag1	88.29(17)

Table S2. Selected bond lengths (Å) and angles (°) for the dimer of **3**(THF).

• **Argentate $(TMP)_2AgLi$**

Method (a) To a solution of TMPH (0.34 mL, 2 mmol) and THF (0.08 mL, 1 mmol) in hexane (3 mL) was added ^{n}BuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) at −78 °C. The solution was returned to room temperature, whereupon it was transferred to a slurry of AgSCN (0.165 g, 1 mmol) in hexane (1 mL) at −78 °C. The mixture darkened upon warming to room temperature to give a black suspension, which was filtered to give a yellow solution. Storage of the filtrate at −27 °C for 24 h gave a few needle-like crystals suitable for diffraction and NMR studies. *Method (b)* To a solution of TMPH (0.34 mL, 2 mmol) in toluene/diisopropyl ether (3 mL/1 mL) was added ^{n}BuLi (1.25 mL, 1.6 M in hexanes, 2 mmol) at −78 °C. The solution was warmed to room temperature and transferred to a slurry of AgSCN (0.165 g, 1 mmol) in toluene/diisopropyl ether (1 mL/1 mL). The mixture was warmed to room temperature to give a dark solution which was filtered to give a straw-colored solution. Storage of the filtrate at −27 °C for 24 h gave a crop of needle-like crystals suitable for bulk analysis. *Method (a)* **^{1}H NMR (500 MHz, 298 K, C_6D_6):** δ 1.06 (s, 1H, TMPH-Me), 1.14 (s, 4H, TMP-3,5), 1.46 (s, 12H, TMP-Me), 1.54 (s, 12H, TMP-Me), 1.63 (m, 2H, TMP-4), 1.70 (m, 4H, TMP-3,5), 1.84 (m, 2H, TMP-4). **^{13}C NMR (125 MHz, 298 K, C_6D_6):** δ 18.4 (s, TMPH-4), 19.5 (s, TMP-4), 31.6 (s, TMPH-Me), 35.5 (s, TMP-Me), 38.2 (s, TMPH-3,5), 40.1 (s, TMP-Me), 41.1 (d, $^3J_{Ag\text{-}C}$ = 6 Hz, TMP-3,5), 49.2 (s, TMPH-2,6), 54.8 (d, $^2J_{Ag\text{-}C}$ = 3 Hz, TMP-2,6). **^{7}Li NMR (194 MHz, 298 K, C_6D_6):** δ 1.06 (s). *Method (b)* **Yield:** 18 % wrt. AgSCN (75 mg). **^{1}H NMR (500 MHz, 298 K, C_6D_6):** δ 1.06 (s, 1H, TMP-Me; TMPH), 1.14 (m, 4H, TMP-3,5; A), 1.38 (s, 1.6H, TMP-Me, unidentified), 1.46 (s, 12H, TMP-Me; A), 1.54 (s, 14H, TMP-Me; A / TMP-3,5; TMPAg), 1.62 (s, 2H, TMP-Me, unidentified), 1.63 (s, 5.5H, TMP-Me; TMPAg), 1.70 (m, 4H, TMP-3,5; A), 1.74 (br, 0.9H, TMP-4; TMPAg), 1.84 (m, 2H, TMP-4; A). A = argentate. (*Method (b)* gave product that incorporated a small quantity of contaminant including TMPAg (confirmed by comparison with an authentic sample) - see also elemental analysis below.) **^{13}C NMR (125 MHz, 298 K, C_6D_6):** δ 19.4 (s, TMP-4, unidentified), 19.5 (s, TMP-4; A), 19.6 (s, TMP-4; TMPAg), 31.6 (s, TMP-Me; TMPH), 35.5 (s, TMP-Me; A), 35.8 (s, TMP-Me, unidentified), 36.8 (s, TMP-Me, unidentified), 38.2 (br, TMP-Me; TMPH), 38.4 (br, m, TMP-Me; TMPAg), 38.5 (br, m, TMP-Me, unidentified), 39.7 (s, TMP-Me, unidentified), 39.8 (s, TMP-Me, unidentified), 40.1 (s, TMP-Me; A), 41.2 (d, $^3J_{Ag\text{-}C}$ = 7 Hz, TMP-3,5, unidentified), 41.3 (d, $^3J_{Ag\text{-}C}$ = 7 Hz, TMP-3,5, unidentified), 41.4 (d, $^3J_{Ag\text{-}C}$ = 6 Hz, TMP-3,5; A), 42.0 (m, TMP-3,5, unidentified), 42.2 (t, $^3J_{Ag\text{-}C}$ = 3 Hz, TMP-3,5; TMPAg), 42.4 (t, $^3J_{Ag\text{-}C}$ = 3 Hz, TMP-3,5, unidentified), 42.5 (m, TMP-2,6, unidentified), 49.2 (s, TMP-2,6; TMPH), 51.9 (s, TMP-2,6, unidentified), 54.8 (m, TMP-2,6; A), 56.7 (m, TMP-2,6; TMPAg), 56.8 (m, TMP-2,6, unidentified). A = argentate. **^{7}Li NMR (194 MHz, 298 K, C_6D_6):** δ 1.06 (s, 1Li), 1.67 (s, 0.27Li). **m.p.**: 173 °C (decomp.). **Anal.:** Calcd for $C_{18}H_{36}AgLiN_2$: C, 54.69; H, 9.18; N, 7.09.* Found: C, 51.84; H, 8.91; N, 7.31. (*Formula from ^{1}H NMR data above ≈ $(TMP)_2Ag_{1.2}Li_{0.8}$ based on TMPAg contamination. Calcd for $C_{18}H_{36}Ag_{1.2}Li_{0.8}$: C, 52.03; H, 8.73; N, 6.74.) **X-ray:** $C_{36}H_{72}Ag_2Li_2N_4$, M = 790.59, monoclinic, space group *C*2/*c*, *a* = 22.1326(5), *b* = 8.3936(2), *c* = 22.8868(6) Å, β = 109.5610(10) °, *V* = 4006.34(17) Å^3, *Z* = 4, ρ_{calcd} = 1.311 g cm^{-3}, Cu-K$_\alpha$ radiation, λ = 1.54184 Å, μ = 8.026 mm^{-1}, *T* = 180(2) K. 18817 data (3517 unique, R_{int} = 0.0489, θ < 66.621 °) were collected. $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.0537, conventional *R* = 0.0257 on *F* values of 3045 reflections with $F^2 > 2\sigma(F^2)$, *S* = 1.128, 208 parameters. Residual electron density extrema ±0.496 eÅ^{-3}.

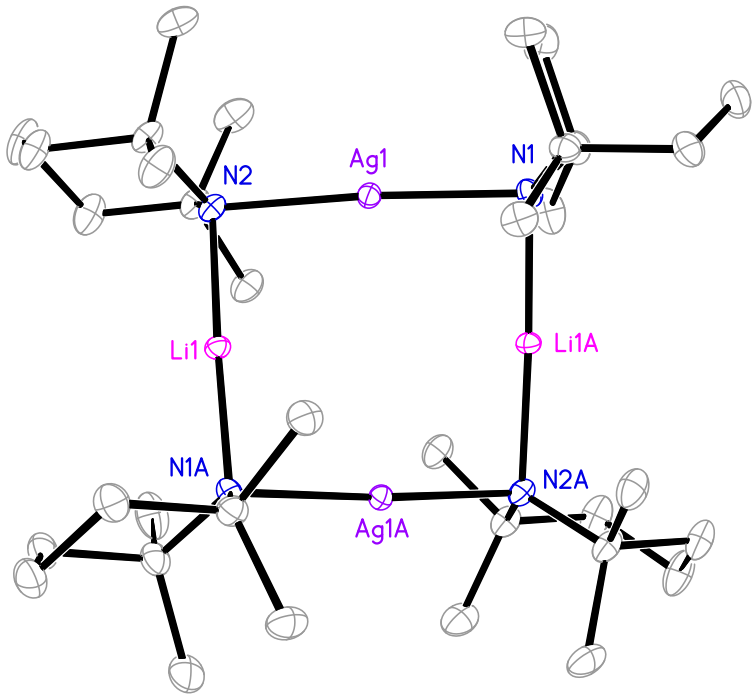


Fig. S2. Molecular structure of the dimer of $(TMP)_2AgLi$ at 30% probability

N1A-Li1	2.014(3)	Li1A–N1–Ag1	88.76(9)
N2-Li1	2.051(3)	Li1–N2-Ag1	87.35(9)
Ag1-N1	2.129(2)	N1A–Li1–N2	177.72(14)
Ag1-N2	2.127(2)	N1–Ag1–N2	176.37(8)

Table S3. Selected bond lengths (Å) and angles (°) for $(TMP)_2AgLi$

3.3. Crystal Structures of Arylargentates

• Arylargentate from the 1 : 1 Reaction of 1a and 3

N,N-Diisopropylbenzamide **1a** (49.3 mg, 0.24 mmol) and dry THF (0.2 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.24 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 30 min at 0 °C. Then, the solvent was removed *in vacuo* and dry hexane (3 mL) was added. This was vigorously stirred and the volatiles were removed *in vacuo* to give a slightly yellow solid. The residue was dissolved in dry benzene (1 mL) and the solution was stored at 4°C for a week to give a few colorless tiny solid.

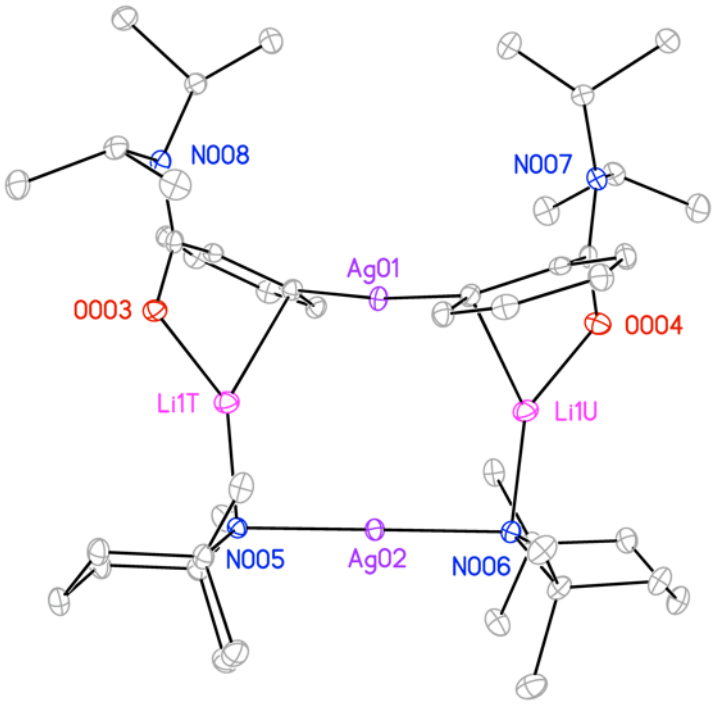


Fig. S3. Molecular structure of the arylargentate from the 1 : 1 reaction of **1a** and **3** at 30% probability

• **Arylargentate from the 2 : 1 Reaction of 1a and 3**

N,N-Diisopropylbenzamide **1a** (205.3 mg, 1.0 mmol) and dry THF (1.0 mL) were added to a heat gun-dried Schlenk tube. The mixture was added to a solution of $(TMP)_2Ag(CN)Li_2$ (0.5 mmol) *via* cannula at –78 °C, and the resulting solution was stirred for 2 hours at 0 °C. During which time, white precipitates appeared. The solvent was removed *via* cannula and the resulted white solids were washed with dry THF. Then, all the volatiles were removed *in vacuo* and dry benzene was added. This was filtered over cotton in the glovebox. The filterate was stored at 4 °C for a week to give a few colorless tiny solid.

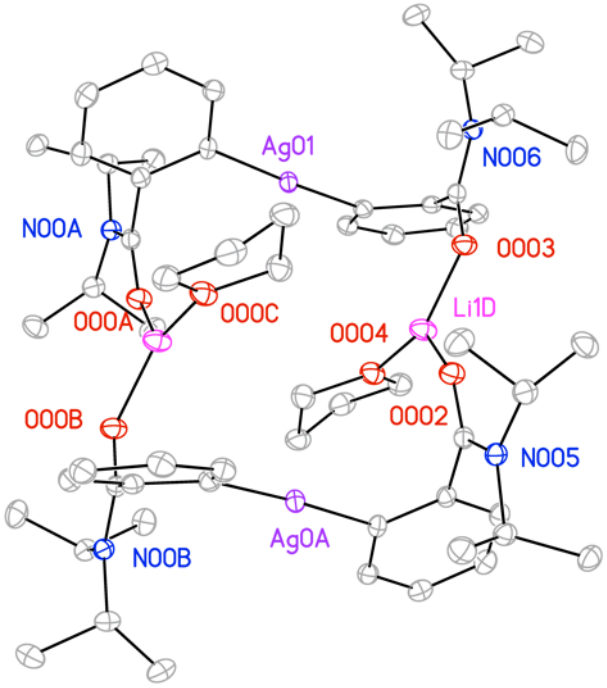


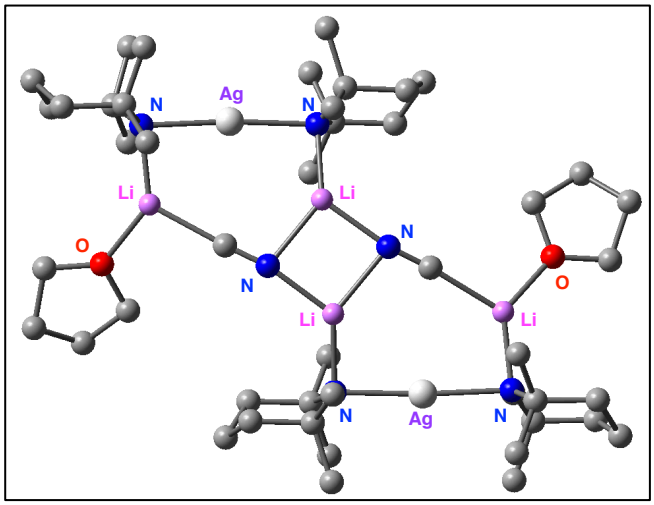
Fig. S4. Molecular structure of the arylargentate from the 2 : 1 reaction of **1a** and **3** at 30% probability

3.4. DFT Calculations

Generals:

All calculations were carried with the Gaussian 16 program package[3]. The molecular structures and harmonic vibrational frequencies were obtained using the hybrid density functional method based on M06 functional[4]. We used LanL2DZ[5] for Ag atom and 6–31+G* for the other atoms. Geometry optimization and vibrational analysis were performed at the same level. All the optimizations were calculated without any symmetry assumptions, and characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima).

• DFT Calculation on 3(THF) (Fig. 2)



The structure of [**3**(THF)]$_2$ calculated at M06/6-31+G*&LanL2DZ(Ag). H atoms were omitted for clarity.

Cartesian Coordinates

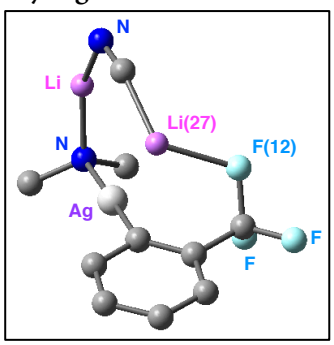
Li	-4.37844800	-1.36886800	0.30063700	C	-3.34445100	-3.74948000	-1.01464500
Ag	-3.88714700	1.45597300	0.17102600	H	-2.90554300	-2.97773400	-1.66255400
C	-1.75351700	2.99877700	-1.39998700	H	-2.61665900	-3.98727700	-0.22371600
C	-1.99095800	3.69140100	1.02082100	C	4.05152400	5.37151000	-1.30000400
Li	-0.91464900	1.10839800	0.53700300	H	4.16834700	5.32247700	-2.39215800
N	-2.05196100	2.62662200	-0.00120800	H	3.41889100	6.23540800	-1.06620500
C	-2.26897800	-1.18457800	0.62754600	C	5.41827200	5.41328200	-0.62404700
N	-1.10903800	-1.01739200	0.71989200	H	5.31995500	5.73479500	0.42270800
N	-5.63943800	0.13923900	0.33163500	H	6.13481000	6.07772100	-1.12021700
C	-6.29480800	0.22837100	1.65172600	C	-3.81195000	-4.98556700	-1.76561000
C	-6.49271700	0.25971200	-0.86678700	H	-3.02919900	-5.75056000	-1.83016800
Li	4.35580200	1.35236900	0.02160500	H	-4.11549400	-4.72495800	-2.78974600
Ag	3.84403000	-1.46273900	0.17206600	C	-5.02828100	-5.41610600	-0.95091600
C	1.67783600	-3.08894100	-1.27603300	H	-5.71743500	-6.06651100	-1.50147800
C	1.98143300	-3.65662900	1.17007500	H	-4.71580700	-5.93992600	-0.03630300
Li	0.89854900	-1.09244900	0.56284300	C	-7.72561500	-0.65612000	-0.76063300
N	2.01097300	-2.64603900	0.09330100	H	-8.38467100	-0.48934200	-1.62881100
C	2.24690400	1.22520400	0.36042100	H	-7.38546300	-1.70644500	-0.81901900
N	1.09943500	1.05775200	0.55280100	C	-7.53693700	-0.68041600	1.71090800
N	5.60906500	-0.15498700	0.24612900	H	-7.19686500	-1.73253200	1.69536200
C	6.23212200	-0.13828600	1.58470200	H	-8.05571300	-0.53397600	2.67257800
C	6.48536800	-0.40608500	-0.91513600	C	-8.48459500	-0.46776300	0.54265400
O	4.61293700	3.21320900	-0.53917300	H	-9.32603400	-1.17442700	0.60056900
C	5.82932800	3.95482600	-0.69290500	H	-8.93264200	0.53794600	0.58757300
H	6.52329700	3.64150300	0.09798100	C	-5.66346800	-0.21416200	-2.06367200
H	6.27772100	3.70647500	-1.66956400	H	-6.26436300	-0.22135800	-2.98518100
C	3.47588500	4.07174400	-0.76562200	H	-4.80011700	0.44880800	-2.23585100
H	2.79195700	3.56616400	-1.45899800	H	-5.28349900	-1.23874000	-1.90972300
H	2.95211500	4.21061400	0.19291900	C	-6.96197500	1.69005000	-1.19614700
O	-4.52244900	-3.20586100	-0.38403600	H	-6.11394800	2.39119100	-1.15317200
C	-5.63937300	-4.07213900	-0.60516700	H	-7.38980900	1.73554900	-2.20996800
H	-6.25595800	-4.06946000	0.30207000	H	-7.72923300	2.06220200	-0.50713100
H	-6.24331800	-3.67866400	-1.44150100	C	-5.30165000	-0.29399200	2.69233800

H	-5.03384300	-1.34933400	2.50940900	H	4.28728800	-0.06773200	2.58296700
H	-4.37134000	0.29550500	2.69125000	H	5.63294000	0.54954500	3.56852100
H	-5.72734000	-0.24896100	3.70526000	H	4.98668200	1.53772000	2.25156200
C	-6.68121300	1.65193800	2.09081900	C	6.57216300	-1.52406000	2.16223500
H	-7.46849200	2.09466700	1.47031700	H	6.90304100	-1.44174900	3.20944000
H	-7.04233500	1.65709200	3.13120600	H	5.68346700	-2.17377900	2.13970700
H	-5.80495600	2.31669600	2.03481900	H	7.36677300	-2.03750100	1.60923400
C	-0.45845100	3.83090900	-1.48209800	C	5.69718100	-0.01197400	-2.16647000
H	-0.30440100	4.16750500	-2.52128500	H	4.80653900	-0.64865500	-2.29282900
H	0.38901600	3.16944600	-1.22956600	H	5.36334500	1.03851500	-2.11658500
C	-0.68787300	4.50392300	0.89359900	H	6.31044600	-0.11576300	-3.07377200
H	-0.70690800	5.34031100	1.61207500	C	6.91630300	-1.87316400	-1.10616100
H	0.15822000	3.85451900	1.18095500	H	7.37460600	-2.01870600	-2.09698100
C	-0.45037800	5.00828700	-0.52105700	H	7.64798000	-2.20761700	-0.36129100
H	0.51337700	5.54006100	-0.57850500	H	6.04489600	-2.54278600	-1.03344200
H	-1.21639700	5.74825500	-0.80538200	C	0.38451000	-3.92759200	-1.27908200
C	-1.50681300	1.70304500	-2.17773000	H	0.19668800	-4.31145000	-2.29668300
H	-0.62888200	1.15903600	-1.79301400	H	-0.45446100	-3.25475100	-1.02888500
H	-2.37846300	1.03050200	-2.12113400	C	0.68232600	-4.48340100	1.11747200
H	-1.31051900	1.91093500	-3.23979300	H	0.72732700	-5.28336900	1.87497700
C	-1.97374000	3.00296100	2.38804300	H	-0.16108100	-3.82709700	1.39614500
H	-2.90003800	2.42958900	2.55544900	C	0.41080500	-5.05808800	-0.26378800
H	-1.11861800	2.31332400	2.49014700	H	-0.55012400	-5.59833100	-0.26750800
H	-1.88450800	3.73706200	3.20211200	H	1.17442200	-5.80572300	-0.53381400
C	-3.19026400	4.65779200	1.03081500	C	1.40399700	-1.83390800	-2.10886300
H	-4.13616400	4.09400500	1.00937100	H	0.53992200	-1.26874000	-1.72112100
H	-3.18411800	5.27749300	1.94126600	H	2.27635100	-1.16059900	-2.11652000
H	-3.19869900	5.34343200	0.17556800	H	1.17018000	-2.09364100	-3.15178100
C	-2.88711400	3.74270900	-2.12757300	C	2.79462900	-3.86426900	-1.99617400
H	-2.64975900	3.86931000	-3.19566200	H	3.72922900	-3.28207500	-1.98417600
H	-3.82464900	3.16938900	-2.05604700	H	3.00856100	-4.83626700	-1.53736900
H	-3.08102600	4.74013800	-1.71694500	H	2.52675100	-4.05036000	-3.04825100
C	7.74456200	0.47827400	-0.86126800	C	1.98925300	-2.89722400	2.49926500
H	8.41828800	0.21024100	-1.69190400	H	2.91488600	-2.31079300	2.61719600
H	7.44110300	1.52770600	-1.02879200	H	1.13157500	-2.20794600	2.58079900
C	7.49845300	0.73827200	1.59197600	H	1.92132400	-3.58750400	3.35277400
H	7.99015700	0.66738500	2.57615000	C	3.18769500	-4.61426000	1.19978300
H	7.18963900	1.79334200	1.47257000	H	3.21119100	-5.18258800	2.14284900
C	8.46627000	0.39167400	0.47340700	H	3.17638600	-5.34649100	0.38381600
H	9.32709500	1.07706600	0.48743600	H	4.12942400	-4.04840700	1.12011800
H	8.88292900	-0.61739300	0.62320800				
C	5.22918800	0.50217800	2.54668400				

• Modeled DFT Calculations on Arylargentates Derived from Ph–CF_3 and Ph–SF_5

Me_2N^- was used as a model for TMP^-.

Arylargentates of Ph–CF_3



The structure of modeled arylargentate derived from Ph–CF_3 calculated at M06/6-31+G*&LanL2DZ(Ag). H atoms were omitted for clarity.

Cartesian Coordinates for Ph–CF_3

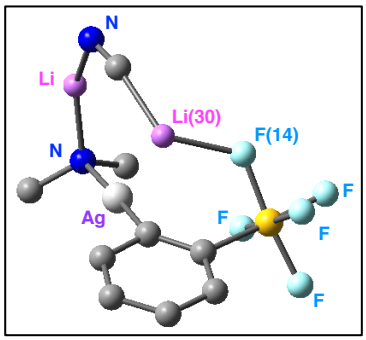
C	3.85464500	-1.69092100	0.09805700	N	-3.07331000	-0.13954600	-0.51398500
C	3.55638400	-0.36579700	-0.19882500	C	-3.72950400	-1.38062300	-0.89481900
C	2.22622200	0.06076400	-0.16385700	H	-4.82260600	-1.23791000	-1.02101700
C	1.14562800	-0.78721300	0.16149200	H	-3.35797500	-1.79195400	-1.85504100
C	1.50504000	-2.11176100	0.47183000	H	-3.58093700	-2.15618400	-0.12856000
C	2.82510200	-2.56283200	0.43984800	C	-3.30005900	0.84264700	-1.56445600
H	4.88678200	-2.03613900	0.06968000	H	-2.91148200	0.52066400	-2.55144500
H	4.35330000	0.32950600	-0.45614600	H	-4.38255800	1.04077500	-1.70599400
H	0.72616000	-2.82635000	0.74413300	H	-2.81389900	1.79926000	-1.32042500
H	3.05045800	-3.60131000	0.68233500	Li	-3.31732200	0.49146800	1.28460600
F	1.09147200	1.70292100	-1.46009000	C	-1.29431600	0.94428800	2.80963800
F	1.29653800	2.06717300	0.66168900	N	-2.45902300	1.02660500	2.94143800
F	3.00577500	2.25535000	-0.65229100	Li	0.50919700	0.60708800	1.89384300
Ag	-0.95397500	-0.43572400	-0.21787900	C	1.92689400	1.50221200	-0.44032800

NBO analysis on F(12)–Li(27) interaction in arylargentate derived from Ph–CF_3:

Interactions		kcal/mol
LP (1) F 12	/LP*(1)Li 27	6.08
LP (2) F 12	/LP*(1)Li 27	4.82
LP (2) F 12	/RY*(2)Li 27	0.39
LP (2) F 12	/RY*(3)Li 27	0.19
LP (2) F 12	/RY*(4)Li 27	0.11
LP (3) F 12	/LP*(1)Li 27	0.77
LP (3) F 12	/RY*(2)Li 27	0.10
LP (3) F 12	/RY*(3)Li 27	0.27

LP: Lone pair. RY: Rydberg orbital. " * " refers to vacant orbital.

Arylargentates of Ph–SF_5



The structure of modeled arylargentate derived from Ph–SF_5 calculated at M06/6-31+G*&LanL2DZ(Ag). H atoms were omitted for clarity.

Cartesian Coordinates for Arylargentate of Ph–SF_5

C	-2.92743600	2.82257000	-0.19639300
C	-3.01500100	1.43706700	-0.24030400
C	-1.83751900	0.70292200	-0.09126200
C	-0.56260200	1.23382100	0.09190700
C	-0.54770000	2.64613300	0.15373000
C	-1.69081400	3.42769700	0.01101700
H	-3.82915600	3.42099100	-0.31315400
H	-3.97857500	0.95654600	-0.38355800
H	0.40468100	3.15464200	0.31293500
H	-1.61721200	4.51364300	0.05982700
S	-2.07832200	-1.13400000	-0.10816400
F	-0.78635300	-1.41803700	-1.03881400
F	-2.26918800	-2.72881500	-0.04665800
F	-1.11800300	-1.32783000	1.26906200
F	-3.37607300	-1.04082300	0.87081100
F	-3.03364100	-1.11572100	-1.40669000
Ag	1.41292900	0.38816900	-0.27653900
N	3.41342800	-0.35621300	-0.58274600
C	4.23625700	0.60556300	-1.30045300
H	5.27057700	0.22822300	-1.43644600
H	3.85351200	0.83381300	-2.31532900
H	4.29769500	1.55776300	-0.75266800
C	3.36570000	-1.59023600	-1.35528000
H	2.95120100	-1.44915500	-2.37334400
H	4.37900700	-2.02151200	-1.48839200
H	2.74325400	-2.34555200	-0.85250500
Li	3.71428500	-0.54936200	1.30707200
C	1.74341300	-0.20349300	2.93590600
N	2.88871800	-0.43742200	3.05493800
Li	-0.07460900	0.14765300	2.05381200

NBO analysis on F(14)–Li(30) interaction in arylargentate derived from Ph–SF_5:

Interactions		kcal/mol
CR (1) F 14	/LP*(1)Li 30	1.34
LP (1) F 14	/LP*(1)Li 30	4.26
LP (2) F 14	/LP*(1)Li 30	0.25
LP (2) F 14	/RY*(3)Li 30	0.07
LP (3) F 14	/LP*(1)Li 30	10.17
LP (3) F 14	/RY*(2)Li 30	0.47
LP (3) F 14	/RY*(3)Li 30	0.14
LP (3) F 14	/RY*(4)Li 30	0.13
LP (4) F 14	/LP*(1)Li 30	1.34
LP (4) F 14	/RY*(2)Li 30	0.17
LP (4) F 14	/RY*(3)Li 30	0.12
LP (4) F 14	/RY*(5)Li 30	0.08

LP: Lone pair. RY: Rydberg orbital. " * " refers to vacant orbital.

4. References

4.1. References for Experimental Section

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4.2. Crystal and Computational Details

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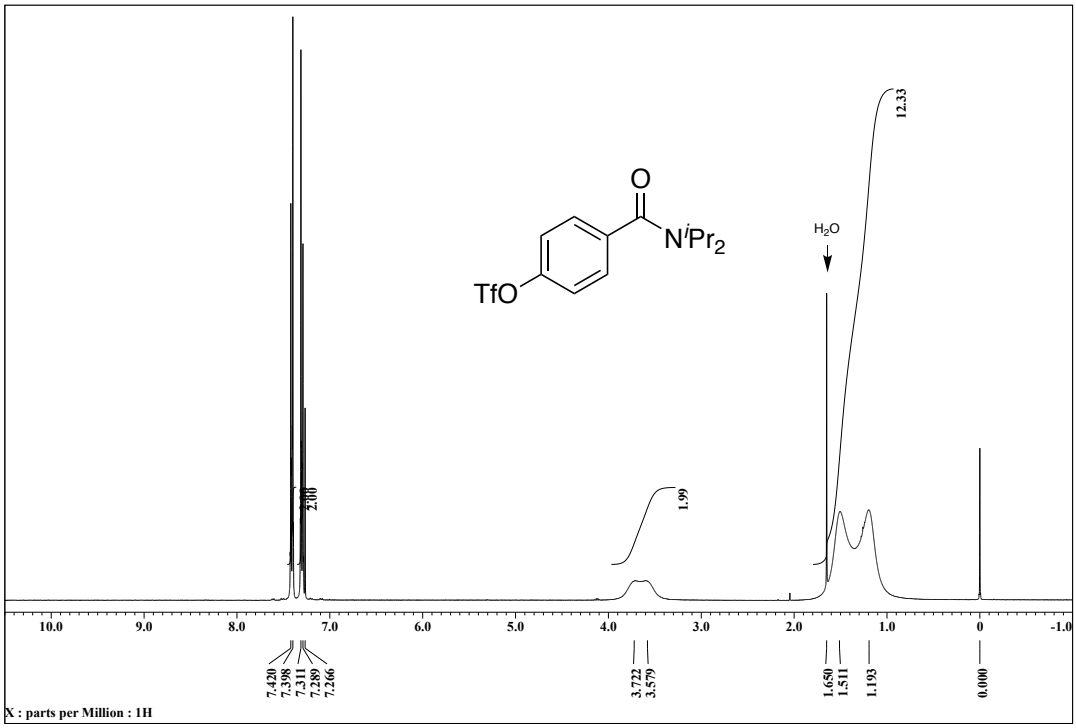
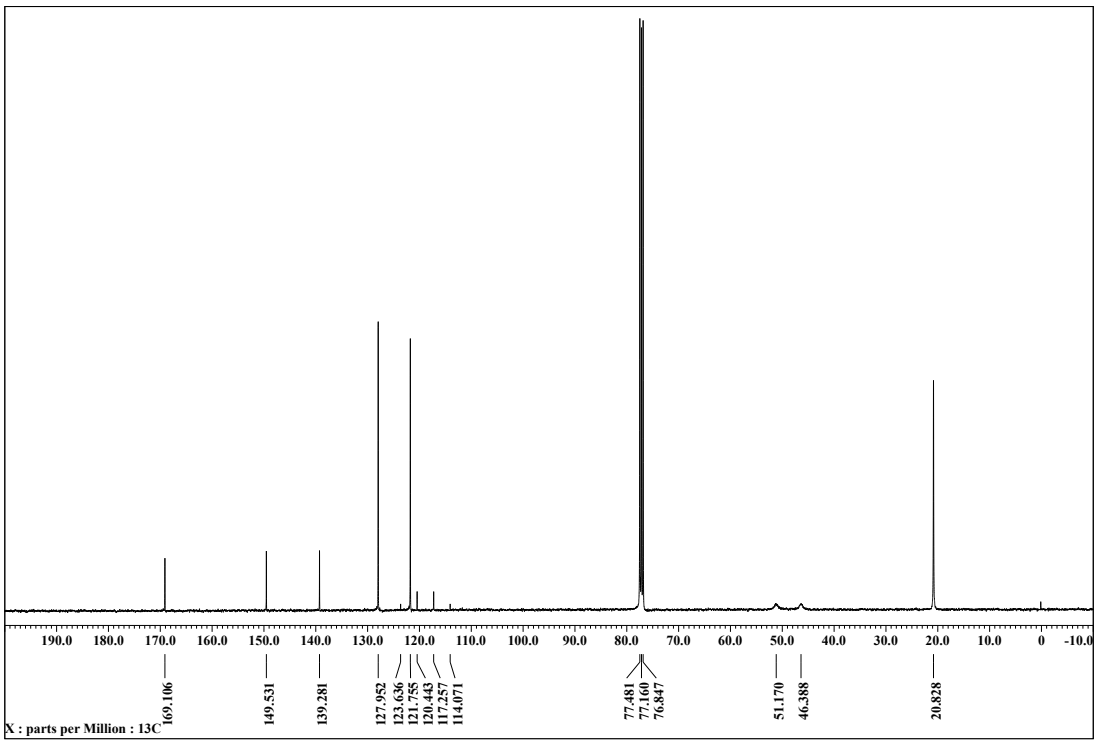
5. Copies of NMR Spectra

4-(Diisopropylcarbamoyl)phenyl trifluoromethanesulfonate (1p)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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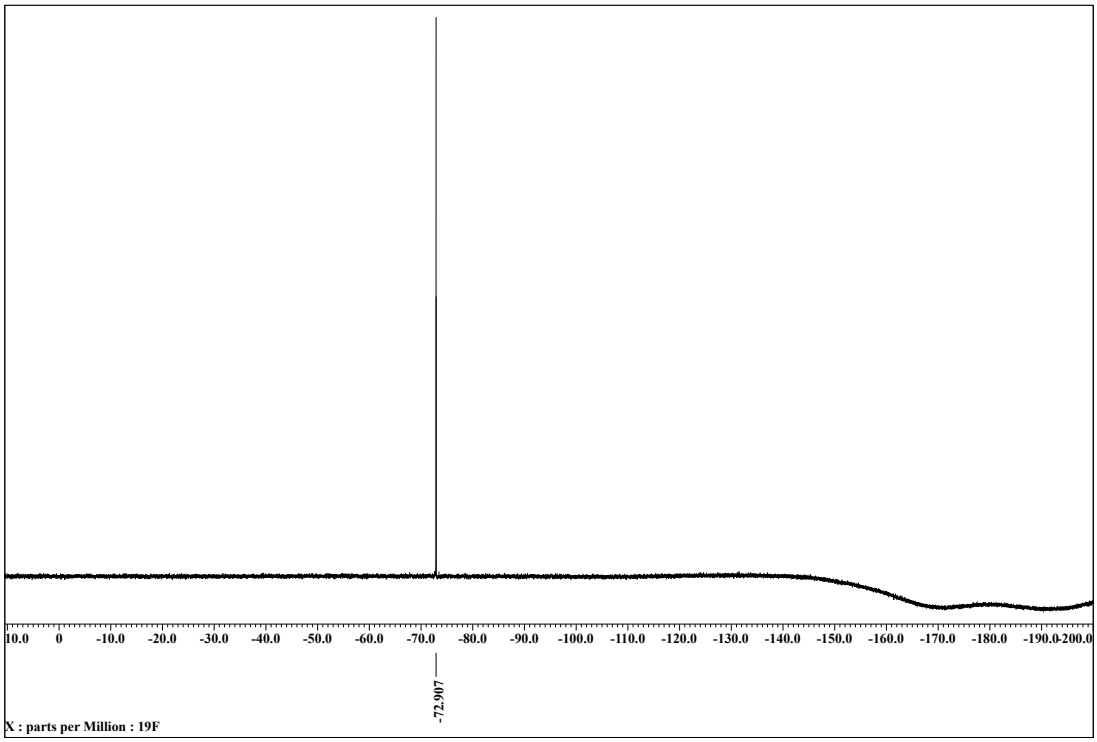
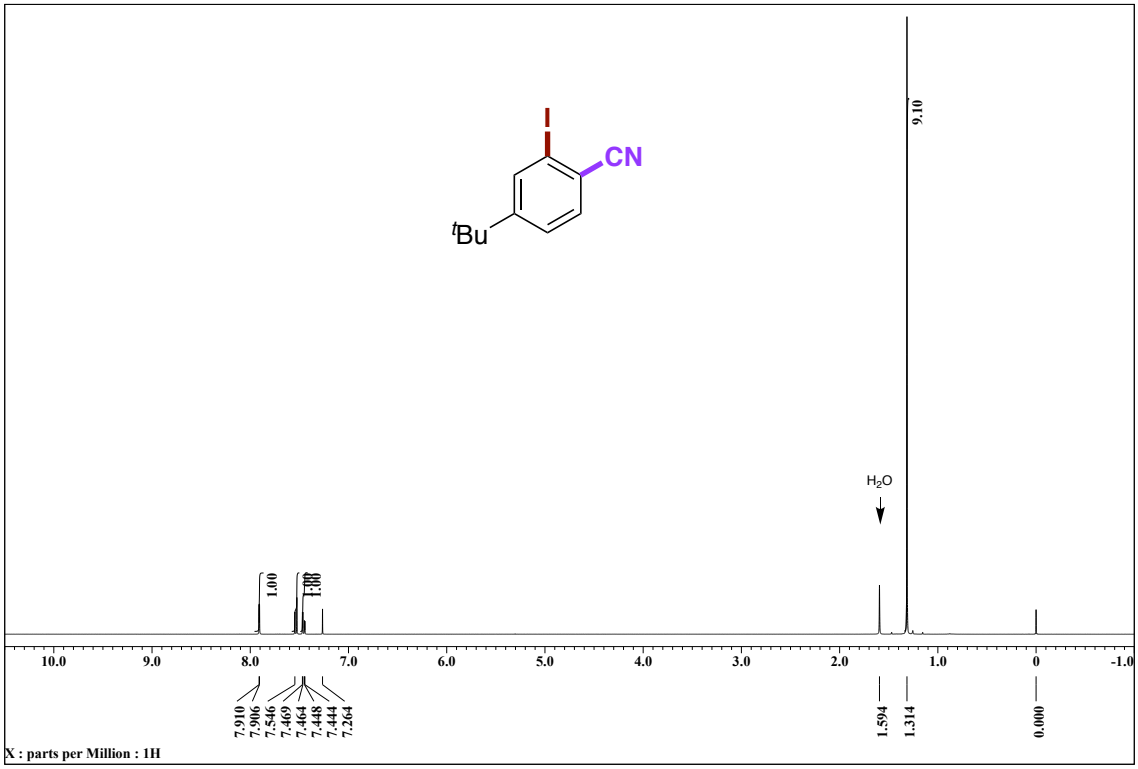
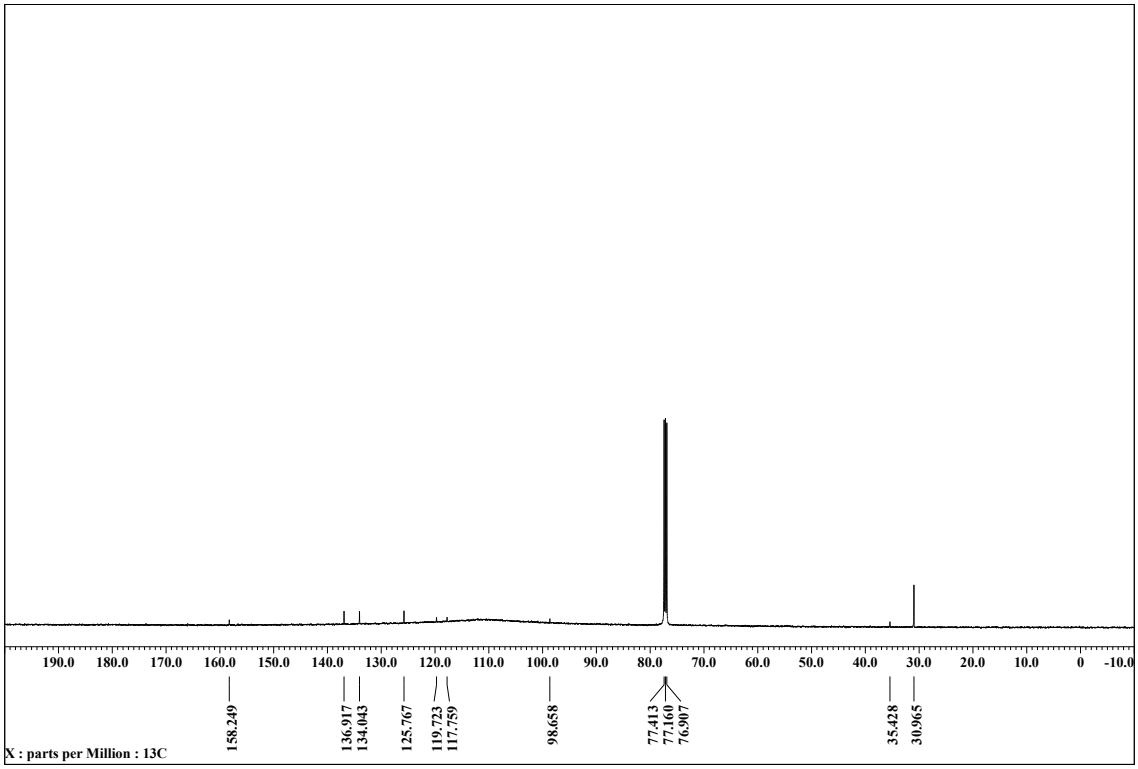


4-(*tert*-butyl)-2-iodobenzonitrile (2d)

^{1}H NMR (400 MHz, $CDCl_3$)

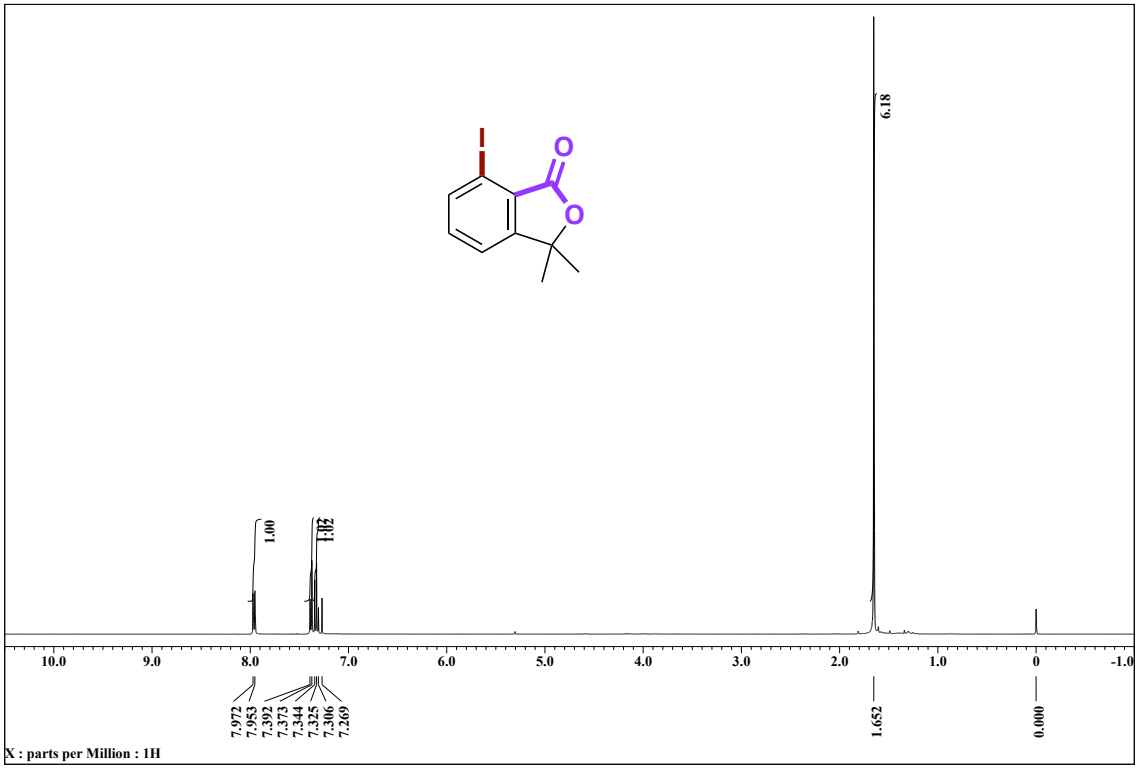


^{13}C NMR (125 MHz, $CDCl_3$)

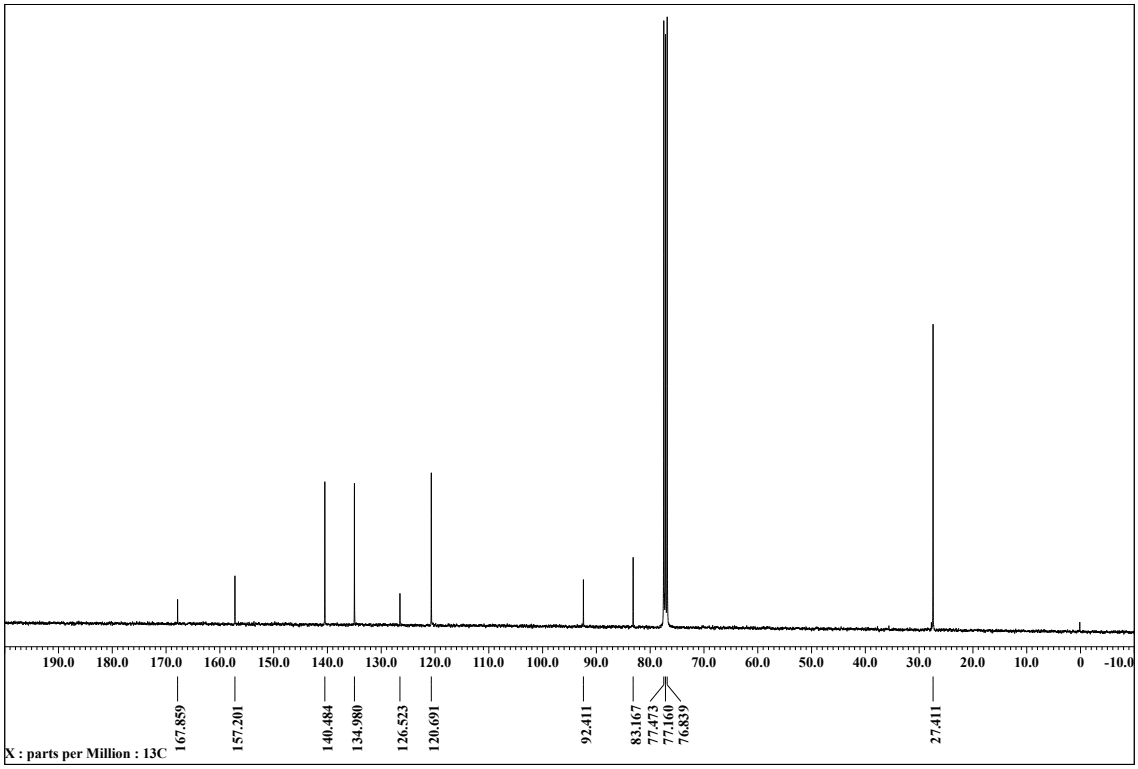


7-Iodo-3,3-dimethylisobenzofuran-1(3*H*)-one (2i)

^{1}H NMR (400 MHz, $CDCl_3$)

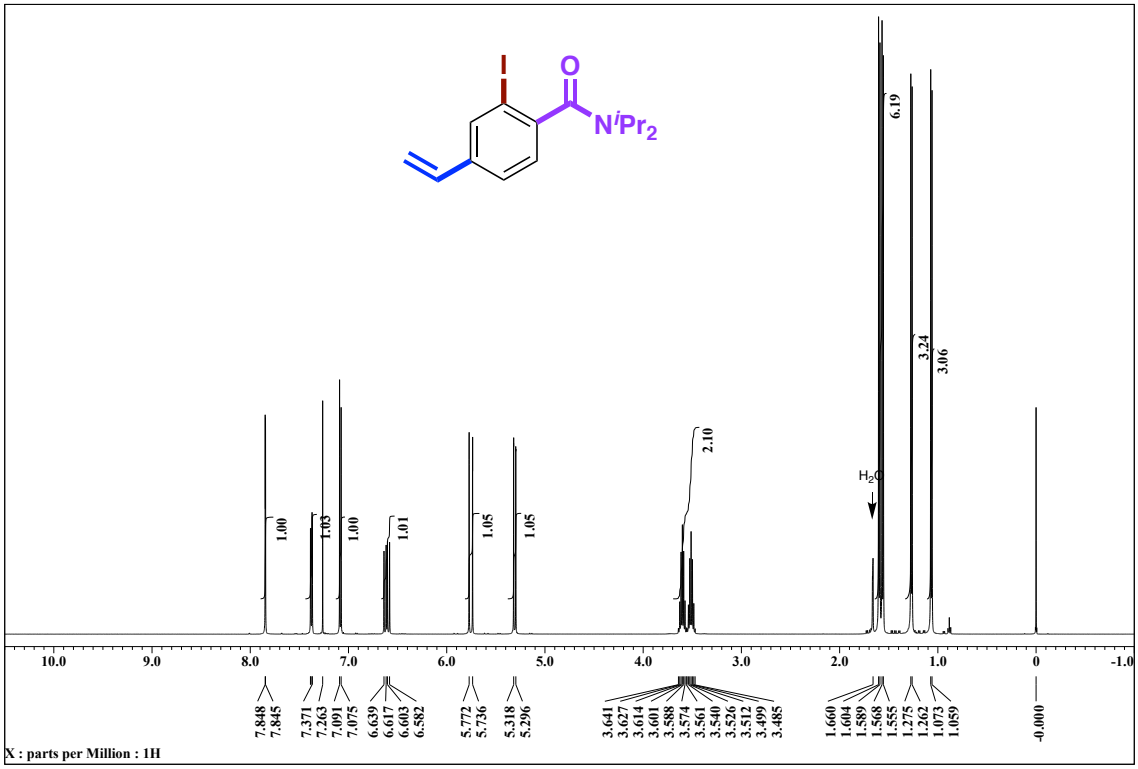


^{13}C NMR (100 MHz, $CDCl_3$)

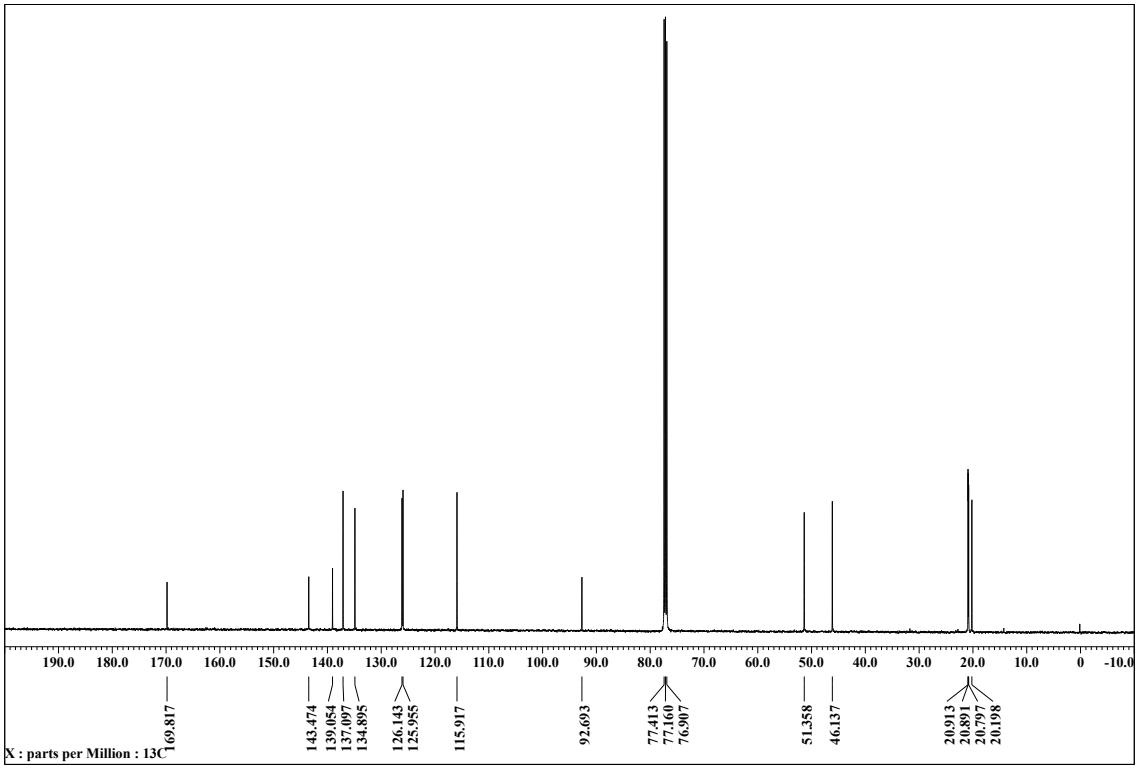


2-Iodo-*N*,*N*-diisopropyl-4-vinylbenzamide (2m)

^{1}H NMR (500 MHz, $CDCl_3$)

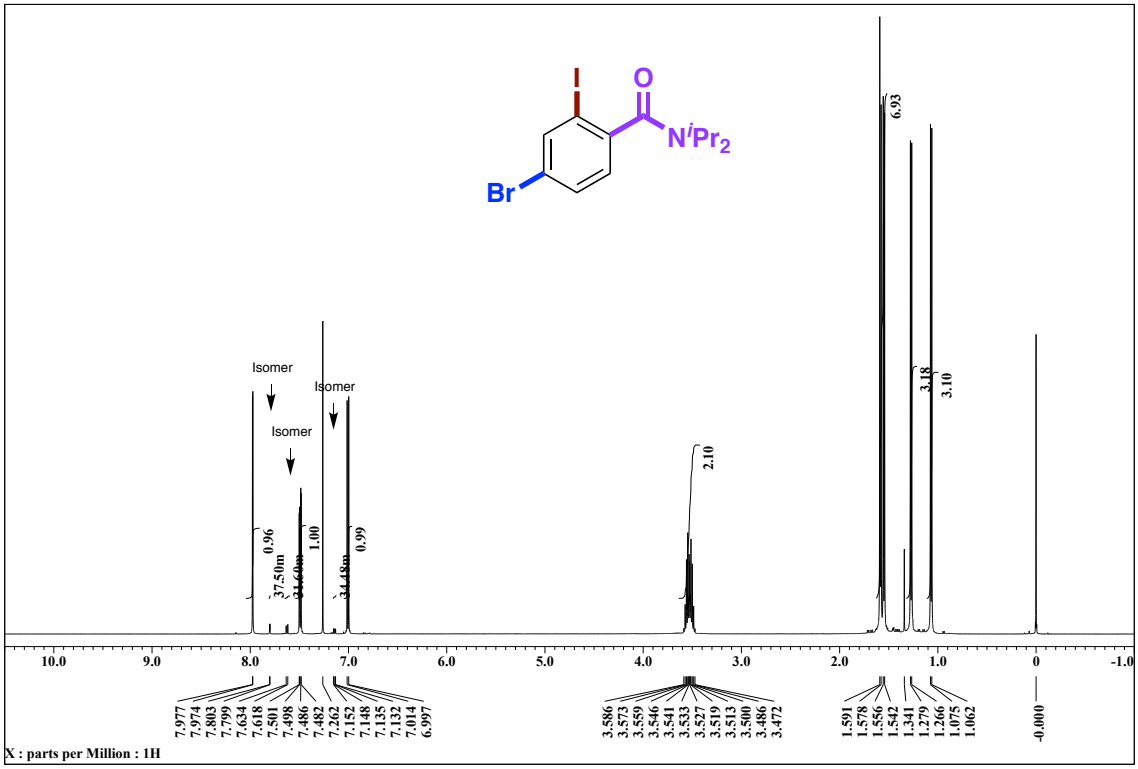


^{13}C NMR (125 MHz, $CDCl_3$)

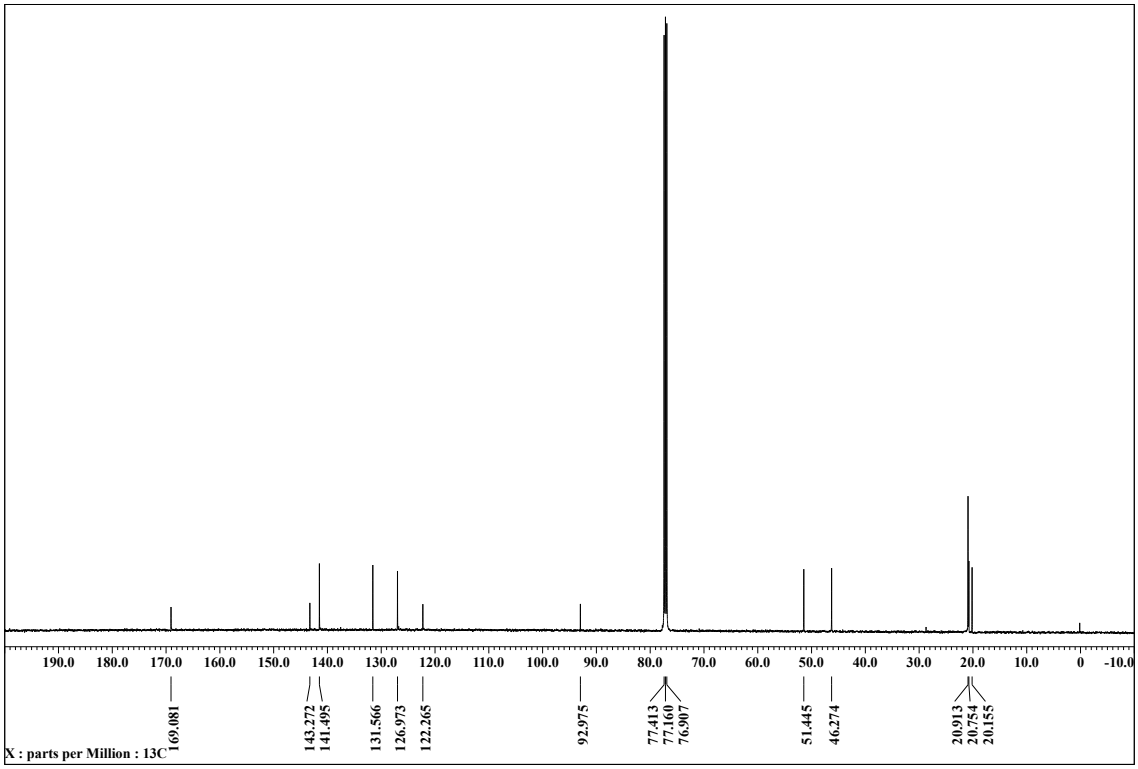


4-Bromo-2-iodo-*N*,*N*-diisopropylbenzamide (2o)

^{1}H NMR (500 MHz, $CDCl_3$)

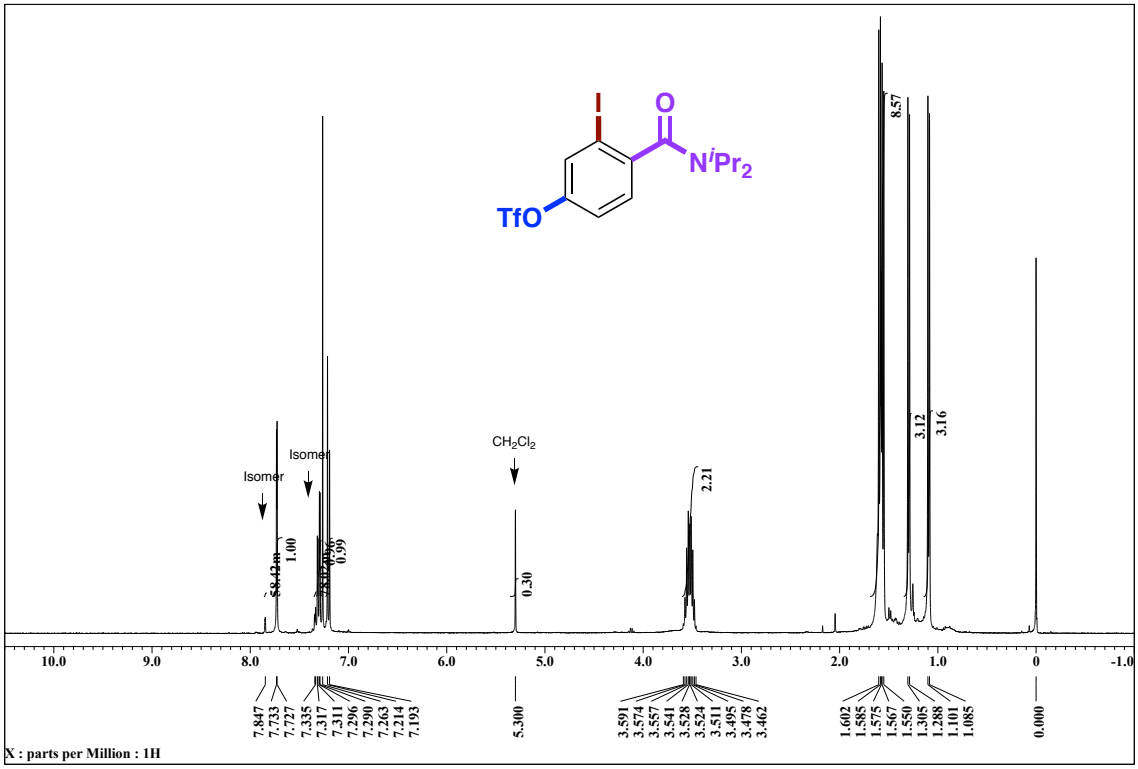


^{13}C NMR (125 MHz, $CDCl_3$)

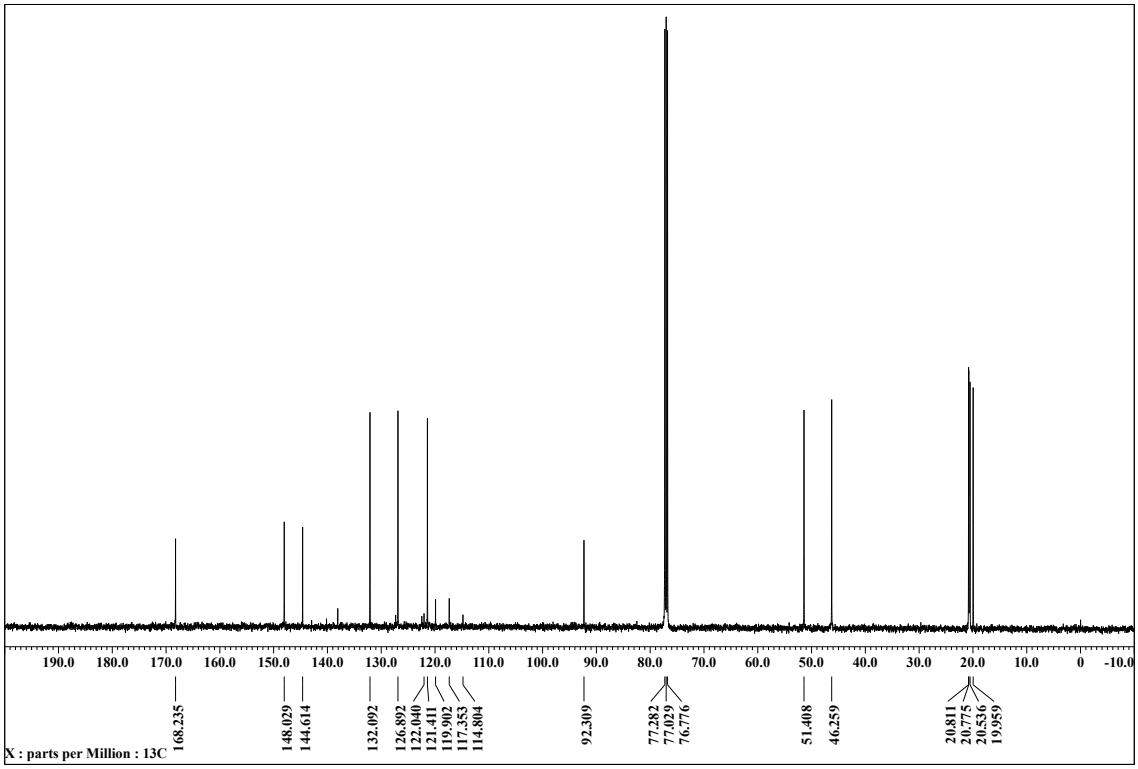


4-(Diisopropylcarbamoyl)-3-iodophenyl trifluoromethanesulfonate (2q)

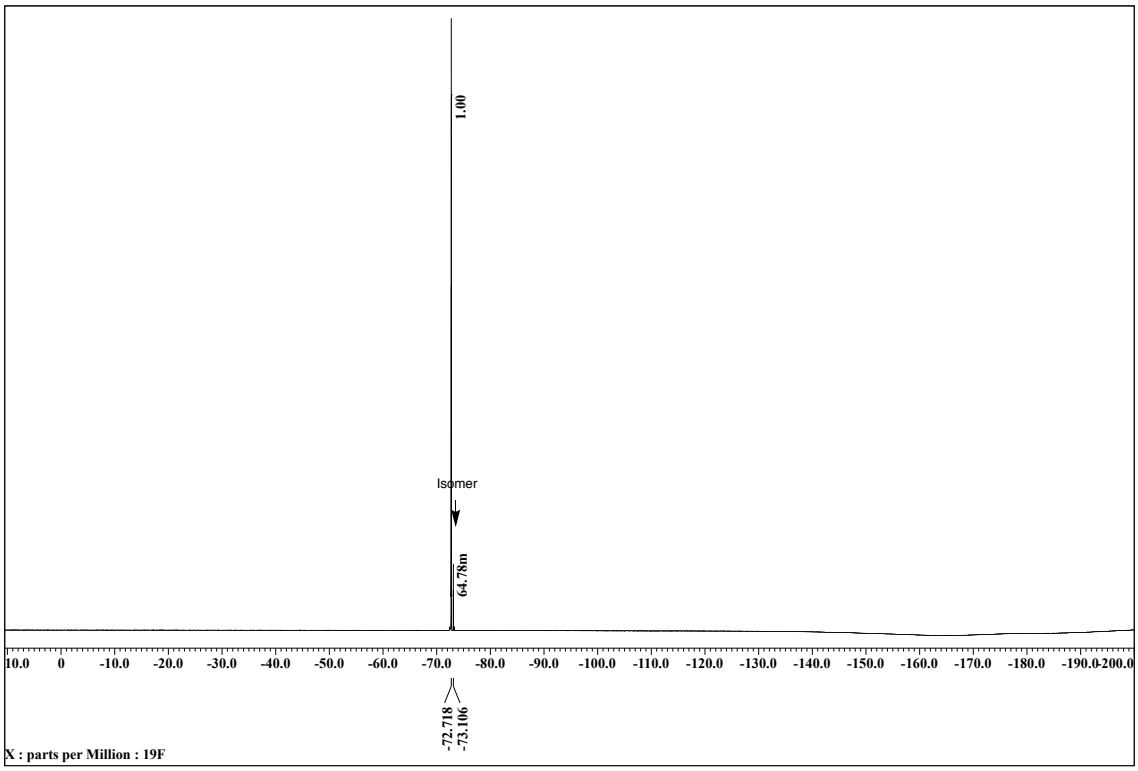
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

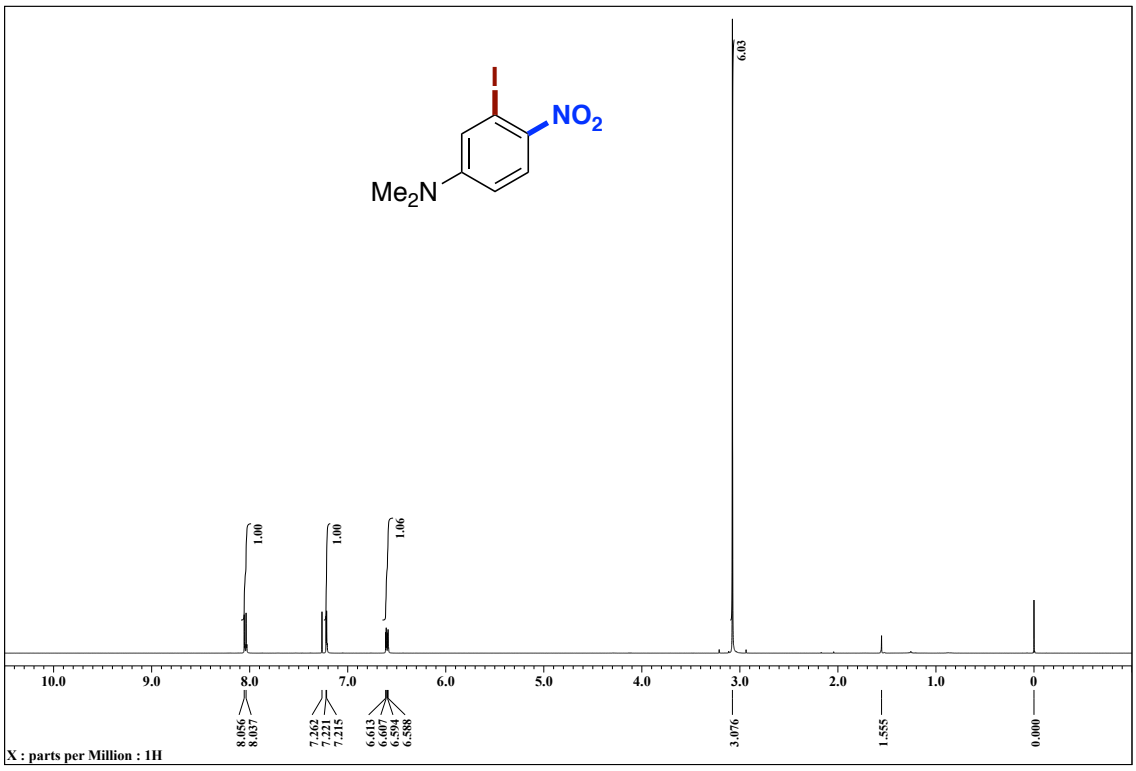


^{19}F NMR (376MHz, $CDCl_3$)

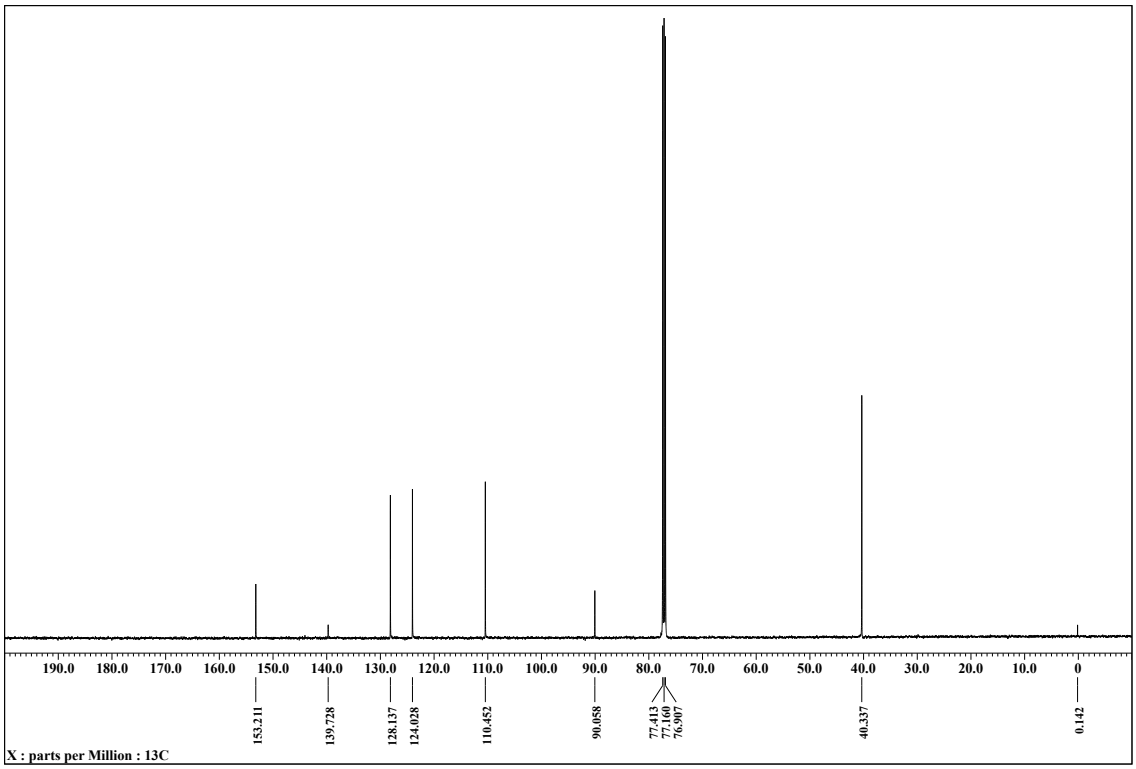


3-Iodo-*N*,*N*-dimethyl-4-nitroaniline (2s)

^{1}H NMR (500 MHz, $CDCl_3$)

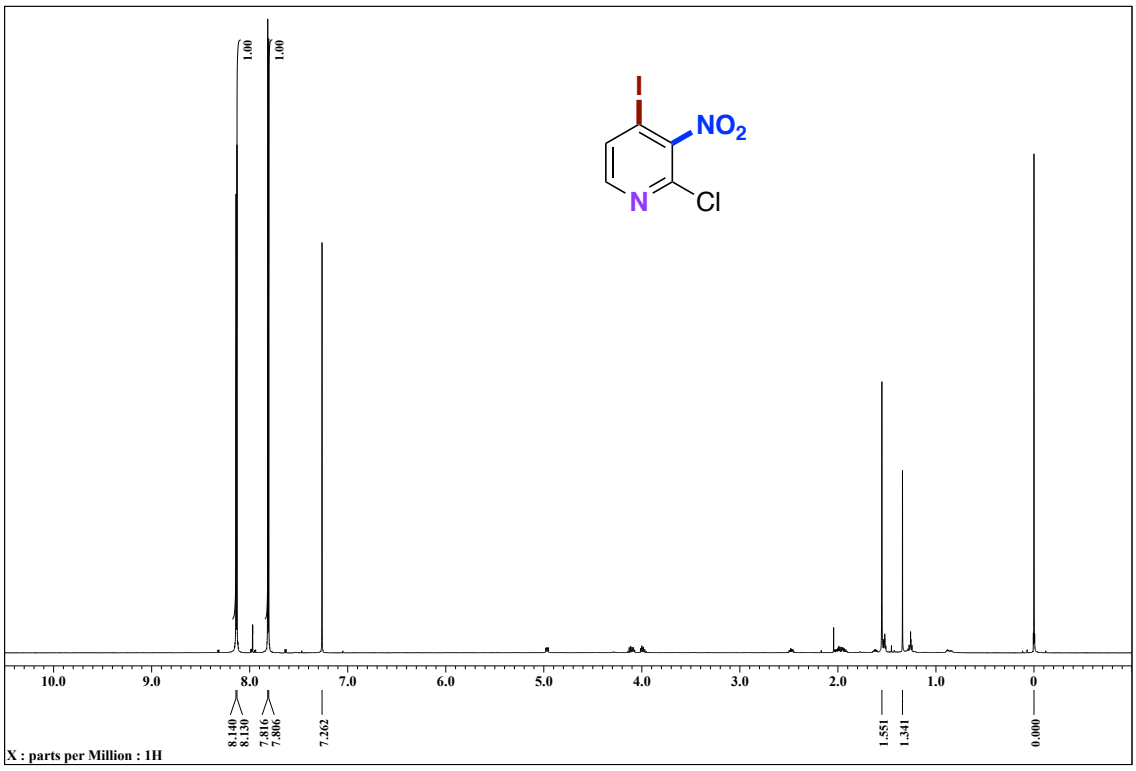


^{13}C NMR (125 MHz, $CDCl_3$)

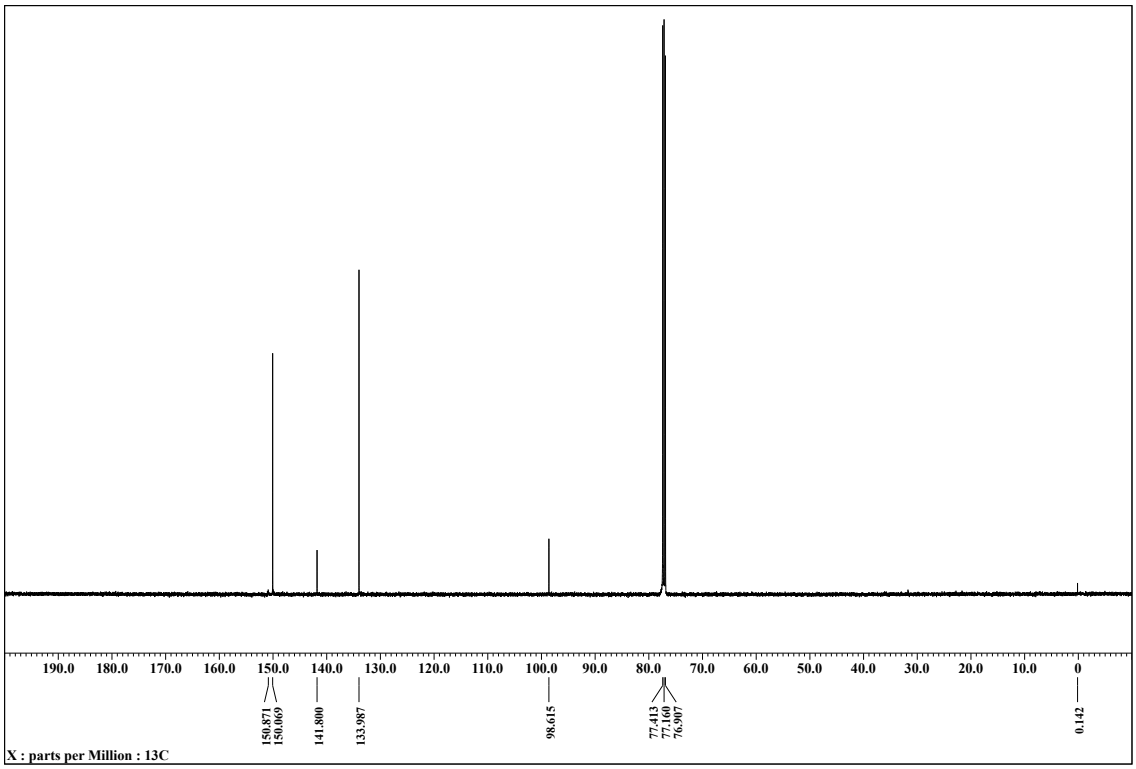


2-Chloro-4-iodo-3-nitropyridine (2t)

^{1}H NMR (500 MHz, $CDCl_3$

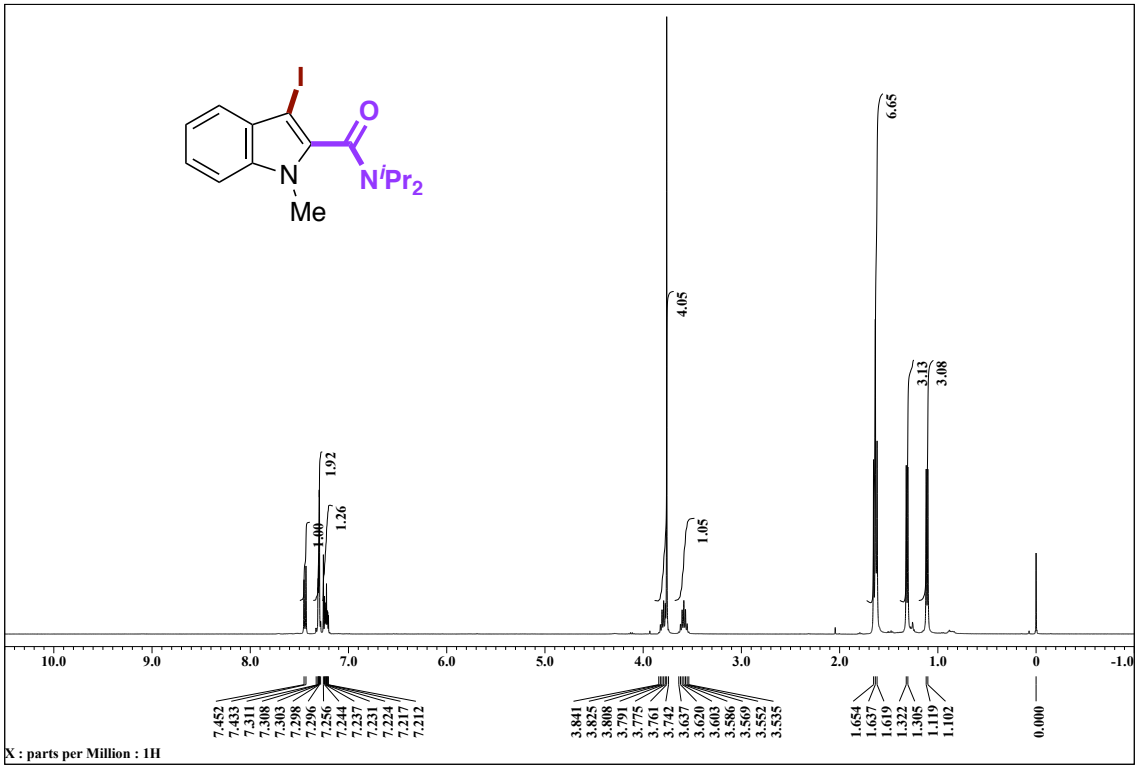


^{13}C NMR (125 MHz, $CDCl_3$)

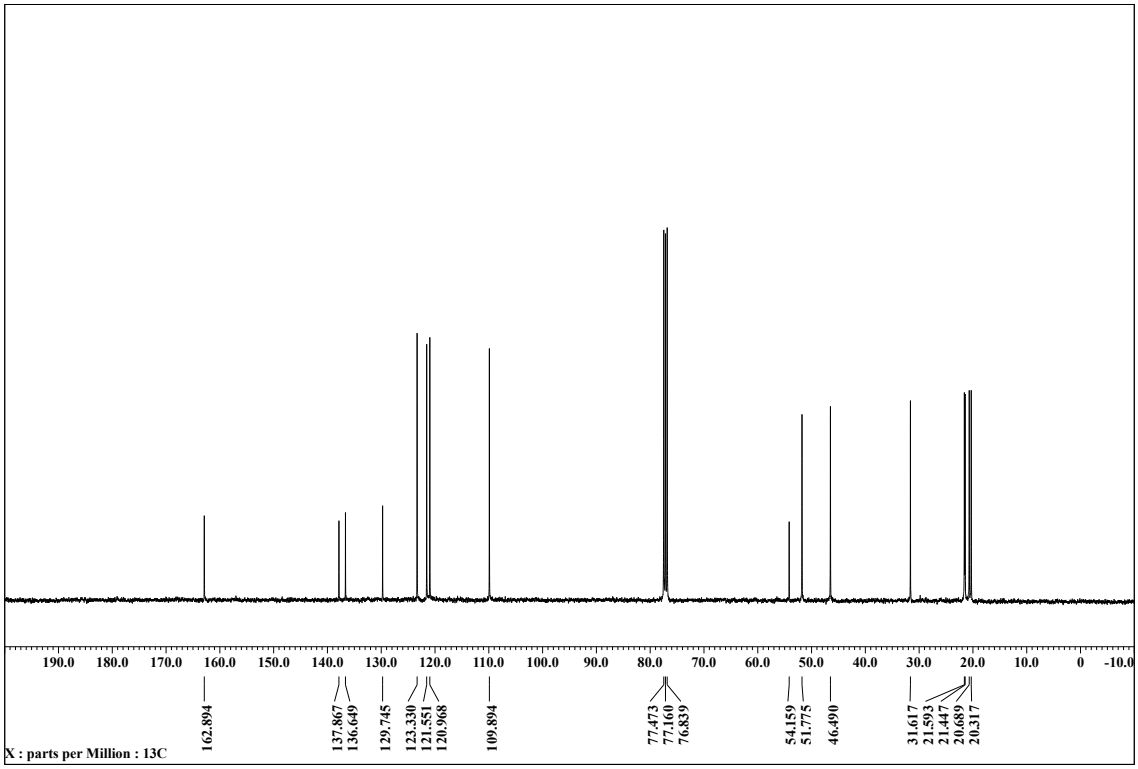


3-Iodo-*N*,*N*-diisopropyl-1-methyl-1*H*-indole-2-carboxamide (2w)

^{1}H NMR (400 MHz, $CDCl_3$)

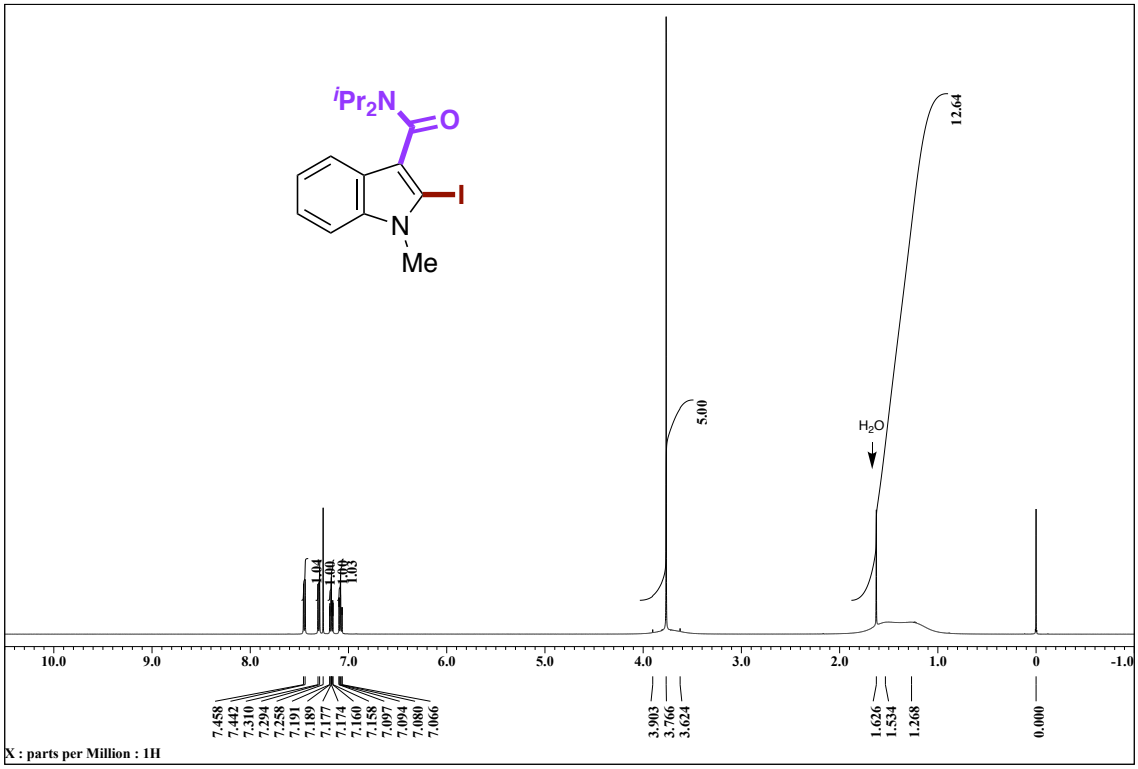


^{13}C NMR (100 MHz, $CDCl_3$)

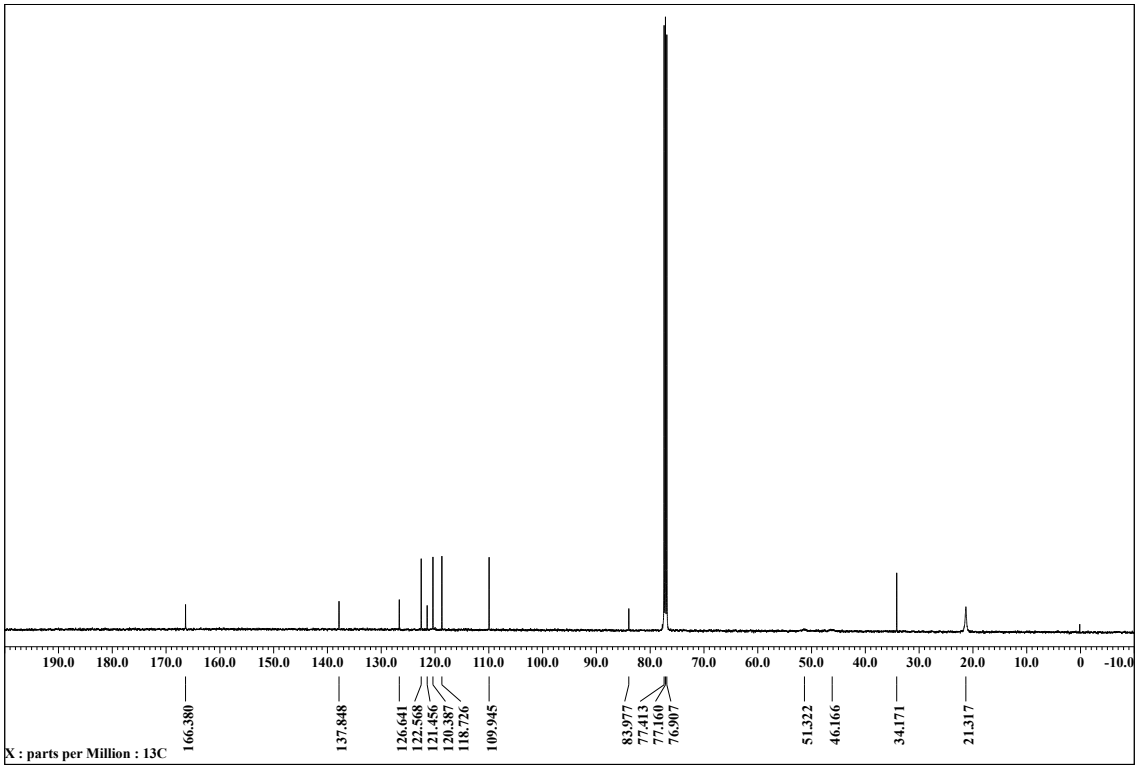


2-Iodo-*N*,*N*-diisopropyl-1-methyl-1*H*-indole-3-carboxamide (2x)

^{1}H NMR (500 MHz, $CDCl_3$)

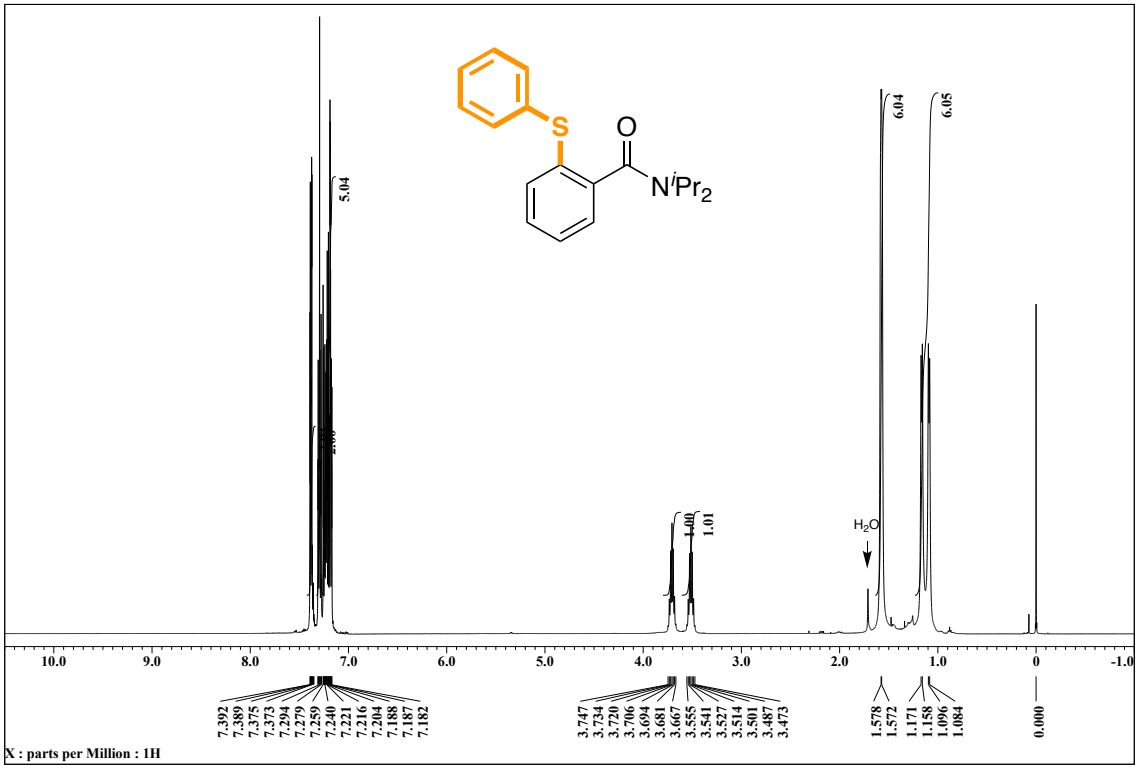


^{13}C NMR (125 MHz, $CDCl_3$)

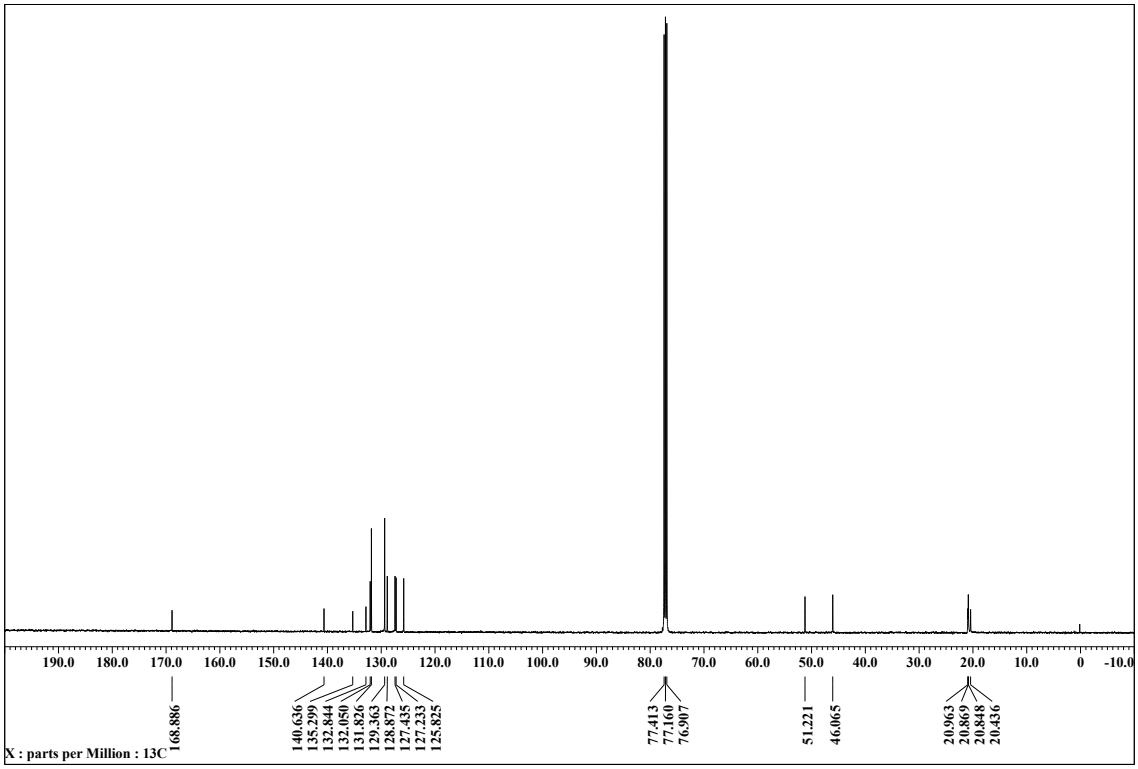


***N*,*N*-Diisopropyl-2-(phenylthio)benzamide (10a)**

^{1}H NMR (500 MHz, $CDCl_3$)

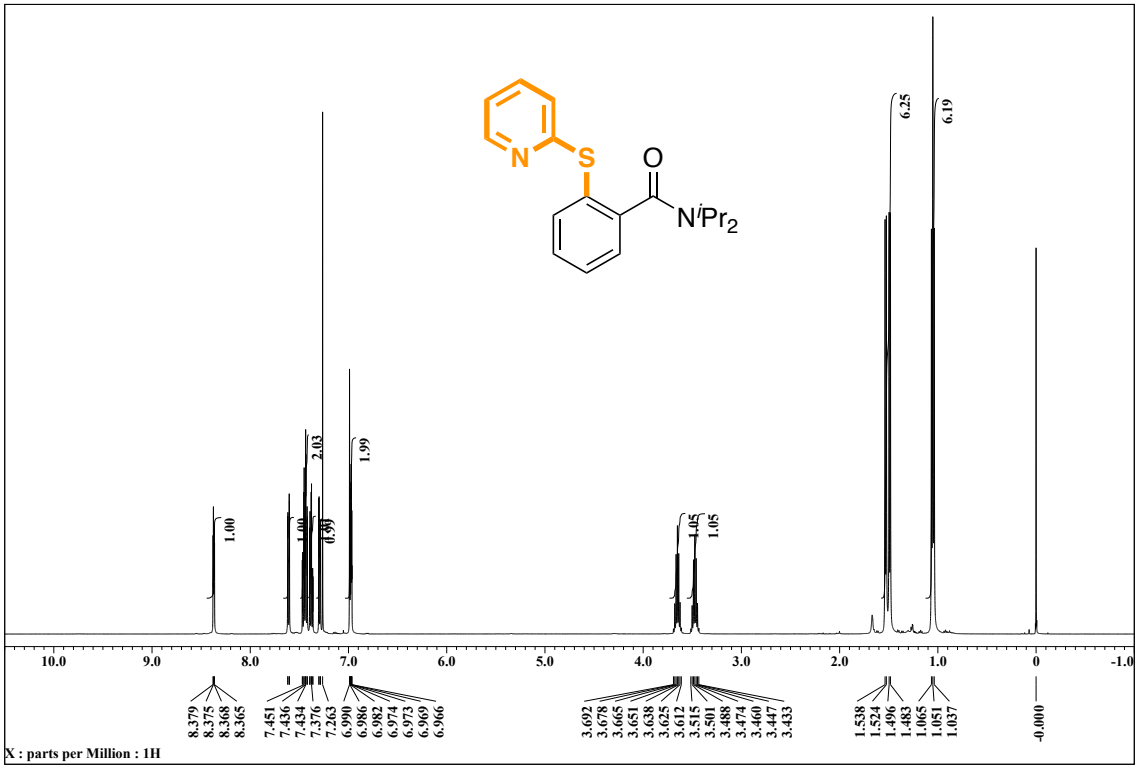


^{13}C NMR (125 MHz, $CDCl_3$)

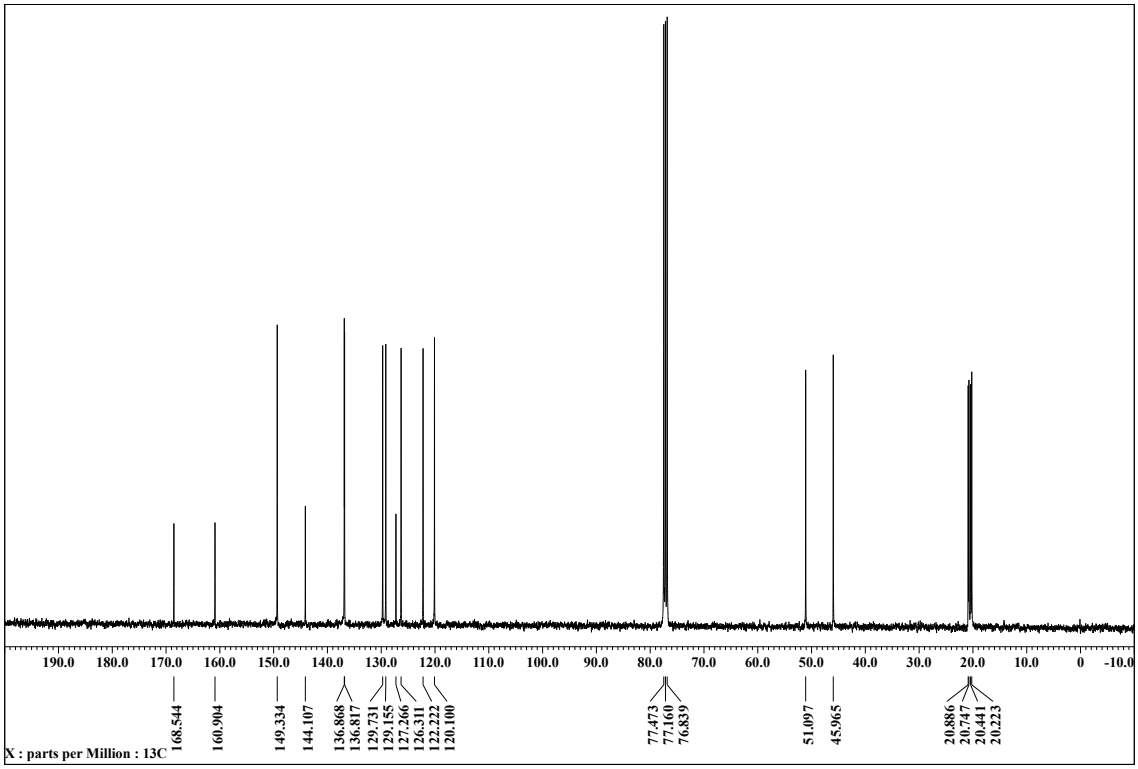


***N*,*N*-Diisopropyl-2-(pyridin-2-ylthio)benzamide (10b)**

^{1}H NMR (500 MHz, $CDCl_3$)

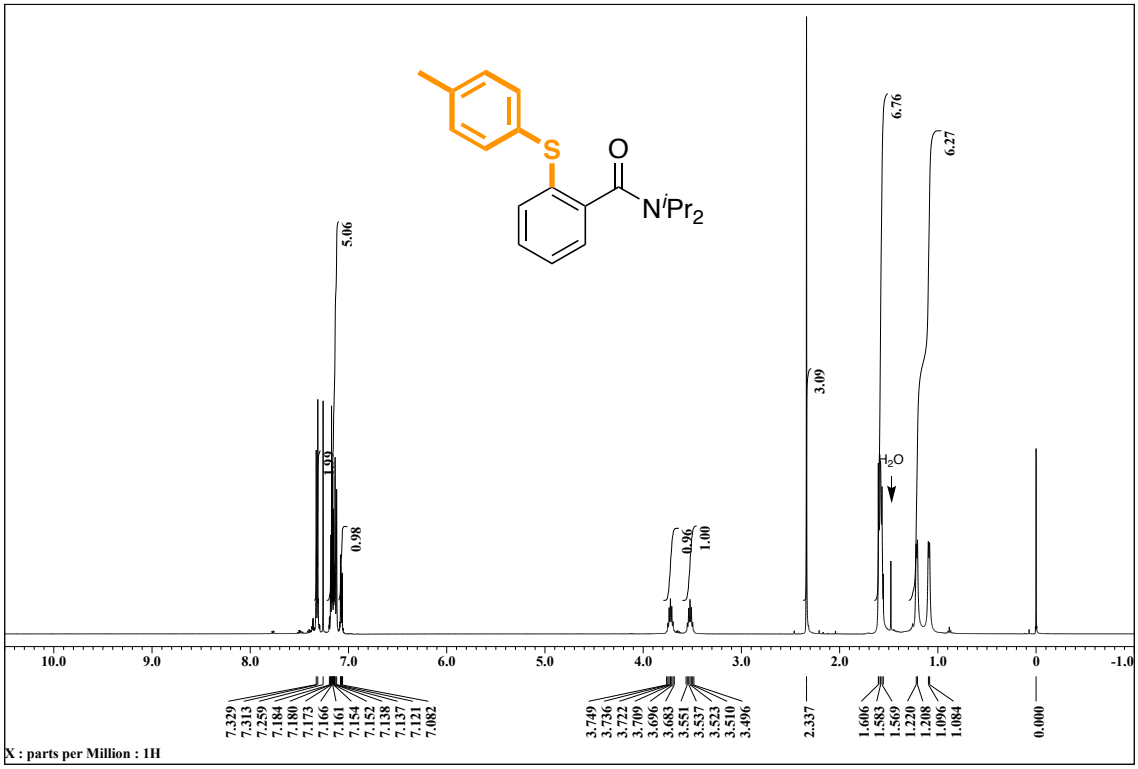


^{13}C NMR (100 MHz, $CDCl_3$)

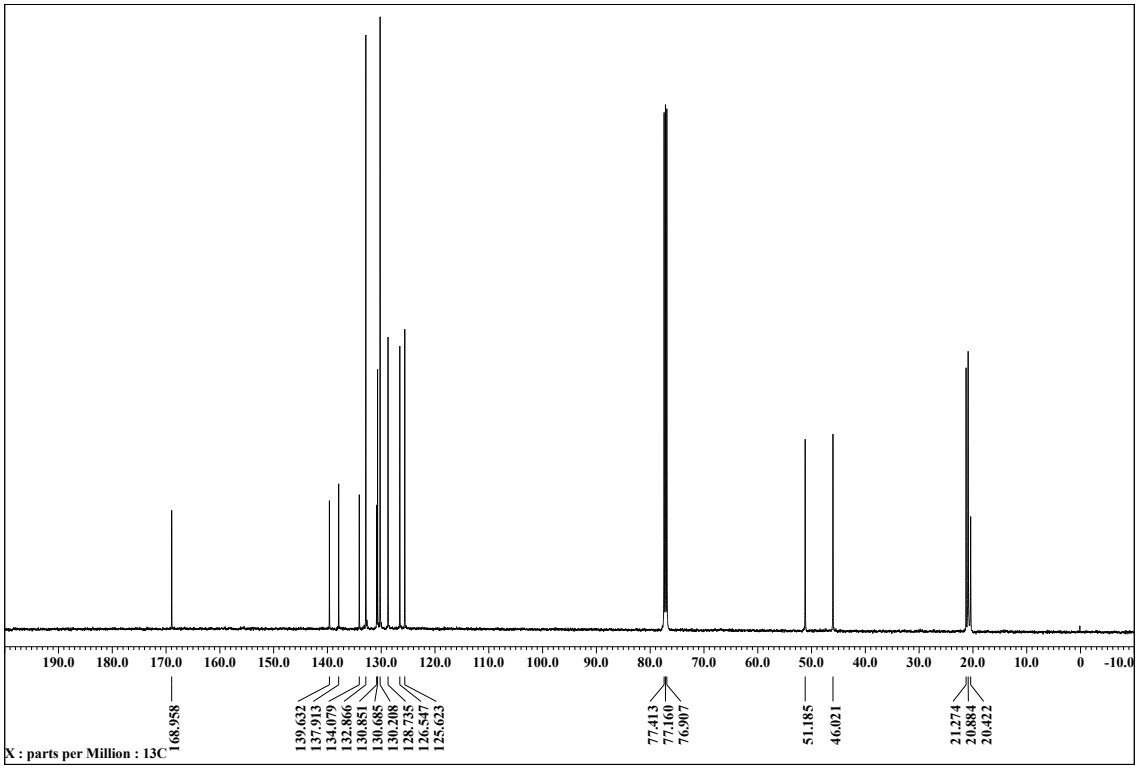


_N,N_-Diisopropyl-2-(_p_-tolylthio)benzamide (10c)

^{1}H NMR (500 MHz, $CDCl_3$)

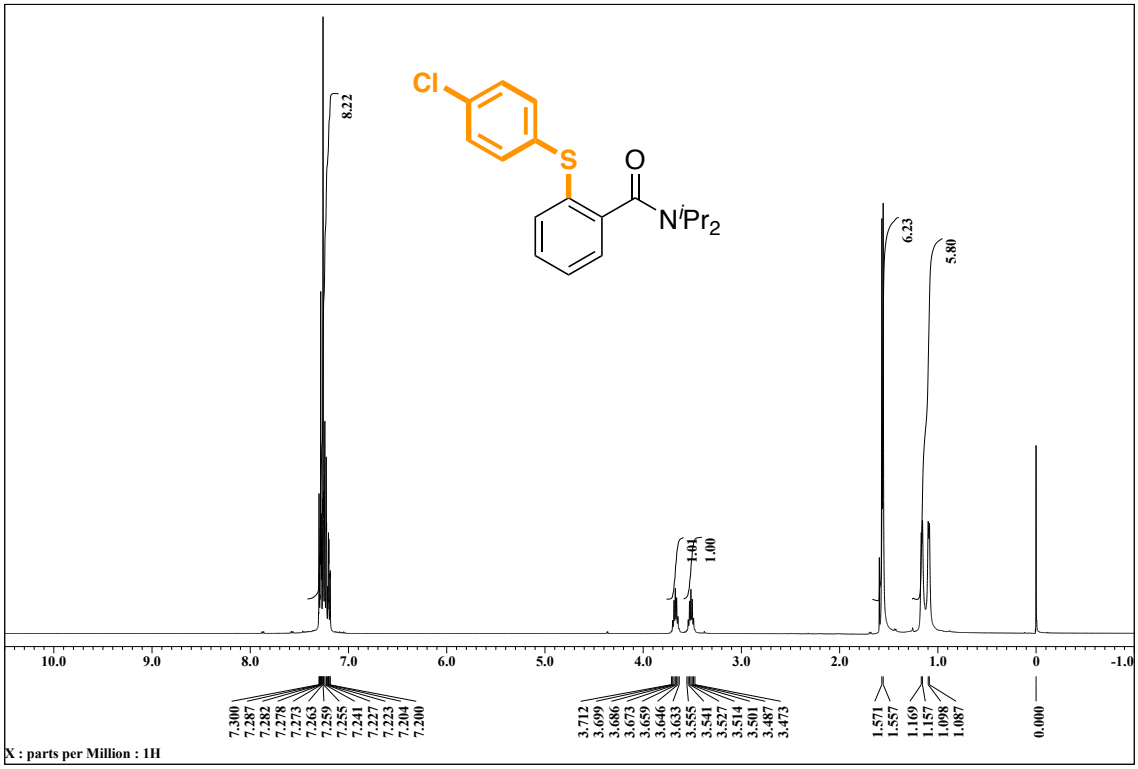


^{13}C NMR (125 MHz, $CDCl_3$)

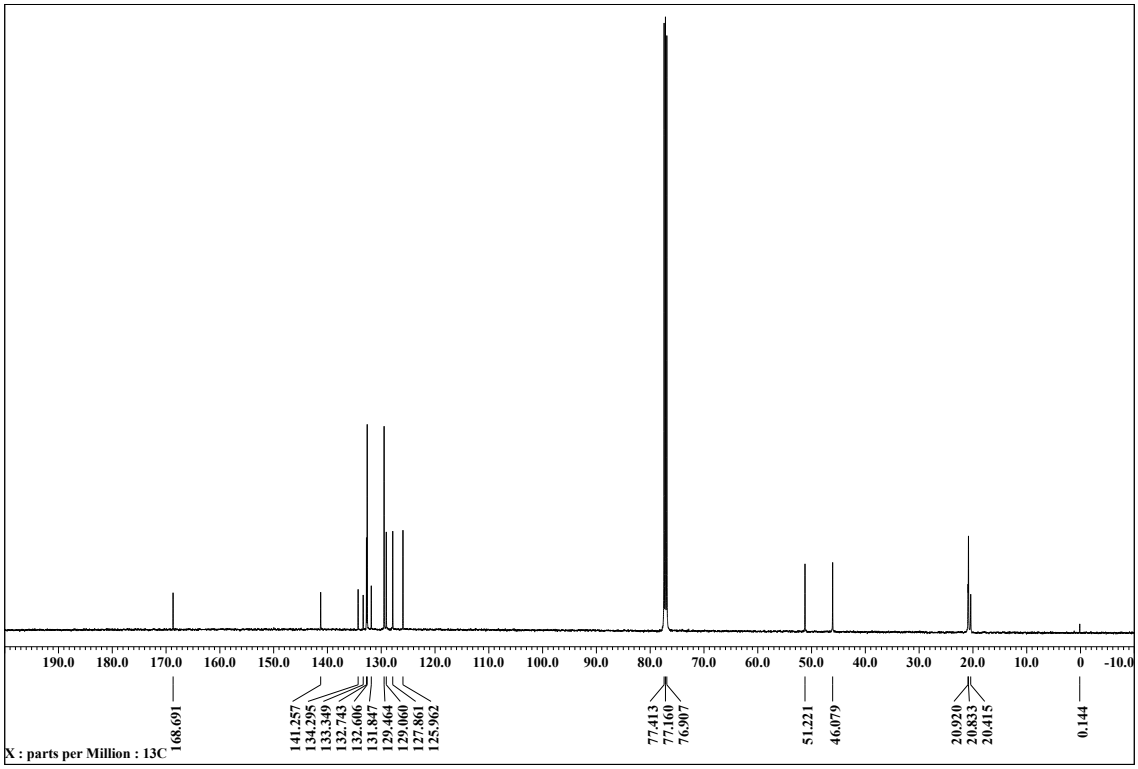


2-((4-Chlorophenyl)thio)-*N,N*-diisopropylbenzamide (10d)

^{1}H NMR (500 MHz, $CDCl_3$)

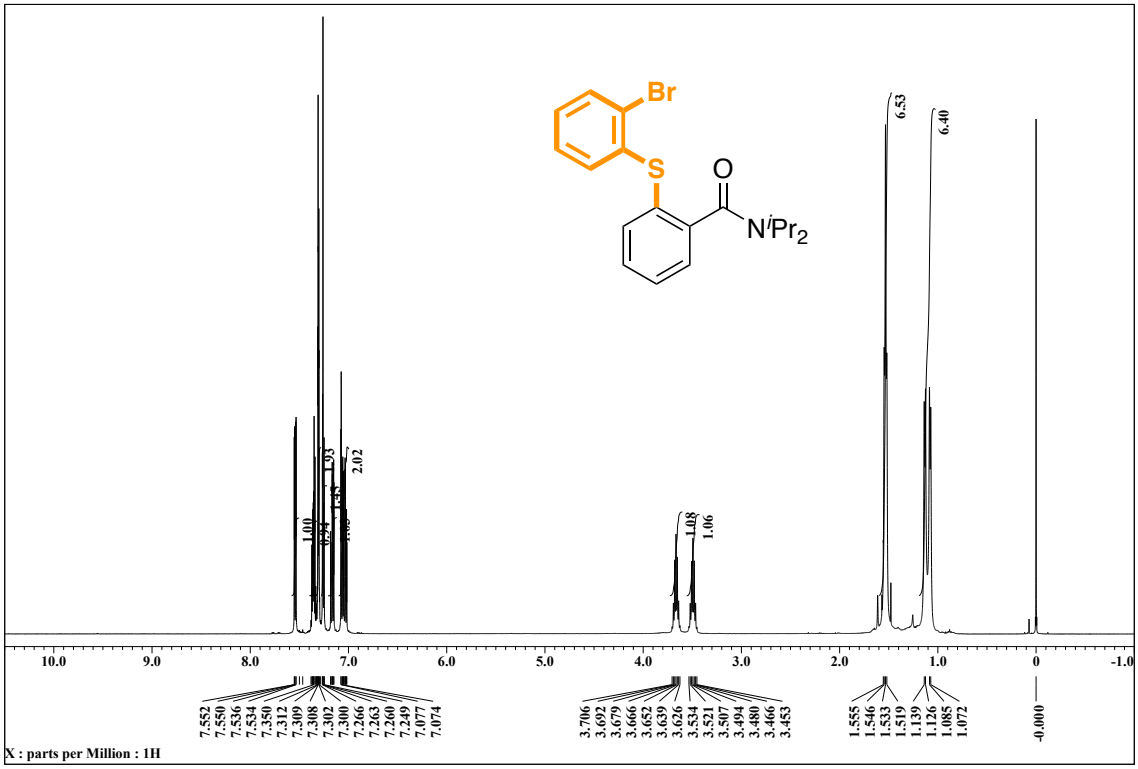


^{13}C NMR (125 MHz, $CDCl_3$)

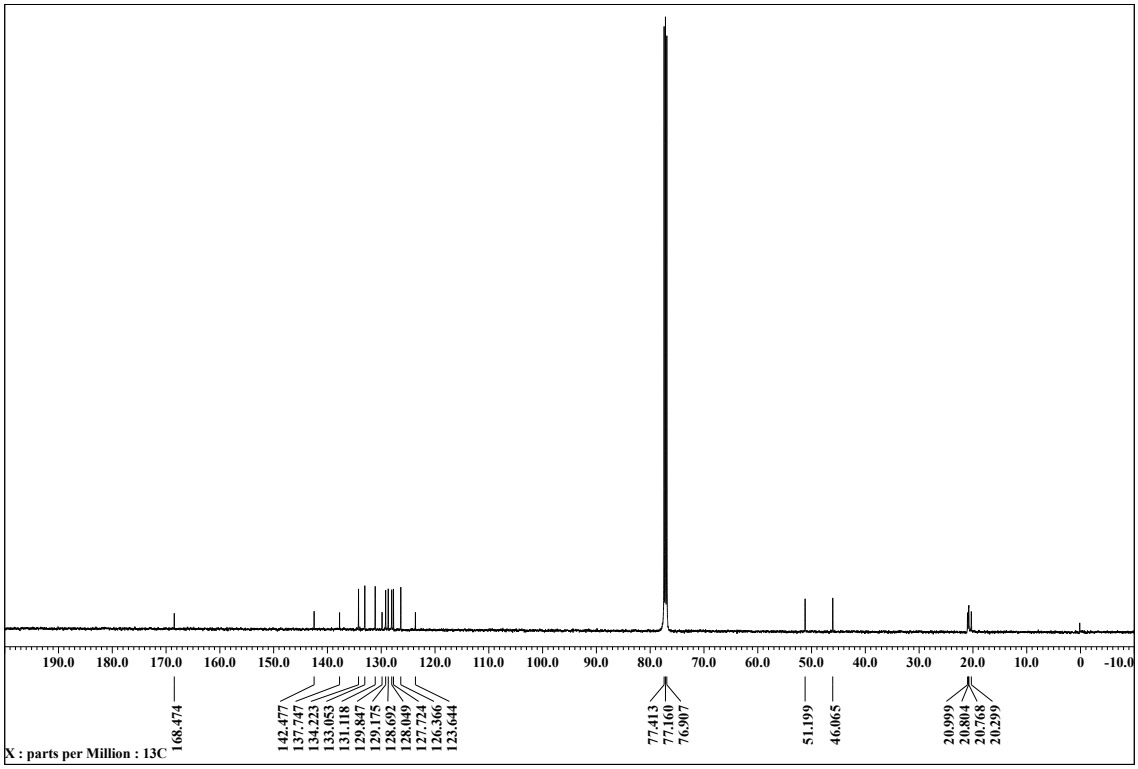


2-((2-Bromophenyl)thio)-*N,N*-diisopropylbenzamide (10e)

^{1}H NMR (500 MHz, $CDCl_3$)

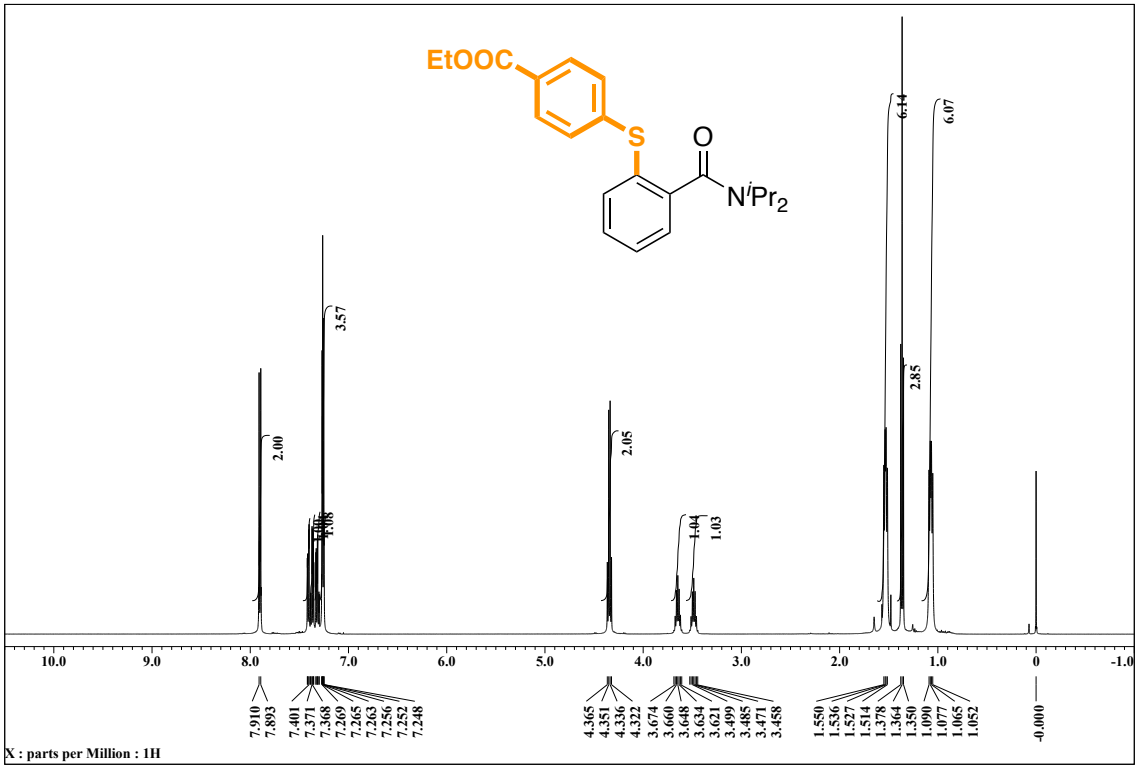


^{13}C NMR (125 MHz, $CDCl_3$)

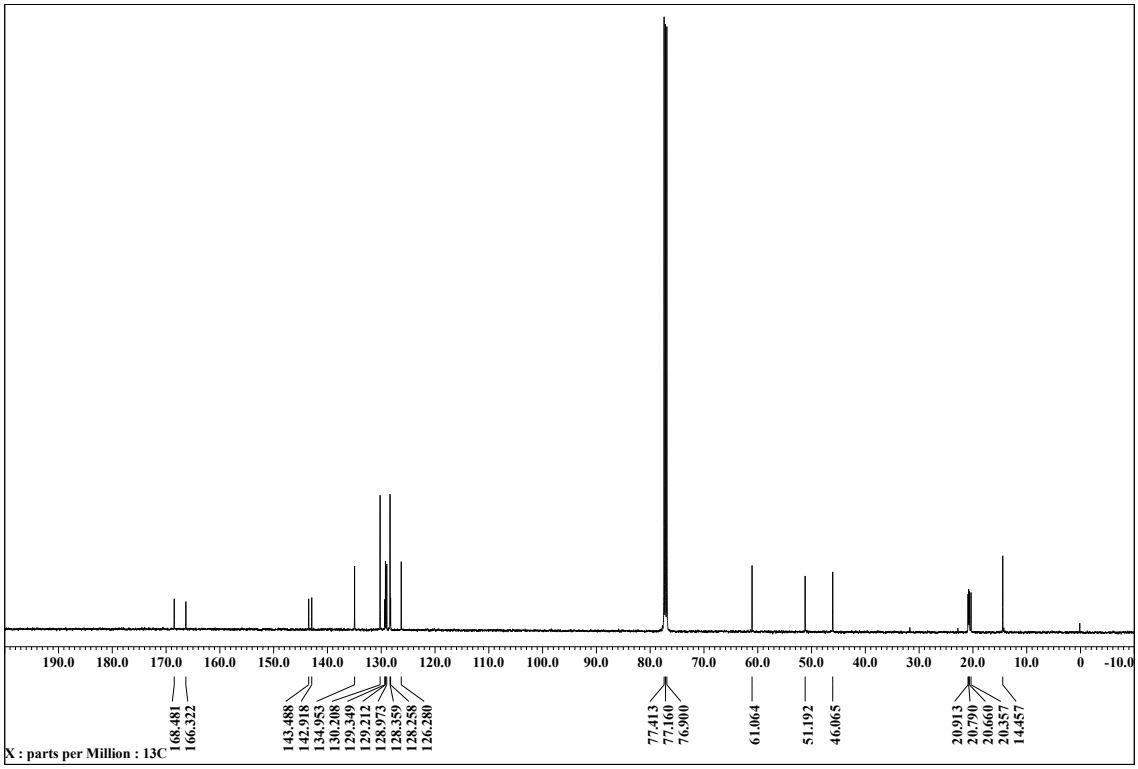


Ethyl 4-((2-(diisopropylcarbamoyl)phenyl)thio)benzoate (10f)

^{1}H NMR (500 MHz, $CDCl_3$)

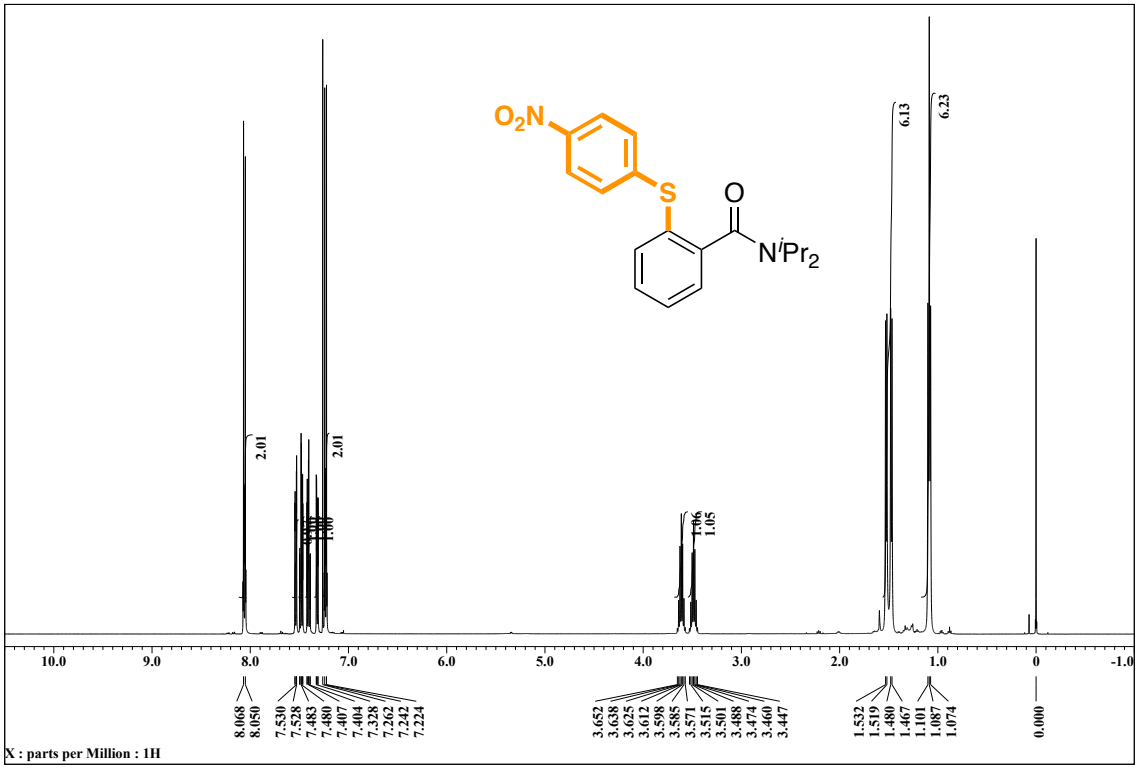


^{13}C NMR (125 MHz, $CDCl_3$)

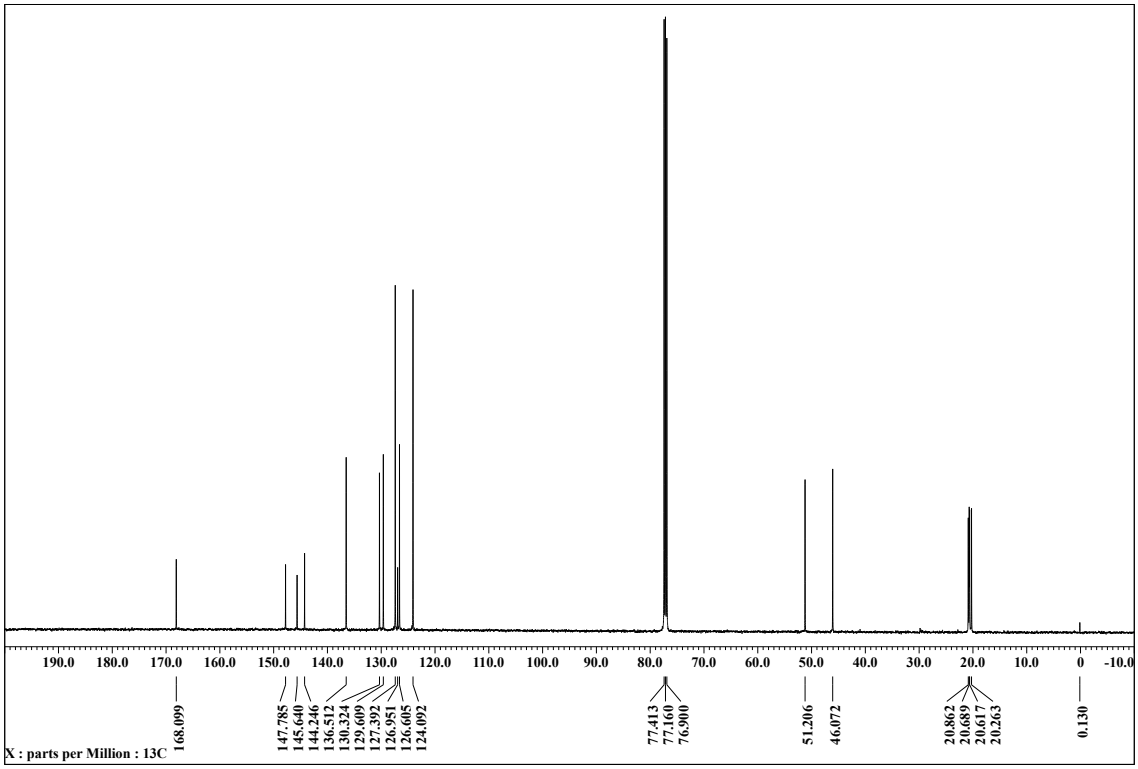


***N*,*N*-Diisopropyl-2-((4-nitrophenyl)thio)benzamide (10g)**

^{1}H NMR (500 MHz, $CDCl_3$)

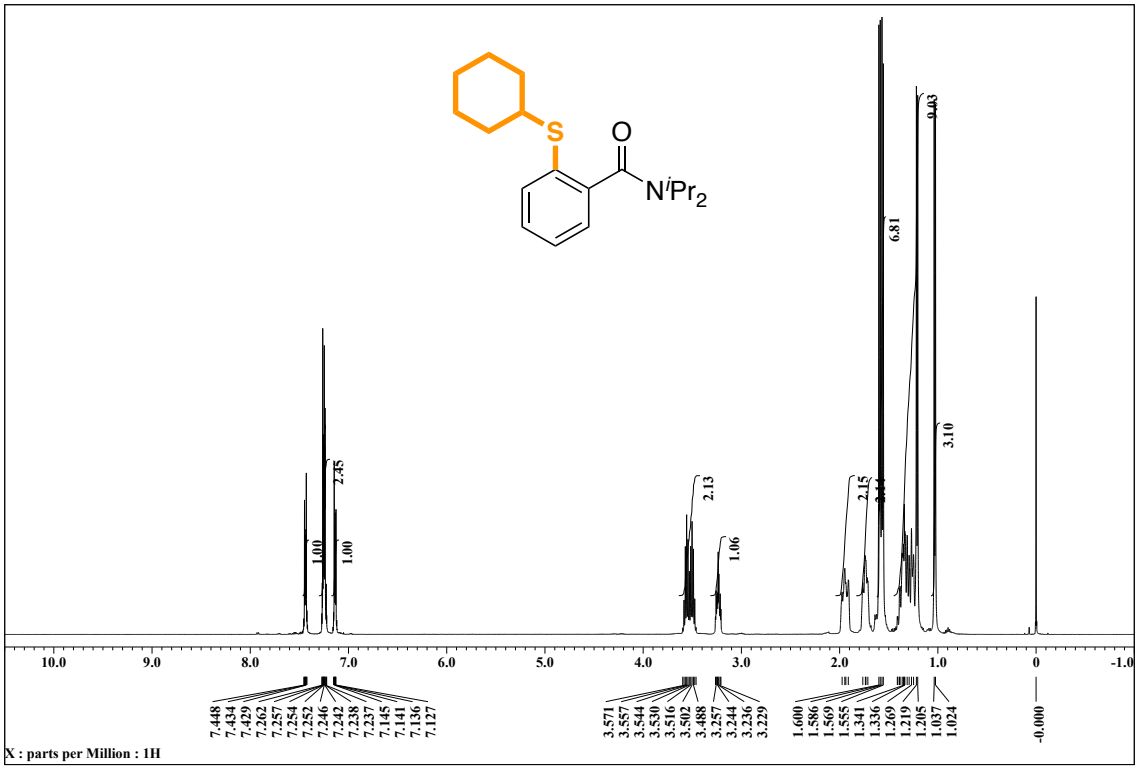


^{13}C NMR (125 MHz, $CDCl_3$)

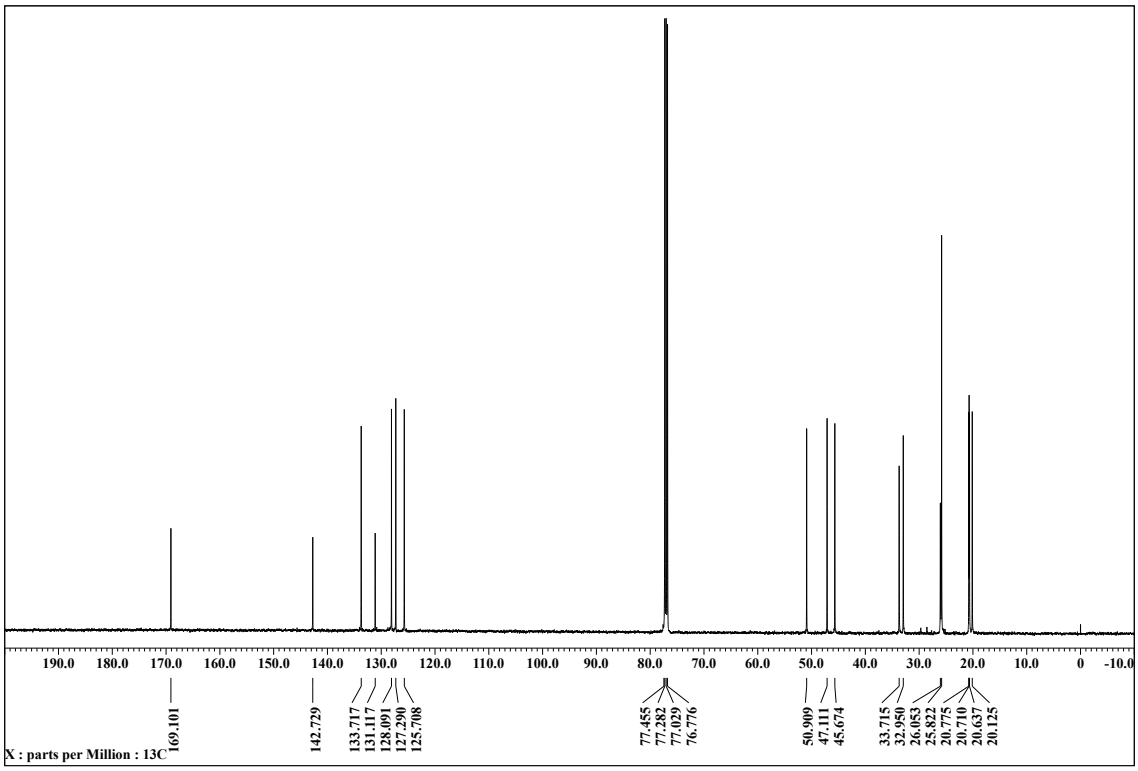


2-(Cyclohexylthio)-*N*,*N*-diisopropylbenzamide (10h)

^{1}H NMR (500 MHz, $CDCl_3$)

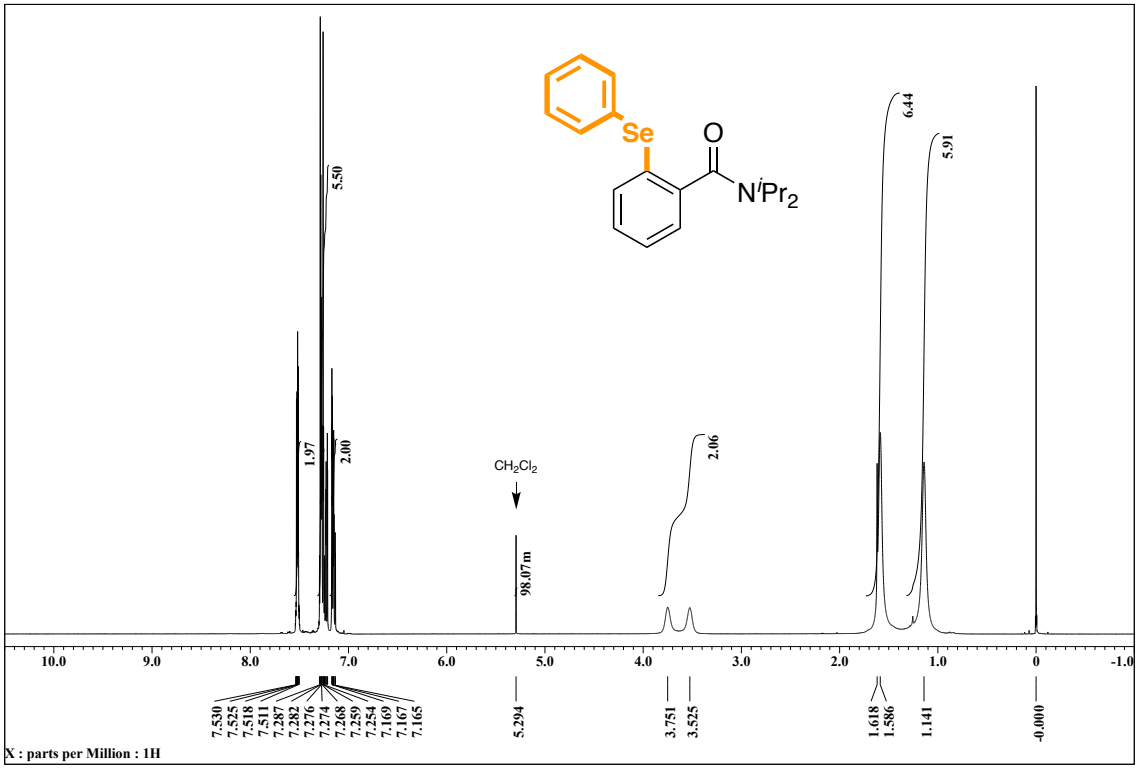


^{13}C NMR (125 MHz, $CDCl_3$)

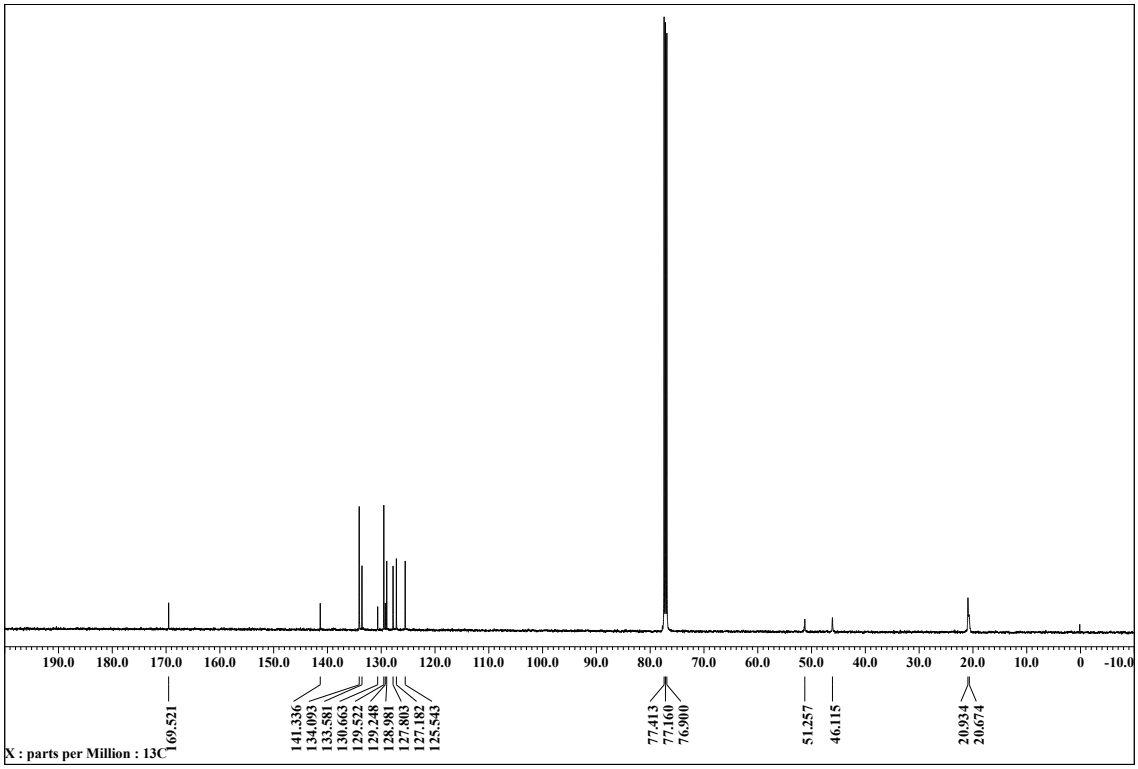


***N*,*N*-Diisopropyl-2-(phenylselanyl)benzamide (10i)**

^{1}H NMR (500 MHz, $CDCl_3$)

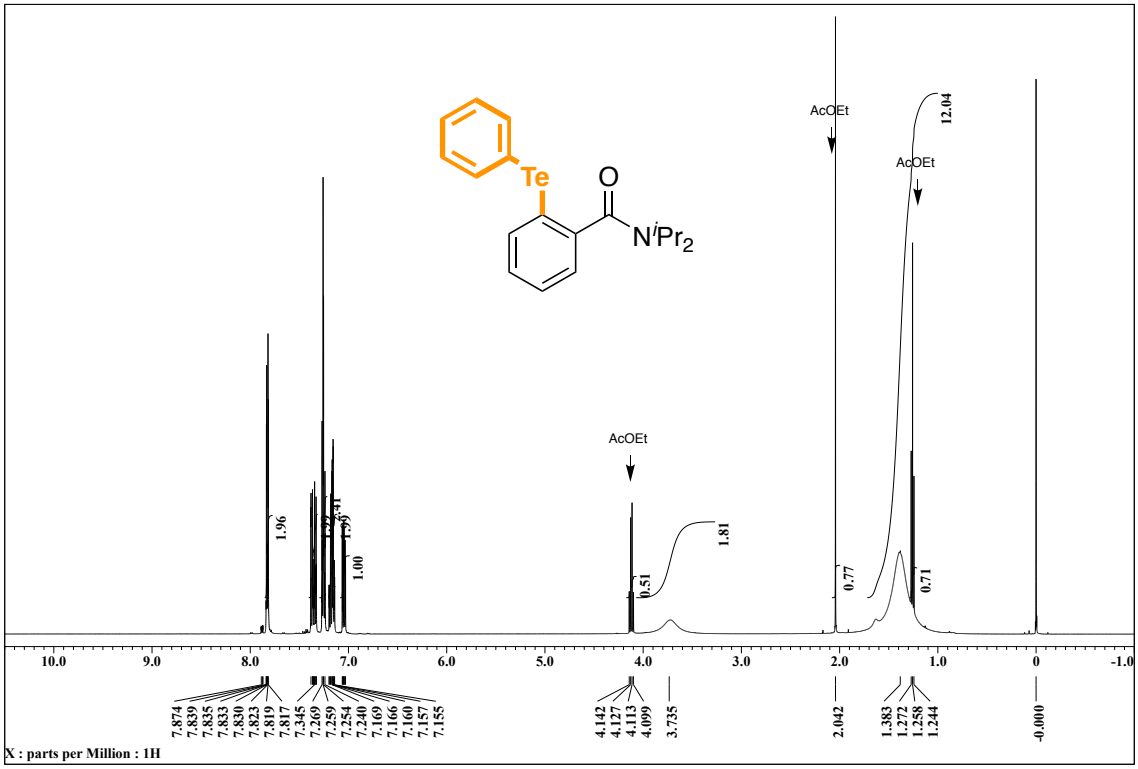


^{13}C NMR (125 MHz, $CDCl_3$)

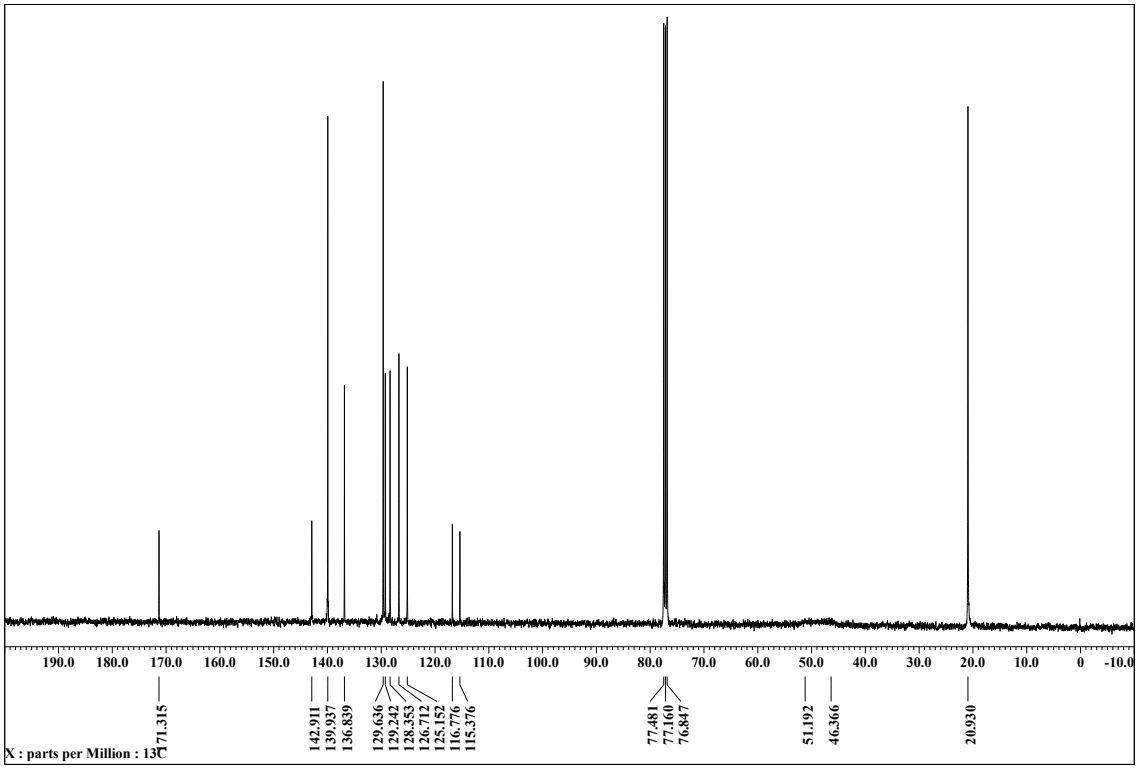


***N*,*N*-Diisopropyl-2-(phenyltellanyl)benzamide (10j)**

^{1}H NMR (500 MHz, $CDCl_3$)

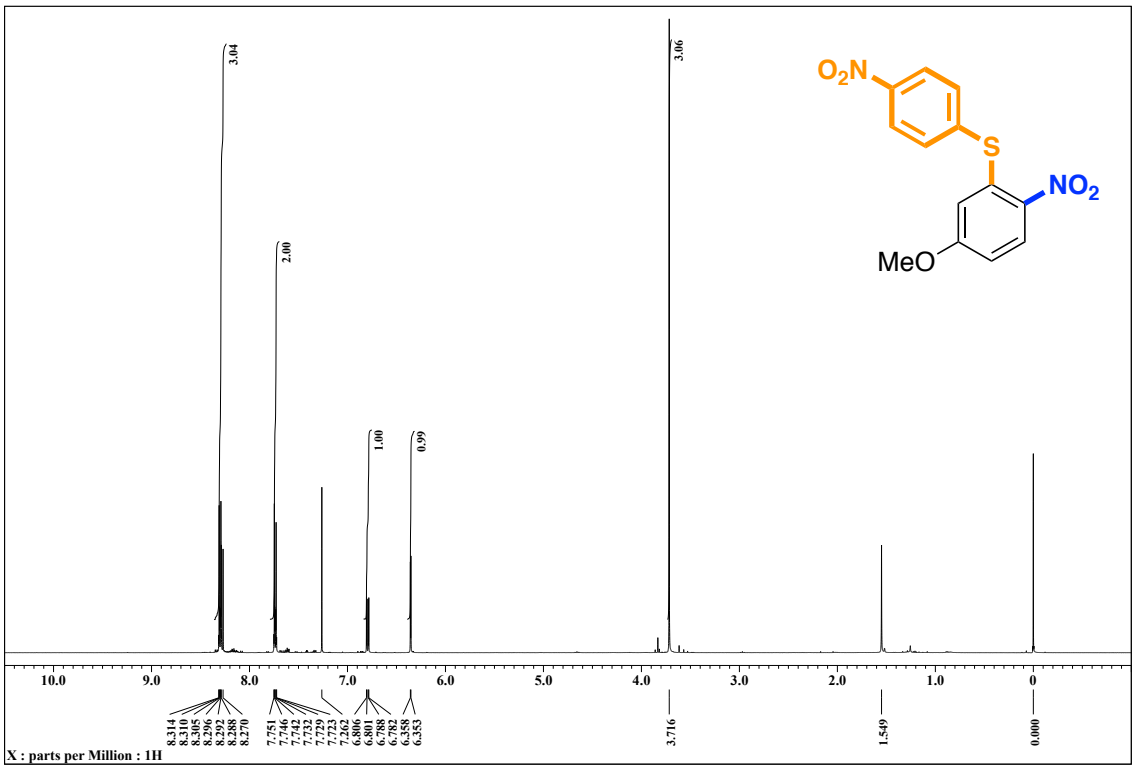


^{13}C NMR (100 MHz, $CDCl_3$, AcOEt was removed by iterative azeotropic evaporation with hexane)

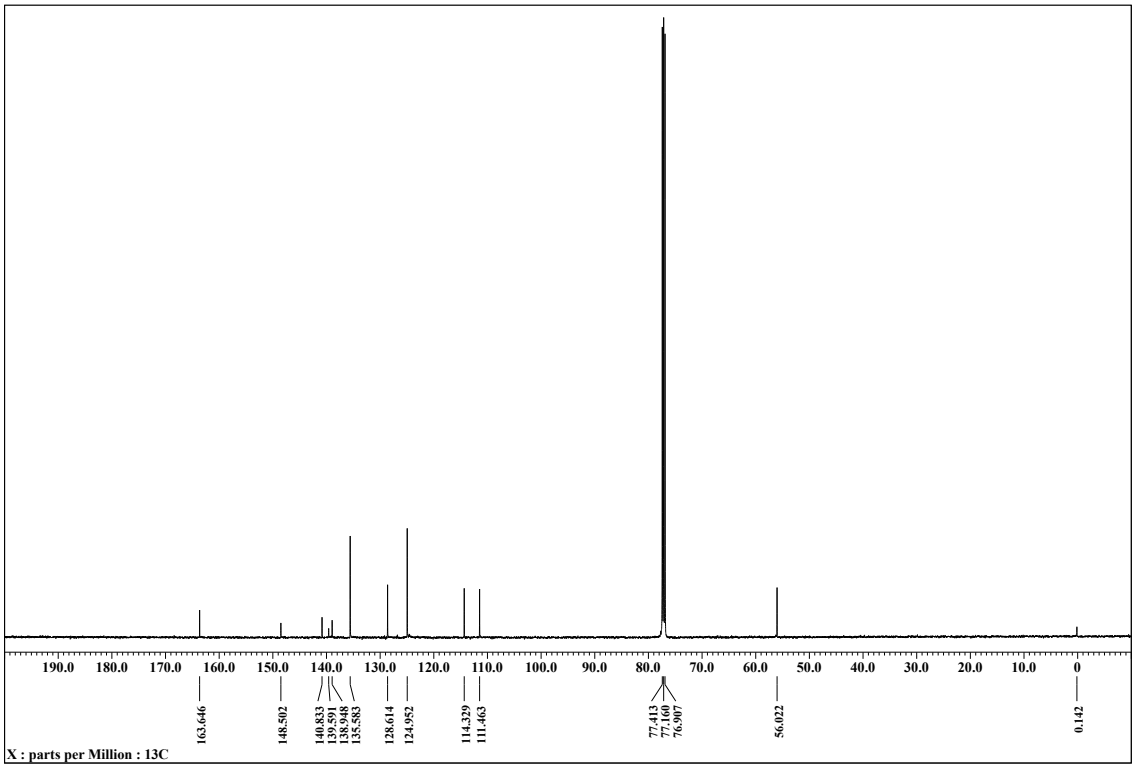


(5-Methoxy-2-nitrophenyl)(4-nitrophenyl)sulfane (10k)

^{1}H NMR (500 MHz, $CDCl_3$)

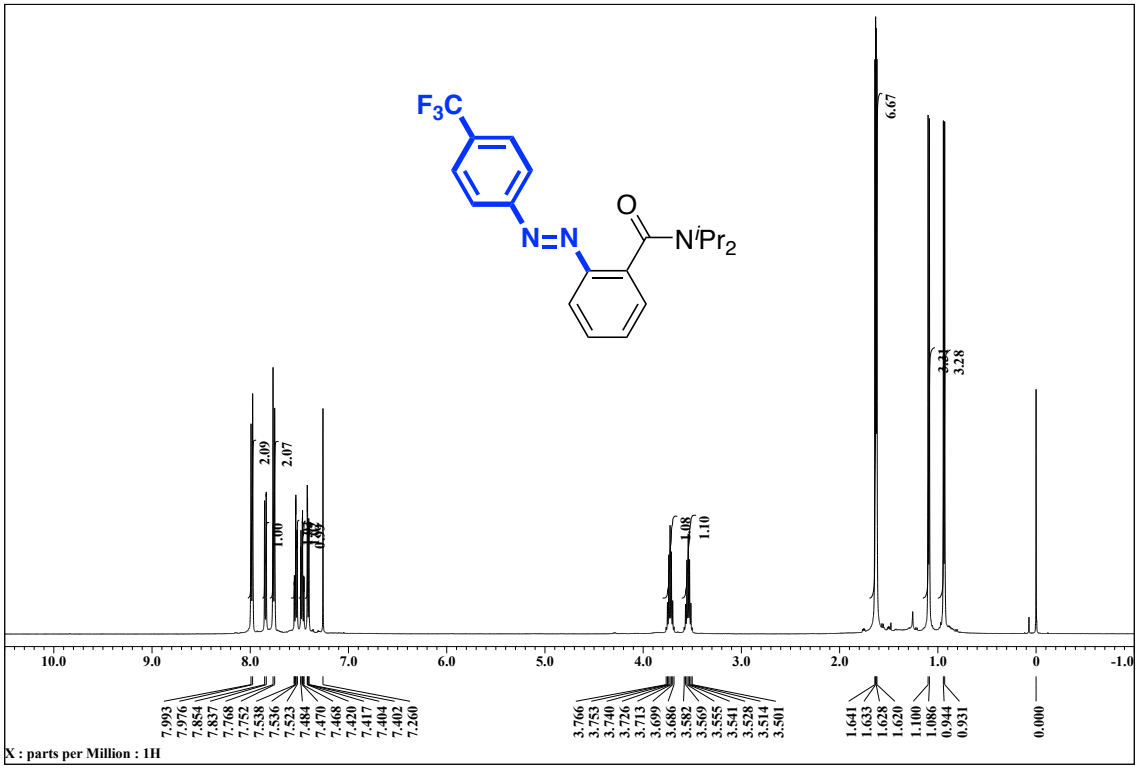


^{13}C NMR (125 MHz, $CDCl_3$)

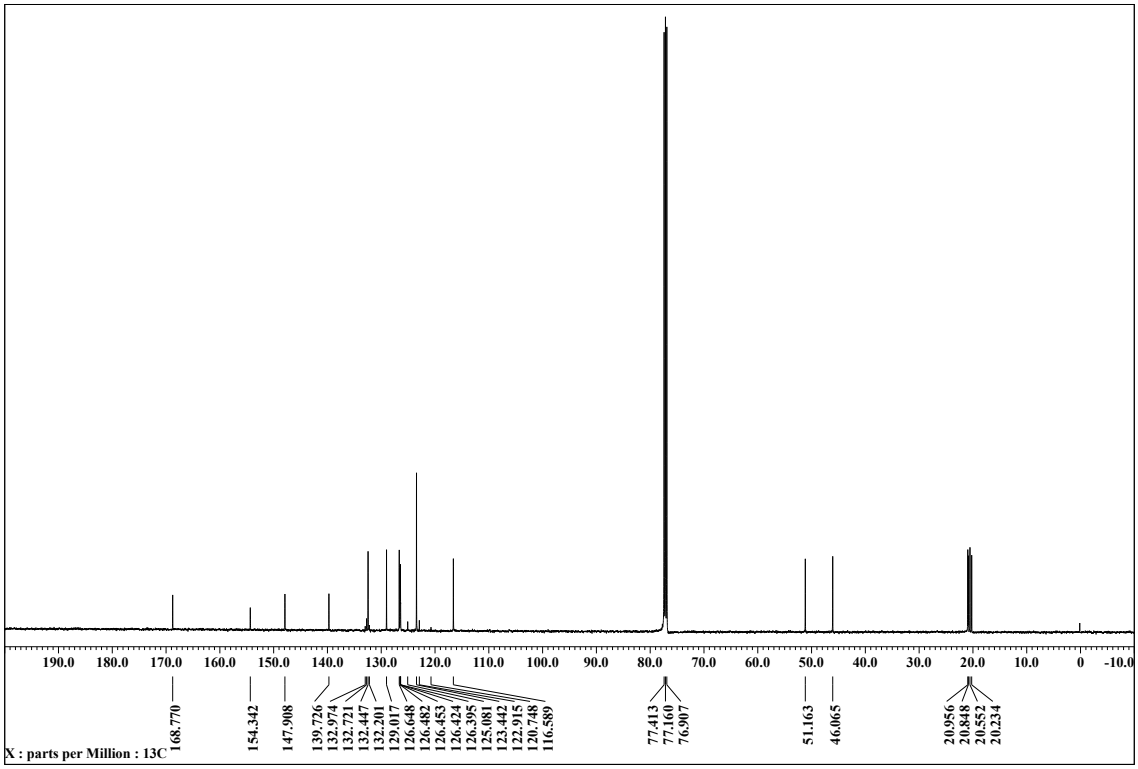


(*E*)-*N*,*N*-Diisopropyl-2-((4-(trifluoromethyl)phenyl)diazenyl)benzamide (11a)

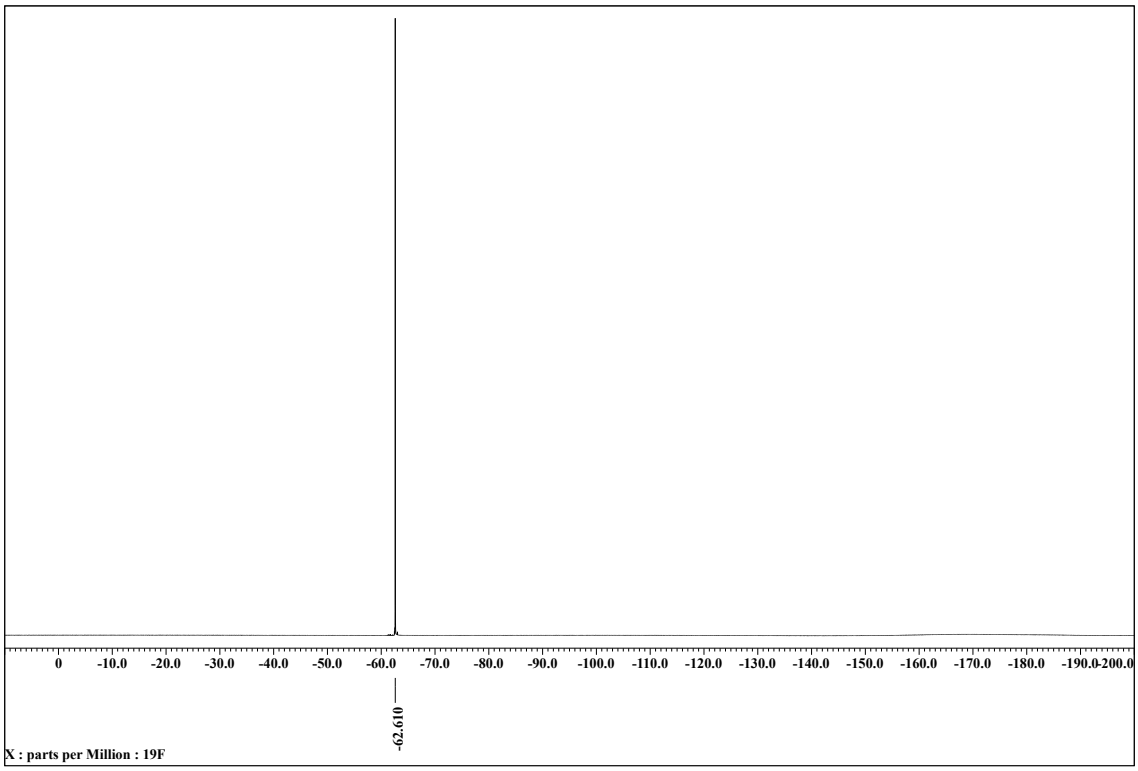
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

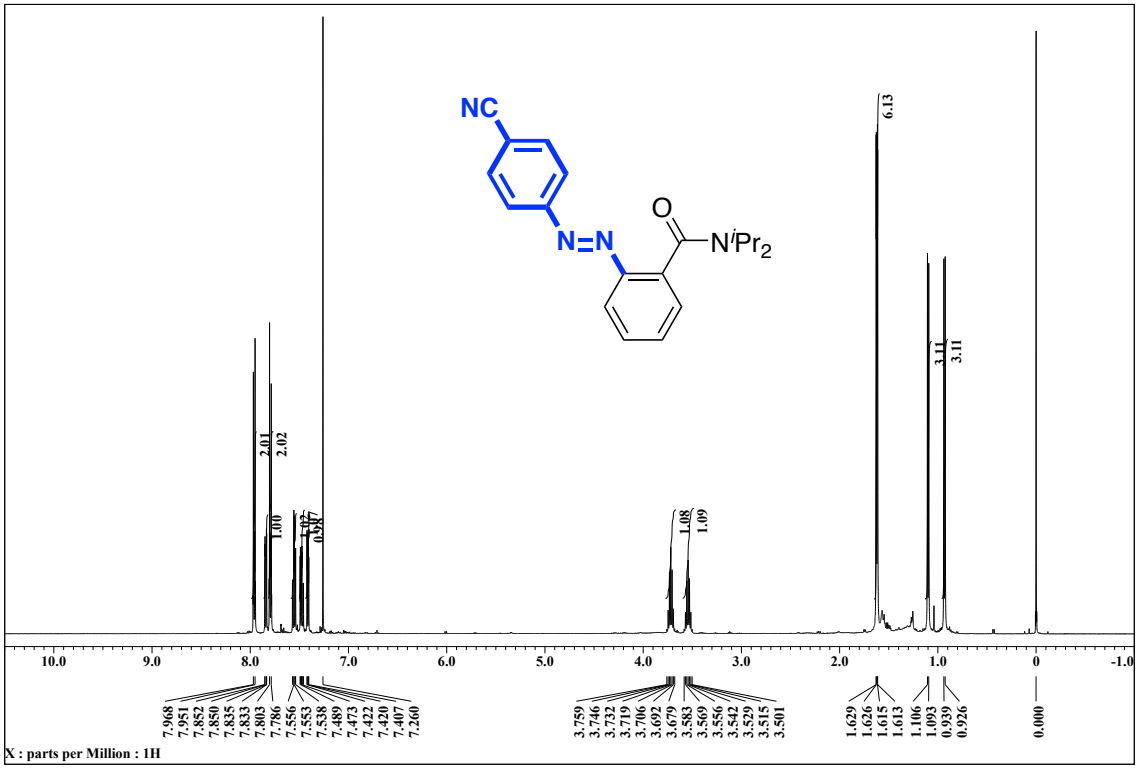


^{19}F NMR (470MHz, $CDCl_3$)

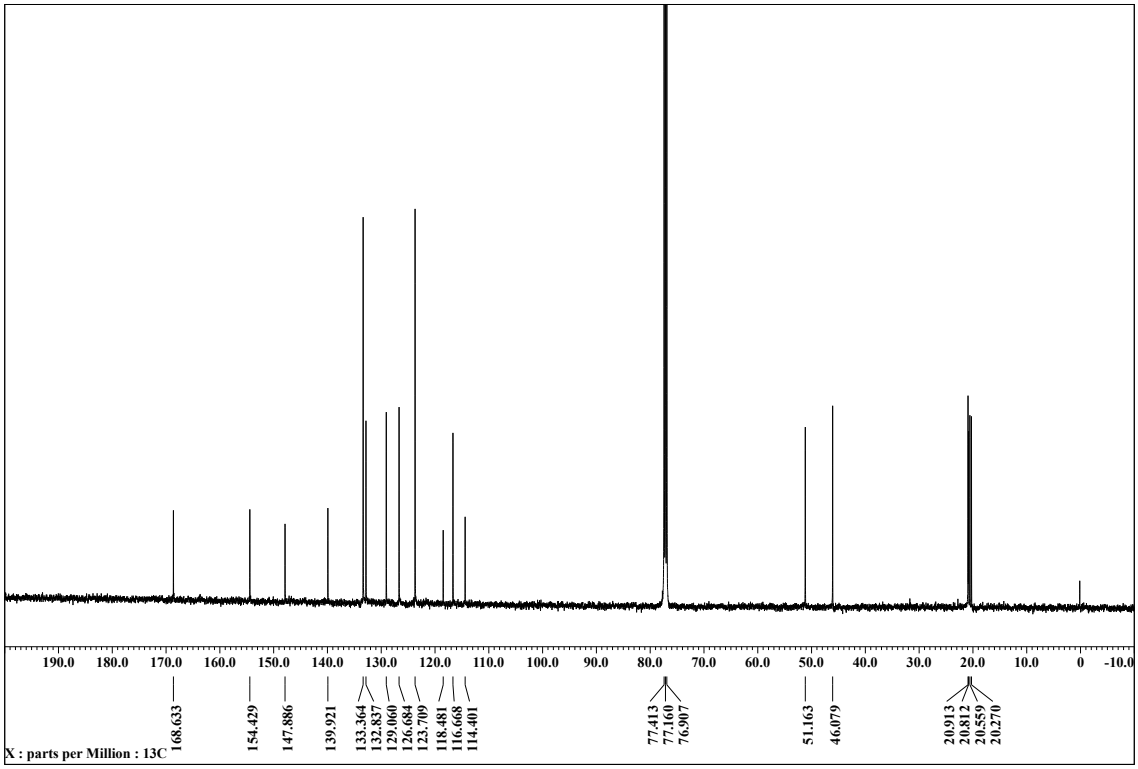


(*E*)-2-((4-Cyanophenyl)diazenyl)-*N*,*N*-diisopropylbenzamide (11b)

^{1}H NMR (500 MHz, $CDCl_3$)

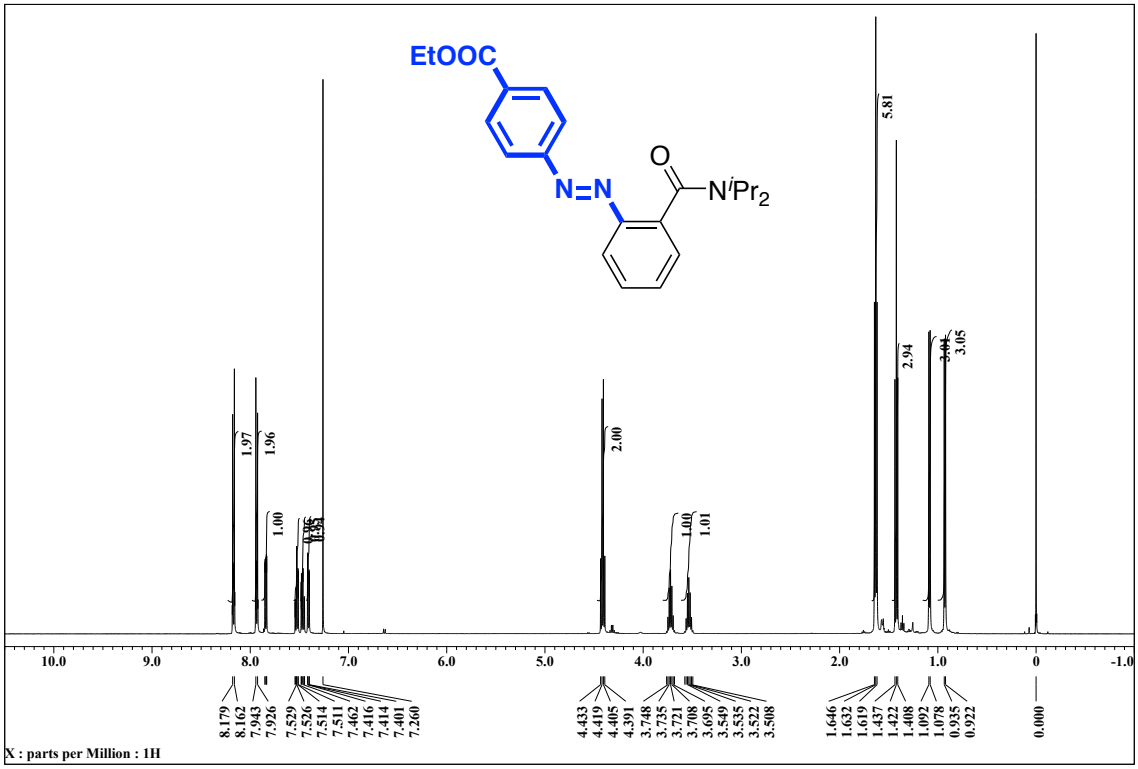


^{13}C NMR (125 MHz, $CDCl_3$)

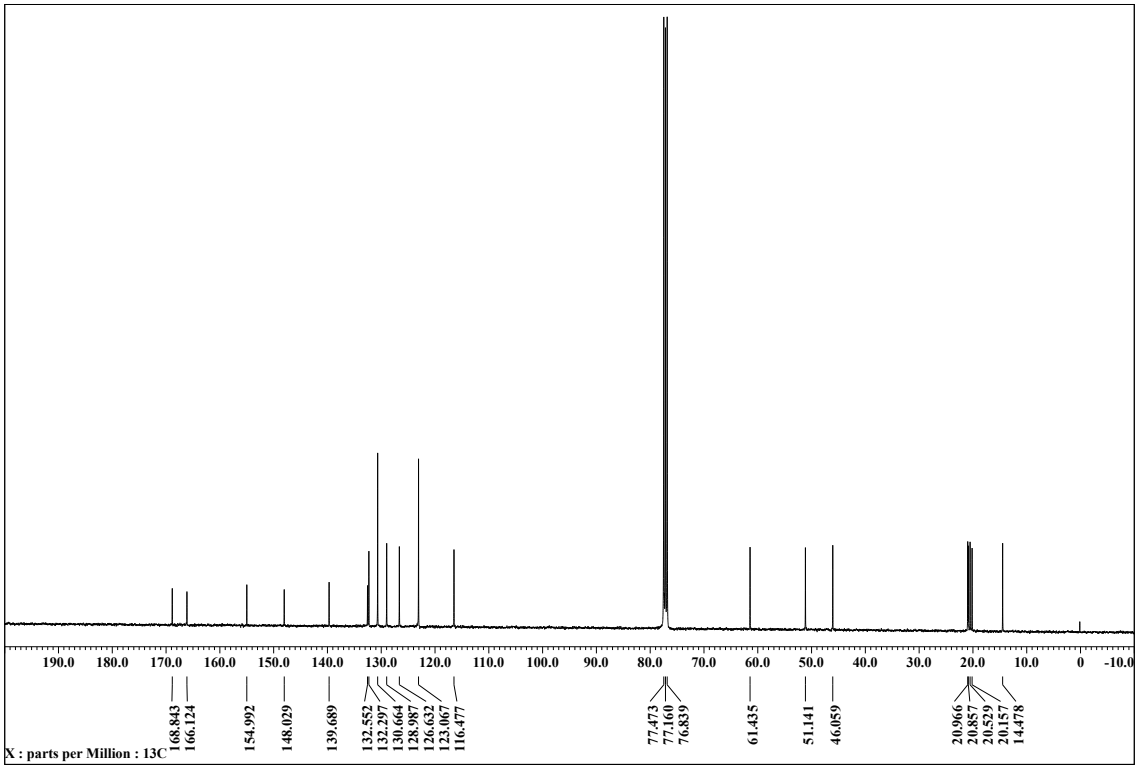


Ethyl (*E*)-4-((2-(diisopropylcarbamoyl)phenyl)diazenyl)benzoate (11c)

^{1}H NMR (500 MHz, $CDCl_3$)

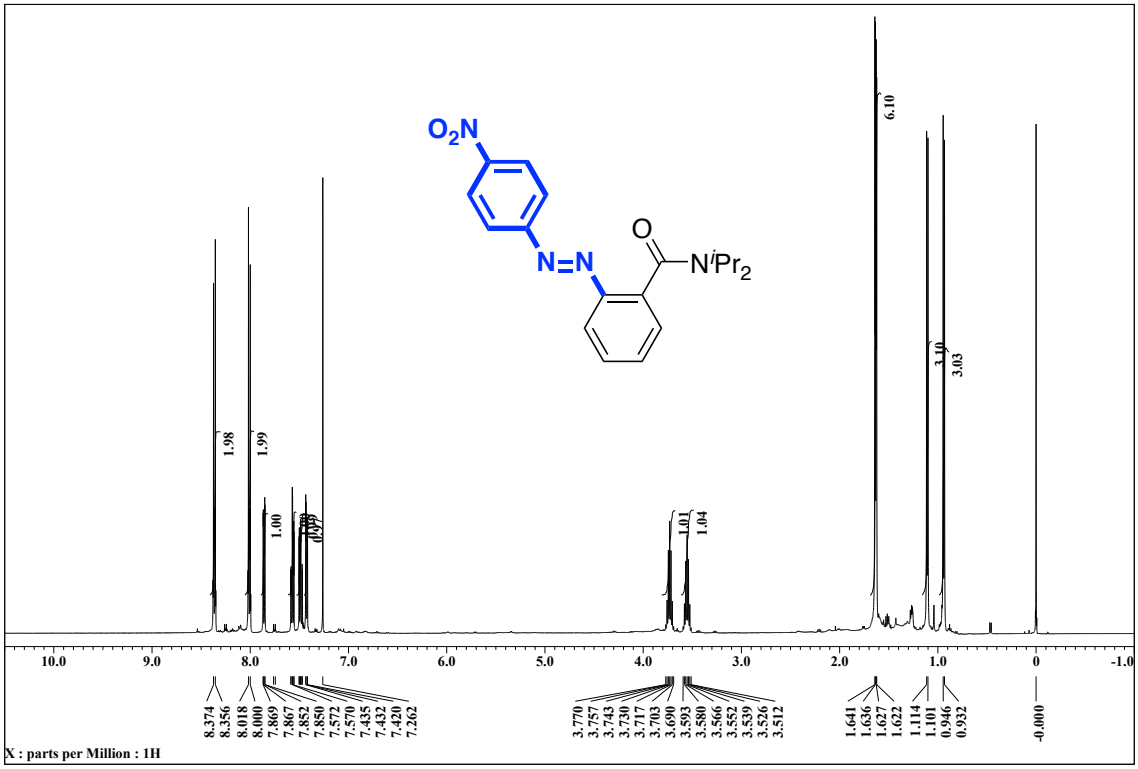


^{13}C NMR (100 MHz, $CDCl_3$)

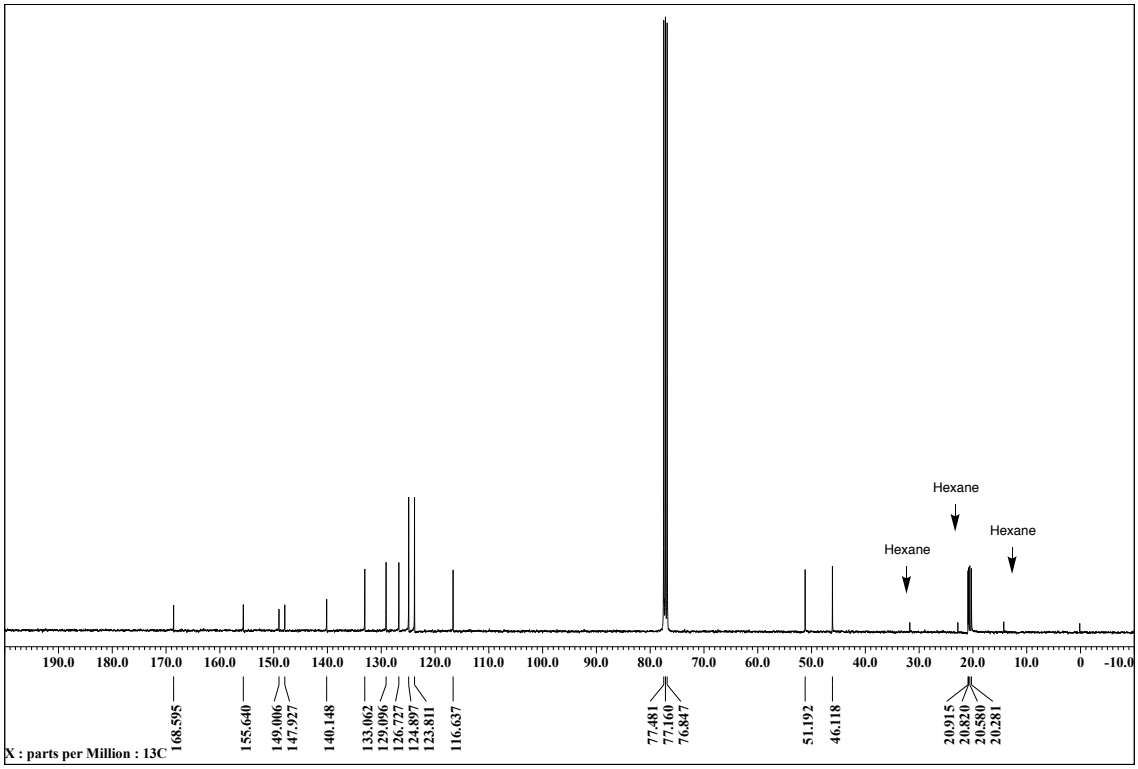


(*E*)-*N*,*N*-Diisopropyl-2-((4-nitrophenyl)diazenyl)benzamide (11d)

^{1}H NMR (500 MHz, $CDCl_3$)

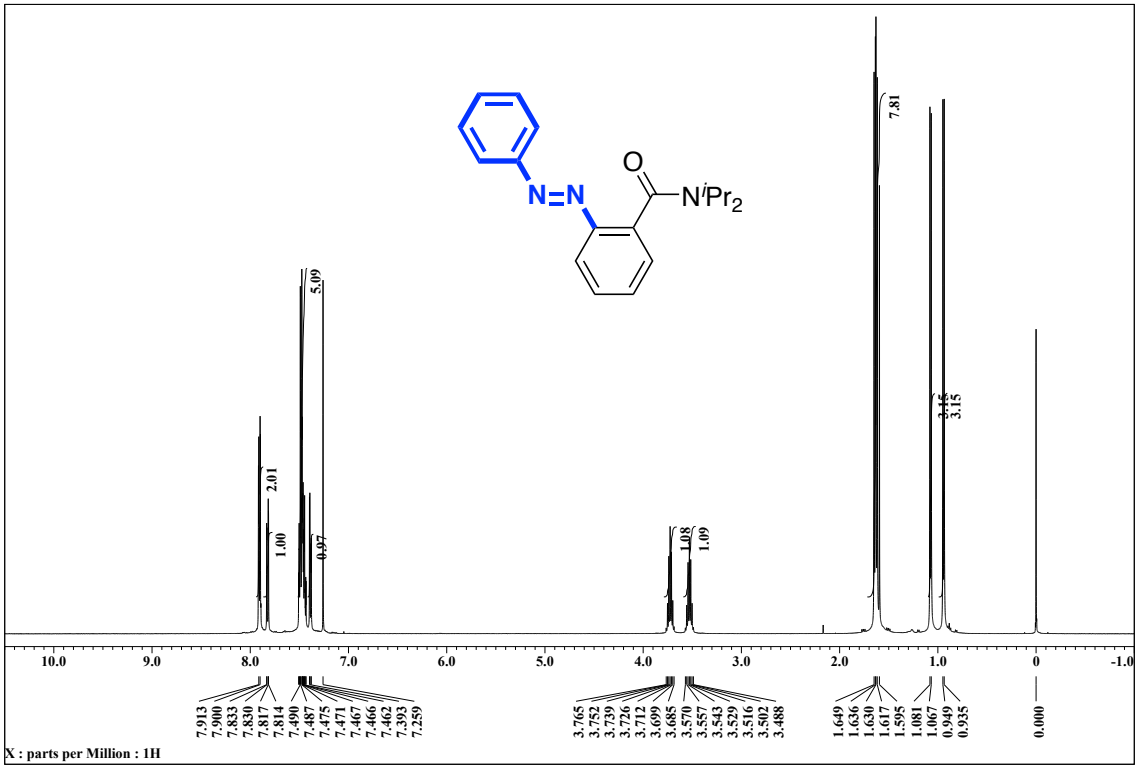


^{13}C NMR (100 MHz, $CDCl_3$)

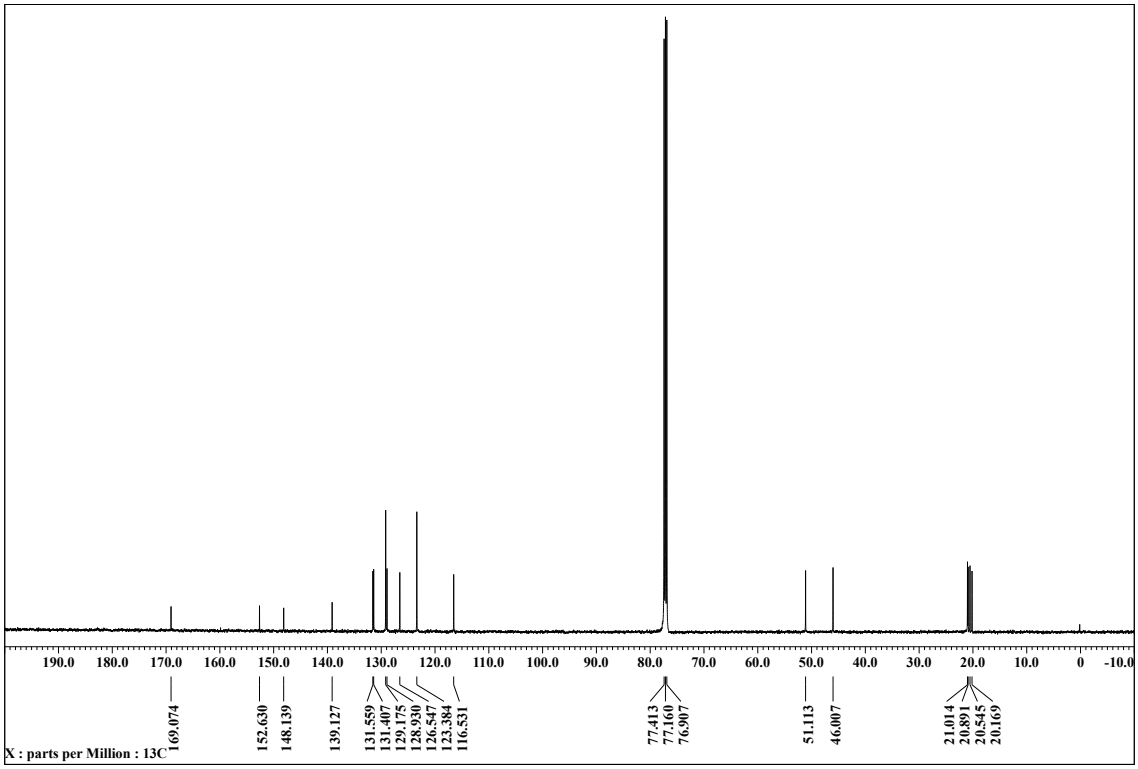


(*E*)-*N*,*N*-Diisopropyl-2-(phenyldiazenyl)benzamide (11e)

^{1}H NMR (500 MHz, $CDCl_3$)

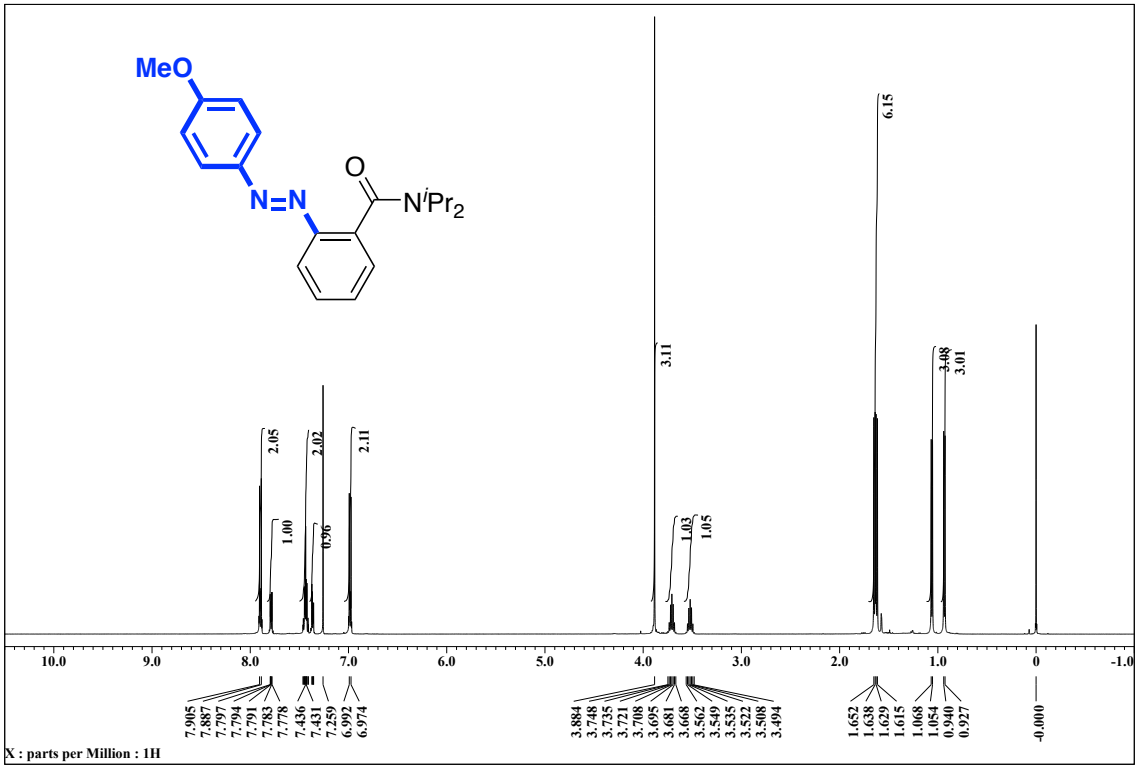


^{13}C NMR (125 MHz, $CDCl_3$)



(*E*)-*N*,*N*-Diisopropyl-2-((4-methoxyphenyl)diazenyl)benzamide (11f)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)