Short Syntheses of 1-Substituted Dibenzothiophene Derivatives

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General Experimental Considerations

Reactions were run under nitrogen, using oven-dried glassware unless otherwise specified. ¹H, ¹³C, and ¹¹B NMR data were collected at 300K on a Bruker AV-500 NMR spectrometer. ¹H NMR spectra are referenced to residual non-deuterated NMR solvent (CHCl₃ =7.26 ppm). ¹³C NMR spectra are referenced to the central CDCl₃ peak (77.16 ppm). Mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University). Optical rotations were obtained in the solvents stated, using a DigiPol 781 Automatic Polarimeter from Rudolph Instruments. Concentrations for optical rotation are given in g/100 mL.

Solvents

Diethyl ether was purchased as anhydrous ACS reagent grade, >99.0% stabilized by BHT in 1L metal cans from Aldrich.

Dichloromethane (ACS grade) was purchased from Fisher. Dichloromethane for reactions was distilled from calcium hydride immediately before use, while no purification was carried out on dichloromethane used for extractive work-ups.

Methanol was purchased from Fisher and used as received.

Tetrahydrofuran was purchased from Aldrich in a Sure/seal® bottle (anhydrous, >99.9%, inhibitor free, catalogue number 401757). Tetrahydrofuran was used directly from this bottle for Grignard reactions and lithiations.

Reagents

Benzaldeyhde, n-Butyllithium, dimethyl formamide, ethylmagnesium bromide in diethyl ether, hydrochloric acid in diethyl ether, magnesium turnings, dimethyl malonitrile, priopionaldehyde, and trifluoroacetic acid were purchased from Aldrich and used directly as received. The n-butyllithium was periodically titrated in THF using 1,10 phenanthroline as an indicator, and 2-butanol as the titrant and concentration varied from 2.5 to 2.6 M.

Sodium borohydride was purchased in a 250 g container from Aldrich and was stored in a solvent-free glovebox to maintain high activity.

N-methoxy-*N*-methytrifluoroacetamide, 2-fluorothiophenol, 2-fluoro-N-methylaniline, 1,2dibromobenzene, 1-bromo-2-fluorobenzene, isopropoxy B(pin), pinacolborane, and titanium ethoxide were purchased from Oakwood Chemical and used directly as received.

4,5-dibromo-o-xylene, 1,2-dibromo-4,5-(methylenedioxy)benzene, 1,2-dibromo-4,5-difluorobenzene, 2,3-dibromopyridine, and N-boc-pyrrolidinone were purchased from Combi-Blocks and used directly as received.

Ellman Sulfinimide Auxiliary was purchased from Oakwood Chemical and configuration was verified by measurement of optical rotation.

X-Ray Crystallography Data

The crystal chosen was attached to the tip of a MicroLoop with Paratone-N oil. Measurements were made on a Bruker D8 VENTURE diffractometer equipped with a PHOTON III CMOS detector using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) from an Incoatec micro-focus sealed tube at 100 K [1]. The initial orientation and unit cell were indexed using a least-squares analysis of the reflections collected from a complete 360° phi-scan, 2 seconds per frame and 1° per frame. For data collection, a strategy was calculated to maximize data completeness and multiplicity, in a reasonable amount of time, and then implemented using the Bruker Apex 3 software suite [1]. The crystal to detector distance was set to 4 cm. Cell refinement and data reduction were performed with the Bruker SAINT [2] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS [3]). The structures were solved using SHELXT-2014 [4] and were refined using a full-matrix least-squares method on F^2 with SHELXL-2018 [4]. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of these hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom or $1.5U_{eq}$ for methyl hydrogens. Hydrogen atoms bonded to nitrogen were allowed to refine isotropically and were not restrained in any way.

Compound **3e** 5 s frames

In the final refinement, there were a number of reflections below $\sin\theta/\lambda = 0.600$ which were missing. These reflections, eight of them strong, were collected but must have saturated the detector during data collection or been partially obscured by the beam stop. They were removed by the software from the data set during processing.

Compound **3f** 10 s frames

The data was cut off at a resolution of 0.63 Å using a SHEL instruction during the refinement. Above this value the reflections were mostly noise, $I/\sigma(I) < 2$.

Compound **3g** 10 s frames

Data was collected to a maximum θ angle of 40.30° (0.55 Å resolution). The highest angle data was weak and noisy (I/ σ (I) < 2), so in the final refinement a SHEL command was used to cut the data off at 36.32° (0.60 Å resolution).

The crystal was found to be a pseudo-merohedral twin. It crystallized as a triclinic unit cell but with two angles close to 90°, and symmetry approximating a *C*-centered monoclinic cell. The only cell that had a reasonable merging-R value (0.056) was triclinic; all higher symmetry cells were above 0.500. There were found to be four complete molecules in the asymmetric unit of the *P*-1 cell. The twin law, determined using the program Platon [5], 0 -1 0 -1 0 0 0 0 -1, was added into the refinement and the BASF scale factor refined to 0.9307(4). The final statistics of the refinement were very reasonable. Attempts were made to refine the structure in a *C*-centered monoclinic cell but no acceptable results were obtained.

Compound 3k 15 s frames

Two reflections were removed from the final refinement as they were partially obscured by the beam stop (1 0 2 and 0 2 0), while one reflection was removed from the final refinement because of poor agreement between F_{obs}^2 and F_{calc}^2 (0 3 6). Data was collected to a maximum θ angle of 40.17° (0.55 Å resolution). The highest angle data was weak and noisy, so in the final refinement a SHEL command was used to cut the data off at 36.32° (0.60 Å resolution).

In the final checkcif file there was one level B alert: Short Intermolecular H...H Contact H4 ...H4(1-x,1-y,1-z) = 1.99 Å. This appears to reflect a true short contact in the structure. H4 is bonded to an aromatic carbon atom of a 6-membered ring, so the geometry of the interaction between two like atoms has little flexibility or chance of the hydrogen atoms being misplaced or misassigned. This contact is part of a network of intermolecular interactions that join several molecules into a close association in this structure (see Figure S15).

Compound 11c 15 s frames

An error occurred during the data collection. The collection stopped after only 8 of 9 runs had been finished and it could not be restarted. However, there was enough data already collected that the structure could be refined and the final cif checked with no problems detected. Data was collected to maximum θ angle of 39.81° (0.56 Å resolution). However, the high angle data was very noisy above 0.65 Å (66.28°). The data was cut off at this value during refinement using a SHEL instruction. One reflection (3 3 0) was removed from the final refinement because of poor agreement between F_{obs}^2 and F_{calc}^2 .

The structure was very disordered. One section of the molecule, involving O1 and the methyl groups of the *t*-butyl group, was modelled with a two part (50:50) disorder. The carbon atoms of the latter group were made equivalent using a SAME command to apply appropriate restraints. No other restraints were required. The other end of the molecule, beyond N1 and including C13, the ethyl group and a portion of the dibenzothiophene group, was also disordered. This included the 5-membered ring and the coordinated 6-membered ring of dibenzothiophene. This portion of the molecule was treated as one unit and was split over two sets of positions. The occupancy of each part was refined using a free variable to a total of one. A SAME instruction was used to set restraints to keep the geometries of the two parts similar. All of the carbon atoms in the two parts were restrained to have similar thermal parameters, as were (separately) S1A and S1B. Bond lengths of the same type between disordered and non-disordered regions of the molecule were restraints were placed over the entire molecule using a RIGU command. The occupancies of the two parts refined to a final ratio of 86.7(3) and 13.3 %.

The molecule was found to crystallize in the chiral space group $P2_12_12_1$, with S chirality at C13 (A and B). The absolute structure of the molecule was reliably determined. Using the program Platon [5] the refined structure was calculated to have a Flack parameter of 0.019(15), a Parsons parameter of 0.024(16) and a Hooft parameter of 0.012(15). These values agree with the Parson's value calculated by the program SHELXL, 0.019(15) from 2398 selected quotients.

The structures reported in this manuscript have been deposited. CCDC 1958921 (**3e**), 2060191 (**3f**), 2060192 (**3g**), 2060190 (**3k**) and 2020652 (**11c**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

N(1)-H(1)O(1A)#1 0.91(3) 2.19(3) 2.886(4) 133(2)	D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)
	N(1)-H(1)O(1A)#1	0.91(3)	2.19(3)	2.886(4)	133(2)
N(1)-H(1)O(1B)#1 0.91(3) 2.06(3) 2.849(4) 145(3)	N(1)-H(1)O(1B)#1	0.91(3)	2.06(3)	2.849(4)	145(3)

 Table S1:
 Hydrogen bonds for compound 11c [Å and °].

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y+1/2,-z+1/2

Table S2: Crystal data and structure refinement details.

Identification code	3e	3f	3g	3k	11c
CCDC deposit number	1958921	2060191	2060192	2060190	2020652
Empirical formula	$C_{18}H_{19}BO_2S$	$C_{13}H_7NS$	$C_{14}H_7F_3O_1S_1\\$	$C_{15}H_{12}OS$	$C_{19}H_{23}NOS_2$
Formula weight	310.20	209.26	280.26	240.31	345.50
Temp (K)	100	125	125	125	100
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_{1}/c$	$P2_{1}/c$	<i>P</i> -1	$P2_{1}/c$	$P2_{1}2_{1}2_{1}$
Unit cell dimensions (Å and °)	a = 11.4270(10)	a = 7.6092(14)	a = 8.2143(4)	<i>a</i> = 6.0539(8)	<i>a</i> = 8.6260(5)
	<i>b</i> = 10.2820(9)	<i>b</i> = 3.8618(7)	<i>b</i> = 8.2225(5)	<i>b</i> = 21.767(3)	<i>b</i> = 9.2018(5)
	c = 13.6992(12)	c = 32.437(7)	c = 35.165(2)	c = 8.6784(12)	<i>c</i> = 22.6467(11)
	$\alpha = 90$	$\alpha = 90$	$\alpha = 89.531(2)$	$\alpha = 90$	$\alpha = 90$
	$\beta = 99.468(3)$	$\beta = 96.374(8)$	$\beta = 89.289(2)$	$\beta = 97.314(5)$	$\beta = 90$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 78.488(2)$	$\gamma = 90$	$\gamma = 90$
Volume (Å ³)	1587.6(2)	947.3(3)	2327.1(2)	1134.3(4)	1797.58(17)
Ζ	4	4	8	4	4
Density (calculated, Mg/m ³)	1.298	1.467	1.600	1.407	1.277
Absorption coefficient (mm ⁻¹)	0.207	0.298	0.304	0.263	0.300
F(000)	656	432	1136	504	736
Crystal size (mm ³)	0.302x0.190x0.128	0.436x0.073x0.040	0.220x0.145x0.063	0.278x0.245x0.050	0.265x0.089x0.068
Theta range of data (°)	3.615 to 46.484	2.527 to 34.336	2.317 to 36.318	2.544 to 36.318	2.389 to 33.141

Index ranges (h, k, l)	-23/23, -20/20, -27/27	-12/12, -6/6, -51/51	-13/13, -13/13, -58/58	-10/10, -36/36, -14/14	-13/13, -14/14, -34/34
Reflections collected	135411	76115	227991	85596	75947
Independent reflections	14090	3958	22572	5501	6840
R(int)	0.0577	0.0563	0.0508	0.0627	0.0537
Completeness to 25.242° (%)	98.8	99.9	100.0	99.8	99.9
Max. and min. transmission	0.7493 and 0.6987	0.7471 and 0.6497	0.7479 and 0.6953	0.7479 and 0.6551	0.7478 and 0.6501
Data / restrains / parameters	14090 / 0 / 203	3958 / 0 / 136	22572 / 0 / 686	5501 / 0 / 156	6840 / 663 / 347
Goodness-of-fit on F^2	1.067	1.126	1.025	1.068	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0414	R1 = 0.0448	R1 = 0.0498	R1 = 0.0479	R1 = 0.0392
	wR2 = 0.1119	wR2 = 0.1131	wR2 = 0.1223	wR2 = 0.1068	wR2 = 0.0849
R indices (all data)	R1 = 0.0600	R1 = 0.0491	R1 = 0.0723	R1 = 0.0648	R1 = 0.0475
	wR2 = 0.1297	wR2 = 0.1159	wR2 = 0.1373	wR2 = 0.1146	wR2 = 0.0894
Absolute structure parameter	n.a.	n.a.	n.a.	n.a.	0.019(15)
Largest diff. peak and hole (e.Å ⁻³)	0.908 and -0.617	0.701 and -0.390	1.163 and -0.760	0.435 and -0.491	0.422 and -0.471



Figure S1. Structure of compound **3e**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have not been labelled.



Figure S2. Packing diagram for compound 3e viewed down the X-axis.



Figure S3. Selected intra- and intermolecular interactions of the types $C-H \cdot \cdot \cdot O$ and $C-H \cdot \cdot \cdot S$ (to the sum of the interacting van der Waals radii + 0.2 Å) in the structure of compound **3e**.



Figure S4. Selected intermolecular stacking and C-H···C_{ring} interactions (to the sum of the interacting van der Waals radii + 0.2 Å) in the structure of compound **3e**.



Figure S5. Structure of compound **3f**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have not been labelled.



Figure S6. Packing diagram for compound 3f viewed down the Y-axis.



Figure S7. Selected intra- and intermolecular interactions (to the sum of the interacting van der Waals radii + 0.2 Å) in the structure of compound **3f**. Note that these interactions occur predominantly in the molecular plane.



Figure S8. Selected intermolecular stacking, $C-H \cdot \cdot \cdot S$ and $C-H \cdot \cdot \cdot C_{ring}$ interactions (to the sum of the interacting van der Waals radii + 0.2 Å) in the structure of compound **3f**. Note that these interactions occur predominantly perpendicular to the molecular plane.



Figure S9. Structure of compound **3g**. There are four unique molecules in the asymmetric unit of the twinned triclinic unit cell. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have not been labelled.



Figure S10. Packing diagram for compound 3g viewed down the X-axis.



Figure S11. Structure of compound **3k**. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have not been labelled.



Figure S12. Packing diagram for compound 3k viewed down the X-axis.



Figure S13. Selected intra- and intermolecular interactions (to the sum of the interacting van der Waals radii + 0.2 Å) in the structure of compound **3k**. Note that these interactions occur predominantly in the molecular plane.



Figure S14. Selected intermolecular C=O···C_{ring} and C-H···C_{ring} interactions (to the sum of the interacting van der Waals radii + 0.2 Å) in the structure of compound **3k**. Note that these interactions occur predominantly perpendicular to the molecular plane.



Figure S15. Structure of compound **11c** including both parts of the disordered model used in the refinement. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have not been labelled.



Figure S16. Structure of compound **11c** including both parts of the disordered model used in the refinement. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have not been labelled.



Figure S17. Packing diagram for compound 11c viewed down the Y-axis.



Figure S18. N-H $\cdot \cdot \cdot$ O hydrogen bonds run in chains through the structure of compound 11c (see Table S1).

Experimental Procedures and Tabulated Data



2-fluorophenyl-2-iodophenyl thioether (2a). (1-bromo-2-fluorobenzene procedure): Magnesium turnings (0.683 g, 28.1 mmmol, 1 equiv.) were placed in a 100 mL three neck flask equipped with a condenser under a nitrogen atmosphere. THF (28 mL) was added. Thiophenol **1a** (3.0 mL, 28.1 mmol, 1 equiv.) was added. Isopropylmagnesium chloride (1.67 M in THF,

16.8 mL, 28.1 mmol, 1 equiv.) was carefully added, which resulted in heating of the reaction to reflux. After bubbling subsided, the reaction was placed in an oil bath at 80 °C. When reflux resumed, halide **6a** (3.07 mL, 28.1 mmol, 1 equiv.) was cautiously added in 5 portions with 10 minutes between each portion. The reaction was heated for a further hour, at which time negligible magnesium remained and the solution was clear and light brown. The reaction was removed from heat, allowed to cool to ambient temperature, and solid iodine was cautiously added with stirring. The reaction self-heated to a gentle reflux, which abated as the reaction was stirred for a further hour. The resulting cloudy brown mixture was poured into 50 mL of saturated aqueous Na₂S₂O₃ and stirred for 10 minutes. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated to give a yellow oil, which slowly solidified. This was dissolved in 100 mL hexanes with heating and placed in a –15 °C freezer. Colourless crystals formed, which were collected by filtration to afford 3.34 g of **2a**. The mother liquor was purified by column chromatography (1% ethyl acetate in hexanes) to afford a further 2.70 g of **2a** (6.04 g total, 18.2 mmol, 65% yield from **1a**). Spectral data agreed with literature values.⁶

(1-bromo-2-fluorobenzene procedure on 18.4 gram scale): The above procedure was repeated with 10 mL (93.6 mmol) of 1a, with appropriate scaling of the other reagents. Rather than adding iodine to the solution of generated organomagnesium at the end of the reaction, the cooled solution was cannulated into a suspension of 23.8 grams of iodine in 100 mL of THF, in a flask equipped with a reflux condenser. This caused the reaction to heat to reflux. At the end of the addition, the colour of the iodine faded, and some solids were noted. The reaction was stirred for an hour, and then worked up according to the above procedure, to give a brown solid. Crystallization from hexanes gave 18.4 grams of product as an off-white solid (55.7 mmol, 59.5% yield). Spectral data agreed with the prior procedure.

1,2-dibromobenzene procedure: The procedure with 3.0 mL of **1a** (28.1 mmol) was carried out on the same manner as the top procedure, except 1,2-dibromobenzene **6b** (3.38 mL, 28.1 mmol) was used instead of **6a**. The crude product was an orange oil, which did not solidify. Chromatography (1% ethyl acetate in hexanes) afforded 3.39 g of product as a colourless solid (10.3 mmol, 37% yield).

Spectral data from 6.04 gram procedure.

The tabulated data, and spectra shown on page S30-S31 are from the 6.04 gram batch. Representative spectra from all the procedures are shown on the next 2 pages for comparison.

¹**H NMR (500 MHz, CDCl₃):** δ 7.85 (dd, *J*= 7.9, 1.4 Hz, 1H), 7.40–7.36 (m, 2H), 7.23–7.14 (m, 3H), 6.96 (ap. d, *J*= 7.9 Hz, 1H), 6.89 (td, *J*= 7.6, 1.6 Hz, 1H).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 162.0 (d, *J*= 248.4 Hz), 140.5, 139.9, 135.2, 130.9 (d, *J*= 8.1 Hz), 129.3, 128.9, 127.9, 125.2 (ap. d, *J*= 3.44 Hz), 121.2 (d, *J*= 18.3 Hz), 116.5 (d, *J*= 22.3 Hz), 99.3.

¹⁹F NMR (470 MHz, CDCl₃): δ -107.0–-107.1 (m).

¹H NMR spectrum of 2a prepared from 1-bromo-2-fluorobenzene (6.04 gram scale)

7,857 7,867 7,864 7,808 7,403 7,737 7,737 7,737 7,737 7,737 7,737 7,737 7,736 7,736 7,736 7,736 7,728 7,728 7,729 7,729 7,729 7,721 6,657 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,716 7,717 7,717



¹H NMR spectrum of 2a prepared from 1-bromo-2-fluorobenzene (18.4 gram scale)



¹H NMR spectrum of 2a prepared from 1,2-dibromobenzene



S19



1-dibenzothiophenecarboxaldehyde (3c) prepared from 2a

Compound **2a** (6.86 g, 20.8 mmol) was dissolved 30 mL THF in a 100 mL Schlenk flask. The mixture was cooled to -78 °C in dry ice/acetone. *N*-Butyllithium (2.5 M in hexanes, 25 mL, 62.5 mmol, 3 equiv.) was added dropwise over 5 minutes. The reaction was stirred for 30 minutes at -78 °C, then moved from the dry ice/acetone bath to an ice bath and stirred for 30

minutes. The reaction was then returned to the dry ice/acetone bath, allowed to cool for 5 minutes, then DMF (4.83 mL, 62.3 mmol, 3 equiv.) was added. The reaction was warmed to room temperature, stirred for 2 hours, then quenched pouring into 100 mL 1 N HCl. The mixture was extracted with 3x 150 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated The residue was purified by column chromatography (7.5 % ethyl acetate in hexanes) to afford **3c** (3.43 g, 16.2 mmol, 78% yield) as a yellow solid. Spectral data were in accordance with literature values.⁷ The tabulated data, and spectra shown on page S30 are from this procedure.

¹**H NMR (500 MHz, CDCl₃)**: δ 10.72 (s, 1H), 8.98 (ap. d, *J*= 7.6 Hz, 1H), 8.11 (ap. d, *J*= 7.9 Hz, 1H), 7.99 (ap. d, *J*= 7.5 Hz, 1H), 7.92 (ap. d, *J*= 7.2 Hz, 1H), 7.61 (ap. t, *J*= 7.7 Hz, 1H), 7.56–7.50 (m, 2H).

¹³C NMR{¹H} (125 MHz, CDCl₃): δ 192.0, 141.6, 140.4, 134.7, 134.6, 134.1, 130.6, 128.6, 127.7, 127.4, 125.9, 125.0, 122.9.

HRMS (ESI): $m/z [M + Na]^+$ calculated for C₁₃H₈NaOS: 235.0188 found: 235.0184.

MP: 96–98 °C

¹H NMR spectrum of 1-dibenzothiophenecarboxaldehyde (3c) prepared from 2a



Single-pot Cascade Reactions:

1-lithiodibenzothiophene (3a-Li): Compound **1a** (0.84 mL, 7.86 mmol, 1 equiv.) was dissolved in 10 mL THF in a 100 mL Schlenk flask. The mixture was cooled to -78 °C in dry ice/acetone. *N*-Butyllithium (2.6 M in hexanes, 3.12 mL, 8.1 mmol, 1 equiv.) was added dropwise over 1 minute. The reaction was stirred for 30 minutes, then dibromobenzene **6b** (0.96 mL, 7.95 mmol, 1) was added. *N*-butyllithium (2.6 M in hexanes, 9.36 mL, 24 mmol, 3 equiv.) was added dropwise over 5 minutes, and the reaction was stirred for 30 minutes. The reaction was moved from the dry ice/acetone bath to an ice bath and stirred for 45 minutes. The reaction was then returned to the dry ice/acetone bath, allowed to cool for 5 minutes, the appropriate quenching agents was added. A tan precipitate usually formed during the warming and second cooling cycle.



1-dibenzothiophenecarboxaldehyde (3c): To the above prepared solution of 1-lithiodibenzothiophene was added DMF (1.81 mL, 23.2 mmol, 3 equiv.). A thick precipitate immediately formed. The reaction was removed from the dry ice/acetone bath, stirred for 2 hours, and then quenched by the addition of 25 mL 1 N HCl. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated The residue was purified by column

chromatography (7.5 % ethyl acetate in hexanes) to afford 3c (667 mg, 3.14 mmol, 40% yield) as a yellow solid. Spectral data were in accordance with literature values.⁷

Spectral data were in agreement with **3c** prepared from **2a**, according to the procedure on page **S18**.

¹H NMR spectrum of 1-dibenzothiophenecarboxaldehyde (3c) prepared from 1a in one pot procedure





1-iododibenzothiophene (3d): To the above prepared solution of 1lithiodibenzothiophene was added solid iodine (3.96 g, 15.6 mmol, 2 equiv.) was added through the top of the flask with a strong countercurrent of nitrogen. The reaction was then moved from the dry ice/acetone bath to the ice bath, stirred for 30 minutes, and then quenched by the addition of 25 mL saturated Na₂S₂O₃. The mixture was extracted with 2x 100 mL portions of

diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The waxy residue was purified by chromatography with pure hexanes, to give an inseparable mixture of 1-iododibenzothiophene and dibenzothiophene. This mixture was placed in a sublimation chamber with a dry-ice finger and evacuated to approximately 5 torr. The residue was heated with a heat gun until it became liquid, and a white sublimate was observed on the cold finger. The chamber was disassembled, the finger cleaned, and the process was repeated twice more, until a negligible amount of sublimation was observed. The remaining material in the bottom of the sublimation chamber (803 mg, 2.59 mmol, 33% yield), was found to be approximately 95% 1-iododibenzothiophene with the balance being dibenzothiophene. No 1-iododibenzothiophene sublimed under these conditions.

¹**H NMR (500 MHz, CDCl₃):** δ 9.41–9.39 (m, 1H), 8.03 (ap. d, *J*= 7.6 Hz, 1H), 7.88–7.86 (m, 2H), 7.57–7.52 (m, 2H), 7.12–7.09 (m, 1H).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 141.7, 140.5, 137.7, 135.7, 134.9, 127.4, 127.2, 124.9, 123.4, 122.9, 122.8, 88.9.

HRMS (APCI): m/z [M radical cation]⁺ calculated for C₁₂H₇IS: 309.9308 found: 309.9298. **MP:** 65–67 °C.



1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan2-yl)-dibenzothiophene (3e): To the above prepared solution of 1-lithiodibenzothiophene was added *i*PrOB(pin) (3.2 mL, 15.7 mmol, 2 equiv.) was added. The cooling bath was removed, and the reaction was stirred for 1 hour, and then quenched by the addition of 15 mL 1 N HCl. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with

brine, dried over Na_2SO_4 , and concentrated. The grey waxy residue was purified by column chromatography with 2.5% ethylacetate/hexanes, then further recrystallized by cooling a solution in hexanes with a few drops of ethyl acetate to give boronate **3e** (804 mg, 2.59 mmol, 33% yield) as white colourless crystals, which were suitable for X-ray analysis.

¹**H NMR (500 MHz, CDCl₃):** δ 9.03–9.02 (m, 1H), 7.96–7.94 (m, 1H), 7.89–7.84 (m, 2H), 7.45–7.43 (m, 3H), 1.50 (s, 12H).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 139.8, 139.7, 138.9, 136.8, 132.7, 126.5, 125.6, 125.5, 125.2, 124.0, 122.7, 122.6, 84.5, 25.1.

¹¹**B NMR (160 MHz, CDCl₃):** δ 32.1 (br. s).

HRMS (ESI): $m/z [M + Na]^+$ calculated for C₁₈H₁₉BNaO₂S: 333.1091 found: 333.1100.



1-Dibenzothiophenecarbonitrile (3f) To the above prepared solution of 1-lithiodibenzothiophene was added a solution of dimethylmalonitrile (1.5 g, 15.7 mmol, 2 equiv.) in 5 mL of THF. The reaction turned blood red and a precipitate formed. The cooling bath was removed, and the reaction was stirred for 1 hour, during which time the precipitate redissolved. The reaction was quenched by addition of 15 mL saturated NH₄Cl_(aq). The mixture was

extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The resulting orange solid was purified by column chromatography with 5–10% ethyl acetate/hexanes, to give nitrile **3f** (601 mg, 2.87 mmol, 36.5% yield) as a white solid. A crystal suitable for X-ray analysis was grown by evaporation of a CDCl₃ solution.

¹**H NMR (500 MHz, CDCl₃):** δ 8.94–8.92 (m, 1H), 8.05 (ap. d, *J*= 8.2 Hz, 1H), 7.89–7.88 (m, 1H), 7.77 (ap. d, *J*= 7.4 Hz, 1H), 7.58–7.53 (m, 2H), 7.48 (ap. t, *J*= 7.7 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 140.9, 140.3, 134.9, 133.3, 130.6, 128.3, 127.5, 125.9, 125.2, 124.1, 122.9, 118.5, 106.2.

HRMS(ESI): m/z [M+Na]⁺ calculated for C₁₃H₇NNaS: 232.0191 found: 232.0190.



1-(1-dibenzothienyl)-2,2,2-trifluoroethanone (3g) To the above prepared solution of 1-lithiodibenzothiophene was added *N*-methoxy-*N*-methytrifluoroacetamide (1.9 mL, 15.7 mmol, 2 equiv.) The cooling bath was removed, and the reaction was stirred for 1 hour, during which time it turned lemon yellow. The reaction was quenched by addition of 15 mL 1 M $HCl_{(aq)}$. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over

 Na_2SO_4 , and concentrated. The resulting dark yellow oil was purified by column chromatography with pure hexanes, to give ketone **3g** (1.01 g, 3.60 mmol, 46% yield) as a white solid. A crystal suitable for X-ray analysis was grown by evaporation of a CDCl₃ solution.

¹**H NMR (500 MHz, CDCl₃):** δ 8.11 (ap. d, *J*= 8.3 Hz, 1H), 8.06 (ap. d, *J*= 8.0 Hz, 1H), 7.87 (ap. d, *J*= 8.0 Hz, 1H), 7.77 (ap. d, *J*= 7.6 Hz, 1H), 7.50 (ap. t, *J*= 7.9 Hz, 2H), 7.43 (ap. t, *J*= 7.2 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 185.2 (²*J*_{C,F}= 71.2 Hz), 141.9, 140.2, 133.3, 133.1, 128.5, 128.1, 127.9, 125.5, 125.2, 124.9, 124.8, 123.0, 116.6 (¹*J*_{C,F}= 585.1 Hz).

¹⁹F NMR (470 MHz, CDCl₃): δ -72.7.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₁₄H₇F₃NaOS: 303.0062 found: 303.0064.



\alpha-phenyl-1-dibenzothiophenemethanol (3h) To the above prepared solution of 1-lithiodibenzothiophene was added benzaldehyde (1.6 mL, 15.7 mmol, 2 equiv.) The cooling bath was removed, and the reaction was stirred for 1 hour, during which time the brown colour faded. The reaction was quenched by addition of 15 mL saturated NH₄Cl_(aq). The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and

concentrated. The resulting pale yellow oil was purified by column chromatography with 5% ethyl acetate/hexanes to give 3h (1.21 g, 4.17 mmol, 53% yield) as a white solid.

¹**H NMR (500 MHz, CDCl₃):** δ 8.30 (ap. d, *J*= 8.2 Hz, 1H), 7.88 (ap. d, *J*= 7.9 Hz, 1H), 7.86–7.83 (m, 1H), 7.45–7.41 (m, 5H), 7.39–7.35 (m, 3H), 7.33–7.30 (m, 1H), 6.81 (br. s, 1H), 2.60 (d, *J*= 3.1 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃): δ 142.0, 140.4, 139.9, 139.8, 134.9, 133.1, 128.7, 128.0, 127.5, 126.3, 126.1, 124.5, 124.2, 122.8, 122.6, 73.4.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₁₉H₁₄NaOS: 313.0658 found: 313.0663.



1-(1-dibenzothienyl)-1-propanol (3i) To the above prepared solution of 1-lithiodibenzothiophene was added propionaldehyde (1.7 mL, 23.6 mmol, 3 equiv.) The cooling bath was removed, and the reaction was stirred for 1 hour, during which time the brown colour faded. The reaction was quenched by addition of 15 mL saturated $NH_4Cl_{(aq)}$. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated. The resulting colourless oil was purified by column

chromatography with 5% ethyl acetate/hexanes to give **3i** (876 mg, 3.61 mmol, 46% yield) as a white solid.

¹**H NMR (500 MHz, CDCl₃):** δ 8.27–8.25 (m, 1H), 7.90–7.88 (m, 1H), 7.79 (ap. dd, *J*= 7.9, 0.7 Hz, 1H), 7.70 (ap. d, *J*= 7.5 Hz, 1H), 7.50–7.45 (m, 3H), 5.70–5.67 (m, 1H), 2.16–2.09 (m, 1H), 2.07 (ap. d, *J*= 3.9 Hz, 1H), 1.95–1.86 (m, 1H), 1.17 (t, *J*= 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 142.3, 140.3, 139.9, 135.2, 132.0, 126.4, 126.1, 125.7, 124.6, 123.1, 122.0, 121.5, 72.3, 30.2, 10.5.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₁₅H₁₄NaOS: 265.0658 found: 265.0657.



N-[4-(1-dibenzothienyl)-4-oxobutyl]-, 1,1-dimethylethyl carbamate (3j) To the above prepared solution of 1-lithiodibenzothiophene was added *N*-Boc-pyrrolidinone (2.68 mL, 15.7 mmol, 2 equiv.) The cooling bath was removed, and the reaction was stirred for 1 hour, during which time the reaction became brown and a precipitate formed. The reaction was quenched by addition of 15 mL saturated $NH_4Cl_{(aq)}$. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated. The resulting pasty solid was purified by column

chromatography with 10% - 30% ethyl acetate/hexanes to give **3j** (1.04 g, 2.81 mmol, 36% yield) as a white solid. Minor signals were observed in the NMR which may be due to Boc rotamers, or equilibria between open and closed forms.

¹**H NMR (500 MHz, CDCl₃):** δ 7.97 (ap. d, *J*= 8.1 Hz, 1H), 7.80 (ap. d, *J*= 7.6 Hz, 1H), 7.83 (ap. d, *J*= 7.9 Hz, 1H), 7.45–7.36 (m, 4H), 4.77 (br. s, 1H), 3.26 (ap. d, *J*= 5.8 Hz, 2H), 3.05 (t, *J*= 7.2 Hz, 2H), 2.03 (p, *J*= 7.0 Hz, 2H). 1.42 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 206.4, 156.1, 140.9, 139.9, 137.8, 133.8, 130.9, 127.1, 125.7, 124.9, 124.6, 124.5, 123.0, 122.9, 40.8, 40.1, 28.5, 24.6.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₂₁H₂₃NNaO₃S: 392.1291 found: 392.1291.



7,8-dimethyl-1-dibenzothiophenecarboxaldehyde (3k): Compound **1a** (0.84 mL, 7.86 mmol, 1 equiv.) was dissolved in 10 mL THF in a 100 mL Schlenk flask. The mixture was cooled to -78 °C in dry ice/acetone. *N*-butyllithium (2.6 M in hexanes, 3.12 mL, 8.1 mmol, 1 equiv.) was added dropwise over 1 minute. The reaction was stirred for 30 minutes, then 3,4-dimethyldibromobenzene **6d** (0.96 mL, 7.95 mmol, 1 equiv.) was added. *N*-butyllithium (2.6 M in hexanes, 9.36 mL, 24 mmol, 3 equiv.) was added

dropwise over 5 minutes, and the reaction was stirred for 30 minutes. The reaction was moved from the dry ice/acetone bath to an ice bath and stirred for 45 minutes. This reaction was much darker than the one with dibromobenzene **6b**. The reaction was then returned to the dry ice/acetone bath, allowed to cool for 5 minutes, and DMF (1.82 mL, 23.6 mmol, 3 equiv.) was added. Adding DMF caused the colour to lighten significantly. The reaction was removed from the dry ice/acetone bath, stirred for 2 hours, and then quenched by the addition of 25 mL 1 N HCl. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography (5 % ethyl acetate in hexanes) to afford **3k** (793 mg, 3.30 mmol, 42% yield) as a yellow solid. A crystal suitable for X-ray analysis was grown by evaporation of a CDCl₃ solution.

¹**H NMR (500 MHz, CDCl₃):** δ 10.66 (s, 1H), 8,49 (s, 1H), 7.95 (ap. dd, *J*= 7.9, 1.1 Hz, 1H), 7,85 (ap. dd, *J*= 7.5, 0.9 Hz, 1H), 7.54 (s, 1H), 7.45 (ap. t, *J*= 7.7 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 191.7, 141.2, 137.9, 137.3, 134.7, 133.8, 133.4, 132.7, 129.2, 128.3, 127.4, 125.0, 122.9, 20.3, 20.2.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₁₅H₁₂NaOS: 262.0501 found: 262.0503.



3,4-dihydro-5-(1-dibenzothienyl)-2H-Pyrrole

Compound **3j** (1.04 g, 2.81 mmol) was dissolved in minimal dichloromethane (approximately 1 mL), and 2 mL of trifluoroacetic acid were added. The dark solution was stirred for 18 hours, then diluted with diethyl ether (30 mL), and washed with 1 M NaOH_(aq). The washings were further extracted with another 30 mL diethyl ether, and the combined organic layers were dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography (10% ethyl acetate in hexanes) to

afford imine 7b (570 mg, 2.27 mmol, 81% yield) as a tan solid.

¹H NMR (500 MHz, CDCl₃): δ 7.95 (ap. d, *J*= 7.9 Hz, 1H), 7.88–7.85 (m, 2H), 7.47–7.42 (m, 2H), 7.39–7.33 (m, 2H), 4.29–4.25 (m, 2H), 3.02–2.98 (m, 2H), 2.26–2.20 (m, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 176.0, 140.4, 139.9, 134.9, 134.3, 132.1, 126.6, 126.1, 124.5, 124.3, 124.2, 123.3, 122.9, 62.4, 39.9, 23.3.

HRMS(APCI): m/z (M+H)⁺ calculated for C₁₆H₁₄NS⁺ 252.0841 found: 252.0845.



2-(1-dibenzothienyl)-pyrrolidine (9b)

Imine **7b** (327 mg, 1.30 mmol) was dissolved in 5 mL of methanol. Sodium borohydride (200 mg, 5.20 mmol, 4 equiv.) was added. The reaction, which bubbled, was stirred for 24 hours. NMR spectroscopy of an aliquot withdrawn after this time showed incomplete conversion. A further 100 mg of sodium borohydride were added. After an additional 24 hours, the starting material was mostly consumed, and other products were growing

in. The reaction was diluted with dichloromethane, and washed with brine. The organic layer was dried with Na₂SO₄, and concentrated. The residue was purified by column chromatography (90% ethyl acetate, 9% methanol, 1% isopropylamine) to afford product **9b** (165 mg, 0.651 mmol, 50% yield) as a yellow oil. Less polar compounds that eluted first were identified as the amine-borane adduct by ¹¹B NMR spectroscopy and mass-spectroscopy, but were not further purified.

¹**H NMR (500 MHz, CDCl₃):** δ 8.43 (ap. d, *J*= 7.4 Hz, 1H), 7.89 (ap. d, *J*= 7.3 Hz, 1H), 7.76 (ap. d, *J*= 7.7 Hz, 2H), 7.50–7.43 (m, 3H), 5.22 (ap. t, *J*= 6.8 Hz, 1H), 3.35–3.31 (m, 1H), 3.22–3.17 (m, 1H), 2.48–2.43 (m, 1H), 2.13 (br. s, 1H), 1.97–1.85 (m, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 142.9, 140.1, 139.8, 135.7, 132.6, 126.3, 125.8, 125.7, 124.4, 122.9, 121.6, 121.2, 59.1, 47.0, 33.0, 25.1.



10: Compound 3c (3.5 g, 16.6 mmol, 1.0 equiv.) and (S)tertbutylsulfinimide (2.0 g, 16.6 mmol, 1.0 equiv.) were placed in a 100 mL Schlenk flask and dissolved in THF (20 mL) followed by the addition of Ti(OEt)₄ (3.8 mL, 20.1 mmol, 1.1 equiv.) and stirred overnight. The resulting orange solution was quenched with water, filtered then extracted with EtOAc (2×100 mL). The combined organic layers were dried over Na₂SO₄ and concentrated. The crude orange oil was purified with column chromatography (60% EtOAc/hex) to yield compound 10 as a yellow solid (2.1 g, 6.65 mmol, 40% yield). Attempts to acquire an optical rotation for

this compound were unsuccessful, as has been common in our experience for yellow coloured compounds.

¹**H NMR (500 MHz, CDCl₃):** δ 9.75 (s, 1H), 8.41–8.39 (m, 1H), 8.05 (ap. d, *J*= 7.6Hz, 1H), 8.00 (ap. d, *J*= 7.8 Hz, 1H), 7.92–7.90 (m, 1H), 7.55–7.50 (m, 3H), 1.35 (s, 9H).

¹³C NMR (125 MHz, CDCl₃): δ 161.6, 140.7, 140.2, 134.8, 134.5, 131.7, 127.2, 126.3, 126.2, 126.1, 125.4, 123.2, 58.2, 22.8.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₁₇H₁₇NNaOS₂: 338.0644 found: 338.0652.



11c: Compound 7 (0.5 g, 1.58 mmol, 1.0 equiv.) was placed in 250 mL flask and dissolved in 15 mL of toluene and cooled to -78° C followed by the addition of ethyl magnesium bromide in diethyl ether (3.0 M, 1.6 mL, 4.75 mmol, 3.0 equiv.) that stirred overnight. The resulting solution was poured into an Erlenmeyer flask containing NH₄Cl_(aq) and extracted with ether (2× 50mL). The organic layers were combined and dried over Na₂SO₄ then concentrated. The crude yellow solid (81:19 *d.r.*) was purified with column chromatography (40% EtOAc/hex) resulting in compound **11c** as a white powder (300 mg, 0.87 mmol, 55% yield). The

minor diastereomer was not obtained as a pure substance. Attempts to acquire an optical rotation for this compound were unsuccessful, potentially due to low intrinsic rotation at the sodium D line. A crystal suitable for X-ray analysis was grown by evaporation of a $CDCl_3$ solution over 4 months during the COVID pandemic, which was used to establish the relative configuration, and confirmed the absolute configuration.

¹H NMR (500 MHz, CDCl₃): δ 8.39 (ap. d, *J*= 6.7 Hz, 1H), 7.88 (ap. d, *J*= 7.3 Hz, 1H), 7.81 (ap. d, *J*= 7.9 Hz, 1H), 7.60 (ap. d, *J*= 6.8 Hz, 1H), 7.49–7.45 (m, 3H), 5.60 (br. s, 1H), 3.76 (ap. d, *J*= 3.4 Hz, 1H), 2.25–2.22 (m, 1H), 2.14–2.11 (m, 1H), 1.23 (s, 9H), 0.96 (ap. t, *J*= 6.6 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 140.5, 139.9, 139.5, 135.1, 132.7, 126.3, 126.2, 125.8, 124.8, 123.1, 122.3, 56.1, 55.2, 28.3, 22.8, 9.6.

HRMS(ESI): m/z (M+Na)⁺ calculated for C₁₈H₂₁ONNaS₂: 354.0957 found: 354.0951.



(S)-(-)-1-amino-1-(1-dibenzothienyl)propane 12: In 20 mL dichloromethane was dissolved 1.30 g of major diastereomer 11c (3.76 mmol, 1 equiv.). To the solution was added 7.5 mL of 2 M HCl in diethyl ether (15 mmol 4 equiv.). A white solid formed within 1 minute. The suspension was stirred for 2 hours, then 40 mL diethyl ether was added. The reaction was filtered, and the white precipitate was collected, washed with diethyl ether, and then suspended in 50 mL of dichloromethane in a separatory funnel. The dichloromethane suspension was treated with 2M

aqueous NaOH and shaken until both layers were clear. The organic layer was dried over Na_2SO_4 and concentrated in vacuo to give 875 mg of amine **12** as an off-yellow solid (3.62 mmol, 97% yield).

The configuration of this compound was known because the absolute and relative configuration of precursor **11c** was known. Furthermore, the negative sign of the optical rotation obtained for this compound is consistent with other (S) configured aryl-alkylamines which also have negative optical rotations.

¹**H NMR (500 MHz, CDCl₃):** δ 8.34 (ap. d, *J*= 7.6 Hz, 1H), 7.90–7.89 (m, 1H), 7.77 (ap. d, *J*= 7.9 Hz, 1H), 7.65 (ap. d, *J*= 7.4 Hz, 1H), 7.50 – 7.44 (m, 3H), 5.02 – 5.00 (m, 1H), 2.12 – 2.07 (m, 1H), 1.85 – 1.75 (m, 1H) 1.69 (br. s, 2H), 1.13 (t, *J*= 7.4 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 144.2, 140.3, 140.0, 135.5, 132.5, 126.5, 126.0, 125.6, 124.6, 123.1, 121.4, 121.3, 53.1, 30.7.

HRMS(ESI): m/z (M+H)⁺ calculated for C₁₅H₁₆NS: 242.0998 found: 242.0990.

Optical Rotation: $[\alpha]^{21}_{D} = -34^{\circ}$ (c= 1.38, CH₂Cl₂)



N-(2-fluorophenyl)-*N*-(2-iodophenyl)-methylamine (13d): Magnesium turnings (0.683 g, 28.1 mmmol, 1 equiv.) were placed in a 100 mL three neck flask equipped with a condenser under a nitrogen atmosphere. THF (28 mL) was added. Aniline 1d (3.52 g, 28.1 mmol, 1 equiv.) was added. Isopropylmagnesium chloride (1.67 M in THF, 16.8 mL, 28.1 mmol, 1 equiv.) was slowly added, which resulted in heating of the reaction to reflux. After bubbling subsided, the reaction was placed in an oil bath at 80 °C. When reflux resumed, halide **6a** (3.07 mL, 28.1 mmol, 1 equiv.) was

cautiously added in 5 portions with 10 minutes between each portion. The reaction was heated for a further hour, at which time negligible magnesium remained and the mixture was clear and dark yellow. The reaction was removed from heat, allowed to cool to ambient temperature, and solid iodine (7.13 g, 28.1 mmol, 1 equiv.) was cautiously added with stirring. The reaction self-heated to a gentle reflux, which abated as the reaction was stirred for a further hour. The resulting black solution was poured into 50 mL of saturated aqueous Na₂S₂O₃ and stirred for 10 minutes. The mixture was extracted with 2x 100 mL portions of diethyl ether, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated to give a black oil. This was purified by column chromatography (2% EtOAc/hexanes) to afford **13d** as a clear colourless oil (3.05 g, 9.32 mmol, 33% yield). Spectral data agreed with literature values.⁶ Minor amounts of co-eluting

impurities were observed in the ¹H, ¹³C, and ¹⁹F NMR spectra, but could not be resolved on TLC or separated by column chromatography.

¹**H NMR (500 MHz, CDCl₃):** δ 7.90 (ap. dd, *J*= 7.9, 1.4 Hz, 1H), 7.34–7.31 (m, 1H), 7.13 (dd, *J*= 7.9, 1.5 Hz, 1H), 7.06–6.98 (m, 2H), 6.93–6.84 (m, 3H), 3.24 (s, 3H).

¹³C{¹H} NMR (125 MHz, CDCl₃): δ 155.0 (d, *J*= 247.2 Hz), 140.4, 138.0 (d, *J*= 8.5 Hz), 135.2, 130.9 (d, *J*= 8.1 Hz), 129.4, 126.7, 125.7, 124.4 (ap. d, *J*= 3.86 Hz), 122.0 (d, *J*= 7.2 Hz), 120.3 (d, *J*= 3.0 Hz), 116.5 (d, *J*= 20.3 Hz), 98.2, 41.4.

¹⁹F NMR (470 MHz, CDCl₃): δ -121.7.

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NMR Data:

7.857 7.854 7.854 7.839 7.839 7.233 7.232 7.232 7.216 7.229 7.214 7.229 7.214 7.214 7.214 7.214 7.214 7.214 7.214 7.214 7.216 7.214 7.216 7.2176 7.216 7.216 7.216 7.2176 7.2176 7.216 7.216 7.2176 7.216 7.216 7.2176 7.216 7.216 7.216 7.2176 7.216 7.2176 7.216 7.2176 7.2176 7.2176 7.2176 7.2176 7.216 7.216 7.2176 7.216 7.216 7.216 7.216 7.216 7.216 7.2176 7.2176 7.216 7.2176 7.2176 7.2176 7.216 7.2176 7.216 7.2176 7.216 7.2176 7.216 7.216 7.216 7.2176 7.216 7.216 7.216 7.216 7.216 7.2176 7.216 7.2176 7.216 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.2176 7.216 7.2176 7.216 7.2

























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8.437 6.437 6.435 6.435 6.435 6.435 6.435 6.435 7.770 7.788 7.788 7.7502 7.487 7.748 7.748 7.748 7.7502 7.447 7.748 7.748 7.7502 7.443 7.748 7.7502 7.748 7.7502 7.748 7.748 7.748 7.748 7.748 7.7502 7.748 7.748 7.748 7.748 7.748 7.748 7.7502 7.748 7.3322 7.3222 7.3222 7.3222 7.3222 7.3222 7.3222 7.3222 7.3222 7.3222 7.3222 7.3222 7.472 7.3222 7.472









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