Facile Preparation of 2-Iodophenyl Trifluoromethanesulfonates: Superior Aryne Precursors

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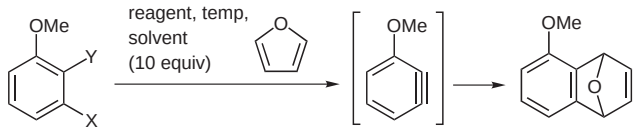
Abstract: A comparative study of 3-methoxyaryne precursors revealed 2-iodo-3-methoxyphenyl triflate as the most effective in nonpolar solvent. Use of Hoppe's *N*-isopropyl carbamate allows for the systematic preparation of a variety of 2-iodophenyl triflates via a directed *ortho*-lithiation–iodination–decarbamation sequence. These steps are possible without isolation of the intermediate iodophenyl carbamates.

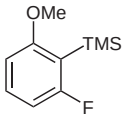
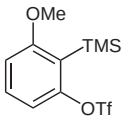
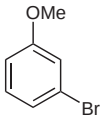
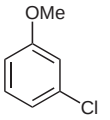
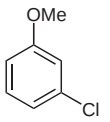
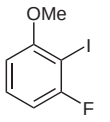
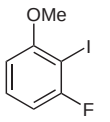
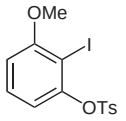
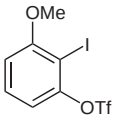
Key words: arynes, carbamate, halogenation, iodophenyl triflate, metalations

Recently, we required a series of methoxyarynes as intermediates toward polysubstituted aromatic products. A benzyne trapping study with various precursors to methoxyarynes (Scheme 1) revealed 2-iodo-3-methoxyphenyl triflate[1] as the most suitable under our constraint of a nonpolar solvent system (Table 1). Although benzyne generation via treatment of aryl silanes with fluoride is effective in polar acetonitrile at ambient temperature,[2] many nucleophiles are not compatible with the reflux conditions required to generate the aryne in tetrahydrofuran (entries 1 and 2). Meanwhile, the use of LiTMP-zincate proved ineffective in our hands (entry 3).[3] *Ortho*-lithiation–LiCl elimination of 3-chloroanisole resulted in unsatisfactory mixtures of bi- and polyaryl products along with the expected cycloadduct (entries 4 and 5).[4] Lithium–halogen exchange with 3-fluoro-2-iodoanisole afforded a 77% yield of the desired cycloadduct in toluene.[5,6] The reaction also produced ca. 15% of 3-fluoro-2-(3-methoxyphenyl) anisole, presumably due to incomplete lithium fluoride elimination and subsequent addition to methoxybenzyne (entry 7). The biaryl formation was even more pronounced when this reaction was conducted in tetrahydrofuran at temperatures ranging from –78 °C to 0 °C (e.g., entry 6).[6] Aryne generation via the iodophenyl tosylate (entry 8) improved upon the lithium fluoride elimination



Scheme 1 Comparative 3-methoxybenzyne trapping study

Table 1 Comparison of *ortho*-Methoxybenzyne Precursors

Entry	Benzyne precursor	Temp (°C)	Solvent	Reagent	Isolated yield (%)
1		Reflux	THF	20% CsF	<10
2		Reflux	THF	CsF	73[a]
3		–78	THF	LTMP, $ZnMe_2$	–[b]
4		–78	THF	*n*-BuLi	22[c]
5		0	THF	*n*-BuLi	Complex mixture
6		–78	THF	*n*-BuLi	55
7		–42	Toluene	*n*-BuLi	77
8		–78	THF	*n*-BuLi	72
9		–78	THF	*n*-BuLi	90

[a] Reaction required 12 h at reflux using 2.0 equiv CsF.
[b] Only 1-(3-methoxyphenyl)-2,2,6,6-tetramethylpiperidine was obtained.
[c] Produced a mixture of polyaryl products and the cycloadduct.

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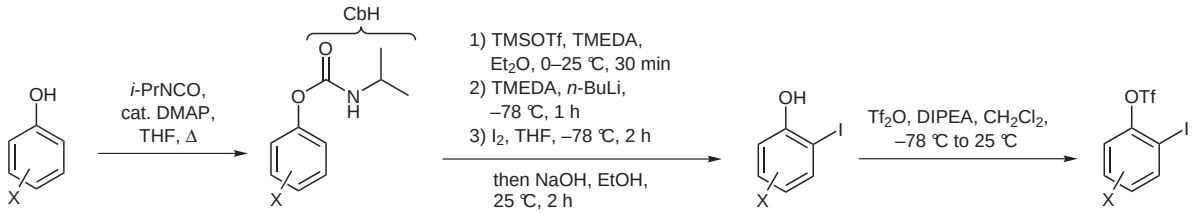
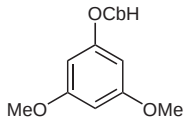
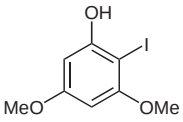
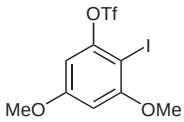
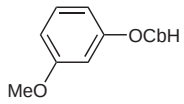
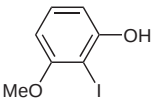
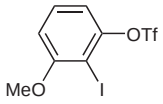
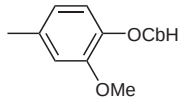
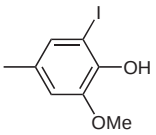
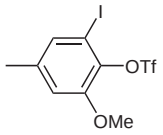
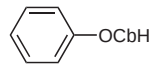
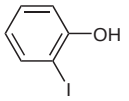
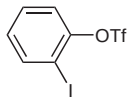
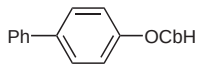
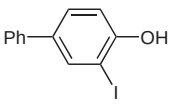
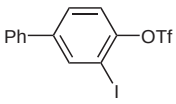
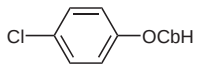
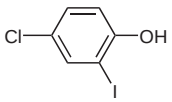
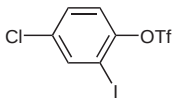
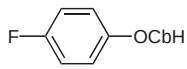
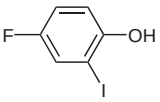
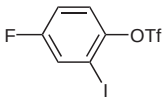
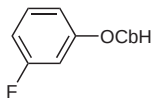
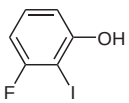
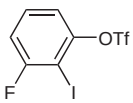
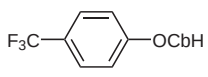
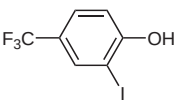
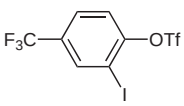
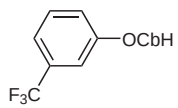
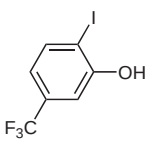
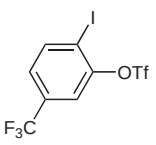


Scheme 2 Preparation of various 2-iodophenyl trifluoromethanesulfonates

in tetrahydrofuran.[7] However, this experiment spawned several minor byproducts along with the cycloadduct. Conducting the reaction at –42 °C offered comparable yields.[8] We ultimately found that introduction of *n*-BuLi to the 2-iodophenyl triflate at –78 °C garnered the desired aryne, which was trapped by furan with negligible side-product formation (entry 9) thereby proving superior to the other examined precursors.

Table 2 Products and Yields Connected with the 2-Iodophenyl Triflate Preparation Outlined in Scheme 2

Entry	Carbamate	Compd	Yield (%)[a]	2-Iodophenol	Compd	Yield (%)[a]	2-Iodophenyl triflate	Compd	Yield (%)[a]
1		**1**	97[10]		**11**	84[10]		**21**	94[31]
2		**2**	96[17]		**12**	74[13]		**22**	92[1b]
3		**3**	98[18]		**13**	77[25]		**23**	92[32]
4		**4**	94[11a]		**14**	75[26]		**24**	93[33]
5		**5**	96[19]		**15**	87[26]		**25**	98[34]
6		**6**	98[20]		**16**	85[27]		**26**	93[35]
7		**7**	98[21]		**17**	76[28]		**27**	92[36]
8		**8**	96[22]		**18**	77[14]		**28**	90[37]
9		**9**	98[23]		**19**	62[29]		**29**	91[38]
10		**10**	92[24]		**20**	58[30]		**30**	91[39]

[a] Isolated yield of purified product. Characterization data is provided under the indicated reference number.

Because of the relative efficiency with which the 2-iodophenyl triflate served as a benzyne precursor, we were surprised that there exists no general procedure for the systematic preparation of such compounds. While direct iodination of substituted phenols has been used en route to 2-iodophenyl triflates, the protocols do not allow for reliable regioselective introduction of the halogen when regioisomeric products are possible or when deactivated substrates are employed.[9]

Hoppe and Kauch reported the preparation of two 2-iodophenols using a directed *ortho*-metalation–iodination approach.[10] The method involves in situ generated N-silylated *N*-isopropyl carbamates to direct the aryl lithiation step. The advantage of the *O*-aryl *N*-isopropyl carbamate (CbH) versus alternative dialkyl carbamates as the directing group is the simple installation and removal of the monoalkylcarbamate under mildly basic conditions.

The *N*-isopropyl carbamates of a variety of phenols were prepared in excellent yields following the method of Hoppe and purified via flash chromatography (Scheme 2).[11] The 3- and 4-trifluoromethylphenols required a minor modification to the reported procedure in that heating at reflux for 72 hours in the presence of 30% DMAP was necessary for complete carbamation. The aryl carbamates were then treated with TMEDA and TMSOTf at 0 °C followed by TMEDA and *n*-BuLi at –78 °C for 1 hour. A solution of I_2 dissolved in THF was then added and stirred for 2 hours at –78 °C. The solution was gradually warmed and the solvent removed by rotary evaporation. After concentrating, the addition of 95% EtOH and powdered NaOH allowed for release of the CbH group without isolation of the 2-iodophenyl isopropylcarbamate. Following purification of the prepared *ortho*-iodophenols, the compounds were smoothly transformed into the desired 2-iodophenyl triflates by standard treatment with triflic anhydride.[1d]

The workup of activated aromatic compounds **11** and **12** (Table 2) required special care to avoid generation of regioisomeric and polyiodinated products. The pH was carefully adjusted to pH 6–8 with 2 N HCl after decarbamation to afford the desired monoiodinated isomers. If the workup was conducted at pH <5, reversible electrophilic iodination ensued, eroding the yields.[9c] Despite the activated nature of **13**, no loss of regioisomeric purity was exhibited when the crude material was treated under acidic conditions.

Competitive dehydrohalogenation did not occur when **6**, **7**, or **8** were subjected to the halogenation protocol. Benzylic deprotonation was also absent with **3** under these conditions. This serves as a testament to the powerful directing effect of the CbH group. The yields of deactivated 2-iodophenols **19** and **20** were improved by using *tert*-butyllithium in place of *n*-BuLi. The regioselective iodination *para* to the trifluoromethyl group in **10** might result from the significant field effect of the trifluoromethyl substituent.[12] This is contrasted by the regioselectivity exhibited by **2**, where the methoxy and CbH substituents share a synergistic directing effect toward lithiation–iodination to give **12** after decarbamation.[13] An analogous regiochemical result was encountered in the iodination of **8**.[14]

We have identified 2-iodophenyl triflates as privileged aryne precursors in nonpolar solvents. The regioselective preparation of both activated and select deactivated iodophenyl triflates is possible using Hoppe's directed *ortho*-lithiation approach.[15,16] Compounds **21**–**30**, which include eight new 2-iodoaryl triflates, likely will find utility in the preparation of disparate polysubstituted aromatics via the popular use of benzynes in organic synthesis. These compounds should also prove useful in transition-metal-catalyzed processes.

Acknowledgment

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References and Notes

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(15) **General Procedure for the Preparation of 2-Iodophenols 11–20**

To a solution of the carbamate (2.5 mmol) dissolved in dry Et_2O (25 mL) under argon was added TMEDA (1.1 equiv, 2.75 mmol) at 0 °C. Then TMSOTf (1.1 equiv, 2.75 mmol) was slowly added to the solution and the reaction mixture was allowed to warm to r.t. over a period of 30 min. After cooling the solution to –78 °C, TMEDA (2.0 equiv, 5.0 mmol) was added followed by the dropwise addition of *n*-BuLi or *t*-BuLi (2.0–2.5 equiv, 5.0–6.2 mmol). The reaction mixture was stirred for 1 h and was then treated with I_2 (1.0 equiv, 2.5 mmol) dissolved in THF (3 mL). After reacting for 2 h, EtOH (0.25 mL) was added and the solvent was removed by rotary evaporation. The resultant residue was dissolved in EtOH (25 mL) and treated with 5 mL of aq 2 N NaOH (4 equiv, 10 mmol). The reaction proceeded for 2 h, after which the pH was adjusted to 6–8 with 2 N HCl. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were washed with a 1 M solution of $Na_2S_2O_3$ (25 mL), then dried and filtered. Upon concentration, the resulting residue was purified using flash chromatography (hexane–EtOAc, 95:5 to 9:1) affording the desired 2-iodophenol.

(16) **General Procedure for the Preparation of 2-Iodophenyl Triflates 21–30**

To a –78 °C solution of 2-iodophenol (1.0 mmol) in CH_2Cl_2 (3 mL) was added anhydrous *i*-Pr_2NEt (1.25 mmol) and Tf_2O (1.25 mmol). After 10 min, the cooling bath was removed and the reaction mixture was allowed to warm to r.t. The reaction was quenched with H_2O (5 mL) after 1–2 h, and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic layers were dried and concentrated. The crude material was then purified by flash chromatography (100% hexane to hexane–EtOAc, 98:2) or recrystallized from hexane to afford the desired 2-iodophenyl triflate.

(17) Compound **2**: white solid, mp 54–55 °C. IR (neat): 3441 (m), 1734 (s), 1507 (m), 908 (m), 732 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 8.2 Hz, 1 H), 6.66 (dt, *J* = 5.0, 2.0 Hz, 2 H), 6.62 (t, *J* = 2.0 Hz, 1 H), 4.79 (d, *J* = 0.7 Hz, 1 H), 3.82 (dt, *J* = 13.2, 6.4 Hz, 1 H), 3.72 (s, 3 H), 1.16 (d, *J* = 6.5 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.3, 153.5, 152.0, 129.5, 113.8, 111.1, 107.5, 55.3, 43.4, 22.8. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{15}NO_3$: 209.1052; found: 209.1056.

(18) Compound **3**: white solid, mp 105–106 °C. IR (neat): 3343 (m), 1739 (s), 1608 (m), 739 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.96 (d, *J* = 8.0 Hz, 1 H), 6.75 (s, 1 H), 6.71 (d, *J* = 8.0 Hz, 1 H), 4.97 (d, *J* = 4.0 Hz, 1 H,), 3.86 (td, *J* = 6.7, 13.1 Hz, 1 H), 3.81 (s, 3 H), 2.32 (s, 3 H), 1.20 (d, *J* = 6.5 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 151.1, 137.6, 136.0, 122.7, 120.9, 113.1, 55.7, 43.3, 22.7, 21.2. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{17}NO_3$: 223.1208; found: 223.1210.

(19) Compound **5**: white solid, mp 151–152 °C. IR (neat): 3391 (m), 1738 (s), 1502 (s), 847 (w), 746 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.5 Hz, 4 H), 7.42 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.1 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 4.89 (d, *J* = 4.9 Hz, 1 H), 3.91 (dd, *J* = 12.8, 6.3 Hz, 1 H), 1.24 (d, *J* = 6.3 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.6, 150.4, 140.5, 138.3, 128.7, 127.9, 127.1, 127.0, 121.8, 43.4, 22.8. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{17}NO_2$: 255.1259; found: 255.1259.

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(21) Compound **7**: white solid, mp 123–124 °C. IR (neat): 3326 (br), 1739 (s), 1495 (s), 845 (s), 746 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.04 (td, *J* = 8.6, 16.7 Hz, 4 H), 4.98 (s, 1 H), 3.87 (dd, *J* = 6.5, 13.1 Hz, 1 H), 1.20 (d, *J* = 6.4 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.7 [d, *J*(CF) = 243.2 Hz], 153.6, 146.8 [d, *J*(CF) = 2.6 Hz], 122.9 [d, *J*(CF) = 8.4 Hz], 115.6 [d, *J*(CF) = 23.4 Hz], 43.4, 22.7. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{10}H_{12}FNO_2$: 197.0852; found: 197.0853.

(22) Compound **8**: white solid, mp 85–86 °C. IR (neat): 3433 (m), 1601 (s), 1508 (m), 748 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29 (dd, *J* = 8.3, 15.3 Hz, 1 H), 6.91 (ddd, *J* = 6.0, 8.1, 6.6 Hz, 3 H), 4.84 (d, *J* = 0.9 Hz, 1 H), 3.89 (qd, *J* = 6.6, 13.4 Hz, 1 H), 1.24 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.7 [d, *J*(CF) = 246.6 Hz], 153.0, 151.9 [d, *J*(CF) = 11.0 Hz], 129.8 [d, *J*(CF) = 9.4 Hz], 117.2 [d, *J*(CF) = 2.0 Hz], 112.0 [d, *J*(CF) = 21.1 Hz], 109.5 [d, *J*(CF) = 24.3 Hz], 43.4, 22.7. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{10}H_{12}FNO_2$: 197.0852; found: 197.0850.

(23) Compound **9**: white solid, mp 119–120 °C. IR (neat): 3316 (br), 1739 (s), 1535 (s), 814 (m), 700 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (m, 3 H), 7.25 (d, *J* = 7.0 Hz, 1 H), 4.93 (d, *J* = 3.9 Hz, 1 H), 3.81 (qd, *J* = 13.5, 6.6 Hz, 1 H), 1.15 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0, 151.1, 131.6 [q, *J*(CF) = 32.8 Hz], 129.6, 125.1, 125.1, 123.6 [q, *J*(CF) = 272.3 Hz], 121.7 [d, *J*(CF) = 3.7 Hz], 118.7 [dd, *J*(CF) = 3.6 Hz, *J* = 7.4 Hz], 43.5, 22.6. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{12}F_3NO_2$: 247.0820; found: 247.0824.

(24) Compound **10**: white solid, mp 88–89 °C. IR (neat): 3339 (br), 1743 (s), 1490 (s), 804 (m), 743 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.46 (m, 2 H), 7.41 (s, 1 H), 7.36 (d, *J* = 7.3 Hz, 1 H), 4.89 (d, *J* = 4.6 Hz, 1 H), 3.90 (qd, *J* = 6.7, 13.4 Hz, 1 H), 1.25 (d, *J* = 6.5 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.05, 151.1, 131.6 [q, *J*(CF) = 32.7 Hz], 129.6, 125.1, 123.6 [q, *J*(CF) = 272.3 Hz], 121.79 [d, *J*(CF) = 3.6 Hz], 118.7 [dd, *J*(CF) = 7.3, 3.5 Hz], 43.5, 22.6. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{11}H_{12}F_3NO_2$: 247.0820; found: 247.0822.

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(31) Compound **21**: recrystallization from hexane, white solid, mp 79–80 °C. IR (neat): 3053 (m), 2987 (w), 1600 (m), 1573 (w), 1456 (m), 1423 (m), 1326 (m), 1265 (s), 1245 (m), 1218 (s), 1160 (m), 1139 (m), 1083 (m), 1059 (m), 1020 (w), 968 (m), 895 (m), 826 (m), 810 (m), 740 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.54 (d, *J* = 2.45 Hz, 1 H), 6.42 (d, *J* = 2.47 Hz, 1 H), 3.88 (s, 3 H), 3.82 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.8, 160.4, 151.4, 118.6 [q, *J*(CF) = 318.5 Hz], 99.8, 98.1, 71.4, 56.8, 55.8. HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_8F_3IO_5S$: 411.9089; found: 411.9106.
(32) Compound **23**: viscous liquid. IR (neat): 2946 (w), 1590 (s), 1504 (s), 1461 (s), 1421 (m), 1301 (m), 1211 (m), 1133 (m), 1041 (m), 946 (m), 873 (m), 836 (m), 798 (m), 769 (m) cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 0.6, 1.8 Hz, 1 H), 6.77 (d, *J* = 1.3 Hz, 1 H), 3.84 (s, 3 H), 2.30 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.1, 140.7, 138.1, 131.6, 122.5, 118.7 [q, *J*(CF) = 321.0 Hz], 89.5, 56.1, 20.9. HRMS (EI): *m/z* $[M]^+$ calcd for $C_9H_8F_3IO_4S$: 395.9140; found: 395.9142.
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(34) Compound **25**: recrystallization from hexane, white needles, mp 41–42 °C. IR (neat): 2925 (w), 1583 (s), 1469 (s), 1425 (s), 1375 (m), 1247 (m), 1213 (s), 1172 (m), 1137 (m), 1031 (m), 885 (m), 833 (m), 798 (m), 761 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 2.2 Hz, 1 H), 7.60 (dd, *J* = 2.2, 8.6 Hz, 1 H), 7.53 (td, *J* = 1.8, 3.3 Hz, 1 H), 7.46 (td, *J* = 1.6, 15.0 Hz, 2 H), 7.46 (d, *J* = 1.6, 4.8 Hz, 1 H), 7.42 (td, *J* = 1.9, 4.8 Hz, 1 H), 7.38 (d, *J* = 8.6 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.5, 143.0, 139.1, 137.9, 129.1, 128.6, 128.5, 127.2, 122.0, 118.7 [q, *J*(CF) = 321.0 Hz], 89.4. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_8F_3IO_3S$: 427.9191; found: 427.9190.
(35) Compound **26**: liquid. IR (neat): 2960 (w), 1569 (s), 1461 (s), 1428 (s), 1371 (m), 1214 (m), 1174 (m), 1137 (m), 1101 (m), 1031 (m), 883 (m), 821 (m), 790 (m), 763 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 2.5 Hz, 1 H), 7.40 (dd, *J* = 2.5, 8.8 Hz, 1 H), 7.25 (d, *J* = 8.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.9, 140.0, 134.6, 130.1, 122.6, 118.6 [q, *J*(CF) = 320.7 Hz], 89.6. HRMS (EI): *m/z* $[M]^+$ calcd for $C_7H_3ClF_3IO_3S$: 385.8488; found: 385.8497.
(36) Compound **27**: liquid. IR (neat): 2985 (w), 1588 (s), 1474 (s), 1428 (s), 1250 (m), 1226 (m), 1139 (m), 1029 (m), 907 (m), 856 (m), 817 (m), 734 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 3.0, 7.3 Hz, 1 H), 7.29 (dd, *J* = 4.6, 9.1 Hz, 1 H), 7.14 (ddd, *J* = 3.0, 7.3, 9.1 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8 [d, *J*(CF) = 254.0 Hz], 146.5 [d, *J*(CF) = 3.4 Hz], 127.5 [d, *J*(CF) = 25.6 Hz], 122.9 [d, *J*(CF) = 9.2 Hz], 118.7 [q, *J*(CF) = 320.6 Hz], 116.9 [d, *J*(CF) = 23.7 Hz], 89.4 [d, *J*(CF) = 8.8 Hz]. HRMS (EI): *m/z* $[M]^+$ calcd for $C_7H_3F_4IO_3S$: 369.8772; found: 369.8778.
(37) Compound **28**: viscous liquid. IR (neat): 3154 (w), 1577 (m), 1457 (s), 1428 (s), 1281 (w), 1248 (m), 1220 (s), 1139 (s), 1096 (w), 1035 (w), 975 (s), 906 (s), 835 (m), 787 (m), 725 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43 (dt, *J* = 8.4, 6.1 Hz, 1 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 7.11 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.0 [d, *J*(CF) = 252.6 Hz], 151.0 [d, *J*(CF) = 4.5 Hz], 130.7 [d, *J*(CF) = 9.0 Hz], 118.7 [q, *J*(CF) = 320.7 Hz], 117.7 [d, *J*(CF) = 2.8 Hz], 115.3 [d, *J*(CF) = 24.2 Hz], 79.2 [d, *J*(CF) = 29.5 Hz]. HRMS (EI): *m/z* $[M]^+$ calcd for $C_7H_3F_4IO_3S$: 369.8784; found: 369.8783.
(38) Compound **29**: recrystallization from hexane, white needles, mp 37–38 °C. IR (neat): 3154 (w), 1606 (s), 1479 (s), 1430 (s), 1398 (m), 1323 (m), 1246 (m), 1221 (m), 1140 (m), 1181 (m), 1080 (m), 1023 (m), 906 (m), 829 (m), 808 (m), 735 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.3 Hz, 1 H), 7.54 (d, *J* = 1.3 Hz, 1 H), 7.38 (dd, *J* = 8.3, 1.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3, 141.6, 132.9 [q, *J*(CF) = 34.2 Hz], 126.1 [q, *J*(CF) = 3.5 Hz], 122.7 [q, *J*(CF) = 272.9 Hz], 119.1 [q, *J*(CF) = 3.6 Hz], 118.7 [q, *J*(CF) = 320.8 Hz], 94.1 [d, *J*(CF) = 0.9 Hz]. HRMS (EI): *m/z* $[M - Tf]^+$ calcd for $C_7H_3F_3IO$: 286.9181; found: 286.9175.
(39) Compound **30**: recrystallization from hexane, white needles, mp 39–40 °C. IR (neat): 2985 (w), 1430 (s), 1399 (m), 1323 (m), 1265 (m), 1246 (m), 1221 (m), 1180 (m), 1139 (m), 1080 (m), 1023 (m), 906 (m), 808 (m), 729 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.08 (dd, *J* = 8.3, 0.5, Hz, 1 H), 7.54 (d, *J* = 1.4 Hz, 1 H), 7.38 (dd, *J* = 8.3, 1.3 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3, 141.6, 132.8 [q, *J*(CF) = 34.2 Hz], 126.1 [q, *J*(CF) = 3.5 Hz], 122.7 [q, *J*(CF) = 272.7 Hz], 119.1 [q, *J*(CF) = 3.3 Hz], 118.6 [q, *J*(CF) = 320.7 Hz], 94.1. HRMS (EI): *m/z* $[M - Tf]^+$ calcd for $C_7H_3F_3IO$: 286.9181; found: 286.9192.