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A simple iodination protocol via in situ generated ICl using NaI/$FeCl_3$

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Abstract—A novel iodination of silyl-enol ethers using hitherto unexplored NaI/$FeCl_3$ system is reported. The procedure has been extended to the iodination of aromatic and hetero aromatic compounds.

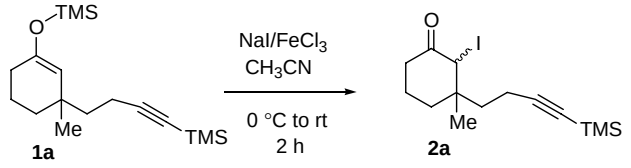
1. Inroduction

In general iodination is a relatively difficult process compared to bromination and hence several additives have been used to enhance the rate of iodination reaction.[1] Olah and co-workers reported an iodination of electron-deficient aromatic compounds using *N*-iodosuccinimide in trifluoromethanesulfonic acid.[2] Tour and Kosynkin reported[3] a facile preparation of iodoanilines using a combination of benzyltriethylammonium dichloroiodate and sodium bicarbonate. A novel synthesis of heterocyclic iodo compounds are reported using potassium dichloroiodate under aqueous condition.[4] Colobert and co-workers reported a mild and regioselective iodination of electron-rich aromatics using *N*-iodosuccinimide in the presence of a catalytic amount of TFA,[5] wherein the iodination was proceeded through the formation of iodotrifluroacetate. Bedekar and co-workers reported[6] an environmentally benign halogenation of aromatic amines, hydrocarbons and naphthols. Recently, Krishnan Mohan et al. reported a regioselective oxiiodination of aromatic compounds using ammonium iodide and oxone.[7] A regioselective bromination of aromatic compounds using LiBr-tetrabutylammonim peroxydisulfate has been observed.[8] Braddock and co-workers reported a similar bromination using LiBr-(diacetoxyiodo)-benzene.[9] Sha and co-workers reported a facile iodination of silyl-enol ether using NaI and *m*-CPBA.[10]

2. Results and discussion

In an ongoing project we required a wide variety of α-bromo/iodo ketones for our work on the synthesis of carbocyclic natural products involving a tandem cyclization of a α-carbonyl radical. The required silyl-enol ethers were smoothly prepared via a CuI promoted 1,4-addition of various Grignards to enones. Initially the iodination/bromination of silyl-enol ether **1a** was tried using NIS/NBS without any success. The existing procedure for iodination using NaI/*m*-CPBA requires the preparation of dry *m*-CPBA, which is somewhat difficult and also problematic. Additionally we had a lot of problems with the reproducibility of this iodination reaction using NaI/*m*-CPBA protocol. Considering the synthetic utility of α-iodo ketones we sought to develop a simple procedure, which can iodinate silyl-enol ether in a reasonable yield. We envisioned that $FeCl_3$[11] could be used for oxidation of the iodide under a mild condition. Our method is based on the generation of electrophilic iodonium ion in situ via the interaction of NaI with $FeCl_3$ in acetonitrile.

As a model reaction silyl-enol ether **1a**[12] was reacted with NaI and $FeCl_3$ (1:2 molar ratio) in acetonitrile at 0 °C to room temperature for 2 h followed by usual workup and column chromatographic purification afforded iodo compound **2a** in 72% yield, Scheme 1. It should be mentioned that when the iodination was performed with 1 mol equiv of NaI/$FeCl_3$ (1:1 molar ratio) it was found to be incomplete.



Scheme 1. Preparation of iodoketone **2a**.

Keywords: Iodination; Silyl-enol ether; Iodo cycloalkanones; Iodoindoles.
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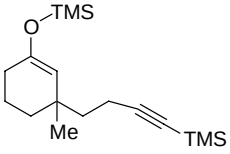
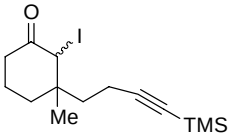
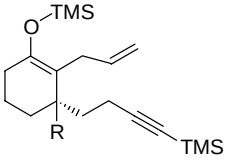
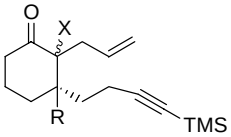
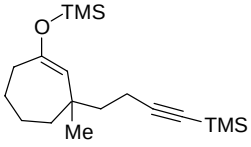
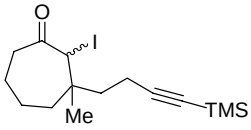
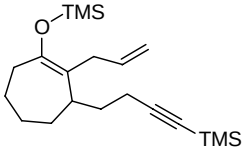
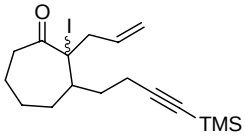
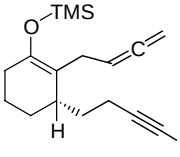
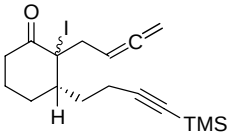
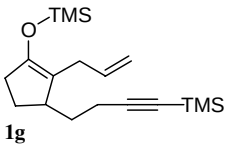
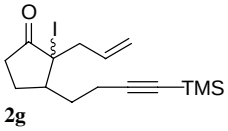
TLC analysis of the pure iodo compound **2a** indicated as a diastereomeric mixture. The ^{1}H NMR spectrum of **2a** confirmed the presence of two diastereomers in the ratio of 1:1, in which the methyl protons appeared as two singlets at δ 0.91 and 0.98 with equal intensity. The ^{13}C NMR spectrum further evidenced the existence of two diastereomers in which twenty-four carbon signals were observed for **2a**. The electron impact mass spectrum of **2a** exhibited $[M-15]^+$ peak at *m*/*z* 347 probably due to the loss of one methyl radical.

Under identical conditions several silyl-enol ethers **1b–g** also underwent a smooth iodination/bromination to afford the respective 2-iodo/bromo cycloalkanones **2b–g** in moderate to good yields. The iodination/bromination details of the silyl-enol ethers and the yield of the respective iodo/bromo compounds are presented in Table 1. The silyl-enol ethers **1b** and **1c** could also be converted into the corresponding α-bromo compounds **2b** and **2c** in 58 and 56% yields under identical conditions using NaBr/$FeCl_3$ (entry 2). Relatively the bromination of silyl-enol ethers **1b** and **1c** are found to be slower than the iodination, and also the yield of α-bromo compounds are almost 5% less than the corresponding iodo compounds (entry 2). The formation of tertiary α-iodo/bromo compounds **2b**, **2c**, **2c′**, **2e**, **2f** and **2g** are found to proceed with somewhat diminished yields (entries 2–6). The ^{1}H NMR spectrum of **2c**, **2c′** and **2d** confirmed the existence of diastereomers in the ratio of 1:1 based on the methyl protons, which appeared as two singlets with equal intensity. The ^{13}C NMR signals for compounds **2b**, **2c**, **2c′** and **2d** were found to be doubled due to the existence of two diastereomers. Surprisingly the compounds **2e**, **2f** and **2g** exhibited only 14, 16 and 14 C-13 signals, respectively. The bromo compound **2b**, **2c** and iodo compound **2c′** exhibited M^+ion peaks at *m*/*z* 340, 354 and 402, respectively. The iodo compound **2d** exhibited $[M-15]^+$ ion peak at *m*/*z* 361.

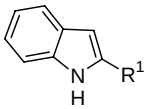
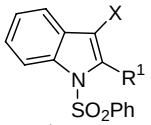
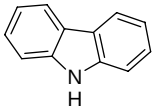
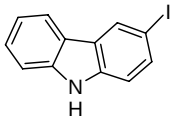
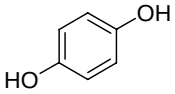
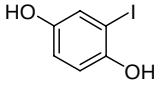
We have extended the mild iodination procedure to the synthesis of various iodoindoles,[13] Table 2. Since the *N*-free iodoindoles are somewhat less stable, the iodination yield

Table 1. Synthesis of halo compounds using NaX/$FeCl_3$

Entry	Substrates	Condition[a]	Iodo/bromo compounds	Yield (%)[b]
1	 **1a**	NaI/$FeCl_3$, 2 h	 **2a**	72
2	 **1b** R=H; **1c** R=Me	NaBr/$FeCl_3$, 4 h NaI/$FeCl_3$, 3 h	 **2b** R=H, X=Br; **2c** R=Me, X=Br; **2c′** R=Me, X=I	58; 56; 60
3	 **1d**	NaI/$FeCl_3$, 3 h	 **2d**	63
4	 **1e**	NaI/$FeCl_3$, 3 h	 **2e**	53
5	 **1f**	NaI/$FeCl_3$, 3 h	 **2f**	55
6	 **1g**	NaI/$FeCl_3$, 3 h	 **2g**	58

[a] CH_3CN used as a solvent.
[b] Isolated yield after column chromatography.

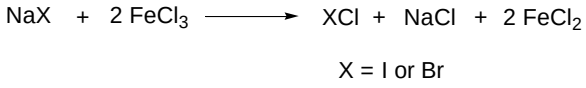
Table 2. Synthesis of halo aromatics using NaX/$FeCl_3$

Entry	Substrates	Condition[a]	Iodo/bromo compounds	Yield (%)[b]
1	 **3** R^1=H; **4** R^1=Me	NaI/$FeCl_3$, 6 h NaBr/$FeCl_3$, 7 h	 **5a** R^1=H, X=I; **5b** R^1=Me, X=I; **6a** R^1=H, X=Br; **6b** R^1=Me, X=Br	72; 81; 74; 76
2	 **7**	NaI/$FeCl_3$, 8 h	 **8**	68
3	 **9**	NaI/$FeCl_3$, 5 h	 **10**	75

[a] CH_3CN used as a solvent.
[b] Isolated yield after column chromatography.

was calculated based on *N*-phenylsufonylated derivative. It should be mentioned that many iodoindoles are utilized as crucial intermediates towards the synthesis of several indole alkaloids.[14] The iodination methodology has been further generalized with the synthesis of iodocarbazole[15] (entry 2) and 2-iodohydroquinone[16] (entry 3).

The observed iodination/bromination may proceed through the intermediacy of ICl/BrCl generated in situ via the oxidation of NaX by the 2 equiv of anhydrous $FeCl_3$ (Scheme 2).



Scheme 2. Mechanism of iodination protocol.

3. Conclusions

In conclusion, we have described a simple and efficient halogenation protocol using NaX/$FeCl_3$ system. Using the procedure several α-iodoketones are prepared in good yields. The α-iodo cycloalkanones **2a–g** could be used as crucial intermediates to the synthesis of angular tricyclic framework of carbocyclic natural products such as dankasterone,[17] laurenene,[18] and guanacastepene.[19] The iodination procedure has been successfully applied to the synthesis of 3-iodoindoles, 3-iodocarbazole and 2-iodohydroquinone. Hopefully this procedure will find wide application since it is mild and environmentally benign. Further application of this methodology and also the synthetic utility of α-iodo cycloalkanones will be explored in due course.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL 400 spectrometer at 400 and 100 MHz and Varian Gemini-300, respectively. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. Elemental analysis were carried out on a Perkin-Elmer 240 B instrument.

4.2. Representative procedure for iodination of silyl-enol ether 2a–g

To a solution of $FeCl_3$ (525 mg, 3.2 mmol) in acetonitrile (20 mL), NaI (243 mg, 1.6 mmol) was added and stirred at 0 °C for 15 min. To this, a solution of silyl-enol ether **1a** (500 mg, 1.6 mmol) in acetonitrile (5 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. It was then quenched (consumption of starting material indicated by TLC) with saturated NH_4Cl solution and reaction mixture was extracted with Et_2O (2×20 mL). The organic layer was separated and washed with saturated $Na_2S_2O_3$ (2×10 mL) solution, water (20 mL) and dried (Na_2SO_4). Removal of solvent followed by flash column chromatographic purification (silica gel, 1% ethyl acetate in hexane) afforded moderately stable iodo compound **2a** as a pale yellow liquid (425 mg, 72%).

4.2.1. 2-Iodo-3-methyl-3-(4-trimethylsilyl-3-butynyl)-1-cyclohexanone 2a. Following the general procedure, compound **2a** was obtained as a pale yellow liquid in 72% yield; (Found: C, 46.32; H, 6.47. $C_{14}H_{23}IOSi$ requires C, 46.41; H, 6.40%); IR (liquid) ν_{max}: 2175, 1710, 844, 763 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.32 and 4.10 (1H, 2s, COC*H*I), 2.13–2.02 (4H, m, CH_2CH_2), 1.77–1.69 (2H, m, CH_2), 1.61–1.48 (4H, m, CH_2CH_2), 0.98 and 0.91 (3H, 2s, *Me*), 0.10 and 0.09 (9H, 2s, Si*Me*$_3$); δ_C (100 MHz, $CDCl_3$) 205.2, 204.7, 106.3, 106.0, 85.4, 84.9, 53.4, 48.6, 46.4, 41.6, 40.9, 35.7, 35.1, 32.2, 31.2, 26.8, 24.5, 21.0, 20.9, 19.7, 14.5, 14.1, 0.1, 0.05; MS (EI) *m/z* (%): 347 $[M-15]^+$, (25%), 221 (41), 179 (21), 149 (26), 128 (54), 82 (100).

4.2.2. 2-Bromo-2-(2-allyl)-3-(4-trimethylsilyl-3-butynyl)-1-cyclohexanone 2b. Following the general procedure, compound **2b** was obtained as a pale yellow liquid in 58% yield; (Found: C, 56.42; H, 7.29. $C_{16}H_{25}BrOSi$ requires C, 56.30; H, 7.38%); IR (liquid) ν_{max}: 2171, 1712, 1610, 845, 759 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.71–5.66 (1H, m, $CH_2CH{=}CH_2$), 5.20–5.08 (2H, m, $CH_2CH{=}CH_2$), 3.32 (1H, dd, $J=5.6$, 5.6 Hz, $CHCH{=}CH_2$), 3.18 (1H, m, CH_2CHCH_2), 2.78 (1H, dd, $J=8.4$, 8.4 Hz, $CHCH{=}CH_2$), 2.42–2.21 (2H, m, CH_2CH_2), 2.02–1.89 (4H, m, CH_2CH_2-CH_2), 1.68–1.51 (4H, m, $CH_2CH_2CH_2$), 0.15 and 0.12 (9H, 2s, $SiMe_3$); δ_C (100 MHz, $CDCl_3$) 203.2, 202.9, 133.4, 132.3, 119.8, 119.3, 107.1, 106.1, 76.71, 75.0, 46.4, 43.3, 41.1, 39.9, 37.1, 36.6, 29.8, 27.7, 26.5, 25.9, 24.4, 24.2, 22.0, 19.4, 17.9, 17.3, 0.16, 0.07; MS (EI) *m/z* (%): 342 $[M+2]^+$, (15%), 340 (M^+, 15), 308 (12), 261 (78), 170 (65), 129 (82), 73 (100).

4.2.3. 2-Bromo-2-(2-allyl)-3-methyl-3-(4-trimethylsilyl-3-butynyl)-1-cyclohexanone 2c. Following the general procedure, compound **2c** was obtained as a pale yellow liquid in 56% yield; (Found: C, 57.56; H, 7.74. $C_{17}H_{27}$-BrOSi requires C, 57.45; H, 7.66%); IR (liquid) ν_{max}: 2173, 1712, 1613, 848, 762 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.58–5.52 (1H, m, $CH_2CH{=}CH_2$), 5.09–5.00 (2H, m, CH_2-$CH{=}CH_2$), 3.89 (1H, d, $J=15.0$ Hz, $CHCH{=}CH_2$), 2.41 (1H, dd, $J=8.3$, 5.4 Hz, $CHCH{=}CH_2$), 2.39–2.07 (2H, m, $CH_2CH_2CH_2$), 1.96–1.60 (4H, m, $CH_2CH_2CH_2$), 1.32–1.19 (4H, m, $CH_2CH_2CH_2$), 1.01 and 0.77 (3H, 2s, *Me*), 0.13 and 0.11 (9H, 2s, $SiMe_3$); δ_C (100 MHz, $CDCl_3$) 204.6, 203.1, 132.1, 131.9, 118.5, 118.0, 107.8, 107.1, 84.3, 84.1, 61.3, 58.3, 45.1, 38.9, 38.5, 37.4, 37.3, 36.4, 33.7, 31.4, 31.2, 25.0, 21.8, 21.6, 19.4, 17.7, 15.0, 14.4, 0.16, 0.07; MS (EI) *m/z* 356 $[M+2]^+$, (18), 354 (M^+, 18), 341 (14), 278 (23), 253 (65), 190 (35), 116 (76), 82 (100%).

4.2.4. 2-Iodo-2-(2-allyl)-3-methyl-3-(4-trimethylsilyl-3-butynyl)-1-cyclohexanone 2c′. Following the general procedure, compound **2c′** was obtained as a pale yellow liquid in 60% yield; (Found: C, 50.87; H, 6.68. $C_{17}H_{27}IOSi$ requires C, 50.74; H, 6.76%); IR (liquid) ν_{max}: 2175, 1710, 1610, 844, 760 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.78–5.66 (1H, m, $CH_2CH{=}CH_2$), 5.46–5.32 (2H, m, $CH_2CH{=}CH_2$), 4.08 (1H, d, $J=13.5$ Hz, $CHCH{=}CH_2$), 2.58 (1H, dd, $J=$ 8.4, 5.6 Hz, $CHCH{=}CH_2$), 2.48–2.16 (2H, m, CH_2CH_2-CH_2), 2.03–1.68 (4H, m, $CH_2CH_2CH_2$), 1.43–1.24 (4H, m, $CH_2CH_2CH_2$), 1.16 and 0.98 (3H, 2s, *Me*), 0.13 and 0.11 (9H, 2s, $SiMe_3$); δ_C (100 MHz, $CDCl_3$) 204.7, 203.4, 132.2, 131.9, 118.4, 118.1, 108.0, 107.3, 84.5, 84.1, 62.8, 59.3, 46.2, 39.2, 38.6, 37.9, 37.4, 36.8, 33.8, 32.5, 32.2, 25.6, 22.4, 21.3, 19.9, 17.3, 15.7, 15.5, 0.19, 0.09; MS (EI) *m/z* 402 (M^+, 13), 277 (31), 261 (6), 234 (4), 127 (95), 82 (100%).

4.2.5. 2-Iodo-3-methyl-3-(4-trimethylsilyl-3-butynyl)-1-cycloheptanone 2d. Following the general procedure, compound **2d** was obtained as a pale yellow liquid in 63% yield; (Found: C, 48.05; H, 6.77. $C_{15}H_{25}IOSi$ requires C, 47.87; H, 6.70%); IR (liquid) ν_{max}: 2173, 1706, 840, 758 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.33 and 4.24 (1H, 2s, $COCHI$), 2.47–2.23 (3H, m, CH_2CHCH_2), 2.16–2.03 (3H, m, CH_2CHCH_2), 1.86–1.71 (2H, m, $CH_2CH_2CH_2$), 1.69–1.24 (4H, m, $CH_2CH_2CH_2$), 0.96 and 0.89 (3H, 2s, *Me*), 0.14 and 0.10 (9H, 2s, $SiMe_3$); δ_C (100 MHz, $CDCl_3$) 205.6, 204.9, 108.3, 107.4, 86.3, 85.7, 65.3, 64.9, 62.4, 61.2, 57.6, 53.4, 49.4, 42.2, 37.8, 30.3, 29.3, 27.8, 24.4, 22.9, 19.6, 19.1, 18.1, 17.4, 0.13, 0.08; MS (EI) *m/z* 361 $[M-15]^+$, (23), 347 (10), 235 (20), 221 (12), 127 (35), 82 (100%).

4.2.6. 2-Iodo-2-(2-allyl)-3-(4-trimethylsilyl-3-butynyl)-1-cycloheptanone 2e. Following the general procedure, compound **2e** was obtained as a pale yellow liquid in 53% yield; IR (liquid) ν_{max}: 2174, 1704, 1610, 842, 760 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.86–5.76 (1H, m, $CH_2CH{=}CH_2$), 5.08–4.96 (2H, m, $CH_2CH{=}CH_2$), 3.30 (1H, dt, $J=2.4$, 11.4 Hz, $CHCH{=}CH_2$), 3.09 (1H, dd, $J=6.1$, 14.4 Hz, CH_2CHCH_2), 2.72 (1H, dd, $J=7.8$, 14.1 Hz, $CHCH{=}CH_2$), 2.58–2.34 (3H, m, CH_2CHCH_2), 2.28–2.08 (3H, m, CH_2CHCH_2), 1.94–1.72 (2H, m, $CH_2CH_2CH_2$), 1.58–1.26 (4H, m, $CH_2CH_2CH_2$), 0.13 and 0.10 (9H, 2s, $SiMe_3$); δ_C (75 MHz, $CDCl_3$) 205.8, 136.8, 117.4, 105.7, 86.0, 64.9, 42.1, 37.9, 30.4, 30.3, 27.3, 18.3, 0.16, 0.09; HRMS (EI): M^+ found 402.0867. $C_{17}H_{27}IOSi$ requires 402.0876.

4.2.7. 2-Iodo-2-(2,3-butadienyl)-3-(4-trimethylsilyl-3-butynyl)-1-cyclohexanone 2f. Following the general procedure, compound **2f** was obtained as a pale yellow liquid in 55% yield; IR (liquid) ν_{max}: 2174, 1950, 1704, 1610, 842, 760 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.02–4.97 (1H, m, $CH{=}C{=}CH_2$), 4.68–4.63 (2H, m, $CH{=}C{=}CH_2$), 3.48–3.36 (2H, m, $CH_2CH{=}C{=}CH_2$), 2.89–2.80 (1H, m, CH_2CHCH_2), 2.38–2.15 (4H, m, $CH_2CH_2CH_2$), 1.98–1.82 (2H, m, $CH_2CH_2CH_2$), 1.55–1.31 (4H, m, $CH_2CH_2CH_2$), 0.12 and 0.06 (9H, 2s, $SiMe_3$); δ_C (75 MHz, $CDCl_3$) 209.3, 203.5, 125.1, 106.0, 87.1, 85.5, 75.2, 43.5, 38.9, 35.8, 32.6, 27.5, 24.3, 17.2, 0.16, 0.09; HRMS (EI): M^+ found 400.0711. $C_{17}H_{27}IOSi$ requires 400.0719.

4.2.8. 2-Iodo-2-(2-allyl)-3-(4-trimethylsilyl-3-butynyl)-1-cyclopentanone 2g. Following the general procedure, compound **2g** was obtained as a pale yellow liquid in 58% yield; (Found: C, 48.27; H, 6.25. $C_{15}H_{23}IOSi$ requires C, 48.13; H, 6.19%); IR (liquid) ν_{max}: 2174, 1704, 1610, 842, 760 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.64–5.57 (1H, m, $CH_2CH{=}CH_2$), 5.12–5.02 (2H, m, $CH_2CH{=}CH_2$), 3.08 (1H, dd, $J=6.7$, 14.5 Hz, $CHCH{=}CH_2$), 2.67 (1H, dd, $J=$ 7.8, 13.8 Hz, CH_2CHCH_2), 2.43 (1H, dd, $J=7.8$, 17.3 Hz, $CHCH{=}CH_2$), 2.38–2.15 (2H, m, CH_2CH_2), 2.14–2.03 (1H, m, CH_2CH), 1.98–1.82 (2H, m, CH_2CH_2), 1.47–1.33 (2H, m, CH_2CH_2), 0.89–0.82 (1H, m, $CHCH_2$), 0.14 and 0.07 (9H, 2s, $SiMe_3$); δ_C (75 MHz, $CDCl_3$) 210.9, 133.9, 119.8, 107.1, 85.6, 63.7, 43.9, 42.8, 34.3, 34.2, 25.2, 16.9, 0.14, 0.08; MS (EI) *m/z* 374 (M^+, 15), 247 (100), 206 (43), 148 (23%).

4.3. Representative procedure for iodination of indole 5a–10

4.3.1. 1-Phenylsulfonyl-3-iodoindole 5a. To a solution of $FeCl_3$ (1.39 g, 8.5 mmol) in acetonitrile (20 mL), NaI (0.64 g, 4.3 mmol) was added and stirred at 0 °C for 15 min. To this, indole **3** (0.5 g, 4.3 mmol) was added and the stirring was continued for an additional 6 h. The reaction mixture was then poured into saturated NH_4Cl solution, extracted with ethyl acetate (2×20 mL). The organic layer

was washed with saturated $Na_2S_2O_3$ solution (20 mL), water (20 mL), dried (Na_2SO_4) and the solvent was removed under vacuo. (0.94 g, 90%). The crude product used as such for next step without any further purification. The crude 3-iodoindole (0.84 g, 3.5 mmol) and phenylsulfonyl chloride (0.5 mL, 3.9 mmol) were dissolved in benzene (20 mL). To this 60% NaOH solution (10 mL) was added along with tetrabutylammonium hydrogensulfate (50 mg). The two-phase system was stirred for 1 h at room temperature. Then the reaction mixture was diluted with water (20 mL), the organic layer separated and dried (Na_2SO_4). Removal of solvent followed by crystallization from MeOH afforded **5a** (0.95 g, 72%) as brown crystals, mp 124 °C; [Found: C, 43.97; H, 2.71; N, 3.59; S, 8.34. $C_{14}H_{10}INO_2S$ requires C, 43.88; H, 2.63; N, 3.66; S, 8.37%]; δ_H (400 MHz, $CDCl_3$) 8.28 (1H, d, $J=8.3$ Hz), 8.14 (2H, d, $J=8.3$ Hz), 7.81 (1H, s), 7.71–7.76 (1H, m), 7.61–7.65 (3H, m), 7.50–7.52 (2H, m); δ_C (100 MHz, $CDCl_3$) 137.8, 134.9, 134.4, 130.2, 129.3, 126.9, 125.9, 125.3, 124.1, 121.2, 113.4, 101.1; MS (EI) *m/z* 383 (M^+, 22), 256 (42), 115 (73), 77 (100%).

4.3.2. 1-Phenylsulfonyl-3-iodo-2-methyindole 5b. Following the general procedure, compound **5b** was obtained as a brown solid in 81% yield; mp 130 °C; [Found: C, 45.41; H, 3.09; N, 3.57; S, 8.13. $C_{15}H_{12}INO_2S$ requires C, 45.35; H, 3.04; N, 3.53; S, 8.07%]; δ_H (300 MHz, $CDCl_3$) 8.16 (1H, d, $J=7.8$ Hz), 7.78 (2H, d, $J=7.5$ Hz), 7.24–7.56 (6H, m), 2.71 (3H, s); δ_C (75 MHz, $CDCl_3$) 138.9, 137.2, 136.5, 134.3, 130.3, 129.5, 126.9, 126.2, 125.3, 119.7, 115.1, 101.7, 14.2; MS (EI) *m/z* 397 (M^+, 15), 256 (48), 129 (46), 77 (100%).

4.3.3. 1-Phenylsulfonyl-3-bromoindole 6a. Following the general procedure, compound **6a** was obtained as a pale yellow solid in 74% yield; mp 120 °C; [Found: C, 50.08; H, 2.94; N, 4.11; S, 9.61. $C_{14}H_{10}BrNO_2S$ requires C, 50.01; H, 3.00; N, 4.17; S, 9.54%]; δ_H (400 MHz, $CDCl_3$) 8.24 (1H, d, $J=8.3$ Hz), 8.12 (2H, d, $J=8.3$ Hz), 7.87 (1H, s), 7.70–7.76 (1H, m), 7.61–7.67 (3H, m), 7.52–7.55 (2H, m); δ_C (100 MHz, $CDCl_3$) 137.7, 134.2, 134.1, 129.3, 126.8, 125.8, 124.7, 123.9, 120.0, 113.5, 99.8; MS (EI) *m/z* 338 $[M+2]^+$, (47%), 336 (M^+, 47), 195 (73), 115 (47), 77 (100%).

4.3.4. 1-Phenylsulfonyl-3-bromo-2-methylindole 6b. Following the general procedure, compound **6b** was obtained as a pale yellow solid in 76% yield; mp 125 °C; [Found: C, 51.38; H, 3.51; N, 3.96; S, 9.11. $C_{15}H_{12}BrNO_2S$ requires C, 51.44; H, 3.45; N, 4.00; S, 9.16%]; IR (KBr) ν_{max}: 1368, 1180 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.19 (1H, d, $J=$ 8.3 Hz), 7.77 (2H, d, $J=7.3$ Hz), 7.49–7.53 (1H, s), 7.38–7.42 (2H, m), 7.24–7.35 (3H, m), 2.63 (3H, s); δ_C (100 MHz, $CDCl_3$) 138.6, 136.9, 135.6, 133.9, 129.3, 128.9, 126.3, 125.2, 124.1, 119.2, 114.5, 101.5, 13.9; MS (EI) *m/z* 352 $[M+2]^+$, (46), 350 (M^+, 46), 209 (100), 129 (44), 77 (49%).

4.3.5. 3-Iodocarbazole 8.[15] Following the general procedure, compound **8** was obtained as a white solid in 68% yield; mp 190 °C (lit.[15] mp 191 °C); [Found: C, 49.28; H, 2.79; N, 4.72. $C_{12}H_8IN$ requires C, 49.17; H, 2.75; N, 4.78%]; δ_H (400 MHz, $CDCl_3$) 10.23 (1H, s), 8.25 (1H, s), 7.96 (1H, d, $J=8.3$ Hz), 7.90 (1H, d, $J=7.8$ Hz), 7.52 (1H, d, $J=8.3$ Hz), 7.29 (1H, t, $J=8.3$ Hz), 7.19 (1H, d, $J=$ 8.3 Hz), 7.09 (1H, t, $J=7.3$ Hz); δ_C (100 MHz, $CDCl_3$) 139.3, 132.8, 124.9, 124.8, 122.2, 119.5, 119.3, 118.4, 117.9, 112.4, 110.4, 80.3; MS (EI) *m/z* 293 (M^+, 42), 272 (24), 209 (15), 164 (100%).

4.3.6. 2-Iodohydroquinone 10.[16] Following the general procedure, compound **10** was obtained as a white solid in 75% yield; mp 115 °C (lit.[16] mp 115–117 °C); [Found: C, 30.67; H, 2.21. $C_6H_5IO_2$ requires C, 30.53; H, 2.14%]; δ_H (400 MHz, $CDCl_3$) 8.09 (1H, s), 8.01 (1H, d, $J=7.6$ Hz), 7.58 (1H, d, $J=8.4$ Hz), 7.43 (1H, d, $J=8.4$ Hz); δ_C (100 MHz, $CDCl_3$) 134.7, 133.9, 131.0, 130.3, 129.9, 128.3; MS (EI) *m/z* 236 (M^+, 46), 167 (26), 158 (38), 139 (48), 117 (66), 109 (53), 101 (57), 97 (47), 68 (100%).

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