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A novel pyrrolidinium ionic liquid with 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate anion as a recyclable reaction medium and efficient catalyst for Friedel–Crafts alkylations of indoles with nitroalkenes

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ABSTRACT

A series of pyrrolidinium-based salts with new fluorine-containing anions were synthesized. Different melting points could be obtained by changing the length of the fluoroalkyl chain of the anions. The pyrrolidinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate ($[C_4H_8NH_2][H(CF_2)_4O(CF_2)_2SO_3]$) is highly fluid even below room temperature. It can be used both as a recyclable solvent and as an efficient catalyst for Friedel–Crafts alkylations of indoles with nitroalkenes.

1. Introduction

Ionic liquids (ILs) have attracted growing academic and industrial interest because of their special properties such as excellent thermal and chemical stability, low vapor pressure and good tunable solubility [1–6]. They have been widely used in organic catalysis, electrochemistry and so on [7–15]. Much attention has been paid on the exploration of new kinds of ILs. Although thousands of ILs were synthesized in the past decades, the most commonly used cations are N,N′-dialkylimidazolium and N-alkylpyridinium. The pyrrolidinium-based ionic liquids have been much less studied. Our experiences in the synthesis and application of biimidazolium and bipyridinium ILs prompted us to extend our investigation to pyrrolidinium ILs [16,17].

Pyrrolidinium salts can be easily obtained from the neutralization of pyrrolidine with Brønsted acids [18–20]. Unfortunately, the melting points of these salts are often higher than room temperature. It is well known that many factors have been identified with respect to lowering melting points of ILs, such as ion asymmetry, large ion size, delocalization of ion charge and so on [21]. And it has been reported that ILs containing highly fluorinated anions such as $[NTf_2]^-$, $[R_fBF_3]^-$ and $[B(Ar_f)_4]^-$, often exhibit lower melting points than those non-fluorine analogues [22–25]. Thus, it occurred to us to explore low melting point pyrrolidinium salts using polyfluoroalkanesulfonate as the anion. Herein, we report the synthesis and applications of pyrrolidinium ionic liquids with polyfluoroalkanesulfonate anions.

2. Results and discussion

Pyrrolidinium salts with perfluoroalkanesulfonate anions were synthesized in quantitative yields by the neutralization of pyrrolidine with the corresponding acids (Scheme 1). However, this direct neutralization could not be applied for the syntheses of pyrrolidinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate ($[C_4H_8NH_2][(H(CF_2)_4O(CF_2)_2SO_3]$) (**1f**). Fortunately, quaternization of pyrrolidine with nitric acid could proceed smoothly to give the corresponding pyrrolidinium nitrate as a yellow solid. Subsequent metathetical reaction with 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate resulted in the formation of **1f** in 95% yield (Scheme 1). The thermal properties of the pyrrolidinium salts were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) as summarized in Table 1.

The melting points of ILs depend largely on the anions. Generally speaking, ILs containing bis(trifluoromethanesulfonyl)imide ion ($(CF_3SO_2)_2N^-$) have lower melting points than others [22,23]. Reviewing the literatures and combining with our result on pyrrolidinium salts, we found that the triflimide (mp = 35 °C) [19] showed a lower melting point than the corresponding

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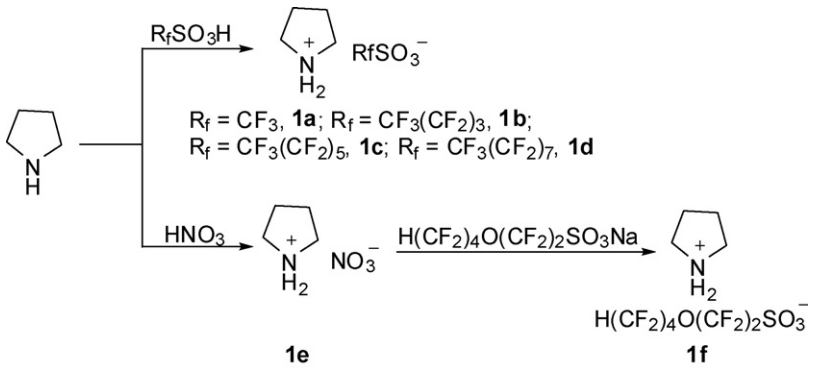


Scheme 1. Preparation of pyrrolidinium salts.

hexafluorophosphate (mp = 282 °C) [18] and tetrafluoroborate (Table 1, entry 1). Using perfluoroalkanesulfonates as the anions, the pyrrolidinium salts are still solid at room temperature and melt above 100 °C (entries 2–5). Much to our surprise, when $H(CF_2)_4O(CF_2)_2SO_3^-$ was employed as the anion, the salt **1f** is liquid and highly fluid even below room temperature (entry 6). The reasons may be rationalized as follows: (a) the charge of the anion is highly delocalized and shielded by the polyfluoroalkyl group from Coulombic interactions with neighboring cations. So ion mobility will be increased [21,26]; (b) long polyfluoroalkyl chain means large anion size, which contributes to lower melting point of ILs [21]; (c) because of repulsive stretching by the 1,3-difluoromethylene groups, perfluorocarbons are rigid, rod-like molecules [27]. However, introducing an oxygen atom into the long fluoroalkyl group can increase ion flexibility. As a result, IL **1f** can be liquid even below room temperature.

Variable solubility of salts in organic solvents is another interesting physicochemical property. The influence of anion on the solubility was then investigated at room temperature (Table 2). It can be seen that all of the salts are completely soluble in water and polar organic solvents like ethanol and tetrahydrofuran (entries 1–3). Unexpectedly, the solubility in water seems not to be affected by the length of the fluoroalkyl chain on the anion (entry 1) [28]. The good water solubility of salts with long fluoroalkyl chain might result from the strong hydratability of the cation. With elongation of the fluoroalkyl chain, most salts are soluble in ethyl acetate, chloroform and dichloromethane (entries 4–6). The salts with long fluoroalkyl chain, e.g., $[C_4H_8NH_2][^nC_8F_{17}SO_3]$ and $[C_4H_8NH_2][H(CF_2)_4O(CF_2)_2SO_3]$ are even soluble in diethyl ether (entry 7). It is well known that an increase in the size of the anion is accompanied by a decrease in the polarity of ionic liquids [25]. Therefore, the above mentioned phenomenon might be interpreted as 'like dissolves like' [29].

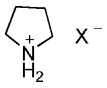
$[C_4H_8NH_2][H(CF_2)_4O(CF_2)_2SO_3]$ **1f** can be regarded as a Brønsted acidic ionic liquid. Brønsted acids are usually used as catalysts for Friedel–Crafts alkylation [30–34]. Friedel–Crafts reaction of indoles with nitroalkenes was always catalyzed by Brønsted acids and Lewis acids [34–37]. But the issue of catalyst recycling and reuse still remains to be addressed. To the best of our knowledge, it has never been reported that ILs were used as both the solvent and catalyst for Friedel–Crafts alkylation of indoles with nitroalkenes. Hence, we explored the application of the Brønsted acidic IL $[C_4H_8NH_2][H(CF_2)_4O(CF_2)_2SO_3]$ as both the recyclable solvent and catalyst for this reaction.

The reaction of indole with trans-β-nitrostyrene was firstly chosen as the model reaction (Table 3). From a preliminary screening, it was found that increasing the temperature led to the significant improvement of the yield (entries 1 and 2). At 50 °C, reducing the ratio of indole to nitrostyrene decreased the yield of **4a** (entries 2–5). Thus, we determined that the ratio 2:1 of indole to nitrostyrene and the temperature of 50 °C were adopted as the optimal conditions for the reaction.

Then a series of different substituted indoles and nitrostyrenes were subjected to this optimal reaction conditions (Table 4). In most cases, the desired Friedel–Crafts alkylated products were obtained in good yields (entries 1–6, 8 and 9). The substituents on indoles had a significant effect on the reactivity. Considerably longer time was necessary for the reaction of indole with bromine on the phenyl ring and the yield became relatively low, which might be resulted from the low electron density of the aromatic ring (entry 7).

IL **1f** could be easily recycled after extraction with toluene and drying under vacuum. It is worth mentioning that the recycled IL can be directly used in the next reaction till the last run without significant decrease in catalytic performance (Table 4, entries 1–9). Determined by ^1H NMR and ^{19}F NMR, the ionic liquid **1f** was found to be in its original state even if it turned brown after 3 runs.

Table 1
Thermal properties of the pyrrolidinium salts.



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Entry	X	T_g (°C)[a]	mp (°C)[b]	T_d (°C)[c]
1	BF_4[d]	−50	74	344
2	CF_3SO_3	−68	109	426
3	$CF_3(CF_2)_3SO_3$	−12	148	371
4	$CF_3(CF_2)_5SO_3$	–	110	408
5	$CF_3(CF_2)_7SO_3$	–	120	393
6	$H(CF_2)_4O(CF_2)_2SO_3$	−74	–	378

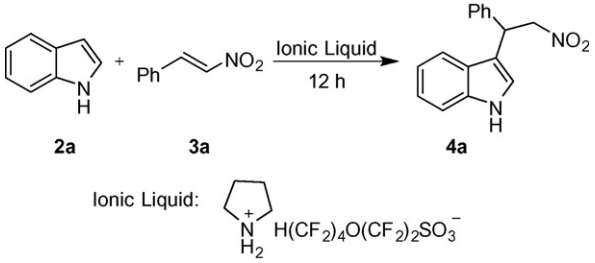
[a] Glass transition temperature (T_g) determined by DSC.
[b] Melting point (mp) determined by DSC.
[c] Thermal degradation (T_d) determined by TGA.
[d] Synthesized according to Ref. [20].

Table 2
Solubility of pyrrolidium salts in organic solvents[a].

Entry	IL	1a	1b	1c	1d	1f
1	H_2O	m	m	m	m	m
2	EtOH	m	m	m	m	m
3	THF	m	m	m	m	m
4	EtOAc	nm	m	m	m	m
5	$CHCl_3$	nm	m	m	m	pm
6	CH_2Cl_2	nm	m	m	m	m
7	Et_2O	nm	nm	nm	m	m
8	Toluene	nm	nm	nm	nm	nm
9	Benzene	nm	nm	nm	nm	nm

[a] Determined at room temperature; m: miscible; nm: non-miscible; pm: partially miscible.

Table 3
Friedel–Crafts reaction of indole with trans-β-nitrostyrene[a].



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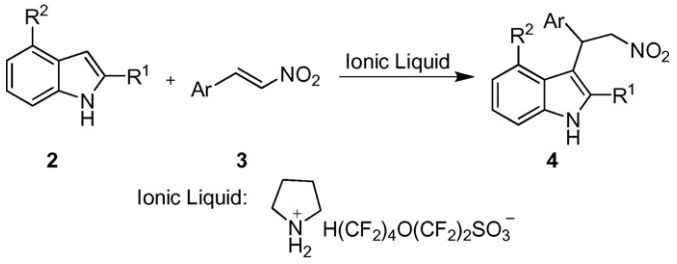
Entry	**2a**/**3a**	*T* (°C)	Yield (%)[b]
1	3/1	25	62
2	3/1	50	94
3	2/1	50	92
4	1.5/1	50	88
5	1/1	50	76

[a] Reaction condition: **2a** and **3a** in IL (2 ml) at indicated temperature.
[b] Isolated yields.

Table 4
Friedel–Crafts alkylation of indoles with nitroalkenes in ionic liquid **1f**[a].



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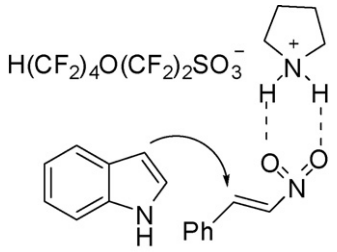
Entry	R^1	R^2	Ar	Time (h)	Product	Yield (%)[b]
1	H	H	Ph	12	**4a**	92
2	H	H	4-MeO-Ph	12	**4b**	91
3	H	H	4-Cl-Ph	12	**4c**	97
4	H	H	4-NO_2-Ph[c]	11	**4d**	96
5	H	H	2-thienyl	24	**4e**	96
6	H	H	2-furyl	24	**4f**	99
7	H	Br	Ph	60	**4g**	55
8	Me	H	Ph	12	**4h**	99
9	H	OMe	Ph	12	**4i**	99

[a] Reaction condition: **2** (1 mmol) and **3** (0.5 mmol) in IL (2 ml).
[b] Isolated yields.
[c] The reaction proceeded at 60 °C.

Combined with the literature reports [38,39], we proposed that the reaction might proceed via an ionic liquid–nitroalkene complex involving an intermolecular double hydrogen bond between the protons on the nitrogen of the cation and the oxygens of the nitro group (Scheme 2). To support the hypothesis,



Scheme 2. The proposed intermediate of the reaction.

IL **1f** was used as the catalyst rather than the solvent for the addition of indole to trans-β-nitrostyrene. No reaction happened in DMSO even if the reaction was performed for 2 days. When CH_2Cl_2 was used as the solvent, the reaction proceeded quite well to give the desired products **4a** in 83% yield. The different catalytic activity of ionic liquid **1f** in DMSO and CH_2Cl_2 might be well explained by the hydrogen bond formation. Hydrogen bonds are easy to form between the nitrogen-protons of the cation and the oxygens of DMSO. Thus, the nitroalkenes could not be activated by ionic liquid **1f**. While in CH_2Cl_2, there would not be such a hydrogen bond interaction between ionic liquid **1f** and CH_2Cl_2.

3. Conclusions

In summary, a series of pyrrolidinium-based salts were synthesized. The ionic liquid $[C_4H_8NH_2][(H(CF_2)_4O(CF_2)_2SO_3]$ is highly fluid even below room temperature. It can be used both as the recyclable solvent and efficient catalyst for Friedel–Crafts alkylations of indoles with nitroalkenes. To the best of our knowledge, this is the first report that an ionic liquid was used as both the solvent and catalyst for this reaction. On the basis of these current efforts, it is likely that a number of acid catalyzed reactions could be performed equally well or perhaps even more effectively in this ionic liquid. Studies to determine applicability to these reactions are currently underway.

4. Experimental

4.1. General information

^{1}H NMR spectra were recorded with a Bruker AM-300 (300 MHz), or Varian VXR (300 MHz) spectrometer. ^{19}F NMR spectra were recorded with a Bruker AM 300 (282 MHz) with $CFCl_3$ as an external standard (negative for up field). ^{13}C NMR spectra were recorded with a Bruker AM 300 (75 MHz) spectrometer. MS was recorded with a Hewlett-Packard HP-5989A spectrometer. Elemental analyses were obtained with a PerkinElmer 2400 Series II Elemental Analyzer. Infrared spectra were measured with a PerkinElmer 983 spectrometer. Glass transition temperature and melting points and were measured by DSC on PYRIS 1. Thermal degradation was measured by TGA on Q500. Unless otherwise noted, reagents were commercially available and used as received.

4.2. Typical procedure for the neutralization of pyrrolidine and perfluoroalkanesulfonic acid (1a–1d)

To a stirred solution of pyrrolidine (4.26 g, 60 mmol) in water (10 ml), trifluoromethanesulfonic acid (7.5 g, 50 mmol) was added slowly at room temperature. Then the reaction was warmed to 60 °C and stirred overnight. The reaction mixture was washed with diethyl ether (50 ml × 3). Removing the solvent at reduced pressure afforded a white solid. A pure product was obtained after recrystallization from ethanol/diethyl ether.

4.3. Procedure for the preparation of pyrrolidinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate (1f)

To a stirred solution of pyrrolidine (40.7 g, 0.55 mol) in water (60 ml), nitric acid (47 g, 65–68%) was added slowly at room temperature. Then the reaction mixture was warmed to 60 °C and stirred overnight. The solution was washed by diethyl ether (50 ml × 3). Removing the solvent at reduced pressure gave pyrrolidinium nitrate as a yellow solid (67 g, 100%).

The solution of pyrrolidinium nitrate (26 g, 194 mmol) in methanol (50 ml) was added slowly to the solution of sodium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate

(87.5 g, 208 mmol) in methanol (70 ml) and stirred for 12 h at room temperature. After filtration, the filtrate was concentrated to give a pale yellow liquid (90.5 g, 99% yield).

4.4. Typical procedure for Friedel–Crafts reaction in ionic liquid

Indole (1 mmol, 117 mg) and trans-β-nitrostyrene (0.5 mmol, 75 mg) were added to ionic liquid **1f** and stirred at 50 °C. After the reaction is complete monitored by TLC, the mixture was extracted by toluene (3 ml × 3). The upper-layer was concentrated and then purified by flash chromatography to afford the Friedel–Crafts alkylated product. The ionic liquid was used directly for the next run after removing the solvent.

4.5. Characterization data

4.5.1. Pyrrolidinium trifluoromethylsulfonate (1a)

White solid: 90% yield; ^{1}H NMR (D_2O, 300 MHz) δ 3.03 (t, J = 6.9 Hz, 4H), 1.75 (t, J = 6.9 Hz, 4H); ^{19}F NMR (D_2O, 282 MHz) δ −79.5 (s, 3F); ^{13}C NMR (D_2O, 75 MHz) δ 122.36 (q, J = 236 Hz), 48.23, 26.24; IR (film) (cm^{-1}): 3192, 3001, 1595, 1464, 1401, 1282, 1228, 1160, 1029, 909, 884, 760, 628, 574, 516; MS (ESI): 149.0 [anion]$^-$; Anal. Calcd. for $C_5H_{10}F_3NO_3S$: C, 27.15; H, 4.56; N, 6.33. Found: C, 27.30; H, 4.62; N, 6.38.

4.5.2. Pyrrolidinium perfluro-n-butylsulfonate (1b)

White solid:92% yield; ^{1}H NMR (D_2O, 300 MHz) δ 3.17–3.12 (m, 4H), 1.89–1.83 (m, 4H); ^{19}F NMR (D_2O, 282 MHz) δ −80.88 to −80.99 (m, 3F), −114.64 to −114.80 (m, 2F), −121.86 to −122.05 (m, 2F), −125.97 to −126.27 (m, 2F); ^{13}C NMR (D_2O, 75 MHz) δ 44.94, 22.97; IR (film) (cm^{-1}): 3204, 1600, 1397, 1358, 1243, 1136, 1062, 1051, 1021, 1006, 848, 806, 739, 657, 533; MS (ESI): 298.9 [anion]$^-$; Anal. Calcd. for $C_8H_{10}F_9NO_3S$: C, 25.88; H, 2.72; N, 3.77. Found: C, 25.83; H, 2.74; N, 3.79.

4.5.3. Pyrrolidinium perfluro-n-hexylsulfonate (1c)

White solid:93% yield; ^{1}H NMR (D_2O, 300 MHz) δ 3.15 (t, J = 7.2 Hz, 4H), 1.89–1.83 (m, 4H); ^{19}F NMR (D_2O, 282 MHz) δ −80.92 (t, J = 8.5 Hz, 3F), −114.54 (t, J = 14.5 Hz, 2F), −120.91 to −121.17 (m, 2F), −121.83 to −122.15 (m, 2F), −122.75 to −123.03 (m, 2F), −126.09 to −126.34 (m, 2F); ^{13}C NMR (D_2O, 75 MHz) δ 45.23, 23.07; IR (film) (cm^{-1}): 3208, 1600, 1398, 1367, 1241, 1200, 1149, 1068, 1033, 892, 703, 644, 623, 567, 525; MS (ESI): 398.9 [anion]$^-$; Anal. Calcd. for $C_{10}H_{10}F_{13}NO_3S$: C, 25.49; H, 2.14; N, 2.97. Found: C, 25.54; H, 2.24; N, 3.12.

4.5.4. Pyrrolidinium perfluro-n-octylsulfonate (1d)

White solid:93% yield; ^{1}H NMR (CD_3OD, 300 MHz) δ 3.24 (t, J = 7.9 Hz, 4H), 2.04–1.97 (m, 4H); ^{19}F NMR (CD_3OD, 282 MHz) δ −81.76 (t, J = 9.9 Hz, 3F), −115.11 (t, J = 16.0 Hz, 2F), −121.09 (s, 2F), −121.88 to −122.53 (m, 6F), −123.13 (s, 2F), −126.69 (s, 2F); ^{13}C NMR (CD_3OD, 75 MHz) δ 45.23, 23.49; IR (film) (cm^{-1}): 3203, 1245, 1202, 1152, 1072, 1039, 941, 645, 624, 558, 524; MS (ESI): 498.9 [anion]$^-$; Anal. Calcd. for $C_{12}H_{10}F_{17}NO_3S$: C, 25.23; H, 1.76; N, 2.45. Found: C, 25.12; H, 1.79; N, 2.42.

4.5.5. Pyrrolidinium nitric (1e) [40]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.39 (br, 2H), 3.23–3.38 (m, 4H), 1.90–2.03 (m, 4H).

4.5.6. Pyrrolidinium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoroethoxy)ethanesulfonate (1f)

^{1}H NMR (CD_3OD, 300 MHz) δ 6.70 (tt, J = 51.1, 6.0 Hz, 1H), 3.16–3.28 (m, 4H), 1.90–2.03 (m, 4H); ^{19}F NMR (CD_3OD, 282 MHz) δ −83.47 to −83.59 (m, 2F), −84.94 to −85.15 (m, 2F), −119.56 (s, 2F), −128.88 to −128.98 (m, 2F), −131.84 to −131.99 (m, 2F), −139.87 to −140.11 (m, 2F); ^{13}C NMR (CD_3OD, 75 MHz) δ 44.80, 23.06; IR (film) (cm^{-1}): 3109, 1610, 1464, 1404, 1349, 1245, 1197, 1148, 1056, 975, 914, 811, 761, 641, 531; MS (ESI): 396.9 [anion]$^-$; Anal. Calcd. for $C_{10}H_{11}F_{12}NO_4S$: C, 25.60; H, 2.36; N, 2.98. Found: C, 25.73; H, 2.49; N, 3.10.

4.5.7. 3-(2-Nitro-1-phenylethyl)-1H-indole (4a) [37]

Yellow oil: 92% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (br s, 1H), 7.47–7.04 (m, 10H), 5.20 (t, J = 8.1 Hz, 1H), 5.07 (dd, J = 12.7, 7.2 Hz, 1H), 4.95 (dd, J = 12.7, 8.1 Hz, 1H).

4.5.8. 3-[1-(4-Methoxyphenyl)-2-nitroethyl]-1H-indole (4b) [37]

White powder: 91% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.07 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.29–7.16 (m, 3H), 7.07 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 6.89–6.82 (m, 2H), 5.14 (t, J = 8.0 Hz, 1H), 5.05 (dd, J = 12.2, 8.0 Hz, 1H), 4.89 (dd, J = 12.2, 8.0 Hz, 1H), 3.77 (s, 3H).

4.5.9. 3-[1-(4-Chlorophenyl)-2-nitroethyl]-1H-indole (4c) [37]

Yellow oil: 97 yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (s, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.33–7.18 (m, 5H), 7.08 (t, J = 7.7 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 5.18 (t, J = 7.7 Hz, 1H), 5.06 (dd, J = 12.3, 7.7 Hz, 1H), 4.91 (dd, J = 7.7, 12.3 Hz, 1H).

4.5.10. 3-[2-Nitro-1-(4-nitrophenyl)ethyl]-1H-indole (4d) [37]

Yellow solid: 96%yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.23–8.17 (m, 3H), 7.53 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 8.6 Hz, 2H), 7.26–7.20 (m, 1H), 7.13–7.06 (m, 2H), 5.31 (t, J = 7.5 Hz, 1H), 5.12 (dd, J = 12.8, 7.5 Hz, 1H), 4.99 (dd, J = 12.8, 7.5 Hz, 1H).

4.5.11. 3-(2-Nitro-1-thiophene-2-ylethyl)-1H-indole (4e) [37]

Yellow oil: 96% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.13 (br, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.25–7.19 (m, 2H), 7.15–7.09 (m, 2H), 7.01–6.92 (m, 2H), 5.47 (t, J = 7.7 Hz, 1H), 4.95–5.10 (m, 2H).

4.5.12. 3-(1-Furan-2-yl-2-nitroethyl)-1H-indole (4f) [37]

Yellow oil: 99% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (br, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.40–7.35 (m, 2H), 7.25–7.19 (m, 1H), 7.17–7.10 (m, 2H), 6.33–6.29 (m, 1H), 6.16 (d, J = 3.3 Hz, 1H), 5.25 (t, J = 7.3 Hz, 1H), 5.06 (dd, J = 12.8, 7.3 Hz, 1H), 4.92 (dd, J = 12.8, 7.3 Hz, 1H).

4.5.13. 4-Bromo-3-(2-Nitro-1-phenylethyl)-1H-indole (4g)

Yellow solid: 55% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.21 (br, 1H), 7.38–7.26 (m, 7H), 7.04 (t, J = 8.3 Hz, 1H), 6.97 (d, J = 2.6 Hz, 1H), 5.97 (dd, J = 7.0 Hz, 9.3 Hz, 1H), 5.17 (dd, J = 13.0, 7.0 Hz, 1H), 4.91 (dd, J = 13.0, 9.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.35, 137.78, 128.83, 128.07, 127.41, 124.80, 124.20, 123.57, 115.15, 113.83, 110.76, 79.54, 40.43; IR (film) (cm^{-1}): 3404, 3060, 3027, 1613, 1542, 1492, 1481, 1452, 1421, 1378, 1336, 1185, 910, 809, 781, 750, 738, 702, 606; MS (EI): 344, 346, 297, 298, 299, 300, 284, 286, 218, 204; Anal. Calcd. for $C_{16}H_{13}BrN_2O_2$: C, 55.67; H, 3.80; N, 8.12. Found: C, 55.64; H, 3.91; N, 8.04.

4.5.14. 2-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (4h) [37]

Yellow solid: 99% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (br s, 1H), 7.22–7.39 (m, 7H), 6.99–7.13 (m, 2H), 5.06–5.27 (m, 3H), 2.42 (s, 3H).

4.5.15. 4-Methoxy-3-(2-nitro-1-phenylethyl)-4-1H-indole (4i)

White solid: 99% yield; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.99 (br, 1H), 7.40–7.26 (m, 5H), 7.12 (t, J = 8.1 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.64 (d, J = 2.5 Hz, 1H), 6.52 (d, J = 7.8 Hz, 1H), 5.51 (dd, J = 10.1, 6.1 Hz, 1H), 5.26 (dd, J = 12.6, 6.1 Hz, 1H), 4.92 (dd, J = 12.6, 10.1 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.20,

139.71, 138.16, 128.63, 127.97, 127.18, 123.55, 121.50, 116.26, 115.41, 104.58, 99.99, 79.81, 55.13, 42.27; IR (film) (cm^{-1}): 3419, 3002, 2970, 2939, 2910, 2839, 1618, 1589, 1540, 1507, 1465, 1453, 1435, 1416, 1377, 1363, 1316, 1259, 1230, 1200, 1120, 1083, 1053, 999, 799, 780, 750, 738, 730, 705, 690, 622, 547; MS (EI): 296, 250, 249, 236, 220; Anal. Calcd. for $C_{17}H1_6N_2O_3$: C, 68.91; H, 5.44; N, 9.45. Found: C, 68.67; H, 5.37; N, 9.41.

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