Supplementary Information

Metal-free Direct Hydrosulfonylation of Azodicarboxylates with Sulfenic acids Leading to Sulfonylhydrazine Derivatives

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1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^1H , 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

2. General procedure for metal-free direct hydrosulfonylation of azodicarboxylates with sulfinic acids

To a mixture of sulfinic acids **1** (0.6 mmol) and azodicarboxylates **2** (0.5 mmol) in a 25 mL round-bottomed flask at room temperature, was added the CH₃OH (2 mL). The reaction vessel was allowed to stir at room temperature for 12h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.

3. Preliminary mechanistic studies.

(1) The reaction of benzenesulfinic acid **1a** and diisopropyl azodicarboxylate **2a** in the presence of TEMPO or BHT.

To a mixture of benzenesulfinic acid **1a** (0.6 mmol), diisopropyl azodicarboxylate **2a** (0.5 mmol) and TEMPO (1.0 mmol) or BHT (1.0 mmol) in a 25 mL round-bottomed flask at room temperature, was added the CH₃OH (2 mL). The reaction vessel was allowed to stir at room temperature for 12h. After the reaction, the solution was concentrated in vacuum, the corresponding product **3a** were obtained in 84% and 85% yields, respectively.

(2) The reaction of benzenesulfonic acid with diisopropyl azodicarboxylate **2a**.

To a mixture of benzenesulfonic acid (0.6 mmol) and diisopropyl azodicarboxylate **2a** (0.5 mmol) in a 25 mL round-bottomed flask at room temperature, was added the CH₃OH (2 mL). The reaction vessel was allowed to stir at room temperature for 12h. After the reaction, the solution was concentrated in vacuum, the corresponding product **3a** was not detected.

(3) The reaction of sodium benzenesulfinate with diisopropyl azodicarboxylate **2a**.

To a mixture of sodium benzenesulfinate (0.6 mmol) and diisopropyl azodicarboxylate **2a** (0.5 mmol) in a 25 mL round-bottomed flask at room temperature, was added the CH₃OH (2 mL). The reaction vessel was allowed to stir at room temperature for 12h. After the reaction, the solution was concentrated in vacuum, only a trace amount of corresponding product **3a** was not detected.

(4) The reaction of sodium benzenesulfinate with diisopropyl azodicarboxylate **2a**.

To a mixture of sodium benzenesulfinate (0.6 mmol), diisopropyl azodicarboxylate **2a** (0.5 mmol) and CF₃COOH (0.5 mmol) in a 25 mL round-bottomed flask at room temperature, was added the CH₃OH (2 mL). The reaction vessel was allowed to stir at room temperature for 12h. After the reaction, the solution was concentrated in vacuum, the corresponding product **3a** was isolated in 95% yield.

4. Characterization data of products 3a-3w

Compound **3a** was obtained in 98% yield according to the general procedure (12h).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.15 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 8.0 Hz, 2H), 7.17 (brs, 1H), 5.01-4.91 (m, 2H), 1.33-1.11(m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 154.6, 150.9, 138.3, 134.0, 129.4, 128.6, 73.0, 71.0, 21.9, 21.5. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 367.0940, found 367.0945.

Diisopropyl 1-(4-methoxyphenylsulfonyl)hydrazine-1,2-dicarboxylate

Compound **3b** was obtained in 97% yield according to the general procedure (12h).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.06 (d, J = 8.5 Hz, 2H), 7.04 (brs, 1H), 7.01 (d, J = 9.0 Hz, 2H), 5.00-4.93 (m, 2H), 3.90 (s, 3H), 1.34-1.17 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 164.1, 154.5, 151.0, 131.9, 129.5, 113.8, 72.8, 70.9, 55.7, 21.9, 21.6. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_7\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 397.1045, found 397.1049.

Compound **3c** was obtained in 86% yield according to the general procedure (12h).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.01 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.03 (brs, 1H), 5.01-4.93 (m, 2H), 2.46 (s, 3H), 1.35-1.16 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 154.5, 150.9, 145.2, 135.3, 129.5, 129.2, 72.9, 70.9, 21.9, 21.7, 21.6. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 381.1096, found 381.1098.

Compound **3d** was obtained in 98% yield according to the general procedure (12h).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.09 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.00 (brs, 1H), 5.01-4.94 (m, 2H), 1.35-1.19 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz,

ppm): 154.5, 150.7, 140.8, 136.6, 131.0, 128.9, 73.2, 71.1, 21.9, 21.6; MS (ESI⁺): [M+H]⁺ 379.1; HRMS (ESI) calcd for C₁₄H₁₉N₂O₆ClNaS (M + Na)⁺ 401.0550, found 401.0551.

diisopropyl1-(4-bromophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compound **3e** was obtained in 81% yield according to the general procedure (12h).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.04 (brs, 1H), 5.02-4.94 (m, 2H), 1.35-1.18 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz, ppm): 154.6, 150.7, 137.2, 131.9, 131.1, 129.5, 73.2, 71.1, 21.9, 21.6, 21.6; MS (ESI⁺): [M+H]⁺ 423.0; HRMS (ESI) calcd for C₁₄H₁₉N₂O₆BrNaS (M + Na)⁺ 445.0045, found 445.0047.

diisopropyl1-(4-fluorophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compound **3f** was obtained in 87% yield according to the general procedure (12h).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.18 (dd, *J*₁ = 8.2 Hz, *J*₂ = 4.8 Hz, 2H), 7.23 (t, *J* = 8.2 Hz, 2H), 7.06 (brs, 1H), 5.02-4.92 (m, 2H), 1.35-1.17 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz, ppm): 166.0 (d, *J* = 255.5 Hz), 154.5, 150.8, 134.1, 132.5 (d, *J* = 9.6 Hz), 115.8 (d, *J* = 22.6 Hz), 73.1, 71.1, 21.9, 21.6; MS (ESI⁺): [M+H]⁺ 363.1; HRMS (ESI) calcd for C₁₄H₁₉N₂O₆FNaS (M + Na)⁺ 385.0846, found 385.0843.

diisopropyl1-(2-bromophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compound **3g** was obtained in 86% yield according to the general procedure (12h).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.36 (brd, *J* = 6.4 Hz, 1H), 7.76 (dd, *J*₁ = 1.2 Hz, *J*₂ = 7.8 Hz, 1H), 7.58-7.49 (m, 2H), 7.01 (brs, 1H), 5.11-5.05 (m, 1H), 4.96-4.90 (m, 1H), 1.34-1.32 (m, 6H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.07-1.03 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz, ppm): 154.8, 150.6, 138.3, 135.2, 134.7, 133.6, 127.7, 120.0, 73.2, 71.1, 21.9, 21.7, 21.5, 21.3; MS (ESI⁺): [M+H]⁺ 423.0; HRMS (ESI) calcd for C₁₄H₁₉N₂O₆BrNaS (M +

Na)⁺ 445.0045, found 445.0048.

Diisopropyl 1-(4-(trifluoromethyl)phenylsulfonyl)hydrazine-1,2-dicarboxylate (new

Compound **3h** was obtained in 87% yield according to the general procedure (12h).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.30 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.07 (brs, 1H), 5.03-4.92 (m, 2H), 1.36-1.17 (m, 12H); ¹³C NMR (CDCl₃, 100 MHz, ppm): 154.5, 150.6, 141.7 (d, *J* = 1.3 Hz), 135.5 (d, *J* = 33.8 Hz), 130.1, 125.7, 123.1 (d, *J* = 271.6 Hz), 73.5, 71.3, 21.8, 21.5; HRMS (ESI) calcd for C₁₅H₁₉N₂O₆F₃NaS (M + Na)⁺ 435.0814, found 435.0815.

diisopropyl 1-(4-acetylphenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compound **3i** was obtained in 93% yield according to the general procedure (12h).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.23(d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H), 7.55 (brs, 1H), 4.97-4.90 (m, 2H), 2.65 (s, 3H), 1.32-1.24 (m, 6H), 1.19-1.12 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz, ppm): 196.9, 154.6, 150.7, 142.0, 140.8, 129.8, 128.3, 73.3, 71.1, 26.9, 21.9, 21.8, 21.6, 21.5; HRMS (ESI) calcd for C₁₆H₂₂N₂O₇NaS (M + Na)⁺ 409.1045, found 409.1041.

diisopropyl 1-(4-nitrophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compound **3j** was obtained in 88% yield according to the general procedure (24h).

¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.41-8.35 (m, 4H), 7.18 (brs, 1H), 5.02-4.93 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.30 (d, *J* = 6.1 Hz, 3H), 1.23-1.19 (m, 6H); ¹³C NMR (CDCl₃, 100 MHz, ppm): 154.5, 150.8, 150.5, 143.7, 131.0, 123.7, 73.7, 71.5, 21.8, 21.6, 21.5; HRMS (ESI) calcd for C₁₄H₁₉N₃O₈NaS (M + Na)⁺ 412.0791, found 412.0790.

Diisopropyl 1-(4-acetamidophenylsulfonyl)hydrazine-1,2-dicarboxylate (new

Compound **3k** was obtained in 97% yield according to the general procedure (12h). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.01 (s, $J = 7.7$ Hz, 2H), 8.00 (brs, 1H), 7.68 (d, $J = 7.6$ Hz, 2H), 7.30 (s, 1H), 5.00-4.91 (m, 2H), 2.21 (s, 3H), 1.33-1.17 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 169.3, 154.8, 151.1, 143.5, 132.2, 130.7, 118.7, 73.1, 71.1, 24.6, 21.9, 21.6; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{24}\text{N}_3\text{O}_7\text{S}$ ($\text{M} + \text{H}$) $^+$ 402.1335, found 402.1331.

Diisopropyl 1-(naphthalen-2-ylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3l** were obtained in 60% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 1H), 8.12 (d, $J = 8.6$ Hz, 1H), 8.04–7.98 (m, 2H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.71-7.62 (m, 2H), 7.06 (brs, 1H), 5.05–4.99 (m, 1H), 4.94–4.88 (m, 1H), 1.37-1.28 (m, 6H), 1.24–1.09 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 151.0, 135.5, 135.0, 131.8, 129.6, 129.4, 128.8, 128.0, 127.5, 123.8, 73.0, 71.0, 21.9, 21.7, 21.6; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 417.1096, found 417.1099.

diisopropyl 1-(trifluoromethylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3m** were obtained in 87% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 7.13 (brs, 1H), 5.18-5.11 (m, 1H), 5.07–5.01 (m, 1H), 1.40-1.36 (m, 6H), 1.31 (d, $J = 6.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 149.6, 130.9 (d, $J = 3.6$ Hz), 128.8 (d, $J = 4.4$ Hz), 119.3 (q, $J = 322.6$ Hz), 75.5, 71.9, 21.7, 21.4, 21.4; HRMS (ESI) calcd for $\text{C}_9\text{H}_{15}\text{N}_2\text{O}_6\text{F}_3\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 359.0501, found 359.0503.

Compound **3n** was obtained in 95% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 7.5$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 8.1$ Hz, 2H), 7.15 (brs, 1H), 4.28–4.20 (m, 4H), 1.34 (t, $J = 6.6$ Hz, 3H), 1.20 (t, $J = 6.9$

Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 150.7, 137.2, 131.9, 131.1, 129.5, 73.2, 71.1, 21.9, 21.6, 21.6; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 339.0627, found 339.0627.

diethyl 1-(4-fluorophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3o** were obtained in 76% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.16 (dd, $J_1 = 8.5$ Hz, $J_2 = 4.6$ Hz, 2H), 7.36 (brs, 1H), 7.22 (t, $J = 8.5$ Hz, 2H), 4.27–4.20 (m, 4H), 1.32 (t, $J = 6.8$ Hz, 3H), 1.21 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1 (d, $J = 255.6$ Hz), 155.0, 151.3, 133.8 (d, $J = 2.6$ Hz), 132.6 (d, $J = 9.7$ Hz), 115.9 (d, $J = 22.8$ Hz), 64.5, 63.0, 14.3, 14.0; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_6\text{FNaS}$ ($\text{M} + \text{Na}$) $^+$ 357.0533, found 357.0533.

diethyl 1-(2-bromophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compound **3p** was obtained in 73% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, $J = 6.8$ Hz, 1H), 7.76 (dd, $J_1 = 1.2$ Hz, $J_2 = 7.8$ Hz, 1H), 7.58–7.48 (m, 2H), 7.13 (brs, 1H), 4.35–4.29 (m, 2H), 4.21–4.15 (m, 2H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.15 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.5, 151.1, 138.0, 135.2, 134.8, 133.8, 127.8, 120.0, 64.5, 63.2, 14.3, 13.9; MS (ESI $^+$): $[\text{M} + \text{H}]^+$ 395.0; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_6\text{BrNaS}$ ($\text{M} + \text{Na}$) $^+$ 416.9732, found 416.9734.

di-tert-butyl 1-(phenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3q** were obtained in 98% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 7.5$ Hz, 2H), 7.65 (t, $J = 7.1$ Hz, 1H), 7.54 (t, $J = 7.9$ Hz, 2H), 6.94 (brs, 1H), 1.51 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 149.8, 138.7, 133.8, 129.0, 128.6, 85.5, 82.5, 28.1, 27.8; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 395.1253, found 395.1258.

di-tert-butyl 1-tosylhydrazine-1,2-dicarboxylate (new compound)

Compounds **3r** were obtained in 84% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 1H), 6.89 (brs, 1H), 2.46 (s, 3H), 1.51 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 149.9, 144.9, 135.7, 129.2, 129.1, 85.3, 82.4, 28.1, 27.8, 21.7; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{26}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 409.1409, found 409.1410.

di-tert-butyl 1-(4-chlorophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3s** were obtained in 84% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.5$ Hz, 2H), 7.51 (d, $J = 8.6$ Hz, 2H), 6.96 (brs, 1H), 1.50 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 149.7, 140.5, 137.1, 130.7, 128.9, 85.8, 82.7, 28.1, 27.8; MS (ESI^+): $[\text{M} + \text{H}]^+$ 407.1; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_6\text{ClNaS}$ ($\text{M} + \text{Na}$) $^+$ 429.0863, found 429.0862.

di-tert-butyl 1-(4-fluorophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3t** were obtained in 83% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 8.17 (dd, $J_1 = 8.4$, $J_2 = 8.0$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 6.92 (brs, 1H), 1.51 (s, 9H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9 (d, $J = 255.0$ Hz), 153.6, 149.7, 134.5 (d, $J = 34.0$ Hz), 132.1 (d, $J = 9.4$ Hz), 115.8 (d, $J = 22.7$ Hz), 85.7, 82.6, 28.1, 27.8; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_6\text{FNaS}$ ($\text{M} + \text{Na}$) $^+$ 413.1159, found 413.1155.

dibenzyl 1-tosylhydrazine-1,2-dicarboxylate (new compound)

Compounds **3u** were obtained in 80% yield according to the general procedure (12h). ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.41 (brs, 1H), 7.37-7.22 (m, 12H), 5.26-5.04 (m, 4H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 151.4, 145.4,

135.3, 134.7, 134.2, 129.6, 129.3, 128.7, 128.6, 128.6, 128.5, 128.4, 128.1, 69.7, 68.3, 21.7; HRMS (ESI) calcd for $C_{23}H_{22}N_2O_6NaS$ ($M + Na$)⁺ 477.1096, found 477.1101.

dibenzyl1-(4-chlorophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3v** were obtained in 83% yield according to the general procedure (12h). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.55 (brs, 1H), 7.37-7.28 (m, 10H), 7.21 (d, *J* = 7.6 Hz, 2H), 5.22-5.08 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 154.9, 151.2, 140.9, 136.1, 135.2, 134.0, 131.1, 130.7, 128.9, 128.9, 128.7, 128.6, 128.5, 128.2, 70.0, 68.5; MS (ESI⁺): [$M+H$]⁺ 475.1; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_6ClNaS$ ($M + Na$)⁺ 497.0550, found 497.0552.

dibenzyl1-(4-bromophenylsulfonyl)hydrazine-1,2-dicarboxylate (new compound)

Compounds **3w** were obtained in 76% yield according to the general procedure (12h). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.44 (brs 1H), 7.37-7.28 (m, 8H), 7.22 (d, *J* = 6.3 Hz, 2H), 5.22-5.08 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 154.9, 151.1, 136.5, 135.1, 133.9, 131.9, 131.1, 130.7, 130.0, 128.9, 128.7, 128.6, 128.5, 128.2, 70.1, 68.6; MS (ESI⁺): [$M+H$]⁺ 519.0; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_6BrNaS$ ($M + Na$)⁺ 541.0045, found 541.0048.

5. Copies of NMR Spectra for 3a–3w