Supporting Information

The Triple Role of Rongalite in Aminosulfonylation of Aryldiazonium Tetrafluoroborates: Synthesis of N-aminosulfonamides via a Radical Coupling Reaction

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S1
1. General.

All kinds of aryldiazonium tetrafluoroborates 2a-2v were prepared according to literature procedures\(^1\) and other substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm\(^{-1}\). \(^1\)H spectra were recorded in DMSO-\(d_6\) on 600 MHz NMR spectrometers and resonances (\(\delta\)) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quadruple), coupling constants (Hz) and integration. \(^{13}\)C spectra were recorded in DMSO-\(d_6\) on 150 MHz NMR spectrometers and resonances (\(\delta\)) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal structure determinations of 3b were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

2. General procedure for the synthesis of 3 (3a as an example).

A mixture of 1 rongalite (1.2 mmol) and 2a (0.6 mmol) in DMSO (3.0 mL) was stirred at rt for 10min in a pressure vessel. The resulting mixture was dropped into 50 mL H\(_2\)O and extracted with EtOAc 3 times (3 ×50 mL). The organic extract was dried with anhydrous Na\(_2\)SO\(_4\), filtered and concentrated. The crude product was purified by column chromatography on silica gel (alkalization with 1% Et\(_3\)N) (eluent: petroleum ether/EtOAc = 5/1) to afford the product 3a as light yellow oil (40.9 mg, 55%).
3. Evidence in support of the mechanism.

(1) We performed a series of radical trapping experiments, and such as TEMPO, BHT, and hydroquinone, no desired product (3l) was observed. And in the reaction containing TEMPO, a TEMPO-PhCO$_2$Et product 4 was detected by GC–MS.

(2) The further radical trapping experiment using 1,1-diphenylethylene (5) as a trapping reagent and ethane-1,1,2-triyltribenzene (6) was obtained.
And the characterization data of 6 are listed below:

**Ethyl 4-(2,2-diphenylethyl)benzoate:**

IR (KBr): 2925, 2361, 1687, 1490, 1416, 1281, 1108, 1026, 1003, 759, 697 cm\(^{-1}\); \(^1\)H NMR (600 MHz, DMSO\(_d6\)) \(\delta = 7.64\) (d, \(J = 7.8\) Hz, 2H), 7.42 (d, \(J = 7.8\) Hz, 4H), 7.24 (t, \(J = 7.8\) Hz, 4H), 7.15 (t, \(J = 7.2\) Hz, 2H), 7.08 (d, \(J = 7.8\) Hz, 2H), 5.85 (d, \(J = 3.6\) Hz, 1H), 4.26-4.23(m, 2H), 3.66 (s, 2H), 1.27 (t, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (150 MHz, DMSO\(_d6\)) \(\delta = 165.8, 147.8, 143.7, 131.1, 127.8, 127.6, 127.3, 126.2, 126.1, 76.8, 60.4, 16.5, 14.2\); HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{21}\)O\(_2\)\(^+\) (M+H)\(^+\) 329.1536, found 329.1536.
(3) The reaction of rongalite (1) and 2l under the standard conditions was stopped at 2 min, the corresponding sulfonyl diazo (7) was obtained in 31% yield, which was then reduced to corresponding sulfonyl hydrazide (3l) in 88% yield by rongalite.

And the characterization data of 7 are listed below:

**ethyl (E)-4-(((4-(ethoxycarbonyl)phenyl)diazene)l sulfonyl)benzoate:**

IR (KBr): 1721, 1626, 1360, 1271, 1166, 1101, 1012, 772, 687, 645, 597 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 8.28 (d, J = 7.8 Hz, 2H), 8.17 (d, J = 7.8 Hz, 2H), 8.06 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 4.47 – 4.40 (m, 4H), 1.45 – 1.41 (m, 6H); ¹³C NMR (150 MHz, CDCl₃) δ = 165.1, 164.8, 151.1, 136.4, 136.1, 135.8, 130.8, 130.5, 130.1, 124.2, 62.0, 61.8, 14.2; HRMS (ESI) m/z calcd for C₁₈H₁₉N₂O₆S⁺ (M+H)⁺ 391.0958, found 391.0953.
(4) The reaction of sodium benzenesulfinate and 2I gave corresponding sulfonyl diazo 8 in 95% yield, which was then reduced to corresponding sulfonyl hydrazide 9 in 91% yield by rongalite.

And the characterization data of 8 and 9 are listed below:

**ethyl (E)-4-((phenylsulfonyl)diazenyl)benzoate:**

IR (KBr): 2978, 2361, 1721, 1604, 1446, 1355, 1272, 1165, 1012, 768, 683, 548 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 8.23 (d, J = 8.4 Hz, 2H), 8.12 (d, J = 7.8 Hz, 2H), 8.04 – 7.99 (m, 3H), 7.88 (t, J = 7.8 Hz, 2H), 4.45 – 4.42 (m, 2H), 1.43 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 164.5, 150.7, 135.7, 135.1, 131.6, 130.8, 130.2, 129.9, 124.2, 61.5, 14.0; HRMS (ESI) m/z calcd for C₁₅H₁₅N₂O₄S⁺ (M+H)⁺ 319.0745, found 319.0745.

**ethyl 4-((2-phenylsulfonyl)hydrazinyl)benzoate:**

IR (KBr): 2361, 1683, 1609, 1340, 1270, 1162, 1021, 874, 724, 614, 553 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.83 (s, 1H), 8.43 (s, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.2 Hz, 1H), 7.63 (t, J = 7.2 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.24 – 4.21 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 165.7, 152.9, 138.8, 133.1, 130.5, 129.3, 127.6, 119.7, 111.6, 59.9, 14.3; HRMS (ESI) m/z calcd for C₁₅H₁₇N₂O₄S⁺ (M+H)⁺ 321.0904, found 321.0901.
(5) To confirm the source of NH in the product of 3, we performed the reaction of deuterated rongalite (1-D) and 2l in the in DMSO-d6 and the deuterated product 3l-D generated in 72% yield with 85% and 91% deuteration of the two N–H groups, respectively. (Since the NH in 3 was too active to exchange with water, we performed the 1H NMR within reaction solution).
(6) We performed cross experiment of 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (2l) and 4-methoxy-benzenediazonium tetrafluoroborate (2c), and only three products was obtained.

It is not easy to determine the structure of the cross product 11, so we try to synthesis the same compound in another way which was list below. The characterization data of 11 are the same with 11'.

And the characterization data of cross product 11 are listed below:

**ethyl 4-(2-((4-methoxyphenyl)sulfonyl)hydrazinyl)benzoate:**

IR (KBr): 2255, 1649, 1319, 1264, 1049, 1026, 1002, 826, 765, 629, 565 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.67 (s, 1H), 8.38 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 7.8 Hz, 2H), 4.28 – 4.26 (m, 2H), 3.89 (s, 3H), 1.33 – 1.31 (m, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ= 165.7, 162.8, 153.0, 130.5, 130.2, 129.9, 119.5, 114.5, 111.6, 60.0, 55.8, 14.4; HRMS (ESI) m/z calcd for C₁₆H₁₉N₂O₅S⁺ (M+H)⁺ 351.1009, found 351.1006.
References:


Figure S1. X-ray crystal structure of 3b.
### Table S1. Crystal data and structure refinement for compound 3b (CCDC: 1839767)

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![Compound 3a](image)

N'-phenylbenzenesulfonohydrazide:

Yield: 55% (40.9 mg); light yellow oil; IR (KBr): 3266, 1640, 1604, 1500, 1158, 732, 687, 517 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.59 (s, 1H), 7.86 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.2 Hz, 2H), 7.61 (t, J = 7.8 Hz, 2H), 7.09 (t, J = 7.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.70 (t, J = 7.2 Hz, 1H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 148.7, 139.2, 132.9, 128.5, 127.5, 119.1, 112.8; HRMS (ESI) m/z calcd for C₁₂H₁₃N₂O₂S⁺ (M+H)⁺ 249.0692, found 249.0689.

![Compound 3b](image)

4-methyl-N'-(p-tolyl)benzenesulfonohydrazide:

Yield: 52% (42.9 mg); gray solid; mp: 128.6-131.0°C; IR (KBr): 1642, 1324, 1159, 1091, 1025, 998, 816, 659, 556 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.40 (s, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 3H), 6.89 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 2.39 (s, 3H), 2.15 (s, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 146.4, 143.1, 136.3, 129.5, 128.9, 127.5, 113.0, 21.0, 20.2; HRMS (ESI) m/z calcd for C₁₄H₁₇N₂O₂S⁺ (M+H)⁺ 277.1005, found 277.1006.

![Compound 3c](image)

4-methoxy-N'-(4-methoxyphenyl)benzenesulfonohydrazide:
Yield: 47% (43.4 mg); gray solid; mp: 110.1-113.2°C; IR (KBr): 3399, 2921, 1644, 1503, 1403, 1260, 831, 803, 559 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.29 (s, 1H), 7.76 – 7.74 (m, 2H), 7.23 (s, 1H), 7.12 – 7.11 (m, 2H), 6.75 – 6.74 (m, 2H), 6.71 – 6.69 (m, 2H), 3.84 (s, 3H), 3.64 (s, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 152.8, 142.4, 130.8, 129.7, 114.2, 113.9, 109.6, 55.7, 55.2; HRMS (ESI) m/z calcd for C₁₄H₁₇N₂O₄S⁺ (M+H)⁺ 309.0904, found 309.0905.

3-methyl-N’-(m-tolyl)benzenesulfonohydrazide:
Yield: 51% (42.2 mg); light yellow solid; mp: 96.8-99.3 °C; IR (KBr): 2253, 1648, 1610, 1333, 1158, 1050, 1028, 1004, 824, 764, 620, 559 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.50 (s, 1H), 7.64 (d, J = 12.6 Hz, 2H), 7.55 (s, 1H), 7.49 – 7.47 (m, 2H), 6.96 (t, J = 7.8 Hz, 1H), 6.60 (s, 2H), 6.51 (d, J = 7.2 Hz, 1H), 2.38 (s, 3H), 2.15 (s, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 148.6, 139.2, 138.8, 137.6, 133.4, 129.0, 128.4, 127.7, 124.7, 119.8, 113.3, 110.2, 21.3, 20.9; HRMS (ESI) m/z calcd for C₁₄H₁₇N₂O₂S⁺ (M+H)⁺ 277.1005, found 277.1003.

4-cyano-N’-(4-cyanophenyl)benzenesulfonohydrazide:
Yield: 81% (72.4 mg); gray solid; mp: 187.1-190.5 °C; IR (KBr): 2219, 1640, 1609, 1164, 1025, 1001, 828, 667, 568 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 10.17 (s, 1H), 8.60 (s, 1H), 8.14 (d, J = 7.2 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 7.55 (d, J = 7.8 Hz, 2H), 6.88 (d, J = 7.8 Hz, 2H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 152.2, 142.6, 133.5, 133.4, 128.4, 119.9, 117.7, 115.6, 112.4, 100.0; HRMS (ESI) m/z calcd for C₁₄H₁₁N₄O₂S⁺ (M+H)⁺ 299.0597, found 299.0598.
4-acetyl-N’-(4-acetylphenyl)benzenesulfonohydrazide:
Yield: 80% (79.6 mg); gray solid; mp: 180.4-183.0 °C; IR (KBr): 3334, 1685, 1643, 1605, 1163, 831, 636, 594 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 10.02 (s, 1H), 8.46 (s, 1H), 8.17 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 2.66 (s, 3H), 2.43 (s, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 197.8, 196.1, 153.1, 142.7, 140.3, 130.3, 129.4, 128.3, 111.8, 27.5, 26.5; HRMS (ESI) m/z calcd for C₁₆H₁₅N₂O₄S+ (M+H)+ 333.0904, found 333.0901.

3-acetyl-N’-(3-acetylphenyl)benzenesulfonohydrazide:
Yield: 67% (66.7 mg); yellow oil; IR (KBr): 3336, 1683, 1593, 1358, 1288, 1260, 1162, 1024, 797, 632, 582 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.88 (s, 1H), 8.35 (s, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.01 (s, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 6.6 Hz, 1H), 2.64 (s, 3H), 2.47 (s, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 197.8, 196.9, 148.7, 139.7, 137.3, 132.6, 131.8 130.0, 129.0, 126.8, 119.5, 117.5, 111.5, 26.9, 26.7; HRMS (ESI) m/z calcd for C₁₆H₁₅N₂O₄S+ (M+H)+ 333.0904, found 333.0904.

2-nitro-N’-(2-nitrophenyl)benzenesulfonohydrazide:
Yield: 45% (45.6 mg); gray solid; mp: 147.6-151.2 °C; IR (KBr): 3257, 1613, 1577, 1524, 1498, 1433, 1334, 1271, 1165, 856, 738, 588 cm⁻¹; ¹H NMR (600 MHz,
DMSO-d$_6$ $\delta$ = 10.45 (s, 1H), 9.20 (s, 1H), 8.06 – 8.04 (m, 3H), 7.93 (t, $J = 7.8$ Hz, 1H), 7.87 (t, $J = 7.8$ Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 6.91 (t, $J = 7.8$ Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-d$_6$) $\delta$= 147.9, 144.3, 136.1, 135.2, 132.8, 132.5, 131.1, 130.3, 125.7, 124.6, 118.9, 115.6; HRMS (ESI) m/z calcd for C$_{12}$H$_{11}$N$_4$O$_6$S$^+$ (M+H)$^+$ 339.0394, found 339.0399.

3-nitro-N’-(3-nitrophenyl)benzenesulfonohydrazide:
Yield: 62% (62.8 mg); yellow oil; IR (KBr): 3090, 1624, 1530, 1352, 1126, 1025, 1001, 876, 780, 732, 672, 586 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$) $\delta$ = 10.23 (s, 1H), 8.58 – 8.55 (m, 2H), 8.46 (s, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 7.94 (t, $J = 7.8$ Hz, 1H), 7.57 – 7.56 (m, 2H), 7.41 (t, $J = 8.4$ Hz, 1H), 7.19 (d, $J = 7.4$ Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-d$_6$) $\delta$= 149.5, 148.4, 147.9, 140.1, 133.8, 131.5, 130.2, 127.8, 122.4, 118.9, 113.7, 106.2; HRMS (ESI) m/z calcd for C$_{12}$H$_{11}$N$_4$O$_6$S$^+$ (M+H)$^+$ 339.0394, found 339.0397.

4-nitro-N’-(4-nitrophenyl)benzenesulfonohydrazide:
Yield: 78% (78.9 mg); yellow solid; mp: 106.8-109.4 °C; IR (KBr): 1632, 1526, 1350, 1325, 1166, 1110, 1022, 987, 780, 686, 615 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$) $\delta$ = 10.39 (s, 1H), 9.02 (s, 1H), 8.49 (d, $J = 6.6$ Hz, 2H), 8.13 (d, $J = 7.2$ Hz, 2H), 8.08 (d, $J = 7.2$ Hz, 2H), 6.92 (d, $J = 7.2$ Hz, 2H); $^{13}$C NMR (150 MHz, DMSO-d$_6$) $\delta$= 154.3, 150.2, 143.8, 138.9, 129.4, 125.7, 124.7, 111.5; HRMS (ESI) m/z calcd for C$_{12}$H$_{10}$N$_4$O$_6$SNa$^+$ (M+Na)$^+$ 361.0213, found 361.0207.
methyl 4-((2-(4-(methoxycarbonyl)phenyl)hydrazinyl)sulfonyl)benzoate:
Yield: 75% (81.9 mg); yellow solid; mp: 87.7-91.3 °C; IR (KBr): 2252, 1644, 1610, 1245, 1111, 1048, 1026, 1003, 826, 774, 692, 604 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 10.00 (s, 1H), 8.43 (s, 1H), 8.17 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 7.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H), 3.76 (s, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 166.1, 165.3, 152.7, 142.7, 133.4, 130.6, 130.1, 128.1, 119.6, 111.6, 52.7, 51.5; HRMS (ESI) m/z calcd for C₁₆H₁₇N₂O₆S⁺ (M+H)⁺ 365.0802, found 365.0803.

ethyl 4-((2-(4-(ethoxycarbonyl)phenyl)hydrazinyl)sulfonyl)benzoate:
Yield: 74% (87.1 mg); yellow solid; mp: 135.8-137.5 °C; IR (KBr): 3327, 3154, 1717, 1682, 1607, 1309, 1175, 1161, 1023, 844, 691, 607, 548 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 10.00 (s, 1H), 8.42 (s, 1H), 8.18 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 4.39 – 4.36 (m, 2H), 4.25 – 4.21 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 165.6, 164.8, 152.6, 142.7, 133.7, 130.5, 130.0, 128.1, 119.9, 111.6, 61.5, 60.0, 14.3, 14.1; HRMS (ESI) m/z calcd for C₁₈H₂₁N₂O₆S⁺ (M+H)⁺ 393.1115, found 393.1113.

4-fluoro-N’-(4-fluorophenyl)benzenesulfonohydrazide:
Yield: 69% (58.7 mg); yellow solid; mp: 130.4-133.7 °C; IR (KBr): 3333, 3246, 1639, 1591, 1506, 1346, 1170, 1091, 1021, 830, 718, 551 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.64 (d, J = 1.2 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.66 (s, 1H), 7.46 (t, J = 9.0 Hz, 2H), 6.95 (t, J = 9.0 Hz, 2H), 6.82 – 6.79 (m, 2H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 165.4, 163.7, 156.9, 155.3, 145.0, 135.3, 130.7, 130.6, 116.4, 116.3, 115.1, 115.0, 114.0; HRMS (ESI) m/z calcd for C₁₂H₁₁F₂N₂O₂S⁺ (M+H)⁺ 285.0504, found 285.0505.

4-chloro-N’-(4-chlorophenyl)benzenesulfonohydrazide:
Yield: 72% (68.4 mg); yellow solid; mp: 214.3-216.7 °C; IR (KBr): 3253, 1594, 1510, 1485, 1327, 1163, 1088, 823, 753, 724, 645, 549 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.74 (s, 1H), 7.86 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 147.5, 137.9, 137.6, 129.5, 129.3, 128.4, 122.4, 114.1; HRMS (ESI) m/z calcd for C₁₂H₁₁Cl₂N₂O₂S⁺ (M+H)⁺ 316.9913, found 316.9908.

4-bromo-N’-(4-bromophenyl)benzenesulfonohydrazide:
Yield: 78% (94.9 mg); gray solid; mp: 125.7-128.1 °C; IR (KBr): 3242, 1637, 1574, 1486, 1389, 1325, 1157, 1089, 1005, 819, 737, 601 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.74 (s, 1H), 7.87 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 147.9, 138.0, 132.3, 131.3, 129.6, 127.0, 114.7, 110.0; (EI-MS) m/z: 403.90.
4-iodo-N'- (4-iodophenyl) benzenesulfonohydrazide:
Yield: 68% (101.8 mg); gray solid; mp: 142.1-144.6 °C; IR (KBr): 3324, 3225, 1637, 1483, 1328, 1252, 1159, 1087, 1003, 815, 732, 496 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.70 (s, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.85 (s, 1H), 7.58 (d, J = 7.8 Hz, 2H), 7.41 (d, J = 7.2 Hz, 2H), 6.65 (d, J = 7.8 Hz, 2H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 148.4, 138.4, 138.1, 137.0, 129.2, 115.2, 101.4, 80.6; (EI-MS) m/z: 499.90.

3-ethynyl-N’-(3-ethynylphenyl) benzenesulfonohydrazide:
Yield: 43% (38.1 mg); gray solid; mp: 136.9-140.3 °C; IR (KBr): 1639, 1330, 1208, 1157, 1024, 994, 782, 688 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.77 (s, 1H), 7.90 (s, 1H), 7.85 (d, J = 6.6 Hz, 2H), 7.79 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 6.88 (s, 1H), 6.82 (d, J = 7.8 Hz, 2H), 4.43 (s, 1H), 4.07 (s, 1H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 149.0, 139.8, 136.3, 130.6, 130.2, 129.4, 128.3, 123.1, 122.9, 122.2, 115.8, 113.9, 84.2, 83.1, 82.3, 80.3; HRMS (ESI) m/z calcd for C₁₆H₁₃N₂O₂S⁺ (M+H)⁺ 297.0692, found 297.0692.

N’-(naphthalen-2-yl)naphthalene-2-sulfonohydrazide:
Yield: 61% (63.6 mg); gray solid; mp: 159.3-162.5 °C; IR (KBr): 3173, 1631, 1605, 1524, 1313, 758, 523 cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ = 9.79 (s, 1H), 8.51 (s, 1H), 8.17 – 8.13 (m, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.70 – 7.60 (m, 4H), 7.54 (d, J = 8.4 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.18 – 7.13 (m, 2H), 7.03 (d, J = 8.8 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 146.1, 135.8, 134.2, 133.8, 131.5, 129.1, 129.0, 128.6, 128.0, 127.7, 127.5, 127.3, 127.2, 125.9, 125.8, 122.2, 115.8, 105.8; HRMS (ESI) m/z calcd for C₂₀H₁₇N₂O₂S⁺ (M+H)⁺ 349.1005, found 349.1002.

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N’-(naphthalen-1-yl)naphthalene-1-sulfonohydrazide:
Yield: 58% (60.5 mg); yellow oil; IR (KBr): 1637, 1383, 1292, 1161, 1024, 995, 781, 713 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 10.01 (s, 1H), 8.85 (d, J = 8.4 Hz, 1H), 8.30 (s, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 6.6 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.75 – 7.68 (m, 3H), 7.61 – 7.59 (m, 1H), 7.40 (d, J = 6.6 Hz, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.92 (d, J = 7.8 Hz, 1H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 142.9, 134.2, 133.6, 133.3, 133.0, 129.3, 128.3, 127.6, 127.1, 126.2, 125.3, 125.1, 124.7, 123.9, 123.8, 121.5, 121.1, 118.3, 106.0; HRMS (ESI) m/z calcd for C₂₀H₁₇N₂O₂S⁺ (M+H)⁺ 349.1005, found 349.1004.

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N’-(9,9-dimethyl-9H-fluoren-3-yl)-9,9-dimethyl-9H-fluorene-2-sulfonohydrazide:
Yield: 63% (90.7 mg); light yellow oil; IR (KBr): 2960, 1613, 1446, 1300, 1212, 1157, 1026, 1001, 761, 735, 670, 567 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 9.62 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.96 – 7.92 (m, 3H), 7.88 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.21 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 6.75 – 6.63 (m, 2H), 1.39 (s, 6H), 1.19 (s, 6H), ¹³C
NMR (150 MHz, DMSO-d6) δ = 154.2, 153.7, 152.3, 148.3, 143.1, 139.0, 137.8, 136.9, 129.9, 128.8, 127.4, 126.8, 126.7, 125.5, 123.0, 122.4, 122.0, 121.2, 120.7, 120.3, 118.6, 111.8, 106.6, 46.8, 46.0, 27.0, 26.3; HRMS (ESI) m/z calcd for C_{30}H_{29}N_{2}O_{2}S + (M+H)^+ 481.1944, found 481.1950.

4-methyl-N’-(4-methyl-2-oxo-2H-chromen-7-yl)-2-oxo-2H-chromene-7-sulfonohydrazide:
Yield: 53% (65.5 mg); yellow solid; mp: 257.1-260.3 °C; IR (KBr): 3251, 2382, 1726, 1618, 1393, 1304, 1162, 864, 583 cm⁻¹; ¹H NMR (600 MHz, DMSO-d6) δ = 10.16 (s, 1H), 8.54 (s, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.71 (s, 1H), 7.50 (d, J = 9.0 Hz, 1H), 6.78 (d, J = 9.0 Hz, 1H), 6.59 (d, J = 8.4 Hz, 2H), 6.04 (s, 1H), 2.47 (s, 3H), 2.31 (s, 3H); ¹³C NMR (150 MHz, DMSO-d6) δ = 160.4, 159.1, 154.6, 153.6, 152.6, 152.3, 152.0, 141.2, 126.9, 126.2, 123.3, 123.0, 116.8, 115.6, 111.6, 109.7, 109.5, 98.3, 18.2, 18.1; HRMS (ESI) m/z calcd for C_{20}H_{17}N_{2}O_{6}S (M+H)^+ 413.0802, found 413.0803.

(1S,4R)-4,7,7-trimethyl-3-oxo-N-(4-((2-(4-((1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxamido)phenyl)hydrazinyl)sulfonyl)phenyl)-2-oxabicyclo[2.2.1]heptane-1-carboxamide:
Yield: 58% (110.8 mg); light yellow oil; IR (KBr): 1788, 1642, 1529, 1440, 1322, 1267, 1162, 1099, 991, 923, 782, 687 cm⁻¹; ¹H NMR (600 MHz, DMSO-d6) δ = 10.24 (s, 1H), 9.55 (s, 1H), 9.47 (s, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.56 (s, 1H), 7.38 (d, J = 9.0 Hz, 2H), 6.74 (d, J = 9.0 Hz, 2H), 1.05 (s, 9H), 1.03 (d, J = 2.4 Hz, 8H), 0.91 (s, 5H), 0.88 (s, 4H); ¹³C NMR (150 MHz, DMSO-d6) δ = 178.0,
177.8, 165.9, 164.5, 141.6, 133.8, 129.5, 128.3, 122.1, 120.6, 112.4, 91.8, 91.7, 54.5, 54.4, 53.7, 53.4, 29.9, 29.8, 28.3, 16.4, 16.3, 9.5; HRMS (ESI) m/z calcd for C₃₂H₃₉N₄O₈S⁺ (M+H)⁺ 639.2483, found 639.2483.

![Chemical Structure](image)

(E)-1-(p-tolyl)-2-tosyl diazene:
IR (KBr): 2361, 1923, 1596, 1459, 1338, 1164, 1039, 885, 808, 656, 579 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 7.86 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.2 Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 147.1, 146.4, 145.8, 130.2, 130.1, 129.8, 124.6, 21.8, 21.7 (5); HRMS (ESI) m/z calcd for C₁₄H₁₃N₂O₂S⁺ (M+H)⁺ 275.0849, found 275.0857.

![Chemical Structure](image)

4-methyl-1,1'-biphenyl:
IR (KBr): 2292, 2361, 1654, 1486, 1262, 1108, 1036, 820, 757, 697 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆) δ = 7.50 (d, J = 7.2 Hz, 4H), 7.22 (d, J = 7.2 Hz, 4H), 2.30 (s, 6H); ¹³C NMR (150 MHz, DMSO-d₆) δ = 137.2, 136.4, 129.6, 126.3, 20.7; HRMS (ESI) m/z calcd for C₁₃H₁₃⁺ (M+H)⁺ 169.1012, found 169.1007.

![Chemical Structure](image)

(E)-1-methyl-4-styryl benzene:
IR (KBr): 2362, 2336, 1652, 1446, 1466, 1264, 1025, 966, 807, 747, 688, 529 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 7.50 (d, J = 7.2 Hz, 2H), 7.41 (d, J = 7.8 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.16 (d, J = 7.2 Hz, 2H), 7.10 – 7.04 (m, 2H), 2.35 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 137.5, 137.4, 134.5, 129.4, 128.6, 128.5, 127.6, 127.4, 126.4, 126.3, 21.3; HRMS (ESI) m/z calcd for C₁₃H₁₅⁺ (M+H)⁺ 195.1168, found 195.1166.

![Chemical Structure](image)

4,4'-dimethyl-1,1'-biphenyl:
IR (KBr): 2922, 2854, 2361, 2336, 1648, 1452, 1397, 1270, 1030, 829, 670, 547 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ = 7.60-7.57 (m, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.46 – 7.41 (m, 2H), 7.36 – 7.31 (m, 1H), 7.25 (t, J = 3.6 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ = 129.5, 128.7, 128.6(8), 127.2, 127.1, 127.0, 126.9, 126.8, 21.1; HRMS (ESI) m/z calcd for C₁₄H₁₅⁺ (M+H)⁺ 183.1168, found 183.1161.
6. Copies of $^1$H NMR, $^{13}$C NMR
$^1$H NMR (400 MHz, DMSO-d$_6$)

$^1$C NMR (100 MHz, DMSO-d$_6$)

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