Supporting Information
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Reactions of Heterocyclic Ketene Aminals with 2-(3-Oxoisobenzofuran-1(3\(H\))-ylidene)malononitrile: Synthesis of a Novel Kind of Polyfunctionalized 1,4-Dihydropyridine-Fused 1,3-Diazaheterocycles

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Supporting Information

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I) General experimental information

All reagents were used as received from commercial sources without further purification or prepared as described in the literature. *N*, *N*-Dimethylformamide and acetonitrile were dried with 4Å molecular sieve before use. Reactions were stirred using Teflon-coated magnetic stirring bars. Analytical TLC was performed with 0.20 mm silica gel 60F plates with 254 nm fluorescent indicator. TLC plates were visualized by ultraviolet light. Melting points are uncorrected. Infrared spectra were recorded on a JASCO FT/IR-480 plus Fourier transform spectrometer. NMR spectra were measured in CDCl₃, DMSO-d₆, CD₃OD (all with TMS as internal standard) on a Bruker AV300 (¹H at 300 MHz, ¹³C at 75 MHz) magnetic resonance spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were in Hz. High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ/FT mass spectrometer or a GCT mass spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

II) General experimental procedure for the preparation of 1,3-diazaheterocycles

The starting materials, heterocyclic ketene aminals 1a-o, were prepared by reactions of the corresponding ketene mecaptans with 1, 2-ethanediamine or 1, 3-propanediamine as described by the literature.¹⁻³ 2-(3-oxoisobenzofuran-1(3H)-ylidene) Malononitrile was prepared according to Moore’s protocol.²

Heterocyclic ketene aminals 1a-o (1mmol) and 2-(3-oxoisobenzofuran-1(3H)-ylidene) malononitrile (0.196 g, 1 mmol) were stirred in *N*, *N*-dimethylformamide (5 ml) at 120 ºC until the reaction was complete as monitored by TLC (c.a. 2-12 hr) and then was cooled to room temperature. Solvents were removed with water in vacuo and the resulting solids were subjected to recrystallization (methyl alcohol / ether, or acetonitrile) to provide the desired fused heterospiro compounds 3a-o.
III) Characterization data for the 1, 3-diazaheterocycles

5-amino-8-benzoyl-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3a)

Starting with 1a (0.198 g, 1.05mmol) and 2 (0.206 g, 1.05mmol) in DMF (10 ml), 3a was obtained as a yellow solid (0.385 g, 95%) after recrystallization from CH3OH / Et2O. mp 342-343 ºC. IR (KBr): 3648, 3397 (NH), 2190 (CN), 1648 (C=O), 1311 (C-O-C) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ = 9.31 (s, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.35-7.30 (m, 2H), 7.24-7.20 (m, 1H), 7.21-7.14 (m, 1H), 7.01 (d, J =7.5 Hz, 1H), 4.12-4.02 (m, 2H), 3.98-3.81 (m, 2H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 193.0, 167.2, 154.8, 152.7, 138.8, 136.5, 136.4, 134.7, 132.0, 130.6, 130.2, 129.3, 128.8, 127.7, 116.7, 104.8, 79.7, 48.8, 46.2. ESI-HRMS: m/z caled for C₂₂H₁₇N₄O₃ [M+H⁺] 385.1301, found 385.1290.

5-amino-8-(p-methylbenzoyl)-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3b)

Starting with 1b (0.209 g, 1.03mmol) and 2 (0.203 g, 1.03mmol) in DMF (10 ml), 3b was obtained as a yellow solid (0.367 g, 89%) after recrystallization from CH₃OH / Et₂O. mp 317-319 ºC. IR (KBr): 3378, 3314 (NH), 2209 (CN), 1645, 1604 (C=O), 1306, 1273, 1172 (C-O-C) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ = 9.31 (s, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.34-7.23 (m, 2H), 7.02-6.99 (m, 3H), 4.17-3.99 (m, 2H), 3.91-3.79 (m, 2H), 2.23 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 192.3, 166.9, 154.1, 152.7, 142.3, 136.7, 135.7, 133.4, 130.5, 130.4, 129.3, 129.1, 128.5, 128.4, 117.1, 106.2, 48.2, 45.9, 21.2. ESI-HRMS: m/z caled for C₂₃H₁₉N₄O₃ [M+H⁺] 399.1452, found 399.1451.

5-amino-8-(p-methoxybenzoyl)-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3c)
Starting with 1c (0.227g, 1.04mmol) and 2 (0.204 g, 1.04mmol) in DMF (10 ml), 3c was obtained as a pale yellow solid (0.414g, 96%) after recrystallization from CH$_2$OH / Et$_2$O. mp 229-231 ºC. IR (KBr): 3386 (NH), 2216 (CN), 1648, 1602 (C=O), 1310, 1258, 1167 (C-O-C) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ = 7.78 (d, $J$= 7.2 Hz, 1H), 7.68 (d, $J$= 8.4 Hz, 2H), 7.34-7.24 (m, 2H), 6.98 (d, $J$= 7.2 Hz, 1H), 6.74 (d, $J$= 8.4 Hz, 2H), 4.26-4.06 (m, 2H), 3.93-3.80 (m, 2H), 3.72 (s, 3H). $^{13}$C NMR (75MHz, DMSO-d$_6$): $\delta$ = 191.2, 166.9, 162.6, 153.9, 152.6, 136.5, 133.7, 131.6, 130.7, 130.4, 129.2, 128.6, 116.9, 113.1, 106.4, 76.4, 61.9, 55.4, 47.8, 46.1. ESI-HRMS: m/z Calcd for C$_{23}$H$_{19}$N$_4$O$_4$ [M+H$^+$] 415.1406, found 415.1402.

5-amino-8-(p-chlorobenzoyl)-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3d)

Starting with 1d (0.230g, 1.03mmol) and 2 (0.203g, 1.04mmol) in DMF (10 ml), 3d was obtained as a yellow solid (0.414g, 96%) after recrystallization from CH$_3$OH / Et$_2$O. mp 332-333 ºC. IR (KBr): 3637, 3371, 3316 (NH), 2214 (CN), 1642 (C=O), 1174, 1089, 1010 (C-O-C) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ = 8.90 (s, 1H), 7.77 (d, $J$= 7.5 Hz, 1H), 7.65 (d, $J$= 8.4 Hz, 2H), 7.36-7.24 (m, 2H), 7.01 (d, $J$= 7.2 Hz, 1H), 6.75 (d, $J$= 8.7 Hz, 2H), 4.13-3.98 (m, 2H), 3.91-3.79 (m, 2H). $^{13}$C-NMR (75 MHz, DMSO-d$_6$): $\delta$ = 191.2, 166.7, 154.4, 152.7, 137.8, 136.9, 136.1, 132.4, 130.7, 130.2, 130.2, 129.5, 128.4, 127.6, 117.0, 47.7, 45.4. ESI-HRMS: m/z Calcd for C$_{22}$H$_{16}$N$_4$O$_3$Cl [M+H$^+$] 419.0905, found 419.0906.

5-amino-8-(p-flurobenzoyl)-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3e)

Starting with 1e (0.207g, 1.00mmol) and 2 (0.197g, 1.00mmol) in DMF (10 ml), 3e was obtained as a yellow solid (0.367g, 91%) after recrystallization from MeOH / Et$_2$O. mp > 340 ºC (partly decomposed). IR (KBr): 3365, 3321 (NH), 1622 (C=O), 1311, 1276, 1164, 1027 (C-O-C) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ = 7.74 (d, $J$= 6.9 Hz, 1H), 7.60-7.55 (m, 2H), 7.38-7.33 (m, 1H), 7.30-7.25 (m, 1H), 7.06-6.96 (m, 3H), 4.11-3.95 (m, 2H), 3.90-3.80 (m, 2H). $^{13}$C NMR (75 MHz, DMSO-d$_6$): $\delta$ = 191.2, 166.8, 165.6, 154.4, 152.7, 136.7, 135.4, 131.5, 131.4, 130.6, 130.3, 129.4, 128.6, 117.0, 114.8, 114.5, 100.0, 45.7. ESI-HRMS: m/z Calcd for C$_{22}$H$_{16}$FN$_4$O$_3$ [M+H$^+$] 403.1206, found 403.1199.

8-(1, 1'-biphenyl) -5-amino-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3f)
Starting with 1f (0.268g, 1.01mmol) and 2 (0.199g, 1.01mmol) in DMF (10 ml), 3f was obtained as a yellow solid (0.408g, 87%) after recrystallization from CH₃OH / Et₂O. mp 306-307 ºC. IR (KBr): 3363, 3331 (NH), 2211 (CN), 1633, 1603 (C=O), 1311 (s) (C-O-C) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ = 7.73 (d, J= 7.5 Hz, 1H), 7.63-7.59 (m, 4H), 7.47-7.44 (m, 4H), 7.40-7.30 (m, 2H), 7.04 (d, J= 7.2 Hz, 1H), 4.22-4.03 (m, 2H), 3.94-3.79 (m, 2H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 192.0, 166.8, 154.4, 152.7, 142.9, 139.2, 137.7, 137.0, 132.5, 130.6, 130.2, 129.5, 129.1, 128.9, 128.3, 128.0, 126.7, 125.8, 117.1, 105.1, 77.9, 48.6, 45.5. ESI-HRMS: m/z calcd for C₂₈H₂₁N₄O₃ [M+H⁺] 461.1614; found 461.1608.

**5-amino-8-nitro-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo [1, 2-a] pyridine-7, 1'-isobenzofuran]-6-carbonitrile (3g)**

Starting with 1g (0.130g, 1.01mmol) and 2 (0.197g, 1.01mmol) in DMF (10 ml), 3g was obtained as a yellow solid (0.322, 98%) after recrystallization from CH₃OH / Et₂O. mp 237-238 ºC. IR (KBr): 3397 (NH), 2224 (CN), 1650 (C=O), 1556, 1320 (NO₂), 1043 (C-O-C) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ = 9.54 (s, 1H), 8.03 (d, J= 7.5 Hz, 1H), 7.67-7.62 (m, 1H), 7.55-7.50 (m, 1H), 7.22 (d, J= 7.8 Hz, 1H), 4.23-4.03 (m, 2H), 3.99-3.92 (m, 2H). ¹³C-NMR (75 MHz, DMSO-d₆): δ = 166.5, 154.1, 152.1, 150.6, 138.6, 132.3, 130.2, 128.9, 128.4, 127.4, 115.5, 112.9, 89.8, 45.2, 43.8. ESI-HRMS: m/z calcd for C₁₅H₁₂N₅O₄ [M+H⁺] 326.0889, found 326.0906.

**5-amino-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo[1, 2-a]pyridine-7, 1'-isobenzofuran]-6,8-dicarbonitrile (3h)**

Starting with 1h (0.110g, 1.01mmol) and 2 (0.198g, 1.01mmol) in DMF (10 ml), 3h was obtained as a yellow solid (0.303g, 98%) after recrystallization from CH₃OH / Et₂O. mp > 300 ºC (decomposed). IR (KBr): 3410, 3330, 3148 (NH), 2217 (CN), 1651 (C=O), 1311, 1253, 1035 (C-O-C) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ = 9.42 (s, 1H), 8.04 (d, J= 7.5 Hz, 1H), 7.73-7.68 (m, 1H), 7.62-7.57 (m, 1H), 7.32 (d, J=7.5 Hz, 1H), 4.05-3.83 (m, 4H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 166.4, 162.0, 153.5, 152.2, 136.5, 132.4, 130.6, 129.8, 129.6, 129.1, 116.4, 116.2, 80.4, 72.2, 52.0, 46.2. ESI-HRMS: m/z calcd for C₁₆H₁₂N₅O₂ [M+H⁺] 306.0991, found 306.0985.

**ethyl 5-amino-6-cyano-3'-oxo-2, 3-dihydro-1H, 3'H-spiro [imidazo[1, 2-a]pyridine-7,**
1'-isobenzofuran]-8-carboxylate (3i)

Starting with 1i (0.157 g, 1.01 mmol) and 2 (0.198 g, 1.01 mmol) in DMF (10 ml), 3i was obtained as a yellow solid (0.353 g, 99%) after recrystallization from CH$_3$OH / Et$_2$O. mp 206-208 °C. IR (KBr): 3360, 3255 (NH), 2219 (CN), 1694 (C=O), 1622 (C=O), 1310, 1257, 1161, 1032 (C-O-C) cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ = 8.48 (s, 1H), 7.77 (d, $J= 7.8$ Hz, 1H), 7.56-7.44 (m, 2H), 7.09 (d, $J=7.2$ Hz, 1H), 4.20-4.04 (m, 2H), 3.91-3.85 (m, 2H), 3.66 (q, $J= 7.1$ Hz, 2H). $^1$C NMR (75 MHz, DMSO-d$_6$): $\delta = 166.8, 164.1, 161.7, 155.9, 152.4, 139.9, 131.1, 130.8, 129.8, 127.7, 127.6, 116.5, 88.5, 87.0, 59.0, 45.0, 43.1, 13.0. ESI-MS: m/z Calcd for C$_{18}$H$_{17}$N$_4$O$_4$ [M+H$^+$] 353.1250, found: 353.1243.

6'-amino-9'-nitro-3-oxo-1', 2', 3', 4'-tetrahydro-3H-spiro[isobenzofuran-1, 8'-pyrido[1, 2-a]pyrimidine]-7'-carbonitrile (3j)

Starting with 1j (0.144 g, 1.01 mmol) and 2 (0.197 g, 1.01 mmol) in DMF (10 ml), 3j was obtained as a yellow solid (0.338 g, 99%) after recrystallization from CH$_3$OH / Et$_2$O. mp 269-270 °C. IR (KBr): 3384, 3304, 3209 (NH), 2222 (CN), 1670, 1624 (C=O), 1567, 1339 (NO$_2$), 1223, 1083, 1016 (C-O-C) cm$^{-1}$. $^1$H-NMR (300 MHz, DMSO-d$_6$): $\delta$ = 10.77 (s, 1H), 8.03 (d, $J= 7.5$ Hz, 1H), 7.66-7.61 (m, 2H), 7.53-7.48 (m, 1H), 7.19 (d, $J= 7.5$ Hz, 1H), 4.06-4.02 (m, 2H), 3.60-3.57 (m, 2H), 2.07 (m, 2H). $^1$C-NMR (75 MHz, DMSO-d$_6$): $\delta = 166.5, 153.4, 152.8, 150.1, 139.5, 132.3, 130.4, 128.5, 128.1, 127.0, 114.3, 113.2, 89.9, 42.6, 18.1. ESI-MS: m/z Calcd for C$_{16}$H$_{14}$N$_5$O$_4$ [M+H$^+$] + 340.1046; found: 340.1031.

6'-amino-9'-benzoyl-3-oxo-1', 2', 3', 4'-tetrahydro-3H-spiro[isobenzofuran-1, 8'-pyrido [1, 2-a]pyrimidine]-7'-carbonitrile (3k)

Starting with 1k (0.204 g, 1.01 mmol) and 2 (0.198 g, 1.01 mmol) in DMF (10 ml), 3k was obtained as a yellow solid (0.383 g, 95%) after recrystallization from CH$_3$OH / Et$_2$O. mp 191-193°C. IR (KBr): 3673, 3425 (NH), 2216 (CN), 1631, 1613 (C=O), 1335, 1280, 1044, 1016 (C-O-C) cm$^{-1}$. $^1$H-NMR (300 MHz, MeOD-d$_4$): $\delta = 7.65$ (d, $J= 7.5$ Hz, 1H), 7.36-7.21 (m, 5H), 7.13-7.08 (m, 2H), 7.01 (d, $J= 7.5$ Hz, 1H), 4.09-3.98 (m, 2H), 3.41 (m, 2H), 2.08-2.05 (m, 2H). $^1$C-NMR (75 MHz, DMSO-d$_6$): $\delta = 194.1, 166.9, 154.9, 152.0, 140.2, 137.4, 133.0, 131.9, 131.8, 130.8, 130.6, 129.3, 128.6, 128.0, 117.3, 105.5, 67.6, 44.1, 19.0. ESI-MS: m/z Calcd for C$_{23}$H$_{19}$N$_4$O$_3$ [M+H$^+$] + 399.1457; found: 399.1438.
6'-amino-9'-(p-methylbenzoyl)-3-oxo-1', 2', 3', 4'-tetrahydro-3H-spiro [isobenzofuran-1, 8'-pyrido [1, 2-a] pyrimidine]-7'-carbonitrile (3l)

Starting with 1l (0.218g, 1.01mmol) and 2 (0.197g, 1.01mmol) in DMF (10 ml), 3l was obtained as a yellow solid (0.375g, 90%) after recrystallization from CH₃OH / Et₂O. mp 211-213 ºC. IR (KBr): 3338, 3288 (NH), 2216 (CN), 1630, 1606 (C=O), 1339, 1281, 1037 (C-O-C) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆): δ = 7.65 (d, 7.5 Hz, 1H), 7.31-7.22 (m, 2H), 7.22-7.15 (m, 2H), 6.96 (d, 7.2 Hz, 1H), 6.89 (d, 8.1 Hz, 2H), 4.06-3.96 (m, 2H), 3.43-3.31 (m, 2H), 2.18 (s, 3H), 2.08-1.92 (m, 2H). ¹³C-NMR (75 MHz, DMSO-d₆): δ = 193.6, 167.0, 155.5, 154.6, 151.4, 141.1, 137.4, 137.0, 133.1, 130.1, 129.8, 128.5, 128.3, 127.9, 117.4, 105.0, 82.0, 48.6, 43.2, 21.0, 18.7. ESI-HRMS: m/z Calcd for C₂₄H₂₁N₄O₃⁺ [M+H]⁺ 413.1614; found: 413.1608.

6'-amino-9'-(p-methoxybenzoyl)-3-oxo-1', 2', 3', 4'-tetrahydro-3H-spiro [isobenzofuran-1, 8'-pyrido [1, 2-a] pyrimidine]-7'-carbonitrile (3m)

Starting with 1m (0.234g, 1.01mmol) and 2 (0.198g, 1.01mmol) in DMF (10 ml), 3m was obtained as a pale yellow solid (0.415g, 96%) after recrystallization from CH₃OH / Et₂O. mp 191-193 ºC. IR (KBr): 3389 (NH), 2203 (CN), 1649 (C=O), 1336, 1262, 1169 (C-O-C) cm⁻¹. ¹H-NMR (300 MHz, DMSO-d₆): δ = 7.77 (d, 7.5 Hz, 1H), 7.59 (d, 8.4 Hz, 2H), 7.40-7.28 (m, 2H), 7.00-6.88 (m, 2H), 6.74 (d, 8.7 Hz, 2H), 4.18-3.94 (m, 2H), 3.74 (s, 3H), 3.44-3.23 (m, 2H), 2.16-1.98 (m, 2H). ¹³C-NMR (75 MHz, DMSO-d₆): δ = 191.2, 166.5, 163.0, 154.1, 150.1, 135.9, 132.5, 131.6, 131.1, 130.8, 130.5, 129.6, 129.1, 116.1, 113.3, 108.1, 80.2, 55.5, 45.0, 18.4. ESI-HRMS: m/z Calcd for C₂₄H₂₁N₄O₃⁺ [M+H]⁺ 429.1563; found: 429.1554.

6'-amino-9'-(p-chlorobenzoyl)-3-oxo-1', 2', 3', 4'-tetrahydro-3H-spiro [isobenzofuran-1, 8'-pyrido [1, 2-a] pyrimidine]-7'-carbonitrile (3n)
Starting with 1n (0.238g, 1.01mmol) and 2 (0.198g, 1.01mmol) in DMF (10 ml), 3n was obtained as a yellow solid (0.385g, 88%) after recrystallization from CH$_2$OH / Et$_2$O. mp 235-237 °C. IR (KBr): 3285 (m) (NH), 2213 (CN), 1631 (C=O), 1606 (s), 1561 (s), 1528 (s) (Ar), 1338 (s), 1281 (m), 1088 (m) (C-O-C) cm$^{-1}$. $^1$H-NMR (300 MHz, DMSO-d$_6$): $\delta$ = 7.64 (d, $J$= 7.2 Hz, 1H), 7.32-7.19 (m, 4H), 7.11-7.09 (m, 2H), 6.99 (d, $J$= 7.2 Hz, 1H), 4.13-3.90 (m, 2H), 3.50-3.31 (m, 2H), 3.08-1.94 (m, 2H). $^{13}$C-NMR (75 MHz, DMSO-d$_6$): $\delta$ = 192.7, 166.9, 154.6, 152.1, 139.4, 137.2, 135.3, 132.6, 130.7, 130.2, 130.1, 129.9, 128.6, 127.4, 117.8, 103.7, 83.2, 48.7, 42.9, 18.6. ESI-HRMS: $m/z$ Calcd for C$_{23}$H$_{18}$ClN$_4$O$_3$ $^+[M+H]^+$ 433.1067; found: 433.1075.

6'-amino-9'-(p-bromobenzoyl)-3-oxo-1', 2', 3', 4'-tetrahydro-3H-spiro [isobenzofuran-1, 8'-pyrido [1, 2-a] pyrimidine]-7'-carbonitrile (3o)

Starting with 1o (0.286g, 1.02mmol) and 2 (0.200g, 1.02mmol) in DMF (10 ml), 3o was obtained as a yellow solid (0.458g, 94%) after recrystallization from CH$_2$OH / Et$_2$O. mp 205-207 °C. IR (KBr): 3282 (NH), 2212 (CN), 1631, 1604 (C=O), 1337, 1280, 1068 (C-O-C) cm$^{-1}$. $^1$H-NMR (300 MHz, DMSO-d$_6$): $\delta$ = 7.63 (d, $J$= 6.9 Hz, 1H), 7.31-7.17 (m, 6H), 7.00 (d, $J$= 6.6 Hz, 1H), 4.02-4.01 (m, 2H), 3.42-3.40 (m, 2H), 2.03-2.00 (m, 2H). $^{13}$C-NMR (75 MHz, DMSO-d$_6$): $\delta$ = 192.7, 166.8, 156.1, 154.5, 152.1, 139.7, 137.2, 132.4, 130.6, 130.2, 130.1, 129.9, 128.5, 124.2, 117.2, 103.2, 83.5, 48.6, 42.8, 18.6. ESI-HR-MS: $m/z$ Calcd for C$_{23}$H$_{18}$N$_4$O$_3$Br $^+[M+H]^+$ 477.0562; found: 477.0571.

IV) Copies of $^1$H and $^{13}$C NMR Spectra

![NMR Spectra Diagram]

Current Data Parameters
NAME: xwy-090
EXPNO: 40
PROCNO: 1

F2 - Acquisition Parameters
Date: 20090206
Time: 17.37
INSTRUM: spect
PROBHD: 5 mm DUL 13C-1
POLARIZATION: ref:
SOLVENT: DMSO
NS: 16
DS: 0
SWH: 8992.806 Hz
FIDRES: 0.137219 Hz
AQ: 3.6438515 sec
RG: 362
DW: 55.600 usec
DE: 6.00 usec
TE: 294.8 K

F2 - Processing Parameters
SI: 32768
SF: 300.1300003 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
Current Data Parameters
NAME    xwy-062
EXPNO  20
PROCNO  1

F2 - Acquisition Parameters
Date    20081222
Time    17:09
INSTRUM spect
PROBHD  5 mm DUL 13C-1
FID      1
TD      65536
SOLVENT DMSO
NS       16
DS       0
SMW     8921.806 Hz
FDRES   0.137219 Hz
AQ      3.6438515 sec
RG      362
DW      55.600 usec
DE      6.00 usec
TE      294.7 K
D1      1.00000000 sec
MCREST 0.00000000 sec
MCWRK  0.01500000 sec

======== CHANNEL f1 ========
NUC1    1H
P1      7.00 usec
PL1    -1.00 dB
SFO1  300.1324010 MHz

F2 - Processing parameters
SI     32768
SF     300.130000 MHz
SWP1  300.130000 MHz

F2 - Processing parameters
SI     32768
SF     300.130000 MHz

N
H
N
H2N
O
O
CN
Cl
N
H
N
H2N
O
O
CN
Cl
Current Data Parameters
NAME: xwy-034
EXPNO: 10
PROCNO: 1

**F2 - Acquisition Parameters**
- Date: 20081116
- Time: 15:59
- INSTRUM: spect
- PROBHD: 5 mm DUL 13C-1
- FIDRES: 0.137219 Hz
- AQ: 3.6438515 sec
- DW: 55.600 usec
- DE: 6.00 usec
- TE: 297.6 K
- MCREST: 1.00000000 sec
- MCWRK: 0.00000000 sec

**F2 - Processing parameters**
- SI: 32768
- SF: 300.1300001 MHz
- SWB: 0
- LB: 0.30 Hz
- GB: 0
- PC: 1.00

**NMR Spectra**
- ppm values range from 2.00 to 7.50
- Peaks at 2.00, 2.05, 7.00, 300.1324010 MHz
- Bruker equipment

**Chemical Structures**
- Molecular structures of compounds with peaks at specific ppm values
- Functional groups: NH, H2N, O, CN, Br