A General Approach to Non-Fullerene Electron Acceptors Based on the Corannulene Motif

Viktor Barát, Maja Budanović, Dzeneta Halilović, June Huh, Richard D. Webster, Surendra H. Mahadevegowda and Mihaiela C. Stuparu*

Email: mstuparu@ntu.edu.sg

Experimental Details

Reactions requiring anhydrous and inert conditions were carried out under an argon atmosphere using oven-dried glassware. Anhydrous DCM was freshly distilled from CaH$_2$ under nitrogen, anhydrous THF was freshly distilled from sodium metal and benzophenone under nitrogen. Anhydrous ethanol was distilled from activated magnesium under nitrogen. All other chemicals were obtained commercially and used as received. 3-Chloroperbenzoic acid was used as a 77% technical grade mixture. Column chromatography was carried out on silica gel 40–63 microns. Reactions were monitored by thin-layer chromatography (TLC) on silica gel-coated aluminium plates (60 F254, Merck) and visualized with UV light ($\lambda = 254$ and 365 nm). Purity of the reported compounds was established by comparing the integrals of the peaks of the desired compounds to the ones arising from impurities. $^1$H NMR spectra were recorded at 300 or 400 MHz Bruker and JEOL ECA instruments (and the corresponding frequencies for $^{13}$C) in CDCl$_3$ unless otherwise noted. Chemical shifts are given in ppm and coupling constants in Hz (CDCl$_3$ $^1$H: 7.26 ppm, $^{13}$C: 77.23 ppm). High-resolution mass spectra (HRMS) were recorded by using JEOL Spiral TOF (JMSS3000) (MALDI) or Waters Q-Tof Premier spectrometer in ESI+ mode with TOF mass analyser.
Voltammetric measurements were performed using a Metrohm Autolab PGSTAT302N potentiostat in a three-electrode setup. A 1 mm diameter planar disk glassy carbon disk (GC, Cypress Systems) was used as a working electrode in conjunction with a platinum wire counter electrode (Metrohm) and a silver wire miniature reference electrode (eDAQ) connected to the test solution via a salt bridge containing 0.5 M tetra-\textit{n}-butylammonium hexafluorophosphate (\textit{n}Bu4NPF\textsubscript{6}) in DMF (Tedia). \textit{n}Bu4NPF\textsubscript{6} was synthetized through a standard procedure according to the literature\textsuperscript{1} and used as the supporting electrolyte. All voltammetric experiments were conducted under an argon atmosphere, at room temperature in a Faraday cage. Prior to each scan, the working electrode was cleaned by polishing with alumina oxide (grain size 0.3 \(\mu\)m) slurry on a Buehler Ultra-pad polishing cloth, rinsing with acetone, and then dried with a lint free tissue. In accordance with IUPAC recommendations, the absolute potentials were calibrated using ferrocene (Fc) as an internal reference, which was added to the test solution at the end of the measurements.

\textbf{Monosulfide 1}

A mixture of monobromocorannulene (28 mg, 0.087 mmol), 4-(methylthio)phenylboronic acid (25 mg, 0.15 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (11 mg, 0.01 mmol) and Na\textsubscript{2}CO\textsubscript{3} (212 mg, 2 mmol) in degassed dioxane:water 1:1 (2.2 mL) was heated to 90°C overnight. The mixture was diluted with DCM and washed three times with water. The organic phase was dried over anhydrous MgSO\textsubscript{4}, filtered and concentrated. The crude product was purified with column chromatography using hexane:DCM 4:1. A colourless solid was obtained: 20 mg (0.053 mmol), 61% yield.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.87 (s, 1H), 7.85 – 7.77 (m, 8H), 7.74 (d, \(J = 8.3\) Hz, 2H), 7.46 (d, \(J = 8.3\) Hz, 2H), 2.60 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 141.33, 138.48, 136.48, 136.65, 136.54,
A solution of **monosulfide 1** (25.8 mg, 0.069 mmol) and mCPBA (15.5 mg, 0.07 mmol) in DCM (2.5 mL) was stirred at room temperature for 60 min. The reaction mixture was washed twice with aq. Na$_2$CO$_3$, the organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using DCM:MeOH 95:5. An off-white solid was obtained: 20.0 mg (0.051 mmol), 75% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.2$ Hz, 2H), 7.90 (s, 1H), 7.89 – 7.72 (m, 10H), 2.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.14, 142.87, 140.28, 136.41, 135.94, 135.75, 135.51, 131.21, 131.11, 131.05, 130.75, 129.24, 127.90, 127.75, 127.63, 127.41, 127.38, 127.14, 127.11, 126.68, 126.66, 124.21, 44.17. HRMS (MALDI-TOF) m/z calcd for C$_{27}$H$_{16}$S [M$^+$]: 372.0967, found: 372.0961.

**Monosulfoxide 2**

A solution of **monosulfide 1** (25.8 mg, 0.069 mmol) and mCPBA (15.5 mg, 0.07 mmol) in DCM (2.5 mL) was stirred at room temperature for 60 min. The reaction mixture was washed twice with aq. Na$_2$CO$_3$, the organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using DCM:MeOH 95:5. An off-white solid was obtained: 20.0 mg (0.051 mmol), 75% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.2$ Hz, 2H), 7.90 (s, 1H), 7.89 – 7.72 (m, 10H), 2.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.14, 142.87, 140.28, 136.41, 135.94, 135.75, 135.51, 131.21, 131.11, 131.05, 130.75, 129.24, 127.90, 127.75, 127.63, 127.41, 127.38, 127.14, 127.11, 126.68, 126.66, 124.21, 44.17. HRMS (MALDI-TOF) m/z calcd for C$_{27}$H$_{17}$OS [M+H$^+$]: 389.0994, found: 389.0976.

**Monosulfone 3**

A solution of **monosulfide 1** (26.4 mg, 0.071 mmol) and mCPBA (95.0 mg, 0.42 mmol) in DCM (2.5 mL) was stirred at room temperature for 60 min. The reaction mixture was washed twice with aq. Na$_2$CO$_3$, the organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using DCM. An off-white solid was obtained: 20.9 mg (0.052 mmol), 73% yield.
$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 8.14 (d, \(J = 8.3\) Hz, 2H), 7.99 (d, \(J = 8.3\) Hz, 2H), 7.91 (s, 1H), 7.89 – 7.78 (m, 7H), 7.73 (d, \(J = 8.9\) Hz, 1H), 3.18 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 145.55, 139.77, 139.55, 136.46, 136.39, 135.95, 135.94, 135.49, 131.27, 131.17, 130.99, 130.60, 128.87, 128.10, 128.04, 127.88, 127.75, 127.58, 127.44, 127.18, 127.13, 127.10, 126.38, 44.84.

HRMS (MALDI-TOF) m/z calcd for C$_{27}$H$_{16}$O$_2$S [M]$^+$: 404.0865, found: 404.0827.

**Monosulfide 4**

To a solution of thiocresol (50 mg, 0.4 mmol) in DMI (5 mL) under argon was added NaH (0.4 mmol) and stirred for 30 minutes. Monobromocorannulene (57 mg, 0.17 mmol) was added and the mixture was heated to 80°C overnight. After cooling, toluene (40 mL) was added and washed with 3x50 mL water. The organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using hexane. A colourless solid was obtained: 42 mg (0.11 mmol), 65% yield.

$^1$H NMR (400 MHz, CDCl$_3$) \(\delta\) 8.00 (d, \(J = 8.8\) Hz, 1H), 7.85 (s, 1H), 7.82-7.73 (m, 6H), 7.67 (d, \(J = 8.7\) Hz, 1H), 7.43 (d, \(J = 8.2\) Hz, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) \(\delta\) 137.15, 136.46, 136.11, 135.94, 135.74, 135.60, 134.81, 133.17, 132.14, 131.11, 131.06, 131.01, 130.80, 130.31, 130.00, 127.80, 127.59, 127.45, 127.29, 127.21, 126.65, 126.30, 21.32. HRMS (MALDI-TOF) m/z calcd for C$_{27}$H$_{16}$S [M]$^+$: 372.0967, found: 372.0952.

**Monosulfoxide 5**

A solution of monosulfide 4 (39.8 mg, 0.107 mmol) and mCPBA (23.9 mg, 0.107 mmol) in DCM (2 mL) was stirred at room temperature for 20 min. The reaction mixture was washed twice with aq. Na$_2$CO$_3$, the organic phase was dried over anhydrous MgSO$_4$, filtered and
concentrated. The crude product was purified with column chromatography using DCM:MeOH 9:1. An off-white solid was obtained: 36.2 mg (0.093 mmol), 87% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.51 (s, 1H), 7.98 (d, \(J = 8.8\) Hz, 1H), 7.90 – 7.74 (m, 9H), 7.31 (d, \(J = 8.1\) Hz, 2H), 2.37 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.21, 142.70, 142.01, 137.10, 136.18, 136.11, 135.51, 135.30, 131.78, 131.07, 130.89, 130.41, 129.83, 128.17, 128.07, 128.04, 127.96, 127.49, 127.31, 127.22, 126.81, 125.85, 124.79, 124.19, 21.60. HRMS (ESI+) m/z calcd for C\(_{27}\)H\(_{17}\)OS [M+H]\(^+\): 389.1000, found: 389.0999.

Monosulfone 6

A solution of monosulfide 4 (13.0 mg, 0.035 mmol) and mCPBA (50.0 mg, 0.223 mmol) in DCM (1 mL) was stirred at room temperature for 20 min. The reaction mixture was washed twice with aq. Na\(_2\)CO\(_3\), the organic phase was dried over anhydrous MgSO\(_4\), filtered and concentrated. The crude product was purified with column chromatography using DCM. An off-white solid was obtained: 6 mg (0.014 mmol), 55% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.81 (s, 1H), 8.44 (d, \(J = 8.9\) Hz, 1H), 8.03 (d, \(J = 8.4\) Hz, 2H), 7.92 – 7.77 (m, 7H), 7.31 (d, \(J = 8.2\) Hz, 2H), 2.37 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.33, 139.58, 138.58, 137.90, 136.43, 136.03, 135.31, 134.92, 132.49, 131.36, 131.18, 131.09, 130.16, 128.75, 128.69, 128.38, 128.27, 128.14, 127.92, 127.53, 127.41, 127.36, 126.19, 125.80, 21.76. HRMS (ESI+) m/z calcd for C\(_{27}\)H\(_{17}\)O\(_2\)S [M+H]\(^+\): 405.0949, found: 405.0980.

Pentasulfide 7

To a freshly prepared solution of NaOEt (1.0 mL EtOH and 53 mg (2.3 mmol) sodium) under argon was added thiocresol (288 mg, 2.3 mmol) and stirred for 40 minutes at room temperature.
The solution was concentrated, and the residue was dissolved in DMI (10 mL) and pentachlorocorannulene (98 mg, 0.23 mmol) was added. The mixture was stirred for 10 days under argon than diluted with 60 mL toluene and washed with 3x100 mL water. The organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using hexane:DCM 6:1. A yellow solid was obtained: 76 mg (0.08 mmol), 38% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.77 (s, 5H), 7.21 (d, $J = 8.1$ Hz, 10H), 7.08 (d, $J = 8.1$ Hz, 10H), 2.36 (s, 15H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.57, 136.39, 135.70, 131.83, 131.62, 130.33, 128.07, 21.41. HRMS (MALDI-TOF) m/z calcd for C$_{55}$H$_{40}$S$_5$ [M]$^+$: 860.1728, found: 860.1718. CCDC number: 1890565.

**Pentasulfone 8**

A solution of pentasulfide 7 (20.7 mg, 0.024 mmol) and mCPBA (161 mg, 0.72 mmol) in DCM (3.0 mL) was stirred at room temperature overnight. The reaction mixture was washed twice with aq. Na$_2$CO$_3$, the organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using CHCl$_3$. An off-white solid was obtained: 23.4 mg (0.023 mmol), 95% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.35 (s, 5H), 7.93 (d, $J = 8.4$ Hz, 10H), 7.31 (d, $J = 8.3$ Hz, 10H), 2.37 (s, 15H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.51, 142.57, 137.81, 137.31, 132.21, 130.62, 128.38, 125.90, 21.86; HRMS (ESI+) m/z calcd for C$_{55}$H$_{44}$NO$_{10}$S$_5$ [M+NH$_4$]$^+$: 1038.1569, found: 1038.1526. CCDC number: 1890567.

**Tetrasulfide 9**
A mixture of tetrabromocorannulene (113 mg, 0.2 mmol), 4-(methylthio)phenylboronic acid (536 mg, 3.2 mmol), Pd(PPh$_3$)$_4$ (92 mg, 0.08 mmol) and Na$_2$CO$_3$ (848 mg, 8 mmol) in degassed dioxane (11.2 mL) and water (4.4 mL) was heated to 120°C for 114 h. The mixture was diluted with DCM and washed three times with water. The organic phase was dried over anhydrous MgSO$_4$, filtered and concentrated. The crude product was purified with column chromatography using hexane:DCM 80:20. A pale yellow solid was obtained: 112 mg (0.15 mmol), 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J$ = 8.8 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.19 (d, $J$ = 5.0 Hz, 16H), 2.52 (s, 6H), 2.51 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.56, 138.46, 138.20, 137.19, 137.14, 135.45, 135.22, 135.18, 134.23, 132.10, 130.81, 130.60, 130.20, 127.44, 127.41, 127.34, 125.80, 15.76. HRMS (MALDI-TOF) m/z calcd for C$_{48}$H$_{34}$S$_4$ [M]$^+$: 738.1537, found: 738.1528.

**Tetrasulfone 10**

To a solution of tetrasulfide 9 (30.0 mg, 0.04 mmol) in DCM (4 mL) was added EtOAc (2 mL), urea-hydrogen peroxide complex (114 mg, 1.21 mmol), phthalic anhydride (180 mg, 1.21 mmol) and the resulting slurry was stirred for 18 hours. The mixture was quenched with water and extracted twice with DCM. The combined organic layers were washed with aq. Na$_2$CO$_3$, dried over anh. MgSO$_4$, filtered and concentrated. The crude product was purified by column chromatography using CHCl$_3$. A colourless solid was obtained: 27.1 mg (0.031 mmol), yield: 78%.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 – 7.85 (m, 10H), 7.54 – 7.43 (m, 12H), 3.13 (s, 6H), 3.11 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.70, 143.67, 139.83, 139.81, 137.92, 137.24, 135.52, 134.51, 132.37, 131.34, 129.96, 129.57, 128.46, 127.32, 127.26, 127.09, 44.65; HRMS (ESI$^+$) m/z calcd for C$_{48}$H$_{35}$O$_8$S$_4$ [M+H]$^+$: 867.1215, found: 867.1185.
**Tetrasulfide 11**

To a freshly prepared solution of NaOEt (1.5 mL EtOH and 62 mg (2.7 mmol) sodium) under argon was added thiocresol (335 mg, 2.7 mmol) and stirred for 40 minutes at room temperature. The solution was concentrated, and the residue was dissolved in DMI (11 mL) and tetrabromocorannulene (153 mg, 0.27 mmol) was added. The mixture was stirred for 10 days under argon then diluted with 60 mL toluene and washed with 3x100 mL water. The organic phase was dried over anhydrous MgSO₄, filtered and concentrated. The crude product was purified with column chromatography using hexane:DCM 5:1. A yellow solid was obtained: 140 mg (0.19 mmol), 70% yield.

\(^1\)H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 8.9 Hz, 2H), 7.75 (s, 2H), 7.61 (d, J = 8.9 Hz, 2H), 7.30 (d, J = 8.2 Hz, 4H), 7.25 (d, J = 8.3 Hz, 4H), 7.07 (dd, J = 14.6, 8.1 Hz, 8H), 2.30 (s, 6H), 2.28 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 138.86, 137.11, 136.67, 136.43, 136.30, 135.98, 135.09, 133.93, 133.82, 131.22, 130.21, 130.18, 129.32, 129.07, 128.96, 128.74, 128.05, 21.29, 21.26. HRMS (ESI+) m/z calcd for C₄₈H₃₄S₄ [M]+: 738.1543, found: 738.1584.

**Tetrasulfone 12**

A solution of tetrasulfide 11 (31.6 mg, 0.043 mmol) and mCPBA (229 mg, 1.02 mmol) in DCM (4.5 mL) was stirred at room temperature for 70 h. The reaction mixture was washed twice with aq. Na₂CO₃, the organic phase was dried over anhydrous MgSO₄, filtered and concentrated. The crude product was purified with column chromatography using CHCl₃. A yellow solid was obtained: 33.9 mg (0.039 mmol), 91% yield.

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.92 – 8.86 (m, 4H), 8.05 (dd, J = 8.3, 4.4 Hz, 8H), 7.97 (d, J = 9.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 8H), 2.43 (s, 12H); \(^{13}\)C NMR (100 MHz, CDCl₃) δ 145.75,
144.55, 144.50, 144.03, 140.72, 140.62, 137.85, 135.11, 132.17, 131.72, 131.12, 129.92, 129.89, 129.36, 128.96, 128.18, 127.07, 126.99, 21.89; HRMS (ESI+) m/z calcd for C_{48}H_{35}O_{8}S_{4} [M+H]^+: 867.1215, found: 867.1171.

**Tetrasulfide 13**

To a solution of benzene-1,2-dithiol (250 mg, 1.76 mmol) in anhydrous DMF (30 mL) was added t-BuOK (394 mg, 3.52 mmol) at room temperature under argon atmosphere. The mixture was stirred for 20 min then tetrabromocorannulene (452 mg, 0.8 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 1 h then heated to 60°C for 21 h. The reaction mixture was quenched with water (100 mL). The mixture was extracted with 4x40 mL CHCl₃. The combined organic layers were washed twice with water and brine; dried oven anhydrous Na₂SO₄, filtered and concentrated. The yellow residue was purified by column chromatography on silica gel (gradient: DCM:Hexane 2:8 to pure DCM) to provide **tetrasulfide 13** as a yellow solid (340 mg, 80%).

^1H NMR (400 MHz, CDCl₃) δ 8.18 (s, 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.50 (m, 4H), 7.18 (dd, J = 5.8, 3.3 Hz, 4H); ^13C NMR (100 MHz, CDCl₃) δ 136.08, 135.31, 135.17, 135.08, 134.31, 133.83, 131.04, 130.76, 130.62, 128.88, 128.85, 128.23, 128.09, 126.76, 126.13. HRMS (MALDI-TOF) m/z calcd for C_{32}H_{14}S_{4} [M]^+: 525.9973, found: 525.9973.

**Tetrasulfone 14**

A solution of tetrasulfide C (650 mg, 1.23 mmol) and mCPBA (6.62 g, 29.65 mmol) in DCM (300 mL) was stirred for 48 h at room temperature. The mixture was washed twice with aq. Na₂CO₃. The organic layer was dried over anh. Na₂SO₄, filtered and concentrated. The residue
was stirred vigorously overnight with 60 mL Et₂O, then filtered and the obtained yellow solid was washed with Et₂O and dried by suction: 462 mg, 58%. CCDC number: 1890566.

1H NMR (400 MHz, CD₂Cl₂) δ 8.93 (s, 2H), 8.86 (d, J = 9.1 Hz, 2H), 8.42 (ddd, J = 5.8, 3.3, 1.8 Hz, 4H), 8.08 (d, J = 9.1 Hz, 2H), 7.97 (dd, J = 5.8, 3.3 Hz, 4H); HRMS (ESI+) m/z calc'd for C₃₂H₁₅O₈S₄ [M+H]^+: 654.9650, found: 654.9639.
Figure S1. Digital pictures of 13 (left) and 14 (right).

Figure S2. X-ray crystal structure of 7. Ellipsoids are drawn at a probability level of 50%.

Figure S3. Crystal packing of 7. Ellipsoids are drawn at a probability level of 50%.
Figure S4. Crystal packing of 8. Each molecule crystallizes with two molecules of chloroform and one molecule of water. Ellipsoids are drawn at a probability level of 50%.

Figure S5. Crystal packing of 14. Each molecule crystallizes with a molecule of dichloromethane. Ellipsoids are drawn at a probability level of 50%.
Figure S6. Cyclic voltammetry at a scan rate of 0.1 V s$^{-1}$ and at a 1 mm diameter glassy carbon electrode showing first reduction process of 1 mM PC$_{61}$BM (black line), 8 (green line), 12 (blue line) and 14 (red line) in DMF containing 0.1 M $n$-Bu$_4$NPF$_6$. 
Figure S7. Cyclic voltammograms showing first reduction process of 1 mM corannulene, sulfides (1, 4, 7, 9, 11, 13), sulfoxide (2, 5), and sulfones (3, 6, 10) in DMF containing 0.1 M $n$Bu$_4$NPF$_6$ at a scan rate of 0.1 V s$^{-1}$ using a 1 mm diameter GC working electrode at 298±2 K in a Faraday cage.
Computational Methods

Geometry optimizations were performed for corannulene and its derivatives using DFT as implemented in Amsterdam density functional (ADF) program\(^2\)\(^3\) with B3LYP functional and all-electron triple zeta double polarization (TZ2P) basis set\(^4\)\(^5\). In the process of optimization, vibrational frequency calculations confirmed no imaginary frequencies for each of optimized molecules, which indicates the optimized structures are at the minima of the potential energy surface.

![Graph](image)

**Figure S8.** DFT-computed LUMO energy plotted against the first reduction potential measured by CV for corannulene (C) and its derivatives (1-14).
References


^1H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 8.8 Hz, 1H), 7.85 (s, 1H), 7.82 – 7.73 (m, 6H), 7.67 (d, J = 8.7 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.15, 136.46, 136.11, 135.94, 135.74, 135.60, 134.81, 133.17, 132.14, 131.11, 131.06, 131.01, 130.80, 130.31, 130.00, 127.80, 127.59, 127.45, 127.29, 127.21, 126.65, 126.30, 21.32.
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.51 (s, 1H), 7.98 (d, $J = 8.8$ Hz, 1H), 7.90 – 7.74 (m, 9H), 7.31 (d, $J = 8.1$ Hz, 2H), 2.37 (s, 3H).
\[^1\text{C}\] NMR (100 MHz, CDCl\textsubscript{3}) $\delta$ 143.21, 142.70, 142.01, 137.10, 136.18, 136.11, 135.51, 135.30, 131.78, 131.07, 130.89, 130.41, 129.83, 128.17, 128.07, 128.04, 127.96, 127.49, 127.31, 127.22, 126.81, 125.85, 124.79, 124.19, 21.60.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (s, 1H), 8.44 (d, $J = 8.9$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 2H), 7.92 – 7.77 (m, 7H), 7.31 (d, $J = 8.2$ Hz, 2H), 2.37 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.33, 139.58, 138.58, 137.90, 136.43, 136.03, 135.31, 134.92, 132.49, 131.36, 131.18, 131.09, 130.16, 128.75, 128.69, 128.38, 128.27, 128.14, 127.92, 127.53, 127.41, 127.36, 126.19, 125.80, 21.76.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (s, 1H), 7.85 – 7.77 (m, 8H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 2.60 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.33, 138.48, 136.65, 136.54, 136.38, 136.04, 135.59, 135.47, 131.16, 131.05, 131.04, 130.90, 130.56, 129.83, 127.63, 127.57, 127.48, 127.31, 127.20, 127.17, 127.11, 126.88, 125.70, 15.99.
$^1$H NMR (400 MHz, CDCl$3$) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.90 (s, 1H), 7.89 – 7.72 (m, 10H), 2.85 (s, 3H).
$\text{^1H NMR (500 MHz, CDCl}_3$) $\delta$ 145.14, 142.87, 140.28, 136.41, 135.94, 135.75, 135.51, 131.21, 131.11, 131.05, 130.75, 129.24, 127.90, 127.75, 127.63, 127.41, 127.38, 127.14, 127.11, 126.68, 126.66, 124.21, 44.17.

$\text{^13C NMR (100 MHz, CDCl}_3$) $\delta$ 145.14, 142.87, 140.28, 136.41, 135.94, 135.75, 135.51, 131.21, 131.11, 131.05, 130.75, 129.24, 127.90, 127.75, 127.63, 127.41, 127.38, 127.14, 127.11, 126.68, 126.66, 124.21, 44.17.
$^1$H NMR (400 MHz, CDCl3) δ 8.14 (d, $J = 8.3$ Hz, 2H), 7.99 (d, $J = 8.3$ Hz, 2H), 7.91 (s, 1H), 7.89 – 7.78 (m, 7H), 7.73 (d, $J = 8.9$ Hz, 1H), 3.18 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl3) δ 145.55, 139.77, 139.55, 136.46, 136.39, 135.95, 135.94, 135.49, 131.27, 131.17, 130.99, 130.60, 128.87, 128.10, 128.04, 127.88, 127.75, 127.58, 127.44, 127.18, 127.13, 127.10, 126.38, 44.84.
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J = 8.9$ Hz, 2H), 7.75 (s, 2H), 7.61 (d, $J = 8.9$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 4H), 7.25 (d, $J = 8.3$ Hz, 4H), 7.07 (dd, $J = 14.6$, 8.1 Hz, 8H), 2.30 (s, 6H), 2.28 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.86, 137.11, 136.67, 136.43, 136.30, 135.98, 135.09, 133.93, 133.82, 131.22, 130.21, 130.18, 129.32, 129.07, 128.96, 128.74, 128.05, 21.29, 21.26.
$^1$H NMR (400 MHz, CDCl3) $\delta$ 8.92 – 8.86 (m, 4H), 8.05 (dd, $J = 8.3$, 4.4 Hz, 8H), 7.97 (d, $J = 9.2$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 8H), 2.43 (s, 12H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.75, 144.55, 144.50, 144.03, 140.72, 140.62, 137.85, 135.11, 132.83, 132.17, 131.72, 131.12, 129.92, 129.89, 129.36, 128.96, 128.18, 127.07, 126.99, 21.89.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.8$ Hz, 2H), 7.64 – 7.55 (m, 4H), 7.19 (d, $J = 5.0$ Hz, 16H), 2.52 (s, 6H), 2.51 (s, 6H).
^13C NMR (100 MHz, CDCl3) δ 138.56, 138.20, 137.19, 137.14, 135.22, 135.18, 134.23, 132.10, 130.81, 130.20, 127.44, 127.41, 127.34, 125.80, 15.76.
$^1$H NMR (400 MHz, CDC13) $\delta$ 7.97 – 7.85 (m, 10H), 7.54 – 7.43 (m, 12H), 3.13 (s, 6H), 3.11 (s, 6H).
$^{13}$C NMR (100 MHz, CDCl₃) δ 143.70, 143.67, 139.83, 139.81, 137.92, 137.24, 135.52, 134.51, 132.37, 131.34, 129.96, 129.57, 128.46, 127.32, 127.26, 127.09, 44.65.
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 2H), 8.10 (d, $J = 8.8$ Hz, 2H), 7.77 (d, $J = 8.8$ Hz, 2H), 7.50 (dd, $J = 3.4$, 1.8 Hz, 4H), 7.18 (dd, $J = 5.8$, 2.2 Hz, 4H)
$^{13}$C NMR (100 MHz, CDC$_3$) \( \delta \) 136.08, 135.31, 135.17, 135.08, 134.31, 133.83, 131.04, 130.76, 130.62, 128.88, 128.85, 128.23, 128.09, 126.76, 126.13.
$^1$H NMR (400 MHz, CD2Cl2) δ 8.93 (s, 2H), 8.86 (d, $J = 9.1$ Hz, 2H), 8.42 (ddd, $J = 5.9$, 3.1, 1.8 Hz, 4H), 8.08 (d, $J = 9.1$ Hz, 2H), 7.97 (dd, $J = 5.8$, 3.3 Hz, 4H).
$^1$H NMR (400 MHz, CDCl₃) δ 7.77 (s, 5H), 7.21 (d, $J = 8.1$ Hz, 10H), 7.08 (d, $J = 8.0$ Hz, 10H), 2.36 (s, 15H).
$^1$C NMR (100 MHz, CDCl$_3$) δ 137.57, 136.39, 135.70, 131.83, 131.62, 130.33, 128.07, 21.41.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.35 (s, 5H), 7.93 (d, $J = 8.4$ Hz, 10H), 7.31 (d, $J = 8.3$ Hz, 10H), 2.37
$^{13}$C NMR (100 MHz, CDCl₃) δ 145.51, 142.57, 137.81, 137.31, 132.21, 130.62, 128.38, 125.90, 81.62