Supporting Information

Copper(I)-Mediated Carboamination of Vinyl Azides by Aryldiazonium Salts: Synthesis of N2-substituted 1,2,3-Triazoles
Zhenhua Liu,† Huimin Ji,† Wen Gao,* Guangyu Zhu, Lili Tong, Fengcai Lei and Bo Tang*
College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Institute of Biomedical Sciences, Shandong Normal University, Jinan 250014, P.R. China.

E-mail: gaowen@sdnu.edu.cn and E-mail: tangb@sdnu.edu.cn

Contents

I. General information .....................................................................................................................S2
II. Synthesis and analytical data of compounds 3 and 4 ............................................................S2-S10
III. Crystallography of compound 3f ...................................................................................... S10-S11
IV. NMR spectra copies ..........................................................................................................S11-S41
I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded at 25 ºC on a Varian 400 MHz and 100 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

II. Synthesis and analytical data of compounds 3 and 4.

Typical synthetic procedure (with 3a as an example): To a solution of $\alpha$-azido styrene (1a) (72.5 mg, 0.5 mmol), 4-methylphenyldiazonium tetrafluoroborate (2a) (309 mg, 1.5 mmol), and 2,6-di-tert-butyl-4-methylphenol (BHT) (55 mg, 0.25 mmol) in DMF (1 mL) at room temperature, CuI (105 mg, 0.55 mmol) was added. The reaction mixture was then stirred for 6 h when TLC conformed that substrate 1a had been consumed. The resulting reaction mixture was then cooled to room temperature and taken up by dichloromethane (3 × 15 mL). The organic layer was washed with brine (3 × 40 mL), dried over MgSO$_4$ and concentrated. Purification of the crude product via flash column chromatography (silica gel; petroleum ether) and concentratinon in vacuo afforded 3a in 83% yield as yellow solid.

(3a) Yellow solid, m.p. 75-76 ºC; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.97−7.95 (d, J = 8.4 Hz, 2H), 7.58−7.52 (m, 2H), 7.45−7.43 (m, J = 8.0 Hz, 2H), 7.33−7.26 (m, 3H), 7.20−7.17 (d, J = 8.5 Hz, 2H), 7.11−7.09 (d, J = 7.9 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$):
145.7, 145.5, 138.4, 137.6, 137.1, 131.0, 129.7, 129.3, 128.5, 128.4, 128.3, 128.37, 128.4, 128.3, 118.6, 21.3, 21.1; HRMS (ESI) m/z calculated for C_{22}H_{20}N_{3} [M+H]^+: 326.1657 found: 326.1669.

(3b) Yellow solid, m.p. 75-76 °C; \textbf{1}H NMR (400 MHz, CDCl$_3$): δ 8.10–8.07 (d, $J = 9.1$ Hz, 2H), 7.67–7.62 (m, 2H), 7.58–7.56 (d, $J = 8.9$ Hz, 2H), 7.44–7.36 (m, 3H), 7.02–7.00 (d, $J = 9.1$ Hz, 2H), 6.94–6.92 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H); \textbf{13}C NMR (100 MHz, CDCl$_3$): 159.8, 158.8, 145.3, 145.1, 133.6, 131.0, 129.7, 128.5, 128.4, 128.3, 123.2, 120.1, 114.3, 114.0, 55.5, 55.3; HRMS (ESI) m/z calculated for C$_{22}$H$_{20}$N$_{3}$O$_{2}$ [M+H]$^+$: 358.1556 found: 358.1551.

(3c) Yellow solid, m.p. 80-81 °C; \textbf{1}H NMR (400 MHz, CDCl$_3$): δ 8.14–8.12 (d, $J = 9.0$ Hz, 1H), 7.68–7.63 (m, 2H), 7.61–7.59 (d, $J = 8.6$ Hz, 2H), 7.44–7.34 (m, 7H), 7.16–7.12 (d, $J = 9.4$ Hz, 4H), 7.10–7.04 (m, 4H), 7.03–7.01 (d, $J = 8.6$ Hz, 2H); \textbf{13}C NMR (100 MHz, CDCl$_3$): 157.9, 156.9, 156.54, 156.51, 145.6, 145.3, 135.3, 130.7, 129.9, 129.83, 129.82, 128.6, 128.4, 125.4, 123.7, 123.6, 120.3, 119.4, 119.3, 119.0, 118.5; HRMS (ESI) m/z calculated for C$_{32}$H$_{24}$N$_{3}$O$_{2}$ [M+H]$^+$: 482.1869 found: 482.1860.

(3d) Yellow solid, m.p. 76-77 °C; \textbf{1}H NMR (400 MHz, CDCl$_3$): δ 8.09–8.07 (d, $J = 8.4$ Hz, 2H), 7.71–7.63 (m, 2H), 7.57–7.55 (d, $J = 8.0$ Hz, 2H), 7.41–7.40 (d, $J = 5.0$ Hz, 3H), 7.33–7.31 (d, $J = 8.2$ Hz, 2H), 7.24–7.22 (d, $J = 7.9$ Hz, 2H), 2.78–2.64 (m, 4H), 1.31–1.24 (m, 6H); \textbf{13}C NMR (100 MHz, CDCl$_3$): 145.7, 145.5, 144.7, 143.5, 137.7, 131.0, 128.6, 128.5, 128.45, 128.4, 128.3, 128.11, 118.7, 120.08, 28.7, 28.4, 15.5, 15.4; HRMS (ESI) m/z calculated for C$_{24}$H$_{24}$N$_{3}$ [M+H]$^+$: 354.1970 found: 354.1976.
(3e) Yellow solid, m.p. 76-77 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.01–7.98 (d, \( J = 8.4 \) Hz, 2H), 7.61–7.55 (m, 2H), 7.50–7.48 (d, \( J = 8.0 \) Hz, 2H), 7.34–7.28 (m, 3H), 7.26–7.24 (d, \( J = 8.4 \) Hz, 2H), 7.18–7.16 (d, \( J = 7.9 \) Hz, 2H), 2.94–2.79 (m, 2H), 1.21–1.18 (t, \( J = 6.0 \) Hz, 12H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): 149.3, 148.1, 145.7, 145.4, 137.7, 131.0, 128.5, 128.43, 128.41, 128.3, 128.2, 127.1, 126.6, 118.7, 33.9, 33.7, 23.94, 23.89; HRMS (ESI) m/z calculated for C\(_{26}\)H\(_{28}\)N\(_3\) [M+H]\(^+\) : 382.2283 found: 382.2281.

(3f) Yellow solid, m.p. 70-71 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.15–8.07 (m, 2H), 7.60–7.54 (m, 4H), 7.56–7.48 (m, 4H), 7.46–7.38 (m, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): 145.9, 143.4, 139.1, 137.8, 137.3, 135.6, 132.3, 129.9, 129.5, 128.6, 128.4, 127.2, 118.2, 21.4, 21.1; HRMS (ESI) m/z calculated for C\(_{20}\)H\(_{16}\)N\(_3\) [M+H]\(^+\) : 298.1344 found: 298.1344.

(3g) Yellow solid, m.p. 77-78 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.07–8.04 (d, \( J = 8.9 \) Hz, 2H), 7.62–7.58 (m, 2H), 7.57–7.55 (d, \( J = 8.6 \) Hz, 2H), 7.46–7.38 (m, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): 146.3, 145.1, 138.5, 132.3, 131.8, 130.2, 129.9, 129.4, 129.0, 128.7, 128.4, 123.0, 121.0, 120.2; HRMS (ESI) m/z calculated for C\(_{20}\)H\(_{14}\)Br\(_2\)N\(_3\) [M+H]\(^+\) : 453.9554 found: 454.9622.

(3h) Yellow solid, m.p. 75-76 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.11–8.09 (d, \( J = 8.9 \) Hz, 2H), 7.62–7.58 (m, 2H), 7.57–7.55 (d, \( J = 8.6 \) Hz, 2H), 7.46–7.44 (d, \( J = 8.9 \) Hz, 2H), 7.42–7.39 (m, 3H), 7.37–7.35 (d, \( J = 8.6 \) Hz, 2H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): 146.3, 145.1, 138.1, 134.8, 133.1, 130.3, 129.6, 129.4, 128.97, 128.95, 128.9, 128.8, 119.9; HRMS (ESI) m/z calculated for C\(_{20}\)H\(_{14}\)Cl\(_2\)N\(_3\) [M+H]\(^+\) : 366.0565 found: 366.0553.
(3i) Yellow solid, m.p. 77-78 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 8.28-8.26\) (d, \(J = 8.6\) Hz, 2H), 8.21-8.19 (d, \(J = 8.6\) Hz, 2H), 8.09-8.07 (d, \(J = 8.1\) Hz, 2H), 7.75-7.73 (d, \(J = 8.1\) Hz, 2H), 7.62-7.01 (d, \(J = 7.3\) Hz, 2H), 7.44-7.43 (d, \(J = 4.8\) Hz, 3H), 1.46-1.38 (m, 6H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): 166.2, 165.9, 147.2, 145.7, 142.4, 134.7, 131.0, 130.7, 130.0, 129.9, 129.3, 129.2, 128.8, 128.5, 128.3, 118.3, 61.24, 61.16; HRMS (ESI) m/z calculated for C\(_{24}\)H\(_{20}\)N\(_3\)O\(_4\) [M+H]\(^+\) : 414.1454 found: 414.1450.

(3j) Yellow solid, m.p. 74-75 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.76-7.74\) (t, \(J = 4.3\) Hz, 1H), 7.59-7.57 (t, \(J = 3.6\) Hz, 2H), 7.42-7.34 (m, 5H), 7.34-7.26 (m, 5H), 2.54 (s, 3H), 2.20 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): 145.6, 145.2, 139.5, 137.4, 132.5, 132.8, 130.8, 130.7, 130.5, 129.0, 128.6, 128.3, 127.0, 126.6, 126.0, 125.0, 20.1, 19.3; HRMS (ESI) m/z calculated for C\(_{22}\)H\(_{20}\)N\(_3\) [M+H]\(^+\) : 326.1657 found: 326.1657.

(3k) Yellow solid, m.p. 78-79 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 7.63-7.53\) (m, 3H), 7.32-7.27 (m, 4H), 6.87-6.78 (m, 4H), 3.86 (s, 6H), 2.45 (s, 3H), 2.16 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): 159.9, 159.4, 145.3, 144.7, 139.0, 134.5, 133.2, 131.7, 131.0, 128.5, 128.1, 126.9, 126.5, 123.2, 116.5, 115.9, 111.6, 111.3, 55.5, 55.2, 20.4, 19.2; HRMS (ESI) m/z calculated for C\(_{24}\)H\(_{24}\)N\(_3\)O\(_2\) [M+H]\(^+\) : 386.1869 found: 386.1880.

(3l) Yellow solid, m.p. 75-76 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta 8.30-8.28\) (d, \(J = 2.5\) Hz, 1H),
8.04–7.99 (m, 1H), 7.80–7.796 (d, J = 1.8 Hz, 1H), 7.62–7.55 (m, 3H), 7.47–7.43 (m, 4H), 7.43–7.40 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): 146.8, 144.3, 138.4, 133.5, 133.1, 133.0, 131.5, 131.0, 130.6, 130.2, 130.0, 129.6, 129.3, 128.9, 128.4, 127.4, 120.5, 117.8; HRMS (ESI) m/z calculated for C$_{20}$H$_{12}$Cl$_4$N$_3$ [M+H]$^+$: 433.9785 found: 433.9779.

(3m) Yellow solid, m.p. 72-73 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 (s, 1H), 8.00–7.95 (d, $J = 8.2$ Hz, 1H), 7.69 (s, 1H), 7.65–7.59 (m, 2H), 7.45–7.40 (m, 3H), 7.38–7.33 (t, $J = 9.2$ Hz, 2H), 7.24–7.22 (d, $J = 7.9$ Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 146.1, 144.8, 138.4, 136.6, 135.3, 135.0, 134.7, 131.4, 131.0, 130.3, 129.7, 128.9, 128.72, 128.69, 128.4, 126.5, 119.3, 116.8, 20.0, 19.7; HRMS (ESI) m/z calculated for C$_{22}$H$_{18}$Cl$_2$N$_3$ [M+H]$^+$: 394.0878 found: 394.0880.

(3n) Yellow solid, m.p. 78-79 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (s, 2H), 7.70–7.64 (m, 2H), 7.41–7.36 (m, 3H), 7.25 (s, 2H), 7.03 (s, 1H), 7.00 (s, 1H), 2.42 (s, 6H), 2.32 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 146.0, 145.6, 139.6, 139.1, 138.1, 130.9, 130.6, 130.3, 129.0, 128.5, 128.3, 126.2, 116.5, 21.4, 21.3; HRMS (ESI) m/z calculated for C$_{24}$H$_{24}$N$_3$ [M+H]$^+$: 354.1970 found: 354.1997.

(4a) Yellow solid, m.p. 113-114 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05–8.03 (d, $J = 8.5$ Hz, 2H), 7.59–7.57 (d, $J = 8.8$ Hz, 2H), 7.55–7.53 (d, $J = 8.0$ Hz, 2H), 7.30–7.27 (d, $J = 8.5$ Hz, 2H), 7.22–7.20 (d, $J = 8.0$ Hz, 2H), 6.94–6.92 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 159.8, 145.4, 145.3, 138.3, 137.6, 137.0, 129.71, 129.68, 129.3, 128.3, 128.1, 123.4, 118.6, 114.0, 55.3, 21.3, 21.0; HRMS (ESI) m/z calculated for C$_{23}$H$_{22}$N$_3$O [M+H]$^+$: 356.1763 found: 356.1777.
(4b) Yellow solid, m.p. 117-118°C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06–8.03 (d, $J$ = 8.5 Hz, 2H), 7.55–7.53 (d, $J$ = 8.5 Hz, 4H), 7.29–7.27 (d, $J$ = 8.2 Hz, 2H), 7.21–7.19 (d, $J$ = 7.9 Hz, 4H), 2.41 (s, 3H), 2.40 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 145.6, 138.3, 137.6, 137.0, 129.7, 129.2, 128.3, 128.1, 118.6, 21.3, 21.0; HRMS (ESI) m/z calculated for C$_{23}$H$_{22}$N$_3$ [M+H]$^+$ : 340.1814 found: 340.1835.

(4c) Yellow solid, m.p. 118-119 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.06–8.04 (d, $J$ = 8.0 Hz, 2H), 7.60–7.51 (m, 4H), 7.30–7.28 (d, $J$ = 7.8 Hz, 2H), 7.22–7.20 (d, $J$ = 7.6 Hz, 4H), 2.70–2.60 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 1.65 (s, 2H), 1.34 (s, 4H), 0.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 145.6, 145.55, 143.4, 138.3, 137.6, 137.0, 132.1, 129.7, 129.2, 128.6, 128.3, 128.2, 128.1, 118.6, 35.8, 31.5, 31.0, 22.5, 21.0, 14.0; HRMS (ESI) m/z calculated for C$_{27}$H$_{29}$N$_3$ [M+H]$^+$ : 396.2440 found: 396.2440.

(4d) Yellow solid, m.p. 123-124 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.08–8.06 (d, $J$ = 8.5 Hz, 2H), 7.75–7.73 (d, $J$ = 8.5 Hz, 2H), 7.68–7.61 (m, 4H), 7.59–7.57 (d, $J$ = 8.1 Hz, 2H), 7.48–7.45 (t, $J$ = 7.8 Hz, 2H), 7.39–7.38 (d, $J$ = 7.2 Hz, 1H), 7.32–7.30 (d, $J$ = 8.1 Hz, 2H), 7.25–7.23 (d, $J$ = 7.9 Hz, 2H) 2.43 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 145.8, 145.1, 141.1, 140.5, 138.5, 137.6, 137.2, 129.9, 129.8, 129.3, 128.8, 128.7, 128.4, 128.0, 127.5, 127.2, 127.0, 118.6, 21.4, 21.1; HRMS (ESI) m/z calculated for C$_{28}$H$_{24}$N$_3$ [M+H]$^+$ : 402.1970 found: 402.1979.

(4e) Yellow solid, m.p. 114-115 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04–8.02 (d, $J$ = 8.5 Hz, 2H), 7.60–7.58 (d, $J$ = 8.6 Hz, 2H), 7.51–7.49 (d, $J$ = 8.1 Hz, 2H), 7.37–7.35 (d, $J$ = 8.6 Hz, 2H), 7.30–7.28 (d, $J$ = 8.2 Hz, 2H), 7.23–7.21 (d, $J$ = 7.9 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR
(100MHz, CDCl₃): 145.8, 144.4, 138.7, 137.6, 137.4, 134.4, 129.8, 129.7, 129.4, 128.8, 128.3, 127.7, 118.7, 21.4, 21.1; HRMS (ESI) m/z calculated for C₂₂H₁₉ClN₃ [M+H]⁺: 360.1268 found: 360.1261.

(4f) Yellow solid, m.p. 103-104 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.06–8.04 (d, J = 8.5 Hz, 2H), 7.98–7.96 (d, J = 8.4 Hz, 2H), 7.78–7.75 (d, J = 8.4 Hz, 2H), 7.51–7.49 (d, J = 8.1 Hz, 2H), 7.30–7.28 (d, J = 8.4 Hz, 2H), 7.23–7.21 (d, J = 8.0 Hz, 2H), 2.62 (s, 3H), 2.41 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): 197.6, 146.3, 144.2, 143.3, 138.8, 137.5, 137.4, 136.6, 135.6, 129.8, 129.4, 128.5, 128.4, 118.7, 26.6, 21.3, 21.0; HRMS (ESI) m/z calculated for C₂₄H₂₃N₃O [M+H]⁺: 384.1763 found: 384.1760.

(4g) Yellow solid, m.p. 100-101 °C; ¹H NMR NMR (400 MHz, CDCl₃): δ 8.04–8.01 (m, 4H), 7.72–7.70 (d, J = 8.3 Hz, 2H), 7.48–7.46 (d, J = 8.0 Hz, 2H), 7.25–7.23 (d, J = 8.2 Hz, 2H), 7.19–7.17 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100MHz, CDCl₃): 166.6, 146.1, 144.1, 138.6, 137.33, 137.31, 135.4, 132.0, 129.71, 129.67, 129.3, 128.3, 128.0, 127.5, 118.5, 52.1, 21.2, 20.9; HRMS (ESI) m/z calculated for C₂₄H₂₂N₂O₂ [M+H]⁺: 384.1712 found: 384.1740.

(4h) Yellow solid, m.p. 119-120 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.04–8.02 (d, J = 8.2 Hz, 2H), 7.80–7.78 (d, J = 8.2 Hz, 2H), 7.67–7.65 (d, J = 8.1 Hz, 2H), 7.48–7.46 (d, J = 7.9 Hz, 2H), 7.31–7.29 (d, J = 8.2 Hz, 2H), 7.25–7.23 (d, J = 7.9 Hz, 2H), 2.42 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): 146.4, 143.4, 139.1, 137.8, 137.3, 135.6, 132.3, 129.9, 129.5, 128.6, 128.4, 127.2, 118.2, 21.4, 21.1; HRMS (ESI) m/z calculated for C₂₃H₁₉N₄ [M+H]⁺: 351.1610 found: 351.1602.
(4i) Yellow solid, m.p. 126-127 °C; \( ^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.06-8.04 \) (d, \( J = 8.5 \) Hz, 2H), 8.01 (s, 1H), 7.76-7.72 (m, 1H), 7.68-7.66 (d, \( J = 7.3 \) Hz, 1H), 7.56-7.46 (m, 5H), 7.31-7.29 (d, \( J = 8.4 \) Hz, 2H), 7.24-7.22 (d, \( J = 8.0 \) Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H); \( ^{13}C\) NMR (100 MHz, CDCl\(_3\)): 193.3, 145.8, 144.2, 144.1, 144.0, 138.8, 137.41, 137.38, 134.8, 134.5, 134.3, 132.0, 129.8, 129.4, 129.2, 128.3, 127.5, 124.4, 124.2, 120.5, 120.4, 118.6, 21.4, 21.0; HRMS (ESI) m/z calculated for C\(_{29}\)H\(_{22}\)N\(_3\)O [M+H]\(^+\): 428.1763 found: 428.1750.

(4j) Yellow solid, m.p. 121-122 °C; \( ^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 8.14 \) (s, 1H), 8.11 (s, 1H), 8.00-7.91 (m, 2H), 7.88-7.86 (s, 1H), 7.62-7.48 (m, 3H), 7.44-7.40 (d, \( J = 8.1 \) Hz, 3H), 7.33-7.31 (d, \( J = 8.3 \) Hz, 2H), 7.04-7.02 (d, \( J = 8.0 \) Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H); \( ^{13}C\) NMR (100 MHz, CDCl\(_3\)): 146.7, 144.3, 138.1, 137.6, 137.2, 133.8, 132.6, 132.0, 129.8, 129.4, 129.2, 128.8, 128.3, 127.4, 127.2, 126.6, 126.1, 125.8, 125.3, 118.7, 21.2, 21.0; HRMS (ESI) m/z calculated for C\(_{26}\)H\(_{22}\)N\(_3\) [M+H]\(^+\): 376.1814 found: 376.1837.

(4k) Yellow solid, m.p. 53-54 °C; \( ^1H\) NMR (400 MHz, CDCl\(_3\)): \( \delta 7.96-7.94 \) (d, \( J = 8.5 \) Hz, 2H), 7.63-7.61 (d, \( J = 8.1 \) Hz, 2H), 7.28-7.24 (d, \( J = 8.1 \) Hz, 2H), 3.58-3.54 (t, \( J = 6.3 \) Hz, 2H), 2.95-2.92 (t, \( J = 7.3 \) Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 1.97-1.84 (m, 4H); \( ^{13}C\) NMR (100 MHz, CDCl\(_3\)): 146.0, 145.8, 138.1, 137.7, 136.8, 129.7, 129.4, 128.1, 127.4, 127.3, 118.4, 44.6, 32.1, 25.9, 25.1, 21.3, 21.0; HRMS (ESI) m/z calculated for C\(_{20}\)H\(_{22}\)ClN\(_3\) [M+H]\(^+\): 340.1581 found: 340.1599.
(4l) Yellow solid, m.p. 64-65 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98–7.96 (d, $J = 8.5$ Hz, 2H), 7.60–7.58 (d, $J = 8.1$ Hz, 2H), 7.33–7.17 (m, 9H), 3.24–3.17 (m, 2H), 3.14–3.07 (m, 2H), 2.39 (s, 6H); $^{13}$C NMR (100MHz, CDCl$_3$): 146.1, 145.7, 141.4, 138.1, 137.7, 136.8, 129.7, 129.4, 128.4, 128.1, 127.4, 126.1, 120.3, 34.9, 28.2, 21.3, 21.0; HRMS (ESI) m/z calculated for C$_{24}$H$_{24}$N$_3$ [M+H]$^+$: 354.1970 found: 354.1988.

(4m) Yellow solid, m.p. 50-51 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96–7.94 (d, $J = 8.0$ Hz, 2H), 7.64–7.62 (d, $J = 7.6$ Hz, 2H), 7.30-7.22 (m, 4H), 2.91–2.87 (t, $J = 7.8$ Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 1.80–1.70 (s, 2H), 1.44–1.36 (s, 2H), 1.33–1.26 (s, 4H), 0.92–0.84 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 146.7, 145.9, 138.0, 137.7, 136.6, 129.7, 129.4, 128.3, 127.4, 118.4, 31.5, 29.1, 28.9, 26.0, 22.6, 21.3, 21.0, 14.1; HRMS (ESI) m/z calculated for C$_{22}$H$_{28}$N$_3$ [M+H]$^+$: 334.2283 found: 334.2296.

(4n) Yellow solid, m.p. 52-53 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03–8.01 (d, $J = 7.8$ Hz, 2H), 7.97–7.95 (d, $J = 8.2$ Hz, 2H), 7.64–7.62 (d, $J = 7.9$ Hz, 2H), 7.56–7.52 (t, $J = 7.4$ Hz, 1H), 7.43–7.40 (t, $J = 8.2$ Hz, 2H), 7.43–7.40 (d, $J = 7.6$ Hz, 2H), 4.37–4.34 (t, $J = 6.0$ Hz, 4H), 3.02–2.98 (t, $J = 7.2$ Hz, 2H), 2.38 (s, 6H), 2.01–1.86 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): 166.6, 145.9, 138.1, 137.6, 136.7, 132.8, 130.3, 129.7, 129.6, 129.5, 129.4, 128.3, 128.1, 127.3, 118.3, 64.6, 28.4, 25.6, 25.2, 21.3, 20.1; HRMS (ESI) m/z calculated for C$_{27}$H$_{38}$N$_3$O$_2$ [M+H]$^+$: 426.5301 found: 426.5312.
**III. Crystallography of compound 3f**

Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a $\omega$ scan technique with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.1 (a) G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Gottingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen, Germany, 1997.

**Table 1. Crystal data and structure refinement.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{20}$H$</em>{15}$N$_{3}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2)K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54184 Å</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 19.5551(4) Å</td>
</tr>
<tr>
<td></td>
<td>alpha = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 7.59507(14) Å</td>
</tr>
<tr>
<td></td>
<td>beta = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>c = 20.2815(4) Å</td>
</tr>
<tr>
<td></td>
<td>gamma = 90 deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>3012.27(10) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.311 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.618 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1248</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.42 x 0.25 x 0.02 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.52 to 67.07 deg.</td>
</tr>
</tbody>
</table>
IV. NMR spectra copies