

Selective Rhodium-Catalyzed C–H Amidation of Azobzenes with Dioxazolones under Mild Conditions

Bomi Jeon, Uiseong Yeon, Jeong-Yu Son, and Phil Ho Lee*

National Creative Research Initiative Center for Catalytic Organic Reactions, Department of Chemistry,
Kangwon National University, Chuncheon 24341, Republic of Korea
FAX: (+)-82-33-259-5667. E-mail: phlee@kangwon.ac.kr

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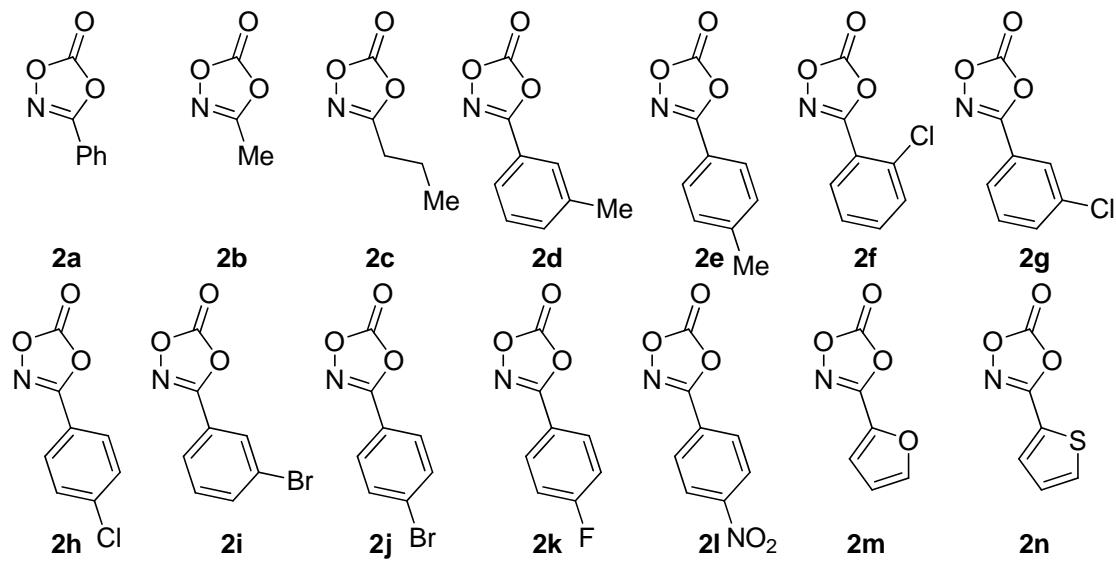
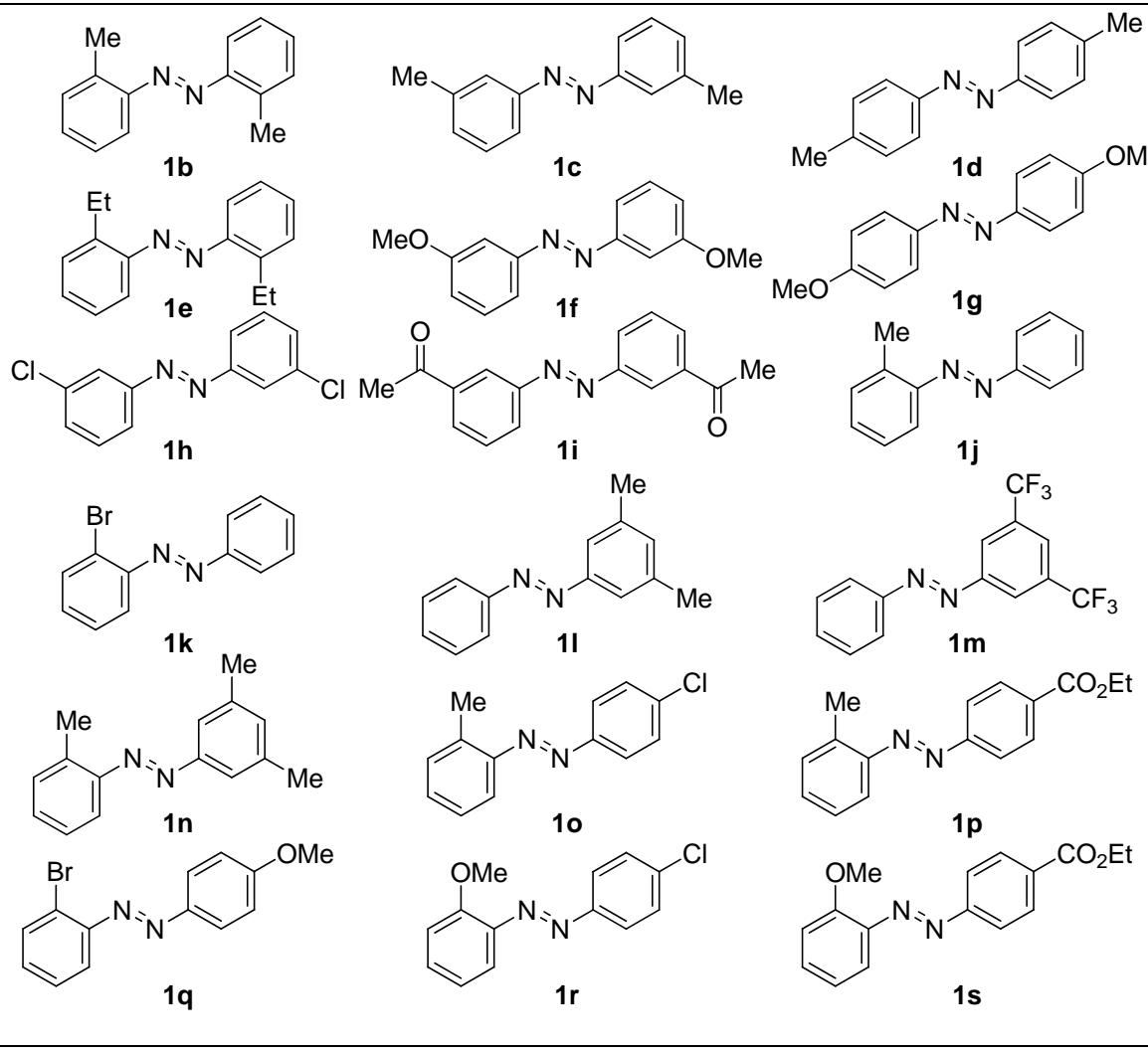
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Experimental Section

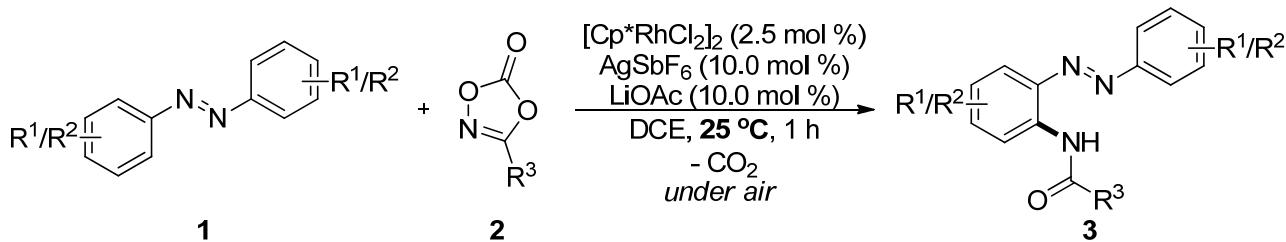
1. General: $[\text{Cp}^*\text{RhCl}_2]_2$, AgSbF₆ and LiOAc were purchased and were used as received. Commercial available reagents were used without purification. DCE was dried with CaH₂. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230-400 mesh). ¹H NMR (400 MHz), ¹³C NMR (100 MHz) and ¹⁹F NMR (376 MHz)spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.26 for ¹H and δ 77.0 for ¹³C). Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. Mass spectra were obtained from the KBSI on high resolution mass spectrometer. Melting points were determined in open capillary tube using Electrothermal 9100 apparatus.

2. Preparation of substrates

Azobzenes (**1**) and 3-substituted 1,4,2-dioxazol-5-ones(**2**) were prepared by reported method.^{1,2}

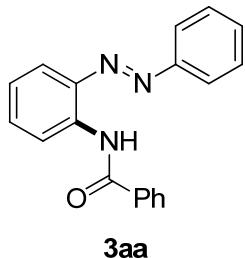


3. General procedure for Rh-catalyzed C–H amidation of azobenzenes with dioxazolones

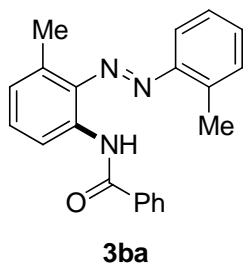


To a test tube were added azobenzene (**1**) (72.9 mg, 0.4 mmol), dioxazolone (**2**) (32.6 mg, 0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol), and LiOAc (1.3 mg, 0.02 mmol) in DCE (1.0 mL). The resulting mixture was stirred at 25 °C for 1 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel using EtOAc:Hexane = 1:7.

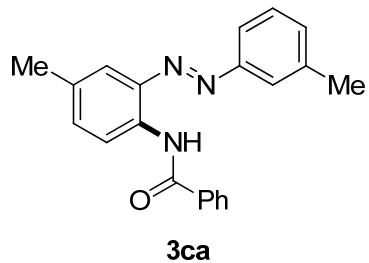
(E)-N-(2-(phenyldiazenyl)phenyl)benzamide (3aa): Yield: 50.6 mg (84%); $R_f = 0.5$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 126-128 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.49 (br, 1H), 8.90 (dd, $J = 8.4, 1.2$ Hz, 1H), 8.01-7.96 (m, 3H), 7.90-7.87 (m, 2H), 7.62-7.48 (m, 7H), 7.25 (td, $J = 7.7, 1.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 152.3, 139.0, 135.4, 135.1, 133.1, 132.1, 131.4, 129.4, 128.9, 127.3, 124.7, 123.6, 122.5, 120.3; IR (film): 3345, 1652, 1592, 1519, 1449, 1316 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}$: 301.1215; found: 301.1216.



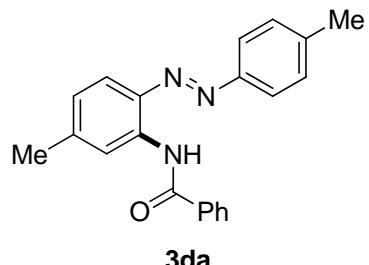
(E)-N-(3-methyl-2-(o-tolyldiazenyl)phenyl)benzamide (3ba): Yield: 60.5 mg (92%); $R_f = 0.2$ (EtOAc:Hexane = 1:20); Orange solid; Melting point: 110-112 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.33 (br, 1H), 8.71 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.56-7.52 (m, 2H), 7.48-7.35 (m, 4H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.15 (d, $J = 7.5$ Hz, 1H), 2.74 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 151.6, 141.1, 137.3, 135.98, 135.96, 132.7, 131.8, 131.5, 131.4, 130.7, 128.7, 127.7, 126.8, 126.2, 118.8, 116.7, 19.9, 18.0; IR (film): 3380, 3184, 3060, 2924, 1680, 1598, 1483, 1212, 707 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$: 329.1528; found: 329.1526.



(E)-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3ca): Yield: 64.4 mg (98%); $R_f = 0.2$ (EtOAc:Hexane = 1:20); Orange solid; Melting point: 90-92 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.40 (br, 1H), 8.78 (d, $J = 8.5$ Hz, 1H), 8.02-7.99 (m, 2H), 7.77 (d, $J = 1.5$ Hz, 1H), 7.71 (s, 1H), 7.70 (d, $J = 8.6$ Hz, 1H), 7.62-7.52 (m, 3H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 8.6$ Hz, 1H), 7.34 (t, $J = 8.8$ Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 152.4, 139.2, 138.8, 135.4, 133.7, 133.3, 132.9, 132.1, 131.9, 129.2, 128.8, 127.2, 124.3, 122.7, 120.1, 120.0, 21.4, 20.8; IR (film): 3390, 2917, 1677, 1591, 1448, 1310, 795 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$: 329.1528; found: 329.1529.

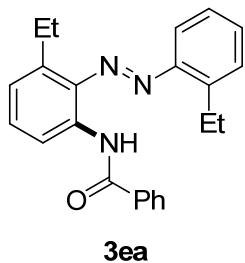


(E)-N-(5-methyl-2-(p-tolyldiazenyl)phenyl)benzamide (3da): Yield: 46.0 mg (70%); $R_f = 0.4$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 198-200 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.62 (br, 1H), 8.72 (d, $J = 0.8$ Hz, 1H), 7.98-7.95 (m, 2H), 7.81 (d, $J = 8.1$ Hz, 1H), 7.73 (d, $J = 8.3$ Hz, 2H), 7.58-7.49 (m, 3H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.02 (dd, $J = 8.2, 1.2$ Hz, 1H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 150.4, 143.8, 141.7, 137.1, 135.4, 134.6, 132.0, 130.0, 128.8, 127.3, 125.3, 124.6, 122.2, 120.4, 22.2, 21.5; IR (film): 3387, 3029, 2919, 1679, 1603, 1426, 1150, 825 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$: 329.1528; found: 329.1525.

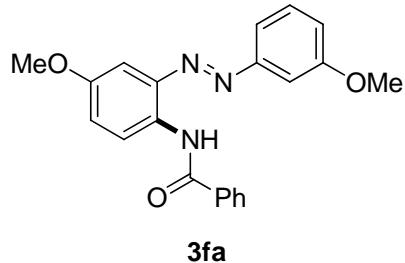


(E)-N-(3-ethyl-2-((2-ethylphenyl)diazenyl)phenyl)benzamide (3ea): Yield: 61.4 mg (86%); $R_f = 0.3$ (EtOAc: Hexane = 1:20); Orange solid; Melting point: 72-74 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.27 (br,

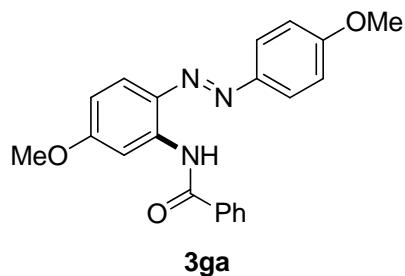
1H), 8.66 (dd, J = 8.4, 1.3 Hz, 1H), 7.86-7.83 (m, 2H), 7.56-7.52 (m, 2H), 7.47-7.39 (m, 4H), 7.33-7.29 (m, 2H), 7.17 (dd, J = 7.5, 1.2 Hz, 1H), 3.17 (q, J = 7.5 Hz, 2H), 2.75 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 151.1, 147.4, 142.1, 136.6, 136.1, 132.8, 131.8, 131.1, 130.9, 129.4, 128.7, 127.7, 126.8, 124.9, 119.0, 116.4, 26.4, 24.5, 16.7, 15.5; IR (film): 3378, 3221, 3063, 2968, 1681, 1580, 1455, 1307 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}$: 357.1841; found: 357.1841.



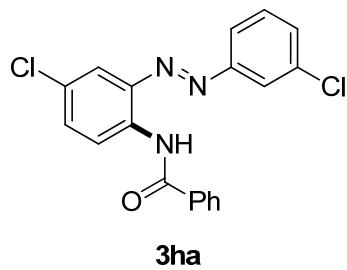
(E)-N-(4-methoxy-2-((3-methoxyphenyl)diazenyl)phenyl)benzamide (3fa): Yield: 41.9 mg (58%); R_f = 0.3 (EtOAc: Hexane = 1:7); Yellow solid; Melting point: 150-152 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.88 (br, 1H), 8.81 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 7.4 Hz, 2H), 7.60-7.42 (m, 7H), 7.15 (dd, J = 9.2, 2.8 Hz, 1H), 7.08 (dt, J = 8.2, 1.2 Hz, 1H), 3.90 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 160.5, 155.8, 153.6, 139.8, 135.4, 131.9, 130.2, 130.1, 128.8, 127.1, 121.6, 120.4, 118.4, 117.1, 105.1, 104.9, 55.7, 55.4; IR (film): 3315, 2837, 1645, 1595, 1521, 1265, 1033 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_3$: 361.1426; found: 361.1425.



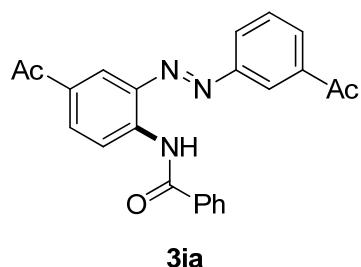
(E)-N-(5-methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)benzamide (3ga): Yield: 46.3 mg (64%); R_f = 0.2 (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 128-130 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.06 (br, 1H), 8.56 (d, J = 2.7 Hz, 1H), 8.00 (d, J = 7.1 Hz, 2H), 7.88 (dd, J = 8.9, 1.4 Hz, 1H), 7.82 (d, J = 8.8 Hz, 2H), 7.63-7.54 (m, 3H), 7.02 (d, J = 8.9 Hz, 2H), 6.78 (dd, J = 8.9, 2.7 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 162.7, 161.7, 146.5, 136.1, 135.4, 133.6, 132.1, 128.9, 128.0, 127.3, 123.7, 114.4, 110.9, 103.5, 55.8, 55.6; IR (film): 3376, 3060, 1676, 1600, 1289, 1254, 836 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_3$: 361.1426; found: 361.1423.



(E)-N-(4-chloro-2-((3-chlorophenyl)diazenyl)phenyl)benzamide (3ha): Yield: 58.4 mg (79%); $R_f = 0.5$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 162-164 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.96 (br, 1H), 8.88 (d, $J = 9.0$ Hz, 1H), 7.98-7.96 (m, 2H), 7.93 (d, $J = 2.4$ Hz, 1H), 7.87 (s, 1H), 7.84-7.80 (m, 1H), 7.65-7.51 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 152.9, 139.3, 135.6, 134.8, 134.7, 133.2, 132.4, 131.6, 130.6, 129.1, 129.0, 127.1, 122.5, 122.0, 121.6, 121.3; IR (film): 3327, 1651, 1587, 1515, 1197, 789, 687 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{N}_3\text{O}$: 369.0436; found: 369.0433.

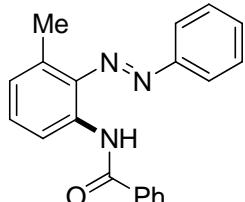


(E)-N-(4-acetyl-2-((3-acetylphenyl)diazenyl)phenyl)benzamide (3ia): Yield: 52.4 mg (68%); $R_f = 0.1$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 172-174 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.65 (br, 1H), 9.04 (d, $J = 8.8$ Hz, 1H), 8.61 (d, $J = 2.1$ Hz, 1H), 8.54 (t, $J = 1.8$ Hz, 1H), 8.19-8.12 (m, 3H), 8.06-8.03 (m, 2H), 7.70 (t, $J = 7.8$ Hz, 1H), 7.67-7.60 (m, 3H), 2.72 (s, 3H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 196.4, 166.0, 152.1, 139.1, 138.3, 138.0, 134.6, 133.2, 132.7, 132.3, 131.2, 129.9, 129.1, 127.3, 127.1, 125.2, 121.9, 120.1, 26.8, 26.6; IR (film): 3420, 1674, 1586, 1276, 798, 696 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_3$: 385.1426; found: 385.1424.



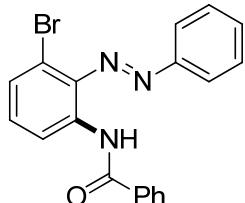
(E)-N-(3-methyl-2-(phenyldiazenyl)phenyl)benzamide (3ja): Yield: 61.2 mg (97%); $R_f = 0.5$ (EtOAc:Hexane = 1:10); Orange solid; Melting point: 102-104 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.13 (br, 1H), 8.81 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 6.8$ Hz, 2H), 7.86 (d, $J = 7.2$ Hz, 2H), 7.62-7.47 (m, 6H),

7.40 (t, $J = 8.0$ Hz, 1H), 7.13 (d, $J = 7.4$ Hz, 1H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 152.3, 142.5, 136.2, 135.8, 133.2, 132.0, 131.7, 131.1, 129.4, 128.8, 127.6, 125.9, 122.2, 118.5, 19.5; IR (film): 3339, 3062, 2925, 1677, 1582, 1459, 1293, 771 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}$: 315.1372; found: 315.1369.



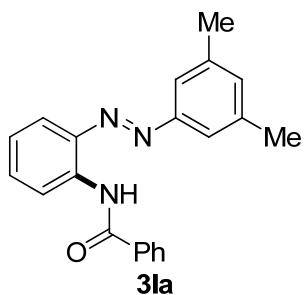
3ja

(E)-N-(3-bromo-2-(phenyldiazenyl)phenyl)benzamide (3ka): Yield: 57.8 mg (76%); $R_f = 0.5$ ($\text{EtOAc:Hexane} = 1:7$); Yellow solid; Melting point: 130-132 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.09 (br, 1H), 8.95 (dd, $J = 8.5, 1.2$ Hz, 1H), 8.02-7.99 (m, 2H), 7.97-7.93 (m, 2H), 7.65-7.53 (m, 7H), 7.34 (t, $J = 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 152.1, 135.4, 134.6, 133.4, 133.0, 132.3, 131.9, 131.0, 129.6, 128.9, 128.5, 127.6, 122.8, 120.1; IR (film): 3297, 3062, 1682, 1575, 1515, 1288, 769, 605 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{14}\text{BrN}_3\text{O}$: 379.0320; found: 379.0323.

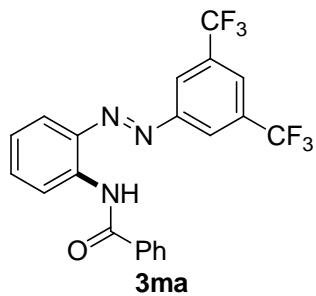


3ka

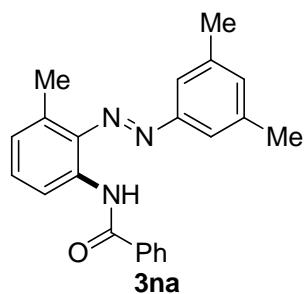
(E)-N-(2-((3,5-dimethylphenyl)diazenyl)phenyl)benzamide (3la): Yield: 38.2 mg (58%); $R_f = 0.4$ ($\text{EtOAc:Hexane} = 1:7$); Orange solid; Melting point: 95-97 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.62 (br, 1H), 8.90 (dd, $J = 8.4, 1.2$ Hz, 1H), 8.03-8.00 (m, 2H), 7.95 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.63-7.50 (m, 6H), 7.27-7.23 (m, 1H), 7.16 (br, 1H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 152.4, 139.1, 138.9, 135.4, 135.1, 133.2, 132.8, 132.1, 128.8, 127.3, 124.7, 123.6, 120.4, 120.2, 21.3; IR (film): 3387, 3060, 2918, 1679, 1595, 1523, 1449, 852 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}$: 329.1528; found: 329.1528.



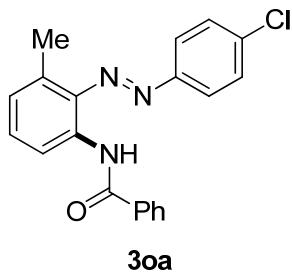
(E)-N-(2-((3,5-bis(trifluoromethyl)phenyl)diazenyl)phenyl)benzamide (3ma): Yield: 38.5 mg (44%); R_f = 0.5 (EtOAc:Hexane = 1:7); Orange solid; Melting point: 133-135 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.16 (br, 1H), 8.93 (dd, J = 8.4, 2.2 Hz, 1H), 8.35 (s, 2H), 8.01-7.97 (m, 4H), 7.64-7.61 (m, 2H), 7.57-7.54 (m, 2H), 7.29-7.25 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 152.6, 138.6, 136.4, 135.0, 134.9, 133.1 (q, J_{CF} = 34.0 Hz), 132.5, 129.0, 127.1, 124.1 (q, J_{CF} = 3.5 Hz), 123.8, 123.4, 122.9 (q, J_{CF} = 267.2 Hz), 122.4 (q, J_{CF} = 3.7 Hz), 120.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0; IR (film): 3329, 1653, 1592, 1368, 1278, 1133, 897 cm⁻¹; HRMS (EI): *m/z* calcd for C₂₁H₁₃F₆N₃O: 437.0963; found: 437.0965.



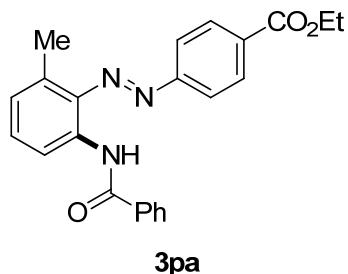
(E)-N-(2-((3,5-dimethylphenyl)diazenyl)-3-methylphenyl)benzamide (3na): Yield: 48.8 mg (71%); R_f = 0.4 (EtOAc:Hexane = 1:7); Orange solid; Melting point: 118-120 °C; ¹H NMR (400 MHz, CDCl₃) δ 13.18 (br, 1H), 8.80 (dd, J = 8.4, 0.5 Hz, 1H), 8.03-8.00 (m, 2H), 7.62-7.52 (m, 3H), 7.48 (br, 2H), 7.38 (t, J = 8.0 Hz, 1H), 7.13 (s, 1H), 7.12 (d, J = 7.6 Hz, 1H), 2.76 (s, 3H), 2.42 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 152.4, 142.2, 139.1, 136.3, 135.9, 132.9, 132.8, 131.9, 131.8, 128.6, 127.7, 125.9, 120.1, 118.5, 21.4, 19.5; IR (film): 3428, 3060, 2920, 1673, 1610, 1584, 1262, 701 cm⁻¹; HRMS (EI): *m/z* calcd for C₂₂H₂₁N₃O: 343.1685; found: 343.1683.



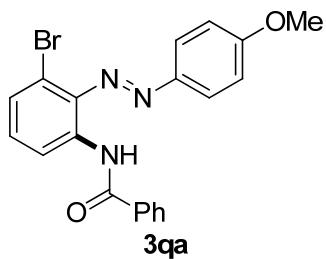
(E)-N-(2-((4-chlorophenyl)diazenyl)-3-methylphenyl)benzamide (3oa): Yield: 55.9 mg (80%); $R_f = 0.4$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 148-150 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.02 (br, 1H), 8.80 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 7.1$ Hz, 2H), 7.79 (d, $J = 8.7$ Hz, 2H), 7.63-7.49 (m, 5H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.14 (d, $J = 7.4$ Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 150.7, 142.6, 137.0, 136.1, 135.8, 133.6, 132.1, 131.8, 129.7, 128.8, 127.5, 126.0, 123.3, 118.5, 19.5; IR (film): 3166, 3055, 1675, 1581, 1262, 1085, 784, 706 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{16}\text{ClN}_3\text{O}$: 349.0982; found: 349.0983.



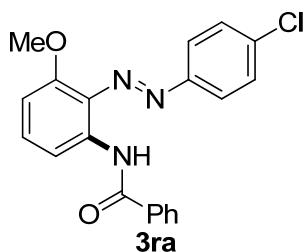
(E)-ethyl 4-((2-benzamido-6-methylphenyl)diazenyl)benzoate (3pa): Yield: 63.5 mg (82%); $R_f = 0.3$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 114-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.05 (br, 1H), 8.81 (d, $J = 8.4$ Hz, 1H), 8.20 (d, $J = 8.4$ Hz, 2H), 7.99 (d, $J = 7.5$ Hz, 2H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.62-7.53 (m, 3H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.14 (d, $J = 7.4$ Hz, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 2.76 (s, 3H), 1.43 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.1, 165.9, 154.7, 143.2, 136.4, 135.7, 134.2, 132.2, 132.1, 131.8, 130.9, 128.8, 127.6, 126.0, 121.9, 118.5, 61.4, 19.5, 14.3; IR (film): 3162, 3076, 2941, 1733, 1681, 1606, 1587, 1273, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_3$: 387.1583; found: 387.1586.



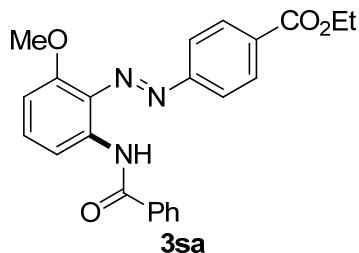
(E)-N-(3-bromo-2-((4-methoxyphenyl)diazenyl)phenyl)benzamide (3qa) : Yield: 60.7 mg (74%); $R_f = 0.3$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 172-174 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.07 (br, 1H), 8.91 (dd, $J = 8.5, 1.1$ Hz, 1H), 7.99-7.97 (m, 2H), 7.94-7.90 (m, 2H), 7.63-7.54 (m, 4H), 7.28 (t, $J = 8.2$ Hz, 1H), 7.03 (d, $J = 9.0$ Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.9, 162.8, 146.5, 135.5, 134.6, 132.8, 132.5, 132.2, 130.1, 128.8, 128.5, 127.6, 124.7, 120.1, 114.7, 55.7; IR (film): 3127, 3063, 1685, 1602, 1578, 1256, 1026, 782, 550 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{16}\text{BrN}_3\text{O}_2$: 409.0426; found: 409.0428.



(E)-N-(2-((4-chlorophenyl)diazenyl)-3-methoxyphenyl)benzamide (3ra): Yield: 69.5 mg (95%); $R_f = 0.2$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 151-153 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.19 (br, 1H), 8.56 (dd, $J = 8.5, 1.0$ Hz, 1H), 7.99-7.96 (m, 2H), 7.81-7.78 (m, 2H), 7.63-7.47 (m, 6H), 6.83 (dd, $J = 8.3, 0.7$ Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 159.2, 150.9, 136.8, 135.6, 135.0, 132.9, 132.1, 129.6, 128.8, 128.5, 127.6, 123.3, 112.5, 106.6, 56.5; IR (film): 3119, 3062, 1677, 1584, 1275, 1122, 701 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{16}\text{ClN}_3\text{O}_2$: 365.0931; found: 365.0929.

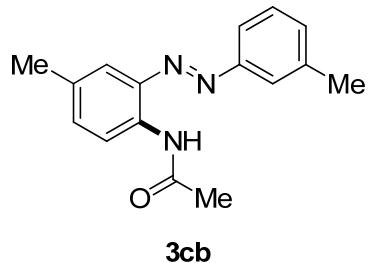


(E)-ethyl 4-((2-benzamido-6-methoxyphenyl)diazenyl)benzoate (3sa): Yield: 60.5 mg (75%); $R_f = 0.1$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 142-143 °C; ^1H NMR (400 MHz, CDCl_3) δ 13.27 (br, 1H), 8.58 (dd, $J = 8.6, 1.2$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 2H), 8.00 (d, $J = 7.2$ Hz, 2H), 7.89 (dt, $J = 8.5, 1.5$ Hz, 2H), 7.63-7.49 (m, 4H), 6.84 (d, $J = 8.3$ Hz, 1H), 4.42 (q, $J = 7.1$ Hz, 2H), 4.04 (s, 1H), 1.43 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 165.9, 159.6, 155.0, 135.6, 135.5, 133.0, 132.2, 132.0, 130.8, 128.8, 128.7, 127.6, 121.9, 112.4, 106.6, 61.3, 56.6, 14.3; IR (film): 3116, 2982, 1682, 1596, 1481, 1274, 1123, 773 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_4$: 403.1532; found: 403.1535.

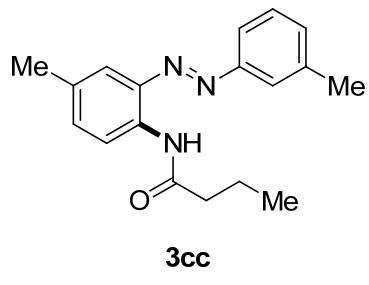


(E)-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)acetamide (3cb): Yield: 52.4 mg (98%); $R_f = 0.2$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 123-125 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.02 (br, 1H), 8.55 (d, $J = 8.4$ Hz, 1H), 7.66-7.64 (m, 3H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.5$ Hz, 1H), 7.29 (dd, $J = 8.5, 1.9$ Hz, 1H), 2.48 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.4,

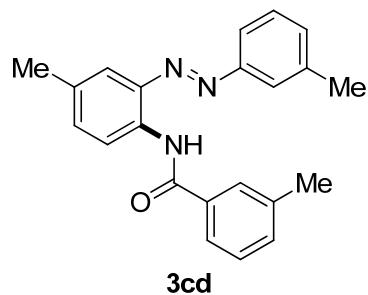
152.5, 139.3, 138.6, 133.59, 133.56, 133.1, 132.1, 129.1, 123.3, 121.2, 120.1, 119.6, 25.4, 21.5, 20.8; IR (film): 3296, 2918, 1660, 1594, 1309, 1292, 818, 687 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}$: 267.1372; found: 267.1371.



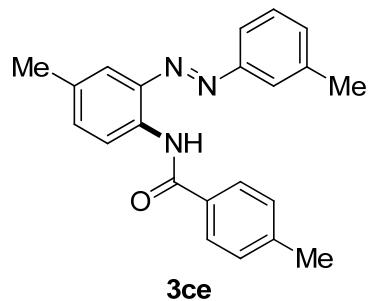
(E)-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)butyramide (3cc): Yield: 43.7 mg (74%); $R_f = 0.4$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 123-125 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 10.05 (br, 1H), 8.58 (d, $J = 8.5$ Hz, 1H), 7.66-7.64 (m, 3H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.5$ Hz, 1H), 7.29 (dd, $J = 8.5, 1.9$ Hz, 1H), 2.48 (s, 3H), 2.45 (t, $J = 7.5$ Hz, 2H), 2.38 (s, 3H), 1.82 (sextet, $J = 7.4$ Hz, 2H), 1.05 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.4, 152.6, 139.3, 138.7, 133.64, 133.59, 133.0, 132.0, 129.1, 123.2, 121.3, 120.2, 119.7, 40.4, 21.5, 20.8, 19.0, 13.8; IR (film): 3298, 2959, 1656, 1593, 1523, 1251, 687 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{18}\text{H}_{21}\text{N}_3\text{O}$: 295.1685; found: 295.1687.



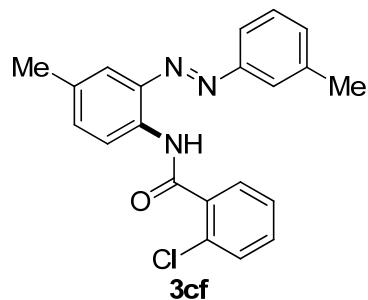
(E)-3-methyl-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3cd): Yield: 48.1 mg (70%); $R_f = 0.5$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 118-120 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 11.41 (br, 1H), 8.79 (d, $J = 8.5$ Hz, 1H), 7.81-7.80 (m, 2H), 7.77 (d, $J = 1.5$ Hz, 1H), 7.72 (s, 1H), 7.71 (d, $J = 6.1$ Hz, 1H), 7.45-7.31 (m, 5H), 2.48 (s, 3H), 2.47 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 152.4, 139.2, 138.8, 138.6, 135.4, 133.7, 133.2, 132.8, 132.7, 132.1, 129.1, 128.7, 127.8, 124.5, 124.4, 122.7, 120.1, 120.0, 21.5, 21.4, 20.8; IR (film): 3395, 3028, 2920, 1674, 1591, 1310, 825 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}$: 343.1685; found: 343.1686.



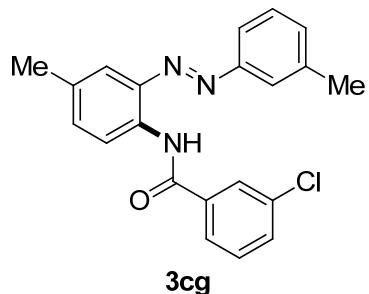
(E)-4-methyl-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3ce): Yield: 39.8 mg (58%); $R_f = 0.5$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 105-107 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.32 (br, 1H), 8.78 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 2H), 7.76 (d, $J = 1.3$ Hz, 1H), 7.71 (s, 1H), 7.70 (d, $J = 8.9$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.35-7.32 (m, 4H), 2.48 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.6, 152.5, 142.5, 139.3, 138.8, 133.8, 133.1, 133.1, 132.6, 132.1, 129.5, 129.2, 127.3, 124.2, 122.7, 120.1, 120.0, 21.6, 21.5, 20.8; IR (film): 3395, 3027, 2917, 1670, 1611, 1590, 1258, 741 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}$: 343.1685; found: 343.1685.



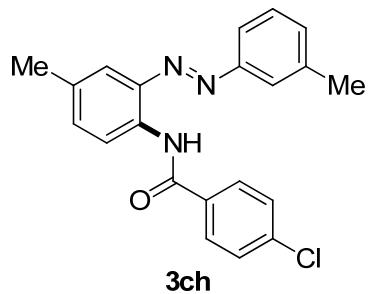
(E)-2-chloro-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3cf): Yield: 30.6 mg (42%); $R_f = 0.4$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 100-102 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.72 (br, 1H), 8.77 (d, $J = 8.5$ Hz, 1H), 7.83 (dd, $J = 7.2, 2.1$ Hz, 1H), 7.70 (d, $J = 1.1$ Hz, 1H), 7.66 (s, 1H), 7.63 (d, $J = 8.4$ Hz, 1H), 7.51-7.49 (m, 1H), 7.47-7.35 (m, 4H), 7.29 (d, $J = 7.5$ Hz, 1H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 152.4, 139.3, 139.1, 135.5, 133.81, 133.76, 133.6, 132.1, 131.8, 130.8, 130.7, 130.6, 129.0, 127.3, 123.1, 120.3 (2C), 120.0, 21.3, 20.9; IR (film): 3367, 3064, 1674, 1592, 1514, 1311, 745 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{ClN}_3\text{O}$: 363.1138; found: 363.1139.



(E)-3-chloro-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3cg): Yield: 65.5 mg (90%); $R_f = 0.6$ (EtOAc: Hexane = 1:7); Orange solid; Melting point: 117-119 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.59 (br, 1H), 8.74 (d, $J = 8.5$ Hz, 1H), 7.95 (br, 1H), 7.89 (d, $J = 7.7$ Hz, 1H), 7.78 (br, 1H), 7.72 (br, 1H), 7.71 (d, $J = 5.9$ Hz, 1H), 7.57-7.54 (m, 1H), 7.47 (t, $J = 7.9$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.34-7.31 (m, 2H), 2.47 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 152.2, 139.4, 138.7, 137.2, 134.9, 133.68, 133.65, 132.3, 132.0, 131.9, 130.2, 129.2, 127.2, 126.0, 125.8, 122.8, 120.1, 119.9, 21.4, 20.8; IR (film): 3391, 3067, 2921, 1680, 1589, 1573, 1312, 736, 685 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{ClN}_3\text{O}$: 363.1138; found: 363.1136.

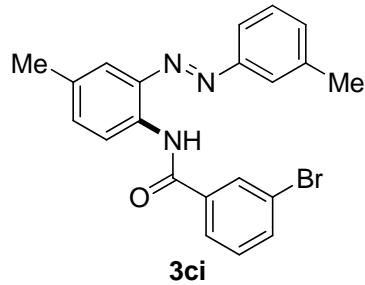


(E)-4-chloro-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3ch): Yield: 70.6 mg (97%); $R_f = 0.6$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 127-129 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.41 (br, 1H), 8.74 (d, $J = 8.5$ Hz, 1H), 7.92 (d, $J = 8.6$ Hz, 2H), 7.77 (d, $J = 1.2$ Hz, 1H), 7.68 (s, 1H), 7.66 (d, $J = 9.9$ Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.36-7.33 (m, 2H), 2.48 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 152.4, 139.4, 138.8, 138.2, 133.8, 133.7, 133.6, 132.5, 132.2, 129.3, 129.1, 128.7, 124.9, 122.6, 120.1, 120.0, 21.5, 20.8; IR (film): 3393, 3029, 2919, 1678, 1595, 1095, 823, 746 cm^{-1} ; HRMS (EI): m/z calcd. for $\text{C}_{21}\text{H}_{18}\text{ClN}_3\text{O}$: 363.1138; found: 363.1135.

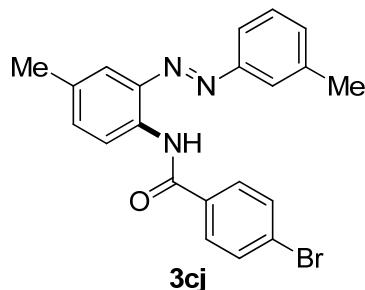


(E)-3-bromo-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3ci): Yield: 75.1 mg (92%); $R_f = 0.6$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 108-110 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.54 (br, 1H), 8.72 (d, $J = 8.5$ Hz, 1H), 8.07 (t, $J = 1.8$ Hz, 1H), 7.92 (dq, $J = 7.8, 0.7$ Hz, 1H), 7.75 (d, $J = 1.4$ Hz, 1H), 7.70-7.68 (m, 3H), 7.40 (q, $J = 7.8$ Hz, 2H), 7.31 (br, 1H), 7.29 (d, $J = 1.2$ Hz, 1H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 152.2, 139.4, 138.7, 137.4, 134.9, 133.7, 133.6, 132.3, 132.0, 130.5, 130.0, 129.2, 126.3, 126.0, 122.9, 122.8, 120.1, 119.9, 21.5, 20.8; IR (film): 3389, 3063,

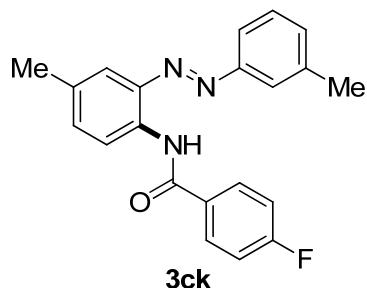
2920, 1678, 1596, 1247, 737, 577 cm^{-1} ; HRMS (EI): m/z cald for $\text{C}_{21}\text{H}_{18}\text{BrN}_3\text{O}$: 407.0633; found: 407.0631.



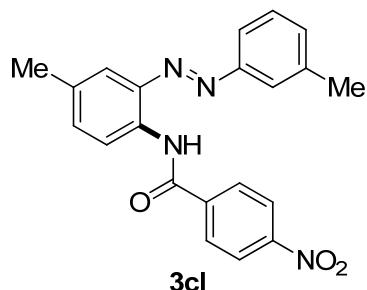
(E)-4-bromo-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3cj): Yield: 71.9 mg (88%); $R_f = 0.6$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 142-144 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 11.38 (br, 1H), 8.72 (d, $J = 8.5$ Hz, 1H), 7.83 (d, $J = 8.5$ Hz, 2H), 7.75 (br, 1H), 7.66-7.63 (m, 4H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.6, 152.3, 139.3, 138.8, 134.2, 133.7, 133.6, 132.4, 132.2, 132.0, 129.3, 128.8, 126.7, 124.9, 122.6, 120.1, 119.9, 21.5, 20.8; IR (film): 3330, 2917, 1653, 1594, 1521, 1315, 745, 588 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{BrN}_3\text{O}$: 407.0633; found: 407.0631.



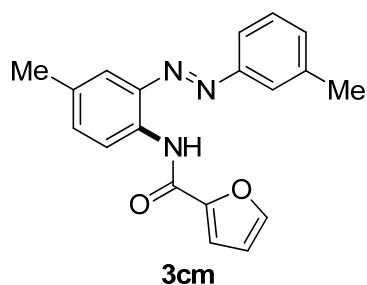
(E)-4-fluoro-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)benzamide (3ck): Yield: 68.1 mg (98%); $R_f = 0.6$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 123-125 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 11.37 (br, 1H), 8.73 (d, $J = 8.5$ Hz, 1H), 8.01-7.96 (m, 2H), 7.75 (d, $J = 1.4$ Hz, 1H), 7.66 (br, 1H), 7.65 (d, $J = 8.9$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.34-7.31 (m, 2H), 7.23-7.17 (m, 2H), 2.46 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.0 (d, $J_{\text{CF}} = 252.9$ Hz), 164.6, 152.4, 139.3, 138.8, 133.7, 133.4, 132.6, 132.2, 131.6 (d, $J_{\text{CF}} = 3.0$ Hz), 129.6 (d, $J_{\text{CF}} = 8.9$ Hz), 129.2, 124.9, 122.6, 120.1, 119.9, 115.9 (d, $J_{\text{CF}} = 21.9$ Hz), 21.5, 20.8; ^{19}F NMR (376 MHz, CDCl_3) δ -107.4; IR (film): 3353, 3074, 1677, 1597, 1315, 1225, 791 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{FN}_3\text{O}$: 347.1434; found: 347.1436.



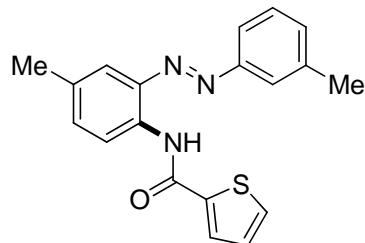
(E)-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)-4-nitrobenzamide (3cl): Yield: 65.9 mg (88%); $R_f = 0.5$ (EtOAc:Hexane = 1:7); Orange solid; Melting point: 163-165 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.60 (br, 1H), 8.72 (d, $J = 8.4$ Hz, 1H), 8.38 (d, $J = 8.6$ Hz, 2H), 8.13 (d, $J = 8.6$ Hz, 2H), 7.79 (s, 1H), 7.66 (s, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 6.9$ Hz, 2H), 2.48 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 152.2, 149.8, 140.9, 139.5, 138.8, 134.2, 133.7, 132.4, 131.8, 129.3, 128.4, 125.6, 124.0, 122.6, 120.1, 119.8, 21.5, 20.8; IR (film): 3347, 2918, 1657, 1594, 1521, 1346, 1313, 710 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_3$: 374.1379; found: 374.1381.



(E)-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)furan-2-carboxamide (3cm): Yield : 31.9 mg (50%); $R_f = 0.2$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 128-129 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.33 (br, 1H), 8.70 (d, $J = 8.4$ Hz, 1H), 7.81 (s, 1H), 7.80 (d, $J = 9.0$ Hz, 1H), 7.74 (d, $J = 1.3$ Hz, 1H), 7.58 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.34-7.32 (m, 2H), 7.27 (dd, $J = 3.5, 0.7$ Hz, 1H), 6.60 (q, $J = 1.7$ Hz, 1H), 2.50 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 152.5, 148.5, 144.2, 139.1, 138.9, 133.6, 133.4, 132.9, 132.1, 129.1, 123.0, 122.5, 120.3, 120.2, 115.2, 112.7, 21.5, 20.9; IR (film): 3363, 2920, 1676, 1597, 1520, 1312, 1163 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}_2$: 319.1321; found: 319.1321.

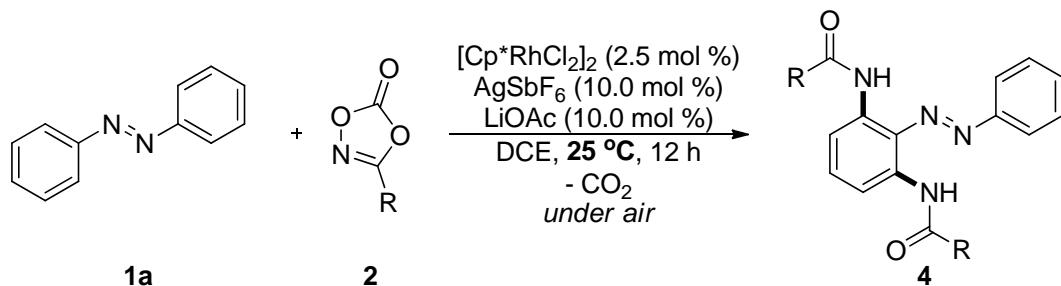


(E)-N-(4-methyl-2-(m-tolyldiazenyl)phenyl)thiophene-2-carboxamide (3cn): Yield: 61.0 mg (91%); R_f = 0.4 (EtOAc:Hexane = 1:7); Orange solid; Melting point: 106-108 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.08 (br, 1H), 8.67 (d, J = 8.5 Hz, 1H), 7.72-7.70 (m, 4H), 7.57 (d, J = 4.9 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 7.16 (t, J = 4.3 Hz, 1H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 152.5, 140.0, 139.3, 138.6, 133.7, 133.3, 132.8, 132.1, 130.8, 129.2, 128.7, 127.9, 123.6, 122.8, 120.1, 119.9, 21.5, 20.8; IR (film): 3383, 3100, 2919, 1665, 1592, 1512, 1311, 1248 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{OS}$: 335.1092; found: 335.1095.



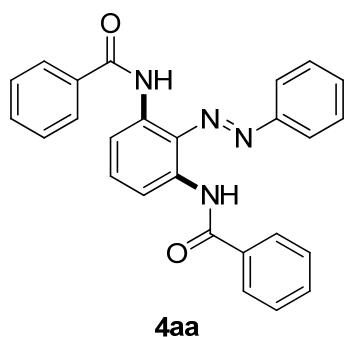
3cn

4. General procedure for diamidation of azobenzene with dioxazolones

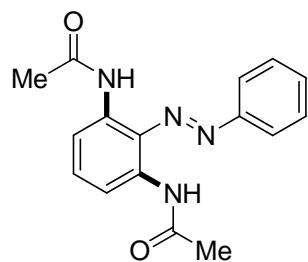


To a test tube were added azobenzene (**1a**) (36.5 mg, 0.2 mmol), dioxazolone (**2**) (97.9 mg, 0.6 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol), and LiOAc (1.3 mg, 0.02 mmol) in DCE (1.0 mL). The resulting mixture was stirred at 25 °C for 12 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel using EtOAc:Hexane = 1:7.

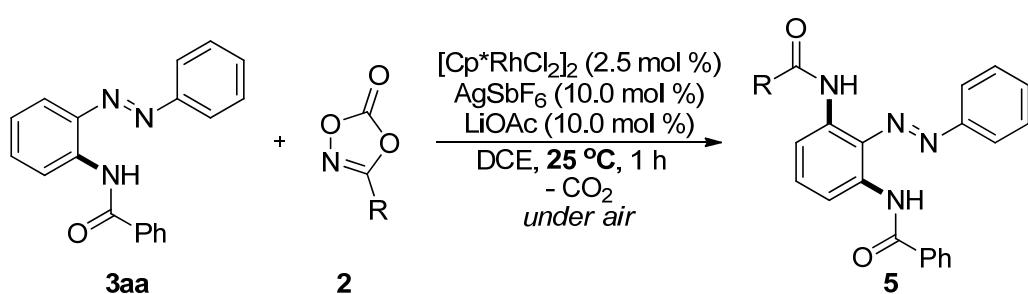
(E)-*N,N'*-(2-(phenyldiazenyl)-1,3-phenylene)dibenzamide (4aa**):** Yield: 71.5 mg (85%); R_f = 0.2 (EtOAc:Hexane = 1:7); Brown solid; Melting point: 227-229 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.76 (br, 2H), 8.66 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 7.0 Hz, 4H), 7.82 (d, J = 1.7 Hz, 1H), 7.80 (d, J = 1.3 Hz, 1H), 7.64-7.54 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 152.2, 136.2, 136.0, 135.3, 132.2, 131.6, 129.8, 128.9, 127.3, 126.2, 121.8, 114.6; IR (film): 3362, 3063, 1684, 1594, 1579, 1302, 776 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}_2$: 420.1586; found: 420.1582.



(E)-N,N'-(2-(phenyldiazenyl)-1,3-phenylene)diacetamide (4ab): Yield: 51.6 mg (87%); $R_f = 0.1$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 231-233 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.83 (br, 2H), 8.38 (d, $J = 8.4$ Hz, 2H), 7.76-7.73 (m, 2H), 7.61-7.52 (m, 3H), 7.45 (t, $J = 8.4$ Hz, 1H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 151.8, 135.7, 135.5, 131.6, 129.7, 129.2, 125.2, 122.0, 114.4, 25.6; IR (film): 3317, 3060, 1673, 1592, 1460, 1296, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2$: 296.1273; found: 296.1271.

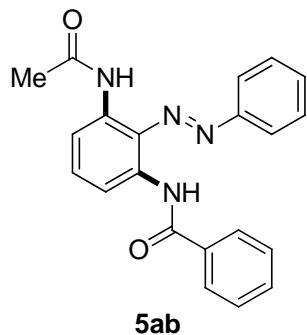


5. General procedure for amidation of mono-amidated azobenzenes

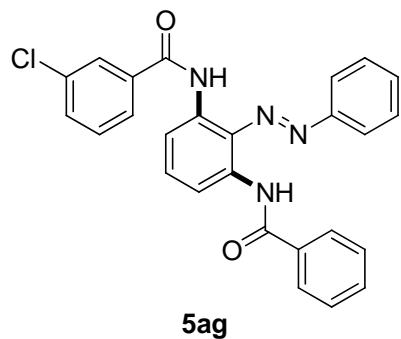


To a test tube were added mono-amidated azobenzene (**3aa**) (120.5 mg, 0.4 mmol), dioxazolone (**2**) (20.2 mg, 0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol), and LiOAc (1.3 mg, 0.02 mmol) in DCE (1.0 mL). The resulting mixture was stirred at 25 °C for 1 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel using EtOAc:Hexane = 1:2.

(E)-N-(3-acetamido-2-(phenyldiazenyl)phenyl)benzamide (5ab): Yield: 43.8 mg (61%); $R_f = 0.3$ (EtOAc:Hexane = 1:2); Brown solid; Melting point: 192-194 °C; ^1H NMR (400 MHz, CDCl_3) δ 12.06 (br, 1H), 10.45 (br, 1H), 8.60 (d, $J = 8.4$ Hz, 1H), 8.42 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 7.9$ Hz, 2H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.62-7.49 (m, 7H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 166.2, 152.0, 136.9, 135.7, 135.4, 135.0, 132.1, 131.6, 129.7, 129.2, 128.9, 127.3, 125.8, 121.9, 114.5, 25.5; IR (film): 3303, 3062, 1681, 1590, 1459, 1285, 770 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_2$: 358.1430; found: 358.1433.

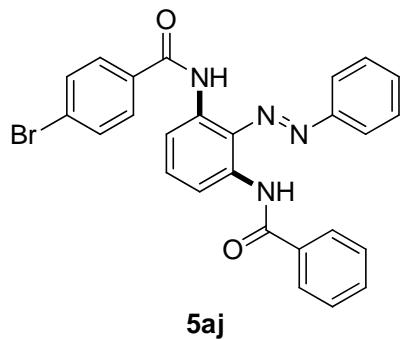


(E)-N-(3-benzamido-2-(phenyldiazenyl)phenyl)-3-chlorobenzamide (5ag): Yield: 57.1 mg (63%); $R_f = 0.3$ (EtOAc:Hexane = 1:2); Yellow solid; Melting point: 209-211 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.81 (br, 1H), 11.63 (br, 1H), 8.66 (dd, $J = 8.4, 1.0$ Hz, 1H), 8.61 (dd, $J = 8.4, 1.0$ Hz, 1H), 8.00-7.96 (m, 3H), 7.90 (d, $J = 7.8$ Hz, 1H), 7.83 (dd, $J = 8.1, 1.4$ Hz, 2H), 7.63-7.53 (m, 8H), 7.49 (t, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 164.3, 152.1, 137.0, 136.5, 135.9, 135.7, 135.3, 135.0, 132.23, 132.17, 131.8, 130.3, 129.8, 128.9, 127.3, 127.2, 126.2, 125.8, 121.9, 114.9, 114.5; IR (film): 3371, 3060, 1684, 1612, 1592, 1298, 768, 680 cm^{-1} ; HRMS (EI): m/z calcd for $\text{C}_{26}\text{H}_{19}\text{ClN}_4\text{O}_2$: 454.1197; found: 454.1201.

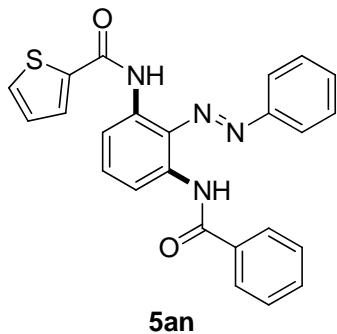


(E)-N-(3-benzamido-2-(phenyldiazenyl)phenyl)-4-bromobenzamide (5aj): Yield: 75.8 mg (76%); $R_f = 0.3$ (EtOAc:Hexane = 1:7); Yellow solid; Melting point: 215-217 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.76 (br, 1H), 11.64 (br, 1H), 8.66 (d, $J = 8.4$ Hz, 1H), 8.61 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 7.0$ Hz, 2H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.63-7.53 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 165.0, 152.2, 136.5, 136.0, 135.8, 135.3, 134.2, 132.25, 132.16, 131.7, 129.9, 128.93, 128.86,

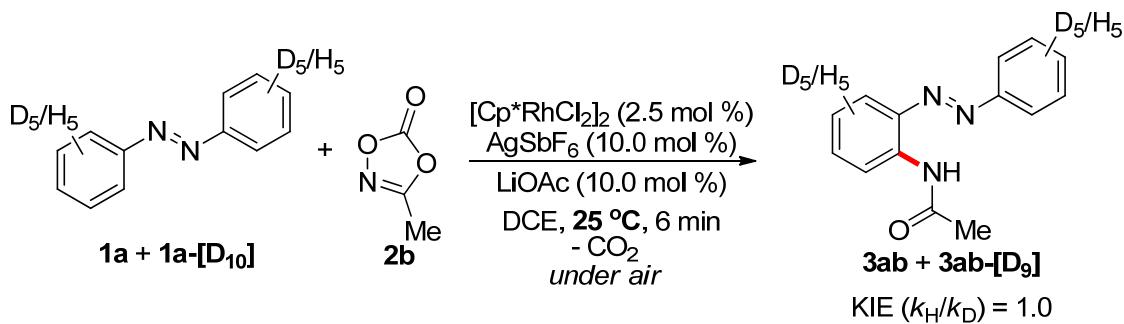
127.3, 127.0, 126.2, 121.7, 114.8, 114.6; IR (film): 3344, 3060, 1683, 1589, 1478, 1295, 697, 614 cm⁻¹; HRMS (EI): *m/z* calcd for C₂₆H₁₉BrN₄O₂: 498.0691; found: 498.0689.



(E)-N-(3-benzamido-2-(phenyldiazenyl)phenyl)thiophene-2-carboxamide (5an): Yield: 47.7 mg (56%); *R*_f = 0.2 (EtOAc:Hexane = 1:2); Yellow solid; Melting point: 214-216 °C; ¹H NMR (400 MHz, CDCl₃) δ 11.84 (br, 1H), 11.43 (br, 1H), 8.63 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.54 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.98 (d, *J* = 7.0 Hz, 2H), 7.85 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.74 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.63-7.53 (m, 8H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 166.0, 160.1, 152.3, 139.7, 136.2, 135.91, 135.85, 135.3, 132.2, 131.6, 131.1, 129.8, 129.2, 128.9, 128.0, 127.3, 126.0, 121.8, 114.62, 114.59; IR (film): 3363, 3063, 1682, 1592, 1298, 703 cm⁻¹; HRMS (EI): *m/z* calcd for C₂₄H₁₈N₄O₂S: 426.1150; found: 426.1154.



6. Studies with isotopically labeled compounds



To a test tube azobenzene (**1a**) (36.5 mg, 0.2 mmol), azobenzene (**1a-[D₁₀]**) (38.5 mg, 0.2 mmol), 3-methyl-1,4,2-dioxazol-5-one (**2b**) (20.2 mg, 0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol), and LiOAc (1.3 mg, 0.02 mmol) in DCE (1.0 mL) were added. The resulting mixture was stirred under air at 25 °C for 6 min. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel using EtOAc:Hexane = 1:7 to yield **3ab + 3ab-[D₉]** (14.2 mg, 23%) as a orange solid. The ratio of **3ab** and **3ab-[D₉]** was determined to be 50/50 (1.0) by ¹H NMR spectroscopy.

7. X-ray crystallography of 3aa

A pink block-like specimen of C₁₉H₁₅N₃O, approximate dimensions 0.080 mm x 0.200 mm x 0.360 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC 1477470).

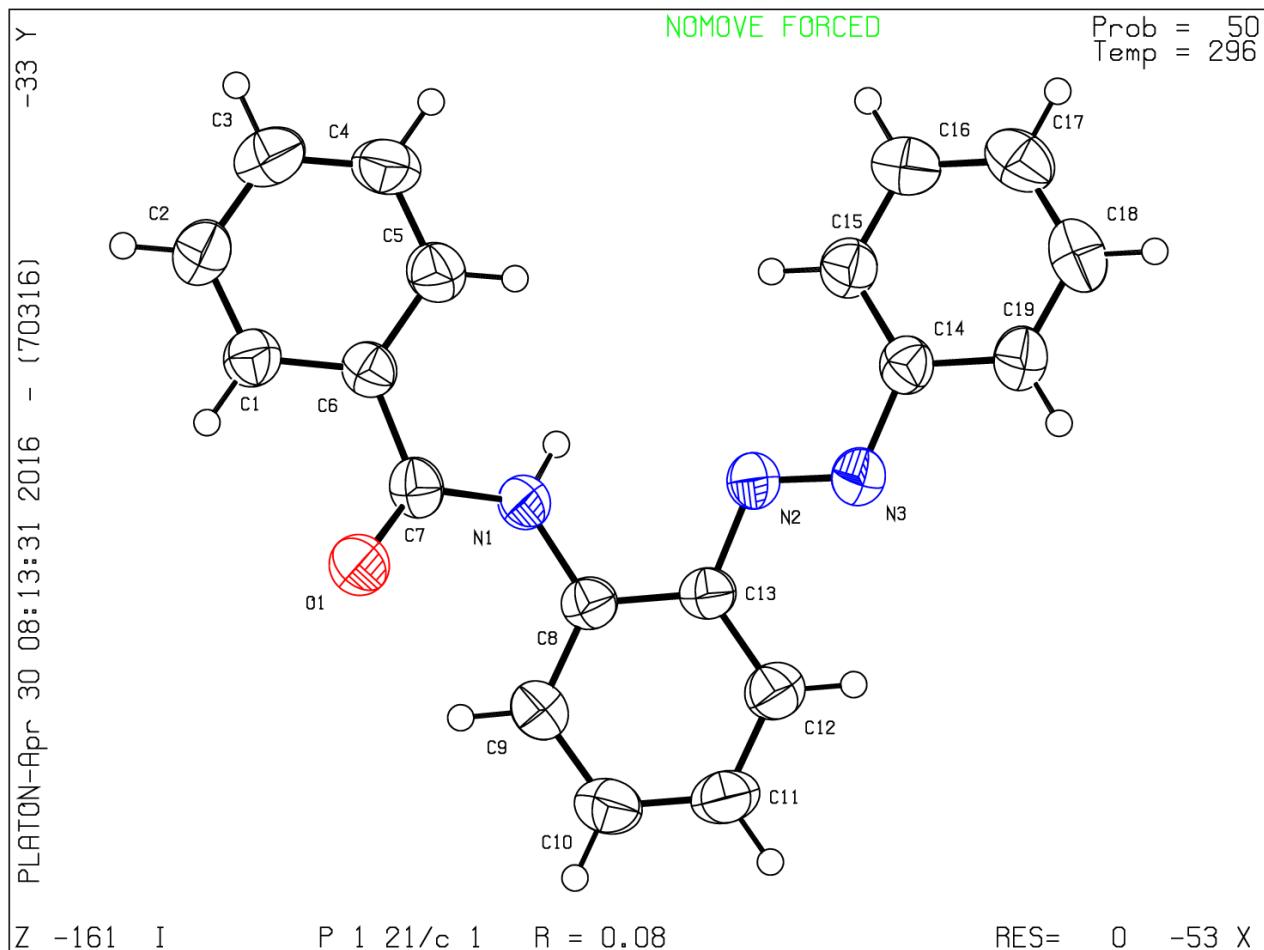


Table 1. Sample and crystal data for 3aa.

Identification code	3aa	
Chemical formula	C ₁₉ H ₁₅ N ₃ O	
Formula weight	301.34	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.200 x 0.360 mm	
Crystal habit	pink block	
Crystal system	monoclinic	
Space group	P 1 2 ₁ /c 1	
Unit cell dimensions	a = 17.259(2) Å	α = 90°
	b = 4.9915(6) Å	β = 111.712(4)°

	$c = 18.893(2) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1512.1(3) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.324 g/cm^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	632	

Table 2. Data collection and structure refinement for 3aa.

Theta range for data collection	2.32 to 28.42°	
Index ranges	$-23 \leq h \leq 23, -6 \leq k \leq 6, -25 \leq l \leq 24$	
Reflections collected	30648	
Independent reflections	3524 [$R(\text{int}) = 0.1233$]	
Coverage of independent reflections	97.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9930 and 0.9700	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3524 / 0 / 209	
Goodness-of-fit on F^2	1.034	
Final R indices	2021 data; $I > 2\sigma(I)$	$R_1 = 0.0777, wR_2 = 0.1899$
	all data	$R_1 = 0.1369, wR_2 = 0.2149$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1184P)^2 + 0.0366P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Extinction coefficient	0.0270(50)	
Largest diff. peak and hole	0.276 and -0.227 e \AA^{-3}	
R.M.S. deviation from mean	0.074 e \AA^{-3}	

Table 3. Bond lengths (Å) for 3aa.

O1-C7	1.233(2)	N2-N3	1.257(3)
N2-C13	1.427(3)	N3-C14	1.429(3)
N1-C7	1.351(3)	N1-C8	1.414(3)
N1-H1	0.86	C8-C9	1.389(3)
C8-C13	1.398(3)	C14-C19	1.379(3)
C14-C15	1.386(3)	C13-C12	1.395(3)
C6-C1	1.382(3)	C6-C5	1.389(3)
C6-C7	1.500(3)	C9-C10	1.388(3)
C9-H9	0.93	C1-C2	1.375(3)
C1-H1A	0.93	C16-C17	1.372(4)
C16-C15	1.380(3)	C16-H16	0.93
C15-H15	0.93	C12-C11	1.375(4)
C12-H12	0.93	C5-C4	1.373(4)
C5-H5	0.93	C19-C18	1.387(4)
C19-H19	0.93	C17-C18	1.373(4)
C17-H17	0.93	C10-C11	1.381(4)
C10-H10	0.93	C18-H18	0.93

C2-C3	1.380(4)	C2-H2	0.93
C11-H11	0.93	C3-C4	1.374(4)
C3-H3	0.93	C4-H4	0.93

Table 4. Bond angles (°) for 3aa.

N3-N2-C13	114.06(18)	N2-N3-C14	114.67(19)
C7-N1-C8	126.72(19)	C7-N1-H1	116.6
C8-N1-H1	116.6	C9-C8-C13	119.7(2)
C9-C8-N1	122.1(2)	C13-C8-N1	118.17(19)
C19-C14-C15	119.6(2)	C19-C14-N3	115.3(2)
C15-C14-N3	125.0(2)	C12-C13-C8	119.8(2)
C12-C13-N2	123.3(2)	C8-C13-N2	116.88(19)
C1-C6-C5	118.9(2)	C1-C6-C7	117.3(2)
C5-C6-C7	123.7(2)	C10-C9-C8	119.4(2)
C10-C9-H9	120.3	C8-C9-H9	120.3
O1-C7-N1	123.2(2)	O1-C7-C6	120.5(2)
N1-C7-C6	116.33(19)	C2-C1-C6	121.2(2)
C2-C1-H1A	119.4	C6-C1-H1A	119.4
C17-C16-C15	120.2(2)	C17-C16-H16	119.9
C15-C16-H16	119.9	C16-C15-C14	119.7(2)
C16-C15-H15	120.2	C14-C15-H15	120.2
C11-C12-C13	120.4(2)	C11-C12-H12	119.8
C13-C12-H12	119.8	C4-C5-C6	120.1(2)
C4-C5-H5	120.0	C6-C5-H5	120.0
C14-C19-C18	120.6(2)	C14-C19-H19	119.7
C18-C19-H19	119.7	C16-C17-C18	120.8(2)
C16-C17-H17	119.6	C18-C17-H17	119.6
C11-C10-C9	121.2(2)	C11-C10-H10	119.4
C9-C10-H10	119.4	C17-C18-C19	119.1(3)
C17-C18-H18	120.5	C19-C18-H18	120.5
C1-C2-C3	119.1(2)	C1-C2-H2	120.4
C3-C2-H2	120.4	C12-C11-C10	119.6(2)
C12-C11-H11	120.2	C10-C11-H11	120.2
C4-C3-C2	120.4(2)	C4-C3-H3	119.8
C2-C3-H3	119.8	C5-C4-C3	120.3(2)
C5-C4-H4	119.9	C3-C4-H4	119.9

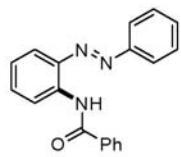
8. References

- (1) (a) Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 6174. (b) Ellman, J. A.; Lavis, L. D.; Bergman, R. G.; Lian, Y. *J. Am. Chem. Soc.* **2013**, *135*, 7122. (c) Wang, J.; He, J.; Zhi, C.; Luo, B.; Pan,

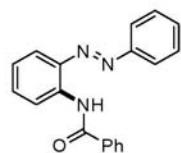
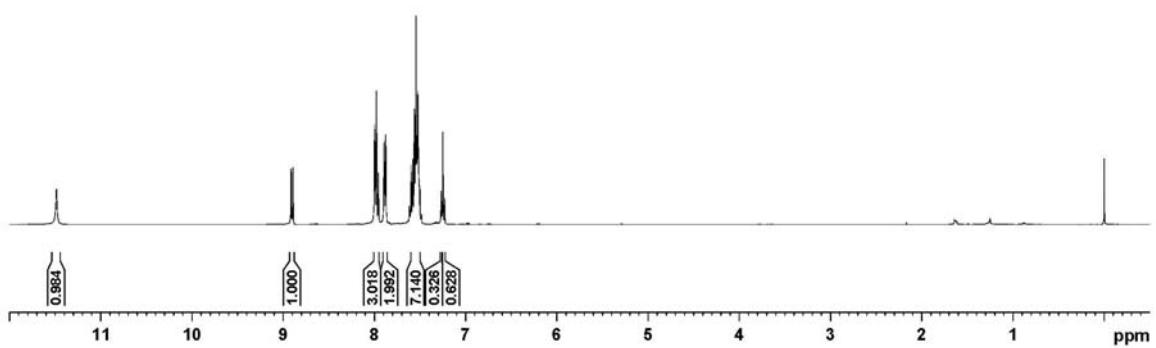
Y.; Cao, X.; Gu, H. *RSC Adv.* **2014**, *4*, 16607. (d) Zhao, R.; Tan, Y.; Xie, Y.; Gao, C.; Liu, H.; Jiang, Y. *Tetrahedron Lett.* **2011**, *52*, 3805. (e) Kaiser, M.; Leitner, S. P.; Hirtenlehner, C.; List, M.; Gerisch, A.; Monkowius, U. *Dalton Trans.* **2013**, *42*, 14749. (f) Badjic, J. D.; Kostic, N. M. *J. Mater. Chem.* **2001**, *11*, 408. (g) Koduri, N. D.; Scott, H.; Hileman, B.; Cox, J. D.; Coffin, M.; Glicksberg, L.; Hussaini, S. R. *Org. Lett.* **2012**, *14*, 440.

(2) Park, Y.; Park, K. T.; Kim, J. G.; Chang, S. *J. Am. Chem. Soc.* **2015**, *137*, 4534.

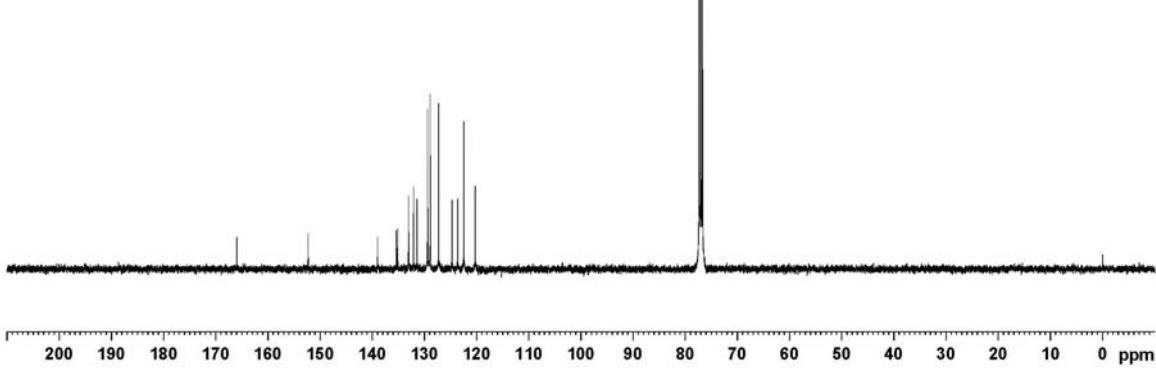
8. ^1H and ^{13}C NMR spectra

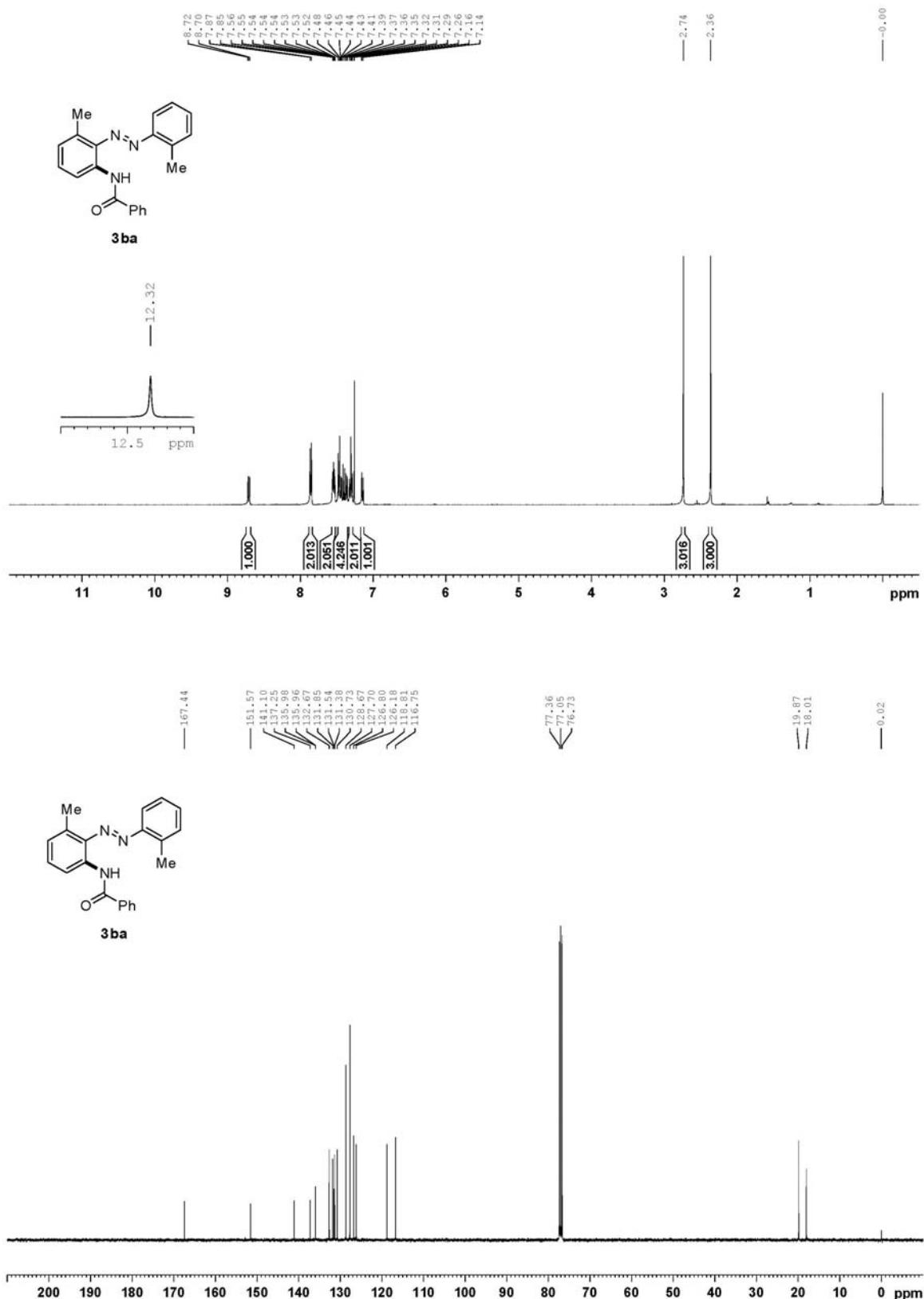


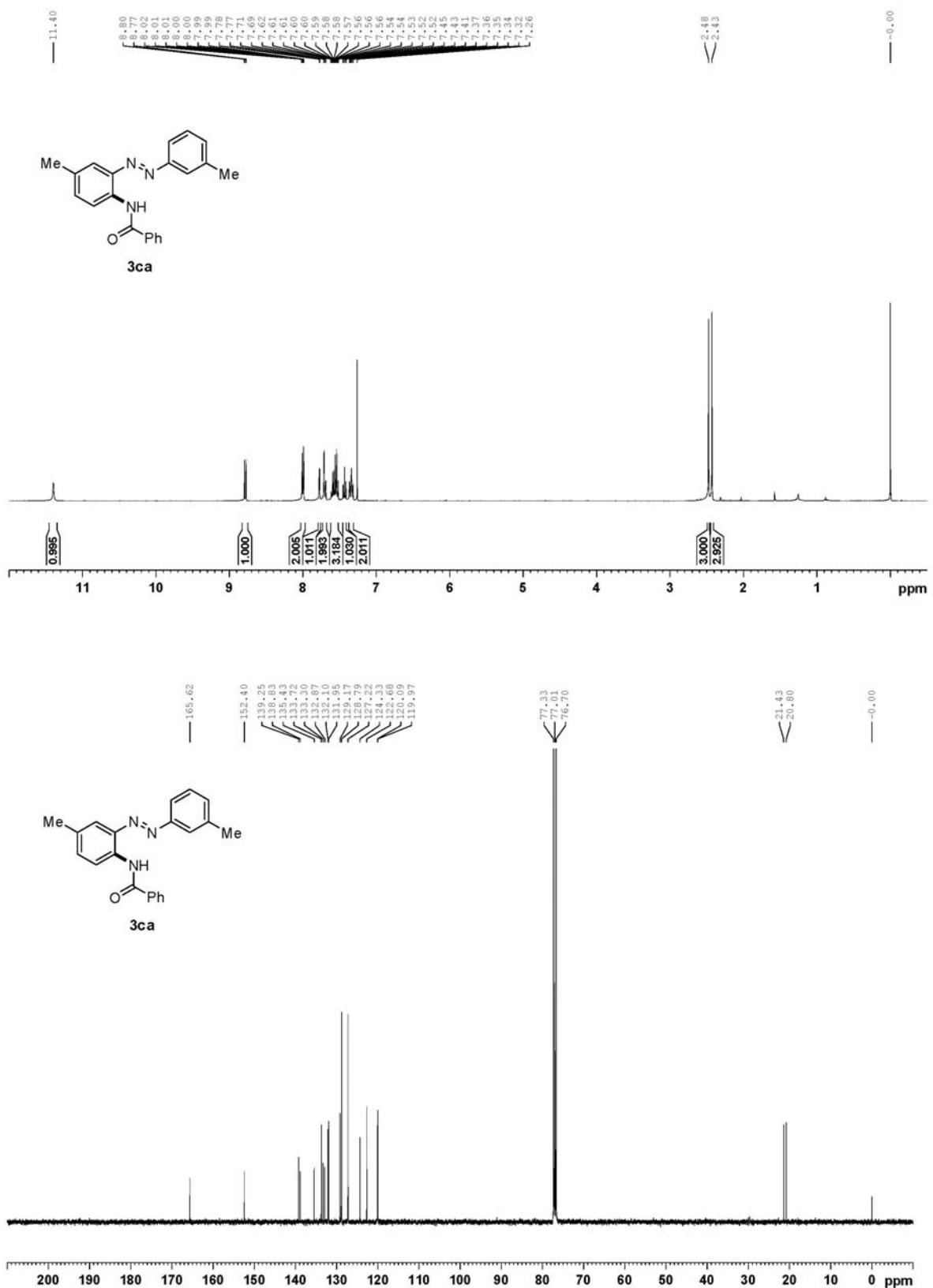
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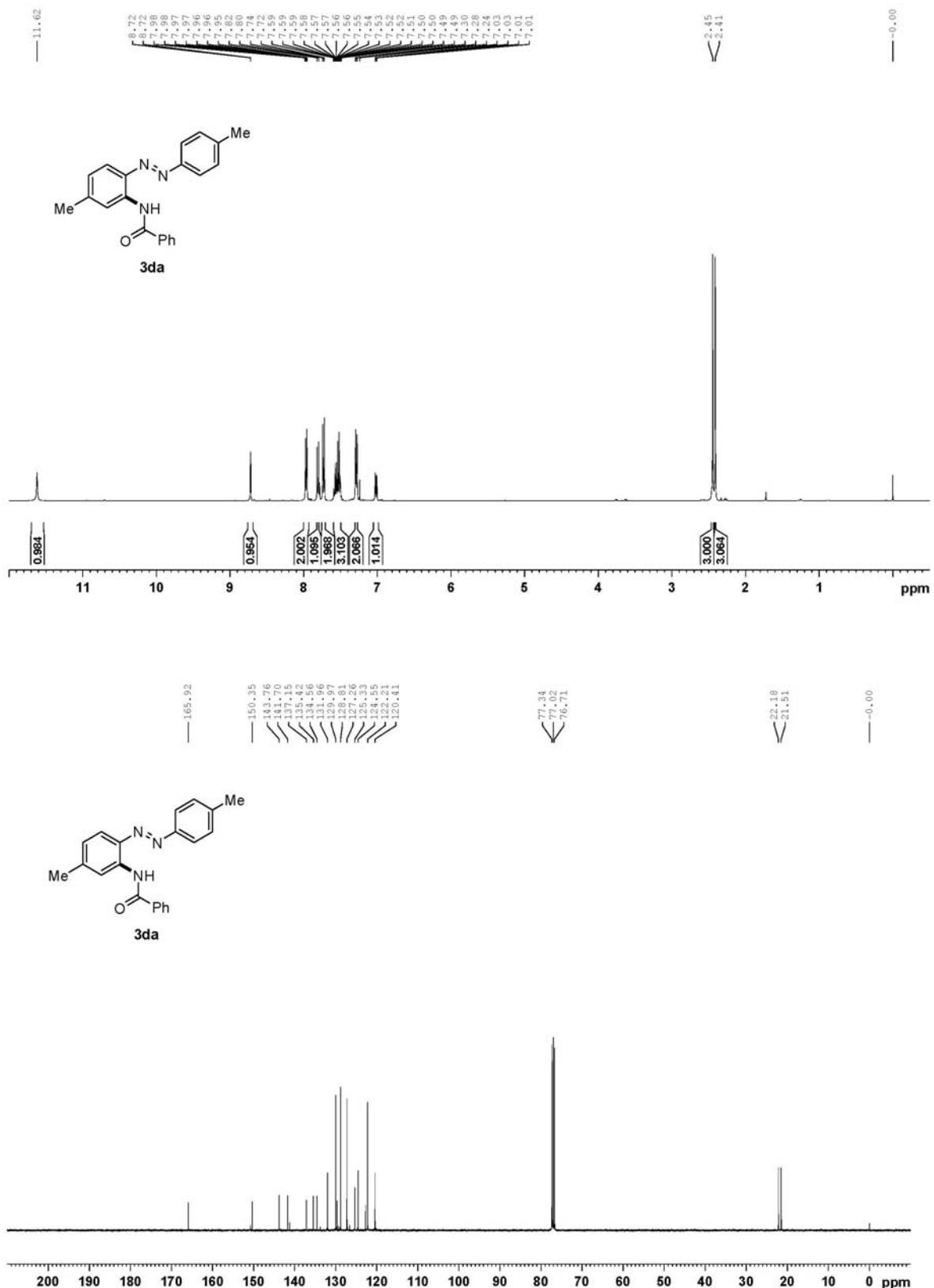


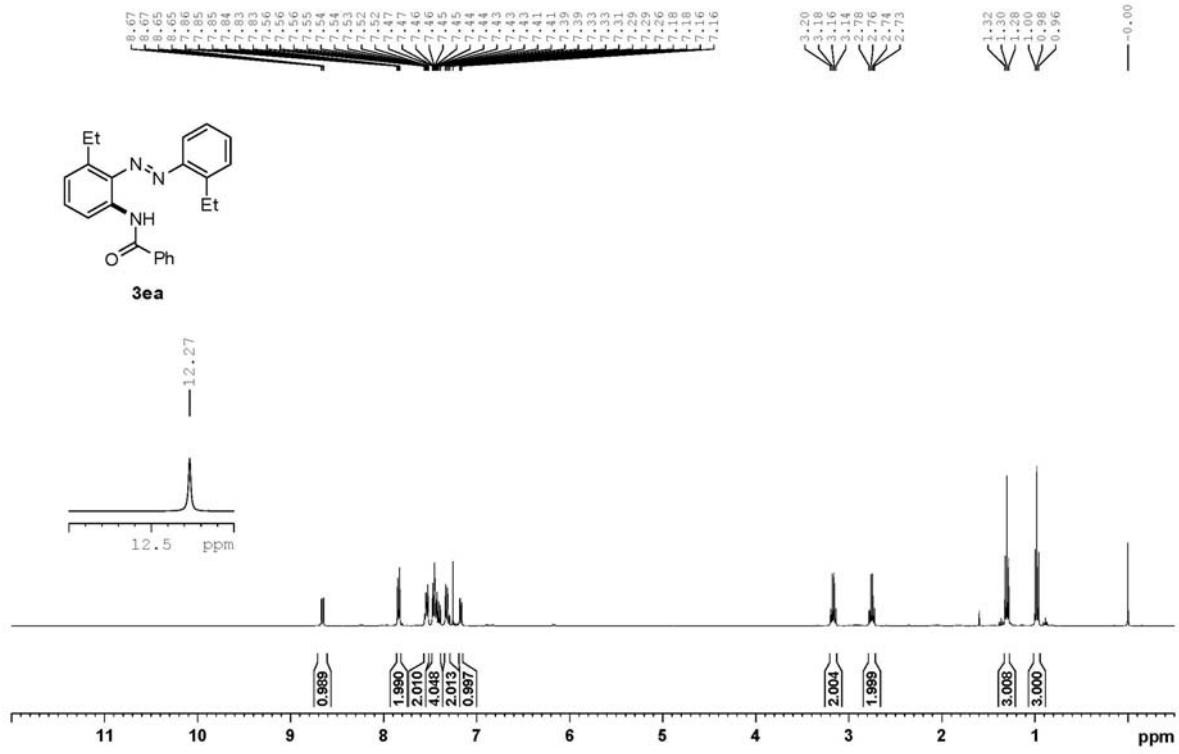
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3ea

