**Bi(OTf)₃-Catalyzed Intramolecular Amination of
Triazenylaryl Allylic Alcohols: a Stereoselective,
High-Yield Synthesis of (*E*)-3-Alkenyl 2*H*-Indazoles**

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A. General Information

Air- or moisture-sensitive reactions were carried out under nitrogen. THF was dried with sodium and freshly distilled. The other materials and solvents were purchased from Aladdin and other commercial suppliers and used without additional purification unless otherwise stated. NMR spectra were recorded on a Bruke Avance operating at for ¹H NMR at 300, 400 or 500 MHz, and

^{13}C NMR at 75, 100 or 125 MHz using TMS as internal standard. Chemical shifts were given relative to CDCl_3 (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR) and $(\text{CD}_3)_2\text{SO}$ (2.50 ppm for ^1H NMR, 40.5 ppm for ^{13}C NMR). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization. Infrared spectra were recorded on a Bruke ATR-FTIR spectrometer. Melting points were measured with WRS-1A digital point apparatus.

B. General Procedure for triazenylaryl allylic alcohol **1** Preparation

triazenylaryl allylic alcohols **1a-t** were prepared from the corresponding triazene benzaldehydes and aryl ketones according to the procedure below.

Triazene benzaldehyde (5 mmol) was taken in a flask (100 mL) and dissolved in EtOH (10 mL). To the solution, substituted aryl ketone (6 mmol) followed by aqueous NaOH solution (3 mL, 3 M) was added. The reaction mixture was stirred at room temperature for 8 h. After Completion, monitored by TLC, the reaction mixture was subjected to filtration to obtain their residue. The residue was thoroughly washed with 20 mL water, followed by 20 mL Et₂O and dried with vacuo to obtain the crude product **S1**.

To a solution of **S1** (3 mmol) in EtOH (5 mL) was added CeCl₃·7H₂O (1119 mg, 3 mmol), followed by NaBH₄ (342 mg, 9 mmol) dropwise in ice bath. The reaction mixture was stirred in ice bath for 1 h before water (20 mL) was added. After stirred at room temperature for 0.5 h, the mixture was extracted with ethyl acetate (40 mL × 4). The organic fractions were dried over Na₂SO₄, concentrated in vacuo and purified by silica gel chromatography to provide the triazenylaryl allylic alcohol **1**.

Ethyl-3-((*E*)-3-hydroxy-3-phenylprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1a**).

Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and acetophenone (720 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1a** (1061 mg, 2.8 mmol, 56%) as a light yellow solid.

R_f = 0.13 (5:1 Petroleum ether/EtOAc); m.p. = 91-93 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.18 (s, 1 H), 7.84 (d, J = 8.8 Hz, 1 H), 7.45-7.41 (m, 3 H), 7.36-7.31 (m, 3 H), 7.28 (t, J = 7.0 Hz, 1 H), 6.50 (dd, J = 16.2, 6.6 Hz, 1 H), 5.41 (d, J = 6.8 Hz, 1 H), 4.33 (q, J = 7.3 Hz, 2 H), 3.94 (br s, 2 H), 3.64 (br s, 2 H), 2.49 (br s, 1 H), 2.02 (br s, 4 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 151.4, 142.9, 132.5, 130.1, 129.3, 128.4, 127.8, 127.4, 126.7, 126.5, 126.3, 116.6, 75.4, 60.7, 51.1, 46.6, 23.7, 23.5, 14.3; IR (ATR-FTIR): 3350, 1705, 1289, 1251, 1220, 1115, 1023, 693 cm^{-1} ; MS (EI): m/z (%): 379 (M^+ , 3), 362 (12), 334 (11), 292 (60), 272 (100), 235 (28), 203 (31), 189 (59), 175 (92), 105 (68); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_3$ (M^+): 379.1896, found: 379.1897.

3-((*E*)-3-hydroxy-3-phenylprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzonitrile (**1b**). Prepared from (*E*)-3-formyl-4-(pyrrolidin-1-yl diazenyl)benzonitrile (1140 mg, 5 mmol) and acetophenone (720 mg, 6 mmol) according to the general procedure. Purification via flash column

chromatography (10-50% EtOAc/Petroleum ether) gave **1b** (780 mg, 2.35 mmol, 47%) as a light yellow solid.

R_f = 0.14 (3:1 Petroleum ether/EtOAc); m.p. = 116-118 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.70 (s, 1 H), 7.46-7.41 (m, 3 H), 7.39-7.34 (m, 3 H), 7.30-7.25 (m, 2 H), 6.40 (dd, *J* = 16.0, 6.4 Hz, 1 H), 5.39 (t, *J* = 4.6 Hz, 1 H), 3.95 (br s, 2 H), 3.63 (br s, 2 H), 2.38 (d, *J* = 4.0 Hz, 1 H), 2.04 (br s, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 151.1, 142.6, 133.5, 131.3, 131.1, 130.4, 128.5, 127.7, 126.3, 125.6, 119.5, 117.4, 107.5, 75.2, 51.3, 47.0, 23.9, 23.4; IR (ATR-FTIR): 3317, 2218, 1389, 1305, 973, 697 cm⁻¹; MS (EI): *m/z* (%): 332 (M⁺, 9), 315 (3), 262 (21), 245 (29), 234 (32), 226 (100), 216 (76), 204 (53), 190 (66), 179 (39), 156 (99), 142 (43), 128 (100), 114 (48), 105 (100); HRMS (EI-TOF) calcd for C₂₀H₂₀N₄O (M⁺): 332.1637, found: 332.1641.

(*E*)-3-(5-chloro-2-((*E*)-pyrrolidin-1-yl-diazenyl)phenyl)-1-phenylprop-2-en-1-ol (**1c**). Prepared from 5-chloro-2-(pyrrolidin-1-ylazo)-benzaldehyde (1185 mg, 5 mmol) and acetophenone (720 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1c** (1262 mg, 3.7 mmol, 74%) as a light yellow solid.

R_f = 0.16 (5:1 Petroleum ether/EtOAc); m.p. = 83-84 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.47-7.40 (m, 3 H), 7.39-7.26 (m, 5 H), 7.13 (dd, *J* = 8.6 Hz, 2.2 Hz, 1 H), 6.37 (dd, *J* = 16.0 Hz, 6.8 Hz, 1 H), 5.38 (d, *J* = 6.0 Hz, 1 H), 3.89 (br s, 2 H), 3.64 (br s, 2 H), 2.44 (d, *J* = 2.4 Hz, 1 H), 2.10-1.93 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 142.7, 132.5, 131.7, 130.3, 128.4, 128.0, 127.5, 126.3, 126.2, 125.6, 118.3, 75.3, 23.7, 23.6; IR (thin film): 3315, 1394, 1310, 1263, 975, 700 cm⁻¹; MS (EI): *m/z* (%): 343 (M⁺, Cl³⁷, 3), 341 (M⁺, Cl³⁵, 8), 271 (10), 234 (100), 225 (20), 207 (14), 190 (11), 189 (21), 178 (55), 165 (57), 137 (71), 105

(57), 77 (57); HRMS (EI-TOF) calcd for C₁₉H₂₀ClN₃O (M⁺): 341.1295, found: 341.1294.

(*E*)-3-(5-bromo-2-((*E*)-pyrrolidin-1-ylidiazenyl)phenyl)-1-phenylprop-2-en-1-ol (**1d**). Prepared from 5-bromo-2-(pyrrolidin-1-ylazo)-benzaldehyde (1410 mg, 5 mmol) and acetophenone (720 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1d** (1232 mg, 3.2 mmol, 64%) as a light yellow solid.

R_f = 0.16 (5:1 Petroleum ether/EtOAc); m.p. = 111-112 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.58 (s, 1 H), 7.46-7.38 (m, 2 H), 7.35 (t, *J* = 7.4 Hz, 2 H), 7.31-7.24 (m, 4 H), 6.35 (dd, *J* = 16.2 Hz, 6.6 Hz, 1 H), 5.37 (d, *J* = 6.8 Hz, 1 H), 3.88 (br s, 2 H), 3.61 (br s, 2 H), 2.34 (br s, 1 H), 2.09-1.90 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 147.0, 142.7, 132.6, 132.1, 130.9, 128.6, 128.5, 127.6, 126.3, 126.1, 118.6, 118.3, 75.3, 50.9, 46.7, 23.7, 23.3; IR (thin film): 3315, 1391, 1310, 976, 700 cm⁻¹; MS (EI): *m/z* (%): 387 (M⁺, Br⁸¹, 13), 385 (M⁺, Br⁷⁹, 12), 298 (16), 280 (89), 209 (38), 195 (16), 189 (25), 179 (57), 165 (32), 105 (100), 85 (75); HRMS (EI-TOF) calcd for C₁₉H₂₀BrN₃O (M⁺): 385.0790, found: 385.0780.

(*E*)-1-(4-methoxyphenyl)-3-(5-methyl-2-((*E*)-pyrrolidin-1-ylidiazenyl)phenyl)prop-2-en-1-ol (**1f**). Prepared from (*E*)-5-methyl-2-(pyrrolidin-1-ylidiazenyl)benzaldehyde (1085 mg, 5 mmol) and *p*-methoxyacetophenone (900 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1f** (913 mg, 2.6 mmol, 52%)

as a yellow solid.

R_f = 0.30 (3:1 Petroleum ether/EtOAc); m.p. = 92-93 °C;

^1H NMR (400 MHz, CDCl_3): δ 7.39-7.31 (m, 4 H), 7.28 (d, J = 8.4 Hz, 1 H), 7.01 (d, J = 8.0 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 6.38 (dd, J = 16.2, 6.6 Hz, 1 H), 5.36 (d, J = 6.0 Hz, 1 H), 3.80 (s, 3 H), 3.77 (br s, 4 H), 2.30 (s, 3 H), 2.25 (s, 1 H), 2.01 (br s, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 145.9, 135.3, 134.5, 131.4, 130.0, 129.1, 127.6, 127.2, 126.3, 116.8, 113.7, 75.1, 55.2, 23.7, 21.0; IR (ATR-FTIR): 3393, 1510, 1402, 1361, 1316, 1245, 1033, 969, 822 cm^{-1} ; MS (EI): m/z (%): 351 (M^+ , 8), 333 (41), 264 (100), 254 (60), 214 (77), 178 (34), 145 (96), 135 (100), 121 (100); HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}$ ($\text{M}^+ - \text{H}_2\text{O}$): 333.1841, found: 333.1838.

(*E*)-1-(4-methoxyphenyl)-3-(2-((*E*)-pyrrolidin-1-yl diazenyl)phenyl)prop-2-en-1-ol (**1g**). Prepared from (*E*)-2-(pyrrolidin-1-yl diazenyl)benzaldehyde (1015 mg, 5 mmol) and *p*-methoxyacetophenone (900 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1g** (1028 mg, 3.05 mmol, 61%) as a light yellow solid.

R_f = 0.27 (3:1 Petroleum ether/EtOAc); m.p. = 73-75 °C;

^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, J = 7.2 Hz, 1 H), 7.41-7.31 (m, 4 H), 7.20 (t, J = 7.6 Hz, 1 H), 7.08 (t, J = 7.4 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 6.40 (dd, J = 15.6, 6.6 Hz, 1 H), 5.36 (d, J = 6.4 Hz, 1 H), 4.17-3.37 (m, 7 H), 2.28 (s, 1 H), 2.01 (br s, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 148.1, 135.2, 131.6, 130.3, 128.2, 127.6, 127.2, 125.9, 125.1, 117.0, 113.7, 75.1, 55.2, 23.7; IR (ATR-FTIR): 3352, 1405, 1314, 1246, 1033, 970, 825, 759 cm^{-1} ; MS (EI): m/z (%): 337 (M^+ , 7), 319 (32), 250 (100), 236 (35), 221 (33), 200 (100), 178 (69), 135 (100), 117 (100), 103 (100), 85 (100); HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_2$ (M^+): 337.1790, found: 337.1786.

Ethyl-4-((*E*)-3-hydroxy-3-(4-methoxyphenyl)prop-1-enyl)-3-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1h**). Prepared from (*E*)-ethyl 4-formyl-3-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and *p*-methoxyacetophenone (900 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1h** (920 mg, 2.25 mmol, 45%) as a light yellow solid.

R_f = 0.22 (3:1 Petroleum ether/EtOAc); m.p. = 134-136 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.03 (s, 1 H), 7.71 (d, J = 8.0 Hz, 1 H), 7.52 (d, J = 8.0 Hz, 1 H), 7.41-7.30 (m, 3 H), 6.89 (d, J = 8.4 Hz, 2 H), 6.49 (dd, J = 15.8, 6.6 Hz, 1 H), 5.36 (d, J = 5.6 Hz, 1 H), 4.35 (q, J = 7.1 Hz, 2 H), 3.93 (br s, 2 H), 3.79 (s, 3 H), 3.65 (br s, 2 H), 2.32 (s, 1 H), 2.02 (br s, 4 H), 1.38 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.7, 159.1, 148.1, 134.9, 134.5, 133.9, 129.9, 127.7, 126.3, 125.8, 125.6, 118.4, 113.8, 74.9, 60.8, 55.2, 23.7, 14.3; IR (ATR-FTIR): 3297, 1707, 1391, 1294, 1251 cm^{-1} ; MS (EI): m/z (%): 410 ($\text{M}^+ + \text{H}$, 8), 391 (75), 322 (100), 293 (45), 272 (29), 189 (53), 175 (51), 135 (42), 121 (45); HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_4$ (M^+): 409.2002, found: 409.1995.

Ethyl-3-((*E*)-3-(4-fluorophenyl)-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1i**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and *p*-fluoroacetophenone (828 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1i** (1092 mg, 2.75 mmol,

55%) as a white solid.

R_f = 0.26 (3:1 Petroleum ether/EtOAc); m.p. = 94-96 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.16 (s, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.44-7.39 (m, 3 H), 7.30 (d, *J* = 16.0 Hz, 1 H), 7.07-6.98 (m, 2 H), 6.46 (dd, *J* = 16.0, 6.8 Hz, 1 H), 5.38 (d, *J* = 6.4 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 3.94 (br s, 2 H), 3.62 (br s, 2 H), 2.48 (br s, 1 H), 2.03 (br s, 4 H), 1.37 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 162.1 (d, *J*_{C-F} = 244.2 Hz), 151.4, 138.6 (d, *J*_{C-F} = 3.0 Hz), 132.3, 129.9, 129.4, 128.1 (d, *J*_{C-F} = 8.1 Hz), 127.8, 127.0, 126.5, 116.7, 115.1 (d, *J*_{C-F} = 20.9 Hz), 74.7, 60.8, 51.1, 46.8, 23.8, 23.4, 14.3; IR (ATR-FTIR): 3304, 1713, 1250, 1219, 1108, 767 cm⁻¹; MS (EI): *m/z* (%): 397 (M⁺, 3), 352 (23), 272 (100), 253 (50), 225 (47), 209 (29), 197 (57), 189 (71), 175 (100), 147 (31), 123 (100), 109 (85); HRMS (EI-TOF) calcd for C₂₂H₂₄FN₃O₃ (M⁺): 397.1802, found: 397.1798.

Ethyl-3-((*E*)-3-(4-chlorophenyl)-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1j**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and *p*-chloroacetophenone (928 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1j** (1017 mg, 2.45 mmol, 49%) as a light yellow solid.

R_f = 0.14 (5:1 Petroleum ether/EtOAc); m.p. = 117-119 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.15 (s, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 7.39-7.36 (m, 2 H), 7.33-7.26 (m, 3 H), 6.44 (dd, *J* = 16.0, 6.8 Hz, 1 H), 5.38 (d, *J* = 4.8 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 3.95 (br s, 2 H), 3.61 (br s, 2 H), 2.37 (d, *J* = 2.8 Hz, 1 H), 2.04 (br s, 4 H), 1.37 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.6, 151.4, 141.3, 133.2, 132.0,

129.8, 129.5, 128.5, 127.80, 127.78, 127.4, 126.5, 116.6, 74.8, 60.8, 46.9, 45.1, 23.9, 23.5, 14.4; IR (ATR-FTIR): 3475, 1693, 1600, 1392, 1226, 1029 cm^{-1} ; MS (EI): m/z (%): 415 (M^+ , Cl^{37} , 3), 413 (M^+ , Cl^{35} , 7), 368 (26), 326 (43), 312 (14), 272 (100), 241 (39), 213 (28), 203 (62), 189 (100), 175 (100), 147 (40), 139 (100), 125 (75); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{22}\text{ClN}_3\text{O}_2$ ($\text{M}^+ - \text{H}_2\text{O}$): 395.1401, found: 395.1397.

Ethyl-3-((*E*)-3-(4-bromophenyl)-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1k**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and *p*-bromoacetophenone (1194 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1k** (1188 mg, 2.6 mmol, 52%) as a yellow solid.

R_f = 0.14 (5:1 Petroleum ether/EtOAc); m.p. = 117-119 $^{\circ}\text{C}$;

^1H NMR (500 MHz, CDCl_3): δ 8.16 (d, J = 2.0 Hz, 1 H), 7.84 (dd, J = 8.3, 1.8 Hz, 1 H), 7.48 (d, J = 8.5 Hz, 2 H), 7.43 (d, J = 8.5 Hz, 1 H), 7.32 (d, J = 8.5 Hz, 2 H), 7.28 (d, J = 16.5 Hz, 1 H), 6.45 (dd, J = 16.0, 6.5 Hz, 1 H), 5.38-5.36 (m, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.95 (br s, 2 H), 3.61 (br s, 2 H), 2.31 (d, J = 3.5 Hz, 1 H), 2.04 (br s, 4 H), 1.38 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.7, 151.5, 141.9, 131.9, 131.5, 129.9, 129.6, 128.2, 127.9, 127.5, 126.6, 121.4, 116.7, 74.8, 60.9, 51.3, 46.9, 24.0, 23.6, 14.5; IR (ATR-FTIR): 3463, 1694, 1395, 1287, 1237 cm^{-1} ; MS (EI): m/z (%): 459 (M^+ , Br^{81} , 2), 457 (M^+ , Br^{79} , 2), 414 (6), 315 (14), 272 (100), 203 (40), 189 (60), 175 (100); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{24}\text{BrN}_3\text{O}_3$ (M^+): 457.1001, found: 457.1002.

Ethyl-3-((*E*)-3-hydroxy-3-(4-iodophenyl)prop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1l**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and *p*-iodoacetophenone (1476 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1l** (1414 mg, 2.8 mmol, 56%) as a light yellow solid.

R_f = 0.27 (3:1 Petroleum ether/EtOAc); m.p. = 105-107 °C;

δ 8.16 (s, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 2 H), 7.43 (d, J = 8.4 Hz, 1 H), 7.28 (d, J = 16.0 Hz, 1 H), 7.20 (d, J = 8.0 Hz, 2 H), 6.45 (dd, J = 16.2, 6.6 Hz, 1 H), 5.37 (d, J = 5.6 Hz, 1 H), 4.35 (q, J = 7.1 Hz, 2 H), 3.96 (br s, 2 H), 3.61 (br s, 2 H), 2.23 (s, 1 H), 2.05 (br s, 4 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 151.4, 142.5, 137.4, 131.8, 129.8, 129.5, 128.4, 127.8, 127.5, 126.6, 116.6, 92.9, 74.9, 60.8, 51.2, 46.8, 23.8, 23.4, 14.4; IR (ATR-FTIR): 3480, 1686, 1362, 1295, 1253, 1225, 1108, 818, 768 cm^{-1} ; MS (EI): m/z (%): 505 (M^+ , 6), 488 (7), 460 (19), 418 (50), 404 (16), 361 (31), 333 (20), 272 (100), 252 (43), 231 (92), 217 (50), 207 (79), 189 (100), 179 (100); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{22}\text{IN}_3\text{O}_2$ ($\text{M}^+ - \text{H}_2\text{O}$): 487.0757, found: 487.0764.

Ethyl-3-((*E*)-3-hydroxy-3-*p*-tolylprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1m**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and

4-acetyltoluene (804 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1m** (865 mg, 2.2 mmol, 44%) as a yellow solid.

R_f = 0.27 (3:1 Petroleum ether/EtOAc); m.p. = 103-105 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.19 (s, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 7.40-7.30 (m, 3 H), 7.18 (d, *J* = 7.6 Hz, 2 H), 6.50 (dd, *J* = 15.6, 6.4 Hz, 1 H), 5.39 (d, *J* = 6.0 Hz, 1 H), 4.35 (q, *J* = 6.8 Hz, 2 H), 3.96 (br s, 2 H), 3.66 (br s, 2 H), 2.35 (s, 3 H), 2.05 (s, 5 H), 1.38 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 151.4, 139.9, 137.3, 132.5, 130.1, 129.3, 129.2, 127.8, 126.6, 126.3, 116.6, 75.4, 60.7, 51.1, 46.8, 23.6, 23.5, 21.1, 14.4; IR (ATR-FTIR): 3481, 1679, 1387, 1293, 1247, 1113 cm⁻¹; MS (EI): *m/z* (%): 393 (M⁺, 2), 375 (9), 348 (10), 306 (78), 272 (83), 249 (25), 221 (23), 203 (44), 189 (64), 175 (100), 119 (66), 105 (50), 85 (79); HRMS (EI-TOF) calcd for C₂₃H₂₇N₃O₃ (M⁺): 393.2052, found: 393.2057.

Ethyl-3-((*E*)-3-hydroxy-3-(4-methoxyphenyl)prop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1n**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and *p*-methoxyacetophenone (900 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1n** (1043 mg, 2.55 mmol, 51%) as a yellow solid.

R_f = 0.28 (3:1 Petroleum ether/EtOAc); m.p. = 77-78 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.19 (s, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 7.40-7.32 (m, 3 H), 7.43 (d, *J* = 8.8 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 6.50 (dd, *J* = 15.8, 6.2 Hz, 1 H), 5.38 (br s, 1 H), 4.35 (q, *J* = 6.9 Hz, 2 H), 3.96 (br s, 2 H), 3.81 (s, 3 H), 3.66 (br s, 2 H), 2.14 (s, 1 H), 2.05 (br s, 4 H), 1.38 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 159.1, 151.4, 135.1, 132.6,

130.1, 129.3, 127.8, 127.7, 126.5, 126.4, 116.6, 113.8, 75.1, 60.8, 55.3, 51.0, 46.6, 23.8, 23.5, 14.4; IR (ATR-FTIR): 3301, 1707, 1247, 1110 cm^{-1} ; MS (EI): m/z (%): 409 (M^+ , 3), 392 (13), 364 (11), 322 (35), 272 (51), 189 (69), 175 (90); HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_4$ (M^+): 409.2002, found: 409.2014.

Ethyl-3-((*E*)-3-hydroxy-3-(3-methoxyphenyl)prop-1-enyl)-4-((*E*)-pyrrolidin-1-yl-diazenyl)benzoate (**1o**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl-diazenyl)benzoate (1375 mg, 5 mmol) and *m*-methoxyacetophenone (900 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1o** (1063 mg, 2.6 mmol, 52%) as a yellow solid.

R_f = 0.28 (3:1 Petroleum ether/EtOAc); m.p. = 93-94 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.17 (s, 1 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.42 (d, J = 8.4 Hz, 1 H), 7.33 (d, J = 16.0 Hz, 1 H), 7.26 (t, J = 8.0 Hz, 1 H), 7.02 (d, J = 2.4 Hz, 2 H), 6.81 (d, J = 8.0 Hz, 1 H), 6.48 (dd, J = 15.8, 6.8 Hz, 1 H), 5.38 (d, J = 6.8 Hz, 1 H), 4.34 (q, J = 6.9 Hz, 2 H), 3.94 (br s, 2 H), 3.80 (s, 3 H), 3.64 (br s, 2 H), 2.60 (br s, 1 H), 2.02 (br s, 4 H), 1.37 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 159.7, 151.4, 144.5, 132.3, 130.1, 129.4, 129.3, 127.8, 126.8, 126.5, 118.7, 116.6, 113.0, 111.7, 75.3, 60.7, 55.2, 51.0, 46.8, 23.8, 23.3, 14.3; IR (ATR-FTIR): 3492, 1684, 1596, 1300, 1256, 1110 cm^{-1} ; MS (EI): m/z (%): 410 ($M^+ + \text{H}$, 34), 392 (43), 364 (22), 322 (100), 293 (29), 272 (100), 265 (58), 203 (59), 189 (95), 175 (100), 135 (91), 85 (95); HRMS (EI-TOF) calcd for $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_4$ (M^+): 409.2002, found: 409.2006.

Ethyl-3-((*E*)-3-(2,4-dimethylphenyl)-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1p**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and 1-(2,4-dimethylphenyl)ethanone (888 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (5-33% EtOAc/Petroleum ether) gave **1p** (936 mg, 2.3 mmol, 46%) as a light yellow solid.

R_f = 0.35 (3:1 Petroleum ether/EtOAc); m.p. = 102-104 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.17 (d, J = 1.2 Hz, 1 H), 7.84 (dd, J = 8.4, 1.6 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.43 (d, J = 8.8 Hz, 1 H), 7.29 (d, J = 16.0 Hz, 1 H), 7.06 (d, J = 8.0 Hz, 1 H), 6.98 (s, 1 H), 6.44 (dd, J = 16.0, 6.4 Hz, 1 H), 5.57 (d, J = 4.8 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.95 (br s, 2 H), 3.61 (br s, 2 H), 2.35 (s, 3 H), 2.31 (s, 3 H), 2.15 (s, 1 H), 2.04 (br s, 4 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 151.3, 137.9, 136.9, 135.1, 131.7, 131.1, 130.3, 129.2, 127.8, 126.8, 126.7, 126.5, 125.8, 116.5, 72.1, 60.7, 51.1, 46.7, 23.9, 23.5, 21.0, 19.1, 14.4; IR (ATR-FTIR): 3552, 1695, 1296, 1243, 1111, 771 cm^{-1} ; MS (EI): m/z (%): 407 (M^+ , 2), 389 (10), 362 (10), 320 (53), 272 (74), 203 (45), 189 (74), 175 (100), 133 (63), 119 (63), 105 (46), 85 (98); HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{29}\text{N}_3\text{O}_3$ (M^+): 407.2209, found: 407.2203.

Ethyl-3-((*E*)-3-(3,4-dimethylphenyl)-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1q**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol)

and 1-(3,4-dimethylphenyl)ethanone (888 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (5-33% EtOAc/Petroleum ether) gave **1q** (651 mg, 1.6 mmol, 32%) as a yellow solid.

R_f = 0.36 (3:1 Petroleum ether/EtOAc); m.p. = 92-94 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.19 (s, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.43 (d, *J* = 8.8 Hz, 1 H), 7.36 (d, *J* = 16.0 Hz, 1 H), 7.23 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 1 H), 7.13 (d, *J* = 8.0 Hz, 1 H), 6.51 (dd, *J* = 16.2, 6.6 Hz, 1 H), 5.36 (d, *J* = 6.4 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.96 (br s, 2 H), 3.67 (br s, 2 H), 2.27 (s, 3 H), 2.26 (s, 3 H), 2.19 (s, 1 H), 2.05 (br s, 4 H), 1.38 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.7, 151.4, 140.4, 136.7, 135.9, 132.6, 130.2, 129.7, 129.2, 127.8, 127.6, 126.5, 126.3, 123.8, 116.6, 75.4, 60.7, 51.1, 46.8, 23.9, 23.5, 19.8, 19.4, 14.4; IR (ATR-FTIR): 3505, 1685, 1384, 1295, 1243, 1103, 768 cm⁻¹; MS (EI): *m/z* (%): 407 (M⁺, 4), 389 (25), 362 (24), 320 (100), 306 (28), 291 (36), 272 (100), 263 (51), 235 (45), 203 (93), 189 (100), 175 (100), 133 (95), 119 (87), 105 (67), 85 (100); HRMS (EI-TOF) calcd for C₂₄H₂₉N₃O₃ (M⁺): 407.2209, found: 407.2209.

Ethyl-3-((*E*)-3-(biphenyl-4-yl)-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl-diazenyl)benzoate (**1r**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl-diazenyl)benzoate (1375 mg, 5 mmol) and 4-acetylbiphenyl (1176 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1r** (524 mg, 1.15 mmol, 23%) as a light yellow solid.

R_f = 0.22 (3:1 Petroleum ether/EtOAc); m.p. = 133-135 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.22 (s, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.64-7.56 (m, 4 H),

7.54-7.52 (m, 2 H), 7.46-7.42 (m, 3 H), 7.40-7.33 (m, 2 H), 6.56 (dd, $J = 15.8, 6.6$ Hz, 1 H), 5.48 (d, $J = 5.6$ Hz, 1 H), 4.36 (q, $J = 7.2$ Hz, 2 H), 3.95 (br s, 2 H), 3.64 (br s, 2 H), 2.35 (s, 1 H), 2.00 (br s, 4 H), 1.39 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 151.4, 141.9, 140.8, 140.5, 132.3, 130.0, 129.4, 128.7, 127.8, 127.22, 127.18, 127.0, 126.95, 126.85, 126.5, 116.6, 75.2, 60.7, 51.0, 46.8, 23.7, 23.2, 14.4; IR (ATR-FTIR): 3468, 1692, 1392, 1302, 1246, 1111 cm^{-1} ; MS (EI): m/z (%): 456 (M^+ , 8), 437 (52), 368 (100), 339 (54), 311 (23), 294 (23), 272 (84), 189 (53), 175 (60), 167 (40), 152 (31); HRMS (EI-TOF) calcd for $\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_3$ (M^+): 455.2209, found: 455.2198.

Ethyl-3-((*E*)-3-hydroxy-3-(naphthalen-2-yl)prop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1s**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and 2-acetylnaphthalene (1020 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1s** (1437 mg, 3.35 mmol, 67%) as a light yellow solid.

$R_f = 0.29$ (3:1 Petroleum ether/EtOAc); m.p. = 128-130 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.20 (s, 1 H), 7.91 (s, 1 H), 7.89-7.77 (m, 4 H), 7.56 (d, $J = 8.4$ Hz, 1 H), 7.51-7.45 (m, 2 H), 7.43 (d, $J = 8.8$ Hz, 1 H), 7.35 (d, $J = 16.0$ Hz, 1 H), 6.59 (dd, $J = 16.0, 6.4$ Hz, 1 H), 5.59 (d, $J = 6.0$ Hz, 1 H), 4.34 (q, $J = 7.1$ Hz, 2 H), 3.92 (br s, 2 H), 3.51 (br s, 2 H), 2.37 (s, 1 H), 1.97 (s, 4 H), 1.37 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 151.4, 140.2, 133.3, 132.9, 132.3, 130.0, 129.4, 128.2, 128.0, 127.8, 127.6, 127.3, 126.5, 126.0, 125.8, 124.9, 124.8, 116.6, 75.5, 60.7, 51.1, 46.6, 23.9, 23.4, 14.4; IR (ATR-FTIR): 3491, 1683, 1393, 1361, 1295, 1254, 1111, 753 cm^{-1} ; MS (EI): m/z (%): 429 (M^+ , 4), 411 (39), 342 (100), 313 (65), 285 (51), 272 (100), 239 (82), 229 (72), 203 (59), 189 (83), 175 (100), 155 (81), 141 (83), 127 (77), 85 (99); HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_3$ (M^+): 429.2052, found: 429.2064.

Ethyl-3-((*E*)-3-cyclopropyl-3-hydroxyprop-1-enyl)-4-((*E*)-pyrrolidin-1-yl diazenyl)benzoate (**1t**). Prepared from (*E*)-ethyl 3-formyl-4-(pyrrolidin-1-yl diazenyl)benzoate (1375 mg, 5 mmol) and 1-cyclopropylethanone (504 mg, 6 mmol) according to the general procedure. Purification via flash column chromatography (10-33% EtOAc/Petroleum ether) gave **1t** (686 mg, 2.0 mmol, 40%) as a yellow solid.

R_f = 0.20 (3:1 Petroleum ether/EtOAc); m.p. = 93-95 °C;

^1H NMR (300 MHz, CDCl_3): δ 8.21 (d, J = 1.5 Hz, 1 H), 7.83 (dd, J = 8.6, 1.7 Hz, 1 H), 7.42 (d, J = 8.4 Hz, 1 H), 7.28 (d, J = 16.2 Hz, 1 H), 6.41 (dd, J = 16.2, 6.3 Hz, 1 H), 4.36 (q, J = 7.1 Hz, 2 H), 3.94 (br s, 2 H), 3.80-3.55 (m, 3 H), 2.18 (br s, 1 H), 2.03 (br s, 4 H), 1.39 (t, J = 7.6 Hz, 3 H), 1.18-1.00 (m, 1 H), 0.66-0.22 (m, 4 H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.7, 151.3, 131.9, 130.4, 129.1, 127.8, 126.5, 126.0, 116.6, 77.3, 60.7, 51.2, 46.8, 23.9, 23.5, 17.5, 14.4, 3.2, 2.2; IR (ATR-FTIR): 3454, 1684, 1239, 978 cm^{-1} ; MS (EI): m/z (%): 343 (M^+ , 6), 298 (37), 272 (97), 256 (31), 227 (31), 200 (34), 189 (100), 175 (46), 155 (41), 145 (44), 129 (61), 115 (52), 85 (84); HRMS (EI-TOF) calcd for $\text{C}_{19}\text{H}_{25}\text{N}_3\text{O}_3$ (M^+): 343.1896, found: 343.1881.

C. General Procedure for Preparation 3-Alkenyl-2-pyrrolidine-2*H*-indazole **2** from triazenylaryl allylic alcohol **1**

3-Alkenyl-2-pyrrolidine-2*H*-indazoles **2a-t** were prepared from the corresponding triazenylaryl allylic alcohol **1a-t** according to the procedure below.

To a solution of triazenylyl allylic alcohol **1** (0.5 mmol) in DCM (2 mL), Bi(OTf)₃ (17 mg, 0.025 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Ethyl acetate and water was added and the resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na₂SO₄, concentrated in vacuo and purified by silica gel chromatography to provide the 3-alkenyl-2-pyrrolidine-2H-indazoles **2**.

(*E*)-ethyl 2-(pyrrolidin-1-yl)-3-styryl-2H-indazole-5-carboxylate (**2a**). Following the general procedure with **1a** (189 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2a** (170 mg, 0.47 mmol, 94%) as a yellow solid.

R_f = 0.30 (10:1 Petroleum ether/EtOAc); m.p. = 102-104 °C;

¹H NMR (500 MHz, CDCl₃): δ 8.79 (s, 1 H), 7.97 (dd, *J* = 8.8 Hz, 1.3 Hz, 1 H), 7.68-7.64 (m, 3 H), 7.61 (d, *J* = 17.0 Hz, 1 H), 7.57 (d, *J* = 17.0 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 4.43 (q, *J* = 7.0 Hz, 2 H), 3.48 (br s, 4 H), 2.10 (br s, 4 H), 1.44 (t, *J* = 7.3 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ 167.0, 147.3, 136.9, 134.1, 132.4, 128.8, 128.4, 126.7, 126.1, 125.0, 123.9, 117.2, 117.1, 115.2, 60.8, 55.1, 23.1, 14.4; IR (ATR-FTIR): 1700, 1281, 1237, 1114, 742 cm⁻¹; MS (EI): *m/z* (%): 361 (M⁺, 10), 292 (100), 263 (15), 247 (12), 218 (12), 189 (12); HRMS (EI-TOF) calcd for C₂₂H₂₃N₃O₂ (M⁺): 361.1790, found: 361.1786.

(*E*)-2-(pyrrolidin-1-yl)-3-styryl-2*H*-indazole-5-carbonitrile (**2b**). Following the general procedure with **1b** (166 mg, 0.5 mmol), purification by column chromatography (5-20% EtOAc/Petroleum ether) gave **2b** (149 mg, 0.475 mmol, 95%) as a light yellow solid.

R_f = 0.29 (5:1 Petroleum ether/EtOAc); m.p. = 185-186 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.40 (s, 1 H), 7.71 (d, J = 9.2 Hz, 1 H), 7.63 (d, J = 7.2 Hz, 2 H), 7.57 (d, J = 16.4 Hz, 1 H), 7.46-7.42 (m, 4 H), 7.35 (t, J = 7.4 Hz, 1 H), 3.55-3.36 (m, 4 H), 2.11 (br s, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 146.1, 136.4, 133.9, 133.1, 128.9, 128.8, 128.5, 127.0, 126.8, 120.1, 118.8, 117.0, 114.7, 104.8, 55.3, 23.1; IR (ATR-FTIR): 2218, 1615, 1341, 1164, 959, 816, 740, 685 cm^{-1} ; MS (EI): m/z (%): 314 (M^+ , 8), 245 (100), 229 (9), 214 (25), 190 (20); HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4$ (M^+): 314.1531, found: 314.1531.

(*E*)-5-chloro-2-(pyrrolidin-1-yl)-3-styryl-2*H*-indazole (**2c**). Following the general procedure with **1c** (171 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2c** (110 mg, 0.34 mmol, 68%) as a light yellow solid.

R_f = 0.44 (10:1 Petroleum ether/EtOAc); m.p. = 128-130 °C;

^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, J = 1.2 Hz, 1 H), 7.64-7.59 (m, 3 H), 7.56 (d, J = 17.2 Hz, 1 H), 7.45-7.23 (m, 5 H), 3.51-3.38 (m, 4 H), 2.15-2.02 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3):

δ 144.2, 137.0, 131.6, 131.0, 128.8, 128.2, 127.6, 127.5, 126.6, 119.6, 119.1, 115.5, 55.2, 23.1; IR (ATR-FTIR): 1942, 1394, 1211, 1110, 956, 805, 685 cm^{-1} ; MS (EI): m/z (%): 325 (M^+ , Cl^{37} , 18), 323 (M^+ , Cl^{35} , 45), 253 (100), 218 (75), 189 (58), 163 (12), 91 (14), 70 (40); HRMS (EI-TOF) calcd for $\text{C}_{19}\text{H}_{18}\text{ClN}_3$ (M^+): 323.1189, found: 323.1187.

(*E*)-5-bromo-2-(pyrrolidin-1-yl)-3-styryl-2*H*-indazole (**2d**). Following the general procedure with **1d** (193 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2d** (121 mg, 0.33 mmol, 66%) as a light yellow solid.

R_f = 0.45 (10:1 Petroleum ether/EtOAc); m.p. = 134-136 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.10 (s, 1 H), 7.60 (d, J = 7.2 Hz, 2 H), 7.58-7.50 (m, 2 H), 7.50-7.23 (m, 5 H), 3.55-3.33 (m, 4 H), 2.15-2.00 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 144.2, 137.0, 131.4, 131.1, 129.7, 128.8, 128.2, 126.6, 122.9, 119.3, 118.8, 115.4, 55.2, 23.1; IR (ATR-FTIR): 1206, 1106, 948, 807, 739, 681 cm^{-1} ; MS (EI): m/z (%): 369 (M^+ , Br^{81} , 6), 367 (M^+ , Br^{79} , 6), 300 (100), 218 (45), 189 (49), 70 (10); HRMS (EI-TOF) calcd for $\text{C}_{19}\text{H}_{18}\text{BrN}_3$ (M^+): 367.0684, found: 367.0681.

(*E*)-3-(4-methoxystyryl)-5-methyl-2-(pyrrolidin-1-yl)-2*H*-indazole (**2f**). Following the general procedure with **1f** (175 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2f** (150 mg, 0.45 mmol, 90%) as a light yellow solid.

R_f = 0.48 (10:1 Petroleum ether/EtOAc); m.p. = 141-142 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 1 H), 7.60 (d, *J* = 9.2 Hz, 1 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 7.48 (d, *J* = 16.8 Hz, 1 H), 7.39 (d, *J* = 16.8 Hz, 1 H), 7.19 (d, *J* = 8.8 Hz, 1 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 3.86 (s, 3 H), 3.46 (br s, 4 H), 2.49 (s, 3 H), 2.08 (br s, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 159.5, 144.7, 131.2, 131.1, 130.3, 129.7, 128.8, 127.7, 119.1, 117.7, 117.2, 114.2, 114.1, 55.3, 54.9, 23.1, 21.9; IR (ATR-FTIR): 1600, 1510, 1251, 1168, 1033, 801 cm⁻¹; MS (EI): *m/z* (%): 333 (M⁺, 20), 264 (100), 249 (20), 220 (26), 189 (19), 165 (13); HRMS (EI-TOF) calcd for C₂₁H₂₃N₃O (M⁺): 333.1841, found: 333.1842.

(*E*)-3-(4-methoxystyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole (**2g**). Following the general procedure with **1g** (169 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2g** (145 mg, 0.455 mmol, 91%) as a white solid.

R_f = 0.61 (3:1 Petroleum ether/EtOAc); m.p. = 92-94 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 1 H), 7.69 (d, *J* = 8.4 Hz, 1 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 16.8 Hz, 1 H), 7.42 (d, *J* = 16.8 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 1 H), 7.16 (t, *J* = 7.6 Hz, 1 H), 6.95 (d, *J* = 8.4 Hz, 2 H), 3.86 (s, 3 H), 3.48 (br s, 4 H), 2.09 (br s, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 159.6, 145.9, 132.0, 130.3, 130.1, 127.8, 126.2, 121.8, 120.8, 117.6, 117.5, 114.2, 114.0, 55.3, 55.0, 23.1; IR (ATR-FTIR): 1510, 1248, 1024, 955, 817, 745 cm⁻¹; MS (EI): *m/z* (%): 319 (M⁺, 10), 250 (100), 235 (12), 206 (34), 178 (20), 152 (12); HRMS (EI-TOF) calcd for C₂₀H₂₁N₃O (M⁺): 319.1685, found: 319.1685.

(*E*)-ethyl 3-(4-methoxystyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-6-carboxylate (**2h**). Following the general procedure with **1h** (204 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2h** (145 mg, 0.37 mmol, 74%) as a light yellow solid.

R_f = 0.33 (10:1 Petroleum ether/EtOAc); m.p. = 156-157 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.48 (s, 1 H), 7.98 (d, *J* = 8.8 Hz, 1 H), 7.77 (dd, *J* = 8.8, 0.8 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 16.8 Hz, 1 H), 7.40 (d, *J* = 16.8 Hz, 1 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 4.41 (q, *J* = 7.1 Hz, 2 H), 3.85 (s, 3 H), 3.47 (br s, 4 H), 2.10 (br s, 4 H), 1.42 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): 167.0, 159.8, 145.1, 132.4, 131.0, 129.8, 128.2, 127.9, 121.4, 121.0, 120.7, 119.7, 114.2, 113.5, 60.9, 55.3, 55.2, 23.1, 14.3; IR (ATR-FTIR): 1705, 1251, 1219, 740 cm⁻¹; MS (EI): *m/z* (%): 391 (M⁺, 18), 346 (8), 322 (100), 293 (37), 250 (14), 205 (22), 176 (27); HRMS (EI-TOF) calcd for C₂₃H₂₅N₃O₃ (M⁺): 391.1896, found: 391.1895.

(*E*)-ethyl 3-(4-fluorostyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2i**). Following the general procedure with **1i** (199 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2i** (161 mg, 0.425 mmol, 85%) as a yellow solid.

R_f = 0.54 (5:1 Petroleum ether/EtOAc); m.p. = 121-122 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.75 (s, 1 H), 7.96 (d, *J* = 8.8 Hz, 1 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 7.62-7.58 (m, 2 H), 7.53 (d, *J* = 18.0 Hz, 1 H), 7.48 (d, *J* = 17.6 Hz, 1 H), 7.10 (t, *J* = 8.4 Hz, 2 H), 4.42 (q, *J* = 7.2 Hz, 2 H), 3.46 (br s, 4 H), 2.09 (br s, 4 H), 1.43 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.0, 162.7 (d, *J*_{C-F} = 247.1 Hz), 147.3, 134.0, 133.1 (d, *J*_{C-F} = 4.0 Hz), 131.1, 128.4 (d, *J*_{C-F} = 7.1 Hz), 126.2, 125.0, 124.0, 117.2, 115.8 (d, *J*_{C-F} = 21.7 Hz), 114.98, 114.96, 60.8, 55.2, 23.2, 14.4; IR (ATR-FTIR): 1700, 1282, 1232, 1114 cm⁻¹; MS (EI): *m/z* (%):

379 (M^+ , 15), 334 (5), 310 (100), 281 (33), 265 (24), 236 (27), 207 (29); HRMS (EI-TOF) calcd for $C_{22}H_{22}FN_3O_2$ (M^+): 379.1696, found: 379.1693.

(*E*)-ethyl 3-(4-chlorostyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2j**). Following the general procedure with **1j** (207 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2j** (170 mg, 0.43 mmol, 86%) as a light yellow solid.

R_f = 0.55 (5:1 Petroleum ether/EtOAc); m.p. = 108-109 °C;

^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1 H), 7.97 (d, J = 9.2 Hz, 1 H), 7.66 (d, J = 8.8 Hz, 1 H), 7.60-7.54 (m, 3 H), 7.50 (d, J = 16.8 Hz, 1 H), 7.39 (d, J = 8.4 Hz, 2 H), 4.43 (q, J = 7.1 Hz, 2 H), 3.47 (br s, 4 H), 2.10 (br s, 4 H), 1.44 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 147.3, 135.5, 134.0, 133.8, 130.9, 129.0, 127.9, 126.2, 124.9, 124.2, 117.27, 117.25, 115.7, 60.9, 55.3, 23.2, 14.4; IR (ATR-FTIR): 1699, 1278, 1240, 1119 cm^{-1} ; MS (EI): m/z (%): 397 (M^+ , Cl^{37} , 3), 395 (M^+ , Cl^{35} , 8), 350 (3), 326 (100), 297 (16), 218 (12), 189 (19); HRMS (EI-TOF) calcd for $C_{22}H_{22}ClN_3O_2$ (M^+): 395.1401, found: 395.1400.

(*E*)-ethyl 3-(4-bromostyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2k**). Following the general procedure with **1k** (228 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2k** (198 mg, 0.45 mmol, 90%) as a light yellow solid.

R_f = 0.55 (5:1 Petroleum ether/EtOAc); m.p. = 109-110 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.75 (s, 1 H), 7.96 (d, $J = 8.8$ Hz, 1 H), 7.66 (d, $J = 8.8$ Hz, 1 H), 7.58 (d, $J = 16.8$ Hz, 1 H), 7.54-7.46 (m, 5 H), 4.43 (q, $J = 7.1$ Hz, 2 H), 3.51-3.39 (m, 4 H), 2.10 (br s, 4 H), 1.44 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 147.3, 135.9, 133.8, 131.9, 130.9, 128.2, 126.2, 124.9, 124.2, 122.2, 117.27, 117.25, 115.8, 60.9, 55.3, 23.2, 14.4; IR (ATR-FTIR): 1697, 1278, 1240, 1117 cm^{-1} ; MS (EI): m/z (%): 441 (M^+ , Br^{81} , 6), 439 (M^+ , Br^{79} , 6), 394 (2), 372 (100), 343 (15), 325 (12), 262 (10), 218 (19), 189 (38); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{22}\text{BrN}_3\text{O}_2$ (M^+): 439.0895, found: 439.0897.

(*E*)-ethyl 3-(4-iodostyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2l**). Following the general procedure with **1l** (252 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2l** (197 mg, 0.405 mmol, 81%) as a light yellow solid.

$R_f = 0.56$ (5:1 Petroleum ether/EtOAc); m.p. = 166-168 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.75 (s, 1 H), 7.96 (d, $J = 9.2$ Hz, 1 H), 7.74 (d, $J = 8.0$ Hz, 2 H), 7.66 (d, $J = 8.8$ Hz, 1 H), 7.59 (d, $J = 16.8$ Hz, 1 H), 7.46 (d, $J = 16.4$ Hz, 1 H), 7.37 (d, $J = 8.0$ Hz, 2 H), 4.43 (q, $J = 7.1$ Hz, 2 H), 3.47 (br s, 4 H), 2.10 (br s, 4 H), 1.44 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 147.3, 137.9, 136.4, 133.7, 131.0, 128.4, 126.2, 124.9, 124.2, 117.28, 117.25, 115.9, 93.8, 60.9, 55.3, 23.2, 14.4; IR (ATR-FTIR): 1694, 1278, 1239, 1117 cm^{-1} ; MS (EI): m/z (%): 487 (M^+ , 15), 442 (4), 418 (100), 390 (22), 373 (17), 262 (19), 218 (26), 189 (52); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{22}\text{IN}_3\text{O}_2$ (M^+): 487.0757, found: 487.0764.

(*E*)-ethyl 3-(4-methylstyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2m**). Following the general procedure with **1m** (197 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2m** (169 mg, 0.45 mmol, 90%) as a light yellow solid.

R_f = 0.33 (10:1 Petroleum ether/EtOAc); m.p. = 113-115 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.79 (s, 1 H), 7.97 (dd, *J* = 9.0, 1.4 Hz, 1 H), 7.66 (d, *J* = 9.2 Hz, 1 H), 7.59-7.51 (m, 4 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 4.43 (q, *J* = 7.1 Hz, 2 H), 3.55-3.40 (m, 4 H), 2.40 (s, 3 H), 2.15-2.03 (m, 4 H), 1.44 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 147.3, 138.5, 134.4, 134.1, 132.5, 129.5, 126.7, 126.1, 125.2, 123.8, 117.2, 117.1, 114.3, 60.9, 55.1, 23.1, 21.3, 14.4; IR (ATR-FTIR): 1701, 1270, 1234, 1195, 743 cm⁻¹; MS (EI): *m/z* (%): 375 (M⁺, 11), 306 (100), 277 (27), 232 (14), 202 (12), 189 (12); HRMS (EI-TOF) calcd for C₂₃H₂₅N₃O₂ (M⁺): 375.1947, found: 375.1949.

(*E*)-ethyl 3-(4-methoxystyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2n**). Following the general procedure with **1n** (205 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2n** (180 mg, 0.46 mmol, 92%) as a yellow solid.

R_f = 0.33 (10:1 Petroleum ether/EtOAc); m.p. = 125-126°C;

¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 1 H), 7.96 (d, *J* = 8.8 Hz, 1 H), 7.65 (d, *J* = 8.8 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* = 16.8 Hz, 1 H), 7.45 (d, *J* = 16.8 Hz, 1 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 3.86 (s, 3 H), 3.47 (s, 4 H), 2.09 (br s, 4 H), 1.44 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 159.9, 147.3, 134.6, 132.2, 129.6, 128.1, 126.1, 125.2, 123.6, 117.0, 114.2, 113.1, 60.9, 55.3, 55.1, 23.1, 14.4; IR (ATR-FTIR): 1694, 1277, 1238, 1111, 1031 cm⁻¹; MS (EI): *m/z* (%): 391 (M⁺, 35), 322 (100), 293 (43), 205 (22), 176 (21); HRMS (EI-TOF) calcd for C₂₃H₂₅N₃O₃ (M⁺): 391.1896, found: 391.1898.

(*E*)-ethyl 3-(3-methoxystyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2o**). Following the general procedure with **1o** (205 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2o** (188 mg, 0.48 mmol, 96%) as a light yellow solid.

R_f = 0.33 (10:1 Petroleum ether/EtOAc); m.p. = 94-96 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 1 H), 7.97 (dd, *J* = 9.4 Hz, 1.0 Hz, 1 H), 7.66 (d, *J* = 9.2 Hz, 1 H), 7.60 (d, *J* = 16.8 Hz, 1 H), 7.53 (d, *J* = 16.8 Hz, 1 H), 7.35 (t, *J* = 8.0 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.17 (s, 1 H), 6.89 (dd, *J* = 8.0 Hz, 2.0 Hz, 1 H), 4.43 (q, *J* = 7.2 Hz, 2 H), 3.89 (s, 3 H), 3.48 (br s, 4 H), 2.10 (br s, 4 H), 1.44 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 159.9, 147.3, 138.4, 134.1, 132.3, 129.8, 126.2, 125.1, 124.0, 119.4, 117.24, 117.15, 115.6, 113.8, 112.3, 60.9, 55.4, 55.2, 23.1, 14.4; IR (ATR-FTIR): 1703, 1268, 1228, 1194, 771, 744 cm⁻¹; MS (EI): *m/z* (%): 391 (M⁺, 31), 322 (100), 293 (21), 277 (13), 249 (11), 205 (12), 176 (8); HRMS (EI-TOF) calcd for C₂₃H₂₅N₃O₃ (M⁺): 391.1896, found: 391.1898.

(*E*)-ethyl 3-(2,4-dimethylstyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2p**). Following the general procedure with **1p** (203 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2p** (183 mg, 0.47 mmol, 94%) as a light yellow solid.

R_f = 0.35 (10:1 Petroleum ether/EtOAc); m.p. = 126-127 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 1 H), 7.97 (dd, *J* = 9.2 Hz, 1.2 Hz, 1 H), 7.83 (d, *J* = 16.8

Hz, 1 H), 7.66 (d, $J = 8.8$ Hz, 1 H), 7.64 (d, $J = 7.6$ Hz, 1 H), 7.45 (d, $J = 16.8$ Hz, 1 H), 7.09 (d, $J = 8.4$ Hz, 1 H), 7.07 (s, 1 H), 4.41 (q, $J = 7.1$ Hz, 2 H), 3.57-3.41 (m, 4 H), 2.49 (s, 3 H), 2.36 (s, 3 H), 2.09 (br s, 4 H), 1.43 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 147.4, 138.4, 136.1, 134.7, 133.0, 131.4, 130.4, 127.1, 126.2, 125.1, 125.0, 123.8, 117.2, 117.1, 115.1, 60.8, 55.0, 23.1, 21.2, 19.8, 14.4; IR (ATR-FTIR): 1707, 1242, 1114, 749 cm^{-1} ; MS (EI): m/z (%): 389 (M^+ , 37), 344 (9), 320 (100), 305 (98), 291 (29), 277 (38), 232 (29), 202 (36); HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_2$ (M^+): 389.2103, found: 389.2113.

(*E*)-ethyl 3-(3,4-dimethylstyryl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2q**). Following the general procedure with **1q** (204 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2q** (192 mg, 0.495 mmol, 99%) as a light yellow solid.

$R_f = 0.35$ (10:1 Petroleum ether/EtOAc); m.p. = 103-105 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.80 (s, 1 H), 7.97 (dd, $J = 9.2, 1.2$ Hz, 1 H), 7.66 (d, $J = 9.2$ Hz, 1 H), 7.56-7.51 (m, 2 H), 7.42-7.39 (m, 2 H), 7.19 (d, $J = 7.6$ Hz, 1 H), 4.44 (q, $J = 7.1$ Hz, 2 H), 3.56-3.39 (m, 4 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 2.16-2.05 (m, 4 H), 1.45 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.1, 147.4, 137.3, 137.0, 134.6, 134.5, 132.8, 130.1, 128.1, 126.1, 125.2, 124.2, 123.8, 117.2, 117.0, 114.1, 60.9, 55.1, 23.2, 19.8, 19.7, 14.4; IR (ATR-FTIR): 1699, 1615, 1279, 1233, 1107, 957, 750 cm^{-1} ; MS (EI): m/z (%): 389 (M^+ , 8), 320 (100), 291 (18), 202 (13); HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_2$ (M^+): 389.2103, found: 389.2101.

(*E*)-ethyl 3-(2-(biphenyl-4-yl)vinyl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2r**).

Following the general procedure with **1r** (228 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2r** (192 mg, 0.44 mmol, 88%) as a light yellow solid.

R_f = 0.60 (5:1 Petroleum ether/EtOAc); m.p. = 126-128 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.81 (s, 1 H), 7.98 (d, *J* = 9.2 Hz, 1 H), 7.77-7.70 (m, 2 H), 7.70-7.61 (m, 6 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 1 H), 7.26 (s, 1 H), 4.44 (q, *J* = 7.1 Hz, 2 H), 3.49 (br s, 4 H), 2.12 (br s, 4 H), 1.45 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 147.4, 141.1, 140.4, 136.0, 134.2, 131.9, 128.8, 127.5, 127.4, 127.2, 126.9, 126.2, 125.1, 124.0, 117.3, 117.2, 115.2, 60.9, 55.2, 23.2, 14.4; IR (ATR-FTIR): 1706, 1272, 1232, 1113, 753 cm⁻¹ MS (EI): *m/z* (%): 437 (M⁺, 10), 368 (100), 339 (29), 294 (16), 265 (20); HRMS (EI-TOF) calcd for C₂₈H₂₇N₃O₂ (M⁺): 437.2103, found: 437.2105.

(*E*)-ethyl 3-(2-(naphthalen-2-yl)vinyl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2s**).

Following the general procedure with **1s** (214 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2s** (195 mg, 0.475 mmol, 95%) as a yellow solid.

R_f = 0.67 (3:1 Petroleum ether/EtOAc); m.p. = 121-122 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.86 (s, 1 H), 8.03-7.96 (m, 2 H), 7.90-7.83 (m, 4 H), 7.78-7.67 (m, 3 H), 7.53-7.46 (m, 2 H), 4.46 (q, *J* = 7.2 Hz, 2 H), 3.60-3.39 (m, 4 H), 2.21-2.06 (m, 4 H), 1.47 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 147.4, 134.4, 134.2, 133.6, 133.3, 132.5, 128.4, 128.1, 127.7, 127.6, 126.5, 126.3, 126.2, 125.1, 124.0, 123.1, 117.3, 117.2, 115.4,

60.9, 55.2, 23.2, 14.4; IR (ATR-FTIR): 1701, 1617, 1271, 1227, 1198, 952, 741 cm^{-1} ; MS (EI): m/z (%): 411 (M^+ , 42), 366 (3), 342 (100), 313 (32), 269 (22), 239 (33); HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{O}_2$ (M^+): 411.1947, found: 411.1947.

(*E*)-ethyl 3-(2-cyclopropylvinyl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2t**). Following the general procedure with **1t** (172 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2t** (150 mg, 0.46 mmol, 92%) as a white solid.

R_f = 0.60 (5:1 Petroleum ether/EtOAc); m.p. = 72-74 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.55 (s, 1 H), 7.89 (dd, J = 9.2, 1.2 Hz, 1 H), 7.58 (d, J = 9.2 Hz, 1 H), 6.97 (d, J = 16.4 Hz, 1 H), 6.22 (dd, J = 16.0, 1.2 Hz, 1 H), 4.39 (q, J = 7.1 Hz, 2 H), 3.49-3.30 (m, 4 H), 2.14-1.96 (m, 4 H), 1.76-1.61 (m, 1 H), 1.40 (t, J = 7.2 Hz, 3 H), 0.97-0.92 (m, 2 H), 0.69-0.65 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.2, 147.2, 140.3, 134.4, 125.9, 125.3, 123.2, 116.81, 116.77, 114.6, 60.7, 54.9, 23.1, 15.7, 14.4, 8.1; IR (ATR-FTIR): 1698, 1277, 1230, 950, 771 cm^{-1} ; MS (EI): m/z (%): 325 (M^+ , 18), 280 (10), 256 (100), 241 (86), 227 (50), 213 (45), 183 (45), 168 (30), 153 (29), 70 (84); HRMS (EI-TOF) calcd for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2$ (M^+): 325.1790, found: 325.1790.

D. General Procedure of 1-Aryl Triazene Cinnamyl Alcohol 3

D1. General Procedure of Compound 3a and 3b

A dry and N₂-flushed 100 mL Schlenk tube, equipped with a magnetic stirrer was charged with *o*-I substituted aryl triazene (8 mmol) in dry THF (10 mL). *i*PrMgCl (5.8 mL, 7.2 mmol, 1.24 M in THF) was then added dropwise at –60 °C. After 2 h, a complete conversion to the corresponding Grignard reagent was observed as indicated by thin layer chromatography (TLC). Cinnamaldehyde (2.643 g, 20 mmol) was added at –60°C. The reaction mixture was slowly warmed to room temperature and stirred overnight. Thereafter, the reaction was quenched by H₂O and the resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na₂SO₄, concentrated in vacuo, and purified by silica gel chromatography.

Ethyl 3-((*E*)-1-hydroxy-3-phenylallyl)-4-((*E*)-pyrrolidin-1-yl)diazenylbenzoate (**3a**). Following the general procedure with (*E*)-ethyl 3-iodo-4-(pyrrolidin-1-yl)diazenylbenzoate (2.98 g, 8 mmol). Purification by column chromatography (10-50% EtOAc/Petroleum ether) gave **3a** (2.58 g, 6.8 mmol, 85%) as brown oil.

R_f = 0.27 (3:1 Petroleum ether/EtOAc);

^1H NMR (500 MHz, CDCl_3): δ 7.97 (d, $J = 1.5$ Hz, 1 H), 7.91 (dd, $J = 9.0$ Hz, 1.5 Hz, 1 H), 7.59 (d, $J = 8.0$ Hz, 1 H), 7.34 (d, $J = 7.5$ Hz, 2 H), 7.27 (t, $J = 7.3$ Hz, 2 H), 7.19 (t, $J = 7.0$ Hz, 1 H), 6.60 (d, $J = 16.0$ Hz, 1 H), 6.51 (dd, $J = 16.0, 5.5$ Hz, 1 H), 5.61-5.50 (m, 1 H), 5.39 (d, $J = 7.5$ Hz, 1 H), 4.36 (q, $J = 7.2$ Hz, 2 H), 4.04-3.91 (m, 2 H), 3.72-3.60 (m, 2 H), 2.09-2.02 (m, 4 H), 1.38 (t, $J = 7.3$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.4, 151.6, 137.0, 135.2, 132.2, 129.50, 129.46, 129.4, 128.4, 127.3, 126.7, 126.5, 116.1, 75.3, 60.7, 51.5, 47.0, 23.8, 23.3, 14.3; IR (ATR-FTIR): 3500, 1705, 1392, 1284, 1262, 1235, 1105 cm^{-1} ; MS (EI): m/z (%): 379 (M^+ , 26), 362 (100), 334 (6), 292 (23), 218 (31), 174 (37), 85 (38); HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_3$ (M^+): 379.1896, found: 379.1894.

3-((*E*)-1-hydroxy-3-phenylallyl)-4-((*E*)-pyrrolidin-1-yl)diazenylbenzonitrile (**3b**). Following the general procedure with (*E*)-3-iodo-4-(pyrrolidin-1-yl)diazenylbenzonitrile (2.61 g, 8 mmol). Purification by column chromatography (10-50% EtOAc/Petroleum ether) gave **3b** (1.22 g, 3.68 mmol, 46%) as a yellow solid.

$R_f = 0.13$ (3:1 Petroleum ether/EtOAc); m.p. = 125-127 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 7.61 (d, $J = 8.4$ Hz, 1 H), 7.59 (d, $J = 1.2$ Hz, 1 H), 7.49 (dd, $J = 8.4$ Hz, 1.6 Hz, 1 H), 7.37-7.35 (m, 2 H), 7.30 (t, $J = 7.2$ Hz, 2 H), 7.24-7.21 (m, 1 H), 6.62 (d, $J = 16.4$ Hz, 1 H), 6.45 (dd, $J = 15.8, 6.2$ Hz, 1 H), 5.56 (t, $J = 6.4$ Hz, 1 H), 5.05 (d, $J = 7.2$ Hz, 1 H), 4.00 (t, $J = 6.6$ Hz, 2 H), 3.69 (t, $J = 6.6$ Hz, 2 H), 2.18-1.99 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.4, 136.6, 136.3, 131.8, 131.6, 131.0, 130.3, 128.5, 127.6, 126.5, 119.4, 116.9, 107.7, 74.1, 51.8, 47.2, 23.8, 23.3; IR (ATR-FTIR): 3359, 2217, 1388, 1309, 692 cm^{-1} ; MS (EI): m/z (%): 332 (M^+ , 23), 315 (35), 263 (12), 247 (35), 190 (25), 171 (75), 128 (40), 91 (75), 85

(100); HRMS (EI-TOF) calcd for $C_{20}H_{20}N_4O$ (M^+): 332.1637, found: 332.1636.

D2. General Procedure of Compound **3s**

Triazene aryl ketone (5 mmol, 1.445 g) was taken in a flask (100 mL) and dissolved in EtOH (15 mL). To the solution, 2-naphthaldehyde (6 mmol, 0.936 g) followed by aqueous NaOH solution (3 mL, 3 M) was added. The reaction mixture was kept in stirred condition at room temperature for 8 h. After Completion, monitored by TLC, the reaction mixture was subjected to filtration to obtain the residue. The residue was thoroughly washed with 40 mL water, followed by 40 mL Et₂O and dried with vacuo to obtain the crude product **3s-1**.

To a solution of **3s-1** (4.15 mmol, 1.777 g) in EtOH (15 mL) was added CeCl₃·7H₂O (5 mmol, 1.865 g) followed by NaBH₄ (475 mg, 12.5 mmol) dropwise in ice bath. The reaction mixture was stirred in ice bath for 1 h before water (20 mL) was added. After stirred at room temperature for 0.5 h the mixture was extracted with ethyl acetate (40 mL × 4). The organic fractions were dried over Na₂SO₄, concentrated in vacuo and purified by silica gel chromatography (10-33% EtOAc/Petroleum ether) to provide the **3s** (1.102 g) as a yellow solid.

R_f = 0.30 (3:1 Petroleum ether/EtOAc); m.p. = 119-121 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.01 (s, 1 H), 7.94 (d, *J* = 8.4 Hz, 1 H), 7.81-7.66 (m, 4 H), 7.61 (d, *J* = 8.8 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 1 H), 7.48-7.36 (m, 2 H), 6.76 (d, *J* = 15.6 Hz, 1 H), 6.64 (dd, *J* = 15.6, 5.6 Hz, 1 H), 5.61 (br s, 1 H), 5.43 (d, *J* = 7.2 Hz, 1 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 3.99 (br s, 2 H), 3.70 (br s, 2 H), 2.19-1.93 (m, 4 H), 1.39 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.4, 151.6, 135.2, 134.4, 133.5, 132.8, 132.7, 129.6, 129.49, 129.45, 128.0, 127.8, 127.5, 126.7, 126.4, 126.1, 125.7, 123.7, 116.2, 75.4, 60.8, 51.5, 47.0, 23.8, 23.3, 14.3; IR

(ATR-FTIR): 3493, 1676, 1385, 1284, 1254, 1109 cm^{-1} ; MS (EI): m/z (%): 429 (M^+ , 7), 411 (8), 384 (10), 356 (9), 342 (95), 313 (24), 239 (47), 218 (100), 141 (72), 85 (52); HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_3$ (M^+): 429.2052, found: 429.2032.

E. General Procedure for Preparation

3-alkenyl-2-pyrrolidine-2*H*-indazole **2** from 1-Aryl Triazene

Cinnamyl Alcohol **3**

(*E*)-ethyl 2-(pyrrolidin-1-yl)-3-styryl-2*H*-indazole-5-carboxylate (**2a**). Following the General Procedure for Preparation 3-Alkenyl-2-pyrrolidine-2*H*-indazole **2** from triazenylaryl allylic alcohol **1** (**C**) with **3a** (189 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2a** (134 mg, 0.37 mmol, 74%) as a yellow solid.

(*E*)-2-(pyrrolidin-1-yl)-3-styryl-2*H*-indazole-5-carbonitrile (**2b**). Following the General Procedure for Preparation 3-Alkenyl-2-pyrrolidine-2*H*-indazole **2** from triazenylaryl allylic alcohol **1** (**C**) with **3b** (166 mg, 0.5 mmol), purification by column chromatography (5-20% EtOAc/Petroleum ether) gave **2b** (119 mg, 0.38 mmol, 76%) as a light yellow solid

(*E*)-ethyl 3-(2-(naphthalen-2-yl)vinyl)-2-(pyrrolidin-1-yl)-2*H*-indazole-5-carboxylate (**2s**). Following the General Procedure for Preparation 3-Alkenyl-2-pyrrolidine-2*H*-indazole **2** from triazenylaryl allylic alcohol **1** (**C**) with **3s** (214 mg, 0.5 mmol), purification by column chromatography (5-10% EtOAc/Petroleum ether) gave **2s** (197 mg, 0.48 mmol, 96%) as a yellow solid.

F. Transformations of the 3-alkenyl-2-pyrrolidine-2*H*-indazole **2a**

To a solution of 3-alkenyl-2-pyrrolidine-2*H*-indazole **2a** (90 mg, 0.25 mmol) in CH₃COOH (2 mL) was added freshly activated Zn (407 mg, 6.25 mmol). The reaction mixture was stirred at 100°C for 12 h. After cooled to room temperature, water was added and the reaction mixture was neutralized with saturated NaHCO₃. The resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na₂SO₄, concentrated in vacuo and purified by silica gel chromatography (20-50% EtOAc/Petroleum ether) to provide the **8a** (54 mg, 0.188 mmol, 75%) as

a white solid.

R_f = 0.15 (5:1 Petroleum ether/EtOAc); m.p. = 140-142 °C;

¹H NMR (400 MHz, CDCl₃): δ 11.54 (br s, 1 H), 8.77 (s, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.68-7.53 (m, 3 H), 7.52-7.35 (m, 4 H), 7.33-7.29 (m, 1 H), 4.46 (q, *J* = 6.9 Hz, 2 H), 1.46 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 145.4, 143.3, 136.7, 132.4, 128.7, 128.2, 127.8, 126.7, 124.1, 123.7, 121.0, 118.8, 109.9, 61.1, 14.4; IR (ATR-FTIR): 3303, 1693, 1277, 1244, 743 cm⁻¹; MS (EI): *m/z* (%): 292 (M⁺, 56), 291 (100), 263 (35), 247 (11), 218 (37), 203 (25), 189 (20), 123 (16), 91 (28), 77 (24); HRMS (EI-TOF) calcd for C₁₈H₁₆N₂O₂ (M⁺): 292.1212, found: 292.1219.

3-Alkenyl-2-pyrrolidine-2H-indazole **2a** (180 mg, 0.5 mmol) was dissolved in 4 mL of EtOH. 10 mg of 10% Pd/C was added and the resulting mixture was shaken under H₂ atmosphere (1 atm) for 3 h. The catalyst was filtered off and washed with ethanol. The combined filtrates were concentrated in vacuo and purified by silica gel chromatography (5-20% EtOAc/Petroleum ether) to provide the **8b** (180 mg, 0.495 mmol, 99%) as a white solid.

R_f = 0.29 (10:1 Petroleum ether/EtOAc); m.p. = 86-87 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.35 (s, 1 H), 7.91 (d, *J* = 8.8 Hz, 1 H), 7.60 (d, *J* = 9.2 Hz, 1 H), 7.34-7.06 (m, 5 H), 4.41 (q, *J* = 6.9 Hz, 2 H), 3.44 (t, *J* = 7.4 Hz, 2 H), 3.27 (br s, 4 H), 3.06 (t, *J* = 7.4 Hz, 2 H), 2.02 (br s, 4 H), 1.44 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.1, 147.0, 140.5, 137.4, 128.4, 128.3, 126.3, 126.0, 124.7, 122.6, 118.0, 116.7, 60.7, 55.2, 35.6, 26.5, 23.1, 14.4; IR (ATR-FTIR): 1708, 1278, 1235, 1110, 750, 697 cm⁻¹; MS (EI): *m/z* (%): 363 (M⁺, 62), 318 (17), 294 (40), 272 (100), 203 (80), 175 (59), 147 (16), 91 (76); HRMS (EI-TOF) calcd for C₂₂H₂₅N₃O₂ (M⁺): 363.1947, found: 363.1953.

To a solution of **8b** (91 mg, 0.25 mmol) in CH₃COOH (2 mL) was added freshly activated Zn (407 mg, 6.25 mmol). The reaction mixture was stirred at 100 °C for 12 h. After cooled to room temperature, water was added and the reaction mixture was neutralized with saturated NaHCO₃. The resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na₂SO₄, concentrated in vacuo and purified by silica gel chromatography (20-50% EtOAc/Petroleum ether) to provide the **8e** (67 mg, 0.228 mmol, 91%) as a white solid.

R_f = 0.14 (5:1 Petroleum ether/EtOAc); m.p. = 82-84 °C;

¹H NMR (400 MHz, CDCl₃): δ 10.77 (s, 1 H), 8.40 (s, 1 H), 8.06 (d, *J* = 8.8 Hz, 1 H), 7.42 (d, *J* = 8.8 Hz, 1 H), 7.34-7.16 (m, 5 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 3.41-3.29 (m, 2 H), 3.22-3.11 (m, 2 H), 1.44 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 166.9, 148.1, 142.8, 141.2, 128.38, 128.35, 127.6, 126.1, 123.6, 122.7, 121.9, 109.5, 61.0, 35.1, 28.9, 14.4; IR (ATR-FTIR): 3142, 3036, 1709, 1264, 1235, 761 cm⁻¹; MS (EI): *m/z* (%): 294 (M⁺, 15), 203 (44), 175 (20), 158 (6), 130 (25), 91 (100); HRMS (EI-TOF) calcd for C₁₈H₁₈N₂O₂ (M⁺): 294.1368, found: 294.1374.

To a solution of **2a** (180 mg, 0.5 mmol) in THF/H₂O (3:1, 4 mL) was added solid NMO (65 mg, 0.55 mmol) followed by OsO₄ (0.05 mmol, 2% in H₂O) dropwise in ice bath. After the reaction mixture was stirred at room temperature for 2 h, it was extracted with ethyl acetate (40 mL × 3). The organic fractions were dried over Na₂SO₄, concentrated in vacuo and purified by silica gel chromatography (10-50% EtOAc/Petroleum ether) to provide the **8c** (178 mg, 0.45 mmol, 90%) as a white solid.

R_f = 0.15 (2:1 Petroleum ether/EtOAc); m.p. = 192-193 °C;

¹H NMR (400 MHz, (CD₃)₂SO): δ 8.54 (s, 1 H), 7.75 (d, *J* = 9.2 Hz, 1 H), 7.54 (d, *J* = 8.8 Hz, 1

H), 7.30-7.08 (m, 3 H), 7.07-6.90 (m, 2 H), 6.03 (s, 1 H), 5.76 (s, 1 H), 5.35 (d, $J = 6.8$ Hz, 1 H), 4.95 (d, $J = 7.2$ Hz, 1 H), 4.34 (q, $J = 6.9$ Hz, 2 H), 3.17-2.93 (m, 2 H), 2.72 (br s, 2 H), 1.84 (s, 4 H), 1.36 (t, $J = 7.0$ Hz, 3 H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$): δ 167.2, 147.2, 142.6, 139.1, 128.5, 128.1, 127.7, 127.2, 126.1, 122.8, 118.5, 117.8, 77.0, 71.8, 61.4, 55.7, 23.5, 15.3; IR (ATR-FTIR): 3440, 3140, 1714, 1676, 1282, 1243, 1050, 748, 695 cm^{-1} ; MS (EI): m/z (%): 396 ($\text{M}^+ + \text{H}$, 19), 350 (18), 288 (100), 219 (43), 191 (55), 173 (39), 107 (38); Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_4$: C, 66.82; H, 6.37; N, 10.63. found: C, 66.23; H, 6.46; N, 10.17.

To a solution of **2a** (180 mg, 0.5 mmol) in DCM (10 mL) was added solid KMnO_4 (474 mg, 3 mmol) and the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was then filtered and the residue was thoroughly washed with DCM (20 mL). The combined filtrates were concentrated in vacuo and purified by silica gel chromatography (5-10% EtOAc/Petroleum ether) to give **8d** (86 mg, 0.3 mmol, 60 %) as a white solid.

$R_f = 0.29$ (10:1 Petroleum ether/EtOAc); m.p. = 96-98 $^{\circ}\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 10.45 (s, 1 H), 8.93 (s, 1 H), 8.04 (dd, $J = 9.0, 1.4$ Hz, 1 H), 7.77 (d, $J = 9.2$ Hz, 1 H), 4.41 (q, $J = 7.2$ Hz, 2 H), 3.57 (t, $J = 6.8$ Hz, 4 H), 2.19-2.07 (m, 4 H), 1.43 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 180.8, 166.5, 146.7, 131.6, 128.2, 127.2, 124.6, 119.5, 117.9, 61.2, 56.6, 23.3, 14.4; IR (ATR-FTIR): 1711, 1661, 1284, 1229, 1123, 1018, 769, 743 cm^{-1} ; MS (EI): m/z (%): 287 (M^+ , 3), 242 (23), 218 (24), 203 (18), 190 (49), 173 (100), 145 (39), 117 (16); HRMS (EI-TOF) calcd for $\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3$ (M^+): 287.1270, found: 287.1263.

1a

^{13}C NMR (100 MHz, CDCl_3)

166.627
151.380
142.873
132.505
130.095
129.264
128.379
127.803
127.449
126.703
126.477
126.346
116.620

77.316
77.000
76.676
75.372

60.686

14.316

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

160 140 120 100 80 60 40 20 0 PPM

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (100 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

8.161
7.850
7.829
7.437
7.416
7.408
7.401
7.387
7.320
7.280
7.260
7.050
7.028
7.006
6.484
6.467
6.444
6.427

5.389
5.373

4.367
4.349
4.332
4.314
3.944

3.621

2.478

2.028

1.388
1.370
1.352

0.001

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

1k

^{13}C NMR (125 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

11

11

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

1o

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (100 MHz, CDCl₃)

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (100 MHz, CDCl₃)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (500 MHz, CDCl_3)

2a

^{13}C NMR (125 MHz, CDCl_3)

2a

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

7.719
7.607
7.584
7.579
7.557
7.500
7.458
7.410
7.368
7.260
7.196
7.174
6.960
6.939

3.855
3.462
3.448

2.490

2.084

0.016

¹H NMR (400 MHz, CDCl₃)

3.03
1.00
1.02
1.02
2.01

3.10

4.06

3.05

4.16

8

7

6

5

4

3

2

1

0

PPM

^{13}C NMR (100 MHz, CDCl_3)

7.982
7.962
7.700
7.678
7.569
7.549
7.516
7.474
7.437
7.395
7.360
7.341
7.322
7.260
7.176
7.157
7.139
6.961
6.939

3.855

3.476

2.093

1.717

0.011

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

2j

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

2k

167.007
147.341
135.881
133.751
131.895
130.934
128.184
126.185
124.891
124.174
122.218
117.274
117.250
115.810

77.317
77.000
76.681

60.915
55.254

23.185

14.415

150

100

50

0 PPM

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (100 MHz, CDCl₃)

167.080
159.890
147.333
138.358
134.070
132.252
129.771
126.154
125.064
123.987
119.394
117.236
117.154
115.565
113.824
112.256

77.316
77.000
76.673

60.901
55.351
55.169

23.133

14.410

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (100 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (125 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

167.107

147.017

140.501

137.417

128.404

128.310

126.302

125.989

124.714

122.566

117.976

116.704

77.314

77.203

77.000

76.672

60.710

55.196

35.558

26.483

23.125

14.410

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)