Supporting Information

Brønsted Acid Catalyzed Enantioselective Addition of Hydrazones to 3-Indolylmethanols

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I. General Information

Unless noted otherwise, all commercially available reagents were used without further purification. Organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. Solvents for chromatography were technical grade and distilled prior to use. Thin layer chromatography (TLC) was carried out on Macherey-Nagel ALUGRAM Xtra SIL G/UV F254, visualized by UV irradiation. Macherey-Nagel silica gel 60 (particle size 0.063-0.2 mm) was used for column chromatography. Solvent mixtures are understood as volume/volume. ¹H-NMR, ¹³C-NMR and ¹⁹F-NMR spectra were recorded on VNMR-400, VNMR-600 or Mercury 300 spectrometer in CDCl₃, CD₂Cl₂ and DMSO-d₆. Carbon NMR (¹³C) spectra were recorded using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the residual proton signals in CDCl₃ (δ = 7.26, 77.16), DMSO-d₆ (δ = 2.50, 39.52) or CD₂Cl₂ (δ = 5.32, 54.00). Coupling constants (J) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010 (column: Equity®-5, length × I.D. 30 m × 0.25 mm, df 0.25 μm, lot # 28089-U, Supelco), High resolution mass spectra (HRMS-ESI) were acquired using a ThermoFisher Scientific LTQ-Orbitrap XL. Infrared Spectra were recorded on a Perkin Elmer Spektrum 100 infrared spectrometre with a Diamant/KRS5 ATR unit. For the most significant bands the wave number ñ is given in cm⁻¹. Signals with transmissions greater than 90% were not reported. Optical rotations were measured with a Perkin-Elmer 241 polarimeter in a 1 dm cuvette using a sodium lamp (589 nm). The optical rotation is given in degrees per mg per ml, sample concentrations are reported in g per 100 mL. Melting points (m.p.) were recorded using a Büchi SMP-20 melting point apparatus and were not corrected. High Performance Liquid Chromatography (HPLC) was carried out on a JASCO UV-2077 Plus with a PU-2080 Plus solvent pump. Operation and analysis were under control of JASCO ChromPass software. As chiral columns for determination of enantiomeric excess the following prefabricated columns from Daicel were used: Chiralpak AD-H (250 x 4.6 mm, 5 μm), Chiralpak IA (250 x 4.6 mm, 5 μm), and Chiralcel OD-H (250 x 4.6 mm, 5 μm). Supercritical Fluid Chromatography (SFC) was carried out using a (S,S)-Whelk-01 column. The chiral SFC methods were calibrated with the corresponding racemic mixtures. The CD-spectrum for the product 8i was recorded on a circular dichroism spectrometer (AVIV Model 62DS) at room temperature in acetonitrile.
II. General Procedures

General Procedure A: Preparation of Hydrazones (2a-e):
A suspension of the corresponding hydrazine hydrochloride (1.47 g, 12.0 mmol) in anhydrous THF (20 mL) was treated with triethylamine (12.0 mmol, 1.21 g) for 15 min before a solution of ethyl glyoxylate (50% in toluene, 2.45 g solution, 12.0 mmol) was added dropwise into the reaction mixture at 0 °C. The mixture was stirred for 30 min at 0 °C, then for 14 h at rt. The solvent was removed in vacuo and the crude product was purified by flash column chromatography (SiO₂ deactivated with NEt₃, n-pentane:ethyl acetate 9:1 to 7:3).

General Procedure B: Preparation of Alcohols (1a-r):
The corresponding bromo compound (3 equiv.) was added slowly to a suspension of magnesium (3.5 equiv.) in dry THF under vigorous stirring. The reaction mixture was stirred for 30 min, then a solution of the corresponding 1H-indole-3-carboxaldehyde (1 equiv.) in dry THF was added slowly to the Grignard solution at 0 °C. The resulting mixture was stirred at 0 °C for 30 min then for 14 h at rt. Water was added to quench the reaction at 0 °C. The reaction mixture was extracted with EtOAc (3x) and the combined organic layers were dried over MgSO₄. The solvent was removed in vacuo and the crude product was purified by flash column chromatography (SiO₂ deactivated with NEt₃, n-pentane:ethyl acetate 9:1 to 7:3). Alcohols 1a-r were synthesized as above, starting from the commercially available Grignard reagent and the corresponding aldehyde.
The products are not very stable at room temperature and should be stored under an atmosphere of argon in the refrigerator.

General Procedure C: Preparation of Racemic Products:
The catalyst (PhO)₂P(O)OH (0.01 mmol) was added to a solution of the corresponding alcohol (0.13 mmol) and hydrazone (0.10 mmol) in dry toluene (1.5 mL). The reaction mixture was stirred for 16 h at rt. The crude product was purified by flash column chromatography (SiO₂, n-pentane:Et₂O 9:1 to 7:3)

General Procedure D: Preparation of Chiral Products:
A solution of catalyst 3h (5 mol %) in toluene (1 mL) was added to a solution of the corresponding alcohol 1 (0.13 mmol) and hydrazone 2 (0.10 mmol) in toluene (1 mL) at -30 °C. The reaction mixture was stirred at -30 °C until complete conversion of the starting material (48-72 h). The crude product was purified by flash column chromatography. The enantiomeric excess was determined by HPLC or SFC analysis, using chiral stationary phases.
III. Characterization of Alcohols 1a-1r:

(2-Methyl-1H-indol-3-yl)(phenyl)methanol (1a)<sup>1</sup>

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (1.59 g, 10 mmol), bromobenzene (4.71 g, 30 mmol) and magnesium (850.5 mg, 35 mmol) using THF (100 mL) as solvent. Purification by column chromatography (SiO<sub>2</sub> (NEt<sub>3</sub>), n-pentane:ethyl acetate 8:2) afforded 1a (2.01 g, 8.45 mmol) as a yellow oil in 85% yield. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 8.03 (s, 1H), 7.50-7.47 (m, 2H), 7.38 (dd, <i>J</i> = 7.9 Hz, 0.8, 1H), 7.34-7.31 (m, 2H), 7.27 (dt, <i>J</i> = 8.1, 0.9 Hz, 1H), 7.24 (dd, <i>J</i> = 7.4, 0.4 Hz, 1H), 7.07 (ddd, <i>J</i> = 8.2, 7.1, 1.2 Hz, 1H), 6.94 (ddd, <i>J</i> = 8.0, 7.1, 1.0 Hz, 1H), 6.17 (s, 1H), 2.44 (s, 3H).<sup>13</sup>C NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ = 144.7, 135.8, 133.1, 128.4, 127.1, 126.2, 121.6, 119.8, 119.6, 114.6, 110.7, 69.4, 12.2. IR (ATR, cm<sup>−1</sup>) ν = 3397, 3055, 1694, 1606, 1454, 1374, 1302, 1241, 1154, 1007, 835, 735. EI-MS: m/z (%) = 237.3 (M<sup>+</sup>, 33), 220.2 (17), 159.9 (24), 131.5 (11), 117.0 (12), 105.1 (74), 82.9 (100), 77.1 (34).

(2-Methyl-1H-indol-3-yl)(p-tolyl)methanol (1b)<sup>1a</sup>

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 4-Me-phenyl bromide (2.57 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO<sub>2</sub> (NEt<sub>3</sub>), n-pentane:ethyl acetate 8:2) afforded 1b (1.10 g, 4.37 mmol) as a yellow oil in 87% yield. <sup>1</sup>H NMR (600 MHz, DMSO-<i>d</i><sub>6</sub>) δ = 10.74 (s, 1H), 7.35 (d, <i>J</i> = 7.9 Hz, 1H), 7.29 (d, <i>J</i> = 8.0 Hz, 2H), 7.20 (d, <i>J</i> = 8.0 Hz, 1H), 7.06 (d, <i>J</i> = 7.9 Hz, 2H), 6.94-6.90 (m, 1H), 6.82-6.78 (m, 1H), 5.95 (d, <i>J</i> = 3.4 Hz, 1H), 5.37 (d, <i>J</i> = 3.5 Hz, 1H), 2.39 (s, 3H), 2.24 (s, 3H).<sup>13</sup>C NMR (150 MHz, DMSO-<i>d</i><sub>6</sub>) δ = 143.1, 135.2, 134.8, 131.8, 128.2, 126.8, 125.7, 119.8, 119.2, 118.0, 114.6, 110.2, 67.4, 20.7, 11.9. IR (ATR, cm<sup>−1</sup>) ν = 3397, 3027, 2922, 1867, 1708, 1609, 1452, 1369, 1305, 1235, 1170, 1109, 1017, 815, 742. EI-MS: m/z (%) = 251.2 (M<sup>+</sup>, 17), 234.3 (43), 232.2 (100), 217.3 (63), 188.9 (27), 157.9 (23), 146.1 (45), 119.0 (52), 90.9 (48).
(2-Methyl-1H-indol-3-yl)(o-tolyl)methanol (1c)\textsuperscript{1a}

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (318.0 mg, 2.0 mmol), 2-Me-phenyl bromide (1.03 g, 6 mmol) and magnesium (170.1 mg, 7.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1c (486 mg, 1.93 mmol) as a yellow oil in 97% yield. \textsuperscript{1H} NMR (600 MHz, DMSO-d\textsubscript{6}) $\delta$ = 10.80 (s, 1H), 7.85 (d, $J$ = 7.7 Hz, 1H), 7.24 (t, $J$ = 7.5 Hz, 1H), 7.21 (d, $J$ = 8.0 Hz, 1H), 7.16 (d, $J$ = 7.9 Hz, 1H), 7.12 (td, $J$ = 7.4, 1.0 Hz, 1H), 7.04 (d, $J$ = 7.4 Hz, 1H), 6.93-6.89 (m, 1H), 6.78-6.74 (m, 1H), 6.01 (d, $J$ = 4.0 Hz, 1H), 5.28 (d, $J$ = 4.0 Hz, 1H), 2.32 (s, 3H), 2.04 (s, 3H). \textsuperscript{13}C NMR (150 MHz, DMSO-d\textsubscript{6}) $\delta$ = 143.3, 135.1, 134.5, 133.0, 129.8, 127.1, 126.1, 126.0, 125.1, 119.7, 118.7, 118.0, 112.2, 110.3, 65.1, 18.9, 11.8. IR (ATR, cm\textsuperscript{-1}) $\tilde{\nu}$ = 3528, 3395, 3058, 2915, 1916, 1716, 1568, 1453, 1247, 992, 846, 738. \textit{EI-MS}: m/z (%) = 251.3 (M\textsuperscript{+}, 100), 234.3 (69), 218.2 (15), 160.2 (15), 132.2 (53), 91.2 (15).

(4-(tert-Butyl)phenyl)(2-methyl-1H-indol-3-yl)methanol (1d)

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (318.0 mg, 2.0 mmol), 4-tBu-phenyl bromide (1.03 g, 6 mmol) and magnesium (170.1 mg, 7.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1d (550 mg, 1.87 mmol) as a yellow oil in 94% yield. \textsuperscript{1H} NMR (600 MHz, DMSO-d\textsubscript{6}) $\delta$ = 10.75 (s, 1H), 7.46 (d, $J$ = 7.9 Hz, 1H), 7.35 (d, $J$ = 8.3 Hz, 2H), 7.28 (d, $J$ = 8.4 Hz, 2H), 7.21 (d, $J$ = 8.0 Hz, 1H), 6.95-6.91 (m, 1H), 6.84-6.80 (m, 1H), 5.97 (d, $J$ = 3.2 Hz, 1H), 5.39 (d, $J$ = 3.3 Hz, 1H), 2.42 (s, 3H), 1.24 (s, 9H). \textsuperscript{13}C NMR (150 MHz, DMSO-d\textsubscript{6}) $\delta$ = 148.2, 143.2, 135.2, 131.6, 126.8, 125.5, 124.4, 119.8, 119.3, 118.0, 114.6, 110.2, 67.8, 34.1, 31.2, 11.9. IR (ATR, cm\textsuperscript{-1}) $\tilde{\nu}$ = 3502, 3397, 329, 2958, 2870, 2711, 2083, 1910, 1709, 1612, 1513, 1458, 161, 1302, 1328, 1104, 1001, 836, 741. \textit{EI-MS}: m/z (%) = 293.3 (M\textsuperscript{+}, 93), 276.3 (100), 260.3 (40), 218.2 (15), 160.2 (20), 132.2 (17), 117.1 (12).
(4-Methoxyphenyl)(2-methyl-1H-indol-3-yl)methanol (1e)\textsuperscript{1b}

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 4-MeO-phenyl bromide (2.57 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1e (565 mg, 2.12 mmol) as a yellow oil in 42% yield. \textsuperscript{1}H NMR (600 MHz, DMSO-d\textsubscript{6}) \(\delta = 10.74\) (s, 1H), 7.35 (d, \(J = 7.9\) Hz, 1H), 7.32 (d, \(J = 8.4\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 1H), 6.94-6.90 (m, 1H), 6.84-6.79 (m, 3H), 5.95 (d, \(J = 3.5\) Hz, 1H), 5.36 (d, \(J = 3.5\) Hz, 1H), 3.70 (s, 3H), 2.39 (s, 3H). \textsuperscript{13}C NMR (150 MHz, DMSO-d\textsubscript{6}) \(\delta = 157.6, 138.2, 135.2, 131.8, 126.9, 126.8, 119.8, 119.2, 118.0, 114.6, 113.1, 110.2, 67.3, 55.0, 11.9.\) IR (ATR, cm\textsuperscript{-1}) \(\tilde{\nu} = 3395, 2936, 1724, 1604, 1576, 1453, 1367, 1299, 1240, 1169, 1024, 831, 743.\) EI-MS: m/z (%) = 267.1 (M\textsuperscript{+}, 93), 250.3 (67), 249.3 (100), 234.2 (13), 205.3 (22), 157.9 (65), 134.9 (50), 116.9 (25), 107.9 (21), 76.8 (33).

(3-Methoxyphenyl)(2-methyl-1H-indol-3-yl)methanol (1f)\textsuperscript{1b}

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (318.0 mg, 2.0 mmol), 3-MeO-phenyl bromide (1.03 g, 6 mmol) and magnesium (170.1 mg, 7.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1f (501 mg, 1.87 mmol) as a yellow oil in 94% yield. \textsuperscript{1}H NMR (600 MHz, DMSO-d\textsubscript{6}) \(\delta = 10.77\) (s, 1H), 7.38 (d, \(J = 7.9\) Hz, 1H), 7.20 (d, \(J = 8.0\) Hz, 1H), 7.16 (t, \(J = 7.9\) Hz, 1H), 7.03 (s, 1H), 6.96-6.90 (m, 2H), 6.84-6.79 (m, 1H), 6.72 (dd, \(J = 8.1, 2.3\) Hz, 1H), 5.96 (d, \(J = 3.4\) Hz, 1H), 5.45 (d, \(J = 3.5\) Hz, 1H), 3.70 (s, 3H), 2.40 (s, 3H). \textsuperscript{13}C NMR (150 MHz, DMSO-d\textsubscript{6}) \(\delta = 158.9, 147.9, 135.2, 132.0, 128.7, 126.8, 119.9, 119.1, 118.2, 118.1, 114.3, 111.6, 111.0, 110.3, 67.5, 54.9, 11.9.\) IR (ATR, cm\textsuperscript{-1}) \(\tilde{\nu} = 3396, 2938, 2076, 1711, 1595, 1455, 1249, 1145, 1034, 862, 744, 690.\) EI-MS: m/z (%) = 267.3 (M\textsuperscript{+}, 100), 250.3 (51), 234.2 (10), 218.2 (7), 160.2 (30), 132.2 (23).
(2-Methoxyphenyl)(2-methyl-1H-indol-3-yl)methanol (1g)

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 2-MeO-phenyl bromide (2.57 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO2 (NEt3), n-pentane:ethyl acetate 8:2) afforded 1g (974 mg, 3.64 mmol) as a yellow solid in 73% yield. m.p. 132 °C. 1H NMR (600 MHz, DMSO-d6) δ = 10.66 (s, 1H), 7.84 (dd, J = 7.6, 1.5 Hz, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.19-7.13 (m, 2H), 6.97 (td, J = 7.5, 0.7 Hz, 1H), 6.92-6.87 (m, 1H), 6.86-6.84 (m, 1H), 6.82 (s, 3H), 6.78 (m, 1H), 6.17 (d, J = 3.5 Hz, 1H), 5.21 (d, J = 3.5 Hz, 1H), 3.68 (s, 3H), 2.40 (s, 3H). 13C NMR (150 MHz, DMSO-d6) δ = 155.6, 135.0, 133.7, 132.0, 127.1, 126.9, 126.5, 119.7, 119.5, 119.3, 117.8, 113.3, 110.3, 110.2, 62.7, 55.2, 11.9. IR (ATR, cm⁻¹) ν = 3511, 3367, 1592, 1490, 1457, 1243, 998, 837, 738. EI-MS: m/z (%) = 267.2 (M⁺, 100), 250.2 (35), 234.2 (13), 218.2 (12), 160.1 (23), 135.1 (35), 132.1 (40), 83.0 (11).

(2-Methyl-1H-indol-3-yl)(4-(trifluoromethyl)phenyl)methanol (1h)

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (572.0 mg, 3.6 mmol), 4-F3C-phenyl bromide (2.42 g, 10.8 mmol) and magnesium (305.7 mg, 12.6 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO2 (NEt3), n-pentane:ethyl acetate 8:2) afforded 1h (749 mg, 2.45 mmol) as a yellow solid in 68% yield. m.p. 82 °C. 1H NMR (400 MHz, DMSO-d6) δ = 10.84 (s, 1H), 7.63 (s, 4H), 7.31 (d, J = 8.0 Hz, 1H), 7.22 (dt, J = 8.0, 0.9 Hz, 1H), 6.93 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 6.81 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 6.07 (d, J = 3.4 Hz, 1H), 5.69 (d, J = 3.5 Hz, 1H), 2.42 (s, 3H). 13C NMR (100 MHz, DMSO-d6) δ = 150.9, 135.2, 132.4, 126.5, 126.4, 124.6 (q, J = 3.7 Hz), 124.5 (q, J = 271.8 Hz), 120.0, 118.8, 118.3, 113.7, 110.4, 67.1, 11.8. 13C{19F} NMR (100 MHz, DMSO-d6) δ = 150.9, 135.2, 132.4, 126.7, 126.5, 126.4, 124.6, 124.5, 120.0, 118.8, 118.3, 113.7, 110.4, 67.1, 11.8. 19F NMR (376 MHz, DMSO-d6) δ = -60.65. IR (ATR, cm⁻¹) ν = 3394, 1703, 1616, 1321, 1163, 1115, 1063, 1014, 836, 745. EI-MS: m/z (%) = 305.2 (M⁺, 100), 288.2 (70), 218.2 (18), 173.1 (61), 160.1 (30), 145.1 (53), 132.1 (20), 117.1 (13), 83.1 (14).
(2-Methyl-1H-indol-3-yl)(naphthalen-1-yl)methanol (1i)

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 1-naphthyl bromide (3.11 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO₂ (NEt₃), n-pentane:ethyl acetate 8:2) afforded 1i (1.43 g, 4.99 mmol) as a yellow oil in 99% yield. \(^1\)H NMR (600 MHz, DMSO-d₆) δ = 10.84 (s, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.57 (dd, J = 8.0, 7.4 Hz, 1H), 7.43-7.38 (m, 1H), 7.37-7.33 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.92-6.87 (m, 1H), 6.75 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.63 (d, J = 4.2 Hz, 1H), 5.54 (d, J = 4.2 Hz, 1H), 2.36 (s, 3H). \(^{13}\)C NMR (150 MHz, DMSO-d₆) δ = 140.6, 135.1, 133.3, 132.8, 130.3, 128.4, 127.2, 127.0, 125.5, 125.2, 125.1, 123.7, 123.6, 119.8, 118.6, 118.2, 113.3, 110.3, 64.9, 12.0. IR (ATR, cm⁻¹) ν = 3534, 3399, 3050, 1724, 1586, 1506, 1451, 1370, 1228, 1154, 1042, 969, 864, 780, 741. EI-MS: m/z (%) = 287.4 (M⁺, 100), 270.2 (77), 254.3 (90), 226.2 (25), 159.4 (63), 131.7 (90), 100.6 (6).

(2-Methyl-1H-indol-3-yl)(naphthalen-2-yl)methanol (1j)\(^{1b}\)

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), 2-naphthyl bromide (3.11 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO₂ (NEt₃), n-pentane:ethyl acetate 8:2) afforded 1j (261 mg, 0.91 mmol) as a yellow oil in 18% yield. \(^1\)H NMR (600 MHz, DMSO-d₆) δ = 10.82 (s, 1H), 8.05 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.49-7.41 (m, 3H), 7.35 (d, J = 7.9 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.93-6.89 (m, 1H), 6.79-6.75 (m, 1H), 6.17 (d, J = 3.1 Hz, 1H), 5.61 (d, J = 3.5 Hz, 1H), 2.46 (s, 3H). \(^{13}\)C NMR (150 MHz, DMSO-d₆) δ = 144.1, 135.6, 133.2, 132.7, 132.3, 128.2, 127.8, 127.6, 127.3, 126.3, 125.7, 125.6, 123.7, 120.3, 119.4, 118.5, 114.6, 110.7, 68.0, 12.3. IR (ATR, cm⁻¹) ν = 3542, 3394, 3050, 1687, 1611, 1455, 1363, 1304, 1227, 1153, 1116, 1010, 859, 818, 741. EI-MS: m/z (%) = 287.4 (M⁺, 25), 269.4 (74), 253.5 (21), 226.2 (37), 157.6 (62), 146.4 (69), 131.4 (75), 127.4 (100), 116.6 (40), 77.0 (61).
(4-Fluorophenyl)(2-methyl-1H-indol-3-yl)methanol (1k)

Iso-propylmagnesium chloride (2 M in hexane, 10.5 mL, 21 mmol) was added dropwise to a solution of 4-iodo-fluorobenzene (4.44 g, 20 mmol) in dry THF (15 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then 1 h at rt. A solution of 2-methyl-1H-indole-3-carboxaldehyde (796 mg, 5.0 mmol) in dry THF (20 mL) was added slowly to the Grignard solution at 0 °C. The resulting mixture was stirred at 0 °C for 15 min, then for 14 h at rt. Water was added to quench the reaction. The reaction mixture was extracted with Et2O (3x25 mL) and the combined organic layer were dried over MgSO4. The crude product was purified by flash chromatography (SiO2 (NEt3), n-pentane:EtOAc 8:2) to yield 1k (1.19 g, 4.67 mmol) as a yellow solid in 93% yield. m.p. 137 °C. 1H NMR (400 MHz, DMSO-d6) δ = 10.79 (s, 1H), 7.46-7.39 (m, 2H), 7.32 (d, J = 7.9 Hz, 1H), 7.23-7.20 (m, 1H), 7.12-7.04 (m, 2H), 6.93 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 6.81 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 5.99 (d, J = 3.2 Hz, 1H), 5.52 (d, J = 3.5 Hz, 1H), 2.40 (s, 3H).

13C NMR (100 MHz, DMSO-d6) δ = 160.65 (d, J = 241.2 Hz), 142.2, 142.2, 135.2, 132.1, 127.56 (d, J = 7.9 Hz), 126.7, 119.9, 119.0, 118.1, 114.33 (d, J = 21.1 Hz), 114.2, 110.3, 67.0, 11.8. 19F NMR (376 MHz, DMSO-d6) δ = -117.51. IR (ATR, cm⁻¹) ν = 3401, 3138, 3021, 1738, 1504, 1450, 1365, 1219, 1022, 831, 743. EI-MS: m/z (%) = 255.2 (M⁺, 100), 238.2 (58), 159.6 (33), 131.7 (33), 122.9 (19), 95.1 (8), 82.9 (8).

Cyclohexyl(2-methyl-1H-indol-3-yl)methanol (1l)

The title compound was synthesized according to general procedure B, starting from 2-methyl-1H-indole-3-carboxaldehyde (796.0 mg, 5.0 mmol), bromo cyclohexane (2.45 g, 15 mmol) and magnesium (425.5 mg, 17.5 mmol) using THF (40 mL) as solvent. Purification by column chromatography (SiO2 (NEt3), n-pentane:ethyl acetate 8:2) afforded 1l (950 mg, 3.9 mmol) as a yellow solid in 78% yield. m.p. 105 °C. 1H NMR (600 MHz, DMSO-d6) δ = 10.65 (s, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.96-6.92 (m, 1H), 6.89-6.84 (m, 1H), 4.63 (d, J = 3.3 Hz, 1H), 4.45 (dd, J = 8.1, 3.3 Hz, 1H), 2.32 (s, 3H), 2.13 (d, J = 12.7 Hz, 1H), 1.80-1.69 (m, 2H), 1.60-1.52 (m, 2H), 1.28 (d, J = 12.8 Hz, 1H), 1.23-1.14 (m, 1H), 1.12-0.95 (m, 3H), 0.87-0.78 (m, 1H). 13C NMR (150 MHz, DMSO-d6) δ = 135.2, 131.7, 127.3, 119.6, 119.5, 117.8, 113.4, 110.2, 71.2, 44.3, 29.9, 29.2, 26.3, 25.8, 25.8, 12.0. IR (ATR, cm⁻¹) ν = 3533, 3258, 2921, 2849, 1709, 1616, 1456, 1298, 1071, 995, 889, 739, 699. EI-MS: m/z (%) = 243.2 (M⁺, 37), 226.2 (7), 174.1 (11), 160.1 (100), 132.1 (36), 117.1 (13).
1-(2-Methyl-1H-indol-3-yl)-3-phenylprop-2-yn-1-ol (1m)

Iso-propylmagnesium chloride (2 M in hexane, 8.0 mL, 16 mmol) was added dropwise to a solution of phenyl acetylene (1.53 g, 1.65 ml, 15 mmol) in dry THF (8 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C, then 1 h at rt. A solution of 2-methyl-1H-indole-3-carboxaldehyde (796 mg, 5.0 mmol) in dry THF (20 mL) was added slowly to the Grignard solution at 0 °C. The resulting mixture was stirred at 0 °C for 15 min, then for 14 h at rt. Water was added to quench the reaction. The reaction mixture was extracted with Et₂O (3x25 mL) and the combined organic layer were dried over MgSO₄. The crude product was purified by flash chromatography (SiO₂ (NEt₃), n-pentane:EtOAc 8:2) to yield 1k (282 mg, 1.08 mmol) as a yellow solid in 22% yield. m.p. 109 °C. ¹H NMR (400 MHz, DMSO-d₆) δ = 10.83 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.46-7.26 (m, 4H), 7.23 (d, J = 7.9 Hz, 1H), 6.98-6.92 (m, 1H), 6.90-6.84 (m, 1H), 5.81 (s, 1H), 2.45 (s, 3H).

(2-Ethyl-1H-indol-3-yl)(phenyl)methanol (1n)

The title compound was synthesized according to general procedure B, starting from 2-ethyl-1H-indole-3-carboxaldehyde (600.0 mg, 3.46 mmol), bromobenzene (1.21 g, 7.71 mmol) and magnesium (218.8 mg, 9.0 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO₂ (NEt₃), n-pentane:ethyl acetate 8:2) afforded 1n (647 mg, 2.57 mmol) as a brown solid in 74% yield. m.p. 77 °C. ¹H NMR (600 MHz, DMSO-d₆) δ = 10.78 (s, 1H), 7.41 (d, J = 7.7 Hz, 2H), 7.35 (d, J = 7.9 Hz, 1H), 7.26 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.14 (t, J = 7.3 Hz, 1H), 6.96-6.91 (m, 1H), 6.80 (t, J = 7.4 Hz, 1H), 6.01 (d, J = 3.3 Hz, 1H), 5.45 (d, J = 3.5 Hz, 1H), 2.81 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). ¹³C NMR (150 MHz, DMSO-d₆) δ = 146.2, 137.9, 135.4, 127.7, 126.6, 125.9, 125.8, 119.9, 119.4, 118.0, 113.6, 110.4, 67.4, 19.2, 14.6. IR (ATR, cm⁻¹) ν = 3470, 3401, 3256, 2972, 1696, 1612, 1491, 1451, 1313, 1009, 834, 730. EI-MS: m/z (%) = 293.2 (M+MeO⁻, 28), 244.1 ([M-OH]⁺, 100), 214.2 (20), 202.1 (14), 102.1 (43).
Phenyl(2-propyl-1H-indol-3-yl)methanol (1o)\textsuperscript{1b}

The title compound was synthesized according to general procedure B, starting from 2-propyl-1H-indole-3-carboxaldehyde (600.0 mg, 3.20 mmol), bromobenzene (993 mg, 6.33 mmol) and magnesium (179.7 mg, 7.39 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1o (561 mg, 2.11 mmol) as a yellow solid in 66% yield. m.p. 75 °C. \textsuperscript{1H} NMR (600 MHz, DMSO-\textit{d}\textsubscript{6}) δ = 10.76 (s, 1H), 7.42 (d, \textit{J} = 7.7 Hz, 2H), 7.33 (d, \textit{J} = 7.9 Hz, 1H), 7.26 (t, \textit{J} = 7.6 Hz, 2H), 7.22 (d, \textit{J} = 8.0 Hz, 1H), 7.15 (t, \textit{J} = 7.4 Hz, 1H), 6.93 (t, \textit{J} = 7.4 Hz, 1H), 6.79 (t, \textit{J} = 7.4 Hz, 1H), 6.00 (d, \textit{J} = 3.4 Hz, 1H), 5.43 (d, \textit{J} = 3.6 Hz, 1H), 2.76 (t, \textit{J} = 7.6 Hz, 2H), 1.73-1.59 (m, 2H), 0.93 (t, \textit{J} = 7.3 Hz, 3H).

\textsuperscript{13}C NMR (150 MHz, DMSO-\textit{d}\textsubscript{6}) δ = 146.1, 136.6, 135.4, 127.6, 126.6, 125.9, 125.8, 119.9, 119.4, 118.0, 114.2, 110.4, 67.4, 27.9, 22.9, 14.0. IR (ATR, cm\textsuperscript{-1}) \textit{v} = 3410, 3058, 2926, 2868, 1887, 1698, 1598, 1457, 1381, 1232, 1179, 1099, 999, 840, 742. \textbf{EI-MS}: m/z (%) = 265.3 (M\textsuperscript{+}, 100), 248.3 (56), 218.2 (39), 188.2 (53), 160.2 (27), 130.2 (13), 118.1 (13), 105.1 (26), 91.1 (11), 77.2 (15).

(2-Isopropyl-1H-indol-3-yl)(phenyl)methanol (1p)

The title compound was synthesized according to general procedure B, starting from 2-isopropyl-1H-indole-3-carboxaldehyde (1.59 g, 3.2 mmol), bromobenzene (1.51 g, 9.6 mmol) and magnesium (272.2 mg, 11.2 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1p (670.0 mg, 2.525 mmol) as a yellow oil in 79% yield. \textsuperscript{1H} NMR (600MHz, DMSO-\textit{d}\textsubscript{6}): δ = 10.75 (s, 1H), 7.42 (d, \textit{J} = 7.7 Hz, 2H), 7.35 (d, \textit{J} = 7.9 Hz, 1H), 7.29-7.23 (m, 3H), 7.14 (t, \textit{J} = 7.3 Hz, 1H), 6.96-6.92 (m, 1H), 6.82-6.78 (m, 1H), 6.04 (d, \textit{J} = 3.2 Hz, 1H), 5.45 (d, \textit{J} = 3.4 Hz, 1H), 3.44 (sept., \textit{J} = 6.9 Hz, 1H), 1.30 (d, \textit{J} = 7.0 Hz, 3H), 1.26 (d, \textit{J} = 7.0 Hz, 3H). \textsuperscript{13}C NMR (150MHz, DMSO-\textit{d}\textsubscript{6}): δ = 146.2 (s), 141.9 (s), 135.5 (s), 127.7 (d, 2C), 126.4 (s), 125.9 (d), 125.7 (d, 2C), 119.9 (d), 119.5 (d), 118.0 (d), 112.7 (s), 110.5 (d), 67.3 (d), 25.2 (q), 22.8 (q), 22.5 (q). IR (ATR, cm\textsuperscript{-1}): \textit{v} = 3856, 3505, 3275, 3062, 2965, 2871, 2733, 2492, 2322, 2106, 192, 1883, 1804, 1680, 1603, 1560, 1453, 1368, 1300, 1231, 1171, 1104, 1064, 1002, 917, 833, 719, 660. \textbf{EI-MS}: m/z (%) = 265.3 (M\textsuperscript{+}, 100), 250.3 (7), 249.3 (10), 248.3 (53), 232.3 (16), 222.2 (14), 188.2 (63), 160.2 (18), 144.2 (9), 118.1 (25), 105.1 (30), 77.2 (12).
(2,7-Dimethyl-1H-indol-3-yl)(phenyl)methanol (1q)\textsuperscript{1a}

The title compound was synthesized according to general procedure B, starting from 2,7-dimethyl-1H-indole-3-carboxaldehyde (152.0 mg, 0.86 mmol), bromobenzene (254.1 mg, 1.62 mmol) and magnesium (46.0 mg, 1.89 mmol) using THF (15 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1q (135 mg, 0.54 mmol) as a yellow oil in 61% yield. \textsuperscript{1H} NMR (600 MHz, DMSO-d\textsubscript{6}) \(\delta = 10.63 \text{ (s, 1H)}, 7.41 \text{ (d, } J = 7.8 \text{ Hz, 2H)}, 7.25 \text{ (t, } J = 7.7 \text{ Hz, 2H)}, 7.20-7.16 \text{ (m, 1H)}, 7.15-7.12 \text{ (m, 1H)}, 6.73-6.69 \text{ (m, 2H)}, 5.98 \text{ (d, } J = 3.4 \text{ Hz, 1H}), 5.41 \text{ (d, } J = 3.5 \text{ Hz, 1H}), 2.42 \text{ (s, 3H)}, 2.39 \text{ (s, 3H)}. \textsuperscript{13}C NMR (150 MHz, DMSO-d\textsubscript{6}) \(\delta = 146.2, 134.6, 131.8, 127.7, 126.4, 125.9, 125.7, 120.5, 119.3, 118.3, 116.8, 114.8, 67.7, 16.8, 11.9. \textsuperscript{IR} (ATR, cm\textsuperscript{-1}) \(\tilde{\nu} = 3499, 3287, 1733, 1618, 1494, 1447, 1377, 1227, 1176, 1037, 997, 868, 836, 784, 751, 699. \textsuperscript{EI-MS}: m/z (%) = 251.2 (M\textsuperscript{+}, 100), 234.2 (59), 218.2 (17), 174.1 (54), 146.1 (48), 131.1 (13) 105.1 (23), 77.2 (10).

(5-Methoxy-2-methyl-1H-indol-3-yl)(phenyl)methanol (1r)\textsuperscript{1b}

The title compound was synthesized according to general procedure B, starting from 5-methoxy-2-methyl-1H-indole-3-carboxaldehyde (193.0 mg, 1.02 mmol), bromobenzene (480.0 mg, 3.06 mmol) and magnesium (89.8 mg, 3.57 mmol) using THF (30 mL) as solvent. Purification by column chromatography (SiO\textsubscript{2} (NEt\textsubscript{3}), n-pentane:ethyl acetate 8:2) afforded 1r (251 mg, 0.94 mmol) as a yellow oil in 92% yield. \textsuperscript{1H} NMR (300 MHz, DMSO-d\textsubscript{6}) \(\delta = 10.61 \text{ (s, 1H)}, 7.42 \text{ (d, } J = 7.6 \text{ Hz, 2H)}, 7.27 \text{ (t, } J = 7.5 \text{ Hz, 2H)}, 7.15 \text{ (t, } J = 7.3 \text{ Hz, 1H)}, 7.09 \text{ (d, } J = 8.7 \text{ Hz, 1H)}, 6.82 \text{ (d, } J = 2.4 \text{ Hz, 1H}), 6.57 \text{ (dd, } J = 8.7 \text{ Hz, 2.4, 1H}), 5.97 \text{ (d, } J = 3.5 \text{ Hz, 1H)}, 5.41 \text{ (d, } J = 3.6 \text{ Hz, 1H)}, 3.61 \text{ (s, 3H)}, 2.37 \text{ (s, 3H)}. \textsuperscript{13}C NMR (75 MHz, DMSO-d\textsubscript{6}) \(\delta = 152.6, 146.0, 132.9, 130.3, 127.7, 127.2, 126.0, 125.8, 114.3, 110.7, 109.2, 101.7, 67.6, 55.2, 12.0. \textsuperscript{IR} (ATR, cm\textsuperscript{-1}) \(\tilde{\nu} = 3788, 3391, 3244, 2932, 2846, 2638, 2322, 2175, 2104, 1970, 1708, 1584, 1457, 1297, 1196, 1107, 1022, 977, 918, 856, 706. \textsuperscript{EI-MS}: m/z (%) = 267.1 (M\textsuperscript{+}, 26), 249.1 (100), 234.1 (31), 206.1 (9), 190.1 (13), 165.0 (17).
IV. Characterization of Products 4a-7a, 8a-r:

**Ethyl (R,Z)-3-(2-methyl-1H-indol-3-yl)-3-phenyl-2-(2-phenylhydrazono)propanoate (4a)**

The title compound was synthesized according to general procedure D, starting from 1a (30.8 mg, 0.13 mmol), 2a (19.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 4a (28.0 mg, 0.068 mmol, 68%) as a yellow oil. 65% ee. **HPLC** (AD-H, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 220 nm) tR = 29.1 min (minor); 35.7 min (major). **1H NMR** (600 MHz, CDCl3) δ = 12.16 (s, 1H), 7.79 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.29-7.25 (m, 3H), 7.23-7.18 (m, 3H), 7.10-7.06 (m, 1H), 6.99-6.93 (m, 3H), 6.92-6.88 (m, 1H), 5.81 (s, 1H), 4.21-4.15 (m, 2H), 2.37 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). **13C NMR** (150 MHz, CDCl3) δ = 163.9, 143.8, 142.5, 135.3, 132.4, 129.8, 129.3, 129.1, 128.7, 127.9, 125.9, 121.8, 120.9, 120.1, 119.3, 113.7, 111.8, 110.1, 60.8, 44.2, 12.7. **IR** (ATR, cm⁻¹) ν = 3406, 3257, 2980, 2923, 1675, 1597, 1544, 1500, 1456, 1225, 1148, 1018, 905, 732. **EI-MS**: m/z (% ) = 411.2 (M⁺, 100), 319.2 (29), 281.1 (19), 245.1 (72), 220.1 (45), 131.1 (70). **HRMS (ESI)**: m/z: calcd. for [M+Na]⁺ = [C26H25O2N3Na]⁺: 434.1839; found 434.1839.

**Ethyl (R,Z)-2-(2-(4-methoxyphenyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-3-phenylpropanoate (5a)**

The title compound was synthesized according to general procedure D, starting from 1a (30.8 mg, 0.13 mmol), 2b (22.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 5a (36.2 mg, 0.082 mmol, 82%) as a yellow oil. 70% ee. **HPLC** (AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 310 nm) tR = 26.9 min (minor); 34.7 min (major). **1H NMR** (600 MHz, CDCl3) δ = 12.17 (s, 1H), 7.79 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.34-7.31 (m, 2H), 7.29-7.24 (m, 3H), 7.23-7.18 (m, 1H), 7.10-7.05 (m, 1H), 6.98-6.94 (m, 1H), 6.92-6.88 (m, 2H), 6.79-6.76 (m, 2H), 5.80 (s, 1H), 4.21-4.14 (m, 2H), 3.76 (s, 3H), 2.36 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). **13C NMR** (150 MHz, CDCl3) δ = 164.0, 155.0, 142.7, 137.8, 135.3, 132.3, 129.1, 128.7, 128.5, 127.9, 125.8, 120.8, 120.2, 119.3, 114.8, 114.7, 112.1, 110.1, 60.6, 55.7, 44.0, 14.2, 12.6. **IR** (ATR, cm⁻¹) ν = 3404, 2935, 1739, 1671, 1510, 1453, 1366, 1217, 1149, 1025, 906, 728. **EI-**
MS: m/z (%) = 441.3 (M+, 100), 319.2 (13), 310.2 (44), 245.1 (52), 220.2 (39), 131.1 (49), 122.1 (25), 107.1 (18). HRMS (ESI): m/z: calcd. for [M+Na]+ = [C27H27O3N3Na]+: 464.1945; found 464.1944.

Ethyl (R,Z)-2-(2-(4-chlorophenyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-3-phenylpropanoate (6a)

The title compound was synthesized according to general procedure D, starting from 1a (30.8 mg, 0.13 mmol), 2c (22.7 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 6a (8.9 mg, 0.02 mmol, 20%) as a yellow oil. 62% ee. HPLC (AD-H, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 220 nm) tR = 23.2 min (minor); 28.2 min (major). 1H NMR (600 MHz, CDCl3) δ = 12.13 (s, 1H), 7.81 (s, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.46-7.28 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.18 (m, 1H), 7.15-7.12 (m, 2H), 7.09-7.05 (m, 1H), 6.97-6.93 (m, 1H), 6.86-6.82 (m, 2H), 5.79 (s, 1H), 4.20-4.14 (m, 2H), 2.37 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ = 163.9, 142.5, 142.3, 135.4, 132.4, 130.5, 129.3, 129.1, 128.7, 127.9, 126.5, 126.0, 120.9, 120.1, 119.4, 114.8, 111.6, 110.2, 60.9, 44.2, 14.1, 12.6. IR (ATR, cm⁻¹) ν = 3404, 2924, 1739, 1676, 1547, 1494, 1456, 1225, 1144, 1093, 1017, 822, 730. EI-MS: m/z (%) = 445.3 (M+, 100), 319.2 (65), 315.2 (27), 273.2 (34), 245.2 (86), 220.2 (78), 169.1 (14), 131.1 (98). HRMS (ESI): m/z: calcd. for [M+Na]+ = [C28H25O2N3ClNa]+: 468.1449; found 468.1454.

Ethyl (R,Z)-3-(2-methyl-1H-indol-3-yl)-2-(2-methylhydrazono)-3-phenylpropanoate (7a)

The title compound was synthesized according to general procedure D, starting from 1a (30.8 mg, 0.13 mmol), 2d (13.0 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL) at 0 °C. Purification by column chromatography (SiO2, hexane / Et2O 8: 2) afforded 7a (14.3 mg, 0.041 mmol, 41%) as a yellow oil. 29% ee. HPLC (AD-H, n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, λ = 220 nm) tR = 29.4 min (minor); 37.9 min (major). 1H NMR (600 MHz, CDCl3) δ = 10.12 (s, 1H), 7.74 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.26-7.20 (m, 5H), 7.16-7.13 (m, 1H), 7.08-7.06 (m, 1H), 6.99-6.96 (m, 1H), 5.71 (s, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.13 (s, 3H), 2.33 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H). 13C NMR (150 MHz, CDCl3) δ = 164.0, 143.6, 135.3, 132.4, 128.9, 128.8, 127.8, 126.6, 125.5, 120.7, 120.6, 119.0,
112.8, 110.0, 60.0, 43.4, 38.7, 14.3, 12.7. **IR** (ATR, cm\(^{-1}\)) \(\tilde{\nu} = 3401, 3279, 2922, 1665, 1535, 1453, 1366, 1103, 908, 855, 733.** **EI-MS:** m/z (%) = 349.3 (M\(^+\), 42), 245.2 (100), 220.2 (48), 204.2 (12), 131.1 (17). **HRMS (ESI):** m/z: calcd. for [M+Na]\(^+\) = [C\(_{21}\)H\(_{23}\)O\(_3\)N\(_3\)Na]\(^+\): 372.1683; found 372.1687.

**Ethyl (R,Z)-2-(2-tert-butylhydrazono)-3-(2-methyl-1H-indol-3-yl)-3-phenylpropanoate (8a)**

The title compound was synthesized according to general procedure D, starting from 1a (30.8 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO\(_2\), n-pentane / Et\(_2\)O 8: 2) afforded 8a (37.6 mg, 0.096 mmol, 96%) as a yellow oil. 93% ee. **HPLC** (AD-H, n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, \(\lambda = 220\) nm) tR = 9.1 min (minor); 10.4 min (major). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta = 10.16\) (s, 1H), 7.74 (s, 1H), 7.48 (d, \(J = 8.0\) Hz, 1H), 7.25-7.24 (m, 3H), 7.22-7.19 (m, 2H), 7.15-7.12 (m, 1H), 7.07-7.04 (m, 1H), 6.96-6.93 (m, 1H), 5.71 (s, 1H), 4.10 (q, \(J = 7.1\) Hz, 2H), 2.33 (s, 3H), 1.16 (t, \(J = 7.1\) Hz, 3H), 1.13 (s, 9H). **\(^{13}\)C NMR** (150 MHz, CDCl\(_3\)) \(\delta = 163.8, 143.4, 135.4, 132.2, 129.2, 128.9, 127.6, 125.8, 125.4, 120.6, 118.9, 112.9, 109.9, 59.9, 54.7, 43.7, 28.9, 14.3, 12.6. **IR** (ATR, cm\(^{-1}\)) \(\tilde{\nu} = 3405, 2974, 2248, 1670, 1531, 1459, 1365, 1201, 1129, 1023, 910, 735.** **EI-MS:** m/z (%) = 391.3 (M\(^+\), 84), 334.2 (5), 261.3 (59), 245.2 (100), 220.2 (38), 131.1 (9), 57.3 (16). **HRMS (ESI):** m/z: calcd. for [M+Na]\(^+\) = [C\(_{21}\)H\(_{23}\)O\(_3\)N\(_3\)Na]\(^+\): 414.2152; found 414.2158.

**Ethyl (R,Z)-ethyl 2-(2-(tert-butyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-3-(p-tolyl)propanoate (8b)**

The title compound was synthesized according to general procedure D, starting from 1b (32.7 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO\(_2\), n-pentane / Et\(_2\)O 8: 2) afforded 8b (40.2 mg, 0.099 mmol, 99%) as a yellow oil. 93% ee. **HPLC** (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, \(\lambda = 220\) nm) tR = 17.5 min (minor); 20.6 min (major). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta = 10.18\) (s, 1H), 7.72 (s, 1H), 7.50 (d, \(J = 7.9\) Hz, 1H), 7.24 (d, \(J = 8.0\) Hz, 1H), 7.14 (d, \(J = 8.0\) Hz, 2H), 7.08-7.04 (m, 1H), 7.03 (d, \(J = 8.0\) Hz, 2H), 6.97-6.93 (m, 1H), 5.69 (s, 1H), 4.11 (q, \(J = 7.1\) Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 1.18 (t, \(J =
7.1 Hz, 3H), 1.15 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 163.9, 140.3, 135.3, 134.7, 132.1, 129.0, 128.9, 128.3, 125.9, 120.7, 120.6, 118.9, 113.1, 109.9, 59.8, 54.7, 43.1, 29.0, 21.1, 14.3, 12.6. IR (ATR, cm$^{-1}$) $\tilde{\nu}$ = 3404, 2972, 2926, 1670, 1525, 1459, 1207, 1129, 1024, 754. EI-MS: m/z (%) = 405.2 (M$^+$, 100), 274.2 (23), 259.1 (70), 234.9 (7).

EI-MS: m/z (%) = 405.2 (M$^+$, 100), 274.2 (23), 259.1 (70), 234.9 (7).

HRMS (ESI): m/z: calcd. for [M+Na]$^+$ = [C$_{25}$H$_{31}$O$_2$N$_3$Na]$^+$: 428.2309; found 428.2296. $[\alpha]_D^{\text{rt}}$: -29.2 (c 1.5, CHCl$_3$).

**Ethyl (R,Z)-2-(2-tert-butylhydrazono)-3-(2-methyl-1H-indol-3-yl)-3-o-tolylpropanoate (8c)**

The title compound was synthesized according to general procedure D, starting from 1c (32.7 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO$_2$, n-pentane / Et$_2$O 8: 2) afforded 8c (34.1 mg, 0.084 mmol, 84%) as a yellow oil. 97% ee. HPLC (AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, $\lambda$ = 220 nm) tR = 8.0 min (minor); 9.7 min (major).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 10.03 (s, 1H), 7.73 (s, 1H), 7.48 (d, $J$ = 8.0 Hz, 1H), 7.25 (d, $J$ = 8.4 Hz, 1H), 7.18 (d, $J$ = 7.6 Hz, 1H), 7.14-6.95 (m, 5H), 5.71 (s, 1H), 4.08 (qd, $J$ = 7.1, 1.6 Hz, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.11 (t, $J$ = 7.1 Hz, 3H), 1.06 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 163.5, 141.6, 136.2, 135.3, 132.2, 129.8, 129.5, 129.0, 125.7, 125.4, 125.2, 120.5, 120.2, 119.0, 111.9, 109.9, 59.8, 54.6, 41.8, 28.8, 19.9, 14.2, 12.6. IR (ATR, cm$^{-1}$) $\tilde{\nu}$ = 3405, 2970, 2249, 1669, 1536, 1458, 1368, 1299, 1288, 19.9, 14.2, 12.6. EI-MS: m/z (%) = 405.2 (M$^+$, 100), 348.2 (5), 274.4 (16), 259.0 (72), 234.1 (12), 216.8 (11). HRMS (ESI): m/z: calcd. for [M+Na]$^+$ = [C$_{25}$H$_{31}$O$_2$N$_3$Na]$^+$: 428.2309; found 428.2296. $[\alpha]_D^{\text{rt}}$: -64.2 (c 2.04, CHCl$_3$).

**Ethyl (R,Z)-2-(2-tert-butylhydrazono)-3-(4-tert-butylphenyl)-3-(2-methyl-1H-indol-3-yl)propanoate (8d)**

The title compound was synthesized according to general procedure D, starting from 1d (38.1 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO$_2$, n-pentane / Et$_2$O 8: 2) afforded 8d (34.2 mg, 0.076 mmol, 76%) as a yellow oil. 95% ee. HPLC (AD-H, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, $\lambda$ = 220 nm) tR = 16.2 min (major); 20.5 min (minor). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 10.14 (s, 1H), 7.71 (s, 1H), 7.52 (d, $J$ = 7.9 Hz, 1H), 7.25-7.22 (m, 3H), 7.18-7.16 (m, 2H), 7.07-7.04 (m, 1H), 6.97-6.93 (m, 1H), 5.69 (s, 1H), 4.10
(q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.29 (s, 9H), 1.17 (t, J = 7.1 Hz, 3H), 1.13 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 163.8, 148.1, 140.3, 135.4, 132.1, 128.9, 128.7, 125.9, 124.4, 120.8, 120.6, 118.8, 113.2, 109.9, 59.8, 54.7, 43.2, 34.4, 31.6, 28.9, 14.3, 12.6. IR (ATR, cm$^{-1}$) ν = 3403, 2964, 1669, 1527, 1459, 1364, 1299, 1192, 1126, 1022, 910, 791, 736. EI-MS: m/z (%) = 447.5 (M$^+$, 42), 317.4 (44), 301.3 (100), 276.3 (21), 246.2 (9), 57.3 (14). HRMS (ESI): m/z: calcd. for [M+Na]$^+$ = [C$_{28}$H$_{37}$O$_2$N$_3$Na]$^+$: 470.2778; found 470.2782. [$\alpha$]D$^\text{rt}$: -33.6 (c 1.50, CHCl$_3$).

**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(4-methoxyphenyl)-3-(2-methyl-1H-indol-3-yl)propanoate (8e)**

The title compound was synthesized according to general procedure D, starting from 1e (34.8 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO$_2$, n-pentane / Et$_2$O 8: 2) afforded 8e (33.7 mg, 0.080 mmol, 80%) as a yellow oil. 90% ee. HPLC (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 23.0 min (minor); 32.6 min (major). $^1$H NMR (600 MHz, CDCl$_3$) δ = 10.16 (s, 1H), 7.74 (s, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.08-7.04 (m, 1H), 6.97-6.93 (m, 1H), 6.79-6.75 (m, 2H), 5.66 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.33 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.15 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 163.8, 157.5, 135.6, 135.3, 132.1, 130.0, 128.8, 126.0, 120.6, 120.6, 118.9, 113.1, 112.9, 109.9, 59.8, 55.3, 54.7, 42.8, 28.9, 14.3, 12.6. IR (ATR, cm$^{-1}$) ν = 3402, 3266, 2970, 1883, 1670, 1610, 1517, 1458, 1367, 1299, 1179, 1030, 753. EI-MS: m/z (%) = 421.2 (M$^+$, 100), 291.8 (9), 274.7 (74), 250.0 (10). HRMS (ESI): m/z: calcd. for [M+H]$^+$ = [C$_{25}$H$_{32}$O$_3$N$_3$]$^+$: 422.2438; found 422.2427. [$\alpha$]D$^\text{rt}$: -42.2 (c 1.18, CHCl$_3$).

**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(3-methoxyphenyl)-3-(2-methyl-1H-indol-3-yl)propanoate (8f)**

The title compound was synthesized according to general procedure D, starting from 1f (34.8 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO$_2$, n-pentane / Et$_2$O 8: 2) afforded 8f (35.9 mg, 0.085 mmol, 85%) as a yellow oil. 96% ee. HPLC (OD-H, n-
hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm) tR = 11.8 min (major); 15.6 min (minor). $^1$H NMR (400 MHz, CDCl$_3$) δ = 10.19 (br s, 1H), 7.73 (br s, 1H), 7.51 (d, $J$ = 7.9 Hz, 1H), 7.23 (dt, $J$ = 8.0 & 0.8 Hz, 1H), 7.13 (t, $J$ = 8.1 Hz, 1H), 7.07-7.03 (m, 1H), 6.97-6.93 (m, 1H), 6.86-6.83 (m, 2H), 6.72-6.69 (m, 1H), 5.70 (s, 1H), 4.11 (q, $J$ = 7.1 Hz, 2H), 3.72 (s, 3H), 2.33 (s, 3H), 1.17 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 163.8, 159.2, 145.2, 135.3, 132.2, 128.9, 128.4, 125.6, 121.8, 120.6, 120.6, 118.9, 115.0, 112.9, 111.0, 109.9, 59.9, 55.3, 54.7, 43.6, 29.0, 14.3, 12.6. IR (ATR, cm$^{-1}$) $\tilde{\nu}$ = 3402, 2970, 1668, 1597, 1530, 1457, 1194, 1040, 909, 736.

EI-MS: m/z (%) = 421.6 ($M^+$, 87), 348.8 (6), 290.7 (34), 274.5 (72), 216.4 (14). HRMS (ESI): m/z: calcd. for [M+H]$^+$ = [C$_{25}$H$_{32}$O$_3$N$_3$]$: 422.2438; found 422.2426. [$\alpha$]$_D^{rt}$: -142.6 (c 1.29, CHCl$_3$).

Ethyl (S,Z)-2-(2-tert-butylhydrazono)-3-(2-methoxyphenyl)-3-(2-methyl-1H-indol-3-yl)propanoate (8g)

The title compound was synthesized according to general procedure D, starting from 1g (34.8 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO$_2$, n-pentane / Et$_2$O 8: 2) afforded 8g (26.5 mg, 0.063 mmol, 63%) as a yellow solid. m.p. 106 °C. 84% ee. HPLC (AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 14.2 min (minor); 18.8 min (major). $^1$H NMR (600 MHz, CDCl$_3$) δ = 9.89 (s, 1H), 7.78 (s, 1H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.30-7.25 (m, 1H), 7.20-7.16 (m, 2H), 7.09 (t, $J$ = 7.5 Hz, 1H), 7.02-6.98 (m, 1H), 6.88-6.84 (m, 1H), 6.80 (td, $J$ = 7.5, 1.0 Hz, 1H), 5.89 (s, 1H), 4.09 (qq, $J$ = 10.9, 7.1 Hz, 2H), 3.82 (s, 3H), 2.38 (s, 3H), 1.13 (t, $J$ = 7.1 Hz, 3H), 1.10 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 163.7, 156.8, 156.8, 135.3, 132.2, 131.9, 130.0, 129.5, 126.7, 126.4, 120.7, 120.4, 119.8, 118.9, 111.7, 109.9, 109.8, 59.6, 55.7, 54.3, 38.7, 28.8, 14.2, 12.5. IR (ATR, cm$^{-1}$) $\tilde{\nu}$ = 3401, 2968, 1669, 1538, 1457, 1184, 1123, 1026, 742. EI-MS: m/z (%) = 421.6 ($M^+$, 87), 348.8 (6), 290.7 (34), 274.5 (72), 216.4 (14). HRMS (ESI): m/z: calcd. for [M+H]$^+$ = [C$_{25}$H$_{32}$O$_3$N$_3$]$: 422.2438; found 422.2426. [$\alpha$]$_D^{rt}$: -142.6 (c 1.29, CHCl$_3$).
**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-3-(4-(trifluoromethyl)phenyl)propanoate (8h)**

The title compound was synthesized according to general procedure D, starting from 1h (39.7 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 8h (43.0 mg, 0.094 mmol, 94%) as a yellow oil. 90% ee. HPLC (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm) tR = 12.7 min (minor); 13.9 min (major). $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 10.21$ (s, 1H), 7.80 (s, 1H), 7.49 - 7.44 (m, 3H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.25-7.28 (m, 1H), 7.11-7.07 (m, 1H), 6.99-6.95 (m, 1H), 5.73 (s, 1H), 4.16-4.06 (m, 2H), 2.35 (s, 3H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.13 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta = 163.6, 147.6, 135.4, 132.4, 129.5, 128.6, 127.7$ (q, $J_{CF} = 32.0$ Hz), 125.0, 124.4 (q, $J_{CF} = 3.6$ Hz), 120.9, 120.4, 119.2, 111.9, 110.1, 60.0, 54.8, 43.7, 28.9, 14.3, 12.5. $^{19}$F NMR (564 MHz, CDCl$_3$) $\delta = -62.12$. IR (ATR, cm$^{-1}$) $\tilde{\nu} = 3400$, 2973, 1736, 1669, 1531, 1459, 1320, 1117, 1019, 736. EI-MS: m/z (%) = 458.9 (M$^+$, 100), 328.5 (24), 313.6 (40), 286.8 (20). HRMS (ESI): m/z: calcd. for [M+Na]$^+$ = [C$_{25}$H$_{28}$O$_2$N$_3$F$_3$Na]$^+$: 482.2026; found 482.2017. $[\alpha]_{D}^{rt}$: -61.9 (c 1.68, CHCl$_3$).

**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-3-(naphthalen-1-yl) propanoate (8i)**

The title compound was synthesized according to general procedure D, starting from 1i (37.4 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 8i (28.2 mg, 0.064 mmol, 64%) as a yellow oil. 98% ee. HPLC (AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 13.7 min (minor); 16.9 min (major). $^1$H NMR (600 MHz, CDCl$_3$) $\delta = 9.93$ (s, 1H), 7.96-7.91 (m, 1H), 7.82-7.78 (m, 1H), 7.74 (s, 1H), 7.67-7.63 (m, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.41-7.35 (m, 2H), 7.27-7.22 (m, 3H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.96 (t, $J = 7.5$ Hz, 1H), 6.27 (s, 1H), 4.13-4.05 (m, 2H), 2.22 (s, 3H), 1.10 (t, $J = 7.1$ Hz, 3H), 0.80 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta = 163.4, 139.1, 135.3, 133.9, 132.5, 129.5, 128.6, 126.6, 126.5, 125.7, 125.5, 125.2, 124.8, 124.8, 120.6, 120.1, 119.2, 112.1, 110.0, 59.9, 54.5, 41.3, 28.6, 14.3, 12.6. IR (ATR, cm$^{-1}$) $\tilde{\nu} = 3406$, 2970, 1669, 1534, 1457, 1300, 1203, 1129, 1026, 755. EI-MS: m/z (%) = 441.3 (M$^+$, 100), 311.4
Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-3-(naphthalen-2-yl) propanoate (8j)

The title compound was synthesized according to general procedure D, starting from 1j (37.4 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 8j (40.3 mg, 0.091 mmol, 91%) as a yellow oil. 96% ee. HPLC (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 24.0 min (minor); 32.9 min (major). 1H NMR (600 MHz, CDCl3) δ = 10.24 (s, 1H), 7.80-7.76 (m, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.69-7.66 (m, 1H), 7.63 (s, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.44 (dd, J = 8.5, 1.7 Hz, 1H), 7.41-7.37 (m, 2H), 7.28-7.25 (m, 1H), 7.10-7.05 (m, 1H), 6.96-6.92 (m, 1H), 5.87 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.12 (s, 9H). 13C NMR (150 MHz, CDCl3) δ = 163.9, 141.1, 135.4, 133.4, 132.4, 130.5, 128.9, 128.8, 128.0, 127.5, 126.8, 126.7, 125.6, 125.5, 125.0, 120.7, 120.5, 119.0, 112.7, 110.0, 59.9, 54.7, 43.7, 29.0, 14.4, 12.7. IR (ATR, cm−1) ν = 3405, 3265, 3052, 2973, 1670, 1530, 1459, 1367, 1205, 1024, 753. EI-MS: m/z (%) = 441.3 (M+, 72), 310.4 (13), 295.2 (100), 270.8 (7). HRMS (ESI): m/z: calcd. for [M+Na]+ = [C28H31O2N3Na]+: 464.2309; found 464.2296. [α]D rt: -149.6 (c 1.38, CHCl3).

Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(4-fluorophenyl)-3-(2-methyl-1H-indol-3-yl) propanoate (8k)

The title compound was synthesized according to general procedure D, starting from 1k (33.2 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 8k (31.1 mg, 0.076 mmol, 76%) as a yellow oil. 95% ee. HPLC (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 17.6 min (minor); 20.0 min (major). 1H NMR (400 MHz, CDCl3) δ = 10.16 (s, 1H), 7.76 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.22-7.16 (m, 2H), 7.07 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 6.96 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 6.93-6.86 (m, 2H), 5.66 (s, 1H), 4.14-4.05 (m, 2H), 2.34 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H), 1.14 (s, 9H). 13C NMR (100 MHz, CDCl3) δ = 163.7, 161.1 (d, Jc,F = 242.7 Hz),
139.0, 135.4, 132.1, 130.6 (d, \( J_{CF} = 5.0 \) Hz), 128.7, 125.6, 120.8, 120.4, 119.0, 114.2 (d, \( J_{CF} = 21.0 \) Hz), 112.7, 110.0, 59.9, 54.7, 43.1, 28.9, 14.3, 12.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta = -118.83 \). IR (ATR, cm\(^{-1}\)) \( \tilde{\nu} = 3401, 3266, 2971, 2250, 1887, 1668, 1603, 1514, 1457, 1369, 1210, 1024, 910, 738, 606 \). EI-MS: m/z (%) = 409.1 (M\(^+\), 87), 278.5 (17), 263.0 (100), 236.6 (13).

HRMS (ESI): m/z: calcd. for \([M+H]^+ = [C_{24}H_{30}O_2N_3F]^+\): 410.2238; found 410.2228.

\([\alpha]_D^{rt}\): -72.1 (c 1.17, CHCl\(_3\)).

**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-cyclohexyl-3-(2-methyl-1H-indol-3-yl)propanoate (8l)**

The title compound was synthesized according to general procedure D, starting from 1l (31.6 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO\(_2\), n-pentane / Et\(_2\)O 8: 2) afforded 8l (37.3 mg, 0.094 mmol, 94%) as a yellow oil. 93 % ee. HPLC (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, \( \lambda = 220 \) nm) \( t_R = 7.7 \) min (minor); 8.3 min (major).

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 10.08 \) (s, 1H), 7.85 (d, \( J = 7.9 \) Hz, 1H), 7.65 (s, 1H), 7.21 (d, \( J = 8.0 \) Hz, 1H), 7.05 (t, \( J = 7.4 \) Hz, 1H), 6.98 (t, \( J = 7.5 \) Hz, 1H), 4.13-4.01 (m, 2H), 3.82 (d, \( J = 10.9 \) Hz, 1H), 2.51 (ddd, \( J = 19.0, 10.9, 3.0 \) Hz, 1H), 2.43 (s, 3H), 2.14-2.07 (m, 1H), 1.77-1.71 (m, 1H), 1.67-1.60 (m, 1H), 1.60-1.52 (m, 1H), 1.36 (s, 9H), 1.34-1.26 (m, 2H), 1.22 (t, \( J = 7.1 \) Hz, 3H), 1.18-1.10 (m, 2H), 0.97-0.88 (m, 1H), 0.80-0.72 (m, 1H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta = 164.2, 135.4, 131.7, 128.5, 125.0, 120.8, 120.5, 118.5, 112.8, 109.9, 59.7, 54.5, 44.6, 38.6, 33.0, 31.6, 29.2, 27.0, 26.8, 26.6, 14.4, 12.4. IR (ATR, cm\(^{-1}\)) \( \tilde{\nu} = 3402, 2922, 2850, 1666, 1528, 1455, 1363, 1299, 1263, 1194, 1142, 1023, 909, 801, 735. EI-MS: m/z (%) = 397.4 (M\(^+\), 58), 314.3 (100), 267.3 (11), 241.2 (9), 195.2 (16), 184.2 (19), 169.2 (16), 144.2 (16), 86.3 (13), 57.3 (24). HRMS (ESI): m/z: calcd. for \([M+H]^+ = [C_{24}H_{36}O_2N_3]^+\): 398.2802; found 398.2798. \([\alpha]_D^{rt}\): -75.4 (c 1.40, CHCl\(_3\)).

**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(2-methyl-1H-indol-3-yl)-5-phenylpent-4-ynoate (8m)**

The title compound was synthesized according to general procedure D, starting from 1m (34.0 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO\(_2\), n-pentane / Et\(_2\)O 8: 2) afforded 8m (9.0 mg,
0.022 mmol, 22%) as a yellow oil. 86% ee. **HPLC** (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 33.6 min (major); 36.5 min (minor). **^1H NMR** (600 MHz, CDCl₃) δ = 10.15 (s, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.73 (s, 1H), 7.43-7.40 (m, 2H), 7.28-7.22 (m, 3H), 7.10-7.03 (m, 2H), 5.47 (s, 1H), 4.21-4.10 (m, 2H), 2.55 (s, 3H), 1.33 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H). **IR** (ATR, cm⁻¹) ν = 3399, 3262, 3054, 2969, 2242, 1886, 1671, 1531, 1455, 1373, 1191, 1026, 911, 742, 611. **EI-MS**: m/z (%) = 415.5 (M⁺, 75), 358.3 (13), 312.7 (22), 284.9 (27), 268.1 (100), 243.8 (85). **HRMS (ESI)**: m/z: calcd. for [M+H]⁺ = [C₂₅H₃₁O₂N₃]⁺: 416.2333; found 416.2329. \[\alpha\]D: -7.9 (c 0.45, CHCl₃).

**Ethyl (R,Z)-2-(2-(tert-butyl)hydrazono)-3-(2-ethyl-1H-indol-3-yl)-3-phenylpropanoate (8n)**

The title compound was synthesized according to general procedure D, starting from 1n (32.7 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO₂, n-pentane / Et₂O 8: 2) afforded 8n (40.5 mg, 0.10 mmol, 99%) as a yellow oil. 98% ee. **HPLC** (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 9.7 min (minor); 11.8 min (major). **^1H NMR** (600 MHz, CDCl₃) δ = 10.17 (s, 1H), 7.81 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.28-7.23 (m, 3H), 7.16-7.12 (m, 1H), 7.09-7.05 (m, 1H), 6.97-6.93 (m, 1H), 5.73 (s, 1H), 4.15-4.05 (m, 2H), 2.82 (dq, J = 15.2, 7.6 Hz, 1H), 2.75 (dq, J = 15.2, 7.6 Hz, 1H), 1.19 (t, J = 7.6 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.13 (s, 9H). **^13C NMR** (150 MHz, CDCl₃) δ = 163.8, 143.6, 137.9, 135.4, 129.1, 128.8, 127.5, 125.8, 125.4, 120.9, 120.6, 118.9, 112.0, 110.0, 59.9, 54.7, 43.6, 28.9, 19.8, 14.3, 14.2. **IR** (ATR, cm⁻¹) ν = 3405, 3266, 3056, 2971, 2248, 1883, 1668, 1534, 1455, 1369, 1314, 1201, 1128, 1023, 910, 735, 629. **EI-MS**: m/z (%) = 405.4 (M⁺, 37), 259.2 (100), 234.2 (34), 218.2 (18), 145.1 (15), 57.2 (13). **HRMS (ESI)**: m/z: calcd. for [M+Na]⁺ = [C₂₆H₃₀O₂N₃Na]⁺: 428.2309; found 428.2299. \[\alpha\]D: -57.5 (c 1.74, CHCl₃).
Ethyl \((R,Z)-2-(2-(\text{tert}-\text{butyl})\text{hydrazono})-3\text{-phenyl}-3-(2\text{-propyl-1H-indol-3-yl})\text{propanoate} (8o)\)

The title compound was synthesized according to general procedure D, starting from 1o (34.5 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et2O 8: 2) afforded 8o (41.2 mg, 0.098 mmol, 98%) as a yellow oil. 96% ee. HPLC (AD-H, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 9.7 min (minor); 13.6 min (major).

\[ ^1H \text{NMR} (600 \text{ MHz, CDCl}_3) \delta = 10.17 (s, 1H), 7.79 (s, 1H), 7.47 (d, J = 8.0 \text{ Hz}, 1H), 7.28-7.23 (m, 3H), 7.23-7.19 (m, 2H), 7.16-7.12 (m, 1H), 7.09-7.05 (m, 1H), 6.96-6.92 (m, 1H), 5.72 (s, 1H), 4.15-4.06 (m, 2H), 2.79 (dt, J = 15.5, 7.7 \text{ Hz}, 1H), 2.69 (dt, J = 14.9, 7.4 \text{ Hz}, 1H), 1.65-1.56 (m, 2H), 1.15 (t, J = 7.1 \text{ Hz}, 3H), 1.13 (s, 9H), 0.91 (t, J = 7.4 \text{ Hz}, 3H). \]

\[ ^{13}C \text{NMR} (150 \text{ MHz, CDCl}_3) \delta = 163.8, 143.6, 136.6, 135.4, 129.1, 128.8, 127.5, 125.8, 125.4, 121.0, 120.6, 118.8, 112.6, 110.0, 59.8, 54.7, 43.7, 28.9, 28.7, 23.1, 14.3, 14.2. IR (ATR, \text{cm}^{-1}) \tilde{\nu} = 3406, 2967, 2872, 2249, 1728, 1668, 1532, 1457, 1369, 1201, 1128, 1024, 910, 735, 627. \]

MS: m/z (%) = 419.5 (M+\(^+\), 45), 273.3 (100), 261.3 (78), 248.3 (34), 218.2 (27), 159.2 (15), 57.2 (16). HRMS (ESI): m/z: calcld. for [M+Na\(^+\)] = [C\(_{26}\)H\(_{33}\)O\(_2\)N\(_3\)Na\(^+\)]: 442.2465; found 442.2462. \([\alpha]_D^{20}: -42.6 (c 1.86, \text{CHCl}_3)\).

Ethyl \((R,Z)-2-(2-(\text{tert}-\text{butyl})\text{hydrazinyliden})-3-(2\text{-isopropyl-1H-indol-3-yl})-3\text{-phenyl propanoat (8p)\)}

The title compound was synthesized according to general procedure D, starting from 1p (34.5 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO2, n-pentane / Et2O 7: 3) afforded 8p (41.5 mg, 0.099 mmol, 99%) as a yellow oil. 70% ee. HPLC (IA, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 220 nm) tR = 7.3 min (minor); 10.2 min (major). \[^1H \text{NMR} (600\text{MHz, CDCl}_3): \delta = 10.17 (s, 1H), 7.84 (s, 1H), 7.47 (d, J = 8.0 \text{ Hz}, 1H), 7.28 (d, J = 8.1 \text{ Hz}, 1H), 7.25-7.18 (m, 4H), 7.15-7.11 (m, 1H), 7.09-7.04 (m, 1H), 6.95-6.91 (m, 1H), 5.75 (s, 1H), 4.16-4.04 (m, 2H), 3.40 (sept., J = 7.0 \text{ Hz}, 1H), 1.31 (d, J = 7.0 \text{ Hz}, 3H), 1.19 (d, J = 7.0 \text{ Hz}, 3H), 1.14 (t, J = 7.2 \text{ Hz}, 3H), 1.13 (s, 9H). \[^{13}C \text{NMR} (151\text{MHz, CDCl}_3): \delta = 163.8, 143.6, 141.6, 135.3, 129.2, 128.7, 127.5, 125.8, 125.4, 121.2, 120.6, 118.9, 111.0, 110.1, 59.9, 54.7, 43.6, 28.9, 25.4, 23.4, 22.2, 14.3. IR (ATR, \text{cm}^{-1}): \tilde{\nu} = 3414, 3270, 3056, 2969, 2248, 1882, \]
Ethyl (R,Z)-2-(2-((tert-butyl)hydrazono)-3-(2,7-dimethyl-1H-indol-3-yl)-3-phenylpropanoate (8q)

The title compound was synthesized according to general procedure D, starting from 1q (32.7 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO₂, n-pentane / Et₂O 8: 2) afforded 8q (32.1 mg, 0.079 mmol, 79%) as a yellow oil. 89% ee. SFC (WHELK-01 column, 5% MeOH/CO₂, flow rate = 4 mL/min, λ = 250 nm) tR = 7.5 min (major); 8.9 min (minor). ¹H NMR (400 MHz, CDCl₃) δ = 10.17 (s, 1H), 7.67 (s, 1H), 7.39-7.33 (m, 1H), 7.26-7.18 (m, 4H), 7.16-7.10 (m, 1H), 6.90-6.96 (m, 2H), 5.72 (s, 1H), 4.11 (qd, J = 7.1, 1.9 Hz, 2H), 2.47 (s, 3H), 2.37 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.14 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ = 163.8, 143.5, 134.8, 131.9, 129.2, 128.4, 127.5, 125.8, 125.4, 121.4, 119.1, 119.0, 118.5, 113.4, 59.9, 54.7, 43.7, 29.0, 16.7, 14.4, 12.7. IR (ATR, cm⁻¹) ν = 3378, 2963, 2925, 2322, 1891, 1647, 1524, 1453, 1366, 1198, 1022, 784, 739, 702. EI-MS: m/z (%) = 405.4 (M⁺, 36), 259.2 (100), 234.2 (26), 145.1 (18). HRMS (ESI): m/z: calcd. for [M+Na]⁺ = [C₂₅H₃₁O₂N₃Na]⁺: 428.2309; found: 428.2308. [α]D^{27}: -44.2 (c 1.87, CHCl₃).

Ethyl (R,Z)-2-(2-((tert-butyl)hydrazono)-3-(5-methoxy-2-methyl-1H-indol-3-yl)-3-phenylpropanoate (8r)

The title compound was synthesized according to general procedure D, starting from 1r (34.8 mg, 0.13 mmol), 2e (17.2 mg, 0.10 mmol) and 3h (3.0 mg, 5 mol%) in toluene (2 mL). Purification by column chromatography (SiO₂, n-pentane / Et₂O 8: 2) afforded 8r (41.8 mg, 0.099 mmol, 99%) as a yellow oil. 90% ee. SFC (WHELK-01 column, 5% MeOH/CO₂, flow rate = 4 mL/min, λ = 250 nm) tR = 10.7 min (major); 12.0 min (minor). ¹H NMR (600 MHz, CDCl₃) δ = 10.15 (s, 1H), 7.63 (s, 1H), 7.26-7.20 (m, 4H), 7.16-7.10 (m, 2H), 6.91 (d, J = 2.2 Hz, 1H), 6.72 (dd, J = 8.7, 2.2 Hz, 1H), 5.66 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 2.30 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H),
1.11 (s, 9H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 163.8, 153.6, 143.3, 133.1, 130.5, 129.5, 129.2, 127.6, 126.0, 125.5, 112.8, 110.5, 110.3, 103.1, 59.9, 56.1, 54.7, 43.9, 28.9, 14.3, 12.7. IR (ATR, cm$^{-1}$) ν = 3403, 2970, 1669, 1449, 1205, 1123, 1028, 910, 720. EI-MS: m/z (%) = 421.3 (M$^+$, 54), 275.2 (100), 261.3 (37), 250.2 (34), 218.2 (11), 161.2 (21). HRMS (ESI): m/z: calcd. for [M+Na]$^+$ = [C$_{25}$H$_{31}$O$_3$N$_3$Na]$^+$: 444.2258; found 444.2254. $[^\alpha]_D$$^\text{rt}$: -39.4 (c 1.71, CHCl$_3$).
V. Determination of the absolute configuration

The structure of product 8i was confirmed by single-crystal X-ray analysis. However, the values of the Flack parameter and standard uncertainty did not allow an unambiguous determination of the absolute configuration. As an alternative, CD-spectroscopy was considered and the recorded and theoretically calculated (TD-DFT/B3LYP/6-31G*/B3LYP/6-31G*) CD-spectra of compound 8i were analyzed (Figure 1).\textsuperscript{2,3} Since the measured spectrum resembles the spectrum calculated for the \((R)\)-enantiomer, we conclude that the absolute configuration of the compound present in our sample is \((R)\).

![Figure 1. Recorded and calculated CD-spectra for 8i.](image)
VI. References:


2. The calculations have been performed by using the facilities and computing resources offered by the Center for Computing and Communication of the RWTH Aachen University.

VII. Copies of $^1$H, $^{13}$C, HPLC and SFC Spectra of the Reported Compounds

$^1$H NMR (600 MHz, CD$_2$Cl$_2$) for 1a

$^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) for 1a
\(^1\)H NMR (600 MHz, DMSO-\(d_6\)) for 1b

\(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) for 1b
$^1$H NMR (600 MHz, DMSO-$_d_6$) for 1c

$^{13}$C NMR (150 MHz, DMSO-$_d_6$) for 1c
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1d

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1d
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1e

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1e
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1f

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1f
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1g

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1g
$^1\text{H NMR}$ (400 MHz, DMSO-$d_6$) for 1h

$^{13}\text{C NMR}$ (100 MHz, DMSO-$d_6$) for 1h
$^{19}$F NMR (376 MHz, DMSO-d$_6$) for 1h
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1i

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1i
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1j

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1j
$^{1}H$ NMR (400 MHz, DMSO-$d_6$) for 1k

$^{13}C$ NMR (100 MHz, DMSO-$d_6$) for 1k
$^{19}$F NMR (376 MHz, DMSO-$d_6$) for 1k
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1l

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1l
$^1$H NMR (400 MHz, DMSO-$d_6$) for 1m

$^{13}$C NMR (100 MHz, DMSO-$d_6$) for 1m
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1n

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1n
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1o

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1o
$^{1}$H NMR (600 MHz, DMSO-$d_6$) for 1p

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1p
$^1$H NMR (600 MHz, DMSO-$d_6$) for 1q

$^{13}$C NMR (150 MHz, DMSO-$d_6$) for 1q
$^{1}H$ NMR (300 MHz, DMSO-$d_6$) for 1r

$^{13}C$ NMR (75 MHz, DMSO-$d_6$) for 1r
$^1$H NMR (600 MHz, CDCl$_3$) for 4a

$^{13}$C NMR (150 MHz, CDCl$_3$) for 4a
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49
$^1$H NMR (600 MHz, CDCl$_3$) for 5a

$^{13}$C NMR (150 MHz, CDCl$_3$) for 5a
$^1$H NMR (600 MHz, CDCl$_3$) for 6a

$^{13}$C NMR (150 MHz, CDCl$_3$) for 6a
$^1$H NMR (600 MHz, CDCl$_3$) for 7a

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$^{13}$C NMR (100 MHz, CDCl$_3$) for 8c
$^1$H NMR (400 MHz, CDCl$_3$) for 8d

$^{13}$C NMR (100 MHz, CDCl$_3$) for 8d
$^{1}H$ NMR (600 MHz, CDCl$_3$) for 8e

$^{13}C$ NMR (150 MHz, CDCl$_3$) for 8e
$^1$H NMR (400 MHz, CDCl$_3$) for 8f

$^{13}$C NMR (100 MHz, CDCl$_3$) for 8f
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Data file: MM 1430_ODH_982_flow1_181.DAT
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$^1$H NMR (600 MHz, CDCl$_3$) for 8g

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8g
$^1$H NMR (600 MHz, CDCl$_3$) for 8h

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8h
$^{19}$F NMR (564 MHz, CDCl$_3$) for 8h
$^1$H NMR (600 MHz, CDCl$_3$) for 8i

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8i
$^1$H NMR (600 MHz, CDCl$_3$) for 8j

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8j
$^1$H NMR (400 MHz, CDCl$_3$) for 8k

$^{13}$C NMR (100 MHz, CDCl$_3$) for 8k
$^{19}\text{F NMR}$ (376 MHz, CDCl$_3$) for 8k
$^1$H NMR (600 MHz, CDCl$_3$) for 8I

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8I
$^1$H NMR (600 MHz, CDCl$_3$) for 8m

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8m
$^1$H NMR (600 MHz, CDCl$_3$) for 8n

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8n
$^1$H NMR (600 MHz, CDCl$_3$) for 8o

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8o
$^1$H NMR (400 MHz, CDCl$_3$) for 8p

$^{13}$C NMR (100 MHz, CDCl$_3$) for 8p
$^1$H NMR (400 MHz, CDCl$_3$) for 8q

$^{13}$C NMR (100 MHz, CDCl$_3$) for 8q
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$^1$H NMR (600 MHz, CDCl$_3$) for 8r

$^{13}$C NMR (150 MHz, CDCl$_3$) for 8r