Supporting information for

Gold(I)-catalyzed Nicholas Reaction with Aromatic Molecules Utilizing a Bifunctional Propargyl Dicobalt Hexacarbonyl Complex

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Table of Contents

1. General procedure ........................................................................................................1
2. Synthesis of Nicholas complex precursors .................................................................2
3. Reagent screening .......................................................................................................13
4. Synthesis of gold catalyst 18g .....................................................................................16
5. Synthesis of substrates ...............................................................................................17
6. Functionalization .......................................................................................................28
7. Decomplexation of dicobalt hexacarbonyl complexes ..............................................46
8. 1-Pot propargylation ..................................................................................................47
9. References ................................................................................................................50
10. NMR spectra ...........................................................................................................51

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1. General procedure
All reactions were carried out under an argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. Dehydrated THF and CH₂Cl₂ were purchased from Kanto Chemical Co., Inc. Other solvents were dehydrated and distilled according to standard protocols. Reagents were obtained from commercial suppliers, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on Silica gel plates (Merck Kieselgel 60 F₂₅₄) or Silica gel plates (Fuji Silysia Chemical Co., Ltd.). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 µm). Flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 µm). Fluorous column chromatography was performed on FluoroFlash® Silica Gel 40 µm (SIGMA-ALDRICH, Co.). All melting points were determined with Yazawa Micro Melting Point BY-2 and are uncorrected. IR spectra were recorded on a JASCO FT/IR-410 Fourier Transform Infrared Spectrophotometer. ¹H-NMR (400 and 600 MHz) and ¹³C-NMR spectra (100 and 150 MHz) were recorded on JEOL JNM-AL-400, JEOL JNM-ECA-600 spectrometers, respectively. ¹⁹F-NMR spectra (560 MHz) are recorded on JEOL JNM-ECA-600 spectrometers. For ¹H-NMR spectra, chemical shifts (δ) are given from TMS (0.00 ppm) or CHCl₃ (7.26 ppm) in CDCl₃ as an internal standard. For ¹³C-NMR spectra, chemical shifts (δ) are given from CDCl₃ (77.0 ppm) as an internal standard. For ¹⁹F-NMR spectra, chemical shifts (δ) are given from C₆F₆ (164.9 ppm) as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, m = multiplet, br = broad. EI mass spectra were recorded on JEOL JMS-DX303, JEOL JMS-700 and JEOL JMS-T 100 GC. FAB mass spectra were recorded on JEOL JMS-700. ESI mass spectra were recorded on Thermo Scientific Exactive Mass Spectrometer.
2. Synthesis of Nicholas complex precursors

2-1. Synthesis of reagent 5

Methyl 2-(hex-1-yn-1-yl)benzoate (S1)

To a solution of methyl 2-iodobenzoate (524 mg, 2.00 mmol) and 1-hexyne (0.28 mL, 2.44 mmol) in Et₃N (6.0 mL) was added Pd(PPh₃)₂Cl₂ (28.0 mg, 39.9 µmol) and CuI (8.97 mg, 47.0 µmol) at room temperature. The reaction mixture was stirred at the same temperature for 24 h, then concentrated under vacuo. CH₂Cl₂ (30 mL) was added to the residue, and the organic layer was washed with water and brine, dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20) to give alkyne S1 (385 mg, 1.78 mmol, 89%). Characterization data were in agreement with previously reported values.¹

2-(Hex-1-yn-1-yl)benzoic acid (S2)

To a solution of benzoate S1 (1.27 g, 5.89 mmol) in MeOH (25 mL) was added 1 M NaOH (25 mL) at room temperature. The reaction mixture was stirred at the same temperature for 5.5 h. The mixture was poured into 1 M HCl (30 mL), and extracted with Et₂O (40 mL × 2). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 1) to give benzoic acid S2 (1.18 g,
mmol, 99%). Characterization data were in agreement with previously reported values.1

**Reagent 5**

To a solution of benzoic acid **S2** (296 mg, 1.46 mmol) in CH₂Cl₂ (4.8 mL) was added (COCl)₂ (150 µL, 1.75 mmol) and DMF (10 µL, 0.13 µmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated under vacuo. To the residue was added CH₂Cl₂ (7.3 mL), pyridine (1.2 mL), and alkyne cobalt complex **S3** (370 mg, 1.10 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (4 mL) and extracted with CH₂Cl₂ (10 mL × 2). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified with silica gel column chromatography (AcOEt : Hexane = 1 : 20) to give complex 5 (471 mg, 0.90 mmol, 82% from **S3**).

5: red oil; IR (neat): 2022 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.43 (td, J = 7.6, 1.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 6.12 (s, 1H), 5.52 (s, 2H), 2.50 (t, J = 7.1 Hz, 2H), 1.69-1.58 (m, 2H), 1.58-1.45 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.1, 165.6, 134.5, 131.8, 131.0, 130.1, 127.1, 125.2, 96.5, 88.7, 79.3, 72.2, 65.4, 30.8, 22.1, 19.6, 13.7; HRMS (ESI): calcd for C₂₂H₁₆O₈Co₂Na([M+Na]⁺): 548.9401, found 548.9393.
2-2. Synthesis of reagent 6

\[
\begin{align*}
\text{Methyl 2-} & ((\text{trimethylsilyl})\text{ethynyl})\text{benzoate (S4)} \\
\text{To a solution of methyl 2-iodobenzoate (5.24 g, 20.0 mmol) and TMS acetylene (3.39 mL, 24.0 mmol) in Et}_3\text{N (60 mL) was added Pd(PPh}_3\text{)}_2\text{Cl}_2 (14.0 mg, 0.02 mmol) and CuI (3.8 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred at the same temperature overnight and concentrated under vacuo. To the residue was added CH}_2\text{Cl}_2 (30 mL) and the organic layer was washed with sat. aq. NH}_4\text{Cl (30 mL), dried over MgSO}_4, and filtered. The filtrate was concentrated under vacuo and purified by column chromatography on silica gel (AcOEt : hexane = 1 : 30) to give alkyne S4 (5.14 g, quant.) Characterization data were in agreement with previously reported values.}^3
\end{align*}
\]

2-Ethynylbenzoic acid (S5)

To a solution of benzoate S4 (996 mg, 4.29 mmol) in MeOH (18 mL) was added 1 M NaOH (18 mL) at room temperature. The reaction mixture was stirred at the same temperature for 3 h. The mixture was poured into conc. HCl (4 mL), and extracted with Et}_2\text{O (30 mL} \times 3). The combined organic layers were washed with brine, dried over MgSO}_4, and filtered. The filtrate was concentrated under vacuo and purified by column chromatography on silica gel (AcOEt : hexane = 4 : 1 to 1 : 1) to give benzoic acid S5 (412 mg, 2.82 mmol, 66%). Characterization data were in agreement with previously
reported values.  

**Reagent 6**

To a solution of benzoic acid **S5** (295 mg, 2.02 mmol) in CH₂Cl₂ (6.8 mL) was added (COCl)₂ (0.21 mL, 2.42 mmol) and DMF (10 µL, 0.13 µmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated in vacuo. To the residue was added CH₂Cl₂ (10 mL), pyridine (1.6 mL) and alkyne cobalt complex **S3** (345 mg, 1.01 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (10 mL) and extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 20) to give complex **6** (395 mg, 0.830 mmol, 82% from **S3**).

**6**: red oil; IR (neat): 2036 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.03 (d, J = 7.4 Hz, 1H), 7.65 (d, J = 7.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 6.13 (s, 1H), 5.54 (s, 2H), 3.44 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.1, 165.3, 135.2, 132.0, 131.7, 130.2, 128.5, 123.1, 88.3, 82.6, 82.0, 72.3, 65.6; HRMS (ESI): calcd for C₁₈H₈O₈Co₂Na ([M+Na]⁺): 492.8775, found 492.8754.
2-3. Synthesis of reagent 7

Methyl 2-ethynylbenzoate (S6)

To a solution of alkyne S4 (2.0 g, 8.6 mmol) in MeOH (45 mL) was added K$_2$CO$_3$ (2.3 g, 17.0 mmol) at room temperature. The mixture was stirred at the same temperature for 3 h. To the mixture was added sat. NH$_4$Cl aq. (30 mL), and the resulting mixture was extracted with Et$_2$O (30 mL × 3). The combined organic layers were dried over MgSO$_4$, filtered, concentrated under vacuo, and purified by column chromatography on silica gel (AcOEt : hexane = 1: 8) to give terminal alkyne S6 (1.3 g, 8.2 mmol, 95%). Characterization data were in agreement with previously reported values.$^3$

Methyl 2-(5,5,6,6,7,7,8,8,8-nonanafuorooct-1-yn-1-yl)benzoate (S8)

To a solution of (π-allyl)$_2$PdCl$_2$ (92 mg, 0.25 mmol), 1,3-di(1-adamantyl)imidazolium hydrochloride (IAd) (198 mg, 0.5 mmol), Cul (216 mg, 1.12 mmol), and Cs$_2$CO$_3$ (2.28 g, 7.0 mmol) in DMF-Et$_2$O (1:2) (10 mL) was added alkyne S6 (0.92 mL, 3.75 mmol) and 2-(nonafluorobutyl)ethyl iodide (S7) (0.86 mL, 5.0 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 24 h, the reaction mixture was concentrated under vacuo and purified by column chromatography on silica gel (CH$_2$Cl$_2$ : Hexane = 1 : 30 to 1 : 8) to give alkyne S8 (1.08 g, 2.70 mmol, 53% from S6).
**S8**: yellow oil; IR (neat): 2955, 1734 cm\(^{-1}\); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta 8.02 \text{ (d, } J = 8.2 \text{ Hz, 1H)}, 7.70 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 7.62 \text{ (t, } J = 7.6 \text{ Hz, 1H)}, 7.53 \text{ (d, } J = 7.6 \text{ Hz, 1H)}, 3.88 \text{ (s, 3H)}, 3.37 \text{ (t, } J = 7.6 \text{ Hz, 2H)}, 2.56-2.41 \text{ (m, 2H)}; \(^1\)C-NMR (150 MHz, CDCl\(_3\)): \(\delta 195.8, 193.3, 167.3, 138.2, 133.4, 131.5, 129.5, 129.2, 129.1, 52.9, 27.9, 24.8 \text{ (t, } ^1J_{\text{CF}} = 23.1 \text{ Hz}); \(^19\)F-NMR (562 MHz, CDCl\(_3\)): \(\delta 84.1 \text{ (s, 3F)}, 117.5 \text{ (s, 2F)}, 127.5 \text{ (s, 2F)}, 129.2 \text{ (s, 2F)}; \text{ HRMS (ESI): calcd for C}_{11}\text{H}_{11}\text{O}_{2}\text{F}_{9}\text{Na ([M+Na]}^+): 429.0508, \text{ found 429.0505.}

2-(5,5,6,6,7,7,8,8,8-Nonafluorooct-1-yn-1-yl)benzoic acid (S9)

To a solution of benzoate S8 (274 mg, 0.67 mmol) in 2,2,2-trifluoroethanol (TFE) (1.8 mL) was added 2 M KOH (1.8 mL) at room temperature. The reaction mixture was and stirred at 50 °C for 16 h. To the mixture was added 1 M HCl (5 mL), and the resulting mixture was extracted with CH\(_2\)Cl\(_2\) (10 mL \times 3). The combined organic layers were dried over MgSO\(_4\), filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20) to give benzoic acid S9 (244 mg, 0.62 mmol, 92%).

**S9**: white solid; mp. 82-84 °C; IR (neat): 1705 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 8.06 \text{ (d, } J = 7.7 \text{ Hz, 1H)}, 7.56 \text{ (d, } J = 7.7 \text{ Hz, 1H)}, 7.51 \text{ (t, } J = 7.7 \text{ Hz, 1H)}, 7.40 \text{ (t, } J = 7.7 \text{ Hz, 1H)}, 2.82 \text{ (t, } J = 7.7 \text{ Hz, 2H)}, 2.64-2.38 \text{ (m, 2H)}; \(^1\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta 170.8, 134.3, 132.6, 131.2, 130.8, 127.9, 124.2, 92.7, 80.2, 30.3 \text{ (t, } ^1J_{\text{CF}} = 21.3 \text{ Hz)}, 11.9 \text{ (t, } ^2J_{\text{CF}} = 4.9 \text{ Hz}); \(^19\)F-NMR (562 MHz, CDCl\(_3\)): \(\delta 84.1 \text{ (s, 3F)}, 118.5 \text{ (s, 2F)} 127.6 \text{ (s, 2F)}, 129.1 \text{ (s, 2F)}; \text{ HRMS (EI): calcd for C}_{15}\text{H}_{9}\text{O}_{2}\text{F}_{9} (M^+) : 392.0459, \text{ found 392.0440.}

**Reagent 7**

To a solution of benzoic acid S9 (196 mg, 0.50 mmol) in CH\(_2\)Cl\(_2\) (1.7 mL) was added (COCl\(_2\)) (58 µL, 0.65 mmol) and DMF (4.0 µL, 0.05 µmol) at room temperature. The
reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated under vacuo. To the residue was added CH$_2$Cl$_2$ (2.5 mL), pyridine (0.38 mL, 5.0 mmol) and then alkyne cobalt complex S3 (128 mg, 0.38 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (5 mL), extracted with CH$_2$Cl$_2$ (10 mL $\times$ 3). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo. The residue was purified with silica gel column chromatography (AcOEt : Hexane = 1 : 100) to give reagent 7 (231 mg, 0.32 mmol, 84% from S3).

7: red oil; IR (neat): 2030, 1732 cm$^{-1}$; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J$ = 8.2 Hz, 1H), 7.54 (d, $J$ = 7.5 Hz, 1H), 7.47 (t, $J$ = 7.5 Hz, 1H), 7.35 (t, $J$ = 7.5 Hz, 1H), 6.13 (s, 1H), 5.53 (s, 2H), 2.82 (t, $J$ = 6.8 Hz, 2H), 2.56-2.43 (m, 2H); $^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta$ 199.0, 165.2, 134.4, 132.0, 131.1, 130.2, 127.7, 124.3, 92.0, 88.6, 80.4, 72.1, 65.4, 30.4 (t, $^1J_{CF}$ = 21.5 Hz), 11.9 (t, $^2J_{CF}$ = 5.7 Hz); $^{19}$F-NMR (562 MHz, CDCl$_3$): $\delta$ 84.1 (s, 3F), 118.6 (s, 2F), 127.7 (s, 2F), 129.9 (s, 2F); HRMS (EI): calcd for C$_{21}$H$_{11}$F$_9$O$_5$Co$_2$ ([M-3CO]$^+$): 631.9127, found: 631.9111.

2-4. Synthesis of reagent 2
**Methyl 2-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodec-1-yn-1-yl)benzoate (S11)**

To a solution of (π-allyl)$_2$PdCl$_2$ (46 mg, 0.13 mmol), IAd (99 mg, 0.25 mmol), CuI (108 mg, 0.56 mmol), and Cs$_2$CO$_3$ (1.14 g, 3.5 mmol) in DMF-Et$_2$O (1:2) (5 mL) was added alkyne S6 (0.46 mL, 1.88 mmol), and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (S10) (0.60 mL, 2.5 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 24 h and concentrated under vacuo and purified by column chromatography on silica gel (CH$_2$Cl$_2$: Hexane = 1 : 30 to 1 : 8) to give alkyne S11 (629 mg, 1.24 mmol, 67% from S6).

S11: yellow oil; IR (neat): 1733 cm$^{-1}$; 1H-NMR (600 MHz, CDCl$_3$): δ 7.91 (d, $J = 7.6$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 3.92 (s, 3H), 2.82 (t, $J = 7.6$ Hz, 2H), 2.56-2.42 (m, 2H); $^{13}$C-NMR (150 MHz, CDCl$_3$): δ 166.6, 134.2, 132.0, 131.6, 130.3, 127.7, 123.6, 91.5, 80.4, 52.0, 30.6 (t, $^1J_{CF} = 21.7$ Hz), 11.9 (t, $^2J_{CF} = 5.8$ Hz); $^{19}$F-NMR (562 MHz, CDCl$_3$): δ 83.9 (s, 3F), 118.3 (s, 2F), 125.1 (s, 2F), 126.0 (s, 2F), 126.7 (s, 2F), 129.3 (s, 2F); HRMS (EI): calcd for C$_{18}$H$_{11}$O$_2$F$_{13}$ (M$^+$): 506.0551, found 506.0543.

**2-(5,5,6,6,7,7,8,8,9,9,10,10-Tridecafluorodec-1-yn-1-yl)benzoic acid (S12)**

To a solution of benzoate S11 (1.37 g, 2.71 mmol) in TFE (7.3 mL) was added 2 M KOH (7.3 mL) at room temperature. The reaction mixture was stirred at 50 °C for 10 h. The mixture was added 1 M HCl (15 mL), and the mixture was extracted with Et$_2$O (20 mL $\times$ 3), and concentrated under vacuo. The crude mixture was dissolved in CH$_2$Cl$_2$ (10 mL) and extracted with 1 M NaOH (15 mL $\times$ 2), and neutralized with 1 M HCl (30 mL), and the mixture was extracted with Et$_2$O (30 mL $\times$ 3). The organic layer was dried over MgSO$_4$, filtered, and concentrated under vacuo to give carboxylic acid S12 (1.24 g, 2.5 mmol, 93%).
**S12**: white solid; mp. 78-80 °C; IR (neat): 1698 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃): δ 8.06 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 2.83 (t, J = 7.6 Hz, 2H), 2.56-2.44 (m, 2H); ¹³C-NMR (150 MHz, CDCl₃): δ 170.5, 134.3, 132.5, 131.2, 130.7, 127.9, 124.1, 92.7, 80.2, 30.4 (t, JCF = 21.7 Hz), 11.9 (t, JCF = 5.8 Hz); ¹⁹F-NMR (562 MHz, CDCl₃): δ 83.9 (s, 3F), 118.3 (s, 2F), 125.1 (s, 2F), 126.0 (s, 2F), 126.7 (s, 2F), 129.3 (s, 2F); HRMS (EI): calcd for C₁₇H₉O₂F₁₃ (M⁺): 492.0395, found 492.0373.

**Reagent 2**

To a solution of benzoic acid S12 (248 mg, 0.50 mmol) in CH₂Cl₂ (5.0 mL) was added (COCl)₂ (56 μL, 0.65 mmol) and DMF (10 μL, 0.13 μmol) at room temperature. The reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was concentrated under vacuo. To the residue was added CH₂Cl₂ (5.0 mL), pyridine (0.38 mL, 5.0 mmol) and then alkyne cobalt complex S3 (128 mg, 0.38 mmol). The reaction mixture was stirred at the same temperature for 2 h. The reaction mixture was quenched with water (10 mL), extracted with CH₂Cl₂ (15 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 100) to give reagent 2 (257 mg, 0.31 mmol, 84% from S3).

**2**: red solid; IR (neat): 2029, 1733 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃): δ 8.01 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 6.13 (s, 1H), 5.52 (s, 2H), 2.83 (t, J = 7.6 Hz, 2H), 2.61-2.45 (m, 2H); ¹³C-NMR (150 MHz, CDCl₃): δ 199.1, 165.2, 134.4, 132.0, 131.1, 130.2, 127.7, 124.3, 92.0, 88.6, 80.4, 72.1, 65.4, 30.5 (t, JCF = 23.1 Hz), 11.9 (t, JCF = 5.8 Hz); ¹⁹F-NMR (562 MHz, CDCl₃): δ 83.9 (s, 3F), 118.3 (s, 2F), 125.0 (s, 2F), 125.9 (s, 2F), 126.6 (s, 2F), 129.2 (s, 2F); HRMS
(ESI): calcd for C_{26}H_{11}O_{8}Co_{2}F_{13}Na ([M+Na]^+): 838.8803, found 838.8793.

2-5. Attempted synthesis of reagent S13

![Reaction scheme](image)

2-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododec-1-yn-1-yl)benzoate (S15)

To a solution of (π-allyl)_{2}PdCl_{2} (28 mg, 75 µmol), IAd (56 mg, 0.15 mmol), Cul (65 mg, 0.34 mmol), Cs_{2}CO_{3} (684 mg, 2.1 mmol) in DMF-Et_{2}O (1:2) (3 mL) was added alkyne S6 (0.16 mL, 1.1 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (S14) (861 mg, 1.5 mmol) at room temperature. The reaction mixture was stirred at 40 °C for 24 h and concentrated under vacuo and purified by column chromatography on silica gel (CH_{2}Cl_{2} : Hexane = 1 : 30 to 1 : 8) to give alkyne S15 (327 mg, 0.54 mmol, 48% from S6).

S15: yellow oil; IR (neat): 2926, 1735 cm^{-1}; ^{1}H-NMR (600 MHz, CDCl_{3}): δ 7.92 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 3.92 (s, 3H), 2.82 (t, J = 7.6 Hz, 2H), 2.57-2.44 (m, 2H); ^{13}C-NMR (150 MHz, CDCl_{3}): δ 166.6, 134.2, 132.0, 131.6, 130.3, 127.7, 123.6, 91.5, 80.4, 52.1, 30.6 (t, \(^{1}J_{CF} = 21.7\) Hz), 11.9 (t, \(^{2}J_{CF} = 5.8\) Hz); ^{19}F-NMR (562 MHz, CDCl_{3}): δ 83.9 (s, 3F), 117.8 (s, 2F), 1118.3 (s, 2F), 124.8 (s, 2F), 125.0 (s, 2F), 125.8 (s, 2F), 126.6 (s, 2F), 129.2 (s, 2F);
HRMS (EI): calcd for C_{20}H_{11}O_{2}F_{17} (M^+): 606.0488, found 606.0482.

3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl)-1H-isochromen-1-one (S16)

To a solution of benzoate S15 (327 mg, 0.54 mmol) in TFE (1.5 mL) was added 2 M KOH (1.5 mL) at room temperature. The reaction mixture was stirred at the same temperature for 26 h. The mixture was added 1 M HCl (5 mL), and the mixture was extracted with Et_2O (15 mL × 2). The combined organic layers were dried over MgSO_4, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20) to give isocoumalin S16 (124 mg, 0.21 mmol, 39%). Carboxylic acid was not obtained.

S16: white solid; mp. 74-76 °C; IR (neat): 1718 cm\(^{-1}\); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): \(\delta\) 8.27 (d, \(J = 7.5\) Hz, 1H), 7.71 (t, \(J = 7.5\) Hz, 1H), 7.51 (t, \(J = 7.5\) Hz, 1H), 7.39 (d, \(J = 8.2\) Hz, 1H), 2.86 (t, \(J = 7.5\) Hz, 2H), 2.62-2.49 (m, 2H); \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)): \(\delta\) 162.4, 154.2, 136.9, 135.0, 129.7, 128.3, 125.3, 120.3, 104.2, 28.7 (t, \(^1J_{CF} = 22.9\) Hz), 25.0 (t, \(^2J_{CF} = 4.3\) Hz); \(^{19}\)F-NMR (562 MHz, CDCl\(_3\)): \(\delta\) 83.9 (s, 3F), 117.5 (s, 2F), 117.9 (s, 2F), 124.8 (s, 2F), 125.0 (s, 2F), 125.8 (s, 2F), 126.5 (s, 2F), 129.2 (s, 2F); HRMS (EI): calcd for C_{19}H_{9}O_{2}F_{17} (M^+): 592.0331, found 592.0310.
3. Reagent screening

3-1. Reaction of reagent 5 with substrate 3

To a solution of 5 (0.1 mmol), naproxen methyl ester 3 (0.2 mmol) and MS4A (50 mg) in CH$_2$Cl$_2$ (1.6 mL) was added a solution of 2.5 mM PPh$_3$AuSbF$_6$ in CH$_2$Cl$_2$ (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. NaHCO$_3$ aq. (2 mL), extracted with CH$_2$Cl$_2$ (4 mL $\times$ 2). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo to give a crude mixture of 4 and 8 and 9. The ratio was determined by $^1$H-NMR used toluene as the internal standard. The analytical samples were obtained by extensive PTLC (AcOEt : hexane = 1 : 8).

8: Characterization data were in agreement with previously reported values.$^5$

9: red oil; IR (neat): 2017 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.33 (d, $J$ = 7.6 Hz, 1H), 7.80 (t, $J$ = 7.6 Hz, 1H), 7.61 (t, $J$ = 7.6, 1H), 7.52 (t, $J$ = 7.6 Hz, 1H), 5.93 (s, 1H), 4.19 (s, 2H), 2.69 (t, $J$ = 7.5 Hz, 2H), 1.77 (quint, $J$ = 7.5 Hz, 2H), 1.45 (sext, $J$ = 7.5 Hz, 2H), 0.98 (t, $J$ = 7.5 Hz, 3H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 199.3, 162.2, 155.6, 137.0, 134.5, 130.2, 127.7, 122.8, 120.8, 111.5, 93.1, 73.8, 30.9, 29.8, 22.5, 13.8; HRMS (EI): calcd for C$_{19}$H$_{16}$O$_5$Co$_2$ ([M-3CO]$^+$): 441.9662, found 441.9668.
3-2. Reaction of reagent 6 with substrate 3

To a solution of 6 (0.1 mmol), naproxen methyl ester 3 (0.2 mmol) and MS4A (50 mg) in CH$_2$Cl$_2$ (1.6 mL) was added a solution of 2.5 mM PPh$_3$AuSbF$_6$ in CH$_2$Cl$_2$ (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. NaHCO$_3$ aq. (2 mL), extracted with CH$_2$Cl$_2$ (4 mL × 2). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo to give crude mixture of 4 and 10 and 11. The ratio was determined by $^1$H-NMR used toluene as the internal standard.

The analytical samples were obtained by PTLC (AcOEt : Hexane 1 : 8).

10: Characterization data were in agreement with previously reported values.$^6$

11: red oil; IR (neat): 2019 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 7.8$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.75 (t, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.4$ Hz, 1H), 6.09 (s, 1H), 6.01 (t, $J = 8.3$ Hz, 1H), 4.11 (d, $J = 8.3$ Hz, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 199.3, 166.5, 146.8, 137.6, 134.5, 130.3, 126.4, 125.9, 122.9, 110.8, 93.2, 72.8, 30.5; HRMS (ESI): calcd for C$_{18}$H$_8$O$_8$Co$_2$Na ([M+Na]$^+$): 492.8775, found 492.8765.
3-3. Reaction of reagent 7 with substrate 3

To a solution of 7 (71.6 mg, 0.1 mmol), naproxen methyl ester 3 (60.6 mg, 0.2 mmol) and MS4A (50 mg) in CH₂Cl₂ (1.6 mL) was added a solution of 2.5 mM PPh₃AuSbF₆ in CH₂Cl₂ (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. aq. NaHCO₃ (2 mL), extracted with CH₂Cl₂ (7 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo to give crude mixture of 3 and 4 and 12. The ratio was determined by ¹H-NMR used toluene as the internal standard.

The analytical samples were obtained by PTLC (AcOEt : Hexane 1 : 8).

12: white solid; mp. 50-52 °C; IR (neat): 1734 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃): δ 8.27 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 6.37 (s, 1H), 2.86 (t, J = 7.6 Hz, 2H), 2.65-2.47 (m, 2H); ¹³C-NMR (150 MHz, CDCl₃): δ 162.3, 154.2, 136.9, 135.0, 129.7, 128.3, 125.3, 120.3, 104.3, 28.6 (t, ¹JCF = 21.7 Hz), 25.0 (t, ²JCF = 4.3 Hz); HRMS (EI): calcd for C₁₅H₉F₉O₂(M⁺): 392.0459, found 392.0477.
3-4. Reaction of reagent 2 with substrate 3

To a solution of 2 (81.6 mg, 0.1 mmol), naproxen methyl ester 3 (60.6 mg, 0.2 mmol) and MS4A (50 mg) in CH₂Cl₂ (1.6 mL) was added a solution of 2.5 mM PPh₃AuSbF₆ in CH₂Cl₂ (0.4 mL) at room temperature. The reaction mixture was stirred at the same temperature for 30 min. The reaction mixture was quenched with sat. aq. NaHCO₃ (2 mL), extracted with CH₂Cl₂ (7 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo to give crude mixture of 3 and 4 and 14. The ratio was determined by ¹H-NMR used toluene as the internal standard.

The analytical samples were obtained by PTLC (AcOEt : Hexane 1 : 8).

14: white solid; mp. 54-56 °C; IR (neat): 1736 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃): δ 8.28 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 6.38 (s, 1H), 2.87 (t, J = 8.2 Hz, 2H), 2.61-2.48 (m, 2H); ¹³C-NMR (150 MHz, CDCl₃): δ 162.3, 154.2, 136.9, 135.0, 129.7, 128.3, 125.3, 120.3, 104.2, 28.7 (t, ¹JCF = 22.9 Hz), 25.0 (t, ²JCF = 4.3 Hz); ¹⁹F-NMR (562 MHz, CDCl₃): δ 83.9 (s, 3F), 117.9 (s, 2F), 125.0 (s, 2F), 126.0 (s, 2F), 126.5 (s, 2F), 129.2 (s, 2F); HRMS (EI): caleed for C₁₇H₉F₁₃O₂ (M⁺): 492.0395, found: 492.0366.

4. Synthesis of gold catalyst 18g
To CH$_2$Cl$_2$ (5.2 mL) was added gold catalyst S17 (164 mg, 0.3 mmol), AgNTf$_2$ (116 mg, 0.3 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 24 h. AgCl was removed by filtration through Celite and concentrated under vacuo to give gold catalyst 18g (211 mg, 0.27 mmol, 89%).

18g: white crystal; IR (neat): 1590, 1496 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.55-7.44 (m, 2H), 7.30-7.19 (m, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 165.5 (dd, $^{1}J_{CF} = 257.2$ Hz, $^{1}J_{CP} = 3.3$ Hz), 136.3 (dd, $^{2}J_{CP} = 15.6$ Hz, $^{2}J_{CF} = 9.0$ Hz), 122.7 (dd, $^{3}J_{CP} = 69.6$ Hz, $^{3}J_{CF} = 3.3$ Hz), 119.4 (q, $^{5}J_{CF} = 322.8$ Hz), 117.5 (dd, $^{4}J_{CF} = 22.1$ Hz, $^{4}J_{CP} = 13.9$ Hz); HRMS (EI): calcd for C$_{20}$H$_{12}$F$_9$N$_4$O$_4$PS$_2$Au (M$^+$): 792.9467, found: 792.9479.

5. Synthesis of substrates

2-Isopropoxynaphthalene (S18)

To a solution of 2-naphthol (446 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added isopropyl iodide (0.50 mL, 5.0 mmol). The reaction mixture was allowed to room temperature and stirred for 2 h. The solution was quenched with sat. NH$_4$Cl aq. (10 mL) at 0 °C and extracted with CH$_2$Cl$_2$ (10 mL $\times$ 3). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give isopropyether S18 (362 mg, 1.88 mmol, 97%). Characterization data were in agreement with previously reported values.$^7$

2-Phenoxy naphthalene (S19)
To solution of 2-bromonaphthalene (414 mg, 2.0 mmol) in toluene (6.7 mL) was added Cs$_2$CO$_3$ (3.26 g, 5.0 mmol), XPhos (76 mg, 0.16 mmol), Pd(db$_3$)$_2$ (18 mg, 40 µmol), and phenol (471 mg, 5.0 mmol) at room temperature. The reaction mixture was heated to reflux and stirred for 10 h. The solution was quenched with H$_2$O (10 mL) at room temperature and extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (Hexane) to give phenyl ether S19 (48.7 mg, 0.22 mmol, 11%). Characterization data were in agreement with previously reported values.

2-(Benzyloxy)naphthalene (20)

To a solution of 2-naphthol (446 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added BnBr (0.36 mL, 3.0 mmol). The reaction mixture was allowed to room temperature and stirred for 2 h. The solution was quenched with MeOH (5.0 mL) and sat. NH$_4$Cl aq. (10 mL) at 0 °C and extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give benzyl ether S20 (322 mg, 1.37 mmol, 69%). Characterization data were in agreement with previously reported values.
2-Allyl-6-methoxynaphthalene (S21)

To a solution of bromide (S22) (120 mg, 0.5 mmol) in DMF (1.7 mL) was added LiCl (64 mg, 1.0 mmol), Pd(PPh₃)₄ (15 mg, 13 µmol), and allyltributyltin (0.2 mL, 0.65 mmol) at room temperature. The reaction mixture was heated to 100 °C and stirred for 5 h. The solution was quenched with sat. NaHCO₃ aq. (2 mL) at room temperature and extracted with Et₂O (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel including 10% K₂CO₃ (AcOEt : Hexane = 1 : 50) to give alkene S21 (98.7 mg, 0.49 mmol, 99%). Characterization data were in agreement with previously reported values.¹⁰

2-(1-Hydroxymethyl)-6-methoxynaphthalene (S23)

To a solution of 6-methoxy-2-naphthaldehyde (376 mg, 2.0 mmol) in EtOH (6.7 mL) added NaBH₄ (151 mg, 4.0 mmol) at 0 °C. The reaction mixture was allowed to room temperature and stirred for 20 min. The solution was added sat. NH₄Cl aq. (10 mL) slowly at 0 °C and extracted with Et₂O (15 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1: 4) to give alcohol S23 (370 mg, 1.96 mmol, 98%). Characterization data were in agreement with previously reported values.¹¹

2-Methoxy-6-((methoxymethoxy)methyl)naphthalene (S24)
To a solution of alcohol S23 (94 mg, 0.5 mmol) in DMF (5.0 mL) was added 60% NaH (50 mg, 1.3 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MOMCl (76 µL, 1.0 mmol). The reaction mixture was allowed to room temperature and stirred for 24 h. The solution was quenched with sat. NH4Cl aq. (5 mL) at 0 °C and extracted with CH2Cl2 (10 mL × 3). The combined organic layers were dried over MgSO4, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 10) to give ether S24 (94 mg, 0.34 mmol, 40%). Characterization data were in agreement with previously reported values.12

**Tert-butyl((6-methoxynaphthalen-2-yl)methoxy)dimethylsilane (40)**

To a solution of alcohol S23 (94 mg, 0.5 mmol) and imidazole (64 mg, 1.0 mmol) in DMF (1.7 mL) was added TBSCl (150 mg, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature. The solution was quenched with sat. NH4Cl aq. (2 mL) at 0 °C and extracted with Et2O (5 mL × 3). The combined organic layers were dried over MgSO4, filtered, and concentrated under vacuo. The residue was concentrated under vacuo and purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give TBS ether 40 (153 mg, quant.).

40: white solid; IR (neat): 1606 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 7.76-7.67 (m, 3H), 7.45 (d, \(J = 8.7\) Hz, 1H), 7.13 (dd, \(J = 7.2\) Hz, \(J = 2.4\) Hz, 1H), 7.12 (s, 1H), 4.86 (s, 2H),
3.92 (s, 3H), 0.96 (s, 9H), 0.12 (s, 6H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 157.4, 136.8, 133.8, 129.3, 128.8, 126.7, 125.3, 124.4, 118.7, 105.8, 65.2, 55.3, 26.0, 18.5, -5.2; HRMS (EI): calcd for C$_{18}$H$_{26}$O$_2$Si (M$^+$): 302.1702, found: 302.1703.

**((6-Methoxynaphthalen-2-yl)methoxy)trimethylsilane (S25)**

\[
\begin{align*}
\text{HO-} & \quad \text{OMe} \\
\text{S23} & \quad \text{TMSCl (3.0 eq)} \\
\text{DMF (0.15 M)} & \quad \text{imidazole (4.0 eq)} \\
& \quad 0 ^\circ \text{C to rt, 1.5 h, 67%}
\end{align*}
\]

To a solution of alcohol S23 (94 mg, 0.5 mmol) and imidazole (136 mg, 2.0 mmol) in DMF (3.3 mL) was dropwised TMSCl (0.19 mL, 1.5 mmol) at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature. The solution was quenched with H$_2$O (2 mL) at 0 °C and extracted with Hexane (5 mL × 2). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 100) to give TMS ether S25 (87.7 mg, 0.34 mmol, 67%).

S25: white solid; IR (neat): 1609 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.84-7.64 (m, 3H), 7.40 (dd, $J = 8.5$ Hz, $J = 1.4$ Hz, 1H), 7.18-7.08 (m, 2H), 4.82 (s, 2H), 3.92 (s, 3H), 0.17 (s, 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 157.5, 136.2, 133.9, 129.3, 128.8, 126.9, 125.7, 125.0, 118.7, 105.7, 64.8, 55.3, -0.3; HRMS (EI): calcd for C$_{15}$H$_{20}$O$_2$Si (M$^+$): 260.1233, found: 260.1233.

**Tert-butyl ((4-nitrophenyl)sulfonyl)carbamate (S26)**

\[
\begin{align*}
\text{O}_3\text{N} & \quad \text{SO}_2\text{NH}_2 \\
\text{Boc}_2\text{O (1.2 eq)} & \quad \text{Et}_3\text{N (1.7 eq)} \\
\text{DMAP (10 mol%)} & \quad \text{CH}_2\text{Cl}_2 (0.5 \text{ M}) \\
& \quad \text{rt, overnight, quant.}
\end{align*}
\]

To a solution of nosylamide (1.04 g, 5.2 mmol) in CH$_2$Cl$_2$ (10 mL) was added Et$_3$N (1.1
mL, 8.7 mmol), DMAP (63 mg, 0.52 mmol), and Boc₂O (1.35 g, 6.2 mmol) at room temperature. The reaction mixture was stirred at the same temperature overnight. The solution was quenched with sat. 1 M HCl (10 mL) at 0 °C and filtered, and washed with Hexane : Et₂O = 1 : 2 (10 mL) to carbamate S₂₆ (1.40 g, quant.). Characterization data were in agreement with previously reported values.¹³

**Tert-butyl ((6-methoxynaphthalen-2-yl)methyl)carbamate (S₂₇)**

To a solution of alcohol S₂₃ (263 mg, 1.38 mmol), carbamate S₂₆ (235 mg, 0.77 mmol), and PPh₃ (367 mg, 1.54 mmol) in benzene (4.5 mL) was dropwised ca. 2.2 M DEAD in toluene (0.71 mL, 1.56 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. The solution was quenched with H₂O (5 mL) at 0 °C and extracted with CH₂Cl₂ (7 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (CHCl₃) to give carbamate S₂₈ (crude).

To a solution of carbamate S₂₈ (crude) in DMF (4.0 mL) was added LiOH•H₂O (130 mg, 3.08 mmol), and thioglycolic acid (0.11 mL, 1.54 mmol) at room temperature. The reaction mixture was stirred overnight. The solution was quenched with sat. NaHCO₃ aq. (5 mL) and extracted with Et₂O (8 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 5) to give carbamate S₂₇ (156 mg,
0.54 mmol, 71% over 2 steps).

**S27**: white solid; IR (neat): 3350 (br), 1697 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8.7, 1H), 7.70 (d, J = 8.7, 1H), 7.64 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.20-7.08 (m, 2H), 4.87 (brs, 1H), 4.44 (d, J = 5.3 Hz, 2H), 3.92 (s, 3H), 1.48 (s, 9H); ¹³C-NMR (100 MHz, CDCl₃): δ 157.5, 155.9, 134.0, 133.7, 129.0, 128.7, 127.0, 126.2, 125.7, 118.8, 105.6, 79.2, 55.1, 44.6, 28.3; HRMS (EI): calcd for C₁₇H₂₁NO₃ (M⁺): 287.1521, found: 287.1504.

**Tert-butyl ((6-methoxynaphthalen-2-yl)methyl)(methyl)carbamate (S29)**

![Chemical structure](image)

To a solution of carbamate S27 (156 mg, 0.54 mmol) in DMF (1.8 mL) was added 60% NaH (82 mg, 1.4 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MeI (86 µL, 1.0 mmol). The reaction mixture was allowed to room temperature and stirred for 5 h. The solution was quenched with sat. NH₄Cl aq. (2 mL) at 0 °C and extracted with Et₂O (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 10) to give carbamate S29 (149 mg, 0.49 mmol, 91%).

**S29** (a mixture of two rotamers): yellowish oil; IR (neat): 1692 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃): δ 7.69 (d, J = 8.3, 1H), 7.68 (d, J = 8.9, 1H), 7.56 (s, 1H), 7.32 (brs, 1H), 7.19-7.05 (m, 2H), 4.52 (s, 2H), 3.88 (s, 3H), 2.86 (brs, 1.5H), 2.79 (brs, 1.5H), 1.50 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃): δ 157.6, 156.2, 155.9, 133.8, 133.2, 129.1, 128.8, 127.2, 126.6, 126.3, 126.0, 125.8, 118.9, 105.7, 79.7, 55.2, 52.7, 52.0, 33.8, 28.5; HRMS
(Ei): calcd for C_{18}H_{23}NO_{3} (M\(^{+}\)) : 301.1678, found: 301.1702.

**(9H-Fluoren-9-yl)methyl ((6-methoxynaphthalen-2-yl)methyl)(methyl)carbamate (S30)**

To a solution of carbamate S29 (160 mg, 0.53 mmol) in CH_{2}Cl_{2} (5.3 mL) was dropwised TFA (0.41 mL, 5.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. The solution was quenched with sat. 1 M NaOH (10 mL) at 0 °C and extracted with CH_{2}Cl_{2} (15 mL × 3). The combined organic layers were dried over MgSO_{4}, filtered, and concentrated under vacuo to give amine S31 (73.8 mg, <0.36 mmol, <67%).

To solution of crude in THF (3.6 mL) was added K_{2}CO_{3} (150 mg, 1.09 mmol) and FmocCl (140 mg, 0.54 mmol) at 0 °C. The reaction mixture was stirred at the same temperature overnight. The solution was quenched with sat. NH_{4}Cl aq. (5 mL) at 0 °C and extracted with Et_{2}O (8 mL × 3). The combined organic layers were dried over MgSO_{4}, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (toluene : Hexane = 1 : 8) to give carbamate S30 (149 mg, 0.35 mmol, 66% over 2 steps).

S30 (a mixture of two rotamers): amorphous; IR (neat): 1699 cm\(^{-1}\); \(^{1}\)H-NMR (400 MHz, CDCl\(_{3}\)): δ 7.85-7.56 (m, 5H), 7.55-7.22 (m, 5H), 7.21-7.07 (m, 4H), 4.63 (s, 1H), 4.51 (s, 3H), 4.30 (brs, 0.5H), 4.25 (brs, 0.5H), 3.93 (s, 3H), 2.92 (brs, 1.5H), 2.87 (brs, 1.5H); \(^{13}\)C-NMR (150 MHz, CDCl\(_{3}\)): δ 157.6, 156.7, 156.3, 144.03, 143.96, 141.3, 133.9,
132.5, 132.3, 129.2, 128.7, 127.6, 127.3, 127.0, 126.5, 125.8, 125.7, 125.0, 124.8, 119.9, 118.9, 105.7, 67.4, 55.2, 52.6, 52.2, 47.4, 47.3, 34.4, 33.4; HRMS (EI): calcd for C_{28}H_{25}NO_{3} (M^+): 423.1834, found: 423.1815.

2-Bromo-6-methoxynaphthalene (S22)

To a solution of 6-bromo-2-naphthol (446 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MeI (0.31 mL, 5.0 mmol). The reaction mixture was allowed to room temperature and stirred overnight. The solution was quenched with sat. NH₄Cl aq. (10 mL) at 0 °C and extracted with CH₂Cl₂ (10mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30) to give methyl ether S22 (446 mg, 1.88 mmol, 94%). Characterization data were in agreement with previously reported values.¹⁴

2-(1-Hydroxyethyl)-6-methoxynaphthalene (S32)

To a solution of 6-methoxy-2-naphthaldehyde (376 mg, 3.0 mmol) in Et₂O (10 mL) was added ca. 3 M MeMgBr in Et₂O (1.0 mL, 3.0 mmol) over 3 min at 0 °C. The reaction mixture was allowed to room temperature and stirred for 1 h. The solution was quenched with 1 M HCl (10 mL) at 0 °C and extracted with Et₂O (15 mL × 3). The combined
organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 8) to give alcohol S32 (276 mg, 1.37 mmol, 68%). Characterization data were in agreement with previously reported values.¹⁵

**2-Acetyl-6-methoxynaphthalene (S33)**

To a solution of alcohol S32 (101 mg, 0.50 mmol), DMAP (2.44 mg, 0.02 mmol), bpy (1.56 mg, 0.01 mmol) and Nor-AZADO (1.52 mg, 0.01 mmol) in MeCN (2.5 mL) was added CuCl (3.64 mg, 0.0368 mmol) at room temperature. The mixture was stirred at the same temperature under O₂ atomosphere overnight. The reaction mixture was quenched with sat. NaHCO₃ aq. (5 mL), extracted with CH₂Cl₂ (7 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1: 20) to give ketone S33 (87 mg, 0.43 mmol, 86%). Characterization data were in agreement with previously reported values.¹⁶

**1-Methoxynaphthalene (S34)**

To a solution of 1-naphthol (288 mg, 2.0 mmol) in DMF (6.1 mL) was added 60% NaH (200 mg, 5.0 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. The reaction mixture cooled to 0 °C and added MeI (0.31 mL, 5.0 mmol).
The reaction mixture was allowed to room temperature and stirred for 2 h. The solution was quenched with sat. NH₄Cl aq. (10 mL) at 0 °C and extracted with CH₂Cl₂ (10 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 100) to give methyl ether S34 (235 mg, 1.49 mmol, 74%). Characterization data were in agreement with previously reported values.¹⁷

(5R,5aR,8aR,9R)-9-((Tert-butyldimethylsilyl)oxy)-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3′,4′:6,7]naphtho[2,3-d][1,3]dioxol-6(5aH)-one (37).

To a solution of podophyllotoxin (207 mg, 0.5 mmol) and imidazole (102 mg, 1.5 mmol) in DMF (1.7 mL) was added TBSCl (150 mg, 1.0 mmol) at 0 °C. The reaction mixture was stirred for 6 h at room temperature. The solution was quenched with sat. NH₄Cl aq. (2 mL) at 0 °C and extracted with Et₂O (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 2) to give TBS ether 37 (211 mg, 0.40 mmol, 80%). Characterization data were in agreement with previously reported values.¹⁸

6. Functionalization
Procedure A

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 µmol), reagent 2 (50 mg, 60 µmol), and DCE (1.0 mL) at room temperature. To the reaction mixture was added gold catalyst 18g (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. NaHCO₃ aq. (2 mL), and extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography to give a desired product.

Procedure B

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 µmol), reagent 2 (50 mg, 60 µmol), DCE (1.0 mL), and HFIP (0.1 mL) at room temperature. To the reaction mixture was added gold catalyst 18g (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. NaHCO₃ aq. (2 mL), and extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography to give a desired product.

Procedure C

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 µmol), reagent 2 (61 mg, 75 µmol), DCE (1.0 mL), and HFIP
(0.1 mL) at room temperature. To the reaction mixture was added gold catalyst 18g (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. NaHCO₃ aq. (2 mL), and extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography to give a desired product.

Procedure D

Two-necked flask containing MS4A (50 mg) was dried using heat gun under vacuo and then cooled to room temperature. After done heating and cooling three times, in the flask was added substrate (50 µmol), reagent 2 (50 mg, 60 µmol), and DCE (1.0 mL) at room temperature. To the reaction mixture was added gold catalyst 18g (5-20 mol%) and stirred at the same temperature for 15 min. The reaction mixture was quenched with sat. NaHCO₃ aq. (2 mL), and extracted with CH₂Cl₂ (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by silica gel column chromatography. After concentrated under vacuo, the residue was purified fluorous silica gel chromatography (H₂O : MeOH = 1 : 4). Fraction was extracted with CH₂Cl₂ (3 mL × 3) and then dried over MgSO₄, filtered, and concentrated under vacuo to give a desired product.

Functionalization of 2-methoxynaphthalene (16)
Procedure A was followed and used gold catalyst 18g (1.98 mg, 2.5 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 17 (23.8 mg, 49.3 µmol, 99%).

17: red oil; IR (neat): 2017 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.7 Hz, 1H), 7.82-7.74 (m, 2H), 7.52 (brt, J = 7.2 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 8.7 Hz, 1H), 5.93 (s, 1H), 4.63 (s, 2H), 3.97 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.8, 154.1, 132.7, 129.2, 128.9, 128.7, 126.5, 123.3, 123.2, 121.3, 112.4, 96.4, 73.6, 55.6, 29.0; HRMS (EI): calc'd for C₁₉H₁₂O₆Co₂ ([M-CO]⁺): 453.9298, found: 453.9312.

Functionalization of 2-isopropoxynaphthalene (S18)

Procedure A was followed and used gold catalyst 18g (1.98 mg, 2.5 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 19 (30.0 mg, 48.9 µmol, 98%).

19: red oil; IR (neat): 2017 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.2 Hz, 1H),
7.77 (d, \( J = 8.2 \) Hz, 1H), 7.73 (d, \( J = 9.2 \) Hz, 1H), 7.52 (t, \( J = 8.2 \) Hz, 1H), 7.35 (t, \( J = 7.7 \) Hz, 1H), 7.23 (d, \( J = 9.2 \) Hz, 1H), 5.91 (s, 1H), 4.72 (quint, \( J = 6.3 \) Hz, 1H), 4.63 (s, 2H), 1.42 (d, \( J = 6.3 \) Hz, 6H); \(^{13}C\)-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 199.9, 152.7, 132.8, 129.2, 128.7, 128.6, 126.4, 123.41, 123.36, 122.6, 115.4, 96.4, 73.9, 71.3, 29.6, 22.4; HRMS (EI): calcd for C\(_{19}\)H\(_{18}\)O\(_4\)Co\(_2\): [M-5CO]\(^+\): 369.9814, found: 369.9786.

**Functionalization of 2-phenoxy naphthalene (S19)**

![Diagram of reaction](attachment:reaction_diagram.png)

Procedure B was followed and used gold catalyst 18g (7.92 mg, 10 \( \mu \)mol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 20 (26.2 mg, 48.2 \( \mu \)mol, 96%).

20: red oil; IR (neat): 2019 cm\(^{-1}\); \(^1H\)-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.08 (d, \( J = 8.7 \) Hz, 1H), 7.84 (d, \( J = 8.2 \) Hz, 1H), 7.74 (d, \( J = 8.7 \) Hz, 1H), 7.60 (dt, \( J = 7.7 \) Hz, \( J = 1.0 \) Hz, 1H), 7.47 (t, \( J = 7.5 \) Hz, 1H), 7.33 (t, \( J = 7.5 \) Hz, 2H), 7.14 (d, \( J = 7.7 \) Hz, 1H), 7.09 (t, \( J = 7.5 \) Hz, 1H), 6.98 (d, \( J = 7.7 \) Hz, 2H), 5.91 (s, 1H), 4.63 (s, 2H); \(^{13}C\)-NMR (100 MHz, CDCl\(_3\)): \( \delta \) 199.6, 157.8, 151.0, 132.7, 131.1, 129.8, 129.2, 128.8, 126.7, 125.9, 124.9, 123.9, 122.8, 119.9, 117.6, 95.5, 73.7, 29.8; HRMS (EI): calcd for C\(_{22}\)H\(_{14}\)O\(_4\)Co\(_2\): [M-3CO]\(^+\): 459.9556, found: 459.9544.

**Functionalization of 2-(benzyloxy)naphthalene (S20)**

31
Procedure B was followed and used gold catalyst $18g$ (3.96 mg, 5.0 µmol). The crude mixture was purified by silica gel column chromatography (Hexane to CH$_2$Cl$_2$ : Hexane = 1 : 50) to give $21$ (26.7 mg, 47.8 µmol, 96%).

$21$: red oil; IR (neat): 2018 cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.99 (d, $J$ = 8.2 Hz, 1H), 7.78 (d, $J$ = 8.2 Hz, 1H), 7.75 (d, $J$ = 9.2 Hz, 1H), 7.53 (dt, $J$ = 8.2 Hz, $J$ = 1.2 Hz, 1H), 7.51-7.45 (m, 2H), 7.43-7.32 (m, 4H), 7.30 (d, $J$ = 9.2 Hz, 1H), 5.90 (s, 1H), 5.26 (s, 2H), 4.68 (s, 2H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 199.7, 153.4, 137.1, 132.7, 129.4, 128.9, 128.64, 128.59, 127.9, 127.3, 126.6, 123.6, 123.4, 122.1, 114.2, 96.1, 73.9, 70.9, 29.5; HRMS (EI): calcd for C$_{23}$H$_{16}$O$_4$Co$_2$ ([M-3CO]$^+$): 473.9713, found: 473.9738.

**Functionalization of 2-allyl-6-methoxynaphthalene (S21)**

Procedure A was followed and used gold catalyst $18g$ (1.98 mg, 2.5 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give $22$ (24.5 mg,
46.8 \mu\text{mol}, 94\%).

22: red oil; IR (neat): 2017 cm\(^{-1}\); \(^{1}\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.88 (d, \(J = 8.7\) Hz, 1H), 7.72 (d, \(J = 8.7\) Hz, 1H), 7.57 (s, 1H), 7.38 (d, \(J = 8.7\) Hz, 1H), 7.22 (d, \(J = 9.2\) Hz, 1H), 6.13-5.98 (m, 1H), 5.92 (s, 1H), 5.14 (d, \(J = 5.8\) Hz, 1H), 5.10 (s, 1H), 4.61 (s, 2H), 3.96 (s, 3H), 3.52 (d, \(J = 6.3\) Hz, 2H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.8, 153.7, 137.4, 134.8, 131.3, 129.3, 128.4, 128.1, 127.4, 123.3, 121.1, 116.0, 112.5, 96.4, 73.6, 55.6, 40.0, 29.0; HRMS (EI): caleld for C\(_{18}\)H\(_{16}\)O\(_2\)Co\(_2\) ([M-5CO]\(^+\)): 381.9814, found: 381.9833.

**Functionalization of 2-methoxy-6-((methoxymethoxy)methyl)naphthalene (S24)**

![chemical structure](image)

Procedure D was followed and used gold catalyst 18g (3.96 mg, 5.0 \mu\text{mol}). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50) and then fluorous silica gel column chromatography to give 23 (16.1 mg, 29 \mu\text{mol}, 58\%).

23: red oil; IR (neat): 2017 cm\(^{-1}\); \(^{1}\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.94 (d, \(J = 8.7\) Hz, 1H), 7.77 (d, \(J = 9.2\) Hz, 1H), 7.76 (s, 1H), 7.52 (dd, \(J = 9.2\) Hz, \(J = 1.9\) Hz, 1H), 7.25 (d, \(J = 9.2\) Hz, 1H), 5.92 (s, 1H), 4.75 (s, 2H), 4.74 (s, 2H), 4.62 (s, 2H), 3.97 (s, 3H), 3.45 (s, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.8, 154.2, 132.6, 132.2, 128.92, 128.88, 127.6, 126.7, 123.6, 121.2, 112.6, 96.2, 73.5, 69.2, 55.6, 55.4, 29.0; HRMS (EI): caleld for C\(_{20}\)H\(_{18}\)O\(_6\)Co\(_2\) ([M-3CO]\(^+\)): 471.9767, found: 471.9776.
Functionalization of tert-butyl((6-methoxynaphthalen-2-yl)methoxy) dimethylsilane (40)

Procedure A was followed and used gold catalyst 18g (3.96 mg, 5.0 µmol). The crude mixture was purified by silica gel column chromatography (CHCl₃ : Hexane = 1 : 20 to CHCl₃ : Hexane = 1 : 15) to give 24 (29.0 mg, quant.).

24: red oil; IR (neat): 2019 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.71 (s, 1H), 7.48 (dd, J = 8.7 Hz, J = 1.0 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 5.92 (s, 1H), 4.88 (s, 2H), 4.62 (s, 2H), 3.96 (s, 3H), 0.97 (s, 9H), 0.13 (s, 6H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.8, 153.9, 136.3, 131.9, 129.0, 128.8, 125.5, 125.3, 123.2, 121.2, 112.4, 96.4, 73.5, 65.1, 55.6, 29.1, 26.0, 18.5, -5.2; HRMS (EI): calcd for C₂₅H₂₈O₆SiCo₂ ([M-2CO⁺]: 570.0319, found: 570.0313.
Functionalization of ((6-methoxynaphthalen-2-yl)methoxy)trimethylsilane (S25)

Procedure A was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (CHCl₃ : Hexane = 1 : 20 to CHCl₃ : Hexane = 1 : 15) to give 25 (<10.46 mg, <17.9 µmol, <36%).

To a solution of 25 (<10.46 mg, <17.9 µmol, <36%) in MeOH (2.0 mL) was added K₂CO₃ (10 mg, 7.23 µmol) at room temperature. The reaction mixture was stirred for 90 min at the same temperature. The solution was quenched with sat. NH₄Cl aq. (1 mL) and extracted with CH₂Cl₂ (3 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 30 to AcOEt : Hexane = 1 : 4) to give S35 (7.86 mg, 15.3 µmol, 31% over 2 steps).

S35: red oil; IR (neat): 3321 (br), 2017 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 8.7 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.76 (s, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.25 (d, J = 8.7 Hz, 1H), 5.92 (s, 1H), 4.84 (s, 2H), 4.62 (s, 2H), 3.97 (s, 3H), 1.70 (brs, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.8, 154.2, 135.7, 132.2, 129.0, 128.9, 126.4, 126.0, 123.7,
121.3, 112.7, 96.3, 73.5, 65.4, 55.6, 29.0; HRMS (EI): calcd for C₁₆H₁₄O₃Co₂ ([M-5CO]⁺): 371.9607, found: 371.9633.

**Functionalization of tert-butyl ((6-methoxynaphthalen-2-yl)methyl)(methyl) carbamate (S29)**

Procedure B was followed and used gold catalyst 18g (3.96 mg, 5.0 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to 1 : 20) to give 26 (23.8 mg, 38.0 µmol, 76%).

26 (a mixture of two rotamers): red oil; IR (neat): 2019, 1694 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃): δ 7.92 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.58 (brs, 1H), 7.41 (brs, 1H), 7.27-7.23 (m, 1H), 5.93 (s, 1H), 4.62 (s, 2H), 4.55 (brs, 2H), 3.97 (s, 3H), 2.88 (brs, 1.5H), 2.80 (brs, 1.5H), 1.49 (s, 9H); ¹³C-NMR (150 MHz, CDCl₃): δ 199.8, 156.3, 155.9, 154.1, 133.0, 131.9, 129.0, 128.6, 127.5, 127.4, 127.3, 126.7, 126.2, 123.7, 121.3, 112.7, 96.3, 79.8, 73.5, 55.6, 52.6, 51.8, 33.9, 33.8, 29.0, 28.5; HRMS (FAB): calcd for C₂₂H₂₅NO₄Co₂ ([M-5CO]⁺): 485.0448, found: 485.0455.
Functionalization of (9H-fluoren-9-yl)methyl ((6-methoxynaphthalen-2-yl) methyl)(methyl)carbamate (S30)

Procedure B was followed and used gold catalyst 18g (3.96 mg, 5.0 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 30 to 1 : 10) to give 27 (35.4 mg, 49.9 µmol, 99%).

27 (a mixture of two rotamers): red oil; IR (neat): 2019, 1702 cm\(^{-1}\); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): δ 7.92 (d, \(J = 8.9\) Hz, 0.5H), 7.87 (d, \(J = 8.2\) Hz, 0.5H), 7.82-7.68 (m, 3H), 7.63 (brs, 1.5H), 7.51 (brd, \(J = 8.2\) Hz, 1.5H), 7.41 (t, \(J = 6.8\) Hz, 1.5H), 7.38-7.29 (m, 2H), 7.26 (d, \(J = 6.8\) Hz, 1H), 7.18 (brd, \(J = 6.8\) Hz, 1.5H), 5.92 (s, 1H), 4.69-4.59 (m, 3H), 4.57-4.46 (m, 3H), 4.31 (brs, 0.5H), 4.25 (brs, 0.5H), 3.97 (s, 3H), 2.92 (brs, 1.5H), 2.88 (brs, 1.5H); \(^1\)C-NMR (150 MHz, CDCl\(_3\)): δ 199.8, 156.8, 156.4, 154.2, 144.0, 141.4, 132.2, 132.0, 128.9, 128.7, 127.7, 127.6, 127.4, 127.0, 126.7, 126.1, 125.0, 124.9, 123.9, 121.3, 120.0, 112.7, 96.2, 73.5, 67.5, 55.6, 52.5, 52.2, 47.4, 34.4, 33.4, 29.7, 29.0; HRMS (FAB): calcd for C\(_{34}\)H\(_{27}\)NO\(_6\)Co\(_2\) ([M-3CO]\(^+\)): 663.0502, found: 663.0504.
Functionalization of 2-bromo-6-methoxynaphthalene (S22)

Procedure B was followed and used gold catalyst 18g (3.96 mg, 5.0 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 28 (25.2 mg, 44.9 µmol, 90%).

28: red oil; IR (neat): 2017 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.94 (d, J = 1.4 \text{ Hz}, 1H), 7.82 (d, J = 9.2 \text{ Hz}, 1H), 7.70 (d, J = 9.2 \text{ Hz}, 1H), 7.58 (dd, J = 9.2 \text{ Hz}, J = 1.4 \text{ Hz}, 1H),\) 7.28 (s, 1H), 5.92 (s, 1H), 4.59 (s, 2H), 3.97 (s, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)):
\[\delta 199.7, 154.3, 131.1, 130.5, 130.2, 129.8, 128.0, 125.0, 121.5, 117.0, 113.4, 95.7, 73.4, 55.6, 28.8; \] HRMS (EI): calcd for C\(_{16}\)H\(_{11}\)\(^{79}\)BrO\(_3\)Co\(_2\) ([M-4CO]\(^+\)): 447.8556, found: 447.8568.

Functionalization of 2-acetyl-6-methoxynaphthalene (S33)

Procedure A was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to
1 : 20) to give 29 (19.5 mg, 37.2 µmol, 74%).

29: red oil; IR (neat): 2017, 1677 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.42 (s, 1H), 8.08 (dd, \(J = 9.2\) Hz, 1.9 Hz, 1H), 7.99 (d, \(J = 9.2\) Hz, 1H), 7.92 (d, \(J = 9.2\) Hz, 1H), 7.33 (d, \(J = 9.2\) Hz, 1H), 5.93 (s, 1H), 4.63 (s, 2H), 4.00 (s, 3H), 2.71 (s, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.7, 197.7, 156.3, 135.0, 132.3, 131.2, 130.9, 127.9, 124.6, 123.6, 121.6, 113.1, 95.6, 73.5, 55.6, 28.8, 26.5; HRMS (EI): calcd for C\(_{17}\)H\(_{14}\)O\(_3\)Co\(_2\) ([M-5CO]\(^+\)): 383.9607, found: 383.9607.

Functionalization of 3-methylbenzofuran

Procedure A was followed and used gold catalyst 18g (1.98 mg, 2.5 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 30 (17.8 mg, 39.0 µmol, 78%).

30: red oil; IR (neat): 2019 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.45 (dd, \(J = 6.8\) Hz, 1.4 Hz, 1H), 7.38 (dd, \(J = 6.8\) Hz, 1.4 Hz, 1H), 7.24 (d, \(J = 7.2\) Hz, 1.9 Hz, 1H), 7.20 (dt, \(J = 7.2\) Hz, 1.4 Hz, 1H), 6.09 (s, 1H), 4.23 (s, 2H), 2.23 (s, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.4, 153.9, 150.9, 129.8, 123.9, 122.2, 119.1, 111.1, 110.9, 93.3, 73.1, 30.4, 7.9; HRMS (EI): calcd for C\(_{17}\)H\(_{10}\)O\(_7\)Co\(_2\) ([M-5CO]\(^+\)): 427.9141, found: 427.9161.
Functionalization of 3-methylbenzothiophene

Procedure B was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 31 (16.2 mg, 34.2 µmol, 68%).

31: red oil; IR (neat): 2018 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.77 (d, \(J = 8.2\) Hz, 1H), 7.63 (d, \(J = 7.7\) Hz, 1H), 7.36 (t, \(J = 7.7\) Hz, 1H), 7.30 (t, \(J = 7.7\) Hz, 1H), 6.10 (s, 1H), 4.37 (s, 2H), 2.40 (s, 3H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.4, 140.3, 138.3, 136.5, 128.1, 124.2, 124.0, 122.2, 121.7, 95.1, 73.6, 32.7, 11.7; HRMS (EI): calcd for C\(_{17}\)H\(_{10}\)OsSCo\(_2\) ([M-CO]\(^+\)): 443.8913, found: 443.8926.

Functionalization of 1-methylindole

Procedure A was followed and used gold catalyst 18g (3.96 mg, 5.0 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 32 (15.7 mg,
34.4 µmol, 69%).

**32**: red oil; IR (neat): 2015 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.63 (d, J = 7.5 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.05 (s, 1H), 4.27 (s, 2H), 3.75 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.7, 137.0, 127.3, 126.9, 121.8, 119.0, 118.7, 114.1, 109.3, 98.9, 73.6, 32.6, 30.1; HRMS (EI): calcd for C₁₆H₁₁NO₄Co₂([M-2CO]⁺): 398.9352, found: 398.9341.

**Functionalization of 1-methoxynaphthalene (S34)**

![Functionalization Diagram]

Procedure A was followed and used gold catalyst 18g (1.98 mg, 2.5 µmol). The crude mixture was purified by silica gel column chromatography (Hexane) to give 33a (16.6 mg, 34.7 µmol, 69%), 33b (5.17 mg, 10.7 µmol, 21%), 33c (3.22 mg, 4.2 µmol, 8%).

**33a**: red oil; IR (neat): 2016 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.30 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 6.74 (d, J = 7.2 Hz, 1H), 5.94 (s, 1H), 4.49 (s, 2H), 3.98 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.6, 155.2, 132.2, 128.8, 126.9, 126.5, 126.1, 125.1, 123.7, 122.8, 103.3, 97.4, 73.7, 55.5, 37.5; HRMS (EI): calcd for C₁₅H₁₂O₂Co₂([M-5CO]⁺): 341.9501,
found: 341.9494.

**33b**: red oil; IR (neat): 2020 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.10 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.54-7.43 (m, 2H), 7.46 (dt, J = 8.2 Hz, J = 1.5 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 6.07 (s, 1H), 4.30 (s, 2H), 3.99 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.7, 153.7, 134.4, 128.4, 128.2, 128.1, 126.0, 125.7, 125.6, 124.3, 122.3, 96.6, 73.6, 62.2, 34.3; HRMS (EI): calcd for C₁₅H₁₂O₂Co₂ ([M-5CO]⁺): 341.9501, found: 341.9510.

**33c**: red oil; IR (neat): 2018 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.15-8.10 (m, 1H), 8.06-8.01 (m, 1H), 7.58-7.50 (m, 2H), 7.30 (s, 1H), 6.05 (s, 1H), 5.97 (s, 1H), 4.51 (s, 2H), 4.28 (s, 2H), 3.90 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 199.7, 153.5, 133.1, 132.0, 129.2, 128.7, 127.9, 126.02, 125.99, 124.3, 123.1, 96.8, 96.2, 73.8, 73.5, 62.2, 37.3, 34.3; HRMS (EI): calcd for C₂₈H₁₄O₂Co₄ ([M-CO]⁺): 777.7813, found: 777.7826.

**Functionalization of naproxen methyl ester (3)**

![Chemical structure](image)

Procedure D was followed and used gold catalyst **18g** (1.98 mg, 2.5 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 30), and then fluorous silica gel column chromatography to give **4** (27.5 mg, 48.4 µmol, 97%). Characterization data were in agreement with previously reported values.¹⁹
Functionalization of estrone methyl ether (34)

![Chemical structure of estrone methyl ether (34)](image)

Procedure C was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 20) to give a mixture of 34a and 34b (62.02 mg). Characterization data were in agreement with previously reported values.¹⁹

Functionalization of indometacin methyl ester (35)

![Chemical structure of indometacin methyl ester (35)](image)

Procedure C was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to AcOEt : Hexane = 1 : 20) to give 35a (15.6 mg, 22.5 µmol, 45%) and 35b (14.52 mg, 20.9 µmol, 42%). Characterization data were in agreement with previously reported
Functionalization of mestranol (36)

Procedure B was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (Pentane) to give a mixture of 36a and 36b (12.56 mg) and a mixture of S36 and S37 (21.98 mg). Characterization data were in agreement with previously reported values.\textsuperscript{19}
Functionalization of (5R,5aR,8aR,9R)-9-((tert-butyldimethylsilyl)oxy)-5-(3,4,5-trimethoxyphenyl)-5,8,8a,9-tetrahydrofuro[3',4':6,7]naphtho[2,3-d][1,3]dioxol-6(5aH)-one (37).

![Chemical structure of 37 and 37a](image)

Procedure C was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (AcOEt : Hexane = 1 : 50 to 1 : 4) to give 37a (9.58 mg, 11.2 µmol, brsm 99%).

37a: red oil; IR (neat): 2019, 1782 cm\(^{-1}\); \(^1\)H-NMR (600 MHz, CDCl\(_3\)): δ 6.96 (s, 1H), 6.39 (s, 1H), 6.061 (s, 1H), 6.055 (s, 1H), 5.98 (s, 1H), 5.97 (s, 1H), 4.93 (d, \(J = 9.6\) Hz, 1H), 4.91 (s, 1H), 4.81 (d, \(J = 9.6\) Hz, 1H), 4.55 (t, \(J = 7.5\) Hz, 1H), 4.43 (d, \(J = 15.7\) Hz, 1H), 4.00 (dt, \(J = 11.1\) Hz, \(J = 8.6\) Hz, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H), 3.11-3.01 (m, 1H), 2.98-2.89 (m, 1H), 0.97 (s, 9H), 0.30 (s, 1H), 0.14 (s, 3H); \(^{13}\)C-NMR (150 MHz, CDCl\(_3\)): δ 173.7, 151.9, 151.8, 147.5, 147.3, 141.4, 133.64, 133.60, 132.1, 127.8, 110.8, 109.0, 106.6, 101.4, 96.8, 72.7, 72.3, 71.5, 60.5, 60.4, 55.8, 44.9, 40.9, 39.5, 31.5, 25.8, 18.0, -3.8, -4.1; HRMS (FAB): calcd for C\(_{32}\)H\(_{38}\)O\(_5\)Co\(_2\) ([M-5CO\(^+\)]: 712.0949, found: 712.0972.
Functionalization of guaiazulene (38)

Procedure C was followed and used gold catalyst 18g (7.92 mg, 10 µmol). The crude mixture was purified by silica gel column chromatography (Pentane) to give 38a (9.05 mg, 19.2 µmol, 38%).

38a: black oil; IR (neat): 2021 cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.06 (d, \(J = 2.0\) Hz, 1H), 7.48 (s, 1H), 7.30 (d, \(J = 11.0\) Hz, 1H), 6.90 (d, \(J = 11.0\) Hz, 1H), 5.99 (s, 1H), 4.71 (s, 2H), 3.09-2.96 (m, 4H), 2.58 (s, 3H), 1.33 (d, \(J = 6.8\) Hz, 6H); \(^1\)C-NMR (150 MHz, CDCl\(_3\)): \(\delta\) 199.8, 144.6, 140.5, 139.6, 138.2, 134.6, 133.7, 131.8, 126.7, 126.0, 124.5, 99.6, 73.9, 37.7, 36.2, 26.5, 24.5, 12.7; HRMS (EI): calcd for C\(_{24}\)H\(_{20}\)O\(_6\)Co\(_2\) ([M]+): 521.9924, found: 521.9934.

7. Decomplexation of dicobalt hexacarbonyl complexes

Decomplexation of 17

To solution of functionalized compound 17 (5.32 mg, 35 µmol) in THF (0.35 mL) and DMF (0.35 mL) was dropwised 1 M TBAF in THF (0.14 mL, 0.14 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 2 h. The solution was quenched with sat. NH\(_4\)Cl aq. (1 mL) at room temperature and extracted
with Et₂O (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (Hexane) to 39 (5.32 mg, 27.1 µmol, 78%).

39: white solid; IR (neat): 3291 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.06 (d, J = 8.3 Hz, 1H), 7.88-7.72 (m, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 4.00 (d, J = 2.9 Hz, 2H), 3.98 (s, 3H), 1.97 (t, J = 2.9 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ 154.0, 132.6, 129.3, 129.0, 128.5, 126.8, 123.6, 123.3, 117.7, 113.6, 82.9, 67.9, 56.9, 14.4; HRMS (EI): calcd for C₁₄H₁₂O ([M]+): 196.0888, found: 196.0895.

8. 1-Pot propargylation

1-Pot propargylation of 40

A solution of reagent 2 (50 mg, 60 µmol), 40 (50 µmol) and MS4A (50 mg) in DCE (1.0 mL) was added gold catalyst 18g (3.96 mg, 5.0 µmol) at room temperature. The reaction mixture was stirred at the same temperature for 15 min. The reaction mixture was concentrated in vacuo. The residue was dissolved in THF (0.5 mL) and DMF (0.5 mL) and dropwised 1 M TBAF in THF (0.25 mL, 0.25 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 3 h. The solution was quenched
with sat. NH₄Cl aq. (2 mL) at room temperature and extracted with Et₂O (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 20 to 1 : 4) to 41 (9.10 mg, 40.2 µmol, 80%).

41: white solid; IR (neat): 3407 (br), 3288 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.07 (d, J = 8.7 Hz, 1H), 7.83-7.75 (m, 2H), 7.55 (dd, J = 9.2 Hz, J = 1.4 Hz, 1H), 7.34 (d, J = 9.2 Hz, 1H), 4.84 (s, 2H), 4.03-3.95 (m, 5H), 1.98 (t, J = 2.7 Hz, 1H), 1.70 (brs, 1H); ¹³C-NMR (100 MHz, CDCl₃): δ 154.1, 136.0, 132.2, 129.2, 128.9, 126.2, 123.9, 120.3, 117.7, 113.9, 82.8, 67.9, 65.4, 56.8, 14.4; HRMS (EI): calcd for C₁₅H₁₄O₂ ([M⁺]: 226.0994, found: 226.0991.

1-Pot propargylation of 3

A solution of reagent 2 (50 mg, 60 µmol), 3 (50 µmol) and MS4A (50 mg) in DCE (1.0 mL) was added gold catalyst 18g (3.96 mg, 5.0 µmol) at room temperature. The reaction mixture was stirred at the same temperature for 15 min. The reaction mixture was concentrated in vacuo. The residue was dissolved in THF (0.5 mL) and DMF (0.5 mL)
and dropwised 1 M TBAF in THF (0.15 mL, 0.15 mmol) at room temperature. The reaction mixture was stirred at the same temperature for 3 h. The solution was quenched with sat. NH₄Cl aq. (2 mL) at room temperature and extracted with Et₂O (5 mL × 3). The combined organic layers were dried over MgSO₄, filtered, and concentrated under vacuo. The residue was purified by column chromatography on silica gel (AcOEt : Hexane = 1 : 50 to 1 : 30) and then fluorous silica gel column chromatography to give 42 (11.4 mg, 40.5 µmol, 81%). Characterization data were in agreement with previously reported values.¹⁹
9. References
10. NMR spectra
Bu sub-isocoumalin 13C

\[
\begin{align*}
\text{O} & \quad \text{Bu} \\
\text{C} & \quad \text{Co}_2\text{(CO)}_8
\end{align*}
\]
acetylene-reagent 1H

\begin{center}
\includegraphics[width=\textwidth]{acetylene-reagent-1H.pdf}
\end{center}
alkyne sdb-cycle 1H

![NMR Spectrogram](image-url)
alkyne seb-cycle 13C

![Chemical Structure of 11](image)

The diagram shows a 13C NMR spectrum with peaks at various ppm values.
C4F9metylester 13C

\[
\text{O} \quad \text{OMe}
\]

\[
S8 \quad \text{C}_4\text{F}_9
\]
C4F9methylester 19F

O

Me

S8

O

C4F9
C4F9carboxylic acid 13C

\[
\begin{align*}
S9
\end{align*}
\]
C4F9 carboxylic acid 19F

\[ \text{S9} \]
C4F9 reagent 1H

The diagram shows the 1H NMR spectrum of the C4F9 reagent. The spectrum is characterized by peaks at various chemical shifts, indicating the presence of different hydrogen atoms with distinct environments.

The chemical shifts are marked along the x-axis, typically ranging from 0.00 to 8.00 ppm. The peaks are labeled with their corresponding chemical shift values, such as 0.98, 1.12, 1.13, 1.17, 1.02, etc., indicating the position of protons in the molecule.

The molecular structure depicted shows the connectivity of the atoms within the molecule, with particular emphasis on the functional groups and the substitution pattern at the carbon and fluorine atoms.
C4F9 reagent 13C
C4F9reagent 19F

\[
\begin{align*}
\text{\textbf{C4F9reagent 19F}}
\end{align*}
\]

\[
\begin{align*}
\text{\textbf{C4F9reagent 19F}}
\end{align*}
\]
C4F9 isocoumalin 1H

![Chemical structure image]

69
C4F9isocoumalin 13C

12
Me ester 13C

![Graph showing chemical structure and data points]
C6F13methylester-19F

S11

\[ \text{C6F13methylester-19F} \]
COOH 19F

![Chemical Structure](image)
C6F13reagent 19F

\[
\begin{align*}
\text{O} & \quad \text{C}_2\text{(CO)}_6 \\
\text{C}_6\text{F}_{13} & \\
\text{2}
\end{align*}
\]
C6F13isocoumalin 13C

\[ \text{C6F13isocoumalin 13C} \]

\[ \begin{array}{c}
\text{14} \\
\text{O} \\
\text{C6F13}
\end{array} \]
C6F13isocoumalin 19F

![Diagram of C6F13isocoumalin 19F](image)
C8F17metyester 19F

\[
\begin{align*}
\text{S15}
\end{align*}
\]
C8F17isocoumalin 13C

\[
\text{S16}
\]

<table>
<thead>
<tr>
<th>Peak (ppm)</th>
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</tr>
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<td>77.000</td>
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<td>77.000</td>
</tr>
</tbody>
</table>

-0.036
F- AuNTf$_2$ 1H

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{F} & \quad \text{AuNTf}_2
\end{align*}
\]

18g
OTBS 13C

TBSO

\[\text{Ome}\]

40
S25
functionalization Me ether 13C
functionalization of iPr ether 13C

$$\text{(OC)}_3\text{Co}_2$$

$$\text{O} - \text{Pr}$$

19
functionalization of Ph ether 1H

\[
\text{(OC)\textsubscript{6}Co\textsubscript{2}}
\]

\[
\begin{array}{c}
\text{OPh} \\
\text{20}
\end{array}
\]
functionalization of Ph ether 13C

(OC)$_6$Co$_2$

20
functionalization Bn ether 1H

```
(OC)_6Co

21
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<th>Chem shift</th>
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</table>

**Functionalization Bn ether 13C**

![Chemical structure](image)
functionalization allyl 13C

```
(OC)_nCo_2

OMe

22
```
functionalization of MOM 1H

(OC)₆CO₂

MOMO

OMe

23
functionalization of MOM 13C

\[
(\text{OC})_6\text{Co}_2
\]

MOMO

\[
\text{OMe}
\]

23
functionalization TBS 1H

$\text{(OC)}_3\text{Co}_2$

TBSO

OMe

24
functionalization TBS 13C

![Chemical Structure](image)

**24**

**NMR Spectra**

- Peak at 199.810 ppm
- Peak at 153.886 ppm
- Peak at 136.265 ppm
- Peak at 131.854 ppm
- Peak at 129.014 ppm
- Peak at 128.767 ppm
- Peak at 125.516 ppm
- Peak at 125.294 ppm
- Peak at 123.245 ppm
- Peak at 121.204 ppm
- Peak at 112.422 ppm
- Peak at 96.390 ppm
- Peak at 77.321 ppm
- Peak at 77.000 ppm
- Peak at 76.679 ppm
- Peak at 73.535 ppm
- Peak at 65.066 ppm
- Peak at 55.561 ppm
- Peak at 29.051 ppm
- Peak at 25.990 ppm
- Peak at 18.484 ppm
- Peak at -5.178 ppm
functionalization TMS 1H

(OC)_6Co_2

S35
Boc functionalization

\[
\text{(OC)\text{\textsubscript{6}}Co\text{\textsubscript{2}}} \\
\begin{array}{c}
\text{N} \\
\text{Boc}
\end{array}
\begin{array}{c}
\text{OMe}
\end{array}
\]

26
functionalization of Fmoc 1H

\[(\text{OC})_6\text{Co}_2\]

Fmoc

\[\text{N}\]

\[\text{O} \text{Me}\]

27
Fmoc functionalization 13C

\[
\text{Fmoc functionalization 13C}
\]

\[
\text{Fmoc functionalization 13C}
\]

\[
\text{Fmoc functionalization 13C}
\]

\[
\text{Fmoc functionalization 13C}
\]
functionalization Br 1H

(OC)₆Co₂

Br

OMe

28
functionalization Br 13C

(OC)₅Co₂

Br

OMe

28
functionalization Ac 1H

(OC)₆Co₂

OMe

29
functionalization of Ac 13C

\[(\text{OC})_2\text{Co}_2\]

\[\text{OMe}\]

29
functionalization furan 1H

```
CO_2(CO)_6
```

1H NMR spectrum with peaks at various ppm values.
functionalization furan 13C
functionalization thiophene 1H

![Diagram of thiophene functionalization](image-url)
functionalization thiophene 13C

\[ \text{Diagram showing carbon-nitrogen structure with functionalization marks.} \]
functionalization of indole 1H

(OC)₅Co₂

32
functionalization of indole $^{13}$C
functionalization of 1-OMe-4 1H
functionalization of 1-OMe-4 13C

OMe

\[ \text{Co}_2(\text{CO})_6 \]

33a
functionalization of 1-OMe-2 1H

![Chemical Structure](image)

33b
functionalization of 1- OMe- 2 13C

33b
functionalization of 1-OMe-2,4 1H

\[
\begin{align*}
\text{OMe} & \quad \text{Co}_2(\text{CO})_6 \\
\text{Co}_2(\text{CO})_6 & \quad 33c
\end{align*}
\]
functionalization of 1-OMe-2,4 13C
functionalization of podophillotoxin 1H
pod functionalization 13C
Functionalization of guaiazulene 1H

\[(\text{OC})_3\text{Co}_2\]

38a
decomplexation of Me ether 1H
decomplexation of Me ether 13C

39
decomplexation of TBS 1H

\[
\begin{align*}
\text{HO} & \quad \text{OMe} \\
\text{41}
\end{align*}
\]
decomplexation of TBS 13C