FeCl₃ Promoted One-step Synthesis of Spiro[4.5]decane Derivatives

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1. General information

Ferric chloride was dried by refluxing the hydrated reagent with thionyl chloride. Excess thionyl chloride was removed in vacuo and the solid further dried and stored in a vacuum desiccator over potassium hydroxide. CHCl₃ was dried by distillation over CaH₂, and THF was dried by distillation over Na/K. Other chemicals were used as received, and all reactions conducted under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography. ¹H NMR, ¹³C NMR, HMBC and NOESY spectra were recorded on Bruker AM-400 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV, and signals were given in m/z with relative intensity (%) in brackets. HRMS data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer.

2. Preparation of Substrates 1a-1k and Analytic Data:

Preparation of Compound 1a

Under Ar atmosphere, 1.6 M t-BuLi (1.5 ml, 2.0 equiv.) was added to a solution of ethynylbenzene (204 mg, 2.0 equiv.) in dry THF (20 ml) at 78 °C. The reaction was warmed to -30°C and then ketones 3 (210 mg) in THF (1 ml) was added dropwise at -78 °C after 40 min. The resulting solution was stirred for 1 h at this temperature and warmed to 0°C for 2.5 h additionally. The mixture was quenched with water (30 ml), extracted with ethyl acetate (3×80 ml), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (4 : 1 P.E. : EtOAc) to afford 1a 216 mg as major isomer(70%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.43-7.40 (m, 2H), 7.32-7.29 (m, 3H), 4.37 (t, J=5.6Hz, 1H), 3.30 (s, 6H), 2.19-2.13 (m, 1H), 2.01-1.32 (m, 14H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 131.6, 128.2, 128.1, 122.9, 104.5, 90.8, 85.9, 78.5, 52.6, 52.5, 51.2,
41.8, 32.4, 31.5, 29.2, 28.1, 24.9, 20.7; **IR** $\nu$ (cm$^{-1}$): 1126, 2224, 2862, 2941, 3421; **MS** (EI) $m/z$ (%): 284 (2), 266, (<1), 253 (2), 235 (2), 209 (2), 157 (6), 129 (21), 115 (12), 91 (12), 75 (100), 71 (30), 55 (27), 41(29); **HRMS** (ESI): calcd for C$_{20}$H$_{28}$O$_3$ [M+NH$_4$]$^+$: 334.2377; Found 334.2375.

The major isomer of 1a-1k was believed to have a cis-structure.$^3$ The minor isomer of 1a-1k was not purified.

**Preparation of Compound 1b**

![chemstructure]

The compound 1b (104mg, 42% yield) was prepared from ketones 3 (142 mg) and 1-ethynyl-2-(trifluoromethyl)benzene (220mg, 2.0 equiv) according to the above procedure for the preparation of 1a. **$^1$H NMR** (400 MHz, CDCl$_3$, ppm): $\delta$ 7.63 (d, $J$=8Hz, 1H), 7.57 (d, $J$=7.6Hz, 1H), 7.48 (t, $J$=7.2Hz, 1H), 7.39 (t, $J$=7.6Hz, 1H), 4.36 (t, $J$=6Hz, 1H), 3.30 (s, 6H), 2.23-2.17 (m, 1H), 2.02-1.93 (m, 3H), 1.80-1.38 (m, 11H); **$^{13}$C NMR** (100 MHz, CDCl$_3$, ppm): $\delta$ 133.9, 131.3, 127.9, 125.8, 125.7, 124.8, 122.1, 121.2, 104.5, 96.8, 81.9, 52.5, 52.4, 51.3, 41.7, 32.3, 31.1, 29.0, 28.1, 24.8, 20.5; **IR** $\nu$ (cm$^{-1}$): 1132, 1318, 2226, 2862, 2941, 3402; **MS** (EI) $m/z$ (%): 352 (<1), 334 (<1), 321 (<1), 303 (2), 239 (1), 235 (2), 205 (3), 169 (4), 151 (4), 97 (6), 75 (100), 71(29), 55 (14), 41 (23); **HRMS** (ESI): calcd for C$_{21}$H$_{27}$O$_3$F$_3$ [M+NH$_4$]$^+$: 402.2251; Found 402.2246.

**Preparation of Compound 1c**

![chemstructure]

The compound 1c (54mg, 48% yield) was prepared from ketones 3 (72 mg) and 1-ethynyl-4-methylbenzene (78mg, 2.0 equiv) according to the above procedure for the preparation of 1a. **$^1$H NMR** (400 MHz, CDCl$_3$, ppm): $\delta$ 7.30 (d, $J$=8Hz, 2H), 7.10 (d, $J$=8Hz, 2H), 4.36 (t, $J$=5.6Hz,
1H), 3.31 (s, 6H), 2.34 (s, 3H), 2.18-1.32 (m, 16H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 138.3, 131.5, 129.0, 119.8, 104.5, 90.1, 86.1, 78.5, 52.6, 52.5, 51.2, 41.8, 32.4, 31.6, 29.2, 28.1, 21.4, 20.8; IR ν (cm$^{-1}$): 1126, 2223, 2862, 2941, 3425; MS (EI) m/z (%): 298 (2), 267 (2), 249 (1), 223 (2), 195 (2), 158 (9), 143 (16), 115 (12), 105 (10), 91 (8), 75 (100), 71 (28), 55 (34), 41 (33); HRMS (ESI): calcd for C$_{21}$H$_{30}$O$_3$ [M+NH$_4$]$^+$: 348.2533; Found 348.2538.

Preparation of Compound 1d

\[
\text{HO} \quad \text{OMe} \\
\text{CH}_3 \\
\text{1d}
\]

The compound 1d (68mg, 59% yield) was prepared from ketones 3 (74 mg) and 1-ethynyl-4-methylbenzene (71mg, 2.0 equiv) according to the above procedure for the preparation of 1a. $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.24-7.11 (m, 4H), 4.37 (t, $J=5.6$Hz, 1H), 3.31 (s, 6H), 2.33 (s, 3H), 2.19-1.37 (m, 16H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 137.9, 132.2, 129.1, 128.7, 128.1, 122.7, 104.5, 90.4, 86.1, 78.5, 52.6, 52.5, 51.2, 41.8, 32.4, 31.5, 29.2, 28.1, 24.9, 21.2, 20.8; IR ν (cm$^{-1}$): 1125, 2224, 2860, 3386; MS (EI) m/z (%): 298 (4), 267 (3), 249 (3), 223 (4), 195 (3), 158 (16), 143 (26), 115 (13), 75 (100), 71 (31), 55 (29), 41 (31); HRMS (ESI): calcd for C$_{21}$H$_{30}$O$_3$ [M+NH$_4$]$^+$: 348.2533; Found 348.2529.

Preparation of Compound 1e

\[
\text{HO} \quad \text{CH}_3 \\
\text{1e}
\]

The compound 1e (63mg, 54% yield) was prepared from ketones 3 (75 mg) and 1-ethynyl-4-methylbenzene (71mg, 2.0 equiv) according to the above procedure for the preparation of 1a. $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.30 (d, $J=8.4$Hz, 2H), 7.10 (d, $J=8.0$Hz, 2H), 4.37 (t, $J=5.6$Hz, 1H), 3.31 (s, 3H), 3.30 (s, 3H), 2.34 (s, 3H), 2.21-1.34 (m, 16H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 138.2, 131.5, 129.0, 119.8, 104.5, 90.1, 86.0, 78.5, 52.6, 52.5, 51.2, 41.8, 32.4, 31.5,
Preparation of Compound 1f

The compound 1f (73mg, 48% yield) was prepared from ketones 3 (102mg) and oct-1-yn-1e (126mg, 2.0 equiv) according to the above procedure for the preparation of 1a. 

$^1$H NMR (400 MHz, CDCl$_3$, ppm): \( \delta \) 4.36 (t, \( J=6.0 \text{Hz} \), 1H), 3.31 (s, 6H), 2.21 (t, \( J=6.8 \text{Hz} \), 2H), 2.04-1.21 (m, 23H), 0.89 (t, \( J=6.8 \text{Hz} \), 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): \( \delta \) 104.5, 86.5, 81.7, 78.2, 52.6, 52.5, 50.9, 41.9, 32.5, 31.5, 31.3, 29.1, 28.8, 28.5, 28.1, 24.9, 22.6, 20.6, 18.7, 14.0; IR \( \nu \) (cm$^{-1}$): 2232, 2860, 3434; MS (EI) m/z (%): 292 (1), 275 (1), 243 (4), 133 (4), 75 (100), 41 (44); HRMS (ESI): calcd for C$_{20}$H$_{36}$O$_3$ [M+ NH$_4$]$^+$: 342.3003; Found 342.3001.

Preparation of Compound 1g

The compound 1g (90mg, 45% yield) was prepared from ketones 3 (140mg) and hept-1-yne (126mg, 2.0 equiv) according to the above procedure for the preparation of 1a. 

$^1$H NMR (400 MHz, CDCl$_3$, ppm): \( \delta \) 4.36 (t, \( J=6.0 \text{Hz} \), 1H), 3.32 (s, 6H), 2.21 (t, \( J=6.8 \text{Hz} \), 2H), 2.05-1.26 (m, 21H), 0.90 (t, \( J=6.8 \text{Hz} \), 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): \( \delta \) 104.5, 86.5, 81.6, 78.2, 52.6, 52.5, 50.9, 41.9, 32.4, 31.5, 31.0, 29.0, 28.5, 28.1, 24.9, 22.1, 20.5, 18.7, 14.0; IR \( \nu \) (cm$^{-1}$): 2236, 2861, 3434; MS (EI) m/z (%): 278 (<1), 260 (<1), 229 (2), 140 (14), 75 (100), 71 (41), 55 (42), 41 (50); HRMS (ESI): calcd for C$_{19}$H$_{34}$O$_3$ [M+ NH$_4$]$^+$: 328.2846; Found 328.2844.

Preparation of Compound 1h
The compound 1h (55mg, 56% yield) was prepared from ketones 3 (50mg) and 4 (114mg, 2.1 equiv) according to the above procedure for the preparation of 1a. 

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm): } \delta 4.36 (t, J=6.0Hz, 1H), 3.63 (t, J=6.0Hz, 2H), 3.32 (s, 6H), 2.24 (t, J=6.8Hz, 2H), 2.04-1.22 (m, 19H), 0.89 (s, 9H), 0.05 (s, 6H); \text{13C NMR (100 MHz, CDCl}_3, \text{ ppm): } \delta 104.5, 86.3, 81.8, 78.2, 62.6, 52.6, 52.6, 50.8, 41.9, 32.5, 31.9, 31.5, 29.0, 28.1, 26.0, 25.3, 24.9, 20.5, 18.5, 18.3, -5.3; \text{IR } v \text{ (cm}^{-1}) : 2239, 2858, 3363; \text{MS (EI) } m/z \text{ (%): } 408 (<1), 394 (<1), 363 (<1), 337 (4), 305 (4), 213 (17), 171 (14), 131 (13), 75 (100), 71 (21), 55 (19), 41 (30); \text{HRMS (ESI): calcd for C}_{24}H_{46}O_4Si [M+ Na]^+ : 449.3058; Found 449.3061. \]

**Preparation of Compound 1i**

\[ \text{HO} \]

Under Ar atmosphere, to a 50 ml three necked RBF containing the Grignard reagent, prepared in Et}_2O (20 ml) from magnesium (65 mg, 2.8 equiv) and bromobenzene (300 mg, 2.0 equiv), was added dropwise a solution of ketones 3 (202 mg) in Et}_2O (5 ml) at 0°C. Then the contents were refluxed for 2 h. After cooling, the mixture was poured onto an ice-cold saturated NH}_4Cl solution and extracted with Et}_2O (3×100 ml). The organic layer was washed with water and a saturated brine solution, dried over Na}_2SO}_4, and concentrated. The concentrate was purified by flash silica gel chromatography (8:1 P.E.: EtOAc). 1i was obtained 194 mg (70%). 

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm): } \delta 7.46-7.21 (m, 5H), 4.28 (t, J=6.0Hz, 1H), 3.27 (s, 6H), 2.12-1.12 (m, 15H); \text{13C NMR (100 MHz, CDCl}_3, \text{ ppm): } \delta 146.1, 128.1, 126.4, 124.9, 104.4, 84.1, 52.6, 50.9, 43.7, 32.3, 29.7, 28.4, 27.9, 24.8, 21.7; \text{IR } v \text{ (cm}^{-1}) : 701; 1051, 2858, 3428; \text{MS (EI) } m/z \text{ (%): } 274 (<1), 260 (1), 228 (5), 207 (19), 192 (7), 164 (13), 133 (23), 105 (55), 75 (100), 55 (47), 41 (50); \text{HRMS (ESI): calcd for C}_{18}H_{26}O_3 [M+NH}_4]^+ : 310.2377; Found 310.2381. \]

**Preparation of Compound 1j**
The compound 6 was prepared from ketones 3 and compound 5 according to the above procedure for the preparation of 1i. TBAF (150 mg) was added to a solution of compound 6 (85 mg) in THF (5 ml) at room temperature. The solution was stirred for 10 h. Water was added and the product was extracted into diethyl ether, the solution dried (MgSO₄) and evaporated. The crude product (57 mg), DMAP (31 mg) and 4-nitrobenzoyl chloride (37 mg) were dissolved in dry dichloromethane (10 ml) and stirred at ambient temperature overnight. Diethyl ether was added and the mixture was washed with saturated aqueous NaHCO₃, brine, the organic solution dried (MgSO₄) and evaporated. The concentrate was purified by flash silica gel chromatography (2:1 P.E.: EtOAc). 1j was obtained 75 mg (91%).

6: ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.31 (d, J=8.4 Hz, 2H), 6.81 (d, J=8.0 Hz, 2H), 4.31 (t, J=6.0 Hz, 1H), 3.29 (s, 6H), 2.08-1.16 (m, 16H), 1.00 (s, 9H), 0.22 (s, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 154.1, 138.7, 126.0, 119.5, 104.4, 83.8, 52.5, 52.5, 50.5, 43.5, 32.3, 29.6, 28.4, 27.9, 25.7, 24.8, 21.5, 18.2, -4.4; IR ν (cm⁻¹): 839, 917, 1258, 1508, 2859, 3468; MS (EI) m/z (%): 422 (<1), 404 (3), 390 (7), 373 (18), 359 (12), 341 (36), 250 (91), 193 (27), 75 (100); HRMS (ESI): calcd for C₂₅H₄₂O₄Si [M+ Na⁺]: 445.2745; Found 445.2751.

1j: ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.40-8.35 (m, 4H), 7.53 (d, J=8.8 Hz, 2H), 7.20 (d, J=8.4 Hz, 2H), 4.30 (t, J=6.0 Hz, 1H), 3.28 (s, 6H), 2.13-1.14 (m, 16H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.3, 150.9, 149.0, 144.4, 135.0, 131.2, 126.4, 123.7, 120.8, 104.4, 83.8, 52.6, 52.5, 51.0, 43.7, 32.3, 29.6, 28.4, 27.9, 24.8, 21.6; IR ν (cm⁻¹): 1079, 1273, 1527, 1738, 2861, 3351; MS (EI) m/z (%): 425 (<1), 407 (1), 393 (1), 376 (2), 285 (20), 150 (100), 75 (88); HRMS (ESI): calcd for C₂₅H₃₁NO₇ [M+ NH₄⁺]: 475.2439; Found 475.2446.
Preparation of Compound 1k

The compound 1k (54mg, 61% yield) was prepared from ketones 3 (78mg) and ethyl bromide (64mg, 2.0 equiv) according to the above procedure for the preparation of 1i. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 4.36 (t, \(J=6.0\)Hz, 1H), 3.31 (t, \(J=6.0\)Hz, 2H), 1.91-1.83 (m, 1H), 1.77-1.15 (m, 16H), 0.93 (t, \(J=7.6\)Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 104.5, 82.7, 52.6, 52.5, 47.8, 37.9, 32.4, 31.8, 30.0, 28.5, 28.4, 24.9, 20.9, 8.9; IR \(\nu\) (cm\(^{-1}\)): 1126, 2860, 3487; MS (EI) \(m/z\) (%): 212 (<1), 195 (<1), 180 (<1), 163 (7), 108 (18), 95 (9), 75 (100), 71 (56), 57 (37), 41 (37); HRMS (ESI): calcd for C\(_{14}\)H\(_{28}\)O\(_3\) [M+ Na\(^+\)]: 267.1931; Found 267.1934.

3. Synthesis of Products 2a-2k and Analytic Data:

General Procedure for cyclization:

Substrates (0.2mmole) in CH\(_2\)Cl\(_2\) (1ml) were added dropwise to the solution of FeCl\(_3\) (1.0 equiv) in CH\(_2\)Cl\(_2\) (4ml) at 0\(^\circ\)C. While the substrates were disappeared by TLC-detected, the mixture was quenched with water (20 ml), extracted with CH\(_2\)Cl\(_2\) (3×30 ml), dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired products 2a-2j.

Synthesis of 2a

Following the General Procedure described above, the title compound 2a (65% yield) was isolated after 20 min. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 7.47-7.45 (m, 2H), 7.33-7.29 (m, 3H), 6.15 (t, \(J=2.8\)Hz, 1H), 3.39 (s, 3H), 3.36-3.32 (dd, \(J=4.4\)Hz, \(J=11.2\)Hz), 2.47-2.41 (m, 2H), 2.09-2.01 (m, 2H), 1.77-1.21 (m, 8H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 137.3, 131.7, 131.5, 128.3, 127.9, 123.8, 91.7, 85.5, 82.4, 57.5, 57.1, 35.2, 31.4, 27.9, 27.1, 24.7, 22.6; IR \(\nu\) (cm\(^{-1}\)): 1100, 1447, 2199, 2855, 2929; MS (EI)
**Synthesis of 2b**

Following the General Procedure described above, the title compound 2b (58% yield) was isolated at room temperature after 20 min. **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.66-7.60 (m, 2H), 7.48 (t, J=7.6Hz, 1H), 7.37 (t, J=7.6Hz, 1H), 6.23 (t, J=2.8Hz, 1H), 3.40 (t, J=6Hz, 1H), 3.36 (s, 6H), 2.50-2.44 (m, 2H), 2.13-1.19 (m, 10H); **13C NMR** (100 MHz, CDCl₃, ppm): δ 139.1, 134.0, 131.4, 131.3, 127.5, 125.8, 125.7, 125.6, 125.0, 122.3, 122.1, 91.5, 87.5, 82.1, 57.3, 57.2, 53.5, 37.2, 27.9, 27.1, 24.7, 22.6; **IR** ν (cm⁻¹): 1132, 1317, 1405, 2201, 2857, 2930; **MS** (EI) m/z (%): 334 (M⁺, 3), 302 (41), 234 (24), 173 (39), 165 (13), 145 (26), 121 (31), 91 (34), 77 (27), 41 (100); **HRMS** (ESI): calcd for C₂₀H₂₁OF₃ [M+NH₄]⁺: 352.1883; Found 352.1890.

**Synthesis of 2c**

Following the General Procedure described above, the title compound 2c (54% yield) was isolated after 20 min. **1H NMR** (400 MHz, CDCl₃, ppm): δ 7.35 (d, J=8Hz, 2H), 7.12 (d, J=8Hz, 2H), 6.12 (t, J=2.8Hz, 1H), 3.39 (s, 3H), 3.35-3.32 (dd, J=4Hz, J=7.2Hz, 1H), 2.45-2.41 (m, 2H), 2.35 (m, 3H), 2.11-2.01 (m, 2H), 1.77-1.18 (m, 8H); **13C NMR** (100 MHz, CDCl₃, ppm): δ 138.0, 136.9, 131.8, 131.4, 129.0, 120.6, 91.8, 84.7, 82.3, 57.5, 57.0, 35.1, 31.3, 27.9, 27.1, 24.7, 22.6, 21.5; **IR** ν (cm⁻¹): 1100, 1449, 2198, 2856, 2928; **MS** (EI) m/z (%): 280 (M⁺, 24), 248 (75), 178 (45), 165 (60), 115 (16), 91 (40), 77 (24), 41 (100); **HRMS** (ESI): calcd for C₂₀H₂₄O [M+H]⁺: 281.1900; Found 281.1896.

**Synthesis of 2d**
Following the General Procedure described above, the title compound 2d (46% yield) was isolated after 20 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.28 (s, 2H), 7.21 (t, $J=7.2$Hz, 1H), 7.11 (d, $J=7.2$Hz, 1H), 6.13 (t, $J=2.8$Hz, 1H), 3.39 (s, 3H), 3.35-3.32 (dd, $J=4$Hz, $J=7.2$Hz, 1H), 2.47-2.41 (m, 2H), 2.34 (s, 3H), 2.10-2.01 (m, 2H), 1.77-1.18 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 137.9, 137.2, 131.7, 128.8, 128.6, 128.2, 123.5, 91.9, 85.1, 82.4, 57.6, 57.1, 35.2, 31.4, 27.9, 27.1, 24.7, 22.6, 21.2; IR $\nu$ (cm$^{-1}$): 1100, 2197, 2856, 2928; MS (EI) m/z (%): 280 (M$^+$, 25), 248 (100), 178 (34), 165 (30), 115 (17), 91 (15), 77 (10), 41 (29); HRMS (ESI): calcd for C$_{20}$H$_{24}$O [M+H]$^+$: 281.1900; Found 281.1904.

**Synthesis of 2e**

Following the General Procedure described above, the title compound 2e (47% yield) was isolated after 20 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.35 (d, $J=8.4$Hz, 2H), 7.12 (d, $J=8.0$Hz, 2H), 6.12 (t, $J=2.8$Hz, 1H), 3.39 (s, 3H), 3.35-3.32 (dd, $J=4$Hz, $J=7.2$Hz, 1H), 2.45-2.41 (m, 2H), 2.35 (s, 3H), 2.11-2.01 (m, 2H), 1.78-1.17 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 138.0, 136.9, 131.8, 131.4, 129.0, 120.6, 91.8, 84.7, 82.3, 57.5, 57.1, 35.2, 31.3, 27.9, 27.1, 24.7, 22.6, 21.5; IR $\nu$ (cm$^{-1}$): 1101, 2198, 2856, 2928; MS (EI) m/z (%): 280 (M$^+$, 26), 248 (100), 178 (29), 165 (24), 115 (13), 91 (12), 77 (7), 41 (18); HRMS (ESI): calcd for C$_{20}$H$_{24}$O [M+H]$^+$: 281.1900; Found 281.1907.

**Synthesis of 2f**

Following the General Procedure described above, the title compound 2f (58% yield) was isolated after
11 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 5.94 (t, $J$=2.8Hz, 1H), 3.36 (s, 3H), 3.27-3.23 (dd, $J$=4.0Hz, $J$=11.2Hz, 1H), 2.37-2.34 (m, 4H), 2.04-1.97 (m, 2H), 1.76-1.17 (m, 16H), 0.90 (t, $J$=6.8Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 135.0, 132.2, 92.6, 82.2, 76.2, 57.4, 56.7, 35.0, 31.3, 30.9, 28.9, 28.6, 27.8, 26.9, 24.8, 22.6, 22.5, 19.5, 14.1; IR $\nu$ (cm$^{-1}$): 1100, 1629, 2206, 2858; MS (EI) m/z (%): 274 (M$^-$, 5), 242 (33), 199 (10), 157 (21), 117 (49), 91 (57), 41 (100); HRMS (ESI): calcd for C$_{19}$H$_{30}$O [M+H]$^+$: 275.2369; Found 275.2367.

Synthesis of 2g

Following the General Procedure described above, the title compound 2g (50% yield) was isolated after 15 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 5.94 (t, $J$=2.4Hz, 1H), 3.36 (s, 3H), 3.26-3.23 (dd, $J$=4.2Hz, $J$=11.2Hz, 1H), 2.37-2.34 (m, 4H), 2.03-1.97 (m, 2H), 1.76-1.14 (m, 14H), 0.91 (t, $J$=7.2Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 135.0, 132.2, 92.6, 82.2, 76.2, 57.4, 56.7, 35.0, 31.1, 30.9, 28.7, 27.8, 26.9, 24.8, 22.6, 22.2, 19.4, 14.0; IR $\nu$ (cm$^{-1}$): 1100, 1565, 2857, 2929; MS (EI) m/z (%): 260 (M$^-$, 12), 228 (61), 129 (84), 91 (81), 77 (44), 41 (100); HRMS (ESI): calcd for C$_{18}$H$_{28}$O [M+NH$_4$]$^+$: 278.2478; Found 278.2475.

Synthesis of 2h

Following the General Procedure described above, the title compound 2h (26% yield) was isolated after 15 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 5.94 (t, $J$=2.4Hz, 1H), 3.64 (t, $J$=6.0Hz, 2H), 3.36 (s, 3H), 3.26-3.22 (dd, $J$=4.4Hz, $J$=11.6Hz, 1H), 2.39-2.35 (m, 4H), 2.04-1.17 (m, 14H), 0.91 (t, $J$=7.2Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 135.1, 132.2, 92.3, 82.2, 77.2, 62.7, 57.4, 56.7, 35.1, 32.0, 30.9, 27.8, 26.9, 25.9, 25.5, 24.8, 22.5, 19.3, 18.3, -5.3; IR $\nu$ (cm$^{-1}$): 1102, 1565, 1726, 2198, 2857, 2930; MS (EI) m/z (%): 376 (M$^-$, 1), 319 (3), 287 (13), 244 (7), 213 (61), 171 (98), 115 (42), 91 (52), 75 (100), 41 (75); HRMS (ESI): calcd for C$_{23}$H$_{40}$O$_2$Si [M+NH$_4$]$^+$: 394.3136; Found 394.3128.

Synthesis of 2i
Following the General Procedure described above, the title compound 2i (64% yield) was isolated after 20 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): 7.35-7.23 (m, 5H), 5.69 (t, J=2.4Hz, 1H), 3.24 (s, 3H), 3.06-3.02 (dd, J=4Hz, J=10.8Hz, 1H), 2.42-2.37 (m, 2H), 2.20-1.13 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 150.0, 138.5, 129.3, 129.2, 128.8, 127.7, 126.6, 126.1, 81.4, 57.2, 55.7, 34.7, 30.0, 28.2, 26.7, 24.6, 22.8; IR ν (cm$^{-1}$): 1101, 1446, 1598, 1727, 2855, 2930; MS (EI) m/z (%): 242 (M$^+$, 38), 210 (100), 169 (41), 141 (84), 115 (91), 91 (96), 58 (90), 41 (85); HRMS (ESI): calcd for C$_{17}$H$_{22}$O [M+ Na$^+$]: 265.1563; Found 265.1570.

**Synthesis of 2j**

Following the General Procedure described above, the title compound 2j (48% yield) was isolated after 40 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 8.40-8.35 (m, 4H), 7.31 (d, J=8.8Hz, 2H), 7.19 (d, J=8.8Hz, 2H), 5.72 (t, J=2.4Hz, 1H), 3.24 (s, 3H), 3.05-3.01 (dd, J=4Hz, J=10.8Hz, 1H), 2.41-2.38 (m, 2H), 2.18-2.13 (m, 1H), 2.05-1.14 (m, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 163.4, 150.9, 149.3, 149.0, 136.8, 135.0, 131.3, 130.0, 123.7, 120.5, 81.3, 57.3, 55.7, 34.6, 30.0, 28.2, 26.6, 24.5, 22.7; IR ν (cm$^{-1}$): 1079, 1269, 1521, 1745, 2852, 2436; MS (EI) m/z (%): 407 (4), 375 (16), 150 (100), 104 (39), 76 (23); HRMS (ESI): calcd for C$_{24}$H$_{25}$NO$_5$ [M+ NH$_4$]$^+$: 425.2071; Found 425.2075.

**Synthesis of 2k**

Following the General Procedure described above, the title compound 2k (22% yield) was isolated after 30 min. $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 5.38 (t, J=2.4Hz, 1H), 3.30 (s, 3H), 3.11-3.07 (dd,
$J$=4.0Hz, $J$=10.8Hz, 1H), 2.24-1.16 (m, 14H), 1.11 (t, $J$=7.6Hz 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 150.7, 122.2, 81.9, 56.5, 55.9, 34.1, 29.3, 28.2, 27.1, 24.9, 22.7, 19.2, 12.1; IR $\nu$ (cm$^{-1}$): 1069, 1652, 2853, 2921; MS (EI) $m/z$ (%): 194 (M$^+$, 7), 162 (13), 121 (18), 91 (37), 75 (75), 41 (100); HRMS (ESI): calcld for C$_{13}$H$_{22}$O [M+ H]$^+$: 195.1743; Found 195.1738.

4. References


5. $^1$H and $^{13}$C NMR Spectra for 1a-1k and 2a-2k: