Electronic Supplementary Information

Strong Lewis acid of air-stable cationic titanocene perfluoroalkyl(aryl)sulfonate complexes as highly efficient and recyclable catalysts for C-C bond forming reactions

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Experiment Section

Typical procedure for the Strecker reaction of benzaldehyde (5a) with aniline (6a) and trimethylsilyl cyanide (7a) catalyzed by 1·THF:

A mixture of PhCHO (106 mg, 1.0 mmol), PhNH₂ (93 mg, 1.0 mmol), trimethylsilylcyanide (119 mg, 1.2 mmol) and Catalyst 1·THF (9 mg, 0.01 mol) was stirred at room temperature until the reaction was complete. It was subject to evaporation in vacuum at room temperature, the residue was dissolved in CH₂Cl₂ (10 ml × 3) and the catalyst was collected by means of filtration for the next cycle of reaction. To the filtrate, after evaporation of the solvent a pale yellow solid mixture was obtained. The products 8a were isolated by silica gel column chromatography on silica gel (petroleum ether:EtOAc = 8:1) in yield 96% (199 mg) as pale yellow solid. Aldehydes and amines and nucleophiles trimethylsilyl cyanide are commercially available. 8a-8l, 8n-8p are known compounds [S1-S4] and 8m is new compound. The spectra data are summarized as follows:

2-Anilino-2-phenylacetonitrile (8a): Light-yellow solid, mp: 85-86 °C; 1H NMR (400 MHz, CDCl₃): δ 7.57 (d, J = 5.6 Hz, 2H, ArH), 7.43 (d, J = 3.0 Hz, 3H, ArH), 7.25 (t, J = 8.0 Hz, 2H, ArH), 6.88 (t, J = 7.2 Hz, 1H, ArH), 6.75 (d, J = 7.6 Hz, 2H, ArH), 5.39 (d, J = 8.4 Hz, 1H, CH), 4.06 (d, J = 8.4 Hz, 1H, NH); 13C NMR (100 MHz, CDCl₃): δ 144.74, 133.98, 129.62, 129.59, 129.38, 127.31, 120.29, 118.31, 114.21, 50.21; MS(70 ev): m/z = 208.1 [M⁺].

2-Anilino-2-(p-methylphenyl)acetonitrile (8b): Light-yellow solid, mp: 77-78 °C; 1H NMR (400 MHz, CDCl₃): δ 7.47 (d, J = 8.0 Hz, 2H, ArH), 7.27 (t, J = 7.8 Hz, 4H, ArH), 6.89 (t, J = 7.4 Hz, 1H, ArH), 6.77 (d, J = 8.0 Hz, 2H, ArH), 5.38 (d, J = 8.0 Hz, 1H, CH), 3.99 (d, J = 8.4 Hz, 1H, NH), 2.39 (s, 3H, CH₃); 13C NMR (100 MHz, CDCl₃): δ 144.76, 139.62, 131.03, 129.99, 129.58, 127.19, 120.21, 118.37, 114.11, 49.99, 21.20; MS(70 ev): m/z = 222.2 [M⁺].

2-Anilino-2-(p-methoxyphenyl)acetonitrile (8c): Light-yellow solid, mp: 94-95 °C; 1H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 8.8 Hz, 2H, ArH), 7.27 (t, J = 8.0 Hz, 2H, ArH), 6.96 (d, J = 8.8 Hz, 2H, ArH), 6.90 (t, J = 7.4 Hz, 1H, ArH), 6.77 (d, J = 8.0 Hz, 2H, ArH), 5.36 (d, J = 8.4 Hz, 1H, CH), 4.00 (s, 1H, NH), 3.83 (s, 3H, OCH₃); 13C
NMR (100 MHz, CDCl₃): δ 160.45, 144.78, 129.58, 128.66, 125.98, 120.19, 118.49, 114.66, 114.13, 55.46, 49.67; MS(70 ev): m/z = 238.1 [M⁺].

2-Anilino-2-(o-fluorophenyl)acetonitrile (8d): Light-yellow solid, mp: 116-117 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.61 (t, J = 7.4 Hz, 1H, ArH), 7.44-7.39 (m, 1H, ArH), 7.28-7.20 (m, 3H, ArH), 7.14 (t, J = 9.2 Hz, 1H, ArH), 6.89 (t, J = 7.2 Hz, 1H, ArH), 6.77 (d, J = 8.0 Hz, 2H, ArH), 5.60 (d, J = 8.4 Hz, 1H, CH), 4.09 (d, J = 8.4 Hz, 1H, N); ¹³C NMR (100 MHz, CDCl₃): δ 161.36, 158.88, 144.48, 131.72, 129.62, 129.01, 125.09, 121.69, 120.53, 117.70, 116.36, 114.42, 44.73; MS(70 ev): m/z = 226.1 [M⁺].

2-Anilino-2-(p-chlorophenyl)acetonitrile (8e): Light-yellow solid, mp: 96-98 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, J = 7.6 Hz, 2H, ArH), 7.38 (d, J = 8.4 Hz, 2H, ArH), 7.24 (t, J = 7.2 Hz, 2H, ArH), 6.89 (t, J = 7.4 Hz, 1H, ArH), 6.73 (d, J = 8.0 Hz, 2H, ArH), 5.37 (d, J = 8.4 Hz, 1H, CH), 4.09 (d, J = 8.4 Hz, 1H, NH); ¹³C NMR (100 MHz, CDCl₃): δ 144.46, 135.55, 132.49, 129.65, 129.54, 128.64, 120.55, 117.97, 114.37, 49.62; MS(70 ev): m/z = 242.1 [M⁺].

2-Anilino-2-(p-bromophenyl)acetonitrile (8f): Light-yellow solid, mp: 86-88 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, J = 8.8 Hz, 2H, ArH), 7.46 (d, J = 8.4 Hz, 2H, ArH), 7.26 (t, J = 7.8 Hz, 2H, ArH), 6.91 (t, J = 7.4 Hz, 1H, ArH), 6.74 (d, J = 8.0 Hz, 2H, ArH), 5.38 (d, J = 8.4 Hz, 1H, CH), 4.06 (d, J = 8.4 Hz, 1H, NH); ¹³C NMR (100 MHz, CDCl₃): δ 144.38, 132.98, 132.52, 129.64, 128.89, 123.74, 120.60, 117.81, 114.34, 49.72; MS(70 ev): m/z = 286.0 [M⁺].

2-(N-Anilino)-2-cinnamylacetonitrile (8g): Pale yellow solid, mp 109-110 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.39-7.25 (m, 5H, ArH), 7.05 (d, J = 16.0 Hz, 1H, ArH), 6.91 (t, J = 7.4 Hz, 1H, ArH), 6.78 (d, J = 8.0 Hz, 2H, ArH), 6.28 (dd, J = 16.0 Hz, 4.8 Hz, 1H, ArH), 5.07 (q, J = 8.4 Hz, 1H, CH), 3.91 (d, J = 9.2 Hz, 1H, NH); ¹³C NMR (100 MHz, CDCl₃): δ 144.46, 135.16, 134.93, 129.64, 128.98, 128.88, 126.97, 120.97, 120.44, 117.70, 114.42, 47.80; MS(70 ev): m/z = 234.0 [M⁺].

2-(furan-2-yl)-2-(phenylamino)acetonitrile (8h): Pale brown solid, mp 69-70 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.48 (s, 1H, ArH), 7.28 (t, J = 7.6 Hz, 2H, ArH), 6.92 (t, J = 7.4 Hz, 1H, ArH), 6.78 (d, J = 8.0 Hz, 2H, ArH), 6.58 (s, 1H, ArH), 6.42 (d, J = 1.2 Hz, 1H, ArH), 5.48 (d, J = 9.2 Hz, 1H, CH), 4.22 (d, J = 7.6 Hz, 1H, NH); ¹³C NMR (100 MHz, CDCl₃): δ 146.08, 144.11, 144.02, 129.63, 120.70, 116.57, 114.53, 110.97, 109.69, 44.39.

2-(phenylamino)pentanenitrile (8i): Colorless oil, ¹H NMR (400 MHz, CDCl₃): δ 7.25 (t, J = 7.0 Hz, 2H, ArH), 6.87 (t, J = 7.0 Hz, 1H, ArH), 6.71 (d, J = 7.6 Hz, 2H, ArH), 4.21 (t, J = 6.8 Hz, 1H, CH), 3.65 (s, 1H, NH), 1.95-1.88 (m, 2H, CH₂), 1.66-1.58 (m, 2H, CH₂), 1.05 (d, J = 7.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 144.84, 129.57, 119.92, 119.61, 114.03, 45.63, 35.48, 18.96, 13.45; MS(70 ev): m/z = 174.1 [M⁺].

2-phenyl-2-(p-methyl-phenylamino)acetonitrile (8j): Light-yellow solid, mp: 82-83 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, J = 6.8 Hz, 2H, ArH), 7.42 (d, J = 5.6 Hz, 3H, ArH), 7.06 (d, J = 7.6 Hz, 2H, ArH), 6.67 (d, J = 7.6 Hz, 2H, ArH), 5.36 (s, 1H, CH), 3.92 (s, 1H, NH), 2.26 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 142.45, 134.16, 130.09, 129.73, 129.48, 129.32, 127.29, 118.43, 114.52, 50.67, 20.52; MS(70 ev): m/z = 222.2 [M⁺].

2-phenyl-2-(p-chlorophenylamino)acetonitrile (8k): Light-yellow solid, mp: 107-109 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.54 (t, J = 3.6 Hz, 2H, ArH), 7.42(t, J = 3.2 Hz, 3H, ArH), 7.18 (d, J = 8.8 Hz, 2H, ArH), 6.66 (d, J =
8.8 Hz, 2H, ArH), 5.35 (s, 1H, CH), 4.14 (s, 1H, NH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.29, 133.54, 129.70, 129.48, 129.43, 127.24, 125.07, 118.03, 115.44, 50.26; MS(70 ev): m/z = 242.1 [M$^+$].

2-phenyl-2-(8-quinolinylamino)acetonitrile (8l): Colorless oil, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.68 (s, 1H, ArH), 8.06 (d, $J$ = 8.0 Hz, 1H, ArH), 7.65 (d, $J$ = 7.2 Hz, 1H, ArH), 7.42 (t, $J$ = 7.2 Hz, 4H, ArH), 7.35 (q, $J$ = 8.4 Hz, 1H, ArH), 7.32 (t, $J$ = 7.8 Hz, 1H, ArH), 7.22 (d, $J$ = 8.0 Hz, 1H, ArH), 6.90 (d, $J$ = 7.6 Hz, 1H, ArH), 6.66 (d, $J$ = 8.0 Hz, 1H, CH), 5.62 (d, $J$ = 8.0 Hz, 1H, NH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.69, 141.36, 138.39, 136.20, 133.87, 133.39, 129.53, 129.41, 128.59, 127.38, 121.87, 118.10, 117.28, 107.06, 49.61; MS(70 ev): m/z = 259.1 [M$^+$].

2-(p-brominephenyl)-2-(p-trifluoromethoxyphenylamino)acetonitrile (8m): Light-yellow solid, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (d, $J$ = 7.6 Hz, 1H, ArH), 7.66 (d, $J$ = 7.6 Hz, 1H, ArH), 7.43 (t, $J$ = 7.6 Hz, 1H, ArH), 7.32 (t, $J$ = 7.8 Hz, 1H, ArH), 7.13 (d, $J$ = 8.4 Hz, 2H, ArH), 6.76 (d, $J$ = 8.4 Hz, 2H, ArH), 5.67 (d, $J$ = 8.0 Hz, 1H, CH), 4.13 (d, $J$ = 7.6 Hz, 1H, NH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.28, 142.64, 133.88, 132.90, 131.45, 129.21, 128.53, 123.61, 122.71, 117.55, 114.84, 50.56; MS(70 ev): m/z = 370.0 [M$^+$]; HRMS Calcd for C$_{15}$H$_{10}$BrF$_3$N$_2$O: 369.9929, [M$^+$]: Found: 369.9925.

2-Anilino-2-phenylpropanenitrile (8n): Yellow solid, 140-142 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 (d, $J$ = 7.2 Hz, 2H, ArH), 7.42-7.33 (m, 3H, ArH), 7.11 (t, $J$ = 7.6 Hz, 2H, ArH), 6.80 (t, $J$ = 7.6 Hz, 1H, ArH), 6.54 (d, $J$ = 8.0 Hz, 2H, ArH), 4.30 (s, 1H, NH), 1.94 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.47, 139.90, 129.26, 129.04, 128.61, 124.89, 120.73, 119.99, 115.77, 57.12, 33.43; MS(70 ev): m/z = 222.1 [M$^+$].

1-Anilino-Cyclohexanecarbonitrile (8o): White solid, 69-71 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.23 (t, $J$ = 7.4 Hz, 2H, ArH), 6.90 (t, $J$ = 9.4 Hz, 3H, ArH), 3.67 (s, 1H, NH), 2.32 (t, $J$ = 11.6 Hz, 2H, CH$_2$), 1.76 (s, 2H, CH$_2$), 1.72-1.59 (m, 5H, CH$_2$), 1.31 (s, 1H, CH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.62, 129.26, 121.22, 120.53, 117.52, 54.39, 36.64, 24.92, 22.24; MS(70 ev): m/z = 200.1 [M$^+$].

1-Anilino-(4-methylcyclohexane)carbonitrile (8p): White solid, mp: 86-88 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.24 (t, $J$ = 7.4 Hz, 2H, ArH), 6.92-6.86 (m, 3H, ArH), 3.63 (s, 1H, NH), 2.28 (d, $J$ = 14.0 Hz, 2H, CH$_2$), 1.93 (t, $J$ = 13.0 Hz, 2H, CH$_2$), 1.64-1.48 (m, 3H, CH$_2$), 1.32-1.24 (m, 2H, CH$_2$), 0.92 (d, $J$ = 6.4 Hz, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 143.64, 129.28, 122.37, 120.26, 116.99, 51.79, 36.96, 34.03, 28.36, 21.27; MS(70 ev): m/z = 214.1 [M$^+$].

Typical procedure for the Mannich-type reaction of benzaldehyde (5a) with aniline (6a) and trimethyl(1-phenyl-vinyloxy)silane (9b) catalyzed by 3: Complex 3 (7 mg, 0.01 mmol), PhCHO (106 mg 1.0 mmol), PhNH$_2$ (93 mg, 1.0 mmol) and trimethyl(1-phenyl-vinyloxy)silane (230 mg, 1.2 mmol) were placed in a 50 mL round-bottomed flask. Then the mixture was stirred at room temperature until the reaction was complete as indicated by TLC. Then the solvents of the resulting mixture were removed by evaporation in vacuum, the residue was dissolved CH$_2$Cl$_2$ and the catalyst was collected by means of filtration for the next cycle of reaction. The filtrate was subject to volatilization and the crude product was obtained, the products 10a-10l were isolated by silica gel column chromatography on silica gel (petroleum ether : EtOAc = 30:1) in yield 94% (283mg) as white solid. Aldehydes and amines and nucleophiles ketene silyl acetals (9a) and enol silyl ethers (9b) are commercially available. 10a-10l are known compounds[S5-S6] and the spectra data are summarized as follows:
1,3-diphenyl-3-(N-phenylamino)propan-1-one (10a): White solid, mp.: 169-171 °C; 1H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.4 Hz, 2H, ArH), 7.55 (t, J = 7.0 Hz, 1H, ArH), 7.45-7.08 (m, 9H, ArH), 6.65 (t, J = 7.4 Hz, 1H, ArH), 6.55 (d, J = 8.0 Hz, 2H, ArH), 5.00 (dd, J = 7.6 Hz, 5.2 Hz, 1H, CH), 4.55 (s, 1H, NH), 3.50 (dd, J = 16.0 Hz, 5.2 Hz, 1H, CH₂), 3.41 (dd, J = 16.0 Hz, 7.6 Hz, 1H, CH₂); 13C NMR (100 MHz, CDCl₃): δ 198.30, 147.00, 142.99, 136.70, 133.45, 129.13, 128.85, 128.72, 128.23, 127.38, 126.39, 117.80, 113.83, 54.80, 46.33; Ms(70 ev): m/z = 301.1 [M⁺].

3-(4-chlorophenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10e): White solid, mp.: 137-138 °C; 1H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.0 Hz, 2H, ArH), 7.55-6.84 (m, 9H, ArH), 6.66 (t, J = 7.0 Hz, 1H, ArH), 6.56 (d, J = 8.4 Hz, 2H, ArH), 4.96 (t, J = 6.4 Hz, 1H, CH), 3.76 (s, 3H, OCH₃), 3.48 (dd, J = 16.4 Hz, 5.2 Hz, 1H, CH₂), 3.40 (dd, J = 16.0 Hz, 7.2 Hz, 1H, CH₂); 13C NMR (100 MHz, CDCl₃): δ 198.47, 158.82, 146.97, 136.77, 134.89, 133.40, 129.12, 128.70, 128.21, 127.49, 117.81, 114.20, 127.88, 118.22, 113.99, 54.32, 46.31; Ms(70 ev): m/z = 331.1 [M⁺].

3-(4-methoxyphenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10c): White solid, mp.: 139-140 °C; IR (KBr): 3450, 3389, 1668 cm⁻¹; 1H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 7.6 Hz, 2H, ArH), 7.55 (t, J = 7.4 Hz, 1H, ArH), 7.45 (d, J = 7.6 Hz, 3H, ArH), 7.20 (d, J = 6.4 Hz, 1H, ArH), 7.11-6.56 (m, 8H, ArH), 5.27 (t, J = 6.2 Hz, 1H, CH), 3.60 (dd, J = 15.6 Hz, 4.8 Hz, 1H, CH₂), 3.41 (dd, J = 16.0 Hz, 8.0 Hz, 1H, CH₂); 13C NMR (100 MHz, CDCl₃): δ 198.28, 161.76, 159.33, 146.43, 136.50, 133.51, 129.18, 128.95, 128.73, 128.56, 128.28, 124.49, 118.15, 115.69, 115.47, 113.83, 49.64, 44.39; Ms(70 ev): m/z = 319.1 [M⁺]; HRMS Calcd for C₂₃H₁₄FNO: 319.1372, [M⁺]; Found: 319.1368.

3-(3-nitrophenyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10g): White solid, mp.: 140-141 °C; 1H NMR (400 MHz, CDCl₃): δ 8.32 (s, 1H, ArH), 8.06 (d, J = 8.0 Hz, 1H, ArH), 7.89 (d, J = 8.0 Hz, 2H, ArH), 7.81 (d, J = 7.6 Hz, 1H, ArH), 7.54-6.84 (m, 9H, ArH), 6.53 (d, J = 7.6 Hz, 2H, ArH), 4.96 (t, J = 6.4 Hz, 1H, CH), 3.46 (dd, J = 16.4 Hz, 5.6 Hz, 1H, CH₂), 3.40 (dd, J = 16.4 Hz, 7.2 Hz, 1H, CH₂); 13C NMR (100 MHz, CDCl₃): δ 197.90, 146.63, 142.04, 136.58, 133.60, 131.93, 129.19, 128.78, 128.25, 128.19, 121.10, 118.18, 113.94, 54.31, 46.05; Ms(70 ev): m/z = 379.1 [M⁺].
CDCl₃, 3.57 (dd, J = 16.0 Hz, 7.6 Hz, 1H, CH), 3.46 (dd, J = 16.0 Hz, 8.0 Hz, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 198.21, 147.08, 140.56, 136.66, 133.52, 132.91, 129.16, 128.76, 128.26, 127.72, 126.20, 125.83, 125.16, 124.58, 117.91, 113.96, 55.05, 46.40; Ms(70 ev): m/z = 353.1 [M⁺].

3-(2-naphthyl)-1-phenyl-3-(N-phenylamino)propan-1-one (10h): White solid, mp.: 133-135 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 8.0 Hz, 3H, ArH), 7.82-7.78 (m, 3H, ArH), 7.58-7.51 (m, 2H, ArH), 7.41 (t, J = 7.2 Hz, 4H, ArH), 7.06 (t, J = 7.2 Hz, 2H, ArH), 6.66-6.58 (m, 3H, ArH), 5.15 (t, J = 6.2 Hz, 1H, CH), 4.62 (s, 1H, NH), 3.57 (dd, J = 16.0 Hz, 4.8 Hz, 1H, CH₂), 3.46 (dd, J = 16.0 Hz, 8.0 Hz, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 198.35, 144.74, 143.19, 136.79, 133.38, 129.62, 128.81, 128.69, 128.22, 127.30, 127.01, 126.62, 114.04, 55.11, 46.38, 20.37; Ms(70 ev): m/z = 315.2 [M⁺].

3-(2-naphthyl)-1-phenyl-3-(N-4-methylphenylamino)propan-1-one (10i): White solid, mp.: 168-169 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J = 8.0 Hz, 2H, ArH), 7.51-7.19 (m, 8H, ArH), 6.88 (t, J = 8.8 Hz, 2H, ArH), 6.47 (d, J = 8.4 Hz, 2H, ArH), 4.93 (t, J = 6.4 Hz, 1H, CH), 4.39 (s, 1H, NH), 3.41 (dd, J = 16.4 Hz, 5.2 Hz, 1H, CH₂), 3.36 (dd, J = 16.0 Hz, 7.6 Hz, 1H, CH), 2.17 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 198.20, 145.42, 142.37, 136.62, 133.55, 128.94, 128.92, 128.74, 128.20, 127.55, 126.33, 122.64, 115.11, 55.09, 46.14; Ms(70 ev): m/z = 335.1 [M⁺].

Methyl 2,2-dimethyl-3-(N-phenylamino)propanoate (10k): White solid, mp.: 169-171 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.22 (m, 5H, ArH), 7.03 (t, J = 7.9 Hz, 2H, ArH), 6.59 (t, J = 7.4 Hz, 1H, ArH), 6.50 (d, J = 8.0 Hz, 2H, ArH), 4.80 (d, J = 8.0 Hz, 1H, CH), 4.49 (d, J = 7.6 Hz, 1H, NH), 3.65 (s, 3H, OCH₃), 1.27 (s, 3H, CH₃), 1.16 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 177.01, 146.89, 139.18, 128.98, 128.24, 127.96, 127.40, 117.22, 113.34, 64.31, 52.06, 46.96, 24.52, 20.66; Ms(70 ev): m/z = 283.1 [M⁺].

Methyl 2,2-dimethyl-3-(N-phenylamino)-3-(4-chlorophenyl)propanoate (10l): White solid, mp.: 108-110 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.20 (m, 4H, ArH), 7.04 (t, J = 7.4 Hz, 2H, ArH), 6.61 (t, J = 7.2 Hz, 1H, ArH), 6.46 (d, J = 8.0 Hz, 2H, ArH), 4.79 (d, J = 6.4 Hz, 1H, CH), 4.45 (d, J = 6.4 Hz, 1H, NH), 3.64 (s, 3H, OCH₃), 1.27 (s, 3H, CH₃), 1.15 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 176.82, 146.64, 137.97, 133.24, 129.64, 129.13, 128.31, 117.60, 113.42, 63.90, 52.24, 46.91, 24.54, 20.84; Ms(70 ev): m/z = 317.1 [M⁺].

Typical procedure for the Mukaiyama-aldol reaction of benzaldehyde (5a) catalyzed by 2·H₂O·THF: Complex 2·H₂O·THF (45 mg, 0.05 mmol), and ketene silyl acetal (9a) (208 mg, 1.2 mmol) were added to a solution of PhCHO (4a) (106 mg, 1.0 mmol) in THF (3.0 mL) at 0 °C. Then the temperature was raised to room temperature slowly. After the mixture was stirred at room temperature for 4 h and monitored by TLC, it was subject to evaporation in vacuum at room temperature, the residue was dissolved in n-hexane (10 mL×3) and the catalyst was collected by means of filtration for the next cycle of reaction. To the combined hexane solution, MeOH and HCl(aq) were added and the mixture was stirred for 15 minutes. NaHCO₃ (aq) was added for neutralization. The mixture was subject to evaporation, and the solids thus obtained were...
dissolved in AcOEt and water. After extraction with AcOEt (three times), the organic layer was washed with NaCl (aq) and dried over MgSO₄. After evaporation, the residue was subject to silica gel column chromatography (petroleum ether : ethyl acetate = 10:1), colourless crystals of (11a) were obtained, (196 mg, isolated yield 95%). Aldehydes and nucleophiles enol silyl ethers and ketene silyl acetals are commercially available. 11a–11e, 11h-p are known compounds[87-90] and 11f, 11g are new compound. The spectra data are summarized as follows:

**Methyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (11a):** White solid, 58-60 ºC. ¹H NMR (400MHz, CDCl₃): δ 7.33-7.25 (m, 5H, ArH), 4.88 (d, J = 3.6 Hz, 1H, CH), 3.71 (s, 3H, OCH₃), 3.14 (d, J = 4.0 Hz, 1H, OH), 1.14 (s, 3H, CH₃), 1.09 (s, 3H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 178.21, 140.00, 127.76, 127.66, 78.68, 52.11, 47.74, 23.01, 19.06; Ms(70 ev): m/z = 208.1 [M⁺].

**Methyl 3-hydroxy-2,2-dimethyl-3-p-tolylpropanoate (11b):** White solid, 70-73 ºC. ¹H NMR (400MHz, CDCl₃): δ 7.18 (d, J = 8.0 Hz, 2H, ArH), 7.11 (d, J = 8.0 Hz, 2H, ArH), 4.84 (d, J = 3.2 Hz, 1H, CH), 3.70 (s, 3H, OCH₃), 3.08 (d, J = 4.0 Hz, 1H, OH), 2.33 (s, 3H, CH₃), 1.13 (s, 3H, CH₃), 1.09 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 178.24, 137.36, 137.05, 128.46, 127.53, 78.56, 52.07, 47.76, 22.98, 21.11, 19.08; Ms(70 ev): m/z = 222.1 [M⁺].

**Methyl 3-(4-chlorophenyl)-3-hydroxy-2,2-dimethylpropanoate (11c):** White solid, 65-66 ºC. ¹H NMR (400MHz, CDCl₃): δ 7.28 (d, J = 8.4 Hz, 2H, ArH), 7.22 (d, J = 8.4 Hz, 2H, ArH), 4.85 (d, J = 4.0 Hz, 1H, CH), 3.71 (s, 3H, OCH₃), 3.29 (d, J = 3.6 Hz, 1H, OH), 1.12 (s, 3H, CH₃), 1.08 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 178.07, 138.46, 133.50, 129.00, 127.93, 77.95, 52.20, 47.65, 22.84, 19.03; Ms(70 ev): m/z = 226.1 [M⁺].

**Methyl 3-hydroxy-2,2-dimethyl-5-phenylpent-4-enoate (11d):** Colorless oil, ¹H NMR (400MHz, CDCl₃): δ 7.38 (d, J = 7.4 Hz, 2H, ArH), 7.32 (t, J = 7.4 Hz, 2H, ArH), 7.24 (t, J = 6.8 Hz, 1H, ArH), 6.63 (d, J = 16.0 Hz, 1H, CH=–), 6.20 (dd, J = 16.0 Hz, 7.2 Hz, 1H, CH=–), 4.35 (d, J = 6.8 Hz, 1H, CH), 3.72 (s, 3H, OCH₃), 2.85 (br, 1H, OH), 1.24 (s, 3H, CH₃), 1.23 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 177.91, 136.60, 132.96, 128.59, 127.82, 127.42, 126.58, 77.85, 52.09, 47.23, 22.81, 20.01; Ms(70 ev): m/z = 234.1 [M⁺].

**Methyl 3-hydroxy-2,2-dimethyl-5-(4-methoxylphenyl)pent-4-enoate (11e):** Colorless oil, ¹H NMR (400MHz, CDCl₃): δ 7.36 (s, 1H, ArH), 7.27-7.22 (m, 3H, ArH), 6.84 (d, J = 15.6 Hz, 1H, CH=–), 6.07 (dd, J = 15.6 Hz, 7.2 Hz, 1H, CH=–), 4.37 (t, J = 6.0 Hz, 1H, CH), 3.72 (s, 3H, OCH₃), 2.80 (d, J = 5.6 Hz, 1H, OH), 2.34 (s, 3H, CH₃), 1.25 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 177.83, 138.49, 134.54, 131.48, 129.81, 129.01, 127.72, 126.40, 124.58, 77.54, 52.15, 47.18, 22.80, 20.08; Ms(70 ev): m/z = 248.1 [M⁺].

**Methyl 3-hydroxy-2,2-dimethyl-5-(4-methoxysulfonyl)pent-4-enoate (11f):** Colorless oil, ¹H NMR (400MHz, CDCl₃): δ 7.31 (d, J = 8.8 Hz, 2H, ArH), 6.85 (d, J = 8.8 Hz, 2H, ArH), 6.56 (d, J = 15.6 Hz, 1H, CH=–), 6.06 (dd, J = 15.6 Hz, 7.2 Hz, 1H, CH=–), 4.32 (t, J = 6.2 Hz, 1H, CH), 3.80 (s, 3H, OCH₃), 3.72 (s, 3H, OCH₃), 2.76 (d, J = 5.6 Hz, 1H, OH), 1.23 (s, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 177.92, 159.39, 132.53, 129.38, 127.77, 125.16, 113.99, 55.30, 52.03, 47.24, 22.80, 19.98; FT-IR (neat, cm⁻¹): 3389, 3009, 2958, 2846, 1718, 1610, 1435, 1299, 1128, 1016, 958; Ms(70 ev): m/z: = 264.1 [M⁺]; HRMS Calcd for C₁₇H₂₆O₃: 264.362; [M⁺] : Found: 264.1359.

**Methyl 3-hydroxy-2,2-dimethyl-5-(3-fluorinephenyl)pent-4-enoate (11g):** Colorless oil, ¹H NMR (400MHz, CDCl₃): δ 7.27 (q, J = 7.2 Hz, 1H, ArH), 7.14 (d, J = 7.6 Hz, 1H, ArH), 7.08 (d, J = 10.0 Hz, 1H, ArH), 6.94 (t, J = 8.4 Hz, 1H, ArH), 6.61 (d, J = 15.6 Hz, 1H, CH=–), 6.22 (dd, J = 16.0 Hz, 6.8 Hz, 1H, CH=–), 4.35 (t, J = 5.6 Hz,
1H, CH), 3.73 (s, 3H, OCH₃), 2.88 (d, J = 5.6 Hz, 1H, OH), 1.25 (s, 3H, CH₂), 1.23 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 177.84, 164.30, 161.86, 138.93, 131.72, 130.03, 128.87, 122.49, 114.70, 114.48, 113.08, 112.86, 52.14, 47.18, 29.70, 22.80, 20.07; FT-IR (neat, cm⁻¹): 3472, 3135, 2928, 1756, 1592, 1438, 1266, 1130, 1112, 1025, 949, 876; Ms(70 ev): m/z = 252.1 [M⁺]; HRMS Calcd for C₁₄H₁₂FO₂: 252.1162, [M⁺]; Found: 252.1158.

(E)-Methyl 3-hydroxy-2,2-dimethyl-5-(3-chlorophenyl)pent-4-enoate (11h): Colorless oil. ¹H NMR (400MHz, CDCl₃): δ 7.41 (d, J = 8.8 Hz, 1H, ArH), 7.18-7.16 (m, 3H, ArH), 6.58 (d, J = 16.0 Hz, 1H, CH=), 6.22 (dd, J = 16.0 Hz, 6.8 Hz, 1H, CH=), 4.34 (d, J = 6.8 Hz, 1H, CH), 3.73 (s, 3H, OCH₃), 2.90 (s, 1H, OH), 1.25 (s, 3H, CH₃), 1.23 (s, 3H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 177.83, 134.49, 134.54, 131.48, 129.81, 129.04, 127.72, 126.40, 124.84, 52.15, 47.18, 22.80, 20.08; Ms(70 ev): m/z = 268.1 [M⁺].

3-Hydroxy-1-phenyl-3-phenylpropan-1-one (11i): Colorless oil. ¹H NMR (400MHz, CDCl₃): δ 7.95 (d, J = 8.0 Hz, 2H, ArH), 7.61-7.28 (m, 8H, ArH), 5.35 (t, J = 5.8 Hz, 1H, CH), 3.60 (s, 1H, CH₂), 3.36 (d, J = 6.0 Hz, 1H, CH₂), 3.21 (dd, J = 13.6 Hz, 5.2 Hz, 1H, CH), 3.74 (s, 1H, OH), 2.90 (s, 1H, OH), 1.25 (s, 3H, CH₃), 1.23 (s, 3H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 200.24, 142.94, 136.56, 136.70, 128.74, 128.61, 128.18, 127.72, 125.78, 70.06, 47.41; Ms(70 ev): m/z = 226.1 [M⁺].

3-Hydroxy-1-phenyl-3-p-tolylpropan-1-one (11j): Colorless oil. ¹H NMR (400MHz, CDCl₃): δ 7.95 (d, J = 7.2 Hz, 2H, ArH), 7.59-7.19 (m, 7H, ArH), 5.32 (t, J = 5.8 Hz, 1H, CH), 3.57 (s, 1H, OH), 3.38 (s, 1H, CH₂), 3.36 (d, J = 5.2 Hz, 1H, CH₃), 2.36 (s, 3H, CH₃), 1.73 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 200.33, 139.96, 137.43, 136.55, 133.70, 129.28, 128.75, 128.18, 125.73, 69.90, 47.42, 21.19; Ms(70 ev): m/z = 240.1 [M⁺].

3-Hydroxy-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (11k): White solid, mp: 101-102 °C; ¹H NMR (400MHz, CDCl₃): δ 7.96 (d, J = 7.6 Hz, 2H, ArH), 7.65-7.46 (m, 7H, ArH), 5.41 (t, J = 4.8 Hz, 1H, CH), 3.75 (s, 1H, OH), 3.37 (d, J = 3.2 Hz, 1H, CH₂), 3.35 (s, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 199.83, 146.90, 136.33, 133.90, 129.66, 128.81, 127.08 (q, J = 262.25 Hz), 125.59, 125.48, 69.47, 47.20; ¹⁹F NMR (376 MHz, CDCl₃): δ ppm 62.43; Ms(70 ev): m/z = 294.1 [M⁺].

3-(2-fluorophenyl)-3-hydroxy-1-phenylpropan-1-one (11l): Yellow solid, mp: 98-100 °C; ¹H NMR (400MHz, CDCl₃): δ 8.00-7.44 (m, 9H, ArH), 5.85 (t, J = 5.2 Hz, 1H, CH), 4.03 (s, 1H, OH), 3.70 (d, J = 16.4 Hz, 1H, CH₂), 3.21 (dd, J = 18.0 Hz, 9.6 Hz, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 199.93, 147.29, 140.36, 138.60, 136.31, 133.85, 128.85, 128.80, 128.26, 124.46, 65.94, 46.48; Ms(70 ev): m/z = 244.1 [M⁺].

3-(4-chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (11m): White solid, mp: 97-98 °C; ¹H NMR (400MHz, CDCl₃): δ 7.61-7.32 (m, 7H, ArH), 7.94 (d, J = 7.6 Hz, 2H, ArH), 5.32 (t, J = 5.0 Hz, 1H, CH), 3.68 (s, 1H, OH), 3.35 (s, 1H, CH₂), 3.33 (d, J = 3.6 Hz, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 199.99, 141.46, 136.36, 133.82, 133.35, 128.78, 128.72, 128.16, 127.18, 69.42, 47.25; Ms(70 ev): m/z = 260.1 [M⁺].

3-(4-Bromophenyl)-3-hydroxy-1-phenylpropan-1-one (11n): White solid, mp: 98-100 °C; ¹H NMR (400MHz, CDCl₃): δ 7.95 (d, J = 7.6 Hz, 2H, ArH), 7.60-7.31 (m, 7H, ArH), 5.31 (t, J = 4.6 Hz, 1H, CH), 3.74 (s, 1H, OH), 3.35 (s, 1H, CH₂), 3.33 (d, J = 3.6 Hz, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 200.01, 141.95, 136.35, 133.86, 131.67, 128.80, 128.17, 127.53, 121.45, 69.44, 47.23; Ms(70 ev): m/z = 304.1 [M⁺].

3-(2-Nitrophenyl)-3-hydroxy-1-phenylpropan-1-one (11o): White solid, mp.: 108-109 °C; ¹H NMR (400MHz, CDCl₃): δ 7.95 (d, J = 7.6 Hz, 2H, ArH), 7.66-7.00 (m, 7H, ArH), 5.62 (t, J = 4.6 Hz, 1H, CH), 3.83 (s, 1H, OH), 3.50 (d, J = 16.8 Hz, 1H, CH₂), 3.23 (dd, J = 17.6 Hz, 9.2 Hz, 1H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δ 200.27,
3-Hydroxy-1-phenyldecane-1-one (11p): Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 7.6\) Hz, 2H, ArH), 7.59 (t, \(J = 7.4\) Hz, 1H, ArH), 7.46 (t, \(J = 7.6\) Hz, 2H, ArH), 4.22 (s, 1H, OH), 3.28 (s, 1H, CH), 3.19 (d, \(J = 2.8\) Hz, 1H, CH\(_2\)), 3.04 (dd, \(J = 17.6\) Hz, 9.2 Hz, 1H, CH\(_2\)), 1.73-1.25 (m, 8H, CH\(_2\)), 0.90-0.87 (m, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 201.07, 136.81, 133.53, 128.69, 128.09, 67.78, 45.04, 36.56, 29.29, 25.57, 14.11; Ms(70 ev): m/z: 234.1 (M\(^+\)).

**Typical procedure for allylation of benzaldehyde (5a) with tetrallyltin (12a) catalyzed by 2·H\(_2\)O·THF**

To a CH\(_3\)CN (3.0 mL) solution of benzaldehyde (106 mg, 1.0 mmol), 2·H\(_2\)O·THF (45 mg, 0.05 mmol) was added. To the mixture was added tetrallyltin (0.3 mmol) at RT. After the mixture was stirred at RT for an hours and monitored by TLC, it was evaporated in vacuum at RT. To the residue, hexane (10 mL × 3) was added; the catalyst precipitated and was recovered by filtration for the next reaction cycle. The combined n-hexane solution was concentrated, and then MeOH and HCl (aq) was added and stirred for 15 mins. NaHCO\(_3\) (aq) was added for neutralization. After the mixture was subject to evaporation, the as-obtained solids were dissolved in AcOEt and water. After extraction with AcOEt (three times), the organic layer was washed with NaCl aq and dried over MgSO\(_4\). After evaporation, GLC yield was measured. Otherwise, the residue was subject to silica gel column chromatography (petroleum ether : ethyl acetate = 8:1), colorless oil (13a) was obtained: 139 mg, isolated yield 95%. Aldehydes and tetrallyltin are commercially available.

**1-Phenyl-3-buten-1-ol (13a):** Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.36-7.27 (m, 5H, ArH), 5.83-5.76 (m, 1H, vinyl), 5.16-5.13 (m, 1H, 2 vinyls), 4.75-4.72 (m, 1H), 2.54-2.47 (m, 2H, CH\(_2\)), 2.11 (br, 1H, OH), \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta\) 143.88, 134.51, 128.45, 127.60, 125.84, 118.50, 73.31, 43.87.

**1-(p-methyphenyl)-3-buten-1-ol (13b):** Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.25 (d, \(J = 6.8\) Hz, 2H, Ar), 7.16 (d, \(J = 8.0\) Hz, 2H, Ar), 5.84-5.76 (m, 1H, vinyl), 5.15-5.12 (m, 2H, 2 vinyls), 4.71 (t, \(J = 6.6\) Hz, 1H, CH), 2.52-2.49 (m, 2H, CH\(_2\)), 2.34 (s, 3H, CH\(_3\)), 2.18 (br, 1H, OH), \(^{13}\)C NMR (100 MHz; CDCl\(_3\)): \(\delta\) 140.90, 137.26, 134.61, 129.13, 125.78, 118.36, 73.18, 43.81, 21.14.

**1-(p-chlorophenyl)-3-buten-1-ol (13c):** Colorless oil, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.33-7.26 (m, 4H, ArH), 5.81-5.73 (m, 1H, vinyl), 5.18-5.14 (m, 2H, 2 vinyls), 4.73-4.70 (m, 1H, CH), 2.52-2.41 (m, 2H, CH\(_2\)), 2.14 (d, \(J = 2.8\) Hz, 1H, OH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.28, 133.99, 133.16, 128.55, 127.22, 118.94, 118.7, 72.54, 43.90.

**Typical procedure for the Mukaiyama-aldol reaction of Benzaldehyde dimethyl acetal (14) with ketene silyl acetics or enol silyl ethers (9) catalyzed by 2·H\(_2\)O·THF:** [The operation method is similar to Mukaiyama-aldol reaction of benzaldehyde (5a) with ketene silyl acetics (9a). The solvent was replaced with CH\(_3\)CN. Benzaldehyde dimethyl acetal (14) and nucleophiles ketene silyl acetics (9a) and enol silyl ethers (9b) are commercially available]. 15a,15b are known compounds\(^{[5]}\) and the spectra data are summarized as follows:

**Methyl 2,2-dimethyl-3-methoxy-3-phenylpropanoate (15a):** Colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.28-7.18 (m, 5H, ArH), 4.41 (s, 1H, CH), 3.63 (s, 1H, OCH\(_2\)), 3.11 (s, 1H, OCH\(_3\)), 1.04 (s, 1H, CH\(_3\)), 0.93 (s, 1H, CH\(_3\)).
1,3-Diphenyl-3-methoxy-1-propanone (15b): Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 7.2 Hz, 2H, ArH), 7.54-7.52 (m, 8H, ArH), 4.90-4.87 (m, 1H, CH), 3.59 (dd, J = 16.4 Hz, 8.4 Hz, 1H, CH₂), 3.24 (s, 1H, OCH₃), 3.08 (d, J = 177.27, 137.33, 128.41, 127.78, 87.88, 57.38, 51.87, 47.96, 22.65, 18.67; Ms(70 ev): m/z: 240.1 (M⁺).

Typical procedure for Friedel-Crafts acylation of anisole (16a) with acetic anhydride (17a) catalyzed by 2·H₂O·THF: To a 50 mL round-bottomed flask was added anisole (16a) (108 mg, 1.0 mmol), acetic anhydride (204 mg, 2.0 mmol) and catalyst (45 mg, 0.05 mmol). Then the mixture was stirred at room temperature until complete consumption of starting material as monitored by TLC or GC-MS analysis. The residue was dissolved in n-hexane and the catalyst was collected by means of filtration for the next cycle of reaction. The filtrate was subject to volatilization and the crude product was obtained, After that, the resulting mixture was removed by evaporation in vacuum and was then subject subject to silica gel column chromatograph; the Friedel-Crafts acylation product (18a) was obtained: 131 mg, isolated yield 87%. Alkyl aryl ethers and anhydride are commercially available. 18a-18i are known compounds [S11-S16] and the spectra data are summarized as follows:

1-(4-methoxyphenyl)ethanone (18a): Oil, ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 7.2 Hz, 2H, ArH), 6.93 (d, J = 7.2 Hz, 2H, ArH), 3.87 (s, 3H, OCH₃), 2.56 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 196.78, 167.52, 130.61, 130.24, 114.71, 55.47, 26.32; Ms(70 ev): m/z: 150.1 (M⁺).

1-(4-ethoxyphenyl)ethanone (18b): Oil, ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J = 7.2 Hz, 2H, ArH), 4.09 (q, J = 6.6 Hz, 2H, CH₂), 2.55 (s, 3H, CH₃), 1.44 (t, J = 5.6 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 196.78, 162.96, 130.61, 130.24, 114.16, 63.77, 26.30, 14.68; Ms(70 ev): m/z: 164.1 (M⁺).

1-(4-butoxyphenyl)ethanone (18c): Oil, ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J = 8.4 Hz, 2H, ArH), 6.92 (d, J = 8.8 Hz, 2H, ArH), 4.07 (t, J = 6.6 Hz, 2H, CH₂), 2.56 (s, 3H, OCH₃), 1.81-1.76 (m, 2H, CH₂), 1.53-1.46 (m, 2H, CH₂), 0.99 (t, J = 7.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 196.86, 163.14, 130.60, 130.10, 114.13, 67.95, 31.14, 26.35, 19.19, 13.82; Ms(70 ev): m/z: 192.1 (M⁺).

1-(4-methoxy-2-methylphenyl)ethanone (18d): Oil, ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 8.4 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.64 (d, J = 7.6 Hz, 1H, ArH), 3.89 (s, 3H, OCH₃), 2.55 (s, 3H, CH₃), 2.24 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 197.16, 161.77, 130.89, 129.82, 128.50, 126.74, 109.15, 55.52, 26.33, 16.25; Ms(70 ev): m/z: 192.1 (M⁺).

1-(4-methoxy-3-methylphenyl)ethanone (18e): Oil, ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 8.0 Hz, 1H, ArH), 6.77-6.73 (m, 2H, ArH), 3.84 (s, 3H, OCH₃), 2.56 (s, 3H, CH₃), 2.54 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 199.50, 161.20, 142.19, 132.50, 121.49, 117.49, 110.60, 55.29, 29.05, 22.56; Ms(70 ev): m/z: 192.1 (M⁺).
1-(4-methoxy-2-chlorophenyl)ethanone (18g): Oil, \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.91 (s, 1H, ArH), 7.78 (d, \(J = 8.4\) Hz, 1H, ArH), 6.89 (d, \(J = 9.0\) Hz, 1H, ArH), 3.90 (s, 3H, OCH\(_3\)), 2.48 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 194.71, 157.76, 129.82, 129.65, 127.74, 121.85, 110.25, 55.36, 25.25; Ms(70 ev): m/z: 184.0 (M\(^+\)).

1-(4-methoxy-2-bromophenyl)ethanone (18h): Oil, \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.15 (d, \(J = 3.6\) Hz, 1H, ArH), 7.91 (t, \(J = 5.8\) Hz, 1H, ArH), 6.93 (t, \(J = 7.2\) Hz, 1H, ArH), 3.96 (s, 3H, OCH\(_3\)), 2.54 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 195.65, 159.60, 143.01, 133.87, 131.16, 129.65, 110.68, 56.50, 26.33; Ms(70 ev): m/z: 228.0 (M\(^+\)).

1-(4-methoxyphenyl)propanone (18i): Oil, \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (d, \(J = 8.8\) Hz, 2H, ArH), 6.93 (d, \(J = 8.8\) Hz, 2H, ArH), 3.87 (s, 3H, OCH\(_3\)), 2.95 (q, \(J = 7.2\) Hz, 2H, CH\(_2\)), 1.21 (t, \(J = 7.2\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.55, 163.30, 130.23, 130.04, 113.67, 55.46, 31.43, 8.46; Ms(70 ev): m/z: 164.1 (M\(^+\)).

Typical procedure for the aza-Friedel-Crafts of benzaldehyde (5a) with indole (19a) and \(N,N\)-dimethylaniline (50a) catalyzed by complex 3: To a 50 mL round-bottomed flask was added benzaldehyde (106 mg, 1.0 mmol), indole (117 mg, 1.0 mmol) and \(N,N\)-dimethylaniline (133 mg, 1.1 mmol), CH\(_2\)CICH\(_2\)Cl (3 mL) and catalyst 3 (14 mg, 0.02 mol). Then the mixture was stirred at 100 °C until complete consumption of starting material as monitored by TLC. Then the reaction mixture was evaporated in vacuum, CH\(_2\)Cl\(_2\) (3×10 mL) was added to the reaction mixture and the catalyst was filtered for the next cycle of reaction. The combined CH\(_2\)Cl\(_2\) solution was removed by evaporation in vacuum and was then subject to silica gel column chromatography; the one-pot three-component aza-Friedel-Crafts product (21a) was obtained, wite solid, 235.0 mg, isolated yield 72%. Aldehydes and indoles such as and nucleophiles \(N,N\)-dialkylaniline are commercially available. \(21a-21c, 21e, 21h-21k\) are known compounds\(^{S17-S18}\) and \(21d, 21f, 21g, 21i\) are new compound. The spectra data are summarized as follows:

4-((1H-indol-3-yl)(phenyl)methyl)-\(N,N\)-dimethylaniline (21a): White solid, mp 159-161 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.85 (s, 1H, NH), 7.30-7.07 (m, 10H, ArH), 6.96 (t, \(J = 6.8\) Hz, 1H, ArH), 6.65 (t, \(J = 8.4\) Hz, 2H, ArH), 6.52 (s, 1H, ArH), 5.57 (s, 1H, CH), 2.89 (s, 6H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.02, 144.68, 136.66, 132.19, 129.52, 128.89, 128.12, 127.05, 125.91, 123.93, 121.88, 120.54, 119.20, 112.58, 110.93, 47.79, 40.71; Ms(70 ev): m/z: 362.0 (M\(^+\)).

4-((1H-indol-3-yl)(p-tolyl)methyl)-\(N,N\)-dimethylaniline (21b): White solid, mp 163-165 °C; \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.91 (s, 1H, NH), 7.32 (d, \(J = 8.4\) Hz, 1H, ArH), 7.25 (d, \(J = 5.2\) Hz, 2H, ArH), 7.16-7.05 (m, 7H, ArH), 6.97 (t, \(J = 7.4\) Hz, 1H, ArH), 6.66 (d, \(J = 8.4\) Hz, 2H, ArH), 6.58 (s, 1H, ArH), 5.54 (s, 1H, CH), 2.90 (s, 6H, CH\(_3\)), 2.31 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 141.72, 136.73, 135.35, 125.39, 128.88, 128.80, 128.16, 123.90, 121.92, 120.83, 120.12, 119.24, 112.68, 119.30, 110.93, 110.90, 47.42, 40.83, 21.07; Ms(70 ev): m/z: 340.2 (M\(^+\)).

4-((1H-indol-3-yl)(p-methoxyphenyl)methyl)-\(N,N\)-dimethylaniline (21c): White solid, mp 160-162 °C; \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.92 (s, 1H, NH), 7.33 (d, \(J = 8.0\) Hz, 1H, ArH), 7.24 (d, \(J = 6.4\) Hz, 2H, ArH), 7.13 (d, \(J = 8.0\) Hz, 2H, ArH), 7.07 (d, \(J = 8.0\) Hz, 2H, ArH), 6.97 (d, \(J = 7.4\) Hz, 1H, ArH), 6.80 (d, \(J = 7.6\) Hz, 2H, ArH), 6.67 (d, \(J = 8.0\) Hz, 2H, ArH), 6.57 (s, 1H, ArH), 5.53 (s, 1H, CH), 3.77 (s, 3H, OCH\(_3\)), 2.91 (s, 6H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 157.78, 149.03, 136.97, 136.76, 132.61, 129.83, 129.48, 127.12, 123.87, 121.93, 121.02, 120.13, 119.24, 113.53, 112.65, 110.94, 55.22, 44.99, 40.80; Ms(70 ev): m/z: 356.2 (M\(^+\)).
4-((1H-indol-3-yl)(o-fluorophenyl)methyl)-N,N-dimethylaniline (21d): White solid, mp 184-186 °C; 1H NMR (400 MHz, CDCl3): δ 7.91 (s, 1H, NH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.19-7.02 (m, 6H, ArH), 6.98 (d, J = 7.6 Hz, 2H, ArH), 6.67 (d, J = 8.0Hz, 2H, ArH), 6.59 (s, 1H, ArH), 5.89 (s, 1H, CH), 2.91 (s, 3H, CH3); 13C NMR (100 MHz, CDCl3): δ 161.93, 159.48, 149.20, 136.78, 131.58 (J = 14.4 Hz), 130.80, 130.48 (J = 4.2 Hz), 129.46, 127.68, 126.94, 124.01, 123.78 (J = 3.4 Hz), 122.05, 119.91, 119.32 (J = 5.4 Hz), 115.20 (J = 22.0 Hz), 112.62, 111.03, 40.74, 40.18 (J = 3.4 Hz); Ms(70 ev): m/z: 344.2 (M+); HRMS Calcd for C23H23FN2: 344.1689, [M+] : Found: 344.1692.

4-((1H-indol-3-yl)(p-chlorophenyl)methyl)-N,N-dimethylaniline (21e): White solid, mp 130-132 °C; 1H NMR (400 MHz, CDCl3): δ 7.95 (s, 1H, NH), 7.34 (d, J = 8.0 Hz, 1H, ArH), 7.22 (d, J = 8.0 Hz, 3H, ArH), 7.15 (d, J = 8.4 Hz, 3H, ArH), 7.05 (d, J = 8.0 Hz, 2H, ArH), 6.99 (t, J = 7.4 Hz, 1H, ArH), 6.66 (d, J = 8.0 Hz, 2H, ArH), 6.57 (s, 1H, ArH), 5.55 (s, 1H, CH), 2.92 (s, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 149.20, 143.29, 136.75, 131.66, 131.58, 130.30, 129.50, 128.31, 126.93, 123.98, 122.12, 120.19, 119.97, 119.41, 112.62, 111.06, 55.20, 47.25, 40.72; Ms(70 ev): m/z: 360.1 (M+).

4-((1H-indol-3-yl)(p-bromophenyl)methyl)-N,N-dimethylaniline (21f): White solid, mp 176-178 °C; 1H NMR (400 MHz, CDCl3): δ 7.91 (s, 1H, NH), 7.56 (d, J = 8.0 Hz, 1H, ArH), 7.31 (d, J = 8.0 Hz, 1H, ArH), 7.21 (d, J = 8.0 Hz, 1H, ArH), 7.16-6.96 (m, 7H, ArH), 6.66 (d, J = 8.4 Hz, 2H, ArH), 6.52 (s, 1H, ArH), 5.98 (s, 1H, CH), 2.91 (s, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 149.14, 143.61, 136.78, 132.88, 130.79, 130.41, 129.85, 127.70, 127.21, 126.98, 125.11, 124.24, 122.09, 119.95, 119.82, 119.38, 112.55, 111.03, 47.01, 40.72; Ms(70 ev): m/z: 404.1 (M+); HRMS Calcd for C23H23BrN2: 404.0888, [M+] : Found: 404.0885.

4-((1H-indol-3-yl)(p-nitrophenyl)methyl)-N,N-dimethylaniline (21g): White solid, mp 156-158 °C; 1H NMR (400 MHz, CDCl3): δ 7.98 (s, 1H, NH), 7.80 (d, J = 8.0 Hz, 1H, ArH), 7.40-7.27 (m, 4H, ArH), 7.21 (d, J = 8.4 Hz, 1H, ArH), 7.14 (d, J = 7.6 Hz, 1H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.98 (d, J = 7.6 Hz, 1H, ArH), 6.64 (d, J = 8.0 Hz, 2H, ArH), 6.53 (s, 1H, ArH), 6.30 (s, 1H, CH), 2.90 (s, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 149.74, 149.32, 138.78, 136.79, 132.33, 131.42, 129.82, 129.70, 127.08, 126.75, 124.40, 124.34, 122.26, 119.71, 119.56, 118.96, 112.61, 111.19, 42.29, 40.66; Ms(70 ev): m/z: 371.1 (M+); HRMS Calcd for C23H17O3N2: 371.1634, [M+] : Found: 371.1630.

4-((1H-2-methyl-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline (21h): White solid, mp 87-89 °C; 1H NMR (400 MHz, CDCl3): δ 7.73 (s, 1H, NH), 7.26-7.16 (m, 6H, ArH), 7.05 (t, J = 7.4 Hz, 4H, ArH), 6.88 (t, J = 7.4 Hz, 1H, ArH), 6.65 (d, J = 8.0 Hz, 2H, ArH), 5.65 (s, 1H, CH), 2.90 (s, 6H, CH3), 2.17 (s, 3H, CH3); 13C NMR (100 MHz, CDCl3): δ 148.99, 144.71, 135.21, 132.01, 131.89, 129.77, 129.16, 128.58, 128.07, 125.81, 120.64, 119.08, 114.64, 112.63, 110.03, 46.79, 40.83, 12.43; Ms(70 ev): m/z: 340.2 (M+).

4-((1H-7-methyl-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline (21i): White solid, mp 84-85 °C; 1H NMR (400 MHz, CDCl3): δ 7.84 (s, 1H, NH), 7.28-7.22 (m, 4H, ArH), 7.18 (d, J = 8.0 Hz, 1H, ArH), 7.09 (t, J = 7.4 Hz, 3H, ArH), 6.95 (d, J = 6.8 Hz, 1H, ArH), 6.90 (d, J = 7.4 Hz, 1H, ArH), 6.66 (d, J = 8.4 Hz, 2H, ArH), 6.58 (s, 1H, ArH), 5.57 (s, 1H, CH), 2.91 (s, 6H, CH3), 2.45 (s, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 149.06, 144.77, 136.28, 132.27, 129.58, 128.96, 128.16, 126.67, 125.93, 123.64, 122.54, 121.21, 120.08, 119.51, 117.84, 112.61, 47.95, 40.77, 16.62; Ms(70 ev): m/z: 340.2 (M+).

4-((1H-6-fluoro-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline (21j): White solid, mp 181-183 °C; 1H NMR (400 MHz, CDCl3): δ 7.89 (s, 1H, NH), 7.26-7.06 (m, 8H, ArH), 7.00 (d, J = 9.6 Hz, 1H, ArH), 6.73 (t, J = 9.2 Hz,
1H, ArH), 6.67 (d, J = 8.4 Hz, 2H, ArH), 6.54 (s, 1H, ArH), 5.53 (s, 1H, CH), 2.93 (s, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 161.11, 149.13, 144.47, 136.70, 136.58, 131.87, 129.51, 128.88, 128.23, 126.08, 124.23, 123.72, 120.83 (d, J = 10 Hz), 112.60, 108.03 (d, J = 24.3 Hz), 97.25 (d, J = 25.8 Hz), 47.83, 40.74; Ms(70 ev): m/z: 344.2 (M+).

4-((1H-5-chloro-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline (21k): White solid, mp 165-166 °C; 1H NMR (400 MHz, CDCl3): δ 7.94 (s, 1H, NH), 7.28-7.17 (m, 7H, ArH), 7.05 (d, J = 8.0 Hz, 3H, ArH), 6.66 (d, J = 8.0 Hz, 2H, ArH), 6.59 (s, 1H, ArH), 5.51 (s, 1H, CH), 2.91 (s, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 149.17, 144.33, 135.06, 131.73, 129.49, 128.86, 128.28, 128.22, 126.15, 125.32, 125.00, 122.34, 120.47, 119.40, 112.68, 112.01, 47.61, 40.76; Ms(70 ev): m/z: 360.1 (M+).

4-((1H-indol-3-yl)(phenyl)methyl)-N,N-dimethylaniline (21i): White solid, mp 78-80 °C; 1H NMR (400 MHz, CDCl3): δ 7.90 (s, 1H, NH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.27-7.23 (m, 5H, ArH), 7.14 (t, J = 7.6 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.97 (d, J = 7.8 Hz, 1H, ArH), 6.62-6.58 (m, 3H, ArH), 5.56 (s, 1H, CH), 3.30 (q, J = 6.8 Hz, 4H, CH2), 1.13 (t, J = 6.8 Hz, 6H, CH3); 13C NMR (100 MHz, CDCl3): δ 146.32, 144.88, 136.73, 130.91, 129.72, 128.97, 128.15, 127.17, 125.91, 123.98, 121.92, 120.80, 120.13, 119.24, 111.77, 110.95, 47.81, 44.33, 12.68; Ms(70 ev): m/z: 354.2 (M+).

References:

$^1$H NMR of Cp$_2$Ti(OH)$_2$(OSO$_2$C$_8$F$_{17}$)$^\cdot$THF in Acetone-$[D_6]$
$^1$H NMR of $\text{Cp}_2\text{Ti(OH)}_2(\text{OSO}_2\text{C}_4\text{F}_9)\cdot\text{H}_2\text{O} \cdot \text{THF}$ in Acetone-$[\text{D}_6]$
$^1$H NMR of [(Cp)$_2$Ti(H$_2$O)$_2$][OSO$_2$C$_4$F$_9$]$_2$ in Acetone-[D$_6$]

$^{19}$F NMR of [(Cp)$_2$Ti(H$_2$O)$_2$][OSO$_2$C$_4$F$_9$]$_2$ in Acetone-[D$_6$]
$^1$H and $^{19}$F NMR Spectra of cauterant sample of complex [(Cp)$_2$Ti(H$_2$O)$_2$][OSO$_2$C$_4$F$_9$]$_2$·H$_2$O·THF after heating at 180 °C for two days in nitrogen atmosphere.

$^1$H NMR of Cp$_2$Ti(OSO$_2$C$_4$F$_9$)$_2$ in Acetone-[D$_6$]

$^{19}$F NMR of Cp$_2$Ti(OSO$_2$C$_4$F$_9$)$_2$ in Acetone-[D$_6$]
$^1$H NMR of [(Cp)$_2$Ti(H$_2$O)$_2$][OSO$_2$C$_6$F$_5$]$_2$ in Acetone-[D$_6$]

$^{19}$F NMR of [(Cp)$_2$Ti(H$_2$O)$_2$][OSO$_2$C$_6$F$_5$]$_2$ in Acetone-[D$_6$]
$^1$H NMR of 8a in CDCl$_3$

$^{13}$C NMR of 8a in CDCl$_3$
$^1$H NMR of 8b in CDCl$_3$

$^{13}$C NMR of 8b in CDCl$_3$
$^1$H NMR of 8c in CDCl$_3$

$^{13}$C NMR of 8c in CDCl$_3$
$^1$H NMR of 8d in CDCl$_3$

$^{13}$C NMR of 8d in CDCl$_3$
$^{1}H$ NMR of 8e in CDCl$_3$

$^{13}$C NMR of 8e in CDCl$_3$
$^1$H NMR of 8f in CDCl$_3$

$^{13}$C NMR of 8f in CDCl$_3$
$^1$H NMR of 8g in CDCl$_3$

$^{13}$C NMR of 8g in CDCl$_3$
$^1$H NMR of 8h in CDCl$_3$

$^{13}$C NMR of 8h in CDCl$_3$
$^1$H NMR of 8i in CDCl$_3$

$^{13}$C NMR of 8i in CDCl$_3$
$^1$H NMR of 8j in CDCl$_3$

$^{13}$C NMR of 8j in CDCl$_3$
$^1$H NMR of 8k in CDCl$_3$

$^{13}$C NMR of 8k in CDCl$_3$
$^1$H NMR of 8l in CDCl$_3$

$^{13}$C NMR of 8l in CDCl$_3$
$^1$H NMR of 8m in CDCl$_3$

$^{13}$C NMR of 8m in CDCl$_3$
$^1$H NMR of 8n in CDCl$_3$

$^{13}$C NMR of 8n in CDCl$_3$
$^1$H NMR of 8o in CDCl$_3$

$^{13}$C NMR of 8o in CDCl$_3$
$^1$H NMR of 8p in CDCl$_3$

$^{13}$C NMR of 8p in CDCl$_3$
$^1$H NMR of 10a in CDCl$_3$

$^{13}$C NMR of 10a in CDCl$_3$
$^1$H NMR of 10b in CDCl$_3$

$^{13}$C NMR of 10b in CDCl$_3$
$^1$H NMR of 10c in CDCl$_3$}

$^{13}$C NMR of 10c in CDCl$_3$
$^1$H NMR of 10d in CDCl$_3$

$^{13}$C NMR of 10d in CDCl$_3$
$^1$H NMR of 10e in CDCl$_3$

$^{13}$C NMR of 10e in CDCl$_3$
$^1$H NMR of 10f in CDCl$_3$

$^{13}$C NMR of 10f in CDCl$_3$
$^1$H NMR of 10g in CDCl$_3$

$^{13}$C NMR of 10g in CDCl$_3$
$^1$H NMR of 10h in CDCl$_3$

$^{13}$C NMR of 10h in CDCl$_3$
$^1$H NMR of 10i in CDCl$_3$

$^{13}$C NMR of 10i in CDCl$_3$
$^1$H NMR of 10j in CDCl$_3$

$^{13}$C NMR of 10j in CDCl$_3$
$^1$H NMR of 10k in CDCl$_3$

$^{13}$C NMR of 10k in CDCl$_3$
$^1$H NMR of 10l in CDCl$_3$

$^{13}$C NMR of 10l in CDCl$_3$
$^1$H NMR of 11a in CDCl$_3$ 

$^{13}$C NMR of 11a in CDCl$_3$
$^1$H NMR of 11b in CDCl$_3$
^{13}C NMR of 11b in CDCl$_3$

^{1}H NMR of 11c in CDCl$_3$
13C NMR of 11c in CDCl3

1H NMR of 11d in CDCl3

13C NMR of 11d in CDCl3
$^1$H NMR of 11e in CDCl$_3$

$^{13}$C NMR of 11e in CDCl$_3$
$^1$H NMR of 11f in CDCl$_3$

$^{13}$C NMR of 11f in CDCl$_3$
$^1$H NMR of $11g$ in CDCl$_3$

$^{13}$C NMR of $11g$ in CDCl$_3$
$^1$H NMR of 11h in CDCl$_3$

$^{13}$C NMR of 11h in CDCl$_3$
$^1$H NMR of 11i in CDCl$_3$

$^{13}$C NMR of 11i in CDCl$_3$
$^1$H NMR of $11j$ in CDCl$_3$

$^{13}$C NMR of $11j$ in CDCl$_3$
$^1$H NMR of $11k$ in CDCl$_3$

$^{13}$C NMR of $11k$ in CDCl$_3$
$^{19}$F NMR of 11k in CDCl$_3$

$^1$H NMR of 11l in CDCl$_3$
$^{13}$C NMR of 111 in CDCl$_3$

$^1$H NMR of 11m in CDCl$_3$
$^{13}$C NMR of 11m in CDCl$_3$

$^1$H NMR of 11n in CDCl$_3$
$^{13}$C NMR of 11n in CDCl$_3$

$^1$H NMR of 11o in CDCl$_3$
$^{13}$C NMR of $\text{11o}$ in CDCl$_3$

$^1$H NMR of $\text{13a}$ in CDCl$_3$
$^{13}$C NMR of 13a in CDCl$_3$

$^1$H NMR of 13b in CDCl$_3$
$^{13}$C NMR of 13b in CDCl$_3$

$^1$H NMR of 13c in CDCl$_3$
$^{13}$C NMR of 13c in CDCl₃

$^1$H NMR of 15a in CDCl₃
$^{13}$C NMR of 15a in CDCl$_3$

$^1$H NMR of 15b in CDCl$_3$
$^{13}$C NMR of 15b in CDCl$_3$

$^1$H NMR of 18a in CDCl$_3$
$^{13}$C NMR of $\textbf{18a}$ in CDCl$_3$

$^1$H NMR of $\textbf{18b}$ in CDCl$_3$
$^{13}$C NMR of 18b in CDCl$_3$

$^1$H NMR of 18c in CDCl$_3$
$^{13}\text{C}$ NMR of 18c in CDCl$_3$

$^1\text{H}$ NMR of 18d in CDCl$_3$
$^{13}$C NMR of 18d in CDCl$_3$

$^1$H NMR of 18e in CDCl$_3$
$^{13}$C NMR of 18e in CDCl$_3$

$^1$H NMR of 18f in CDCl$_3$
$^{13}$C NMR of 18f in CDCl$_3$

$^1$H NMR of 18g in CDCl$_3$
$^{13}$C NMR of $18g$ in CDCl$_3$

$^1$H NMR of $18h$ in CDCl$_3$
$^{13}$C NMR of 18h in CDCl$_3$

$^1$H NMR of 18i in CDCl$_3$
$^{13}$C NMR of 18i in CDCl$_3$

$^1$H NMR of 21a in CDCl$_3$
$^{13}$C NMR of 21a in CDCl$_3$

$^1$H NMR of 21b in CDCl$_3$
$^{13}$C NMR of 21b in CDCl$_3$

$^1$H NMR of 21c in CDCl$_3$
$^{13}$C NMR of 21c in CDCl$_3$

$^1$H NMR of 21d in CDCl$_3$
$^{13}$C NMR of 21d in CDCl$_3$

$^1$H NMR of 21e in CDCl$_3$
$^{13}$C NMR of 21e in CDCl$_3$

$^1$H NMR of 21f in CDCl$_3$
$^{13}$C NMR of 21f in CDCl$_3$

$^1$H NMR of 21g in CDCl$_3$
$^{13}$C NMR of 21g in CDCl$_3$

$^1$H NMR of 21h in CDCl$_3$
$^{13}$C NMR of 21h in CDCl$_3$

$^1$H NMR of 21i in CDCl$_3$
$^{13}$C NMR of 21i in CDCl$_3$

$^1$H NMR of 21j in CDCl$_3$
$^{13}$C NMR of 21j in CDCl$_3$

$^1$H NMR of 21k in CDCl$_3$
$^{13}$C NMR of 21k in CDCl$_3$

$^1$H NMR of 21i in CDCl$_3$
$^{13}$C NMR of 21i in CDCl$_3$