Supplementary Material (ESI) for Chemical Communications

Supporting Information

Noncatalytic Conversion of C-F Bonds of Benzotrifluorides to C-C Bonds Using Organoaluminum Reagents

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General

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts are given in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass analyses (EI) were run using a JEOL JMS-mate operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. Elemental analyses were performed on a Perkin Elmer 240C apparatus.

***t*-Butyl benzene** CAS Registry Number: 18899-19-9, 35507-09-6, 74533-92-9.

Into a dichloroethane (1 mL) solution of benzotrifluoride (29.2 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. The mixture was warmed to 25 ^{o}C and a saturated $NaHCO_3$ solution (50 mL) was added. The product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 33.6 mg (90%) of *t*-butyl benzene: IR(NaCl): 3060, 2965, 1600, 1496, 1446, 1366, 1269, 1114, 1032, 762, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.41-7.39 (m, 2H), 7.33-7.29 (m, 2H), 7.19-7.16 (m, 1H), 1.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ128.0, 125.4, 125.2, 31.3, 28.4; MS (EI) m/z (relative intensity, %) 134 (M^+, 27), 119 (100), 103 (5), 91 (44), 77 (8); HRMS calcd for $C_{10}H_{14}$: 134.1096, found 134.1086; Anal, Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.28; H, 10.51.

1-*tert*-Butyl-4- methoxy benzene

Into a dichloroethane (1 mL) solution of 1-methyl-4-trifluoromethyl-benzene (33.6 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that menthioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 31.2 mg (95%) of 4-methoxy 1-*tert*-butyl benzene: IR(NaCl): 3854, 3676, 2962, 2869, 2835, 1614, 1582, 1515, 1464, 1394, 1364, 1300, 1249, 1184,

1116, 1039, 828, 794, 656 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.31 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ157.3, 143.3, 126.2, 113.3, 113.2, 55.2, 34.0, 31.5; MS (EI) m/z (relative intensity, %) 164 (M^+, 25), 149 (100), 133 (2), 121 (16), 109 (11), 91 (7), 77 (5); HRMS calcd for $C_{11}H_{16}O$: 164.1201, found 164.1202; Anal, Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.16; H, 9.81.

1-*tert*-Butyl-4-phenyl benzene

Into a dichloroethane (1 mL) solution of 1-phenyl-4-trifluoromethyl-benzene (44.4 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that menthioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 40.2 mg (93%) of 4-phenyl-1-*tert*-butyl benzene: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ7.67-7.60 (m, 4H), 7.55-7.47 (m, 4H), 7.39-7.37 (m, 1H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ157.3, 143.3, 126.2, 113.3, 113.2, 55.2, 34.0, 31.5; MS (EI) m/z (relative intensity, %) 210 (M^+, 38), 195 (100), 178 (7), 167 (15), 155 (8), 152 (6), 128 (1), 115 (2), 98 (2). 84 (6), 77 (2); HRMS calcd for $C_{16}H_{18}$: 210.1409, found 210.1407; Anal, Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.20; H, 8.53.

1-*tert*-Butyl-4-fluoro benzene

Into a dichloroethane (1 mL) solution of 1-fluoro-4-trifluoromethyl-benzene (32.8 mg, 0.2 mmol) was added trimethylaluminum chloride (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that menthioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 29.8 mg (98%) of 4-fluoro-1-*tert*-butyl benzene: IR(NaCl): 3854, 3822, 3676, 2966, 1512, 1234, 1165, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.35-7.32 (m, 2H), 7.00-6.95 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ162.0, 146.7, 126.7, 114.7, 114.5, 34.3, 31.5; MS (EI) m/z (relative intensity, %) 152 (M^+, 18), 137 (100), 121 (3), 109 (41), 97 (5), 96 (2), 75 (2); HRMS calcd for $C_{10}H_{13}F$: 152.1001, found 152.1008

1-*tert*-Butyl-4-chloro benzene

Into a dichloroethane (1 mL) solution of 1-chloro-4-trifluoromethyl-benzene (36.1 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 32.8 mg (97%) of 4-chloro-1-*tert*-butyl benzene: IR(NaCl): 3822, 3676, 2964, 2904, 2869, 1896, 1648, 1497, 1481, 1459, 1400, 1364, 1268, 1112, 1096, 1012, 826, 741, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.32-7.30 (m, 2H), 7.26-7.24 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ149.6, 131.1, 128.1, 126.8, 34.5, 31.3; MS (EI) m/z (relative intensity, %) 168 (M^+, 24), 153 (100), 137 (2), 125 (29), 115 (5), 102 (3), 101 (3), 77 (5); HRMS calcd for $C_{10}H_{13}Cl$: 168.0706, found 168.0716; Anal, Calcd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77. Found: C, 71.14; H, 7.52.

1-*tert*-Butyl-4-bromo benzene

Into a dichloroethane (1 mL) solution of 1-bromo-4-trifluoromethyl-benzene (45.0 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 38.9 mg (89%) of 4-bromo-1-*tert*-butyl benzene: IR(NaCl): 2964, 2905, 2868, 1495, 1478, 1396, 1364, 1267, 1203, 1109, 1071, 1008, 823, 726, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.41-7.40 (m, 2H), 7.25-7.24 (m, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ150.1, 131.0, 127.2, 119.2, 34.5, 31.2; MS (EI) m/z (relative intensity, %) 212 (M^+, 24), 197 (100), 183 (2), 171 (18), 169 (16), 157 (2), 133 (1), 118 (26), 117 (9), 102 (7), 77 (7); HRMS calcd for $C_{10}H_{13}Br$: 212.0201, found 212.0181; Anal, Calcd for $C_{10}H_{13}Br$: C, 56.36; H, 6.15. Found: C, 56.39; H, 5.87.

1-*tert*-Butyl-4-iodo benzene

Into a dichloroethane (1 mL) solution of 1-iodo-4-trifluoromethyl-benzene (54.4 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 24 h at 50 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 42.1 mg (81%) of 4-iodo-1-*tert*-butyl benzene: IR(NaCl): 3855, 3651, 2963, 2903, 2867, 1492, 1392, 1364, 1267, 1202, 1109, 1004, 819, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.63-7.61 (m, 2H), 7.16-7.14 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ150.8, 137.0, 127.6, 90.6, 34.6, 31.1; MS (EI) m/z (relative intensity, %) 260 (M^+, 42), 245 (100), 229 (0.8), 217 (12), 203 (0.2), 127 (0.5), 118 (16), 117 (8), 91 (3), 77 (3); HRMS calcd for $C_{10}H_{13}I$: 260.0062, found 260.0049; Anal, Calcd for $C_{10}H_{13}I$: C, 46.17; H, 5.04. Found: C, 46.19; H, 4.84.

Trichloromethyl benzene

Into a dichloromethane (1 mL) solution of trifluoromethyl-benzene (29.2 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at -78 ^{o}C under nitrogen. After stirring for 24 h the same temperature, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that menthioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 38.3 mg (98%) of trichloromethyl-benzene: IR(NaCl): 3064, 1486, 1448, 1315, 1190, 1182, 869, 803, 722, 708, 688, 628 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.95-7.93 (m, 2H), 7.47-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ44.2, 30.3, 28.3, 25.5; MS (EI) m/z (relative intensity, %) 194 (M^+, 5), 161 (61), 159 (100), 133 (1), 123 (5), 107 (0.5), 89 (10), 79 (4); HRMS calcd for $C_7H_5Cl_3$: 193.9457, found 193.9440; Anal, Calcd for $C_7H_5Cl_3$: C, 43.01; H, 2.58. Found: C, 42.92; H, 2.63.

1-Isobutyl-4-isopropyl benzene (6)

Into a dichloroethane (1 mL) solution of 1-difluoromethyl-4-isobutyl-benzene (36.8 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 30 min at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product.

Purification by Silica gel column chromatography with hexane as the eluent afforded 34.9 mg (99%) of 1-isobutyl-4-isopropyl benzene: IR(NaCl): 3010, 2958, 2925, 2869, 1513, 1464, 1422, 1383, 1366, 1168, 1116, 1052, 1020, 843, 797 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.15-7.05 (m, 4H), 2.88 (m, 1H), 2.44 (d, J = 7.3 Hz, 2H), 1.84 (m, 1H), 1.24 (d, J = 6.8 Hz, 6H), 0.90 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ146.0, 139.0, 129.0, 126.1, 45.0, 33.7, 30.2, 24.1, 22.4; MS (EI) m/z (relative intensity, %) 176 (M^+, 28), 161 (30), 145 (0.8), 133 (100), 119 (18), 105 (12), 91 (13), 77 (3); HRMS calcd for $C_{13}H_{20}$: 176.1565, found 176.1563; Anal, Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.30; H, 11.26.

1-Dichloromethyl-4-isobutyl benzene (7)

Into a dichloromethane (1 mL) solution of 1-difluoromethyl-4-isobutyl benzene (36.8 mg, 0.2 mmol) was added trichloroaluminum (1 mL, 1 mmol, 1 M in hexane) at -78 ^{o}C under nitrogen. After stirring for 8 h at -78 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 36.5 mg (84%) of 1-dichloromethyl-4-isobutyl-benzene: IR(NaCl): 2957, 2925, 2868, 1612, 1511, 1465, 1418, 1384, 1366, 1251, 1209, 1180, 1120, 1020, 849, 812, 790, 739, 694, 632 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.48-7.46 (m, 2H), 7.19-7.16 (m, 2H), 6.70 (s, 1H), 2.49 (d, J = 7.3 Hz, 2H), 1.87 (m, 1H), 0.91 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ43.9, 37.8, 29.4, 25.8, 71.9, 45.1, 30.1, 22.3; MS (EI) m/z (relative intensity, %) 216 (M^+, 12), 201 (0.7), 181 (100), 173 (16), 165 (1), 138 (39), 125 (3), 115 (3), 103 (7), 91 (5), 77 (6); HRMS calcd for $C_{11}H_{14}Cl_2$: 216.0473, found 216.0484; Anal, Calcd for $C_{11}H_{14}Cl_2$: C, 60.85; H, 6.50. Found: C, 60.85; H, 6.52.

1-Isobutyl 4-diphenylmethyl benzene (8)

Into a hexane (1 mL) solution of 1-difluoromethyl-4-isobutyl benzene (36.8 mg, 0.2 mmol) was added triphenylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 30 min at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 50.5 mg (84%) of 1-isobutyl-4-diphenylmethyl benzene: ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.30-7.00 (m, 14H), 5.52 (s, 1H), 2.44 (d, J = 7.1 Hz, 2H), 1.84 (m, 1H), 0.89 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ144.2, 141.0, 139.6, 129.4, 129.1, 129.0, 128.2, 126.2, 56.5, 45.0, 30.2, 22.4; MS (EI) m/z (relative intensity, %) 300 (M^+, 51), 299 (4), 285 (0.9), 257 (33), 243 (100), 241 (5), 223 (12), 215 (3), 202 (2), 179 (21), 165 (29), 152 (5), 141 (2), 115 (3), 103 (1), 91 (12), 77 (1); HRMS calcd for $C_{23}H_{24}$: 300.1878, found 300.1883; Anal, Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.66; H, 8.18.

9, 9'-Diphenylfluorene (11)

Into a xylene (1 mL) solution of diiodobiphenyl (243.6 mg, 0.6 mmol) was added *tert*-buthyllitium (1.5 mL, 2.4 mmol, 1.59 M in pentane) at -78 ^{o}C under nitrogen. After stirring for 10 min at -78 ^{o}C, the reaction mixture was warmed up to 25 ^{o}C. $^{n}BuLi$ (0.4 ml, 0.6 mmol, 1.59M in hexane) and $AlBr_3$ (146.7 mg, 0.55 mmol) were successively added to the reaction mixture at 25 ^{o}C. After stirring for 30 min, a hexane (0.5 mL) solution of

difluorodiphenylmethane (102.1 mg, 0.5 mmol) was added by a syringe pump to the reaction mixture over 1 h at 25 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 132.1 mg (83%) of 9,9'-diphenylfluorene:^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.77-7.75 (m, 2H), 7.42-7.40 (m, 2H), 7.37-7.33 (m, 2H), 7.28-7.20 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ151.1, 145.9, 140.1, 128.2, 128.1, 127.7, 127.4, 126.6, 126.2, 120.1, 65.5; MS (EI) m/z (relative intensity, %) 318 (M^+, 100), 317 (23), 289 (2), 287 (0.9), 276 (0.8), 243 (1), 241 (42), 215 (3), 213 (2), 202 (1), 189 (0.9), 159 (7), 151 (2), 145 (1), 138 (1), 120 (0.8), 85 (1), 77 (1); HRMS calcd for $C_{25}H_{18}$: 318.1409, found 318.1403; Anal, Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.17; H, 5.78.

1-(2,2,3,3,4,4,4-Heptafluoro-1,1-dimethyl-butyl)-4-methoxy benzene (13)

Into a dichloroethane (1 mL) solution of 1-methoxy-4-nonafluorobutyl-benzene (65.2 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 30 min at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 60.1 mg (96%) of **13**: IR(NaCl): 3000, 2960, 2841, 1614, 1584, 1518, 1484, 1468, 1444, 1399, 1375, 1341, 1300, 1258, 1228, 1191, 1116, 1102, 1037, 946, 897, 875, 832, 808, 732, 681 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.42-7.39 (m, 2H), 6.89-6.87 (m, 2H), 3.81 (s, 3H), 1.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ158.8, 132.1, 128.9, 113.3, 55.2. 44.1, 23.4; MS (EI) m/z (relative intensity, %) 318 (M^+, 23), 303 (2), 299 (2), 287 (0.2), 215 (0.2), 207 (0.7), 184 (3), 180 (2), 169 (1), 149 (100), 133 (3), 121 (9), 109 (5), 91 (4), 77 (2); HRMS calcd for $C_{13}H_{13}F_7O$: 318.0855, found 318.0850; Anal, Calcd for $C_{13}H_{13}F_7O$: C, 49.06; H, 4.12. Found: C, 49.11; H, 4.09.

1-(1, 1-Dichloro 2, 2, 3, 3, 4, 4-heptafluorobutyl) 4-methoxy benzene (14)

Into a dichloroethane (1 mL) solution of 1-methoxy-4-nonafluorobutyl-benzene (65.2 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 30 min at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 69.7 mg (97%) of **14:** ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.77-7.74 (m, 2H), 6.94-6.92 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ161.2, 130.4, 126.1, 113.4, 55.4; MS (EI) m/z (relative intensity, %) 358 (M^+, 15), 339 (2), 323 (100), 303 (2), 288 (1), 269 (1), 235 (1), 220 (2), 204 (57), 189 (69), 169 (20), 161 (11), 138 (4), 125 (6), 119 (3), 111 (3). 75 (4); HRMS calcd for $C_{11}H_7Cl_2F_7O$: 357.9762, found 357.9767; Anal, Calcd for $C_{11}H_7Cl_2F_7O$: C, 36.79; H, 1.96. Found: C, 37.04; H, 2.24.

9, 9'-Dimethylfluorene (17)

Into a dichloroethane (1 mL) solution of 1-phenyl-2-trifluoromethyl-benzene (44.4 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 30 h at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product.

Purification by Silica gel column chromatography with hexane as the eluent afforded 18.6 mg (97%) of 9, 9'-dimethylfluorene: ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ7.73-7.71 (m, 2H), 7.44-7.42 (m, 2H), 7.35-7.29 (m, 4H), 1.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ53.5, 39.2, 27.2, 26.9, 27.2, 26.9, 22.6, 20.0, 46.8, 27.1; MS (EI) m/z (relative intensity, %) 194 (M^+, 41), 179 (100), 178 (36), 152 (5), 151 (3), 139 (0.7), 126 (0.6), 96 (2), 89 (11), 88 (5), 76 (4); HRMS calcd for $C_{15}H_{14}$: 194.1096, found 194.1096; Anal, Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.48; H, 7.20.

2, 3-Dimethoxy-9, 9'-dimethylfluorene (**20**)

Into a dichloroethane (1.4 mL) solution of 3,4-dimethoxy-2'-trifluoromethyl-biphenyl (56.5 mg, 0.2 mmol) was added trimethylaluminum (1.4 mL, 1.4 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 96 h at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 39.7 mg (78%) of **20**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ7.62-7.60 (m, 1H), 7.41-7.39 (m, 1H), 7.33-7.23 (m, 3H), 6.94 (s, 1H), 4.10 (s, 3H), 3.84 (s, 3H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ153.6, 149.1, 148.6, 146.1, 139.4, 131.3, 126.9, 125.9, 122.3, 118.9, 105.7, 103.1, 56.1, 46.7, 27.2; HRMS calcd for $C_{17}H_{18}O_2$: 254.1307, found 254.1304; Anal, Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.14; H, 6.87.

2-Isopropenyl-1,3,5-trimethyl-benzene (**24**)

Into a dichloroethane (1 mL) solution of 1-phenyl-2-trifluoromethyl benzene (37.6 mg, 0.2 mmol) was added trimethylaluminum (1 mL, 1 mmol, 1 M in hexane) at 25 ^{o}C under nitrogen. After stirring for 96 h at 25 ^{o}C, the reaction mixture was quenched with 1N HCl at 0 ^{o}C. Similar workup that mentioned above afforded a crude product. Purification by Silica gel column chromatography with hexane as the eluent afforded 31.1 mg (97%) of **24**:IR(NaCl): 3074, 2964, 2919, 2859, 2731, 2362, 1642, 1612, 1574, 1482, 1431, 1376, 1283, 1174, 1132, 1096, 1033, 898, 849, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$,25 ^{o}C, TMS): δ6.91 (s, 2H), 5.30 (s, 1H), 4.79 (s, 1H), 2.32 (s, 3H), 2.27 (s, 6H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ144.7, 140.4, 135.8, 134.6, 128.0, 114.7, 23.7, 20.9, 19.5; MS (EI) m/z (relative intensity, %) 160 (M^+, 95), 145 (100), 130 (24), 129 (17), 115 (13), 105 (13), 91 (8), 77 (6); HRMS calcd for $C_{12}H_{16}$: 160.1252, found 160.1246; Anal, Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.74; H, 9.97.