Supporting Information for

Syntheses of 2-(2,2,2-Trifluoroethylidene)/(2,2-Difluoroethyl)-1,3-Dicarbonyl Compounds and Their Fungicidal Activities
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General information

$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra were recorded using Bruker AVIII 400 spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as the external standard and low field is positive. Coupling constants ($J$) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: $^1$H NMR (chloroform $\delta$ 7.26) and $^{13}$C NMR (chloroform $\delta$ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on Waters GCT-TOF and State Key Discipline Testing Center for Physical Chemistry of Fuzhou University. Reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.
General procedure for synthesis of 1,3-dicarbonyl substrates 1

To a suspension of ketone (10 mmol) in THF (40 mL) was added NaH (0.80 g, 20 mmol, 60%). After the reaction mixture was stirred at 0 °C for about 1 h, the ester (10 mmol) was added dropwise at the same temperature. Then the mixture was stirred at room temperature until TLC indicated the total consumption of the ketone. The reaction mixture was poured into ice-water (100 mL), acidified with aqueous HCl (3 M) to pH 2~3 and extracted with EtOAc (100 mL × 3). The combined organic layer was dried over Na₂SO₄ and evaporated under reduced pressure. The resulting 1,3-diketones were used for the next step without further purification.

1-(4-Bromophenyl)-3-(4-fluorophenyl)propane-1,3-dione (1s)

Obtained as a pale yellow solid. M.p. 130–131 °C. \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 16.82 (s, 1H), 8.16 – 7.95 (m, 2H), 7.87 (d, \(J = 7.2\) Hz, 2H), 7.66 (d, \(J = 7.2\) Hz, 2H), 7.26 – 7.13 (m, 2H), 6.78 (s, 1H). \(^13\)C NMR (101 MHz, CDCl₃): \(\delta\) 185.3 (s), 184.0 (s), 134.2 (s), 132.0 (s), 129.7 (s), 129.6 (s), 128.6 (s), 127.4 (s), 116.0 (s), 115.8 (s), 92.7 (s). \(^19\)F NMR (376 MHz, CDCl₃) \(\delta\) -105.5 – -106.0 (m, 1F). IR (KBr): \(\nu\) 3064, 1579, 1506, 1471, 1293, 1177, 1092, 1049, 1008, 843, 775, 691, 627, 533 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C₁₃H₁₀FO₂Br: 319.9848; found: 319.9842.
1-(4-Bromophenyl)-3-(4-chlorophenyl)propane-1,3-dione (1y)

Obtained as a pale yellow solid. M.p. 175–176 °C. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 16.77 (s, 1H), 7.94 (d, \(J = 7.8\) Hz, 2H), 7.86 (d, \(J = 7.8\) Hz, 2H), 7.65 (d, \(J = 7.4\) Hz, 2H), 7.49 (d, \(J = 7.4\) Hz, 2H), 6.79 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 184.7 (s), 184.6 (s), 139.0 (s), 134.2 (s), 133.8 (s), 132.0 (s), 129.1 (s), 128.7 (s), 128.6 (s), 127.5 (s), 92.9 (s). IR (KBr): \(\nu\) 3059, 1588, 1500, 1466, 1304, 1222, 1175, 1110, 1071, 1007, 884, 776, 736, 681, 627, 586 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C\(_{15}\)H\(_{10}\)O\(_2\)ClBr: 335.9553; found: 335.9549.
General procedure of synthesis of 2-(2,2,2-trifluoroethylidene)/(2,2-difluoroethyl)-substituted 1,3-dicarbonyl compounds

The 1,3-dicarbonyl substrates (1) (0.50 mmol), trifluoroacetic anhydride (2a) or difluoroacetic anhydride (2b) (2.50 mmol, 5.0 equiv), Et₃N (3.5 mmol, 7.0 equiv), and toluene (5.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C or 130 °C for 20 h. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting products 3 or 4 were purified by column chromatography over silica gel (n-pentanes/dichloromethane = 5:1 or 2:1).
Procedure for gram scale reaction for synthesis of 3-(1-chloro-2,2,2-trifluoroethylidene)-1-methylpyrrolidin-2-one (3a)

![Chemical Structure Diagram]

The 1,3-diphenylpropane-1,3-dione (1a) (2.24 g, 10.0 mmol), trifluoroacetic anhydride (2) (10.5 g, 50.0 mmol, 5.0 equiv), Et$_3$N (70 mmol, 7.0 equiv), and toluene (30 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 100 °C for 20 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (80 mL), washed with saturated brine (100 mL), and water (400 mL), dried over MgSO$_4$. The solvent was removed by rotary evaporation and the resulting product 3a was purified by column chromatography over silica gel (n-pentanes/dichloroethane = 5:1).
The procedure for the synthesis of compound 5

![Chemical structure of 3a and 5](image)

1,3-Diphenyl-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3a) (152.0 mg, 0.50 mmol), sodium borohydride (37.0 mg, 1.0 mmol, 2.0 equiv), dry 1,4-dioxane (5 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at room temperature for 8 h. The reaction mixture was then diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the product 5 was purified by column chromatography over silica gel (n-pentanes/ethyl acetate = 5:1).
The procedure for the synthesis of compound 6

1,3-Diphenyl-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3a) (60.8 mg, 0.20 mmol), 4-methylbenzenethiol (0.20 mmol, 1.0 equiv), ethanol (2 mL) were added to a reaction tube equipped with a stir bar. The resulting mixture was heated at 80 °C for 24 h. The reaction mixture was diluted with ethyl acetate (30 mL), washed with saturated brine (30 mL), and water (20 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting residue was purified by recrystallization.
Data for compounds 3–6.

1,3-Diphenyl-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3a)
Obtained as a pale yellow oil in 85% yield (129 mg). $R_f$ (n-pentane/dichloroethane = 5:1) = 0.30. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (d, $J$ = 7.3 Hz, 4H), 7.65 (dd, $J$ = 14.2, 7.1 Hz, 2H), 7.53 (dd, $J$ = 12.4, 7.2 Hz, 4H), 6.35 (q, $J$ = 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 191.1 (s), 190.9 (s), 148.9 (q, $J$ = 4.6 Hz), 135.2 (s), 134.9 (s), 134.6 (s), 134.5 (s), 130.3 (s), 129.8 (s), 129.0 (s), 128.9 (s), 124.7 (q, $J$ = 36.3 Hz), 121.7 (q, $J$ = 272.6 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -60.1 (d, $J$ = 7.5 Hz, 3F). IR (KBr): ν 3066, 2254, 1659, 1597, 1580, 1345, 1256, 1161, 1066, 860, 803, 684, 584, 480 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{17}$H$_{11}$F$_3$O$_2$: 304.0711; found: 304.0709.

1,3-di-p-Tolyl-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3b)
Obtained as a pale yellow oil in 82% yield (136 mg). $R_f$ (n-pentane/dichloroethane = 5:1) = 0.20. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 – 7.86 (m, 4H), 7.40 – 7.29 (m, 4H), 6.27 (q, $J$ = 7.5 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 190.6 (s), 190.5 (s), 149.6 (q, $J$ = 4.6 Hz), 145.8 (s), 145.7 (s), 132.9 (q, $J$ = 0.9 Hz), 132.3 (s), 130.5 (s), 130.0 (s), 129.7 (s), 129.6 (s), 123.8 (q, $J$ = 36.2 Hz), 121.7 (q, $J$ = 272.5 Hz), 21.9 (s), 21.8 (s). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -60.1 (d, $J$ = 7.5 Hz, 3F). IR (KBr): ν 2925, 2254, 1659, 1605, 1572, 1409, 1344, 1259, 1160, 1141, 1072, 828, 569, 485 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{19}$H$_{15}$F$_3$O$_2$: 332.1024; found: 332.1017.
1,3-di-"m"-Tolyl-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3c)

Obtained as a pale yellow oil in 81% yield (134 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.30. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.87 – 7.77 (m, 4H), 7.52 – 7.38 (m, 4H), 6.34 (q, \( J = 7.5 \) Hz, 1H), 2.45 (s, 3H), 2.44 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 191.3 (s), 191.1 (s), 149.2 (q, \( J = 4.5 \) Hz), 139.0 (s), 138.8 (s), 135.5 (s), 135.3 (s), 135.2 (s), 135.0 (s), 130.5 (s), 129.9 (s), 128.7 (s), 127.6 (s), 127.4 (s), 124.6 (q, \( J = 36.2 \) Hz), 121.7 (q, \( J = 272.5 \) Hz), 21.3 (s), 21.2 (s). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -60.0 (d, \( J = 7.5 \) Hz, 3F). IR (KBr): \( \nu \) 3078, 2255, 1663, 1597, 1506, 1413, 1344, 1239, 1152, 1071, 983, 846, 568, 505 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C\(_{19}\)H\(_{15}\)F\(_3\)O\(_2\): 332.1024; found: 332.1030.

1,3-di-"o"-Tolyl-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3d)

Obtained as a pale yellow oil in 81% yield (134 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.40. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.71 (d, \( J = 7.7 \) Hz, 1H), 7.59 (d, \( J = 7.7 \) Hz, 1H), 7.51 – 7.39 (m, 2H), 7.38 – 7.21 (m, 4H), 6.37 (q, \( J = 7.8 \) Hz, 1H), 2.58 (s, 3H), 2.40 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 194.4 (s), 193.0 (s), 150.1 (q, \( J = 4.5 \) Hz), 140.9 (s), 138.3 (s), 135.4 (s), 134.3 (s), 133.2 (s), 132.4 (s), 132.2 (s), 132.1 (s), 131.7 (s), 129.6 (s), 126.7 (q, \( J = 36.3 \) Hz), 125.9 (s), 125.6 (s), 121.9 (q, \( J = 272.5 \) Hz), 21.5 (s), 20.1 (s). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -60.1 (d, \( J = 7.8 \) Hz, 3F). IR (KBr): \( \nu \) 2970, 1665, 1600, 1571, 1275, 1244, 1162, 1129, 1069, 974, 884, 858, 835, 597, 459 cm\(^{-1}\). HR-MS (ESI): m/z calcd. for C\(_{19}\)H\(_{16}\)F\(_3\)O\(_2\) [M+H]\(^+\): 333.1103; found: 333.1097.
1,3-Bis(4-(tert-butyl)phenyl)-2-(2,2,2-trifluoroethyldiene)propane-1,3-dione (3e)

Obtained as a pale yellow oil in 82% yield (170 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.60. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.11 – 7.91 (m, 4H), 7.62 – 7.48 (m, 4H), 6.30 (q, \( J = 7.5 \) Hz, 1H), 1.37 (s, 9H), 1.36 (s, 9H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 190.6 (s), 190.4 (s), 158.6 (s), 158.5 (s), 149.7 (q, \( J = 4.6 \) Hz), 132.7 (s), 132.3 (s), 130.4 (s), 129.9 (s), 126.0 (s), 125.9 (s), 123.7 (q, \( J = 36.2 \) Hz), 121.5 (q, \( J = 272.6 \) Hz), 35.3 (s), 31.0 (s). \( ^19F \) NMR (376 MHz, CDCl\(_3\)): \( \delta \) -60.1 (d, \( J = 7.5 \) Hz, 3F). IR (KBr): v 3062, 2965, 2870, 2258, 1659, 1602, 1565, 1463, 1344, 1259, 1159, 1134, 1108, 1069, 983, 873, 843, 569 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C\(_{25}\)H\(_{27}\)F\(_3\)O\(_2\): 416.1963; found: 416.1958.

1,3-Bis(4-methoxyphenyl)-2-(2,2,2-trifluoroethyldiene)propane-1,3-dione (3f)

Obtained as a pale yellow solid in 77% yield (140 mg). M.p. 97–99 °C. \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.30. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.05 (d, \( J = 8.0 \) Hz, 2H), 8.01 (d, \( J = 8.0 \) Hz, 2H), 7.07 – 6.90 (m, 4H), 6.19 (q, \( J = 7.2 \) Hz, 1H), 3.90 (s, 6H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 189.3 (s), 189.2 (s), 164.8 (s), 164.7 (s), 150.5 (q, \( J = 5.0 \) Hz), 133.1 (s), 132.5 (s), 128.4 (s), 127.7 (s), 122.5 (q, \( J = 36.1 \) Hz), 121.8 (q, \( J = 272.5 \) Hz), 114.2 (s), 114.1 (s), 55.6 (s), 55.5 (s). \( ^19F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -60.1 (d, \( J = 7.2 \) Hz, 3F). IR (KBr): v 3011, 2960, 2870, 1509, 1459, 1307, 1252, 1153, 1072, 1026, 981, 887, 841, 790, 570, 512 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C\(_{19}\)H\(_{15}\)F\(_3\)O\(_4\): 364.0922; found: 364.0928.
1,3-Bis(3-methoxyphenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3g)

Obtained as a pale yellow oil in 79% yield (143 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.40. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.66 – 7.50 (m, 3H), 7.47 (s, 1H), 7.45 – 7.35 (m, 2H), 7.17 (d, \( J = 7.9 \) Hz, 2H), 6.38 (q, \( J = 7.4 \) Hz, 1H), 3.83 (s, 6H). \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 190.7 (s), 190.6 (s), 160.0 (s), 159.9 (s), 149.0 (q, \( J = 4.6 \) Hz), 136.5 (s), 136.1 (s), 129.9 (s), 124.9 (q, \( J = 36.2 \) Hz), 123.0 (s), 122.9 (s), 121.7 (q, \( J = 272.6 \) Hz), 121.5 (s), 121.1 (s), 114.0 (s), 113.0 (s), 55.4 (s), 55.3 (s). \( ^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -60.1 (d, \( J = 7.4 \) Hz, 3F). IR (KBr): \( \nu \) 3075, 3008, 2942, 2838, 2254, 1663, 1596, 1551, 1458, 1430, 1341, 1264, 1151, 1077, 1033, 878, 832, 680, 607, 558 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C\(_{19}\)H\(_{15}\)F\(_3\)O\(_4\): 364.0922; found: 364.0929.

4,4’-(2-(2,2,2-Trifluoroethylidene)malonyl)dibenzonitrile (3h)

Obtained as a pale yellow solid in 50% yield (88 mg). M.p. 60–63 °C. \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.40. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.08 (d, \( J = 8.2 \) Hz, 4H), 7.92 – 7.83 (m, 4H), 6.40 (q, \( J = 7.3 \) Hz, 1H). \( ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 189.8 (s), 189.5 (s), 146.8 (q, \( J = 4.5 \) Hz), 137.7 (s), 137.6 (s), 132.9 (s), 132.8 (s), 130.5 (s), 130.0 (s), 126.3 (q, \( J = 36.7 \) Hz), 121.2 (q, \( J = 273.0 \) Hz), 118.1 (s), 118.0 (s), 117.5 (s), 117.4 (s). \( ^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) -60.1 (d, \( J = 7.3 \) Hz, 3F). IR (KBr): \( \nu \) 3138, 2255, 1655, 1565, 1461, 1384, 1275, 1181, 1144, 1018, 884, 850, 590, 480 cm\(^{-1}\). HR-MS (ESI): m/z calcd. for C\(_{19}\)H\(_{10}\)F\(_3\)N\(_2\)O\(_2\) [M+H]\(^+\): 355.0695; found: 355.0698.

1,3-Bis(4-fluorophenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3i)

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Obtained as a pale yellow solid in 79% yield (134 mg). Mp: 58–60 °C. $R_f$ ($n$-pentane/dichloroethane = 5:1) = 0.30. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.19 – 7.98 (m, 4H), 7.29 – 7.11 (m, 4H), 6.29 (q, $J$ = 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 189.3 (s), 189.2 (s), 167.9 (d, $J$ = 4.4 Hz), 165.4 (d, $J$ = 4.6 Hz), 148.9 (q, $J$ = 4.6 Hz), 133.2 (d, $J$ = 9.8 Hz), 132.7 (d, $J$ = 9.9 Hz), 131.6 (s), 131.1 (d, $J$ = 2.9 Hz), 123.9 (q, $J$ = 36.4 Hz), 121.5 (q, $J$ = 272.6 Hz), 116.4 (d, $J$ = 6.0 Hz), 116.1 (d, $J$ = 6.1 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -60.2 (d, $J$ = 7.5 Hz, 3F), -101.6 (tt, $J$ = 8.3, 5.4 Hz, 1F), -101.8 (tt, $J$ = 8.3, 5.4 Hz, 1F). IR (KBr): $\mu$ 3078, 2617, 1663, 1597, 1506, 1413, 1344, 1239, 1071, 1012, 983, 872, 864, 568, 505 cm$^{-1}$. HR-MS (ESI): m/z calcd. for C$_{17}$H$_{10}$F$_5$O$_2$ [M+H]$^+$: 341.0599; found: 341.0595.

1,3-Bis(4-chlorophenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3j)

Obtained as a pale yellow oil in 72% yield (134 mg). $R_f$ ($n$-pentane/dichloroethane = 5:1) = 0.50. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05 – 7.87 (m, 4H), 7.60 – 7.45 (m, 4H), 6.31 (q, $J$ = 7.4 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 189.7 (s), 189.6 (s), 148.4 (q, $J$ = 4.6 Hz), 141.6 (s), 141.5 (s), 133.5 (s), 133.0 (s), 131.7 (s), 131.2 (s), 129.4 (s), 129.3 (s), 124.5 (q, $J$ = 36.4 Hz), 121.5 (q, $J$ = 272.7 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -60.1 (d, $J$ = 7.4 Hz, 3F). IR (KBr): $\nu$ 3065, 2257, 2200, 1662, 1586, 1487, 1401, 1343, 1252, 1160, 1090, 1012, 869, 838, 782, 534, 486 cm$^{-1}$. HR-MS (ESI): m/z calcd. for C$_{17}$H$_{10}$Cl$_2$F$_3$O$_2$ [M+H]$^+$: 373.0009; found: 373.0004.

1,3-Bis(4-bromophenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3k)

Obtained as a pale yellow oil in 82% yield (189 mg). $R_f$ ($n$-pentane/dichloroethane = 5:1) = 0.50. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 – 7.80 (m, 4H), 7.75 – 7.63 (m, 4H),
6.31 (q, J = 7.4 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 189.9 (s), 189.8 (s), 148.3 (q, J = 4.6 Hz), 133.8 (s), 133.4 (s), 132.4 (s), 132.3 (s), 131.8 (s), 131.2 (s), 130.5 (s), 130.4 (s), 124.7 (q, J = 36.4 Hz), 121.5 (q, J = 272.7 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -60.1 (d, J = 7.4 Hz, 3F). IR (KBr): ν 3066, 2924, 2205, 1668, 1565, 1470, 1422, 1353, 1275, 1241, 1158, 1138, 1068, 995, 793, 769, 672, 591, 454 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{17}$H$_{10}$Br$_2$F$_3$O$_2$ [M+H]$^+$: 462.8980; found: 462.8974.

**1,3-Bis(3-bromophenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3l)**

Obtained as a pale yellow oil in 72% yield (166 mg). $R_f$ (n-pentane/dichloroethane = 5:1) = 0.60. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.12 (s, 1H), 8.08 (s, 1H), 7.89 (t, J = 8.5 Hz, 2H), 7.78 (t, J = 6.6 Hz, 2H), 7.47 – 7.35 (m, 2H), 6.38 (q, J = 7.4 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 189.7 (s), 189.5 (s), 147.5 (q, J = 4.5 Hz), 137.6 (s), 137.4 (s), 136.8 (s), 136.4 (s), 132.7 (s), 132.2 (s), 130.5 (s), 130.4 (s), 128.9 (s), 128.6 (s), 125.6 (q, J = 36.5 Hz), 123.4 (s), 123.3 (s), 121.4 (q, J = 272.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -60.0 (d, J = 7.4 Hz, 3F). IR (KBr): ν 3066, 2924, 2205, 1668, 1565, 1470, 1422, 1353, 1275, 1241, 1158, 1138, 1068, 995, 793, 769, 672, 591, 454 cm$^{-1}$. HR-MS (ESI): m/z calcd. for C$_{17}$H$_{10}$Br$_2$F$_3$O$_2$ [M+H]$^+$: 462.8980; found: 462.8974.

**1,3-Di(naphthalen-2-yl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3m)**

Obtained as a pale yellow oil solid in 89% yield (179 mg). M.p. 118–120 °C. $R_f$ (n-pentane/dichloroethane = 5:1) = 0.40. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.66 (s, 1H), 8.59 (s, 1H), 8.14 – 8.00 (m, 4H), 7.99 – 7.87 (m, 4H), 7.73 – 7.55 (m, 4H), 6.47 (q, J = 7.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 191.0 (s), 190.9 (s), 149.7 (q, J = 4.5 Hz, 1H), 141.0 (s), 136.9 (s), 136.8 (s), 128.6 (s), 125.6 (q, J = 36.5 Hz), 123.4 (s), 123.3 (s), 121.4 (q, J = 272.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -60.0 (d, J = 7.4 Hz, 3F). IR (KBr): ν 3066, 2924, 2205, 1668, 1565, 1470, 1422, 1353, 1275, 1241, 1158, 1138, 1068, 995, 793, 769, 672, 591, 454 cm$^{-1}$. HR-MS (ESI): m/z calcd. for C$_{17}$H$_{10}$Br$_2$F$_3$O$_2$ [M+H]$^+$: 462.8980; found: 462.8974.
Hz), 136.3 (s), 136.1 (s), 133.7 (s), 132.8 (s), 132.4 (s), 132.3 (s), 132.2 (s), 130.1 (s), 130.0 (s), 129.6 (s), 129.5 (s), 129.1 (s), 128.9 (s), 127.9 (s), 127.8 (s), 127.3 (s), 127.1 (s), 124.5 (s), 124.3 (q, J = 36.7 Hz), 123.9 (s), 121.2 (q, J = 273.0 Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -59.9 (d, J = 7.5 Hz, 3F).

\(1\)H NMR (376 MHz, CDCl\(_3\)): δ 7.66 (s, 2H), 7.38 (d, J = 3.7 Hz, 1H), 7.28 (d, J = 3.7 Hz, 1H), 6.75 (q, J = 7.6 Hz, 1H), 6.59 (dd, J = 3.4, 1.2 Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 177.6 (s), 175.5 (s), 151.5 (s), 150.6 (s), 148.7 (s), 148.5 (s), 145.5 (q, J = 4.6 Hz), 127.2 (q, J = 36.5 Hz), 122.5 (s), 121.6 (q, J = 272.4 Hz), 121.1 (s), 113.2 (s), 113.1 (s). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -59.9 (d, J = 7.6 Hz, 3F).

\(1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.94 (d, J = 3.9 Hz, 1H), 7.85 – 7.73 (m, 3H), 7.24 – 7.12 (m, 2H), 6.46 (q, J = 7.5 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 182.2 (s), 181.4 (s), 148.3 (q, J = 4.7 Hz), 142.4 (s), 141.3 (s), 137.3 (s), 137.0 (s), 136.9 (s), 136.7 (s), 128.9 (s), 128.8 (s), 124.4 (q, J = 36.4 Hz), 121.5 (q, J = 272.6 Hz).

**1,3-Di(furan-2-yl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3n)**

Obtained as a pale yellow oil in 85% yield (120 mg). \(R_f\) (n-pentane/dichloroethane = 5:1) = 0.50. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): δ 7.66 (s, 2H), 7.38 (d, J = 3.7 Hz, 1H), 7.28 (d, J = 3.7 Hz, 1H), 6.75 (q, J = 7.6 Hz, 1H), 6.59 (dd, J = 3.4, 1.2 Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 177.6 (s), 175.5 (s), 151.5 (s), 150.6 (s), 148.7 (s), 148.5 (s), 145.5 (q, J = 4.6 Hz), 127.2 (q, J = 36.5 Hz), 122.5 (s), 121.6 (q, J = 272.4 Hz), 121.1 (s), 113.2 (s), 113.1 (s). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -59.9 (d, J = 7.5 Hz, 3F).

**1,3-Di(thiophen-2-yl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3o)**

Obtained as a pale yellow oil in 82% yield (129 mg). \(R_f\) (n-pentane/dichloroethane = 5:1) = 0.20. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): δ 7.94 (d, J = 3.9 Hz, 1H), 7.85 – 7.73 (m, 3H), 7.24 – 7.12 (m, 2H), 6.46 (q, J = 7.5 Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ 182.2 (s), 181.4 (s), 148.3 (q, J = 4.7 Hz), 142.4 (s), 141.3 (s), 137.3 (s), 137.0 (s), 136.9 (s), 136.7 (s), 128.9 (s), 128.8 (s), 124.4 (q, J = 36.4 Hz), 121.5 (q, J = 272.6 Hz).
Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -60.1 (d, $J =$ 7.5 Hz, 3F). IR (KBr): ν 3103, 1632, 1512, 1407, 1354, 1261, 1158, 1132, 1068, 1034, 912, 851, 610, 569, 476 cm$^{-1}$. HR-MS (ESI): m/z calcd. for C$_{13}$H$_7$F$_3$O$_2$: 315.9840; found: 315.9841.

1-(4-Fluorophenyl)-3-(m-tolyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione

(3p)

Obtained as a pale yellow oil in 83% yield (139 mg). $R_f$ (n-pentane/dichloroethane = 5:1) = 0.40. $^1$H NMR (400 MHz, CDCl$_3$) $E + Z$: $\delta$ 8.15 – 7.97 (m, 2H), 7.91 – 7.71 (m, 2H), 7.57 – 7.36 (m, 2H), 7.21 (t, $J =$ 7.6 Hz, 2H), 6.38 – 6.21 (m, 1H), 2.53 – 2.38 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $E + Z$: $\delta$ 191.2 (s), 190.9 (s), 189.4 (s), 189.3 (s), 167.9 (s), 167.8 (s), 165.4 (s), 165.3 (s), 149.5 (q, $J =$ 4.6 Hz), 148.8 (q, $J =$ 4.7 Hz), 139.1 (s), 138.9 (s), 135.6 (s), 135.4 (s), 134.8 (s), 133.3 (s), 133.2 (s), 132.7 (s), 132.6 (s), 130.5 (s), 130.0 (s), 128.8 (s), 128.7 (d, $J =$ 6.1 Hz), 127.7 (s), 127.5 (s), 124.4 (q, $J =$ 36.5 Hz), 124.0 (q, $J =$ 36.5 Hz), 121.6 (q, $J =$ 273.5 Hz), 121.5 (q, $J =$ 273.5 Hz), 116.4 (s), 116.3 (s), 116.2 (s), 116.1 (s), 21.3 (s), 21.2 (s). $^{19}$F NMR (376 MHz, CDCl$_3$) $E + Z$: $\delta$ -60.1 (t, $J =$ 9.8 Hz), -101.8 – -102.0 (m), -102.1 (dd, $J =$ 6.7, 5.0 Hz). IR (KBr): ν 3153, 2254, 1661, 1598, 1506, 1466, 1412, 1264, 1152, 848, 816, 576, 503 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{18}$H$_{12}$F$_4$O$_2$: 336.0773; found: 336.0777.

1-(4-Bromophenyl)-3-(p-tolyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione

(3q)

Obtained as a pale yellow oil in 85% yield (168 mg). $R_f$ (n-pentane/dichloroethane = 5:1) = 0.40. $^1$H NMR (400 MHz, CDCl$_3$) $E + Z$: $\delta$ 7.81 – 8.00 (m, 4H), 7.66 (d, $J =$ 8.5 Hz, 2H), 7.32 (t, $J =$ 7.3 Hz, 2H), 6.38 – 6.24 (m, 1H), 2.53 – 2.33 (m, 3H). $^{13}$C
NMR (101 MHz, CDCl₃) E + Z: δ 190.4 (s), 190.2 (s), 190.1 (s), 190.0 (s), 149.1 (q, J = 4.6 Hz), 148.6 (q, J = 4.6 Hz), 146.2 (s), 146.1 (s), 134.0 (s), 133.6 (s), 132.7 (s), 132.3 (s), 132.2 (s), 132.1 (s), 131.7 (s), 131.2 (s), 130.5 (s), 130.2 (s), 130.1 (s), 130.0 (s), 129.7 (s), 129.6 (s), 124.3 (q, J = 36.2 Hz), 124.2 (q, J = 36.2 Hz), 121.6 (q, J = 272.6 Hz), 121.5 (q, J = 272.6 Hz), 21.9 (s), 21.8 (s).

19F NMR (376 MHz, CDCl₃) E + Z: δ -60.0 (d, J = 7.5 Hz, 3F), -60.1 (d, J = 7.4 Hz, 3F).

IR (KBr): ν 3063, 2923, 2253, 2196, 1661, 1584, 1545, 1483, 1430, 1399, 1343, 1265, 1158, 1136, 1070, 1010, 979, 868, 828, 774, 575, 489 cm⁻¹. HR-MS (EI): m/z calcd. for C₁₈H₁₂BrF₃O₂: 395.9973; found: 395.9976.

1-(4-Bromophenyl)-3-(4-(tert-butyl)phenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3r)

Obtained as a pale yellow oil in 75% yield (164 mg). R₁ (n-pentane/dichloroethane = 5:1) = 0.40. 1H NMR (400 MHz, CDCl₃) E + Z: δ 7.99 – 7.82 (m, 4H), 7.74 – 7.51 (m, 4H), 6.30 (qd, J = 7.4, 2.7 Hz, 1H), 1.45 – 1.33 (m, 9H). 13C NMR (101 MHz, CDCl₃) E + Z: δ 190.40 (s), 190.4 (s), 190.1 (s), 189.9 (s), 189.8 (s), 158.9 (s), 158.8 (s), 156.6 (s), 148.7 (q, J = 4.6 Hz), 148.6 (q, J = 4.6 Hz), 134.6 (s), 134.0 (s), 132.4 (s), 132.3 (s), 132.2 (s), 132.1 (s), 132.0 (d, J = 6.7 Hz), 131.9 (s), 131.7 (s), 131.3 (s), 131.2 (d, J = 4.3 Hz), 131.1 (s), 130.4 (s), 130.2 (s), 128.6 (s), 127.2 (s), 126.1 (s), 125.8 (s), 125.7 (d, J = 7.6 Hz), 124.4 (s), 124.2 (q, J = 36.3 Hz), 124.0 (s), 121.6 (q, J = 272.4 Hz), 35.4 (s), 35.1 (s), 31.1 (s), 31.0 (d, J = 14.3 Hz), 30.9 (s). 19F NMR (376 MHz, CDCl₃) E + Z: δ -60.2 (d, J = 7.5 Hz, 3F), -60.1 (d, J = 7.4 Hz, 3F). IR (KBr): ν 2965, 2253, 1661, 1584, 1483, 1399, 1261, 1162, 1011, 982, 841, 788, 626, 571, 542 cm⁻¹. HR-MS (EI): m/z calcd. for C₂₁H₁₈BrF₃O₄: 438.0442; found: 438.0451.
1-(4-Bromophenyl)-3-(4-fluorophenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3s)

Obtained as a pale yellow oil in 81% yield (162 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.30. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) 8.19 – 7.95 (m, 2H), 7.86 (d, \( J = 7.1 \) Hz, 2H), 7.65 (d, \( J = 7.6 \) Hz, 2H), 7.29 – 7.09 (m, 2H), 6.39 – 6.22 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) 190.0 (s), 189.8 (s), 189.2 (s), 189.1 (s), 167.9 (d, \( J = 4.6 \) Hz), 165.4 (d, \( J = 4.8 \) Hz), 148.6 (d, \( J = 4.3 \) Hz), 148.5 (d, \( J = 4.3 \) Hz), 133.9 (s), 133.4 (s), 133.2 (s), 133.1 (s), 132.7 (s), 132.6 (s), 132.3 (d, \( J = 2.8 \) Hz), 131.7 (s), 131.2 (s), 130.4 (s), 130.2 (s), 124.3 (q, \( J = 36.3 \) Hz), 124.2 (q, \( J = 36.3 \) Hz), 121.5 (q, \( J = 272.7 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) -60.1 (d, \( J = 7.2 \) Hz, 3F), -60.2 (d, \( J = 6.5 \) Hz, 3F), -101.4 – -101.5 (m, 1F), -101.5 – -101.7 (m, 1F). IR (KBr): \( \nu \) 3076, 2255, 1661, 1597, 1567, 1506, 1254, 1152, 1071, 982, 871, 838, 780, 575, 502 cm\(^{-1}\). HR-MS (EI): m/z calcd. for C\(_{17}\)H\(_9\)BrF\(_4\)O\(_2\): 399.9722; found: 399.9727.

1-(4-Bromophenyl)-3-(4-methoxyphenyl)-2-(2,2,2-trifluoroethylidene)propane-1,3-dione (3t)

Obtained as a pale yellow oil in 80% yield (164 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.50. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) 8.14 – 7.79 (m, 4H), 7.65 (d, \( J = 8.3 \) Hz, 2H), 7.07 – 6.92 (m, 2H), 6.34 – 6.19 (m, 1H), 3.95 – 3.80 (m, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) 190.2 (s), 190.1 (s), 188.8 (s), 188.7 (s), 164.9 (s), 164.8 (s), 149.4 (q, \( J = 4.6 \) Hz), 149.2 (q, \( J = 4.6 \) Hz), 134.0 (s), 133.6 (s), 133.0 (s), 132.4 (s), 132.2 (s), 131.7 (s), 131.3 (s), 130.2 (s), 130.0 (s), 129.4 (s), 128.5 (s), 128.3 (s), 127.4 (s), 123.9 (q, \( J = 36.3 \) Hz), 123.3 (q, \( J = 36.1 \) Hz), 121.7 (q, \( J = 272.6 \) Hz), 121.6 (q, \( J = 272.6 \) Hz), 114.3 (s), 114.2 (s), 55.6 (s), 55.5 (s). \(^{19}\)F NMR (376 MHz,
CDCl₃) E + Z: δ -60.0 (d, J = 7.4 Hz, 3F), -60.1 (d, J = 7.3 Hz, 3F). IR (KBr): v 3061, 2964, 2255, 1645, 1595, 1509, 1482, 1345, 1251, 1155, 1070, 1010, 867, 839, 780, 573, 510 cm⁻¹. HR-MS (EI): m/z calcd. for C₁₉H₁₂BrF₃O₃: 411.9922; found: 411.9923.

1-(4-methoxyphenyl)-2-(2,2,2-trifluoroethylidene)-3-(4-(trifluoromethyl)phenyl)propane-1,3-dione (3u)

Obtained as a pale yellow oil in 72% yield (144 mg). Rᵢ (n-pentane/dichloroethane = 5:1) = 0.60. ¹H NMR (400 MHz, CDCl₃) E + Z: δ 8.22 – 8.08 (m, 2H), 8.07 – 7.90 (m, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 8.5 Hz, 2H), 6.38 – 6.23 (m, 1H), 3.95 – 3.87 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) E + Z: δ 190.5 (s), 190.4 (s), 188.8 (s), 188.7 (s), 165.1 (s), 165.0 (s), 149.0 (q, J = 4.4 Hz), 148.8 (q, J = 4.6 Hz), 137.8 (s), 137.7 (s), 136.0 (s), 135.7 (s), 135.6 (s), 135.4 (s), 135.3 (s), 135.2 (s), 133.0 (s), 132.3 (s), 130.5 (s), 130.2 (s), 128.3 (s), 127.3 (s), 125.9 (q, J = 3.6 Hz), 124.7 (q, J = 36.7 Hz), 123.6 (q, J = 36.4 Hz), 123.8 (s), 123.5 (s), 121.6 (q, J = 272.0 Hz), 121.5 (q, J = 272.0 Hz), 114.4 (s), 114.3 (s), 55.6 (s), 55.5 (s). ¹⁹F NMR (376 MHz, CDCl₃) E + Z: δ -60.1 (d, J = 7.4 Hz, 3F), -60.3 (d, J = 7.4 Hz, 3F), -63.3 (s, 3F), -63.4 (s, 3F). IR (KBr): v 3067, 2963, 2844, 2188, 1661, 1657, 1596, 1573, 1462, 1410, 1323, 1254, 1129, 1065, 1016, 982, 870, 843, 798, 592, 511 m⁻¹. HR-MS (ESI): m/z calcd. for C₁₉H₁₃F₆O₃ [M+H]: 403.0768; found: 403.0763.

Ethyl 2-benzoyl-4,4,4-trifluorobut-2-enoate (3v)

Obtained as a pale yellow oil in 80% yield (108 mg). Rᵢ (n-pentane/dichloroethane = 5:1) = 0.30. ¹H NMR (400 MHz, CDCl₃) E + Z: δ 7.89 (d, J = 7.5 Hz, 2H), 7.66 (t, J =
7.3 Hz, 1H), 7.53 (t, \( J = 7.5 \) Hz, 2H), 7.00 (q, \( J = 7.8 \) Hz, 1H), 4.27 (q, \( J = 7.0 \) Hz, 2H), 1.22 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) 190.2 (s), 162.4 (s), 141.1 (q, \( J = 4.7 \) Hz), 135.2 (s), 134.4 (s), 129.0 (s), 128.9 (s), 128.0 (q, \( J = 36.4 \) Hz), 121.4 (q, \( J = 271.9 \) Hz), 62.9 (s), 13.8 (s).

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( E + Z \): \( \delta \) -60.8 (d, \( J = 7.8 \) Hz, 3F).

IR (KBr): \( \nu \) 2987, 2943, 1739, 1673, 1468, 1394, 1375, 1349, 1281, 1252, 1137, 1096, 1053, 1018, 1003, 868, 796, 760, 660, 619, 546, 507 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_{13}\)H\(_{12}\)F\(_3\)O\(_3\) \([M+H]^+\): 273.0733; found: 273.0732.

**Diethyl 2-(2,2,2-trifluoroethylidene)malonate (3w)**

Obtained as a pale yellow oil in 74% yield (88 mg). \( R_f \) (n-pentane/dichloroethane = 5:1) = 0.60. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.75 (q, \( J = 7.5 \) Hz, 1H), 4.32 (dq, \( J = 13.9, 7.1 \) Hz, 4H), 1.31 (t, \( J = 7.0 \) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 162.5 (s), 161.4 (s), 135.6 (q, \( J = 5.0 \) Hz), 127.7 (q, \( J = 36.7 \) Hz), 121.2 (q, \( J = 271.4 \) Hz), 62.8 (s), 62.4 (s), 13.8 (s), 13.7 (s). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -62.5 (d, \( J = 7.6 \) Hz, 3F). IR (KBr): \( \nu \) 2987, 2943, 1739, 1673, 1468, 1394, 1375, 1349, 1281, 1252, 1234, 1137, 1096, 1053, 1018, 1003, 868, 796, 760, 660, 619, 546, 507 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_9\)H\(_{12}\)F\(_3\)O\(_4\) \([M+H]^+\): 241.0688; found: 241.0682.

**2-(2,2,2-Trifluoroethyl)-1H-indene-1,3(2H)-dione (3x)**

Obtained as a pale yellow solid in 60% yield (68 mg). M.p. 138–140 °C. \( R_f \) (n-pentane/dichloroethane = 2:1) = 0.20. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.07 – 7.96 (m, 2H), 7.93 – 7.86 (m, 2H), 3.31 (t, \( J = 5.1 \) Hz, 1H), 2.81 (qd, \( J = 10.8, 5.2 \) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 196.7 (s), 141.7 (s), 136.1 (s), 125.8 (q, \( J = 277.4 \) Hz), 123.6 (s), 48.4 (q, \( J = 2.1 \) Hz), 29.8 (q, \( J = 31.1 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \)
-63.5 (t, J = 10.8 Hz, 3F). IR (KBr): v 3458, 2956, 2894, 2050, 1980, 1757, 1706, 1603, 1424, 1346, 1392, 1346, 1262, 1219, 1100, 967, 868, 798, 699, 599, 518 cm⁻¹. HR-MS (ED): m/z calcd. for C₁₃H₇F₃O₂: 228.0398; found: 228.0402.

2-(2,2-Difluoroethyl)-1,3-diphenylpropane-1,3-dione (4a)

Obtained as a pale yellow oil in 30% yield (43 mg). R_f (n-pentane/dichloroethane = 2:1) = 0.30. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 7.7 Hz, 4H), 7.62 (t, J = 7.3 Hz, 2H), 7.50 (t, J = 7.4 Hz, 4H), 6.06 (t, J = 56.7 Hz, 1H), 5.58 (t, J = 6.4 Hz, 1H), 2.70 (tt, J = 16.7, 4.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 194.7 (s), 135.2 (s), 134.0 (s), 129.1 (s), 128.7 (s), 115.7 (t, J = 239.6 Hz), 50.1 (t, J = 4.3 Hz), 33.4 (t, J = 22.4 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -115.9 (dt, J = 56.7, 17.0 Hz, 2F). IR (KBr): v 3065, 2935, 2253, 1697, 1677, 1596, 1448, 1364, 1270, 1181, 1069, 984, 704, 691, 601, 509 cm⁻¹. DART-HRMS m/z: calcd. for C₁₃H₁₃F₂O₂ [M+H]^+: 289.1036; found: 229.1034.

2-(2,2-Difluoroethyl)-1,3-dip-tolylpropane-1,3-dione (4b)

Obtained as a pale yellow solid in 22% yield (34 mg). Mp: 110-112 °C. R_f (n-pentane/dichloroethane = 2:1) = 0.40. ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 7.4 Hz, 4H), 7.28 (d, J = 7.4 Hz, 4H), 6.03 (t, J = 56.7 Hz, 1H), 5.48 (t, J = 6.3 Hz, 1H), 2.67 (tt, J = 16.8, 3.2 Hz, 2H), 2.43 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 194.3 (s), 145.0 (s), 132.8 (s), 129.8 (s), 128.8 (s), 115.8 (t, J = 239.5 Hz), 50.0 (t, J = 4.3 Hz), 33.6 (t, J = 22.4 Hz), 21.7 (s). ¹⁹F NMR (376 MHz, CDCl₃): δ -116.0 (dt, J = 56.7, 16.8 Hz, 2F). IR (KBr): v 3032, 2923, 1690, 1672, 1605, 1571, 1509, 1407,
1,3-Bis(4-(tert-butyl)phenyl)-2-(2,2-difluoroethyl)propane-1,3-dione (4e)

Obtained as a pale yellow oil in 22% yield (44mg). $R_f$ (n-pentane/dichloroethane = 2:1) = 0.40. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 7.6$ Hz, 4H), 7.52 (d, $J = 7.6$ Hz, 4H), 6.03 (t, $J = 56.7$ Hz, 1H), 5.53 (t, $J = 6.4$ Hz, 1H), 2.68 (tt, $J = 16.8$, 5.2 Hz, 2H), 1.36 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 194.3 (s), 157.9 (s), 132.6 (s), 128.7 (s), 126.1 (s), 115.9 (t, $J = 239.5$ Hz), 50.0 (t, $J = 4.4$ Hz), 35.2 (s), 33.5 (t, $J = 22.5$ Hz), 31.0 (s). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -116.0 (dt, $J = 56.7$, 16.8 Hz, 2F). IR (KBr): ν 2965, 2870, 1691, 1603, 1564, 1463, 1407, 1364, 1321, 1269, 1189, 1108, 1073, 1041, 986, 961, 621, 546, 508 cm$^{-1}$. DART-HRMS m/z: calcd. for C$_{25}$H$_{31}$F$_2$O$_2$ [M+H]$^+$: 401.2287; found: 401.2286.

2-(2,2-difluoroethyl)-1,3-bis(4-fluorophenyl)propane-1,3-dione (4i)

Obtained as a pale yellow oil in 20% yield (32 mg). $R_f$ (n-pentane/dichloroethane = 2:1) = 0.40. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 – 7.88 (m, 4H), 7.16 (t, $J = 8.1$ Hz, 4H), 6.03 (tt, $J = 56.6$, 3.8 Hz, 1H), 5.44 (t, $J = 6.5$ Hz, 1H), 2.68 (tt, $J = 17.2$, 5.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 192.9 (s), 167.5 (s), 165.0 (s), 131.4 (d, $J = 9.6$ Hz), 116.4 (d, $J = 22.1$ Hz), 115.6 (t, $J = 239.7$ Hz), 50.1 (t, $J = 4.2$ Hz), 33.4 (t, $J = 22.3$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -102.9 – -103.0 (m, 2F), -116.1 (dt, $J = 56.6$, 17.2 Hz, 2F). IR (KBr): ν 3078, 2924, 2853, 1696, 1675, 1596, 1507, 1409, 1346, 1320, 1270, 1238, 1157, 1118, 1071, 1040, 986, 961, 845, 811, 600, 586 cm$^{-1}$. DART-HRMS m/z: calcd. for C$_{17}$H$_{13}$F$_4$O$_2$ [M+H]$^+$: 325.0852; found: 325.0846.
1,3-Bis(4-chlorophenyl)-2-(2,2-difluoroethyl)propane-1,3-dione (4j)

Obtained as a pale yellow oil in 21% yield (37 mg). \( R_f \) (n-pentane/dichloroethane = 2:1) = 0.50. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.91 (d, \( J = 8.2 \) Hz, 4H), 7.48 (d, \( J = 8.2 \) Hz, 4H), 6.03 (tt, \( J = 56.5, 3.7 \) Hz, 1H), 5.42 (t, \( J = 6.5 \) Hz, 1H), 2.68 (tt, \( J = 17.2, 5.6 \) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 193.2 (s), 140.8 (s), 133.4 (s), 130.0 (s), 129.5 (s), 115.5 (t, \( J = 239.8 \) Hz), 50.1 (t, \( J = 4.1 \) Hz), 33.3 (t, \( J = 22.2 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -116.1 (dt, \( J = 56.6, 17.2 \) Hz, 2F). IR (KBr): \( \nu \) 3093, 2925, 2853, 1697, 1588, 1569, 1400, 1320, 1270, 1119, 1092, 1072, 907, 840, 817, 628, 611, 537 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_{17}\)H\(_{13}\)Cl\(_2\)F\(_2\)O\(_2\) [M+H]\(^+\): 357.0261; found: 357.0255.

1,3-Bis(4-bromophenyl)-2-(2,2-difluoroethyl)propane-1,3-dione (4k)

Obtained as a pale yellow solid in 20% yield (44 mg). Mp: 130–132 °C. \( R_f \) (n-pentane/dichloroethane = 2:1) = 0.30. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.82 (d, \( J = 7.9 \) Hz, 4H), 7.63 (d, \( J = 7.9 \) Hz, 4H), 6.03 (tt, \( J = 56.6, 3.6 \) Hz, 1H), 5.41 (t, \( J = 6.5 \) Hz, 1H), 2.67 (tt, \( J = 17.2, 5.6 \) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 193.4 (s), 133.8 (s), 132.5 (s), 130.1 (s), 129.6 (s), 115.5 (t, \( J = 239.8 \) Hz), 50.0 (t, \( J = 4.1 \) Hz), 33.3 (t, \( J = 22.2 \) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -116.0 (dt, \( J = 56.6, 17.2 \) Hz, 2F). IR (KBr): \( \nu \) 3091, 2940, 1697, 1676, 1584, 1566, 1396, 1364, 1320, 1249, 1195, 1178, 1118, 1071, 1041, 1009, 985, 960, 837, 814, 605, 520 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_{17}\)H\(_{13}\)Br\(_2\)F\(_2\)O\(_2\) [M+H]\(^+\): 444.9245; found: 444.9245.
Obtained as a pale yellow solid in 32% yield (60 mg). Mp: 130–132 °C. 

\[ RL \] (n-pentane/dichloroethane = 2:1) = 0.30. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 6 7.89 (d, 6 = 7.5 Hz, 2H), 7.82 (d, 6 = 7.6 Hz, 2H), 7.61 (d, 6 = 7.7 Hz, 2H), 7.30 (d, 6 = 7.8 Hz, 2H), 6.03 (tt, 6 = 56.7, 3.8 Hz, 1H), 5.45 (t, 6 = 6.5 Hz, 1H), 2.82 – 2.52 (m, 2H), 2.44 (s, 3H). 

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): 6 194.1 (s), 193.7 (s), 145.4 (s), 134.1 (s), 132.5 (s), 132.4 (s), 130.1 (s), 129.9 (s), 129.2 (s), 128.9 (s), 115.7 (t, 6 = 239.6 Hz), 50.0 (t, 6 = 4.2 Hz), 33.4 (t, 6 = 22.3 Hz), 21.7 (s). 

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): 6 -115.1 (dt, 6 = 56.6, 16.8 Hz, 2F), -115.9 (dt, 6 = 55.4, 16.2 Hz, 2F), -116.1 (dt, 6 = 34.7, 16.5 Hz, 2F), -116.9 (dt, 6 = 56.7, 17.3 Hz, 2F). IR (KBr): 6 2923, 2852, 1694, 1673, 1605, 1585, 1484, 1397, 1321, 1270, 1179, 1118, 1070, 1042, 1010, 984, 960, 813, 626, 588, 518 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_{18}\)H\(_{16}\)BrF\(_2\)O\(_2\) [M+H]+: 381.0302; found: 381.0296.

Obtained as a pale yellow oil in 21% yield (40 mg). R\(_f\) (n-pentane/dichloroethane = 2:1) = 0.40. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 6 8.06 – 7.94 (m, 2H), 7.83 (d, 6 = 7.5 Hz, 2H), 7.64 (d, 6 = 7.5 Hz, 2H), 7.18 (t, 6 = 8.0 Hz, 2H), 6.03 (tt, 6 = 56.7, 3.5 Hz, 1H), 5.42 (t, 6 = 6.4 Hz, 1H), 2.68 (tt, 6 = 17.2, 5.6 Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): 6 193.5 (s), 192.8 (s), 166.3 (d, 6 = 257.2 Hz), 133.9 (s), 132.5 (s), 131.5 (s), 131.4 (s), 130.1 (s), 129.5 (s), 116.4 (d, 6 = 22.1 Hz), 115.5 (t, 6 = 239.7 Hz), 50.1 (t, 6 = 4.2 Hz), 33.3 (t, 6 = 22.2 Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): 6 -102.7 – -102.9 (m, 1F), -116.1 (dt, 6 = 56.7, 17.2, 3.3 Hz, 2F). IR (KBr): 6 3076, 2925, 2853, 1695, 1674,
1584, 1567, 1485, 1397, 1364, 1320, 1303, 1270, 1238, 1193, 1180, 1157, 1118, 1070, 984, 842, 681, 587, 508 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_{17}\)H\(_{13}\)BrF\(_3\)O\(_2\) [M+H]\(^{+}\): 385.0051; found: 385.0045.

1-(4-Bromophenyl)-2-(2,2-difluoroethyl)-3-(4-methoxyphenyl)propane-1,3-dione (4t)

Obtained as a pale yellow oil in 30% yield (59 mg). \(R_f\) (n-pentane/dichloroethane = 2:1) = 0.40. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.98 (d, \(J = 7.8\) Hz, 2H), 7.82 (d, \(J = 7.6\) Hz, 2H), 7.61 (d, \(J = 7.7\) Hz, 2H), 6.98 (d, \(J = 7.8\) Hz, 2H), 6.02 (t, \(J = 56.6\) Hz, 1H), 5.40 (t, \(J = 6.0\) Hz, 1H), 3.90 (s, 3H), 2.86 – 2.50 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 193.7 (s), 192.8 (s), 164.4 (s), 134.2 (s), 132.3 (s), 131.2 (s), 130.0 (s), 129.2 (s), 127.8 (s), 115.7 (t, \(J = 239.6\) Hz), 114.4 (s), 55.6 (s), 50.0 (t, \(J = 4.0\) Hz), 33.5 (t, \(J = 22.3\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -115.1 (dt, \(J = 56.7, 16.7\) Hz, 2F), -115.8 (dt, \(J = 56.6, 16.7\) Hz, 2F), -116.2 (dt, \(J = 56.8, 17.4\) Hz, 2F), -117.0 (dt, \(J = 56.9, 17.4\) Hz, 2F). IR (KBr): \(\nu\) 3059, 2961, 2842, 1691, 1665, 1597, 1584, 1573, 1510, 1485, 1431, 1396, 1318, 1260, 1169, 1117, 1070, 1028, 983, 960, 839, 625, 590, 511 cm\(^{-1}\). DART-HRMS m/z: calcd. for C\(_{18}\)H\(_{16}\)BrF\(_2\)O\(_3\) [M+H]\(^{+}\): 397.0251; found: 397.0245.

1-(4-Bromophenyl)-3-(4-chlorophenyl)-2-(2,2-difluoroethyl)propane-1,3-dione (4y)

Obtained as a pale yellow solid in 20% yield (40 mg). Mp: 112-113 °C. \(R_f\) (n-pentane/dichloroethane = 2:1) = 0.40. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.91 (d, \(J = 7.6\) Hz, 2H), 7.83 (d, \(J = 7.7\) Hz, 2H), 7.65 (d, \(J = 7.5\) Hz, 2H), 7.48 (d, \(J = 7.5\) Hz,
2H), 6.03 (t, J = 5.6 Hz, 1H), 2.68 (tt, J = 17.2, 2.8 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 193.4 (s), 193.2 (s), 140.8 (s), 133.8 (s), 133.4 (s), 132.5 (s), 130.1 (s), 130.0 (s), 129.6 (s), 129.5 (s), 115.4 (t, J = 239.9 Hz), 50.1 (t, J = 4.1 Hz), 33.3 (t, J = 22.3 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -116.0 (dt, J = 56.6, 17.2 Hz, 2F).

IR (KBr): ν 3091, 2926, 2854, 2253, 1697, 1675, 1585, 1568, 1487, 1399, 1320, 1270, 1118, 1092, 1071, 1043, 986, 904, 856, 839, 816, 608, 536 cm$^{-1}$.

DART-HRMS m/z: calcd. for C$_{17}$H$_{13}$BrClF$_2$O$_2$ [M+H]$^+$: 400.9756; found: 400.9750.

2-(2,2-Difluoroethyl)-1H-indene-1,3(2H)-dione (4x)

Obtained as a pale yellow solid in 20% yield (21 mg). Mp: 87–90 °C. $R_f$ (n-pentane/dichloroethane = 3:1) = 0.30. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07 – 7.97 (m, 2H), 7.93 – 7.86 (m, 2H), 6.29 (tt, J = 56.8, 4.3 Hz, 1H), 3.27 (t, J = 6.4 Hz, 1H), 2.44 (tt, J = 16.1, 5.6 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 198.3 (s), 141.8 (s), 136.0 (s), 123.5 (s), 115.0 (t, J = 240.0 Hz), 48.5 (t, J = 5.3 Hz), 30.6 (t, J = 23.7 Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$): δ -116.4 (dt, J = 56.7, 16.1 Hz, 2F).

IR (KBr): ν 3447, 2936, 2254, 1751, 1711, 1600, 1401, 1347, 1282, 1201, 1119, 1075, 1043, 1014, 955, 904, 787, 601, 531 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{11}$H$_8$F$_2$O$_2$: 210.0492; found: 210.0486.

1,3-Diphenyl-2-(2,2,2-trifluoroethyl)propane-1,3-dione (5)

Obtained as a pale yellow oil in 78% yield (44 mg). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, J = 7.8 Hz, 4H), 7.62 (t, J = 7.4 Hz, 2H), 7.49 (t, J = 7.3 Hz, 4H), 5.62 (t, J = 6.0 Hz, 1H), 3.07 (qd, J = 10.5, 6.7 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): δ 193.2 (s), 135.1 (s), 134.1 (s), 129.1 (s), 128.7 (s), 126.3 (q, J = 276.8 Hz), 50.2 (s), 33.1 (q, J = 6.7 Hz, 2H).
29.9 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -64.9 (t, $J = 10.7$ Hz, 3F). IR (KBr): $\nu$ 3065, 2961, 2258, 1700, 1596, 1581, 1448, 1336, 1257, 1112, 1000, 873, 785, 688, 588 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{17}$H$_{13}$F$_3$O$_2$: 306.0868; found: 306.0858.

1,3-Diphenyl-2-(2,2,2-trifluoro-1-(p-tolylthio)ethyl)propane-1,3-dione (6)

Obtained as a red-brown solid in 80% yield (68 mg). Mp: 167–168 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J = 7.6$ Hz, 2H), 7.97 (d, $J = 7.6$ Hz, 2H), 7.70 – 7.36 (m, 8H), 7.15 (d, $J = 7.3$ Hz, 2H), 5.95 (d, $J = 10.1$ Hz, 1H), 4.89 – 4.71 (m, 1H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 191.1 (s), 191.0 (s), 139.3 (s), 136.8 (s), 135.6 (s), 134.1 (s), 134.0 (s), 133.6 (s), 130.1 (s), 129.7 (s), 129.1 (s), 129.0 (s), 128.9 (s), 128.7 (s), 126.5 (q, $J = 279.3$ Hz), 54.7 (s), 53.0 (q, $J = 28.6$ Hz), 21.2 (s). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -68.0 (d, $J = 8.1$ Hz, 3F). IR (KBr): $\nu$ 3063, 2254, 1701, 1675, 1596, 1492, 1448, 1292, 1247, 1176, 1101, 963, 810, 685, 595, 574 cm$^{-1}$. HR-MS (EI): m/z calcd. for C$_{24}$H$_{20}$F$_3$O$_2$S [M+H]$^+$: 429.1131; found: 429.1126.
Crystal structure analyses

The suitable crystals of 3f (CCDC 1837087), and 4k (CCDC 1859309) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using MoKα radiation (λ = 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.
ORTEP diagrams of 3f.
ORTEP diagrams of 4k.
The procedure for the evaluation of fungicidal activities

Each of the test compounds (4 mg) was first dissolved in 5 mL of mixture of acetone and methanol (1:1 by volume), and then 5 mL of water containing 0.1% Tween 80 was added to generate a 10 mL stock solution of 400 mg/L concentration.

Briefly, a whole plant is used in this test, and the testing solution is sprayed to the host plant by a special plant sprayer. The plant is inoculated with fungus after 24 h. According to the infecting characteristics of fungus, the plant is stored in a humidity chamber and then transferred into a greenhouse after infection is finished. The other plants are placed in a greenhouse directly. The activity of each compound was estimated by visual inspection after 4-7 days, and screening results were reported as a range from 0% (no control) to 100% (complete control).
References:


(3) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.
Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

$^1$H-NMR spectrum of 1s in CDCl$_3$

$^{13}$C-NMR spectrum of 1s in CDCl$_3$
$^{19}$F-NMR spectrum of 1s in CDCl$_3$

$^1$H-NMR spectrum of 1y in CDCl$_3$
$^{13}$C-NMR spectrum of 1y in CDCl$_3$

$^1$H-NMR spectrum of 3a in CDCl$_3$
$^{13}$C-NMR spectrum of 3a in CDCl$_3$

$^{19}$F-NMR spectrum of 3a in CDCl$_3$
$^1$H-NMR spectrum of 3b in CDCl$_3$

$^{13}$C-NMR spectrum of 3b in CDCl$_3$
$^{19}$F-NMR spectrum of 3b in CDCl$_3$

$^1$H-NMR spectrum of 3c in CDCl$_3$
$^{13}$C-NMR spectrum of 3c in CDCl$_3$

$^{19}$F-NMR spectrum of 3c in CDCl$_3$
$^1$H-NMR spectrum of 3d in CDCl$_3$

$^{13}$C-NMR spectrum of 3d in CDCl$_3$
$^{19}$F-NMR spectrum of 3d in CDCl$_3$

$^1$H-NMR spectrum of 3e in CDCl$_3$
$^{13}$C-NMR spectrum of $3e$ in CDCl$_3$

$^{19}$F-NMR spectrum of $3e$ in CDCl$_3$
$^{1}{H}$-NMR spectrum of $3f$ in CDCl$_3$

$^{13}$C-NMR spectrum of $3f$ in CDCl$_3$
$^{19}$F-NMR spectrum of 3f in CDCl$_3$

$^1$H-NMR spectrum of 3g in CDCl$_3$
$^{13}$C-NMR spectrum of 3g in CDCl$_3$

$^{19}$F-NMR spectrum of 3g in CDCl$_3$
$^1$H-NMR spectrum of 3h in CDCl$_3$

$^{13}$C-NMR spectrum of 3h in CDCl$_3$
$^{19}$F-NMR spectrum of 3h in CDCl$_3$

$^1$H-NMR spectrum of 3i in CDCl$_3$
$^{13}$C-NMR spectrum of 3i in CDCl$_3$

$^{19}$F-NMR spectrum of 3i in CDCl$_3$
$^1$H-NMR spectrum of 3j in CDCl$_3$

$^{13}$C-NMR spectrum of 3j in CDCl$_3$
$^{19}F$-NMR spectrum of 3j in CDCl$_3$

$^1$H-NMR spectrum of 3k in CDCl$_3$
$^{13}$C-NMR spectrum of $3k$ in CDCl$_3$

$^{19}$F-NMR spectrum of $3k$ in CDCl$_3$
$^1$H-NMR spectrum of 3l in CDCl$_3$

$^{13}$C-NMR spectrum of 3l in CDCl$_3$
$^{19}$F-NMR spectrum of 3l in CDCl$_3$

$^1$H-NMR spectrum of 3m in CDCl$_3$
$^{13}$C-NMR spectrum of 3m in CDCl$_3$

$^{19}$F-NMR spectrum of 3m in CDCl$_3$
\( ^1 \text{H-NMR} \) spectrum of 3n in \( \text{CDCl}_3 \)

\( ^{13} \text{C-NMR} \) spectrum of 3n in \( \text{CDCl}_3 \)
$^{19}$F-NMR spectrum of 3n in CDCl$_3$

$^1$H-NMR spectrum of 3o in CDCl$_3$
$^{13}$C-NMR spectrum of 3o in CDCl$_3$

$^{19}$F-NMR spectrum of 3o in CDCl$_3$
$^1$H-NMR spectrum of 3p in CDCl$_3$

$^{13}$C-NMR spectrum of 3p in CDCl$_3$
$^{19}$F-NMR spectrum of $3p$ in CDCl$_3$

$^1$H-NMR spectrum of $3q$ in CDCl$_3$
$^{13}$C-NMR spectrum of 3q in CDCl$_3$

$^{19}$F-NMR spectrum of 3q in CDCl$_3$
$^1$H-NMR spectrum of 3r in CDCl$_3$

$^{13}$C-NMR spectrum of 3r in CDCl$_3$
$^{19}$F-NMR spectrum of $3r$ in CDCl$_3$

$^1$H-NMR spectrum of $3s$ in CDCl$_3$
$^{13}$C-NMR spectrum of 3s in CDCl$_3$

$^{19}$F-NMR spectrum of 3s in CDCl$_3$
$^1$H-NMR spectrum of 3t in CDCl$_3$

$^{13}$C-NMR spectrum of 3t in CDCl$_3$
\( ^{19}\text{F-NMR spectrum of } 3t \text{ in CDCl}_3 \)

\( ^1\text{H-NMR spectrum of } 3u \text{ in CDCl}_3 \)
$^{13}$C-NMR spectrum of 3u in CDCl$_3$

$^{19}$F-NMR spectrum of 3u in CDCl$_3$
$^1$H-NMR spectrum of 3v in CDCl$_3$

$^{13}$C-NMR spectrum of 3v in CDCl$_3$
$^{19}$F-NMR spectrum of 3v in CDCl$_3$

$^1$H-NMR spectrum of 3w in CDCl$_3$
$^{13}$C-NMR spectrum of 3w in CDCl$_3$

$^{19}$F-NMR spectrum of 3w in CDCl$_3$
$^1$H-NMR spectrum of 3x in CDCl$_3$

[C-NMR spectrum of 3x in CDCl$_3$]
$^{19}$F-NMR spectrum of 3x in CDCl$_3$

$^1$H-NMR spectrum of 4a in CDCl$_3$
$^{13}$C-NMR spectrum of 4a in CDCl$_3$

$^{19}$F-NMR spectrum of 4a in CDCl$_3$
$^1$H-NMR spectrum of 4b in CDCl$_3$

$^{13}$C-NMR spectrum of 4b in CDCl$_3$
$^{19}$F-NMR spectrum of $4b$ in CDCl$_3$

$^1$H-NMR spectrum of $4e$ in CDCl$_3$
$^{13}$C-NMR spectrum of 4e in CDCl$_3$

$^{19}$F-NMR spectrum of 4e in CDCl$_3$
$^1$H-NMR spectrum of 4i in CDCl$_3$

$^{13}$C-NMR spectrum of 4i in CDCl$_3$
$^{19}$F-NMR spectrum of 4i in CDCl$_3$

$^1$H-NMR spectrum of 4j in CDCl$_3$
\[ ^{13}\text{C-NMR spectrum of 4j in CDCl}_3 \]

\[ \text{C-F spectrum of 4j in CDCl}_3 \]

\[ ^{19}\text{F-NMR spectrum of 4j in CDCl}_3 \]
$^1$H-NMR spectrum of 4k in CDCl$_3$

$^{13}$C-NMR spectrum of 4k in CDCl$_3$
$^{19}$F-NMR spectrum of 4k in CDCl$_3$

$^1$H-NMR spectrum of 4q in CDCl$_3$
$^{13}$C-NMR spectrum of 4q in CDCl$_3$

![$^{13}$C-NMR spectrum of 4q in CDCl$_3$](image)

$^{19}$F-NMR spectrum of 4q in CDCl$_3$

![$^{19}$F-NMR spectrum of 4q in CDCl$_3$](image)
$^1$H-NMR spectrum of $4s$ in CDCl$_3$

$^{13}$C-NMR spectrum of $4s$ in CDCl$_3$
$^{19}\text{F-NMR spectrum of } 4s \text{ in CDCl}_3$

$^{1}\text{H-NMR spectrum of } 4t \text{ in CDCl}_3$
$^{13}$C-NMR spectrum of 4t in CDCl$_3$

$^{19}$F-NMR spectrum of 4t in CDCl$_3$
$^1$H-NMR spectrum of 4y in CDCl$_3$

$^{13}$C-NMR spectrum of 4y in CDCl$_3$
$^{19}$F-NMR spectrum of 4y in CDCl$_3$ 

$^1$H-NMR spectrum of 4x in CDCl$_3$
$^{13}$C-NMR spectrum of $4x$ in CDCl$_3$

$^{19}$F-NMR spectrum of $4x$ in CDCl$_3$
$^1$H-NMR spectrum of 5 in CDCl$_3$

$^{13}$C-NMR spectrum of 5 in CDCl$_3$
$^{19}$F-NMR spectrum of 5 in CDCl$_3$

$^1$H-NMR spectrum of 6 in CDCl$_3$
$^1$C-NMR spectrum of 6 in CDCl$_3$

$^{19}$F-NMR spectrum of 6 in CDCl$_3$