SUPPORTING INFORMATION

Acid Mediated Electrocyclic Domino Transformations of 5,5-Disubstituted 1-Amino-1-azapenta-1,4-dien-3-ones into Dihydrospiroindenepyrazole and Dihydroindenodiazepine Derivatives

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Experimental Section

Melting points are uncorrected. ^{1}H, ^{13}C, ^{19}F, ^{31}P, GCOSY, GHSQC, GHMBC and 1D-NOE NMR spectroscopy: TMS (^{1}H) (0.00 ppm), $CDCl_3$ (^{13}C) (77.0 ppm), $CFCl_3$ (^{19}F) (0.0 ppm) were used as internal reference, 85 % H_3PO_4 (^{31}P) (0.0 ppm) was used as external reference. When necessary, the experiments were carried out with complete exclusion of moisture.

General Procedure: Preparation of hydrazones 2

Hydrazones **2** were prepared from α-ketoesters and the corresponding hydrazines. α -Ketoester (1 eq.) was dissolved in abs. ethanol (1 mmol of the compound in 2 mL of solvent) and hydrazine (1-1.1 eq.) in abs. ethanol (1 mmol of the compound in 0.5 mL of solvent) was added slowly at 0°C. In case of the synthesis of compounds **2e** and **2f** acetic acid (1 eq.) and a small amount of sodium acetate were added to the reaction mixture in order to maintain pH 5-6. The reaction mixture was stirred at RT for 4 h. The reaction mixture was filtered and the solvent was evaporated. The hydrazones **2** were purified by distillation at reduced pressure.

Ethyl 2-(2,2-dimethylhydrazono)propanoate (2a).[1] **2a** was obtained from ethylpyruvate (2.32 g, 20 mmol) and *N,N*-dimethylhydrazine (1.26 g, 21 mmol) according to the general procedure. The subsequent distillation (0.09 mbar, 38°C, (0.1 torr, 90°C[1]) gave 2.45 g (15.51 mmol, 78%, (87%[1]) **2a** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, J= 7.1 Hz, 3H, CH_3), 2.13 (s, 3H, CH_3), 2.85 (s, 6H, CH_3N), 4.30 (q, J = 7.1 Hz, 2H, CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH_3), 15.7 (CH_3), 46.9 (CH_3N), 61.4 (CH_2O), 145.5 (C=N), 165.3 (COO) ppm.

Ethyl 2-(2-ethyl-2-methylhydrazono)propanoate (2b). 2b was obtained from ethylpyruvate (2.32 g, 20 mmol) and *N*-ethyl-*N*-methylhydrazine (1.48 g, 20 mmol) according to the general procedure. The subsequent distillation (0.3 mbar, 42-45°C) gave 2.81 g (16.33 mmol, 82%) **2b** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, J = 7.2 Hz, 3H, CH_3CH_2N), 1.34 (t, J = 7.1 Hz, 3H, CH_3CH_2O), 2.13 (s, 3H, CH_3), 2.78 (s, 3H, CH_3N), 3.14 (q, J = 7.2 Hz, 2H, CH_3CH_2N), 4.29 (q, J = 7.1 Hz, 2H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8 (CH_3CH_2N), 14.2 (CH_3CH_2O), 15.7 (CH_3), 43.2 (CH_3N), 54.7 ($CH_3\mathit{C}H_2N$), 61.2 ($CH_3\mathit{C}H_2O$), 144.6 (*C*=N), 165.4 (*C*OO) ppm. IR (film): nu(tilde) = 3395 (w), 2937 (m), 2905 (w), 2870 (w), 2855 (w), 1734 (m), 1707 (s), 1580 (w), 1460 (m), 1447 (m), 1369 (m), 1310 (s), 1227 (m), 1173 (m), 1138 (s), 1096 (m), 1069 (m), 1036 (m), 995 (w), 939 (w), 860 (w), 797 (w), 754 (w), 708 (w), 665 (m) cm^{-1}. HRMS (ESI): calcd. for $C_8H_{16}N_2O_2Na$ 195.1104; found 195.1109. $C_8H_{16}N_2O_2$ (172.22): calcd. C 55.79, H 9.36, N 16.27; found C 55.44, H 9.60, N 16.46.

Ethyl 2-(2-isopropyl-2-methylhydrazono)propanoate (2c). 2c was obtained from ethylpyruvate (2.32 g, 20 mmol) and *N*-isopropyl-*N*-methylhydrazine (1.76 g, 20 mmol) according to the general procedure. The subsequent distillation (0.5 mbar, 50-52°C) gave 3.13g (16.83 mmol, 84%) **2c** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, J = 6.6 Hz, 6H, $C\mathit{H}_3$), 1.32 (t, J = 7.1 Hz, 3H, $C\mathit{H}_3CH_2O$), 2.12 (s, 3H, $C\mathit{H}_3$), 2.76 (s, 3H, $C\mathit{H}_3N$), 3.42 (sept, J = 6.6 Hz, 1H, C*H*), 4.25 (q, J = 7.1 Hz, 2H, $CH_3C\mathit{H}_2O$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 ($\mathit{C}H_3$), 15.9 ($\mathit{C}H_3$), 19.7 ($\mathit{C}H_3$), 39.2 ($\mathit{C}H_3N$), 59.1 (*C*HN), 61.0 ($\mathit{C}H_3CH_2O$), 140.1 (*C*=N), 166.0 (*C*OO) ppm. IR (film): nu(tilde) = 3379 (w), 2976 (m), 2934 (m), 2912 (m), 2874 (w), 2855 (w), 1734 (m), 1703 (s), 1580 (m), 1460 (m), 1448 (m), 1366 (m), 1310 (s), 1229 (m), 1173 (m), 1136 (s), 1121 (s), 1076 (m), 1034 (m), 961 (w), 891 (w), 866 (w), 847 (w), 793 (w), 756 (w), 700 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_9H_{18}N_2O_2Na$ 209.1260; found 209.1273. $C_9H_{18}N_2O_2$ (186.25): calcd. C 58.04, H 9.74, N 15.04; found C 57.88; H 10.01, N 15.03.

Ethyl 2-(2-butyl-2-methylhydrazono)propanoate (2d). 2d was obtained from ethylpyruvate (2.32 g, 20 mmol) and *N*-butyl-*N*-methylhydrazine (2.17 g, 20 mmol) according to the general procedure. The subsequent distillation (0.2 mbar, 57-60°C) gave 3.68 g (18.4 mmol, 92%) **2d** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H, $C\mathit{H}_3$), 1.28-1.41 (m, 5H, $C\mathit{H}_3$, $C\mathit{H}_2$) , 1.50-1.60 (m, 2H, $C\mathit{H}_2$), 2.13 (s, 3H, $C\mathit{H}_3$), 2.79 (s, 3H, $C\mathit{H}_3N$), 3.08-3.13 (m, 2H, $C\mathit{H}_2N$), 4.29 (q, J = 7.1 Hz, 2H, $C\mathit{H}_2O$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9 ($\mathit{C}H_3$), 14.2 ($\mathit{C}H_3$), 15.7 ($\mathit{C}H_3$), 20.0 ($\mathit{C}H_2$), 30.0 ($\mathit{C}H_2$), 43.7 ($\mathit{C}H_3$), 60.4 ($\mathit{C}H_2$), 61.3 ($\mathit{C}H_2$), 144.1 (*C*=N), 165.5 (*C*OO) ppm. IR (film): nu(tilde) = 3398 (w), 2961 (m), 2934 (m), 2872 (m), 1736 (m), 1709 (s), 1655 (w), 1578 (m), 1560 (w), 1466 (m), 1448 (m), 1367 (m), 1310 (m), 1244 (m), 1219 (m), 1173 (m), 1138 (s), 1094 (m), 1074 (m), 1032 (m), 966 (w), 945 (w), 895 (w), 864 (w), 827 (w), 789 (w), 754 (w), 702 (w), 665 (w), 644 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{20}N_2O_2Na$ 223.1417; found 223.1417. $C_{10}H_{20}N_2O_2$ (200.28): calcd. C 59.97, H 10.07, N 13.99; found C 59.80, H 10.16, N 13.85.

Methyl 2-(2,2-dimethylhydrazono)-2-phenylacetate (2e). 2e was obtained from phenylglyoxylic acid methyl ester (1.64 g, 10 mmol) and *N,N*-dimethylhydrazine (0.66 g, 11 mmol) according to the general procedure. The subsequent distillation (0.01 mbar, 84-88°C) gave 1.28 g (6.21mmol, 62%) **2e** as a yellow oil. Mixture of *E*- and *Z*- isomers 1:1.4 ratio. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84, 2.87 (s, 6H, CH_3N), 3.77, 3.90 (s, 3H, CH_3O), 7.25-7.36 (m, 4H, *H*-arom.), 7.55-7.58 (m, 1H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.91, 46.94 (CH_3N), 51.9, 52.2 (CH_3O), 126. 2 (*C*H-arom.), 127.6 (*C*H-arom.), 128.0 (*C*H-arom.), 128.4 (*C*H-arom.), 129.2 (*C*H-arom.), 130.0 (*C*H-arom.), 134.1, 135.5 (*C*-ipso), 145.7 (*C*=N), 166.4 (*C*OO), 166.8 (*C*OO) ppm. IR (film): nu(tilde) = 3059 (w), 3024 (w), 2991 (w), 2951 (m), 2899 (w), 2866 (w), 2791 (w), 1722 (s), 1703 (s), 1597 (w), 1557 (s), 1493 (m), 1466 (w), 1445 (m), 1435 (m), 1423 (m), 1298 (m), 1277 (m), 1246 (m), 1202 (s), 1159 (w), 1128 (w), 1057 (s), 1022 (m), 1007 (w), 945 (w), 835 (w), 766 (w), 756 (w), 729 (w), 698 (m), 652 (w), 621(w), 588 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}N_2O_2Na$ 229.0947; found 229.0944.

Ethyl 2-(2,2-dimethylhydrazono)-2-(2-thienyl)acetate (2f). 2f was obtained from 2-thiophene glyoxylic acid ethyl ester (1.25 g, 6.8 mmol) and *N,N*-dimethylhydrazine (0.45 g, 7.5 mmol) according to the general procedure. The subsequent distillation (0.01 mbar, 88-92°C) gave 1.14 g (5.04 mmol, 74%) **2f** as an orange oil. Mixture of *E*- and *Z*-isomers, 1:1 ratio. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, J = 7.1 Hz, 3H, CH_3), 1.39 (t, J = 7.1 Hz, 3H, CH_3), 2.88 (s, 6H, CH_3N), 2.91 (s, 6H, CH_3N), 4.29 (q, J = 7.1 Hz, 3H, CH_2), 4.39 (q, J = 7.1 Hz, 3H, CH_2), 6.96-7.05 (m, 3H, *H*-thiophene), 7.12 (dd, J = 3.6, 1.1 Hz, 1H, *H*-thiophene), 7.23 (dd, J = 5.1, 1.1 Hz, 1H, *H*-thiophene), 7.42 (dd, J = 5.1, 1.1 Hz, 1H, *H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1 (CH_3), 14.3 (CH_3), 46.5 (CH_3N), 47.0 (CH_3N), 61.3 (CH_2O), 61.5 (CH_3O), 125.7 (*C*H-arom.), 125.8 (*C*H-arom.), 126.4 (*C*H-arom.), 127.2 (*C*H-arom.), 128. 4 (*C*H-arom.), 128.6, 128.8, 130.6 (*C*H-arom.), 133.7, 137.2, 137.4, 138.9 (*C*=N), 140.1 (*C*=N), 164.9 (*C*OO), 165.5(*C*OO) ppm. IR (film): nu(tilde) = 3103 (w), 3076 (w), 2982 (w), 2959 (w), 2901 (w), 2866 (w), 2824 (w), 2791 (w), 1720 (m), 1670 (w), 1665 (w), 1578 (w), 1560 (w), 1553 (w), 1510 (w), 1501 (w), 1491 (w), 1466 (w), 1420 (w), 1391 (w), 1367 (w), 1354 (w), 1304 (w), 1223 (w), 1192 (m), 1069 (m), 1045 (m), 1020 (w), 976 (w), 945 (w), 847 (w), 704 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{14}N_2O_2SNa$ 249.0668; found 249.0667.

Ethyl 2-(2-allyl-2-methylhydrazono)propanoate (2g). 2g was obtained from ethylpyruvate (2.32 g, 20 mmol) and *N*-allyl-*N*-methylhydrazine (1.72 g, 20 mmol) according to the general procedure. The subsequent distillation (0.2 mbar, 55-58°C) gave 2.68 g (14.57 mmol, 73%) **2g** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7.1 Hz, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.79 (s, 3H, CH_3N), 3.73 (m, 2H, CH_2), 4.29 (q, J = 7.1 Hz, 2H, CH_2O), 5.19-5.28 (m, 2H, CH_2-vinyl), 5.91 (tdd, J = 16.4, 10.2, 6.2 Hz, 1H, C*H*-vinyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (*C*H_3), 15.8 (*C*H_3), 43.2 (*C*H_3N), 61.4 (*C*H_2), 63.3 (*C*H_2), 117.9 (*C*H_2-vinyl), 134.0 (*C*H-vinyl), 144.7 (*C*=N), 165.4 (*C*OO) ppm. IR (film): nu(tilde) = 3398 (w) **,** 3080 (m), 2982 (s), 2947 (s), 2907 (s), 2874 (s), 1848 (w), 1734 (s), 1707 (s), 1646 (s), 1584 (s), 1504 (m), 1460 (s), 1447 (s), 1393 (s), 1383 (s), 1310 (s), 1223 (s), 1167 (s), 1140 (s), 1098 (s)**,** 1024 (s), 924 (s), 864 (m), 826 (m), 791 (m), 756 (s), 665 (w), 636 (w) cm^{-1}. HRMS (ESI): calcd. for $C_9H_{16}N_2O_2Na$ 207.1104; found 207.1106. $C_9H_{16}N_2O_2$ (184.24): calcd. C 58.67, H 8.75, N 15.21; found C 58.30, H 8.82, N 15.00.

Ethyl 2-(2-benzyl-2-methylhydrazono)propanoate (2h). 2h was obtained from ethylpyruvate (2.27 g, 19.6 mmol) and *N*-aminomorpholine (2.66 g, 19.6 mmol) according to the general procedure. The subsequent distillation (0.1 mbar, 105-110°C) gave 2.70 g (11.54 mmol, 59%) **2h** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, J = 7.1 Hz, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.75 (s, 3H, CH_3N), 4.30 (s, 2H, CH_2Ph), 4.30 (q, J = 7.1 Hz, 2H, CH_2O), 7.27-7.37 (m, 5H, *H*-arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (*C*H_3), 15.7 (*C*H_3), 43.0 (*C*H_3), 61.4 (*C*H_2), 64.7 (*C*H_2), 127.3 (*C*H-arom.), 128.3 (*C*H-arom.), 128.5 (*C*H-arom.), 137.6 (*C*-ipso), 144.9 (*C*=N), 165.5 (*C*OO) ppm. IR (film): nu(tilde) = 3398 (w), 3086 (w), 3063 (w), 3030 (w), 2982 (s), 2936 (m), 2905 (m), 2872 (m), 2849 (m), 2802 (w), 1732 (s), 1711 (s), 1651 (w), 1585 (m), 1495 (w), 1454 (s), 1447 (m), 1391 (w), 1367 (m), 1306 (s), 1232 (m), 1198 (s), 1171 (m), 1146 (s), 1101 (m), 1084 (w), 1028 (m), 959 (w), 912 (w), 864 (w), 837 (w), 789 (w), 756 (w), 731 (m), 725 (w), 698 (m), 644 (w), 592 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{18}N_2O_2Na$ 257.1260; found 257.1253. $C_{13}H_{18}N_2O_2$ (234.29): calcd. C 66.64, H 7.74, N 11.96; found C 66.39, H 7.70, N 12.11.

Ethyl 2-(pyrrolidin-1-ylimino)propanoate (2i). 2i was obtained from ethylpyruvate (4.64 g, 40 mmol) and *N*-aminopyrrolidine hydrochloride (5 g, 41 mmol) according to the general procedure. The subsequent distillation (0.1 mbar, 75°C) gave 3.44 g (18.70 mmol, 63%) **2i** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H, CH_3CH_2), 1.86-1.90 (m, 4H, CH_2), 2.12 (s, 3H, CH_3), 3.42-3.45 (m, 4H, CH_2N), 4.28 (q, J = 7.1 Hz, 2H, CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (CH_3), 16.1 (CH_3), 24.4 (CH_2), 55.9 (CH_2N), 61.1 (CH_2O), 144.7 (C=N), 165.9 (COO) ppm. IR (film): nu(tilde) = 3379 (w), 2974 (s), 2872 (m), 1699 (s), 1572 (m), 1475 (w), 1458 (m), 1448 (m), 1393 (w), 1369 (m), 1346 (m), 1302 (s), 1258 (m), 1240 (m), 1209 (m), 1151 (s), 1124 (s), 1030 (m), 974 (w), 932 (w), 916 (w), 864 (w), 787 (w), 758 (m), 723 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_9H_{16}N_2O_2Na$ 207.1104; found 207.1103. $C_9H_{16}N_2O_2$ (184.24): calcd. C 58.67, H 8.75, N 15.21; found C 58.12, H 8.84, N 15.29.

Ethyl 2-(piperidin-1-ylimino)propanoate (2j). 2j was obtained from ethylpyruvate (1.16 g, 10 mmol) and *N*-aminopiperidine (1.05 g, 10.5 mmol) according to the general procedure. The subsequent distillation (0.09 mbar, 61°C) gave 1.82 g (9.2 mmol, 92%) **2j** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (t, J = 7.1 Hz, 3H, CH_3), 1.46-1.54 (m, 2H, CH_2), 1.67-1.74 (m, 4H, CH_2), 2.13 (s, 3H, CH_3), 2.94-2.98 (m, 4H, CH_2N), 4.31 (q, J = 7.1 Hz, 2H, CH_2O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 15.9 (CH_3), 23.8 (CH_2), 25.3 (CH_2), 55.5 (CH_2N), 61.6 (CH_2O), 150.8 (C=N), 165.1 (COO) ppm. IR (film): nu(tilde) = 3451 (w), 3406 (w), 2980 (m), 2937 (s), 2856 (m), 2820 (m), 2725 (w), 2698 (w), 2667 (w), 1734 (s), 1713 (s), 1649 (w), 1603 (w), 1474 (m), 1443 (m), 1391 (w), 1366 (m), 1306 (s), 1277 (m), 1229 (m), 1173 (m), 1140 (s), 1103 (m), 1065 (m), 1036 (m), 1003 (m), 953 (w), 914 (w), 860 (m), 785 (w), 746 (m), 706 (w), 665 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{18}N_2O_2Na$ 221.1260; found 221.1260. $C_{10}H_{18}N_2O_2$ (198.26): calcd. C 60.58, H 9.15, N 14.14; found C 60.22, H 9.21, N 14.02.

Ethyl 2-(azepan-1-ylimino)propanoate (2k). 2k was obtained from ethylpyruvate (1.16 g, 10 mmol) and *N*-aminohomopiperidine (1.20 g, 10.5 mmol) according to the general procedure. The subsequent distillation (0.01 mbar, 84°C) gave 1.84 g (8.7 mmol, 87%) **2k** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H, CH_3), 1.58-1.62 (m, 4H, CH_2), 1.70-1.75 (m, 4H, CH_2), 2.12 (s, 3H, CH_3), 3.47-3.51 (m, 4H, CH_2N), 4.25 (q, *J* = 7.1 Hz, 2H, CH_2O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3 (CH$_3$), 15.9 (CH$_3$), 27.1 (CH$_2$), 27.9 (CH$_2$), 57.7 (CH$_2$N), 61.0 (CH$_2$O), 147.0 (*C*=N), 166.4 (*C*OO) ppm. IR (film): nu(tilde) = 3368 (w), 2978 (m), 2930 (m), 2856 (m), 2687 (w), 1697 (s), 1570 (m), 1450 (m), 1366 (m), 1302 (m), 1281 (m), 1227 (m), 1175 (m), 1126 (s), 1094 (m), 1034 (m), 1013 (w), 968 (w), 907 (w), 856 (w), 785 (w), 760 (w), 733 (w), 665 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{20}N_2O_2Na$ 235.1417; found 235.1413. $C_{11}H_{20}N_2O_2$ (212.29): calcd. C 62.24, H, 9.50, N 13.20; found C 61.73; H 9.52, N 13.01.

Ethyl 2-(morpholine-4-ylimino)propanoate (2l). 2l was obtained from ethylpyruvate (1.16 g, 10 mmol) and *N*-aminomorpholine (1.06 g, 10.4 mmol) according to the general procedure. The subsequent distillation (0.2 mbar, 62°C) gave 1.67 g (8.37 mmol, 84%) **2l** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H, CH_3), 2.16 (s, 3H, CH_3), 3.02 (m, 4H, CH_2N), 3.84 (m, 4H, CH_2O), 4.32 (q, *J* = 7.1 Hz, 2H, CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH$_3$), 15.9 (CH$_3$), 54.5 (CH$_2$N), 61.8 (CH$_2$O), 66.2 (CH$_2$O), 152.9 (*C*=N), 164.8 (*C*OO) ppm. IR (film): nu(tilde) = 3456 (w), 2964 (m), 2920 (w), 2897 (w), 2855 (m), 2843 (m), 1734 (s), 1649 (w), 1614 (w), 1456 (m), 1435 (w), 1389 (w), 1367 (m), 1304 (m), 1263 (m), 1177 (m), 1148 (m), 1113 (s), 1011 (m), 961 (m), 920 (w), 868 (m), 787 (w), 746 (w), 652 (w) cm^{-1}. MS (EI): *m/z* = 200 $[M]^+$, 171, 127, 113, 86, 69, 56. $C_9H_{16}N_2O_3$ (200.23): calcd. C 53.98; H, 8.05, N 13.99; found C 53.65; H, 8.07, N 13.88.

General Procedure: Preparation of Ketophosphonates 3

Dimethyl methylphosphonate (1 eq.) (d = 1.161) was dissolved in abs. THF (1 mmol of the compound in 1.5 mL of solvent), cooled to -78°C and *n*-BuLi (1.6 M in hexane, 1 eq.) was added slowly. The reaction mixture was stirred for 1h at -78°C. Then, hydrazone **2** (1 eq.) in abs. THF (1 mmol of the compound in 0.5 mL) was added. The reaction mixture was stirred for 4 h at -78°C, and then quenched with AcOH (1 eq.) and water (~10 eq.). After evaporation of the solvent the residue was dissolved in dichloromethane, washed first with water, and then with saturated aqueous $NaHCO_3$ solution and again with water. The residue was dried over $MgSO_4$ and purified by column chromatography.

Dimethyl 3-(2,2-dimethylhydrazono)-2-oxobutylphosphonate (3a). 3a was obtained from compound **2a** (1.71 g, 10.81 mmol) and dimethyl methylphosphonate (1.34 g, 10.81 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/acetone, 2:1) gave 1.53g (6.48 mmol, 60%) **3a** as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 2.06 (s, 3H, CH_3), 3.11 (s, 6H, CH_3N), 3.58 (d, J = 22.2 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH$_3$), 33.9 (d, J = 132.3 Hz, CH$_2$P), 46.7 (CH$_3$N), 52.6 (d, J = 6.2 Hz, CH$_3$O), 141.9 (C=N), 191.2 (d, J = 6.3 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.8 ppm. IR (film): nu(tilde) = 3532 (w), 3464 (w), 2990 (w), 2957 (m), 2876 (w), 2853 (w), 2795 (w), 1665 (s), 1557 (s), 1448 (m), 1387 (w), 1367 (w), 1259 (s), 1204 (w), 1148 (w), 1132 (w), 1063 (m), 1030 (s), 947 (w), 878 (w), 845 (w), 804 (m), 754 (w), 745 (w), 689 (w) cm^{-1}. HRMS (ESI): calcd. for $C_8H_{17}N_2PO_4Na$ 259.0818; found 259.0804. $C_8H_{17}N_2PO_4$ (236.21): calcd. C 40.68, H 7.25, N 11.86; found C 40.66, H 7.27, N 11.89.

Dimethyl 3-(2-ethyl-2-methylhydrazono)-2-oxobutylphosphonate (3b). 3b was obtained from compound **2b** (1.72 g, 10.00 mmol) and dimethyl methylphosphonate (1.24 g, 10.00 mmol) according to the general procedure. The subsequent chromatographic purification (acetone) gave 1.40g (5.60 mmol, 56%) **3b** as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (t, J = 7.2 Hz, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.11 (s, 3H, CH_3N), 3.40 (q, J = 7.2 Hz, 2H, CH_2), 3.60 (d, J = 22.2 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5 (CH$_3$), 12.6 (CH$_3$), 34.0 (d, J = 132.4 Hz, CH$_2$P), 42.5 (CH$_3$N), 52.7 (d, J = 6.3 Hz, CH$_3$O), 55.3 (CH$_2$N), 140.8 (C=N), 191.2 (d, J = 6.5 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.4 ppm. IR (film): nu(tilde) = 3476 (w), 3304 (w), 2972 (m), 2957 (m), 2874 (w), 2853 (w), 1663 (s), 1555 (s), 1448 (w), 1383 (w), 1369 (w), 1317 (m), 1256 (s), 1205 (m), 1148 (m), 1065 (m), 1034 (s), 972 (w), 928 (w), 876 (w), 845 (w), 806 (m), 770 (w), 743 (w), 665 (m) cm^{-1}. HRMS (ESI): calcd. for $C_9H_{19}N_2PO_4Na$ 273.0975; found 273.0973. $C_9H_{19}N_2PO_4$ (250.23): calcd. C 43.20, H 7.65, N 11.19; found C 42.90, H 7.71, N 11.11.

Dimethyl 3-(2-isopropyl-2-methylhydrazono)-2-oxobutylphosphonate (3c). 3c was obtained from compound **2c** (1.16 g, 6.23 mmol) and dimethyl methylphosphonate (0.77 g, 6.23 mmol) according to the general procedure. The subsequent chromatographic purification (acetone) gave 1.20g (4.55 mmol, 73%) **3c** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, J = 6.6 Hz, 6H, CH_3), 2.09 (s, 3H, CH_3), 3.10 (s, 3H, CH_3N), 3.56 (sept, J = 6.6 Hz, 1H, CH), 3.59 (d, J = 22.2 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8 (CH$_3$), 20.0 (CH$_3$), 34.1 (d, J = 132.9 Hz, CH$_2$P), 39.8 (CH$_3$N), 52.6 (d, J = 6.4 Hz, CH$_3$O), 60.7 (CH), 138.8 (C=N), 191.2 (d, J = 6.4 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.4 ppm. IR (film): nu(tilde) = 3476 (w), 3312 (w), 2974 (m), 2853 (w), 1663 (s), 1555 (s), 1460 (m), 1448 (m), 1387 (m), 1366 (m), 1323 (m), 1258 (s), 1207 (m), 1159 (m), 1124 (m), 1063 (s), 1040 (s), 939 (w), 872 (m), 845 (m), 808 (m), 739 (w), 692 (w), 665 (w), 644 (w), 606 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{21}N_2PO_4Na$ 287.1131; found 287.1127. $C_{10}H_{21}N_2PO_4$ (264.26): calcd. C 45.45, H 8.01, N 10.60; found C 45.26, H 8.17, N 10.97.

Dimethyl 3-(2-butyl-2-methylhydrazono)-2-oxobutylphosphonate (3d). 3d was obtained from compound **2d** (1.57 g, 7.83 mmol) and dimethyl methylphosphonate (0.97 g, 7.83 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/acetone, 1:1) gave 1.72 g (6.19 mmol, 79%) **3d** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H, CH_3), 1.30-1.42 (m, 2H, CH_2), 1.59-1.69 (m, 2H, CH_2), 2.09 (s, 3H, CH_3), 3.15 (s, 3H, CH_3N), 3.33-3.38 (m, 2H, CH_2N), 3.59 (d, J = 22.1 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH$_3$), 13.8 (CH$_3$), 19.9 (CH$_2$), 29.8 (CH$_2$), 33.9 (d, J = 132.6 Hz, CH$_2$P), 42.9 (CH$_3$N), 52.7 (d, J = 6.3 Hz, CH$_3$O), 60.8 (CH$_2$), 139.6 (C=N), 191.1 (d, J = 6.4 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.5 ppm. IR (film): nu(tilde) = 3475 (w), 2957 (s), 2934 (s), 2872 (m), 1663 (m), 1553 (s), 1460 (m), 1450 (m), 1383 (m), 1367 (m), 1317 (s), 1258 (s), 1202 (s), 1146 (m), 1109 (m), 1065 (s), 1032 (s), 953 (w), 876 (m), 845 (m), 806 (m), 781 (w), 748 (w), 694 (w), 665 (w), 644 (w), 606 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{23}N_2PO_4Na$ 301.1288; found 301.1278. $C_{11}H_{23}N_2PO_4$ (278.29): calcd. C 47.48, H 8.33, N 10.07; found C 47.43, H 8.56, N 10.00.

Dimethyl 3-(2,2-dimethylhydrazono)-2-oxo-3-phenylpropylphosphonate (3e). 3e was obtained from compound **2e** (1.78 g, 8.65 mmol) and dimethyl methylphosphonate (1.07 g, 8.65 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/acetone, 2:1) gave 1.16 g (3.89 mmol, 45%) **3e** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.95 (s, 6H, CH_3N), 3.70 (d, J = 22.0 Hz, 2H, CH_2P), 3.80(d, J = 11.1 Hz, 6H, CH_3O), 7.15-7.18 (m, 2H, *H*-arom.), 7.31-7.33 (m, 3H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6 (d, J = 132.0 Hz, *C*H_2P), 46.8 (*C*H_3N), 52.8 (d, J = 6.3 Hz, *C*H_3O), 127.5 (*C*H-arom.), 128.0 (*C*H-arom.), 130.2 (*C*H-arom.), 134.1 (*C*-ipso), 137.6 (d, J = 2.7 Hz, *C*=N), 190.3 (d, J = 6.3 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.1 ppm. IR (film): nu(tilde) = 3530 (m), 3474 (m), 3298 (w), 3055 (m), 3020 (s), 2995 (s), 2955 (s), 2851 (s), 2797 (m), 1967 (w), 1881 (w), 1819 (w), 1659 (s), 1601 (s), 1549 (s), 1491 (s), 1460 (s), 1445 (s), 1427 (s), 1406 (s), 1387 (s), 1302 (s), 1258 (s), 1186 (s), 1126 (s), 1059 (s), 1030 (s), 953 (s), 912 (s), 878 (s), 847 (s), 810 (s), 758 (m), 739 (s), 708 (s), 638 (s), 617 (m), 584 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{19}N_2O_4PNa$ 321.0975; found 321.0973.

Dimethyl 3-(2,2-dimethylhydrazono)-2-oxo-3-(2-thienyl)propylphosphonate (3f). 3f was obtained from compound **2f** (1.07 g, 4.72 mmol) and dimethyl methylphosphonate (0.59 g, 4.72 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/acetone, 2:1) gave 0.861 g (2.83 mmol, 60%) **3f** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.08 (s, 6H, CH_3N), 3.67 (d, J = 22.0 Hz, 2H, CH_2P), 3.79 (d, J = 11.1 Hz, 6H, CH_3O), 6.93 (dd, J = 3.5, 1.2 Hz, 1H, *H*-thiophene), 7.02 (dd, J = 5.1, 3.5 Hz, 1H, *H*-thiophene), 7.41 (dd, J = 5.1, 1.2 Hz, 1H, *H*-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8 (d, J = 132.5 Hz, *C*H_2P), 46.5 (*C*H_3N), 52.8 (d, J = 6.4 Hz, *C*H_3O), 125.9 (*C*H-thiophene), 127.5 (*C*H-thiophene), 130.0 (*C*H-thiophene), 130.2 (*C*=N), 132.8 (*C*-ipso), 189.9 (d, J = 6.2 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.1 ppm. IR (film): nu(tilde) = 3518 (s), 3470 (s), 3296 (m), 3198 (m), 3078 (s), 2993 (s), 2953 (s), 2851 (s), 2797 (m), 1902 (w), 1823 (w), 1666 (s), 1661 (s), 1651 (s), 1557 (s), 1514 (s), 1506 (s), 1454 (s), 1447 (s), 1416 (s), 1387 (s), 1350 (s), 1296 (s), 1244 (s), 1198 (s), 1186 (s), 1157 (s), 1126 (s), 1018 (s), 930 (s), 878 (s), 849 (s), 806 (s), 762 (s), 721 (s), 636 (m), 586 (w), 550 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{17}N_2O_4PSNa$ 327.0539; found 327.0546.

Dimethyl 3-(2-allyl-2-methylhydrazono)-2-oxobutylphosphonate (3g). 3g was obtained from compound **2g** (2.59 g, 14.09 mmol) and dimethyl methylphosphonate (1.75 g, 14.09 mmol) according to the general procedure. The subsequent chromatographic purification (acetone) gave 2.40 g (9.16 mmol, 65%) **3g** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H, CH_3), 3.10 (s, 3H, CH_3N), 3.59 (d, J = 22.2 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O), 3.94-3.98 (m, 2H, CH_2N), 5.22-5.29 (m, 2H, CH_2-vinyl), 5.86-5.99 (m, 1H, C*H*-vinyl) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (*C*H_3), 33.9 (d, J = 132.4 Hz, *C*H_2P), 42.6 (*C*H_3N), 52.7 (d, J = 6.3 Hz, *C*H_3O), 63.3 (*C*H_2N), 118.2 (*C*H_2-vinyl), 133.1 (*C*H-vinyl), 140.5 (*C*=N), 191.3 (d, J = 6.4 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.3 ppm. **IR** (film): nu(tilde) = 3479 (m), 3082 (w), 2984 (m), 2957 (m), 2853 (m), 1663 (s), 1555 (s), 1456 (m), 1447 (m), 1421 (m), 1387 (m), 1367 (m), 1312 (m), 1254 (s), 1204 (m), 1186 (m), 1148 (m), 1032 (s), 934 (m), 878 (m), 845 (m), 806 (m), 783 (w), 752 (w), 700 (w), 665 (w), 650 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{19}N_2PO_4Na$ 285.0975; found 285.0972.

Dimethyl 3-(2-benzyl-2-methylhydrazono)-2-oxobutylphosphonate (3h). 3h was obtained from compound **2h** (1.81 g, 7.75 mmol) and dimethyl methylphosphonate (0.96 g, 7.75 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/acetone, 1:1) gave 1.62 g (5.19 mmol, 67%) **3h** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 3H, CH_3), 3.10 (s, 3H, CH_3N), 3.60 (d, J = 22.2 Hz, 2H, CH_2P), 3.76 (d, J = 11.1 Hz, 6H, CH_3O), 4.56 (s, 2H, CH_2Ph), 7.28-7.40 (m, 5H, *H*-arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (*C*H_3), 34.0 (d, J = 132.5 Hz, *C*H_2P), 42.4 (*C*H_3N), 52.7 (d, J = 6.3 Hz, *C*H_3O), 65.0 (*C*H_2Ph), 127.7 (*C*H-arom.), 128.1 (*C*H-arom.), 128.6 (*C*H-arom.), 136.8 (*C*-ipso), 140.5 (*C*=N), 191.3 (d, J = 6.5 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.3 ppm. IR (film): nu(tilde) = 3470 (m), 3310 (w), 3086 (w), 3061 (w), 3028 (m), 2991 (m), 2955 (m), 2851 (m), 1661 (s), 1555 (s), 1497 (m), 1454 (s), 1387 (m), 1367 (m), 1312 (s), 1258 (s), 1202 (m), 1180 (m), 1030 (s), 966 (w), 941(w), 878 (m), 844 (m), 806 (s), 739 (m), 702 (m), 665 (w), 625 (w), 596 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{21}N_2PO_4Na$ 335.1131; found 335.1128. $C_{14}H_{21}N_2PO_4$ (312.30): calcd. C 53.84, H 6.78, N 8.97; found C 53.92, H 6.90, N 8.88.

Dimethyl 2-oxo-3-(pyrrolidin-1-ylimino)butylphosphonate (3i). 3i was obtained from compound **2i** (2.72 g., 14.79 mmol) and dimethyl methylphosphonate (1.83 g, 14.79 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/acetone, 1:4) gave 1.55g (5.92 mmol, 40%) **3i** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91-1.94 (m, 4H, CH_2), 2.06 (s, 3H, CH_3), 3.55-3.59 (m, 4H, CH_2N), 3.59 (d, J = 22.2 Hz, 2H, CH_2P), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5 (*C*H_3), 24.3 (*C*H_2), 25.2 (*C*H_2), 33.8 (d, J = 132.2 Hz, *C*H_2P), 52.7 (d, J = 6.2 Hz, *C*H_3O), 55.5 (*C*H_2N), 139.0 (*C*=N), 191.0 (d, J = 6.4 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.2 ppm. IR (film): nu(tilde) = 3476 (m), 2957 (s), 2874 (m), 2860 (m), 1657 (s), 1551 (s), 1456 (s), 1387 (m), 1367 (m), 1304 (s), 1259 (s), 1219 (s), 1161 (s), 1140 (s), 1063 (s), 1026 (s), 949 (w), 876 (m), 847 (s), 808 (s), 745 (m), 694 (m), 652 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{19}N_2O_4PNa$ 285.0975; found 285.0965.

Dimethyl 2-oxo-3-(piperidin-1-ylimino)butylphosphonate (3j). 3j was obtained from compound **2j** (0.60 g, 3.00 mmol) and dimethyl methylphosphonate (0.37 g, 3.00 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/acetone, 3:1) gave 0.62 g (2.23 mmol, 74%) **3j** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57-1.63 (m, 2H, CH_2), 1.68-1.75 (m, 4H, CH_2), 2.03 (s, 3H, CH_3), 3.27-3.30 (m, 4H, CH_2N), 3.63 (d, J = 22.3 Hz, 2H, CH_2P), 3.78 (d, J = 11.2 Hz, 6H, CH_3O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3 (*C*H_3), 24.0 (*C*H_2), 25.2 (*C*H_2), 34.0 (d, J = 132.0 Hz, *C*H_2P), 52.8 (d, J = 6.2 Hz, *C*H_3O), 55.1 (*C*H_2N), 134.9 (*C*=N), 191.7 (d, J = 6.3 Hz, *C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.5 ppm. IR (film): nu(tilde) = 3476 (w), 2939 (m), 2855 (m), 1676 (s), 1560 (m), 1445 (m), 1387 (m), 1364 (m), 1304 (s), 1258 (s), 1202 (m), 1184 (m), 1159 (m), 1063 (s), 1030 (s), 988 (m), 941 (m), 916 (w), 878 (m), 843 (m), 808 (m), 783 (m), 741 (w), 665 (m) cm^{-1}. MS (EI): *m/z* =276 $[M]^+$, 245, 220, 194, 162, 151, 124, 109, 84, 56.

Dimethyl 3-(azepan-1-ylimino)-2-oxobutylphosphonate (3k). 3k was obtained from compound **2k** (1.07 g, 5.00 mmol) and dimethyl methylphosphonate (0.62 g, 5.00 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/acetone, 4:1) gave 0.630 g (2.17 mmol, 43%) **3k** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58-1.61 (m, 4H, CH_2), 1.74-1.76 (m, 4H, CH_2), 2.08 (s, 3H, CH_3), 3.60 (d, J = 22.3 Hz, 2H, CH_2P), 3.64-3.68 (m, 4H, CH_2N), 3.77 (d, J = 11.1 Hz, 6H, CH_3O) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ 12.3 (CH$_3$), 27.0 (CH$_2$), 28.1 (CH$_2$), 33.9 (d, J = 132.4 Hz, CH$_2$P), 52.6 (d, J = 6.2 Hz, CH$_3$O), 56.8 (CH$_2$N), 134.9 (C=N), 190.9 (d, J = 6.5 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, CDCl$_3$) δ 24.5 ppm. IR (film): nu(tilde) = 3476 (m), 3304 (w), 2930 (m), 2855 (m), 2685 (w), 1655 (s), 1547 (s), 1450 (m), 1383 (m), 1367 (m), 1310 (s), 1254 (s), 1211 (m), 1186 (m), 1144 (m), 1099 (m), 1030 (s), 986 (m), 905 (m), 878 (m), 847 (m), 806 (m), 748 (m), 690 (m), 665 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{23}N_2O_4PNa$ 313.1288; found 313.1291.

Dimethyl 3-(morpholine-4-ylimino)-2-oxobutylphosphonate (3l). 3l was obtained from compound **2l** (0.60 g, 3.00 mmol) and dimethyl methylphosphonate (0.37 g, 3.00 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/acetone, 4:1) gave 0.49 g (1.76 mmol, 58%) **3l** as a yellow solid. m.p. 70-71 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.03 (s, 3H, CH_3), 3.22 (m, 4H, CH_2N), 3.63 (d, J = 22.3 Hz, 2H, CH_2P), 3.78 (d, J = 11.2 Hz, 6H, CH_3O), 3.85 (m, 4H, CH_2O) ppm. ^{13}C NMR (75 MHz, CDCl$_3$) δ 13.4 (CH$_3$), 31.4 (d, J = 132.2 Hz, CH$_2$P), 52.8 (d, J = 6.1 Hz, CH$_3$O), 54.6 (CH$_2$N), 66.1 (CH$_2$O), 151.6 (C=N), 191.8 (d, J = 6.9 Hz, CO) ppm. ^{31}P NMR (121.5 MHz, CDCl$_3$) δ 22.8 ppm. IR (KBr): nu(tilde) = 3530 (m), 3476 (m), 2959 (m), 2926 (m), 2899 (m), 2853 (m), 2768 (w), 2720 (w), 2687 (w), 2369 (w), 2338 (w), 2087 (w), 1684 (s), 1572 (m), 1458 (m), 1389 (m), 1364 (m), 1302 (s), 1256 (s), 1207 (m), 1182 (m), 1115 (s), 1067 (s), 1032 (s), 947 (m), 880 (m), 845 (m), 808 (m), 770 (m), 741 (m), 636 (m) cm^{-1}. MS (EI): m/z =278 [M]$^+$, 194, 162, 151, 124, 109, 94, 86, 56. $C_{10}H_{19}N_2PO_5$ (278.24): calcd. C 43.17, H 6.88, N 10.07; found C 43.45, H 6.87, N 9.93.

X-ray crystal structure analysis of **3l**:[2] formula $C_{10}H_{19}N_2O_5P$, M = 278.24, colourless crystal 0.30 x 0.20 x 0.15 mm, a = 7.691(1), b = 10.311(1), c = 17.038(1)Å, β = 96.56(1)°, V = 1342.3(2) Å^3, ρ_{calc} = 1.377 g cm^{-3}, μ= 0.220 mm^{-1}, empirical absorption correction (0.937 ≤ T ≤ 0.968), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 0.71073 Å, T = 198(2) K, ω and φ scans, 11459 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 3212 independent (R_{int} = 0.068) and 2086 observed reflections [$I \geq 2\,\sigma(I)$], 186 refined parameters, R = 0.047, wR^2 = 0.120, max. (min.) residual electron density 0.26 (-0.41) e Å^{-3}, group O16-C18 refined with split positions, hydrogen atoms calculated and refined as riding atoms.

General Procedure: Preparation of Azapenta-dienones 4

t-BuOK (1 eq.) was dissolved in abs. THF (1 mmol of the base in 10 mL of solvent) and ketophosphonate (1 eq.) **3** in THF (1 mmol of the compound in 2 mL of solvent) was added. The reaction mixture was stirred for 1h at RT and trifluoroacetylketone (1 eq.) in THF was added. The reaction mixture was stirred for 4 h at RT. Then, the solvent was evaporated. The residue was dissolved in dichloromethane, washed with brine, dried over $MgSO_4$, concentrated and purified using column chromatography. In all cases the *E*-isomers were the main products. ^{1}H and ^{13}C signals are assigned for the main *E*-product. The stereochemistry and the ratios of *E*- and *Z*-isomers were determined by comparing the ^{19}F chemical shifts to compounds with known stereochemistry from the crude reaction mixtures.[3]

2-(2,2-Dimethylhydrazono)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4a). 4a was obtained from ketophosphonate **3a** (0.408 g, 1.72 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 1:1) gave 0.372 g (1.31 mmol, 76%) **4a** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H, C*H*$_3$), 3.08 (s, 6H, C*H*$_3$N), 7.23-7.26 (m, 2H, *H*-arom.), 7.31-7.35 (m, 3H, *H*-arom.), 7.46 (q, J = 1.45 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (*C*H$_3$), 46.7 (*C*H$_3$), 123.2 (q, J = 273.9 Hz, *C*F$_3$), 128.0 (*C*H-arom.), 128.6 (*C*H-arom.), 129.0 (*C*H-arom.), 130.8 (q, J = 5.4 Hz, *C*H-olef.), 132.4 (*C*-ipso), 136.2 (q, J = 30.1 Hz, *C*CF$_3$), 142.3 (*C*=N), 189.2 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9 ppm (*E*-isomer), -59.8 (*Z*-isomer), ratio 19:1. IR (film): nu(tilde) = 3289 (w), 3088 (w), 3061 (m), 3026 (m), 2926 (m), 2878 (m), 2841 (m), 2795 (w), 1956 (w), 1882 (w), 1751 (w), 1715 (w), 1665 (s), 1555 (s), 1497 (s), 1445 (s), 1429 (s), 1404 (m), 1369 (s), 1269 (s), 1236 (s), 1171 (s), 1096 (s), 1080 (s), 1034 (s), 1003 (m), 970 (s), 945 (m), 914 (m), 878 (m), 837 (m), 808 (m), 779 (m), 756 (m), 700 (s), 646 (s), 615 (m) cm^{-1}. MS (EI): *m/z* =284 $[M]^+$, 215, 199, 151, 127, 85, 57. $C_{14}H_{15}F_3N_2O$ (284.28): calcd. C 59.15, H 5.32, N 9.85; found C 59.10, H 5.21, N 9.64.

2-(2-Ethyl-2-methylhydrazono)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4b). 4b was obtained from ketophosphonate **3b** (0.500g, 2.00 mmol) according to the general procedure. The subsequent chromatographic purification (TBME) gave 0.581 g (1.95 mmol, 98%) **4b** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H, CH_3), 1.98 (s, 3H, CH_3), 3.09 (s, 3H, CH_3N), 3.39 (q, J = 7.2 Hz, 2H, CH_2), 7.24-7.36 (m, 5H, *H*-arom.), 7.48 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5 (CH_3), 12.7 (CH_3), 42.6 (CH_3), 55.3 (CH_2N), 123.2 (q, J = 274.2 Hz, CF_3), 128.0 (*C*H-arom.), 128.6 (*C*H-arom.), 128.9 (*C*H-arom.), 131.2 (q, J = 5.4 Hz, *C*H-olef.), 132.2 (*C*-ipso), 135.6 (q, J = 30.1 Hz, *C*-olef.), 141.1 (*C*=N), 189.2 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9 ppm (*E*-isomer), -60.0 (*Z*-isomer), ratio 8:1. IR (film): nu(tilde) = 3314 (w), 3088 (w), 3061 (w), 3026 (w), 2978 (w), 2934 (w), 2874 (w), 1663 (s), 1553 (s), 1499 (w), 1458 (w), 1445 (w), 1371 (m), 1310 (m), 1271 (s), 1240 (m), 1171 (s), 1123 (s), 1076 (m), 1045 (w), 1001 (w), 970 (w), 914 (w), 876 (w), 824 (w), 799 (w), 777 (w), 756 (w), 700 (m), 665 (w), 646 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{17}F_3N_2ONa$ 321.1185; found 321.1181. $C_{15}H_{17}F_3N_2O$ (298.30): calcd. C 60.40, H 5.74, N 9.39; found C 61.05, H 5.72, N 9.61.

6,6,6-Trifluoro-2-(2-isopropyl-2-methylhydrazono)-5-phenylhex-4-en-3-one (4c). 4c was obtained from ketophosphonate **3c** (0.792 g, 3 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 3:1) gave 0.840g (2.69 mmol, 90%) **4c** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (d, J = 6.5 Hz, 6H, CH_3), 2.02 (s, 3H, CH_3), 3.10 (s, 3H, CH_3N), 3.54 (sept, J = 6.5 Hz, 1H, C*H*), 7.26-7.29 (m, 2H, *H*-arom.), 7.33-7.36 (m, 3H, *H*-arom.), 7.48 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.6 (CH_3), 20.3 (CH_3), 40.3 (CH_3N), 61.0 (*C*HN), 123.3 (q, J = 274.2 Hz, CF_3), 128.0 (*C*H-arom.), 128.6 (*C*H-arom.), 128.9 (*C*H-arom.), 132.1(*C*-ipso), 132.4 (q, J = 5.3 Hz, *C*H-olef.), 134.6 (q, J = 30.1 Hz, *C*-olef.), 139.5 (*C*=N), 189.4 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.8 ppm (*E*-isomer), -60.1 (*Z*-isomer), ratio 11:1. IR (film): nu(tilde) = 3294 (w), 3088 (w), 3061 (w), 2978 (m), 2936 (m), 2878 (w), 1663 (m), 1553 (s), 1499 (m), 1458 (m), 1373 (m), 1317 (m), 1269 (s), 1238 (s), 1169 (s), 1123 (s), 1088 (m), 1030 (m), 1003 (w), 968 (m), 939 (w), 914 (w), 885 (w), 874 (w), 816 (w), 785 (w), 779 (w), 756 (w), 700 (m), 660 (w), 644 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}F_3N_2ONa$ 335.1342; found 335.1344. $C_{16}H_{19}F_3N_2O$ (312.33): calcd. C 61.53, H 6.13, N 8.97; found C 61.47, H 6.21, N 9.33.

2-(2-Butyl-2-methylhydrazono)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4d). **4d** was obtained from ketophosphonate **3d** (1.72 g, 6.19 mmol) according to the general procedure. The subsequent chromatographic purification (TBME) gave 1.85g (5.69 mmol, 92%) **4d** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.3 Hz, 3H, CH_3), 1.33-1.40 (m, 2H, CH_2), 1.58-1.66 (m, 2H, CH_2), 2.00 (s, 3H, CH_3), 3.13 (s, 3H, CH_3N), 3.34-3.38 (m, 2H, CH_2N), 7.26-7.28 (m, 2H, *H*-arom.), 7.31-7.36 (m, 3H, *H*-arom.), 7.47 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH_3), 13.8 (CH_3), 19.8 (CH_2), 29.8 (CH_2), 42.9 (CH_3), 60.7 (CH_2), 123.2 (q, J = 274.0 Hz, CF_3), 128.0 (*C*H-arom.), 128.6 (*C*H-arom.), 128.9 (*C*H-arom.), 131.5 (q, J = 5.3 Hz, *C*H-olef.), 132.3 (*C*-ipso), 135.3 (q, J = 30.4 Hz, *C*CF_3), 139.8 (*C*=N), 189.2 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9 ppm (*E*-isomer), -60.0 (Z-isomer), ratio 13:1. IR (film): nu(tilde) = 3078 (w), 3059 (w), 2961 (m), 2932 (m), 2874 (w), 1663 (m), 1551 (s), 1499 (w), 1460 (w), 1445 (w), 1367 (m), 1310 (m), 1271 (s), 1231 (m), 1169 (s), 1123 (s), 1067 (w), 1001 (w), 970 (w), 914 (w), 876 (w), 843 (w), 779 (w), 754 (w), 698 (m), 665 (w), 646 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{21}F_3N_2ONa$ 349.1498; found 349.1501. $C_{17}H_{21}F_3N_2O$ (326.36): C 62.56, H 6.49, N 8.58; found C 62.52, H 6.69, N 8.44.

1-(2,2-Dimethylhydrazono)-5,5,5-trifluoro-1,4-diphenylpent-3-en-2-one (4e). **4e** was obtained from ketophosphonate **3e** (0.200 g, 0.67 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:3) gave 0.168 g (0.49 mmol, 72%) **4e** as a yellow solid, m.p. 84-85°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (s, 6H, CH_3N), 6.93-6.95 (m, 2H, *H*-arom.), 7.24-7.26 (m, 3H, *H*-arom.), 7.32-7.35 (m, 5H, *H*-arom.), 7.42 (q, J = 1.5 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.9 (CH_3N), 123.3 (q, J = 274.1 Hz, CF_3), 127.5, 128.0, 128.1, 128.6, 129.1, 130.1, 132.3 (q, J = 5.5 Hz, *C*H-olef.), 132.5, 133.9, 138.4 (*C*=N), 189.3 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.6 ppm (*E*-isomer), -59.8 (Z-isomer), ratio 7:1. IR (KBr): nu(tilde) = 3082 (m), 3055 (m), 3022 (m), 2961 (m), 2922 (m), 2893 (m), 2874 (m), 2799 (w), 1962 (w), 1884 (w), 1821 (w), 1765 (w), 1663 (s), 1624 (s), 1599 (m), 1547 (s), 1535 (s), 1493 (s), 1485 (s), 1443 (m), 1425 (s), 1381 (s), 1331 (s), 1302 (s), 1277 (s), 1259 (s), 1246 (s), 1186 (s), 1171 (s), 1146 (s), 1119 (s), 1078 (s), 1030 (s), 1001 (m), 972 (s), 957 (s), 914 (m), 895 (m), 837 (s), 795 (m), 746 (m), 735 (m), 729 (m), 719 (m), 698 (s), 656 (s), 617 (s), 567 (m), 511 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{17}F_3N_2ONa$ 369.1185; found 369.1193.

1-(2,2-Dimethylhydrazono)-5,5,5-trifluoro-4-phenyl-1-(2-thienyl)pent-3-en-2-one (4f). 4f was obtained from ketophosphonate **3f** (0.282 g, 0.93 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:1) gave 0.196 g (0.56 mmol, 60%) **4f** as a yellow solid, m.p 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (s, 6H, C*H*$_3$N), 6.72 (dd, J = 3.5, 1.1 Hz, 1H, *H*-thiophene), 6.94 (dd, J = 5.1, 3.5 Hz, 1H, *H*-thiophene), 7.30-7.35 (m, 6H, *H*-arom.), 7.38 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.6 (*C*H$_3$N), 123.3 (q, J = 274.3 Hz, *C*F$_3$), 126.0, 127.6, 128.1, 129.0, 130.0, 130.9, 131.9 (q, J = 5.2 Hz, *C*H-olef.), 132.4, 132.6, 142.9 (*C*=N), 189.0 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.6 ppm (*E*-isomer), -59.9 (*Z*-isomer), ratio 7:1. IR (KBr): nu(tilde) = 3244 (m), 3109 (m), 3096 (m), 3063 (s), 3044 (m), 3028 (m), 3001 (m), 2928 (s), 2795 (m), 1960 (w), 1888 (w), 1805 (w), 1705 (s), 1659 (s), 1628 (s), 1601 (s), 1547 (s), 1508 (s), 1445 (s), 1414 (s), 1379 (s), 1367 (s), 1348 (s), 1333 (s), 1288 (s), 1273 (s), 1244 (s), 1211 (s), 1171 (s), 1119 (s), 1080 (s), 1061 (s), 1034 (s), 1003 (m), 972 (s), 937 (m), 903 (m), 853 (s), 833 (s), 787 (m), 764 (s), 756 (s), 700 (s), 660 (m), 617 (m), 581 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{15}F_3N_2OSNa$ 375.0749; found 375.0737.

2-(2,2-Dimethylhydrazono)-6,6,6-trifluoro-5-p-tolylhex-4-en-3-one (4g). 4g was obtained from ketophosphonate **3a** (0.119 g, 0.5 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.105 g (0.35 mmol, 70%) **4g** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 3.10 (s, 6H, C*H*$_3$N), 7.15 (br s, 4H, *H*-arom.), 7.48 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (*C*H$_3$), 21.3 (*C*H$_3$), 46.7 (*C*H$_3$), 123.2 (q, J = 274.2 Hz, *C*F$_3$), 128.78 (*C*H-arom.), 128.80 (*C*H-arom.), 129.3 (*C*-ipso), 130.2 (q, J = 5.4 Hz, *C*H-olef.), 136.3 (q, J = 30.0 Hz, *C*CF$_3$), 138.5, 142.1 (*C*=N), 189.1(*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.0 ppm (*E*-isomer), -59.9 (*Z*-isomer), ratio 15:1. IR (film): nu(tilde) = 3290 (w), 3030 (w), 2963 (w), 2924 (w), 2876 (w), 2841 (w), 2793 (w), 1665 (m), 1612 (w), 1557 (s), 1514 (m), 1448 (m), 1429 (w), 1406 (w), 1369 (m), 1271 (s), 1169 (s), 1123 (s), 1094 (m), 1070 (m), 970 (m), 939 (w), 876 (w), 839 (w), 822 (w), 816 (w), 723 (w), 646 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{17}F_3N_2ONa$ 321.1185; found 321.1169. $C_{15}H_{17}F_3N_2O$ (298.30): calcd. C 60.40, H 5.74, N 9.39; found C 60.30, H 5.62, N 9.13.

2-(2,2-Dimethylhydrazono)-5-(2,4-dimethylphenyl)-6,6,6-trifluorohex-4-en-3-one (4h). 4h was obtained from ketophosphonate **3a** (0.118 g, 0.5 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:5) gave 0.106 g (0.34 mmol, 68%) **4h** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.12 (s, 6H, CH_3N), 6.98-7.16 (m, 3H, *H*-arom.), 7.74 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) (for the mixture of *E* and *Z*-isomers) δ 12.4 (CH_3), 19.5 (CH_3), 19.7 (CH_3), 21.1(CH_3), 21.2 (CH_3), 46.7 (CH_3), 122.8 (q, J = 275.3 Hz, CF_3), 123.3 (q, J = 274.4 Hz, CF_3), 126.0, 126.1, 128.7, 129.5, 130.6, 131.0, 129.3 (*C*-ipso), 136.4 (q, J = 30.2 Hz, CCF_3), 136.9, 137.0, 138.1, 138.4, 141.4 (*C*=N), 142.6 (*C*=N), 187.7 (*C*O), 190.8(*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.5 ppm (*E*-isomer), -59.4 (*Z*-isomer), ratio 1.6:1. IR (film): nu(tilde) = 3314 (w), 2961 (w), 2924 (w), 2876 (w), 2795 (w), 1665 (m), 1558 (m), 1456 (w), 1367 (m), 1271 (m), 1234 (m), 1196 (m), 1169 (m), 1124 (m), 1090 (m), 1038 (w), 970 (w), 945 (w), 912 (w), 878 (w), 820 (w), 737 (w), 712 (w), 665 (w), 644 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}F_3N_2ONa$ 335.1342; found 335.1339. $C_{16}H_{19}F_3N_2O$ (312.33): calcd. C 61.53, H 6.13, N 8.97; found C 61.68, H 6.00, N 8.76.

2-(2,2-Dimethylhydrazono)- 6,6,6-trifluoro-5-(naphthalen-1-yl)hex-4-en-3-one (4i). 4i was obtained from ketophosphonate **3a** (0.236 g, 10 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:2) gave 0.206 g (0.62 mmol, 62%) **4i** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) (for the mixure of *E*- and *Z*- isomers) δ 1.81 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.13 (s, 6H, CH_3N), 3.25 (s, 6H, CH_3N), 6.78 (s, 1H, *H*-olef), 7.36-7.53 (m, 7H, *H*-arom.), 7.78-7.90 (m, 5H, *H*-arom.), 7.94 (q, J = 1.4 Hz, 1H, *H*-olef.), 8.28-8.31 (m, 1H, *H*-arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH_3), 12.6 (CH_3), 46.7 (CH_3), 46.8 (CH_3), 124.9, 125.0, 125.4, 125.8, 126.0, 126.1, 126.3, 127.0, 127.1, 128.2, 128.3, 128.99, 129.04, 129.6, 129.8, 130.1, 131.7, 131.8, 131.9, 132.4, 133.3, 133.6, 134.7, 139.9 (q, J = 3.6 Hz, *C*H-olef.), 141.3(*C*=N), 142.4 (*C*=N), 187.7

(*C*O), 191.0 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.3 ppm (*E*-isomer), -61.5 (*Z*-isomer), ratio 1 : 1. IR (film): nu(tilde) = 3275 (w), 3055 (w), 2950 (w), 2920 (m), 2899 (w), 2802 (w), 2795 (m), 1657 (s), 1638 (s), 1593 (m), 1543 (s), 1508 (m), 1439 (w), 1423 (w), 1400 (w), 1366 (m), 1339 (w), 1288 (m), 1267 (m), 1165 (m), 1121 (m), 1065 (m), 1045 (w), 980 (w), 955 (w), 928 (m), 916 (w), 899 (w), 885 (w), 849 (w), 827 (m), 808 (m), 779 (m), 748 (w), 737 (w), 712 (w), 687 (w), 673 (w), 627 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{17}F_3N_2ONa$ 357.1185; found 357.1178. $C_{17}H_{14}F_3NO_2$ (334.34): calcd. C 64.66, H 5.13, N 8.38; found C 64.45, H 5.11, N 8.30.

2-(2-Allyl-2-methylhydrazono)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4j). 4j was obtained from ketophosphonate **3g** (0.925 g, 3.53 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 3:1) gave 0.911 g (2.94 mmol, 83%) **4j** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, C*H*$_3$), 3.07 (s, 3H, C*H*$_3$N), 3.93-3.95 (m, 2H, C*H*$_2$N), 5.21-5.27 (m, 2H, C*H*$_2$-vinyl), 5.89 (tdd, *J* = 16.4, 10.3, 6.0 Hz, 1H, C*H*-vinyl), 7.24-7.27 (m, 2H, *H*-arom.), 7.32-7.35 (m, 3H, *H*-arom.), 7.48 (q, *J* = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.3 (*C*H$_3$), 42.8 (*C*H$_3$), 63.3 (*C*H$_2$), 118.4 (*C*H$_2$-vinyl), 123.2 (q, *J* = 274.1 Hz, *C*F$_3$), 128.0 (*C*H-arom.), 128.6 (*C*H-arom.), 128.9 (*C*H-arom.), 131.0 (q, *J* = 5.4 Hz, *C*H-olef.), 132.3 (*C*-ipso), 133.0 (*C*H-vinyl), 134.8 (q, *J* = 30.1 Hz, *C*CF$_3$), 141.1 (*C*=N), 189.3 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.0 ppm (*E*-isomer), -60.0 (*Z*-isomer), ratio 8:1. IR (film): nu(tilde) = 3406 (w), 3086 (w), 3063 (w), 3026 (w), 2978 (w), 2959 (w), 2926 (w), 2883 (w), 2858 (w), 1751 (w), 1665 (m), 1649 (m), 1555 (s), 1497 (w), 1444 (w), 1420 (w), 1369 (m), 1304 (m), 1271 (s), 1231 (m), 1171 (s), 1124 (s), 1067 (m), 993 (w), 970 (w), 928 (w), 876 (w), 837 (w), 806 (w), 756 (w), 700 (m), 646 (w), 588 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2ONa$ 333.1185; found 333.1186. $C_{16}H_{17}F_3N_2O$ (310.31): calcd. C 61.93, H 5.52, N 9.03; found C 62.03, H 5.50, N 9.04.

2-(2-Benzyl-2-methylhydrazono)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4k). 4k was obtained from ketophosphonate **3h** (1.55g, 4.97 mmol) according to the general procedure. The subsequent chromatographic purification (acetone) gave 1.68 g (4.67 mmol, 94%) **4k** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, C*H*$_3$), 3.07 (s, 3H, C*H*$_3$N), 4.51 (s, 2H, C*H*$_2$Ph), 7.23-7.39 (m, 10H, *H*-

arom.), 7.48 (q, *J* = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH_3), 42.5 (CH_3), 65.1 (CH_2), 123.2 (q, *J* = 274.3 Hz, CF_3), 127.9 (*C*H-arom.), 128.1 (*C*H-arom.), 128.4 (*C*H-arom.), 128.6 (*C*H-arom.), 128.7 (*C*H-arom.), 129.0 (*C*H-arom.), 131.4 (q, *J* = 5.2 Hz, *C*H-olef.), 132.2 (*C*-ipso), 136.6 (*C*-ipso), 141.6 (*C*=N), 189.3 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9 ppm (*E*-isomer), -55.9 (*Z*-isomer), ratio 15:1. IR (film): nu(tilde) = 3292 (w), 3088 (m), 3063 (m), 3032 (m), 2959 (m), 2928 (m), 2812 (w), 1956 (w), 1882 (w), 1811 (w), 1751 (w), 1719 (w), 1665 (s), 1657 (s), 1601 (m), 1560 (s), 1553 (s), 1497 (m), 1454 (m), 1445 (m), 1420 (m), 1369 (s), 1304 (s), 1269 (s), 1169 (s), 1123 (s), 1078 (s), 1030 (m), 1003 (w), 968 (m), 941 (w), 914 (w), 876 (m), 843 (w), 806 (w), 779 (m), 754 (m), 735 (m), 700 (m), 667 (m), 648 (m), 602 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{19}F_3N_2ONa$ 383.1342; found 383.1337.

6,6,6-Trifluoro-5-phenyl-2-(pyrrolidin-1-ylimino)hex-4-en-3-one (4l). 4l was obtained from ketophosphonate **3i** (0.158 g, 0.60 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:2) gave 0.140 g (0.45 mmol, 75%) **4l** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88-1.92 (m, 4H, CH_2), 1.94 (s, 3H, CH_3), 3.50-3.54 (m, 4H, CH_2N), 7.25-7.38 (m, 5H, *H*-arom.), 7.49 (br s, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4 (CH_3), 24.4 (CH_2), 55.2 (CH_2N), 123.3 (q, *J* = 274.1 Hz, CF_3), 128.0 (*C*H-arom.), 128.5 (*C*H-arom.), 129.0 (*C*H-arom.), 130.8 (q, *J* = 5.3 Hz, *C*H-olef.), 132.5 (*C*-ipso), 135.4 (q, *J* = 30.0 Hz, CCF_3), 140.1 (*C*=N), 189.0 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.9 ppm (*E*-isomer), -59.8 (*Z*-isomer), ratio 10:1. IR (film): nu(tilde) = 3391 (w), 3246 (w), 3065 (w), 3040 (w), 2976 (m), 2959 (m), 2926 (m), 2874 (m), 1719 (w), 1657 (m), 1632 (s), 1543 (s), 1487 (m), 1369 (s), 1352 (m), 1340 (m), 1263 (s), 1219 (s), 1163 (s), 1119 (s), 1070 (s), 1036 (m), 1001 (w), 970 (m), 941 (w), 912 (w), 885 (m), 856 (w), 820 (m), 779 (m), 760 (m), 700 (s), 679 (m), 650 (w), 635 (m), 600 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2ONa$ 333.1185; found 333.1197. $C_{16}H_{17}F_3N_2O$ (310.31): calcd. C 61.93, H 5.52, N 9.03; found C 62.09, H 5.44, N 8.45.

6,6,6-Trifluoro-5-phenyl-2-(piperidin-1-ylimino)hex-4-en-3-one (4m). 4m was obtained from ketophosphonate **3j** (0.221 g, 0.80 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 1:10) gave 0.205 g (0.63 mmol, 79%) **4m** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50-1.66 (m, 6H, C*H*$_2$), 1.86 (s, 3H, C*H*$_3$), 3.21-3.24 (m, 4H, C*H*$_2$N), 7.17-7.30 (m, 4H, *H*-arom.), 7.44 (q, *J* = 1.4 Hz, 1H, *H*-olef.), 7.47-7.51 (m, 1H, *H*-arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2 (*C*H$_3$), 23.9 (*C*H$_2$), 25.4 (*C*H$_2$), 55.5 (*C*H$_2$N), 122.8 (*C*H-arom.), 124.6 (q, *J* = 273.8 Hz, *C*F$_3$), 128.1 (*C*H-arom.), 128.7 (*C*H-arom.), 129.0 (*C*H-arom.), 129.1 (*C*H-arom.), 129.7 (*C*H-olef.), 130.2 (q, *J* = 25.4 Hz, *C*CF$_3$), 130.8 (*C*-ipso), 141.3 (*C*=N), 185.0 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.0 ppm (*E*-isomer), -59.9 (*Z*-isomer), ratio 18:1. IR (film): nu(tilde) = 3339 (w), 3088 (w), 3061 (w), 2963 (m), 2930 (m), 2856 (w), 2361 (m), 2343 (w), 1720 (w), 1670 (w), 1655 (w), 1639 (w), 1578 (w), 1560 (w), 1535 (w), 1531 (w), 1508 (w), 1499 (w), 1491 (w), 1447 (w), 1400 (w), 1366 (w), 1296 (m), 1261 (s), 1205 (m), 1175 (m), 1121 (s), 1016 (s), 972 (w), 941 (w), 862 (m), 800 (s), 698 (m), 667 (m), 644 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{19}F_3N_2ONa$ 347.1342; found 347.1341. $C_{17}H_{19}F_3N_2O$ (324.34): calcd. C 62.95, H 5.90, N 8.64; found C 62.68, H 5.84, N 8.98.

2-(Azepan-1-ylimino)-6,6,6-trifluoro-5-phenylhex-4-en-3-one (4n). 4n was obtained from ketophosphonate **3k** (0.232 g, 0.80 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/Pentane, 1:2) gave 0.204 g (0.60 mmol, 75%) **4n** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55-1.58 (m, 4H, C*H*$_2$), 1.71-1.73 (m, 4H, C*H*$_2$), 1.97 (s, 3H, C*H*$_3$), 3.61-3.64 (m, 4H, C*H*$_2$N), 7.27-7.37 (m, 5H, *H*-arom.), 7.48 (q, *J* = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.3 (*C*H$_3$), 27.1 (*C*H$_2$), 28.1 (*C*H$_2$), 57.0 (*C*H$_2$N), 123.4 (q, *J* = 274.0 Hz, *C*F$_3$), 128.0 (*C*H-arom.), 128.5 (*C*H-arom.), 129.0 (*C*H-arom.), 132.1 (q, *J* = 5.3 Hz, *C*H-olef.), 132.5 (*C*-ipso), 134.5 (q, *J* = 29.8 Hz, *C*CF$_3$), 136.2 (*C*=N), 189.2 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.2 ppm (*E*-isomer), -59.6 (*Z*-isomer), ratio 9:1. IR (film): nu(tilde) = 3290 (w), 3088 (w), 3059 (w), 3026 (w), 2932 (m), 2858 (m), 2683 (w), 1655 (m), 1545 (s), 1499 (m), 1448 (m), 1367 (m), 1304 (s), 1273 (s), 1256 (s), 1234 (m), 1169 (s), 1123 (s), 1078 (m), 1003 (w), 988 (w), 968 (m), 903 (w), 878 (w), 820 (w), 775 (w), 756 (w), 700 (s), 646 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{21}F_3N_2ONa$ 361.1498; found 361.1500. $C_{18}H_{21}F_3N_2O$ (338.37): calcd. C 63.89, H 6.26, N 8.28; found C 63.76, H 6.08, N 8.05.

6,6,6-Trifluoro-2-(morpholine-4-ylimino)-5-phenylhex-4-en-3-one (4o). **4o** was obtained from ketophosphonate **3l** (0.695 g, 2.50 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane, 3:5) gave 0.612 g (1.88 mmol, 75%) **4o** as a yellow solid, m.p 73.5-74.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (s, 3H, C*H*$_3$), 3.18-3.20 (m, 4H, C*H*$_2$), 3.81-3.83 (m, 4H, C*H*$_2$), 7.23-7.26 (m, 2H, *H*-arom.), 7.35-7.37 (m, 3H, *H*-arom.), 7.48 (q, J = 1.4 Hz, 1H, *H*-olef.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4 (*C*H$_3$), 54.6 (*C*H$_2$N), 66.1 (*C*H$_2$O), 122.8 (*C*H-arom.), 123.9 (q, J = 277.1 Hz, *C*F$_3$), 128.2 (*C*H-arom.), 128.9 (*C*H-arom.), 129.4 (q, J = 5.0 Hz, *C*H-olef.), 132.0 (*C*-ipso), 151.7 (*C*=N), 189.4 (*C*O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.2 ppm (*E*-isomer), -59.8 (*Z*-isomer), ratio 20:1. IR (KBr): nu(tilde) = 3445 (w), 3071 (w), 3028 (w), 2972 (m), 2928 (w), 2909 (w), 2870 (m), 1670 (s), 1655 (m), 1582 (m), 1497 (w), 1448 (m), 1427 (w), 1377 (m), 1362 (m), 1331 (m), 1296 (s), 1273 (s), 1252 (s), 1169 (s), 1151 (s), 1119 (s), 1101 (s), 1067 (s), 1018 (s), 966 (m), 947 (m), 918 (w), 880 (m), 864 (m), 816 (w), 775 (m), 756 (m), 702 (s), 675 (m), 644 (s), 633 (m), 609 (m), 513 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2O_2Na$ 349.1134; found 349.1131. $C_{16}H_{17}F_3N_2O_2$ (326.31): calcd. C 58.89, H 5.25, N 8.58; found C 58.80, H 5.13, N 8.28.

X-ray crystal structure analysis of **4o**:[2] formula $C_{16}H_{17}F_3N_2O_2$, M = 326.32, colorless crystal 0.25 x 0.10 x 0.03 mm, a = 9.075(1), b = 9.616(1), c = 10.500(1)Å, α = 75.02(1), β = 84.11(1), γ = 61.97(1)°, V = 781.1(1) Å^3, ρ_{calc} = 1.387 g cm^{-3}, μ= 0.116 mm^{-1}, empirical absorption correction (0.972 ≤ T ≤ 0.997), Z = 2, triclinic, space group *P*1bar (No. 2), λ= 0.71073 Å, T = 198(2) K, ω and φ scans, 8144 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.67 Å^{-1}, 3733 independent (R_{int} = 0.080) and 2136 observed reflections [$I \geq 2\ \sigma(I)$], 209 refined parameters, R = 0.065, wR^2 = 0.142, max. (min.) residual electron density 0.31 (-0.23) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General Procedure: Cyclization of Aza-penta-dienones with the Use of Trifluoromethanesulfonic Acid

A solution of trifluoromethanesulfonic acid (10 eq.) in dry dichloromethane (1 mL of acid in 50 mL of solvent) was cooled to –10°C. A solution of the 1-azapenta-1,4-dienone **4** (1 eq.) in dry dichloromethane (1 mmol of the compound in 5 mL of solvent) was added dropwise with stirring. After complete addition stirring was continued for 1h. Then the reaction mixture was treated with acetic anhydride (20 eq.) and stirred at 0°C for 1h. A saturated solution of sodium hydrogen carbonate was added carefully for neutralization of the acidic mixture. The organic layer was washed with saturated sodium hydrogen carbonate solution until the aqueous layer became neutral. Then the organic layer was washed with water, dried with $MgSO_4$ and the solvent was evaporated. The substances were purified by column chromatography. Identity of diastereomers was determined on the basis of NOE experiments. The ratio of diastereomers was determined from ^{19}F spectra for the crude reaction mixtures. Compounds are thermally unstable and GC results can not be used as a measure of purity. In cases where the CHN analysis results are not indicated the purity of the products was determined from the NMR experiments and is more than 90%.

1',3'-Dimethyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5a). 5a was obtained from azadienone **4a** (0.207 g, 0.73 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 4:1) gave 0.062 g (0.23 mmol, 32%) **5a** as a red solid m.p. 52-53°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 3H, CH_3), 2.92 (s, 3H, CH_3N), 3.32 (d, J = 9.7 Hz, 1H, CH_2), 3.46 (d, J = 9.7 Hz, 1H, CH_2), 6.82 (q, J = 1.65 Hz, 1H, CH), 7.35 (dt, J = 7.4, 1.0 Hz, 1H, H-arom.), 7.40 (dt, J = 7.5, 1.2 Hz, 1H, H-arom.), 7.47-7.50 (m, 2H, H-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (CH$_3$), 43.6 (CH$_3$N), 64.0 (CH$_2$), 69.0 (C-spiro), 121.0 (CH-arom.), 122.0 (q, J = 270.3 Hz, CF$_3$), 123.3 (CH-arom.), 127.6 (CH-arom.), 128.4 (CH-arom.), 128.8, 130.9, 135.5 (q, J = 34.9 Hz, CCF$_3$), 137.7, 138.1 (q, J = 4.9 Hz, CH), 145.6 (C=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.7 ppm. IR (KBr): nu(tilde) = 3431 (m), 3067 (s), 2999 (m), 2968 (m), 2916 (m), 2878 (m), 2862 (m), 2843 (s), 2828 (s), 2793 (m), 1975 (w), 1935 (w), 1898 (w), 1746 (w), 1719 (w), 1630 (s), 1612 (s), 1580 (m), 1543 (w), 1458 (s), 1381 (s), 1335 (m), 1313 (s), 1302 (s), 1275 (s), 1259 (m), 1234 (s), 1196 (s), 1177 (s), 1140 (s), 1111 (s), 1057 (s), 1040 (m), 1016 (m), 1007 (m), 964 (s), 907 (s), 878 (m), 851 (s), 770 (s), 706 (m), 652 (s), 638 (m), 621 (m), 606 (m), 561 (m), 546 (w), 521 (w), 488 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{13}F_3N_2H$ 267.1104; found 267.1094. $C_{14}H_{13}F_3N_2$ (266.26): calcd. C 63.15, H 4.92, N 10.52; found C 62.91, H 5.09, N 10.29.

2,4-Dimethyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6a). **6a** was obtained from azadienone **4a** (0.207 g, 0.73 mmol) according to the general procedure. The subsequent chromatographic purification (TBME/pentane, 4:1) gave 0.070 g (0.26 mmol, 36%) **6a** as a red solid, m.p. 125°C (dec). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.34 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 4.16 (br d, 1H, CH_2), 4.33 (br d, 1H, CH_2), 6.82 (s, 1H, N*H*), 6.93 (dd, *J* = 7.3, 0.6 Hz, 1H, *H*-arom.), 7.17 (t, *J* = 7.6 Hz, 1H, *H*-arom.), 7.23 (q, *J* = 1.4 Hz, 1H, C*H*), 7.55 (d, *J* = 7.8 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.8 (CH_3), 40.5 (CH_3N), 62.1 (CH_2), 109.1 (*C*-olef.), 118.6 (*C*H-arom.), 120.2 (q, *J* = 34.3 Hz, *C*CF_3), 122.2 (*C*H-arom.), 123.2 (*C*H-arom.), 124.5 (q, *J* = 281.9 Hz, *C*F_3), 127.0 (q, *J* = 4.9 Hz, *C*H), 131.6, 132.5, 134.2 (q, *J* = 1.7 Hz), 154.0 (*C*-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.8 ppm. IR (KBr): nu(tilde) = 3256 (s), 3076 (m), 3022 (m), 2968 (m), 2928 (m), 2797 (w), 1697 (w), 1607 (s), 1595 (s), 1547 (s), 1514 (s),1483 (s), 1431 (s), 1387 (s), 1356 (s), 1337 (s), 1319 (s), 1261 (m), 1240 (s), 1221 (s), 1198 (s), 1169 (s), 1151 (s), 1124 (s), 1099 (s), 1084 (s), 1049 (s), 1034 (s), 957 (m), 943 (m), 889 (w), 851 (m), 795 (s), 766 (s), 708 (m), 689 (m), 671 (m), 660 (m), 629 (m), 604 (w), 565 (s), 511 (m), 482 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{13}F_3N_2H$ 267.1104; found 267.1110. $C_{20}H_{16}F_3N_5O_7$ (picrate) (495.37): C 48.49, H 3.26, N 14.14; found C 48.51, H 3.32, N 13.82.

X-ray crystal structure analysis of **6a**:[2] formula $C_{14}H_{18}F_3N_2$, *M* = 266.26, colorless crystal 0.40 x 0.25 x 0.20 mm, a = 21.159(1), b = 8.921(1), c = 16.079(3)Å, β = 123.22(1)°, V = 2539.1(3) Å^3, ρ_{calc} = 1.393 g cm^{-3}, μ= 0.979 mm^{-1}, empirical absorption correction (0.640 ≤ *T* ≤ 0.828), *Z* = 8, monoclinic, space group *C*2/c (No. 15), λ= 1.54178 Å, *T* = 293(2) K, ω and φ scans, 17000 reflections collected (±*h*, ±*k*, ± *l*), [(sinθ)/λ] = 0.60 Å^{-1}, 2230 independent (R_{int} = 0.031) and 2130 observed reflections [$I \geq 2\,\sigma(I)$], 178 refined parameters, *R* = 0.048, wR^2 = 0.130, max. (min.) residual electron density 0.25 (-0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

1'-Ethyl-3'-methyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5b). **5b** was obtained from azadienone **4b** (0.480g, 1.61 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/TBME, 3:2) gave 0.150g (0.54 mmol, 34%) **5b** as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H, CH_3) 1.48 (s, 3H, CH_3), 3.10 (m, 2H, CH_2), 3.31 (d,

J = 9.7 Hz, 1H, CH_2), 3.48 (d, J = 9.7 Hz, 1H, CH_2), 6.84 (q, J = 1.7 Hz, 1H, CH), 7.28-7.40 (m, 2H, H-arom.), 7.47-7.50 (m, 2H, H-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (CH_3), 12.9 (CH_3), 51.0 (CH_2N), 61.7 (CH_2N), 68.1 (C-spiro), 121.0 (CH-arom.), 122.0 (q, J = 270.2 Hz, CF_3), 123.3 (CH-arom.), 125.3, 126.1, 127.5 (CH-arom.), 128.3 (CH-arom.), 135.4 (q, J = 34.6 Hz, CCF_3), 137.7, 138.4 (q, J = 4.9 Hz, CH), 145.9 (C=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.7 ppm. IR (film): nu(tilde) = 3265 (w), 3072 (w), 3049 (w), 2976 (m), 2939 (m), 2918 (w), 2870 (w), 2822 (m), 1618 (m), 1603 (m), 1580 (w), 1545 (w), 1466 (m), 1460 (m), 1437 (m), 1379 (m), 1352 (w), 1313 (m), 1294 (m), 1265 (m), 1234 (m), 1215 (m), 1144 (s), 1126 (s), 1105 (m), 1059 (w), 1020 (w), 982 (m), 966 (m), 943 (w), 893 (w), 856 (w), 843 (m), 806 (w), 756 (m), 700 (w), 665 (w), 654 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{15}F_3N_2H$ 281.1260; found 281.1251. $C_{15}H_{15}F_3N_2$ (280.29): calcd. C 64.28, H 5.39, N 9.99; found C 64.28, H 5.40, N 10.01.

2-Ethyl-4-methyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6b). 6b was obtained from azadienone **4b** (0.480g, 1.61 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/TBME, 2:1) gave 0.070 g (0.25 mmol, 16%) **6b** as green solid, m.p. 111-112°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, J = 7.2 Hz, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.63 (br s, 1H, CH_2), 2.77 (br s, 1H, CH_2), 4.30 (br d, 1H, CH_2), 4.36 (br d, 1H, CH_2), 6.87 (s, 1H, NH), 6.92 (dd, J = 7.3, 0.7 Hz, 1H, H-arom.), 7.15 (dd, J = 7.7, 7.4 Hz, 1H, H-arom.), 7.22 (q, J = 1.4 Hz, 1H, CH), 7.53 (d, J = 7.8 Hz, 1H, CH-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.6 (CH_3), 18.8 (CH_3), 46.5 (CH_2), 60.5 (CH_2), 109.5 (C-olef.), 118.6 (CH-arom.), 120.2 (q, J = 34.1 Hz, CCF_3), 122.2 (CH-arom.), 123.2 (CH-arom.), 124.4 (q, J = 267.8 Hz, CF_3), 127.0 (q, J = 5.0 Hz, CH), 131.7, 132.7, 134.2 (q, J = 1.8 Hz), 154.1 (C-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.8 ppm. IR (KBr): nu(tilde) = 3499 (w), 3217 (s), 3074 (m), 3040 (s), 3009 (s), 2980 (s), 2949 (s), 2928 (s), 2878 (s), 1896 (w), 1830 (w), 1771 (w), 1688 (w), 1678 (w), 1607 (s), 1593 (s), 1543 (s), 1518 (s), 1479 (s), 1425 (s), 1387 (s), 1362 (s), 1315 (s), 1275 (m), 1238 (s), 1221 (s), 1173 (s), 1144 (s), 1123 (s), 1090 (s), 1040 (s), 988 (s), 961 (s), 926 (m), 895 (m), 881 (m), 841 (m), 802 (m), 781 (m), 750 (s), 710 (s), 690 (m), 663 (m), 627 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{15}F_3N_2H$ 281.1260; found 281.1255.

X-ray crystal structure analysis of **6b**:[2] formula $C_{15}H_{15}F_3N_2$, M = 280.29, light yellow crystal 0.50 x 0.35 x 0.30 mm, a = 17.1113(4), b = 17.2951(4), c = 18.4728(5)Å, V = 5466.9(2) Å^3, ρ_{calc} = 1.362 g cm^{-3}, μ= 0.979 mm^{-1}, empirical absorption correction (0.652 ≤ T ≤ 0.767), Z = 16, orthorhombic, space group Pbca (No. 61), λ= 1.54178 Å, T = 223(2) K, ω and φ scans scans, 46104 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4935 independent (R_{int} = 0.041) and 4493 observed reflections [$I \geq 2\,\sigma(I)$], 373 refined parameters, R = 0.054, wR^2 = 0.152, max. (min.) residual electron density 0.43 (-0.36) e Å^{-3}, two almost identical molecules in the asymmetric unit, hydrogen atoms at N5 from difference Fourier calculations and refined free, others calculated and refined as riding atoms.

1'-Isopropyl-3'-methyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5c). 5c was obtained from azadienone **4c** (0.312 g, 1.00 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 7:1) gave 0.130 g (0.44 mmol, 44%) **5c** as a brown solid, m.p. 48-49°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (d, J = 6.4 Hz, 3H, CH_3), 1.28 (d, J = 6.4 Hz, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.22 (sept., J = 6.4 Hz, 1H, CH), 3.37 (d, J = 9.7 Hz, 1H, CH_2), 3.52 (d, J = 9.7 Hz, 1H, CH_2), 6.86 (q, J = 1.2 Hz, 1H, CH), 7.32-7.42 (m, 2H, H-arom.), 7.47-7.50 (m, 2H, H-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9 (CH$_3$), 20.0 (CH$_3$), 20.2 (CH$_3$), 55.0 (CH$_2$N), 58.6 (CHN), 67.9 (C-spiro), 121.0 (CH-arom.), 122.0 (q, J = 270.2 Hz, CF$_3$), 123.3 (CH-arom.), 125.3, 126.1, 127.5 (CH-arom.), 128.3 (CH-arom.), 135.2 (q, J = 34.5 Hz, CCF$_3$), 137.7, 138.6 (q, J = 4.8 Hz, CH), 146.1 (C=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.7 ppm. IR (KBr): nu(tilde) = 3071 (w), 2970 (m), 2943 (w), 2918 (w), 2874 (w), 2831 (w), 1715 (w), 1622 (m), 1614 (m), 1580 (w), 1466 (m), 1435 (m), 1381 (m), 1348 (w), 1312 (m), 1294 (m), 1267 (m), 1234 (m), 1217 (m), 1177 (s), 1150 (s), 1126 (s), 1078 (w), 1063 (w), 1038 (w), 1009 (w), 984 (m), 966 (m), 943 (w), 889 (w), 874 (w), 831 (w), 775 (w), 764 (m), 696 (w), 654 (w), 644 (w), 604 (w), 573 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2H$ 295.1417; found 295.1416. $C_{16}H_{17}F_3N_2$ (294.31): calcd. C 65.29, H 5.82, N 9.52; found C 65.39, H 5.64, N 9.08.

2-Isopropyl-4-methyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6c). 6c was obtained from azadienone **4c** (0.312 g, 1.00 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 1:2) gave 0.070 g (0.24 mmol, 24%) **6c** as a red solid, m.p. 77-79 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (d, J = 6.2 Hz, 6H, CH_3), 2.38 (s, 3H, CH_3), 3.08 (sept., J = 6.2 Hz, 1H, CH), 4.33 (br d, 1H, CH_2), 4.46 (br d, 1H, CH_2), 6.87 (s, 1H, NH), 6.94 (d, J = 7.2 Hz, 1H, H-arom.), 7.16 (t, J = 7.5 Hz, 1H, H-arom.), 7.22 (q, J = 1.4 Hz, 1H, CH), 7.53 (d, J = 7.8 Hz, 1H, H-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.7 (CH$_3$), 49.9 (CH$_2$), 58.0 (CHN), 109.8 (C-olef.), 118.6 (CH-arom.), 120.1 (q, J = 34.2 Hz, CCF$_3$), 122.1 (CH-arom.), 123.3 (CH-arom.), 124.4 (q, J = 267.8 Hz, CF$_3$), 126.9 (q, J = 5.0 Hz, CH), 131.5, 133.2, 134.2 (q, J = 1.8 Hz), 154.3 (C-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.8 ppm. IR (KBr): nu(tilde) = 3283 (s), 3040 (m), 2974 (m), 2926 (m), 2876 (m), 1697 (m), 1655 (m), 1647 (m), 1607 (s), 1595 (s), 1528 (s), 1481 (s), 1458 (m), 1429 (s), 1389 (s), 1358 (s), 1333 (s), 1317 (s), 1265 (m), 1240 (s), 1221 (s), 1173 (s), 1146 (s), 1126 (s), 1097 (s), 1072 (s), 1047 (s), 1032 (s), 999 (m), 970 (m), 934 (m), 889 (m), 858 (m), 845 (m), 795 (m), 754 (s), 733 (m), 692 (m), 662 (m), 638 (m), 592 (w), 550 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2H$ 295.1417; found 295.1410.

1'-Butyl-3'-methyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5d). 5d was obtained from azadienone **4d** (0.326 g, 1.00 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/acetone, 16:1) gave 0.125 g (0.41 mmol, 41%) **5d** as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3H, CH_3), 1.47 (m, 2H, CH_2), 1.48 (s, 3H, CH_3), 1.67 (m, 2H, CH_2), 3.05 (m, 2H, CH_2N), 3.32 (d, J = 9.7 Hz, 1H, CH_2), 3.46 (d, J = 9.7 Hz, 1H, CH_2), 6.83 (q, J = 1.7 Hz, 1H, CH), 7.32-7.40 (m, 2H, H-arom.), 7.47-7.50 (m, 2H, H-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (CH$_3$), 14.0 (CH$_3$), 20.4 (CH$_2$), 30.0 (CH$_2$), 56.7 (CH$_2$N), 62.1 (CH$_2$N), 68.1 (C-spiro), 120.9 (CH-arom.), 122.0 (q, J = 270.2 Hz, CF$_3$), 123.3 (CH-arom.), 125.2, 127.5 (CH-arom.), 128.3 (CH-arom.), 135.4 (q, J = 34.7 Hz, CCF$_3$), 137.6, 138.4 (q, J = 4.9 Hz, CH), 145.9 (C=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.7 ppm. IR (film): nu(tilde) = 3406 (w), 3072 (w), 3049 (w), 3024 (w), 2961 (m), 2932 (m), 2872 (m), 2816 (m), 1767 (w), 1715 (w), 1620 (w), 1605 (w), 1580 (w), 1466 (m), 1437 (w), 1379 (m), 1313 (m), 1294 (m), 1261 (m), 1234 (m), 1219 (w), 1175 (m), 1128 (m), 1063 (w), 1038 (w), 1016 (w), 995 (w), 974 (w), 966 (w), 945 (w), 891 (w), 860 (w), 845 (w), 800 (w), 756 (m), 714 (w), 698 (w), 667 (w), 644 (w), 606 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{19}F_3N_2H$ 309.1573; found 309.1565. $C_{17}H_{19}F_3N_2$ (308.34): calcd. C 66.22, H 6.21, N 9.09; found C 66.71, H 6.39, N 8.79.

2-Butyl-4-methyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6d). 6d was obtained from azadienone **4d** (0.326 g, 1.00 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Acetone, 5:1) gave 0.035 g (0.11 mmol, 11%) **6d** as a red solid. m.p. 98-99°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3H, CH_3), 1.27 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 2.36 (s, 3H, CH_3), 2.53-2.71 (br d, 2H, CH_2), 4.24 (br d, J = 15.4 Hz, 1H, CH_2), 4.36 (br d, J = 15.4 Hz, 1H, CH_2), 6.81 (s, 1H, N*H*), 6.92 (d, J = 7.3 Hz, 1H, *H*-arom.), 7.16 (dd, J = 7.5, 7.5 Hz, 1H, *H*-arom.), 7.23 (q, J = 1.4 Hz, 1H, C*H*), 7.54 (d, J = 7.8 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0 (*C*H_3), 18.8 (*C*H_3), 20.1 (*C*H_2), 29.7 (*C*H_2), 51.9 (*C*H_2N), 60.9 (*C*H_2N), 109.4 (*C*-olef.), 118.5 (*C*H-arom.), 120.1 (q, J = 34.1 Hz, *C*CF_3), 122.1 (*C*H-arom.), 123.1 (*C*H-arom.), 124.5 (q, J = 267.8 Hz, *C*F_3), 126.9 (q, J = 4.9 Hz, *C*H), 132.0, 132.6, 134.2 (q, J = 1.6 Hz), 154.3 (*C*-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -59.8 ppm. IR (KBr): nu(tilde) = 3250 (s), 3018 (s), 2959 (s), 2932 (s), 2874 (s), 1915 (w), 1846 (w), 1744 (w), 1690 (m), 1607 (s), 1593 (s), 1541 (s), 1516 (s), 1481 (s), 1435 (s), 1427 (s), 1387 (s), 1358 (s), 1335 (s), 1319 (s), 1263 (s), 1240 (s), 1221 (s), 1169 (s), 1146 (s), 1128 (s), 1094 (s), 1036 (s), 972 (s), 934 (s), 899 (m), 885 (m), 849 (m), 802 (w), 791 (m), 758 (s), 714 (s), 690 (m), 665 (m), 625 (m), 592 (m), 511 (m) cm^{-1}. HRMS (ESI): calcd. for: $C_{17}H_{19}F_3N_2H$ 309.1573; found 309.1568. $C_{17}H_{19}F_3N_2$ (308.34): calcd. C 66.22, H 6.21, N 9.09; found C 66.28, H 6.24, N 9.32.

1'-Methyl-3'-phenyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5e). 5e was obtained from azadienone **4e** (0.130g, 0.376 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 8:1) gave 0.033 g (0.10 mmol, 26%) **5e** as a yellowish solid, m.p. 90-91°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 3H, CH_3N), 3.41 (d, J = 9.6 Hz, 1H, CH_2), 3.56 (d, J = 9.6 Hz, 1H, CH_2), 7.01 (q, J = 1.8 Hz, 1H, C*H*), 7.06-7.16 (m, 5H, *H*-arom.), 7.30 (dt, J = 7.5, 0.8 Hz, 1H, *H*-arom.), 7.41 (dt, J = 7.6, 1.1 Hz, 1H, *H*-arom.), 7.49 (d, J = 7.5 Hz, 1H, *H*-arom.), 7.57 (dd, J = 7.6, 0.6 Hz, 1H, *H*-arom.). ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.2 (*C*H_3N), 65.8 (*C*H_2), 67.0 (*C*-spiro), 121.4 (*C*H-arom.), 122.0 (q, J = 270.2 Hz, *C*F_3), 123.7 (*C*H-arom.), 125.5 (*C*H-arom.), 127.9

(*C*H-arom.), 128.3 (*C*H-arom.), 128.4 (*C*H-arom.), 128.8 (*C*H-arom.), 131.3, 135.0 (q, J = 34.7 Hz, *C*CF_3), 137.1, 139.9 (q, J = 4.9 Hz, *C*H), 146.8, 149.7 (*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.8 ppm. IR (KBr): nu(tilde) = 3437 (w), 3086 (w), 3078 (w), 3044 (w), 2995 (w), 2963 (w), 2918 (w), 2880 (w), 2860 (w), 2839 (w), 2829 (w), 2795 (w), 1662 (w), 1582 (w), 1547 (w), 1493 (w), 1464 (w), 1458 (m), 1445 (w), 1414 (w), 1379 (m), 1335 (w), 1313 (m), 1294 (m), 1277 (w), 1234 (m), 1196 (m), 1173 (s), 1148 (s), 1117 (s), 1070 (m), 1049 (m), 1030 (w), 1018 (w), 995 (m), 974 (m), 959 (m), 916 (w), 893 (w), 870 (m), 845 (w), 806 (w), 768 (s), 739 (w), 710 (w), 687 (m), 673 (m), 656 (w), 646 (w), 619 (w), 602 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{15}F_3N_2Na$ 351.1080; found 351.1078.

X-ray crystal structure analysis of **5e**:[2] formula $C_{19}H_{15}F_3N_2$, M = 328.33, light yellow crystal 0.40 x 0.20 x 0.15 mm, a = 5.9468(1), b = 9.2592(2), c = 15.2291(4)Å, α = 107.113(1), β = 91.035(1), γ = 90.367(2)°, V = 801.24(3) Å^3, ρ_{calc} = 1.361 g cm^{-3}, μ= 0.105 mm^{-1}, empirical absorption correction (0.959 ≤ T ≤ 0.984), Z = 2, triclinic, space group P1bar (No. 2), λ= 0.71073 Å, T = 223(2) K, ω and φ scans, 8458 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 3892 independent (R_{int} = 0.036) and 2608 observed reflections [$I \geq 2\ \sigma(I)$], 218 refined parameters, R = 0.055, wR^2 = 0.145, max. (min.) residual electron density 0.23 (-0.32) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-Methyl-4-phenyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6e). 6e was obtained from azadienone **4e** (0.130g, 0.376 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 8:1) gave 0.035 g (0.11 mmol, 28%) **6e** as a yellow solid, m.p. 170 °C (dec). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.66 (s, 3H, CH_3), 4.25 (br d, 1H, CH_2), 4.66 (br d, 1H, CH_2), 6.85 (q, J = 1.4 Hz, C*H*), 6.93 (s, 1H, N*H*), 6.93 (dd, J = 7.3, 0.6 Hz, 1H, *H*-arom.), 7.01 (d, J = 7.3 Hz, 1H, *H*-arom.), 7.24 (t, J = 7.5 Hz, 1H, *H*-arom.), 7.48-7.60 (m, 5H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 40.5 (*C*H_3N), 63.0 (*C*H_2), 110.0 (*C*-olef.), 118.8 (*C*H-arom.), 122.7 (*C*H-arom.), 123.2 (q, J = 267.3 Hz, *C*F_3), 123.8 (*C*H-arom.), 125.8 (q, J = 33.7 Hz, *C*CF_3), 128.7 (*C*H-arom.), 129.7 (q, J = 4.9 Hz, *C*H), 130.2 131.0, 131.7, 132.6, 134.8, 155.9 (*C*-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ - 61.1 ppm. IR (KBr): nu(tilde) = 3451 (w), 3208 (w), 3051 (w), 2961 (m), 2920 (m), 2853 (w), 1603 (m), 1587 (s), 1572 (m), 1551 (s), 1502 (s), 1481 (s), 1445 (m), 1423 (s), 1385 (m), 1354 (m), 1339 (m), 1319 (s), 1310 (s), 1286 (m), 1250 (m), 1234 (s), 1205 (s), 1182 (w), 1169 (m), 1159 (m), 1126 (s), 1101 (s), 1067 (m), 1043 (s), 1009 (m), 999 (m), 974 (w), 949 (w), 918 (m), 870 (w), 862 (w), 849 (w), 791 (w), 770 (m), 754 (s), 700 (s), 679 (w), 665 (w), 631 (m), 592 (m), 552 (w) cm $^{-1}$. HRMS (ESI): calcd. for $C_{19}H_{15}F_3N_2Na$ 351.1080; found 351.1088. $C_{19}H_{15}F_3N_2$ (328.33): C 69.50, H 4.60, N 8.53; found C 69.67, H 4.63, N 8.16.

X-ray crystal structure analysis of **6e**:[2] formula $C_{19}H_{15}F_3N_2$, M = 328.33, light yellow crystal 0.30 x 0.10 x 0.03 mm, a = 10.2968(5), b = 11.3686(5), c = 14.3731(8)Å, α = 102.061(2), β = 94.523(2), γ = 101.547(4)°, V = 1599.24(14) Å^3, ρ_{calc} = 1.364 g cm^{-3}, μ= 0.890 mm^{-1}, empirical absorption correction (0.776 ≤ T ≤ 0.974), Z = 4, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 22644 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5612 independent (R_{int} = 0.068) and 4457 observed reflections [I ≥ 2 σ(I)], 441 refined parameters, R = 0.067, wR^2 = 0.180, max. (min.) residual electron density 0.33 (-0.43) e Å^{-3}, two almost identical molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms.

1'-Methyl-3'-(2-thienyl)-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5f). 5f was obtained from azadienone **4f** (0.130 g, 0.37 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 3:1) gave 0.038g (0.11 mmol, 31%) **5f** as a brown solid, m.p. 94-95°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (s, 3H, CH_3N), 3.46 (d, J = 9.7 Hz, 1H, CH_2), 3.63 (d, J = 9.7 Hz, 1H, CH_2), 6.20 (dd, J = 3.7, 1.0 Hz, 1H, H-thiophene), 6.71 (dd, J = 5.1, 3.8 Hz, 1H, CH-thiophene), 7.01 (q, J = 1.7 Hz, 1H, CH), 7.12 (dd, J = 5.1, 1.0 Hz, 1H, H-thiophene), 7.34 (dt, J = 7.6, 0.9 Hz, 1H, H-arom.), 7.43 (dt, J = 7.5, 1.1 Hz, 1H, H-arom.), 7.51-7.57 (m, 2H, H-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.2 (CH_3N), 65.4 (CH_2), 67.1 (C-spiro), 121.3 (CH-arom.), 122.0 (q, J = 270.2 Hz, CF_3), 123.8 (CH-arom.), 125.1 (CH-arom.), 126.5 (CH-arom.), 127.3 (CH-arom.), 127.9 (CH-arom.), 128.7 (CH-arom.), 133.8, 135.3 (q, J = 34.7 Hz, CCF_3), 137.5, 139.2 (q, J = 4.9 Hz, CH), 145.9, 146.1 (C=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.9 ppm. IR (KBr): nu(tilde) = 3437 (w), 3074 (w), 2993 (w), 2993 (w), 2963 (m), 2920 (w), 2891 (w), 2835 (w), 2801 (w), 1620 (m), 1580 (w), 1560 (w), 1543 (w), 1512 (w), 1466 (m), 1460 (m), 1435 (w), 1412 (w), 1381 (m), 1352 (w), 1317 (m), 1294 (m), 1277 (m), 1263 (m), 1232 (s), 1194 (m), 1175 (s), 1144 (s), 1128 (s), 1082 (m), 1049 (m), 1018 (m), 982 (m), 887 (w), 862 (m), 851 (m), 820 (m), 766 (m), 710 (s), 669 (w), 640 (w), 592 (w) cm $^{-1}$. HRMS (ESI): calcd. for $C_{17}H_{13}F_3N_2SNa$ 357.0644; found 357.0646.

2-Methyl-4-(2-thienyl)-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6f). Compound **6f** was obtained from azadienone **4f** (0.130 g, 0.37 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 1:1) gave 0.022 g (0.07 mmol, 18%) **6f** as a yellow solid, m.p. 150-151°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (s, 3H, CH_3), 4.26 (d, J = 15.3 Hz, 1H, CH_2), 4.44 (d, J = 15.3 Hz, 1H, CH_2), 6.92 (s, 1H, N*H*), 7.00 (d, J = 7.3 Hz, 1H, *H*-arom.), 7.21-7.23 (m, 3H, *H*-arom.), 7.46 (dd, J = 3.7, 1.1 Hz, 1H, *H*-arom.), 7.57-7.59 (m, 2H, C*H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4 (*C*H_3N), 63.2 (*C*H_2), 110.4 (*C*-olef.), 118.9 (*C*H-arom.), 122.2 (q, J = 34.3 Hz, *C*CF_3), 122.8 (*C*H-arom.), 124.3 (q, J = 268.1 Hz, *C*F_3), 128.2 (*C*H-arom.), 129.2 (q, J = 5.0 Hz, *C*H), 129.7 (*C*H-arom.), 131.8 (*C*H-arom.), 132.3, 132.4, 135.1, 136.0, 148.3 (*C*-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ - 60.2 ppm. IR (KBr): nu(tilde) = 3449 (w), 3219 (m), 2964 (w), 2949 (m), 2924 (m), 2853 (w), 1578 (s), 1549 (s), 1524 (m), 1508 (m), 1479 (s), 1421 (s), 1385 (m), 1344 (w), 1335 (w), 1306 (s), 1263 (w), 1248 (m), 1232 (s), 1204 (m), 1169 (m), 1150 (s), 1126 (s), 1097 (s), 1040 (s), 1007 (m), 951 (w), 905 (w), 878 (w), 853 (w), 843 (m), 802 (w), 789 (w), 756 (m), 716 (s), 662 (w), 633 (w), 598 (w) cm $^{-1}$. HRMS (ESI): calcd. for $C_{17}H_{13}F_3N_2SH$ 335.0824; found 335.0828.

X-ray crystal structure analysis of **6f**:[2] formula $C_{17}H_{13}F_3N_2S$, M = 334.35, yellow crystal 0.30 x 0.30 x 0.25 mm, a = 8.7915(5), b = 16.0920(10), c = 11.1759(7)Å, β = 106.315(1)°, V = 1517.4(2) Å^3, ρ_{calc} = 1.464 g cm^{-3}, μ= 2.200 mm^{-1}, empirical absorption correction (0.558 ≤ T ≤ 0.609), Z = 4, monoclinic, space group $P2_1$/n (No. 14), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 10753 reflections collected (± h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 2680 independent (R_{int} = 0.032) and 2511 observed reflections [$I \geq 2\sigma(I)$], 220 refined parameters, R = 0.037, wR^2 = 0.096, max. (min.) residual electron density 0.23 (-0.432) e Å^{-3}, C20 and S23 refined with split positions, hydrogen atom at from difference Fourier calculations and refined free, others calculated and refined as riding atoms.

2,4,9-Trimethyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6g). Compound **6g** was obtained from azadienone **4g** (0.105 g, 0.35 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O 1:2) gave 0.033g (0.12 mmol, 34%) **6g** as a red solid, m.p. 138°C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H, C*H*$_3$), 2.35 (s, 3H, C*H*$_3$), 2.53 (s, 3H, C*H*$_3$N), 4.09-4.13 (br d, 1H, C*H*$_2$), 4.50-4.54 (br d, 1H, C*H*$_2$), 6.75 (s, 1H, N*H*), 7.01 (d, *J* = 7.8 Hz, 1H, *H*-arom.), 7.16 (q, *J* = 1.4 Hz, 1H, C*H*), 7.42 (d, *J* = 7.8 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8 (*C*H$_3$), 19.1 (*C*H$_3$), 40.6 (*C*H$_3$N), 58.0 (*C*H$_2$), 109.2 (*C*-olef.), 118.3 (*C*H-arom.), 120.0 (q, *J* = 33.8 Hz, *C*CF$_3$), 124.5 (q, *J* = 267.8 Hz, *C*F$_3$), 125.7 (*C*H-arom.),126.5 (q, *J* = 5.0 Hz, *C*H), 129.7, 130.1, 133.0 (q, *J* = 1.7 Hz), 133.1, 153.4 (*C*-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -60.0 ppm. IR (KBr): nu(tilde) = 3437 (w), 3256 (s), 3034 (s), 2963 (m), 2926 (m), 2891 (m), 2870 (m), 2798 (w), 1686 (w), 1605 (s), 1524 (s), 1475 (s), 1443 (s), 1425 (s), 1385 (s), 1358 (s), 1335 (m), 1310 (s), 1292 (s), 1254 (s), 1227 (s), 1196 (s), 1169 (s), 1151 (s), 1122 (s), 1088 (s), 1047 (s), 1032 (s), 955 (m), 903 (m), 845 (m), 829 (m), 812 (s), 773 (m), 727 (m), 708 (m), 662 (w), 644 (w), 629 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{15}F_3N_2H$ 281.1260; found 281.1261.

2,4,7,9-Tetramethyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6h). **6h** was obtained from azadienone **4h** (0.106 g, 0.34 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O 1:2) gave 0.066g (0.22 mmol, 66%) **6h** as a yellow solid, m.p. 141-142°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H, C*H*$_3$), 2.34 (s, 3H, C*H*$_3$), 2.49 (s, 3H, C*H*$_3$), 2.54 (s, 3H, C*H*$_3$), 3.98-4.05 (m, 1H, C*H*$_2$), 4.50-4.53 (br d, 1H, C*H*$_2$), 6.83 (s, 2H, N*H* and *H*-arom.), 7.26 (q, *J* = 1.0 Hz, 1H, C*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8 (*C*H$_3$), 18.9 (*C*H$_3$), 20.0 (q, *J* = 4.7 Hz, *C*H$_3$), 40.5 (*C*H$_3$N), 57.6 (*C*H$_2$), 108.5 (*C*-olef.), 119.4 (q, *J* = 34.0 Hz, *C*CF$_3$), 124.7 (q, *J* = 267.0 Hz, *C*F$_3$), 126.9 (*C*H-arom.), 128.4 (q, *J* = 6.3 Hz, *C*H), 128.5, 128.8, 130.3, 133.1 (q, *J* = 1.3 Hz), 134.3, 153.1 (*C*-N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.0 ppm. IR (KBr): nu(tilde) = 3416 (w), 3252 (s), 3017 (s), 2968 (s), 2936 (s), 2891 (s), 2874 (s), 2799 (m), 2745 (m), 1676 (m), 1595 (s), 1543 (s), 1510 (s), 1483 (s), 1464 (s), 1447 (s), 1412 (s), 1398 (s), 1385 (s), 1358 (s), 1339 (s), 1315 (s), 1292 (s), 1269 (s), 1238 (s), 1225 (s), 1198 (s), 1165 (s), 1124 (s), 1117 (s), 1082 (s), 1028 (s), 997 (s), 976 (s), 962 (s), 953 (s), 908 (m), 893 (s), 854 (s), 839 (s), 802 (s), 775 (m), 721 (m), 690 (m), 667 (s), 611 (s), 586 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{17}F_3N_2H$ 295.1417; found 295.1426.

1',3'-Dimethyl-1-(trifluoromethyl)-1',5'-dihydrospiro(cyclopenta[a]naphthalene-3,4'-pyrazole) (5g). Compound **5g** was obtained from azadienone **4i** (0.134 g, 0.40 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O/pentane 2:1) gave 0.047 g (0.15 mmol, 37%) **5g** as a brown solid, m.p. 83-84°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (s, 3H, CH_3), 2.95 (s, 3H, CH_3N), 3.42 (d, J = 9.7 Hz, 1H, CH_2), 3.51 (d, J = 9.7 Hz, 1H, CH_2), 7.09 (q, J = 1.17 Hz, 1H, CH), 7.48-7.71 (m, 3H, H-arom.), 7.86-7.94 (m, 2H, H-arom.), 8.31 (d, J = 8.5 Hz, 1H, H-arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.8 (CH$_3$), 43.7 (CH$_3$N), 63.6 (CH$_2$), 68.7 (C-spiro), 120.7 (CH-arom.), 122.7 (q, J = 269.8 Hz, CF$_3$), 124.3 (q, J = 5.4 Hz, CH-arom.), 125.9 (CH-arom.), 127.2 (CH-arom.), 128.4, 129.0 (CH-arom.), 129.3 (CH-arom.), 133.2, 134.1, 135.7 (q, J = 34.5 Hz, CCF$_3$), 140.6 (q, J = 6.2 Hz, CH), 145.4, 150.7 (C=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.2 ppm. IR (KBr): nu(tilde) = 3414 (m), 3073 (s), 3001 (m), 2966 (m), 2914 (m), 2883 (m), 2858 (m), 2843 (s), 2816 (m), 2789 (m), 1946 (w), 1913 (w), 1832 (w), 1809 (w), 1765 (w), 1686 (m), 1603 (s), 1584 (s), 1558 (m), 1520 (m), 1458 (s), 1445 (s), 1400 (s), 1379 (s), 1360 (m), 1348 (s), 1337 (s), 1325 (s), 1298 (s), 1275 (s), 1252 (s), 1213 (s), 1200 (s), 1178 (s), 1161 (s), 1146 (s), 1121 (s), 1092 (s), 1061 (s), 1032 (s), 1009 (s), 962 (s), 937 (s), 922 (s), 887 (m), 872 (s), 858 (s), 820 (s), 743 (s), 729 (s), 714 (s), 702 (s), 679 (m), 656 (m), 638 (m), 627 (m), 617 (m), 571 (m), 540 (s), 519 (m), 503 (s), 480 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{15}F_3N_2H$ 317.1266; found 317.1276.

1'-Allyl-3'-methyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5h). 5h was obtained from azadienone **4j** (0.873 g, 2.82 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/TBME, 3:2) gave 0.057g (0.20 mmol, 7%) **5h** as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49 (s, 3H, CH_3), 3.35 (d, J = 9.9 Hz, 1H, CH_2), 3.48 (d, J = 9.9 Hz, 1H, CH_2), 3.73 (tdd, J = 13.8, 6.6, 1.2 Hz, 1H, CH$_2$=CHCH_2), 3.80 (tdd, J = 13.9, 6.5, 1.3 Hz, 1H, CH$_2$=CHCH_2), 5.25 (dd, J = 10.2, 1.3 Hz, 1H, CH_2=CHCH$_2$), 5.32 (qd, J = 17.2, 1.4 Hz, 1H, CH_2=CHCH$_2$), 6.02 (tdd, J = 16.8, 10.2, 6.5 Hz, CH$_2$=CHCH$_2$), 6.83 (q, J = 1.7 Hz, 1H, CH), 7.35 (dt, J

= 7.4, 1.1 Hz, 1H, *H*-arom.), 7.35 (dt, *J* = 7.5, 1.3 Hz, 1H, *H*-arom.), 7.48-7.50 (m, 2H, *H*-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (CH_3), 59.3 (CH_2N), 61.2 (CH_2N), 68.2 (*C*-spiro), 118.6 , 121.0 (*C*H-arom.), 122.0 (q, *J* = 270.2 Hz, CF_3), 123.3 (*C*H-arom.), 127.6 (*C*H-arom.), 128.4 (*C*H-arom.), 135.4, 137.7 (q, *J* = 1 Hz), 138.2 (q, *J* = 4.9 Hz, *C*H), 145.7 (C=N) ppm. ^{19}F NMR (282 MHz, CDCl3) δ -64.7 ppm. IR (film): nu(tilde) = 3379 (w), 3074 (w), 2957 (w), 2922 (w), 2855 (w), 2816 (w), 1736 (w), 1618 (w), 1580 (w), 1466 (w), 1460 (w), 1437 (w), 1379 (m), 1313 (w), 1294 (w), 1273 (w), 1248 (w), 1234 (m), 1213 (w), 1194 (w), 1175 (m), 1128 (s), 1074 (w), 991 (w), 966 (w), 922 (w), 860 (w), 764 (w), 756 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2H$ 293.1260; found 293.1258.

1',3'-Dimethyl-3-(trifluoromethyl)-5'-vinyl-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5j). 5j was obtained from azadienone **4j** (0.873 g, 2.82 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/TBME, 3:2) gave 0.055g (0.20 mmol, 7%) **5j** as an orange oil. Compound was obtained as a mixture of diastereomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (s, 3H, CH_3), 2.85 (s, 3H, CH_3N), 3.80 (d, *J* = 8.3 Hz, 1H, C*H*), 5.02-5.03 (m, 1H, *H*-vinyl), 5.05 (br s, 1H, *H*-vinyl), 5.61-5.67 (m, 1H, *H*-vinyl), 6.87 (q, *J* = 1.7 Hz, 1H, C*H*), 7.35 (dt, *J* = 7.4, 1.1 Hz, 1H, *H*-arom.), 7.38-7.50 (m, 3H, *H*-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.2 (CH_3), 41.3 (CH_3N), 72.3 (*C*-spiro), 81.5 (*C*HN) 120.2 (*C*H), 120.9, 121.1 (*C*H-arom.), 121.9 (q, *J* = 270.2 Hz, CF_3), 123.2 (*C*H-arom.), 127.4 (*C*H-arom.), 131.2 (*C*H-arom.), 135.5 (q, *J* = 4.9 Hz, *C*H), 138.8, 144.6 (*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.60 (1R,5'R; 1S,5'S), -64.57 (1R,5'S; 1S,5'R) ppm, ratio 3.6: 1. IR (film): nu(tilde) = 3391 (w), 3074 (w), 2986 (w), 2961 (w), 2922 (w), 2864 (w), 2789 (w), 1773 (w), 1717 (w), 1620 (w), 1582 (w), 1460 (w), 1448 (w), 1435 (w), 1379 (m), 1315 (w), 1288 (w), 1269 (w), 1231 (m), 1169 (m), 1144 (m), 1126 (m), 991(w), 961 (w), 932 (w), 789 (w), 772 (w), 758 (w), 750 (w), 667 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2H$ 293.1260; found 293.1274.

2-Allyl-4-methyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6i). 6i was obtained from azadienone **4j** (0.873 g, 2.82 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/TBME, 3:2) gave 0.118 g (0.40 mmol, 14%) **6i** as a brown solid, m.p. 109-110°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H, CH_3), 3.23 (br s, 1H, CH_2), 3.32 (br s, 1H,

CH_2), 4.29 (br s, 1H, CH_2), 4.38 (br s, 1H, CH_2), 5.01 (ddd, J = 17.1, 3.2, 1.4 Hz, 1H, CH_2=CHCH$_2$), 5.11-5.14 (m, 1H, CH_2=CHCH$_2$), 5.92 (tdd, J = 16.7, 10.1, 6.6 Hz, CH$_2$=C*H*CH$_2$), 6.78 (s, 1H, N*H*), 6.91 (dd, J = 7.2, 0.7 Hz, 1H, *H*-arom.), 7.16 (t, J = 7.5 Hz, 1H, *H*-arom.), 7.23 (q, J = 1.4 Hz, 1H, C*H*), 7.54 (d, J = 7.8 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 18.6 (CH$_3$), 55.2 (CH$_2$N), 60.9 (CH$_2$N), 109.8 (*C*-olef.), 118.6 (*C*H-arom.), 119.1 (CH$_2$=CHCH$_2$), 120.4 (q, J = 34.0 Hz, *C*CF$_3$), 122.2 (*C*H-arom.), 123.3 (*C*H-arom.), 124.4 (q, J = 267.8 Hz, *C*F$_3$), 127.0 (q, J = 5.0 Hz, *C*H), 131.8, 132.6, 133.9 (CH$_2$=*C*HCH$_2$), 134.4 (q, J = 1.7 Hz), 154.1 (*C*-N) ppm. ^{19}F NMR (282 MHz, CDCl$_3$) δ -59.9 ppm. IR (KBr): nu(tilde) = 3414 (w), 3356 (m), 3233 (m), 3072 (w), 3011 (m), 2922 (m), 2855 (m), 1709 (m), 1639 (m), 1605 (s), 1593 (s), 1549 (s), 1526 (s), 1499 (m), 1479 (s), 1458 (m), 1431 (m), 1387 (m), 1352 (s), 1335 (s), 1315 (s), 1261 (s), 1240 (s), 1221 (s), 1148 (s), 1128 (s), 1096 (s), 1038 (s), 995 (m), 986 (m), 955 (m), 926 (m), 910 (m), 851 (w), 791 (m), 756 (m), 733 (m), 716 (m), 692 (w), 644 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2H$ 293.1260; found 293.1263.

1'-Benzyl-3'-methyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5i). 5i was obtained from azadienone **4k** (0.540 g, 1.50 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et$_2$O, 4:1) gave 0.100 g (0.29 mmol, 19%) **5i** as a yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.50 (s, 3H, C*H*$_3$), 3.28 (d, J = 9.8 Hz, 1H, C*H*$_2$), 3.38 (d, J = 9.8 Hz, 1H, C*H*$_2$), 4.29 (d, J = 13.4 Hz, 1H, C*H*$_2$), 4.35 (d, J = 13.4 Hz, 1H, C*H*$_2$), 6.78 (q, J = 1.7 Hz, 1H, C*H*), 6.93 (dd, J = 7.3, 0.6 Hz, 1H, *H*-arom.), 7.28-7.47(m, 8H, *H*-arom.) ppm. ^{13}C NMR (125 MHz, CDCl$_3$) δ 11.8 (*C*H$_3$), 60.7 (*C*H$_2$N), 61.3 (*C*H$_2$N), 68.2 (*C*-spiro), 120.9 (*C*H-arom.), 122.0 (q, J = 270.1 Hz, *C*F$_3$), 123.3 (*C*H-arom.), 127.5, 127.6 (*C*H-arom.), 128.3(*C*H-arom.),128.4 (*C*H-arom.), 129.0 (*C*H-arom.), 135.4 (q, J = 34.8 Hz, *C*CF$_3$), 136.8, 137.6, 138.3 (q, J = 4.9 Hz, *C*H), 145.9 (*C*=N) ppm. ^{19}F NMR (282 MHz, CDCl$_3$) δ -64.7 ppm. IR (film): nu(tilde) = 3370 (w), 3088 (w), 3069 (w), 3030 (w), 3007 (w), 2957 (w), 2918 (w), 2849 (w), 2828 (w), 1747 (w), 1732 (m), 1626 (w), 1582 (w), 1497 (w), 1458 (w), 1433 (w), 1381 (w), 1360 (w), 1315 (w), 1292 (w), 1267 (m), 1236 (m), 1209 (m), 1177 (m), 1128 (m), 1057 (w), 1022 (w), 993 (w), 964 (w), 955 (w), 939 (w), 862 (w), 756 (w), 712 (w), 698 (w), 667 (w), 640 (w), 608 (w), 588 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{17}F_3N_2H$ 343.1417; found 343.1422.

1',3'-Dimethyl-5'-phenyl-3-(trifluoromethyl)-1',5'-dihydrospiro(indene-1,4'-pyrazole) (5k). Compound **5k** was obtained from azadienone **4k** (0.540 g, 1.50 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 4:1) gave 0.060g (0.18 mmol, 12%) **5k** as a brown viscose oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 3H, C*H*$_3$), 2.90 (s, 3H, C*H*$_3$), 4.51 (s, 1H, C*H*), 6.63 (q, *J* = 1.7 Hz, 1H, C*H*), 6.98-7.19 (m, 4H, *H*-arom.), 7.39-7.48 (m, 4H, *H*-arom.), 7.60-7.62 (m, 1H, *H*-arom.) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5 (*C*H$_3$), 41.8 (*C*H$_3$N), 72.9 (*C*-spiro), 81.7 (*C*HN), 121.1 (*C*H-arom.), 121.8 (q, *J* = 268.1 Hz, *C*F$_3$), 123.3 (*C*H-arom.), 126.3 (*C*H-arom.), 126.9 (*C*H-arom.), 127.5 (*C*H-arom.), 127.8 (*C*H-arom.), 128.1 (*C*H-arom.), 128.3 (*C*H-arom.), 128.5 (*C*H-arom.), 128.9 (*C*H-arom.), 129.0 (*C*H-arom.), 134.4, 135.2 (q, *J* = 34.1 Hz, *C*CF$_3$), 136.4 (q, *J* = 5.1 Hz, *C*H), 144.8(*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.9 (1R,5'R; 1S,5'S), -64.7 (1R,5'S; 1S,5'R), ppm, ratio 1.8:1. IR (KBr): nu(tilde) = 3449 (m), 3069 (m), 3030 (w), 2955 (w), 2914 (w), 2864 (w), 2793 (w), 1686 (m), 1655 (w), 1647 (w), 1638 (w), 1624 (m), 1607 (m), 1580 (w), 1499 (w), 1458 (m), 1433 (m), 1408 (m), 1379 (s), 1358 (w), 1315 (m), 1298 (m), 1271 (m), 1236 (m), 1209 (m), 1169 (s), 1146 (s), 1123 (s), 1076 (m), 1043 (w), 1028 (w), 1015 (m), 968 (m), 953 (w), 943 (w), 895 (w), 881 (w), 795 (m), 773 (m), 754 (m), 741 (m), 714 (m), 698 (s), 669 (m), 652 (w), 582 (m) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{17}F_3N_2H$ 343.1417; found 343.1402.

2-Benzyl-4-methyl-6-(trifluoromethyl)-2,3-dihydro-1H-indeno[7,1-de][1,2]diazepine (6j). 6j was obtained from azadienone **4k** (0.540 g, 1.50 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 4:1) gave 0.085g (0.25 mmol, 17%) **6j** as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H, C*H*$_3$), 3.73 (d, *J* = 11.9 Hz, 1H, C*H*$_2$), 3.83 (d, *J* = 11.9 Hz, 1H, C*H*$_2$), 4.31 (d, *J* = 16.1 Hz, 1H, C*H*$_2$), 4.48 (d, *J* = 16.1 Hz, 1H, C*H*$_2$), 6.56 (s, 1H, N*H*), 6.92 (d, *J* = 7.3 Hz, 1H, *H*-arom.), 7.17-7.34 (m, 7H, *H*-arom.), 7.57 (d, *J* = 7.8 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.6 (*C*H$_3$), 56.1 (*C*H$_2$), 61.2 (*C*H$_2$), 109.9 (*C*-olef.), 118.8 (*C*H-arom.), 122.7 (*C*H-arom.), 123.2 (q, *J* = 267.3 Hz, *C*F$_3$), 123.8 (*C*H-arom.), 125.8 (q, *J* = 33.7 Hz, *C*CF$_3$), 128.7 (*C*H-arom.), 129.7 (q, *J* = 4.9 Hz, *C*H), 130.2, 131.0, 131.7, 132.6, 134.7, 134.9, 155.9 (*C*-N) ppm. ^{19}F NMR (282 MHz, CDCl3) δ - 59.8 ppm. IR (film): nu(tilde) = 3416 (w), 3364 (m), 3256 (m), 3063 (w), 3030 (m), 2976 (m), 2936 (m), 2916 (m), 2853 (w), 1605 (m), 1595 (m), 1549 (m), 1528 (m), 1495 (m), 1479 (m), 1456 (m), 1429 (m), 1387 (m), 1352 (m), 1335 (m), 1315 (s), 1240 (s), 1221 (m), 1202 (m), 1167 (m), 1148 (m), 1128 (m), 1097 (s), 1074 (m), 1038 (s), 988 (w), 939 (w), 897 (w), 849 (m), 793 (w), 756 (m), 710 (m), 698 (w), 665 (w), 644 (w), 613 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{17}F_3N_2H$ 343.1417; found 343.1417.

2'-Methyl-3-(trifluoromethyl)-3a',4',5',6'-tetrahydrospiro(indene-1,3'-pyrrolo[1,2-b]pyrazole) (5l). **5l** was obtained from azadienone **4l** (0.138 g, 0.45 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O) gave 0.070 g (0.24 mmol, 54%) **5l** as a yellow solid, m.p. 100-101°C. ^{1}H and ^{13}C spectral data are given for main diastereomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.50 (s, 3H, C*H*$_3$), 1.77-1.81 (m, 2H, C*H*$_2$), 1.88-1.94 (m, 2H, C*H*$_2$), 3.31-3.36 (m, 1H, C*H*$_2$), 3.61-3.65 (m, 1H, C*H*$_2$), 3.82-3.84 (m, 1H, C*H*N), 6.79 (q, *J* = 1.7 Hz, 1H, C*H*), 7.31 (dt, *J* = 7.5, 0.9 Hz, 1H, *H*-arom.), 7.36 (dt, *J* = 7.6, 1.2 Hz, 1H, *H*-arom.), 7.46 (dd, *J* = 7.6, 0.6 Hz, 1H, *H*-arom.), 7.58 (d, *J* = 7.5 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.0 (*C*H$_3$), 24.9 (*C*H$_2$), 28.0 (*C*H$_2$), 54.0 (*C*H$_2$N), 71.4 (*C*-spiro), 72.9 (*C*HN), 121.9 (q, *J* = 270.2 Hz, *C*F$_3$), 123.4 (*C*H-arom.), 125.3 (*C*H-arom.), 128.0 (*C*H-arom.), 128.2 (*C*H-arom.), 128.4, 136.3, 136.5 (*C*H), 147.8 (*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.6 (1R, 3a'R; 1S, 3a'S), -60.1 (1R, 3a'S; 1S, 3a'R) ppm, ratio 9:1. IR (KBr): nu(tilde) = 3433 (w), 3069 (m), 2980 (w), 2953 (w), 2943 (m), 2876 (w), 1719 (w), 1626 (m), 1611 (m), 1580 (w), 1543 (w), 1468 (m), 1437 (w), 1381 (m), 1315 (m), 1290 (m), 1271 (m), 1258 (m), 1217 (m), 1177 (s), 1151 (s), 1123 (s), 1007 (m), 978 (m), 955 (w), 941 (w), 907 (w), 880 (w), 847 (w), 777 (m), 758 (m), 700 (w), 660 (w), 642 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2H$ 293.1260; found 293.1258. $C_{22}H_{18}F_3N_5O_7$ (521.40): calcd. C 50.68, H 3.48, N 13.43; found C 50.37, H 3.27, N 13.35 (for picrate).

2'-Methyl-3-(trifluoromethyl)-4',5',6',7'-tetrahydro-3a'H-spiro(indene-1,3'-pyrazolo[1,5-a]pyridine) (5m). Compound **5m** was obtained from azadienone **4m** (0.162 g, 0.50 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O) gave 0.060 g (0.20 mmol, 39%) **5m** as a brown oil. ^{1}H and ^{13}C spectral data are given for main diastereomer. ^{1}H NMR (600 MHz,

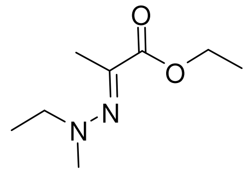
$CDCl_3$) δ 1.19-1.30 (m, 3H, CH_2), 1.49 (s, 3H, CH_3), 1.72-1.80 (m, 3H, CH_2), 2.69 (dt, J = 11.0, 3.2 Hz, 1H, CH_2N), 3.23 (dd, J = 11.7, 2.6 Hz,1H, C*H*N), 3.82-3.85 (m, 1H, CH_2N), 6.91 (q, J = 1.7 Hz, 1H, C*H*), 7.36 (dt, J = 7.4, 1.2 Hz, 1H, *H*-arom.), 7.40 (dt, J = 7.5, 1.3 Hz, 1H, *H*-arom.), 7.42-7.44 (m, 1H, *H*-arom.), 7.49-7.51 (m, 1H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.5 (CH_3), 24.1 (CH_2), 24.8 (CH_2), 25.3 (CH_2), 52.9 (CH_2N), 70.4 (*C*-spiro), 75.7 (*C*HN), 121.1 (*C*H-arom.), 122.0 (q, J = 270.3 Hz, CF_3), 123.2 (*C*H-arom.), 127.2 (*C*H-arom.), 128.3 (*C*H-arom.), 135.4, 135.6 (q, J = 4.9 Hz, *C*H), 135.9, 138.8, 144.7 (*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.5 (1R, 3a'S; 1S, 3a'R), -64.5 (1R, 3a'R; 1S, 3a'S) ppm, ratio 1:4.5. IR (film): nu(tilde) = 3423 (w), 3071 (w), 2941 (m), 2856 (w), 2801 (w), 1736 (w), 1624 (w), 1438 (w), 1380 (m), 1315 (m), 1254 (m), 1230 (m), 1177 (m), 1155 (s), 1126 (s), 1038 (w), 980 (w), 943 (w), 858 (w), 835 (w), 770 (w), 756 (w), 709 (w), 665 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{17}F_3N_2H$ 307.1417; found 307.1405

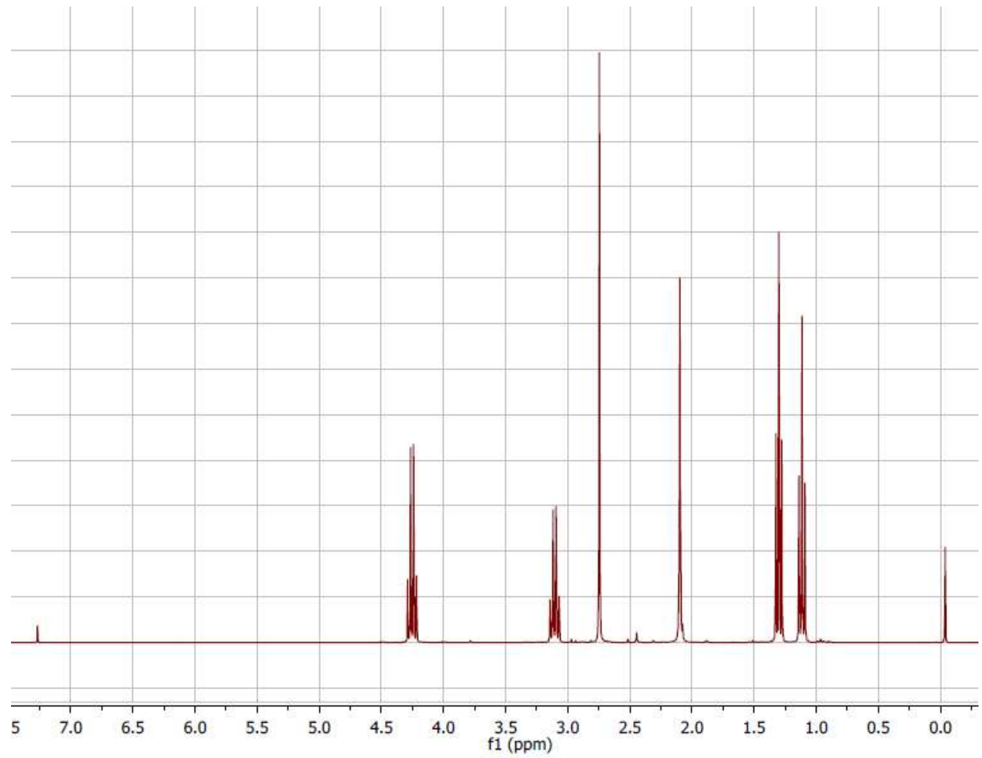
2'-Methyl-3-(trifluoromethyl)-3a',4',5',6',7',8'-hexahydrospiro(indene-1,3'-pyrazolo[1,5-a]azepine) (5n). 5n was obtained from azadienone **4n** (0.210 g, 0.62 mmol) according to the general procedure. The subsequent chromatographic purification (Et_2O) gave 0.143 g (0.45 mmol, 72%) **5n** as a red solid, m.p. 89-90°C. ^{1}H and ^{13}C spectral data are given for main diastereomer. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.25-1.91 (m, 3H, CH_2), 1.42 (s, 3H, CH_3), 1.58-1.89 (m, 5H, CH_2), 2.76-2.82 (m, 1H, C*H*N), 3.51-3.56 (m, 1H, CH_2N), 3.93-3.99 (m, 1H, CH_2N), 6.87 (q, J = 1.7 Hz, 1H, C*H*), 7.28-7.51 (m, 4H, *H*-arom.) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 12.2 (CH_3), 25.6 (CH_2), 25.7 (CH_2), 26.8 (CH_2), 27.3 (CH_2), 56.8 (CH_2N), 72.8 (*C*-spiro), 77.3 (*C*HN), 121.1 (*C*H-arom.), 121.9 (q, J = 270.2 Hz, CF_3), 123.2 (*C*H-arom.), 127.3 (*C*H-arom.), 128.3 (*C*H-arom.), 135.3 (q, J = 34.6 Hz, CCF_3), 136.8 (q, J = 4.9 Hz, *C*H), 138.4, 145.5 (*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.6 (1R, 3a'S; 1S, 3a'R), -64.5 (1R, 3a'R; 1S, 3a'S) ppm, ratio 1:2.2. IR (KBr): nu(tilde) = 3433 (w), 3067 (w), 2932 (s), 2858 (m), 2820 (m), 2720 (w), 2694 (w), 1773 (w), 1618 (m), 1580 (w), 1543 (w), 1466 (m), 1458 (m), 1435 (m), 1381 (s), 1315 (m), 1296 (m), 1263 (s), 1227 (s), 1177 (s), 1134 (s), 1049 (m), 1018 (m), 997 (m), 972 (m), 959 (m), 947 (m), 872 (w), 814 (m), 804 (m), 773 (m), 758 (m), 712 (w), 660 (w), 638 (w), 604 (w), 569 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{19}F_3N_2H$ 321.1573; found 321.1576. $C_{24}H_{22}F_3N_5O_7$ (549.46): calcd. C 52.46, H 4.04, N 12.75; found C 52.32, H 3.80, N 12.71 (for picrate).

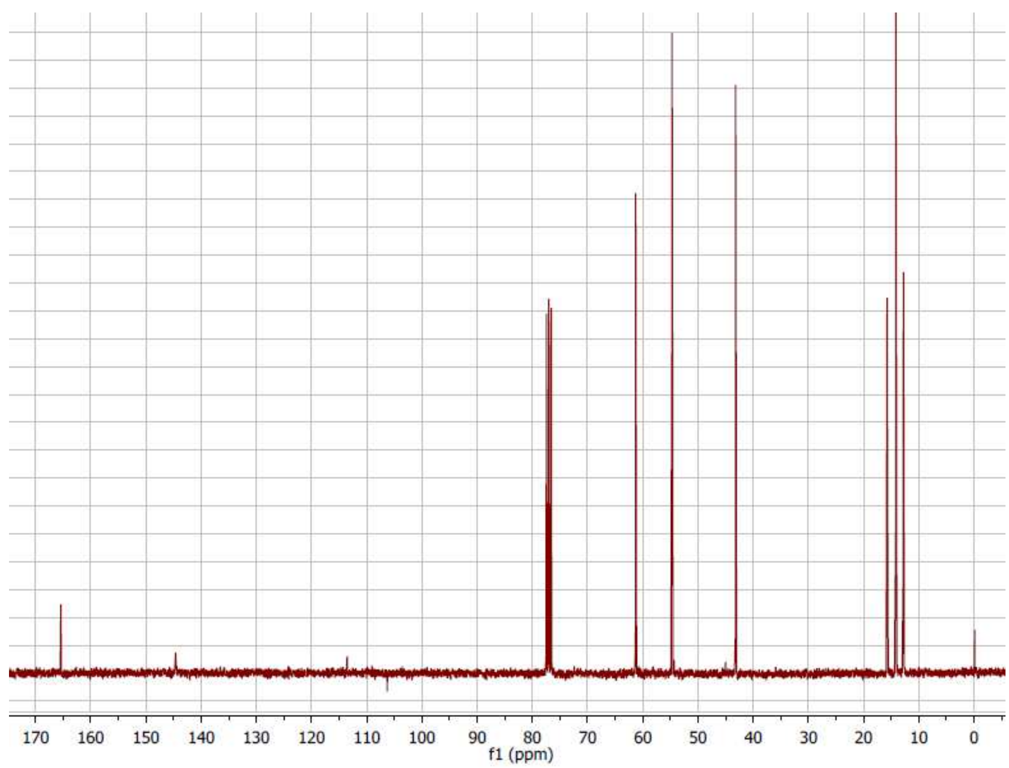
2'-Methyl-3-(trifluoromethyl)-3a',4',6',7'-tetrahydrospiro(indene-1,3'-pyrazolo[5,1-c][1,4]oxazine) (5o). Compound **5o** was obtained from azadienone **4o** (0.163 g, 0.50 mmol) according to the general procedure. The subsequent chromatographic purification (pentane/Et_2O, 2:1) gave 0.080 g (0.26 mmol, 52%) **5o** as a red solid, m.p. 135-136°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51 (s, 3H, C*H*$_3$), 3.22 (dt, *J* = 11.8, 3.6 Hz, 1H, C*H*$_2$N), 3.50-3.53 (m, 1H, C*H*$_2$), 3.65-3.69 (m, 3H, C*H*N, CH_2), 3.74 (dt, *J* = 11.5, 2.8 Hz, 1H, C*H*$_2$), 3.88-3.91 (m, 1H, C*H*$_2$), 6.82 (q, *J* = 1.7 Hz, 1H, C*H*), 7.37 (dt, *J* = 7.4, 1.2 Hz, 1H, *H*-arom.), 7.41 (dt, *J* = 7.5, 1.3 Hz, 1H, *H*-arom.), 7.47-7.51 (m, 1H, *H*-arom.), 7.54 (ddd, *J* = 7.4, 1.2, 0.75 Hz, 1H, *H*-arom.) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.1 (*C*H$_3$), 51.6 (*C*H$_2$), 65.7 (*C*H$_2$), 66.1 (*C*H$_2$), 69.2 (*C*-spiro), 71.0 (*C*HN), 121.1 (*C*H-arom.), 121.8 (q, *J* = 270.4 Hz, *C*F$_3$), 123.3 (*C*H-arom.), 125.0, 127.2, 128.6 (*C*H-arom.), 133.6 (q, *J* = 4.9 Hz, *C*H), 136.8 (d, J = 34.7 Hz, *C*CF$_3$), 144.4 (*C*=N) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.64 (1R, 3a'S; 1S, 3a'R), -64.67 (1R, 3a'R; 1S, 3a'S), ppm, ratio 1:6. IR (KBr): nu(tilde) = 3437 (w), 3063 (w), 2991 (w), 2968 (w), 2912 (m), 2862 (m), 2835 (m), 1719 (w), 1620 (w), 1601 (w), 1580 (w), 1462 (m), 1435 (w), 1379 (s), 1350 (w), 1317 (m), 1302 (m), 1252 (m), 1225 (m), 1178 (s), 1151 (s), 1123 (s), 1097 (s), 1051 (m), 955 (m), 914 (w), 881 (m), 841 (m), 820 (w), 775 (m), 746 (m), 721 (m), 679 (w), 662 (w), 636 (w), 604 (w) cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}F_3N_2OH$ 309.1209; found 309.1208. $C_{16}H_{15}F_3N_2O$ (308.30): calcd. C 62.33, H 4.90, N 9.09; found C 62.59, H 4.94, N 9.17.

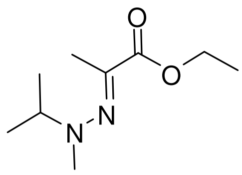
X-ray crystal structure analysis of **5o**:[2] formula $C_{16}H_{15}F_3N_2$, M = 308.30, light yellow crystal 0.45 x 0.15 x 0.05 mm, a = 7.026(1), b = 16.043(5), c = 26.047(4)Å, V = 2936.0(11) Å^3, ρ_{calc} = 1.395 g cm^{-3}, μ= 0.979 mm^{-1}, empirical absorption correction (0.667 ≤ T ≤ 0.953), Z = 8, orthorhombic, space group *P*bca (No. 61), λ= 1.54178 Å, T = 223(2) K, $\omega/2\theta$ scans, 3489 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.62 Å^{-1}, 2986 independent (R_{int} = 0.036) and 1786 observed reflections [$I \geq 2\ \sigma(I)$], 201 refined parameters, R = 0.058, wR^2 = 0.181, max. (min.) residual electron density 0.35 (-0.11) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

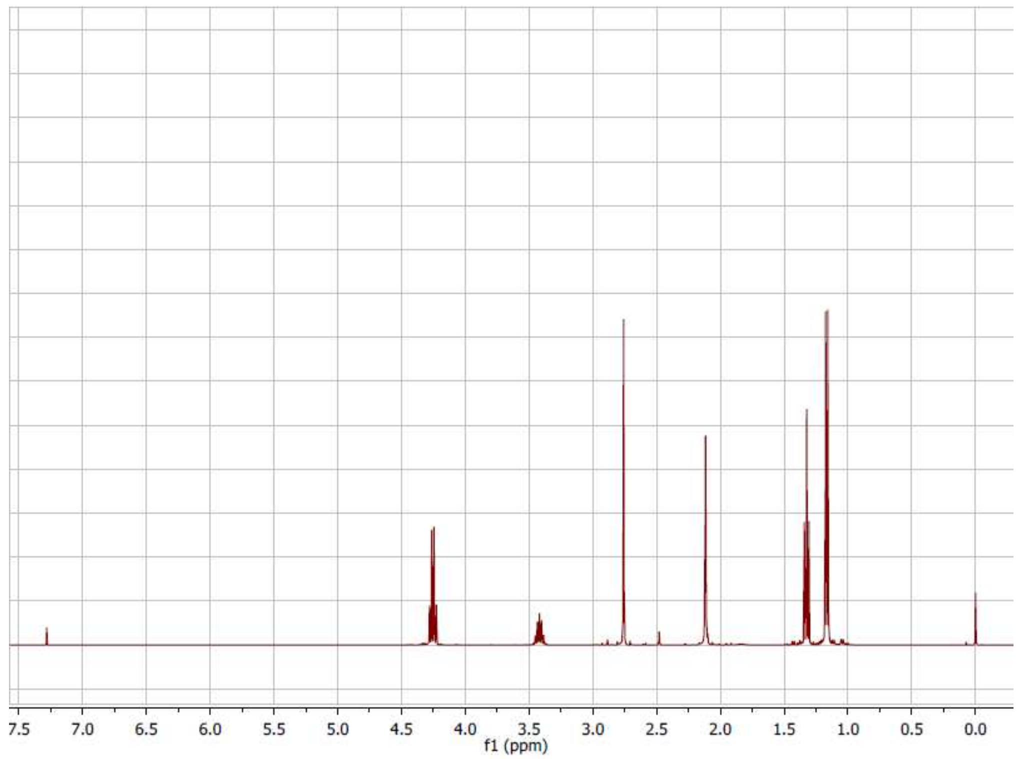
^{1}H and ^{13}C spectra for the new compounds

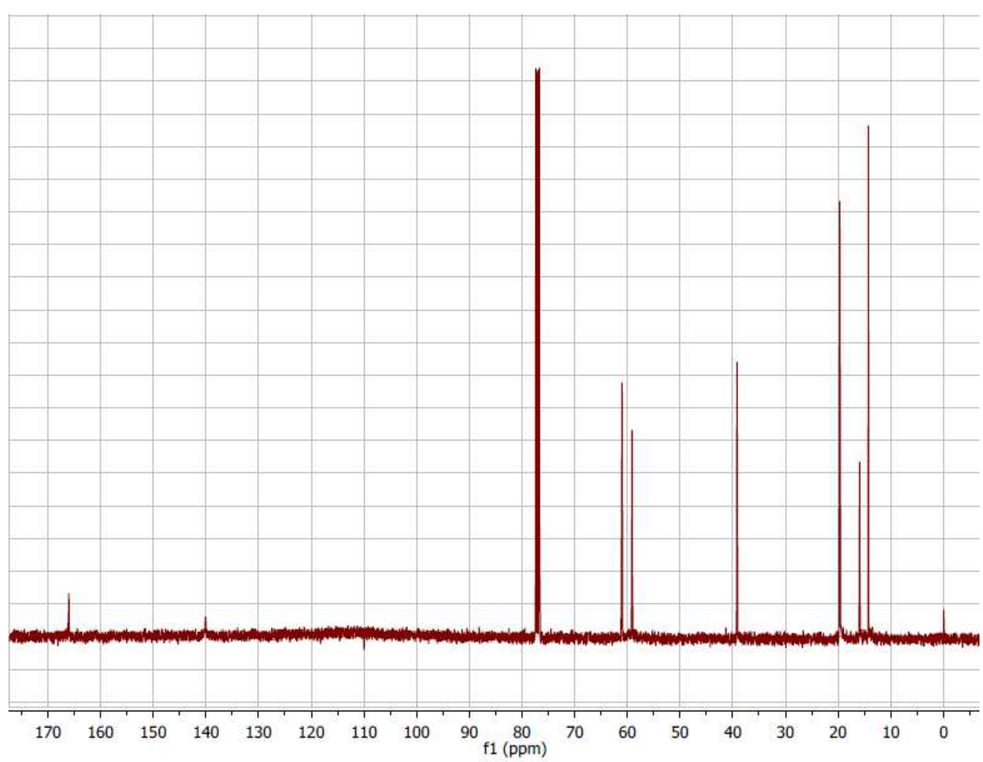
^{1}H and ^{13}C Spectra of  **2b**

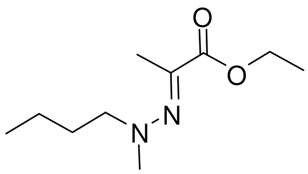




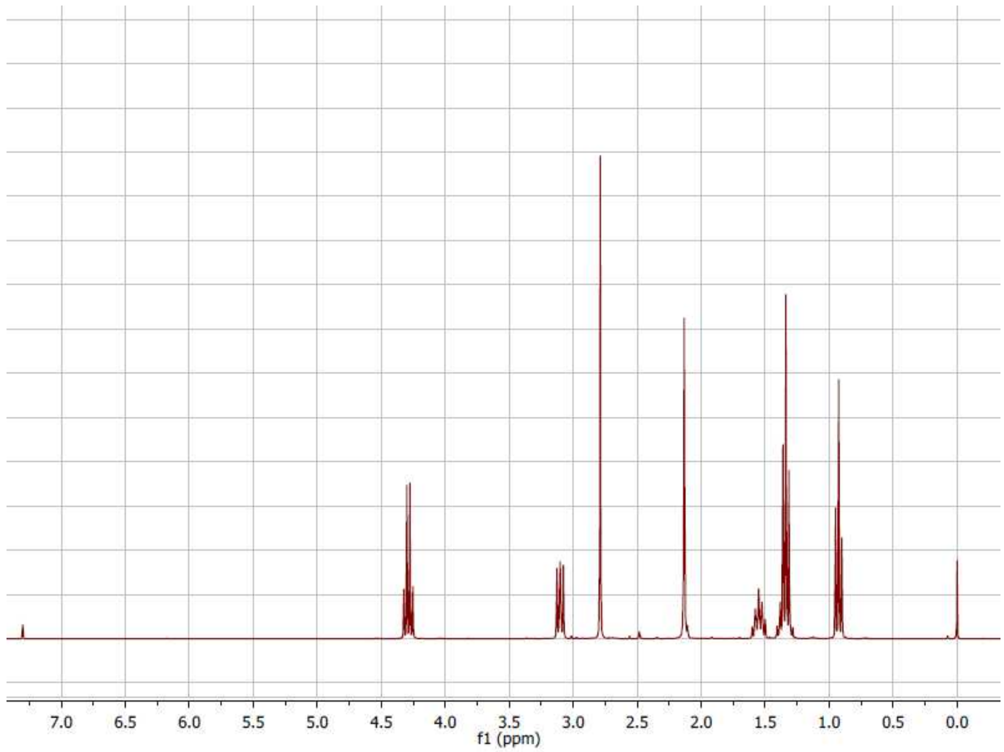
^{1}H and ^{13}C Spectra of  **2c**

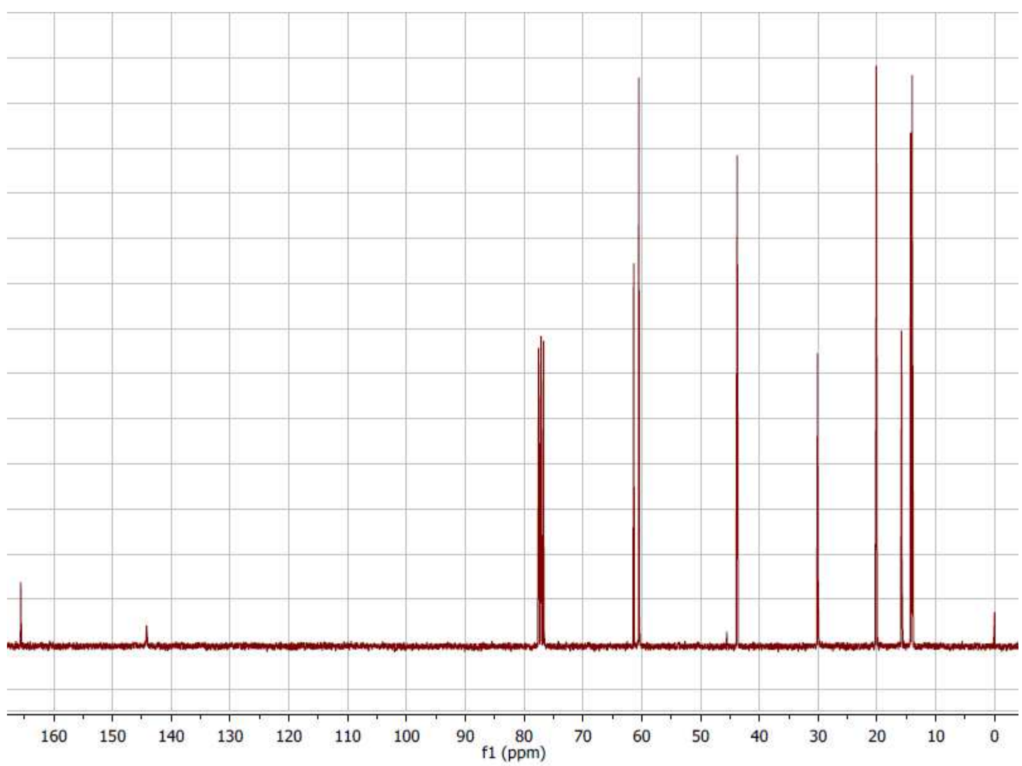


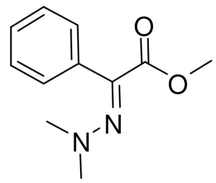


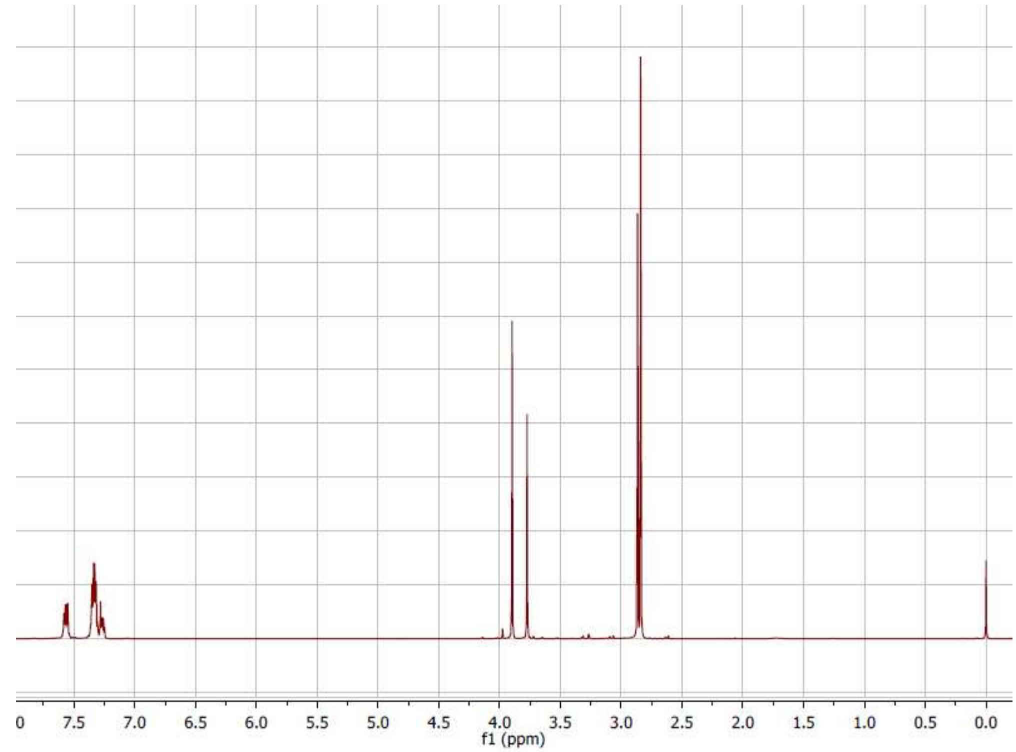
[1]H and [13]C Spectra of 

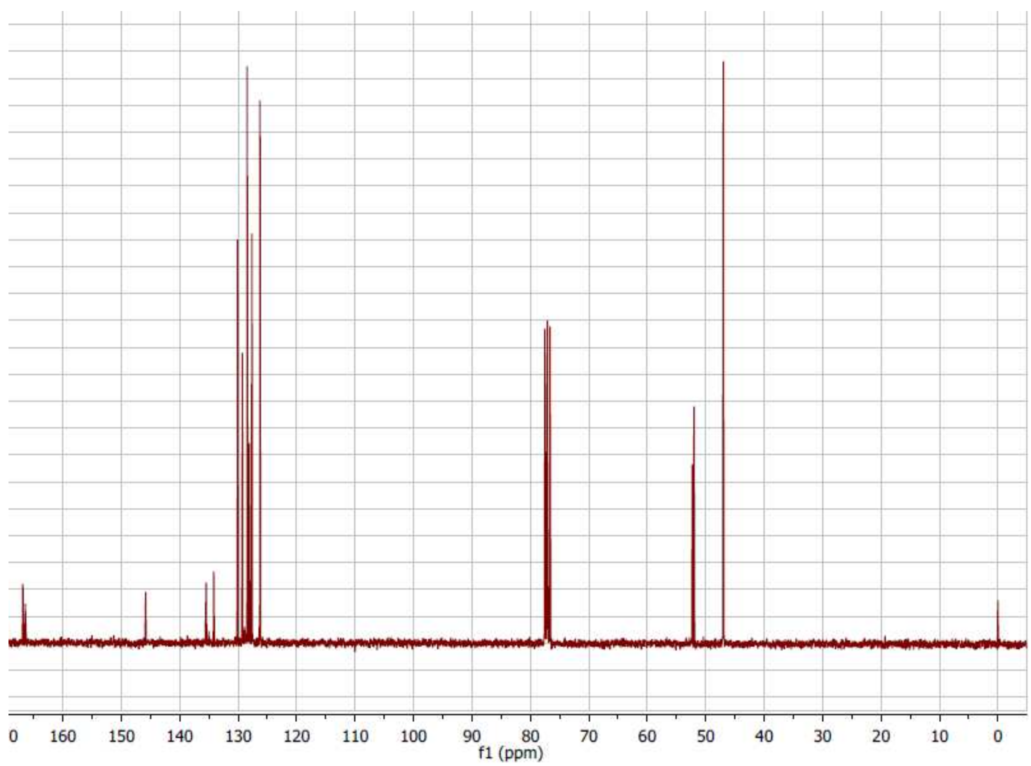
2d

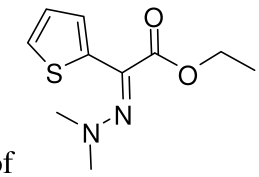


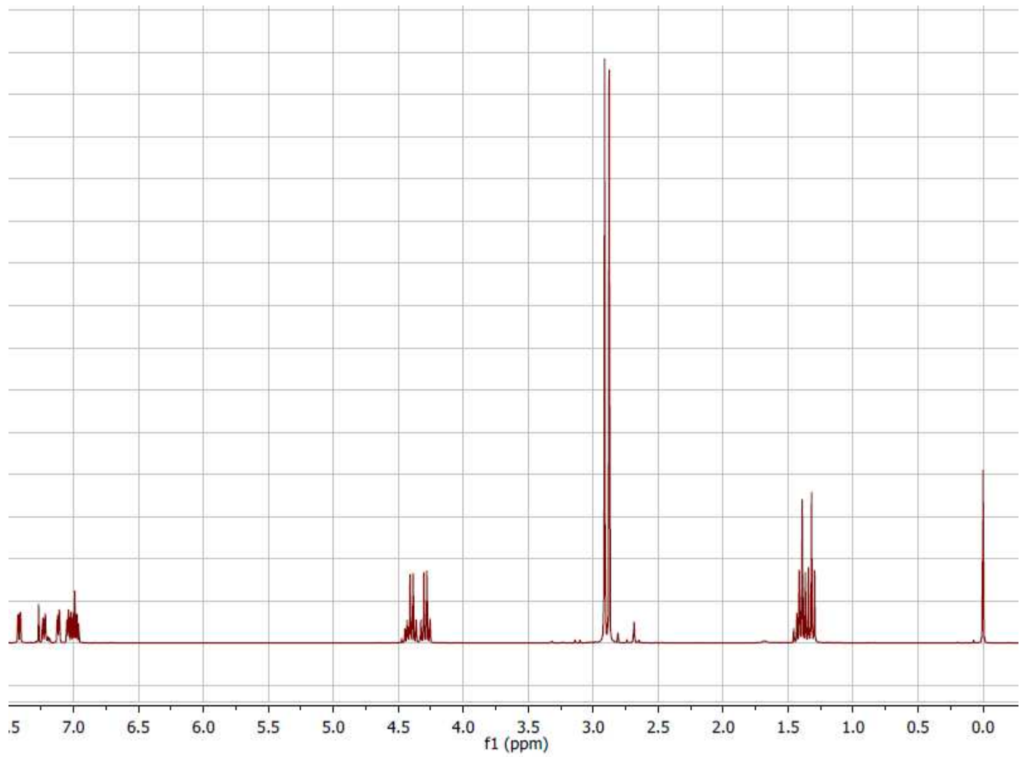


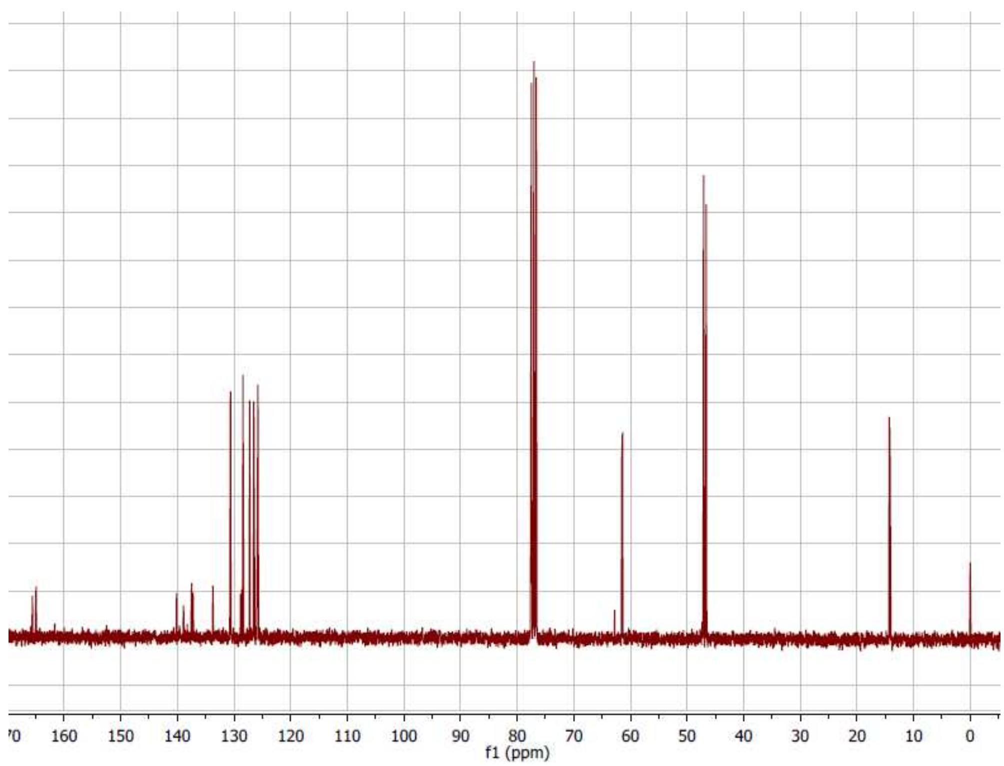
^{1}H and ^{13}C Spectra of  **2e**

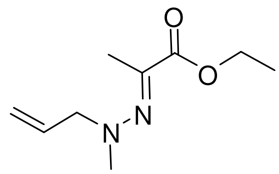


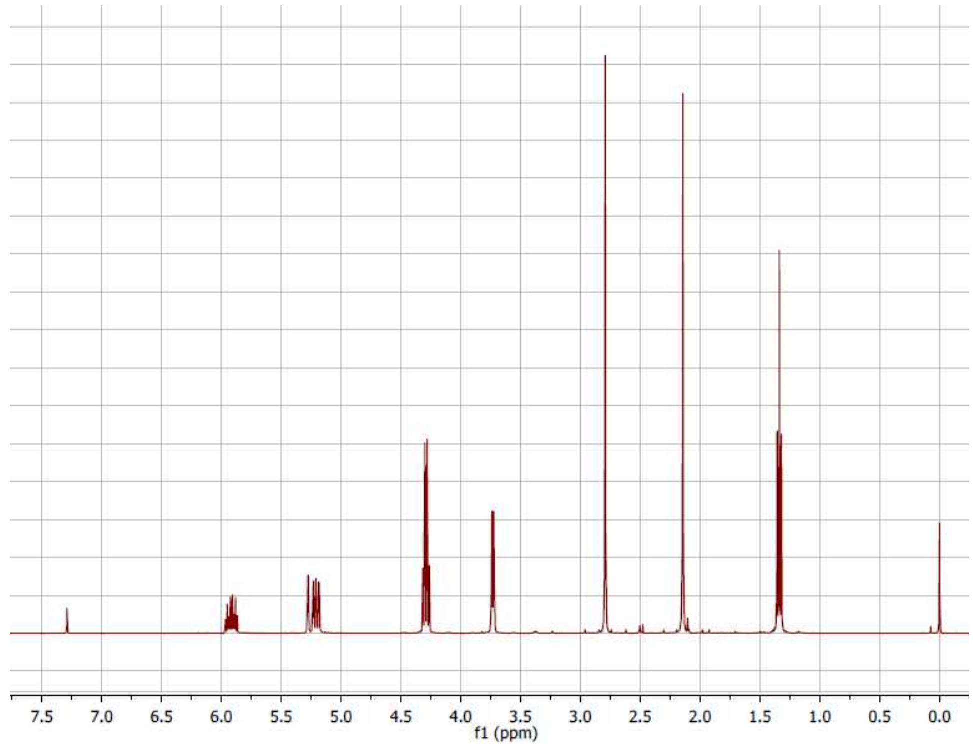


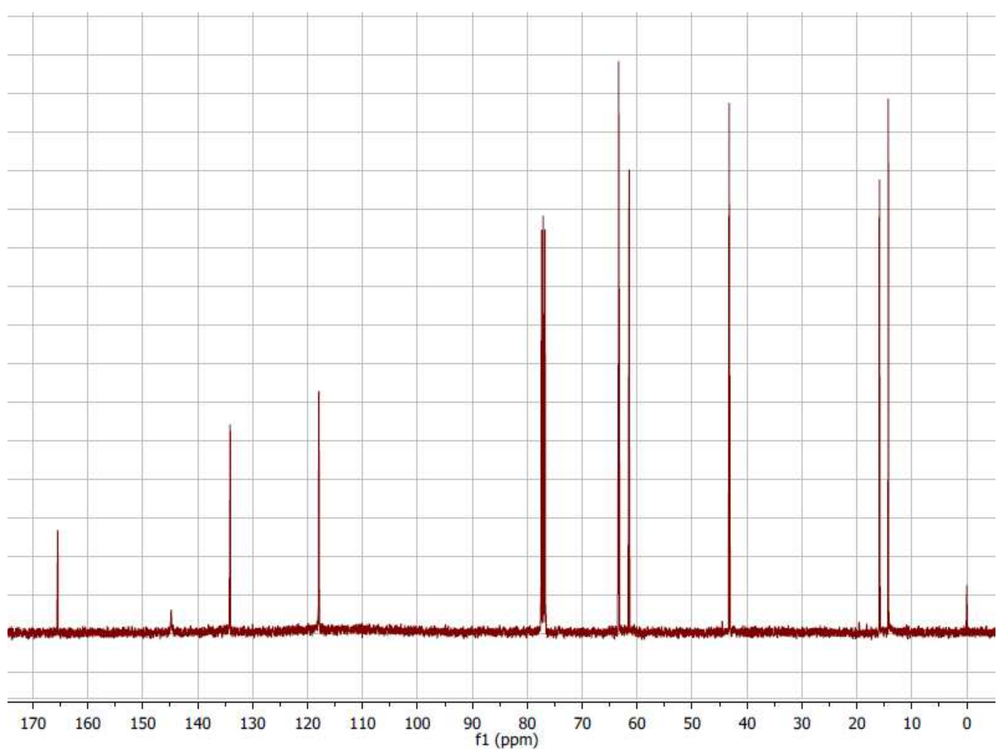
^{1}H and ^{13}C Spectra of  **2f**

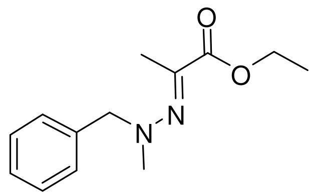


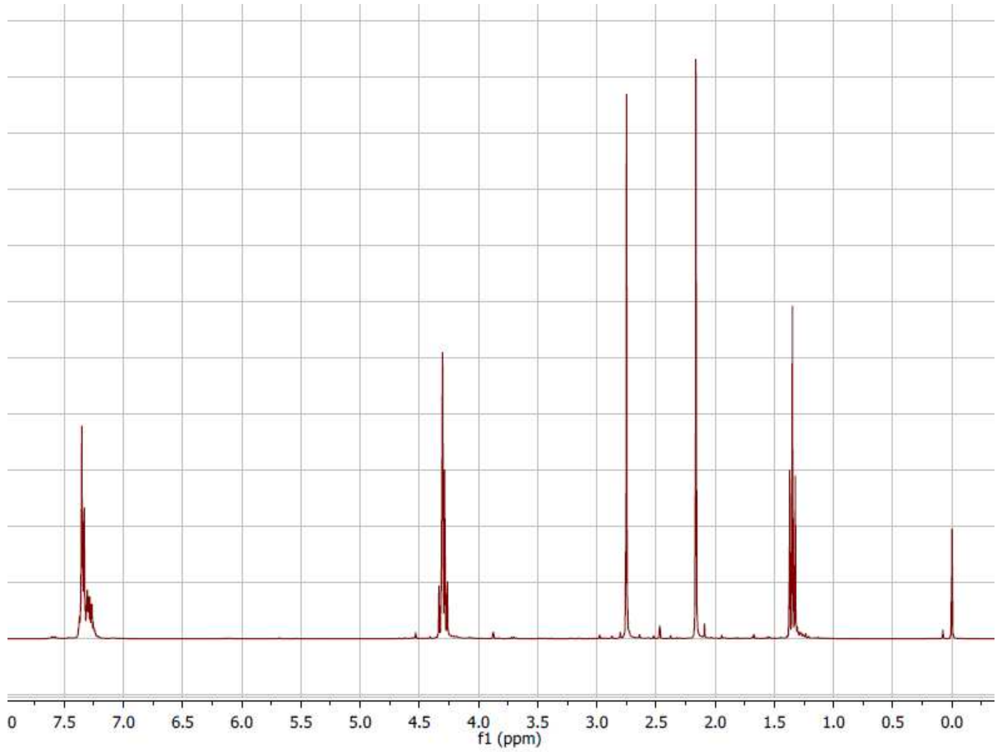


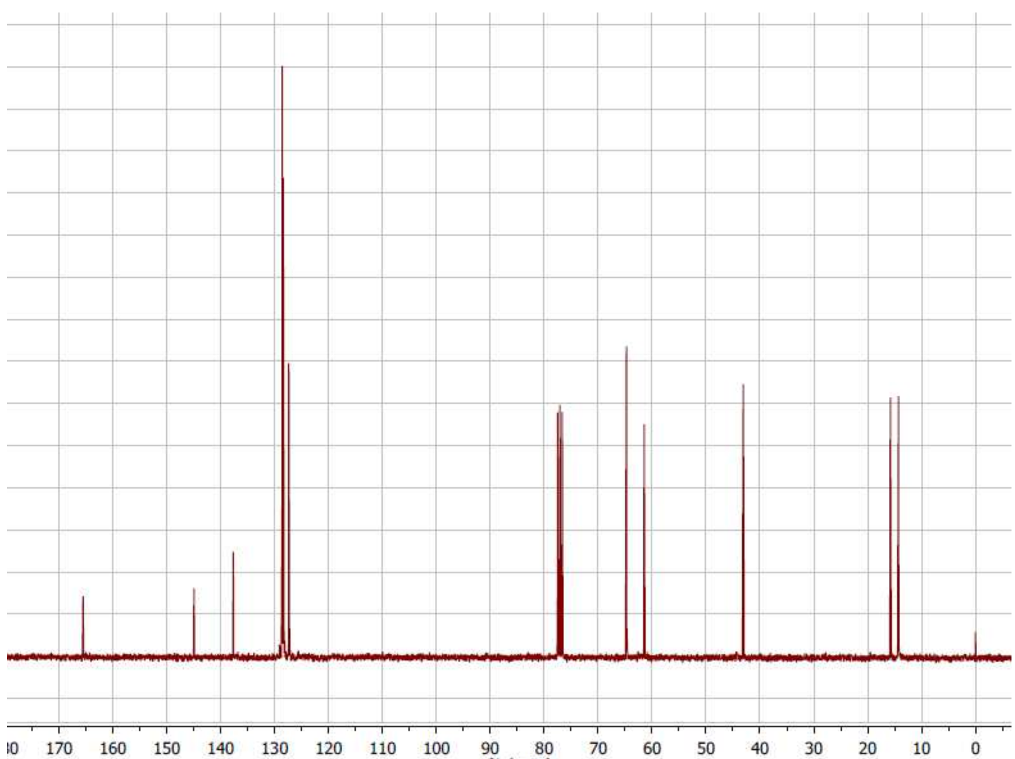
^{1}H and ^{13}C Spectra of  **2g**

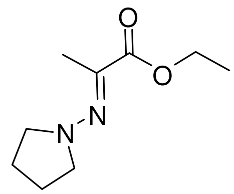


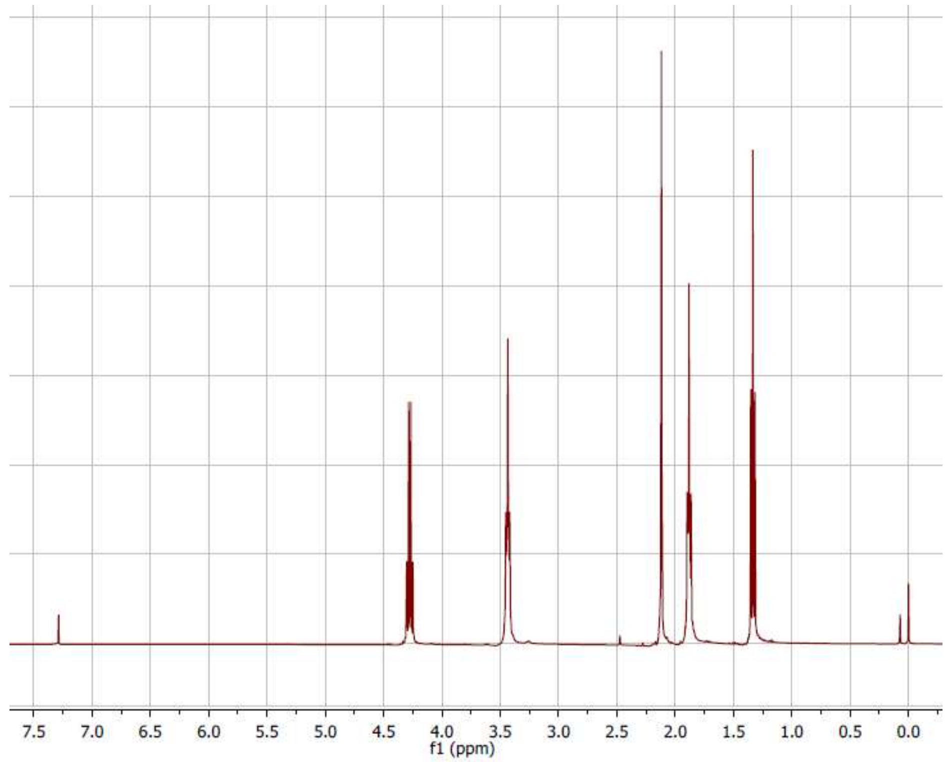


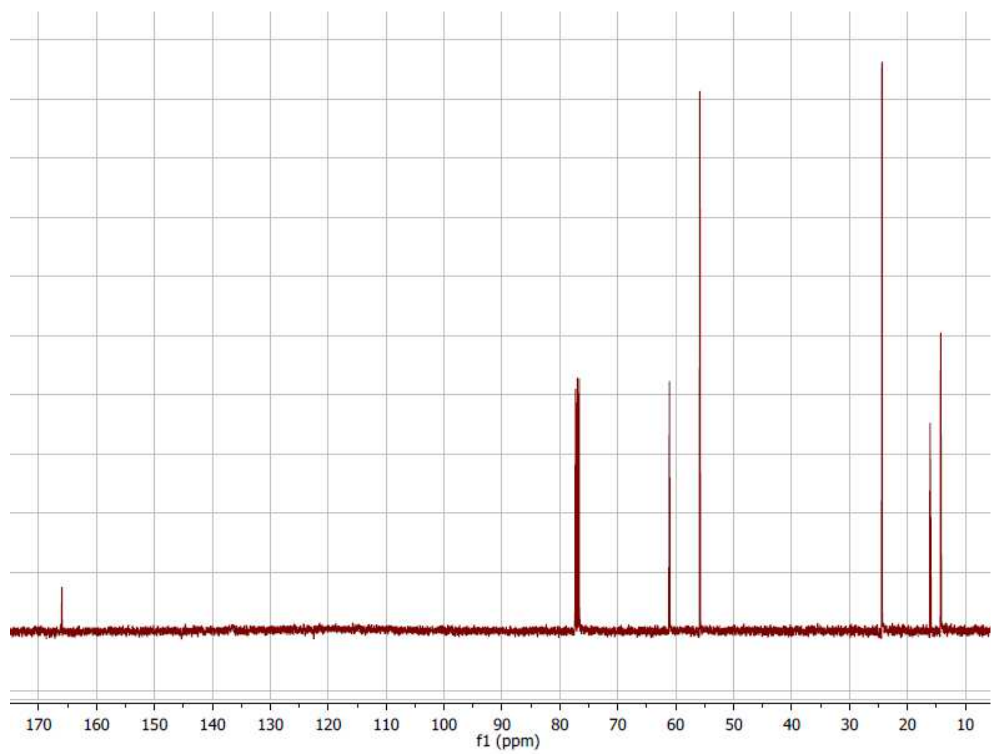
^{1}H and ^{13}C Spectra of  **2h**

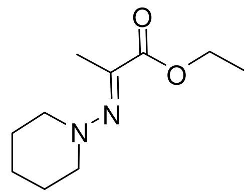




[1]H and [13]C Spectra of  **2i**





^{1}H and ^{13}C Spectra of 

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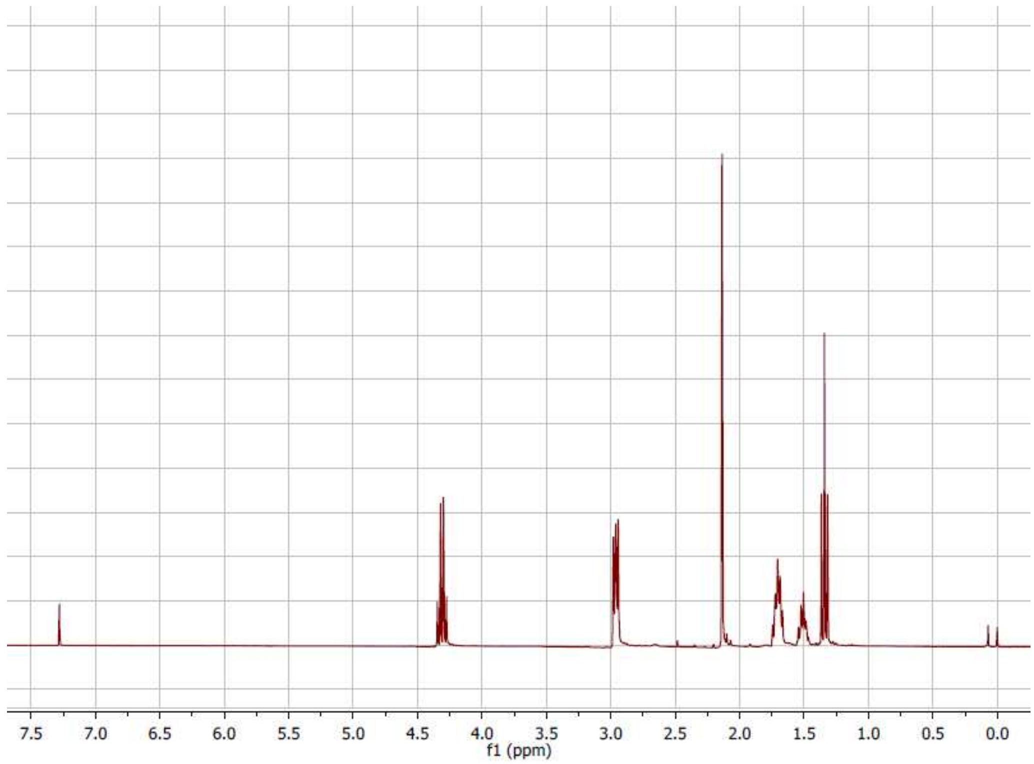
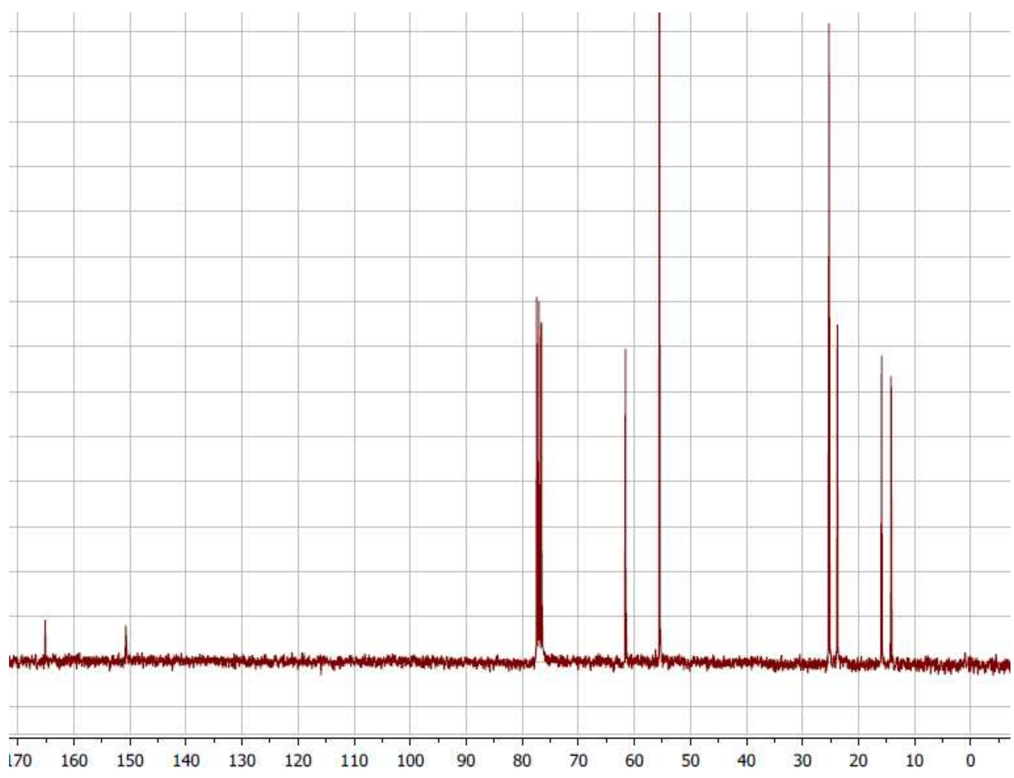
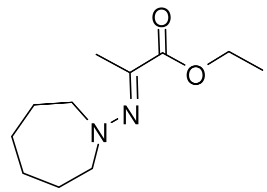
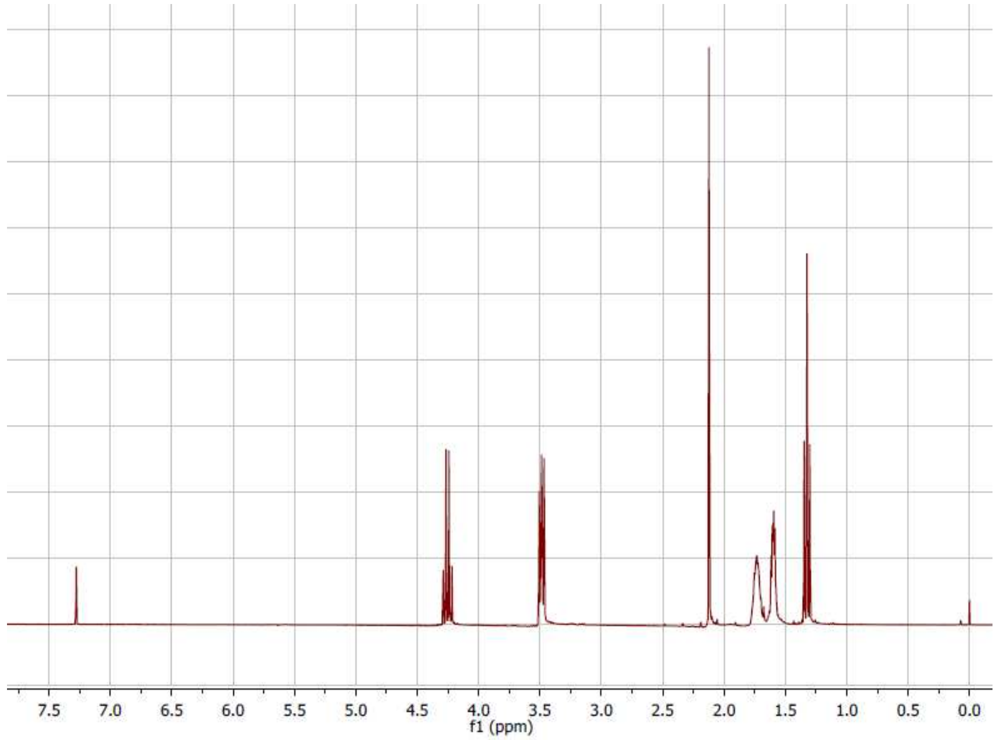
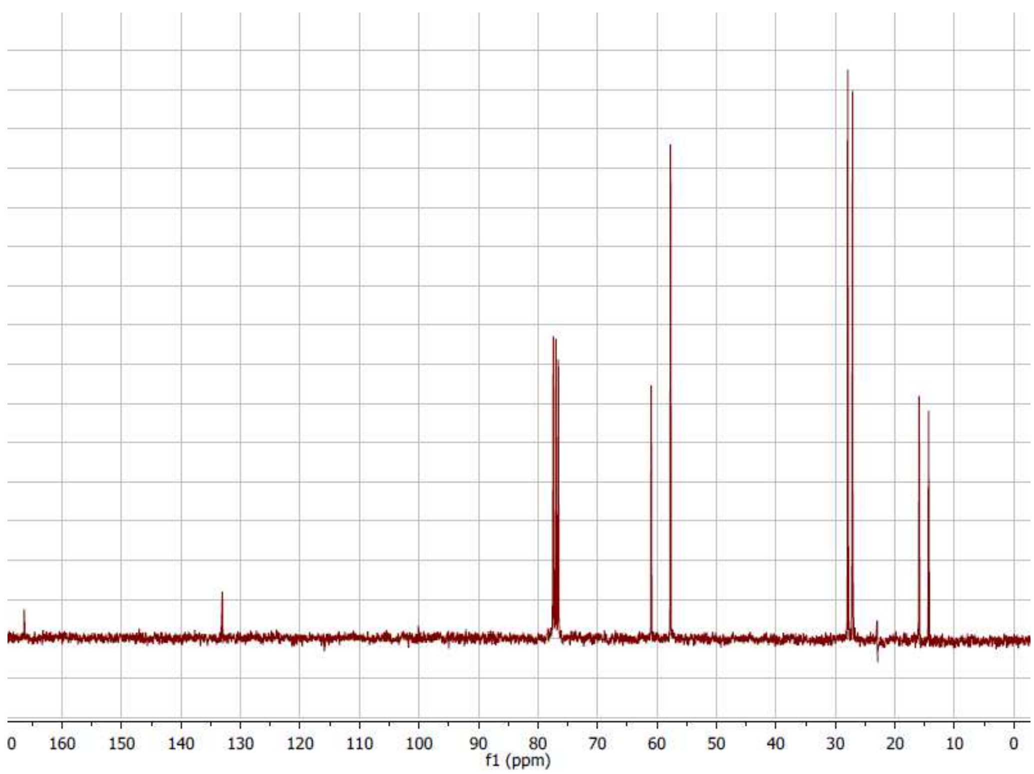
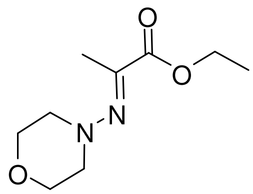


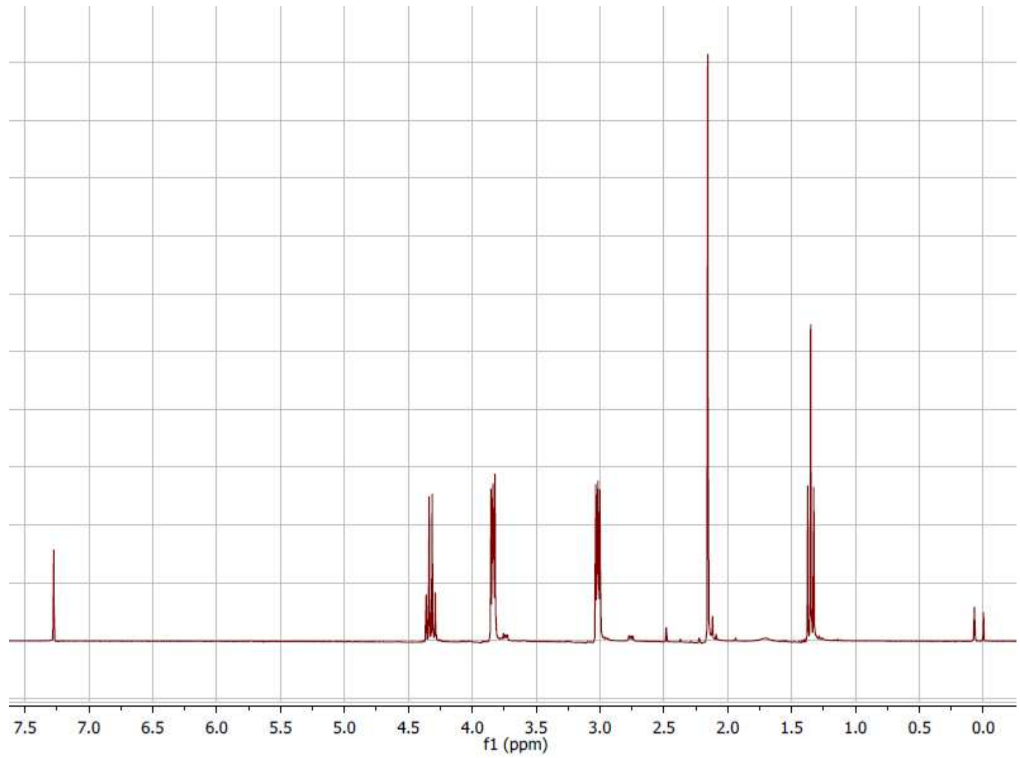


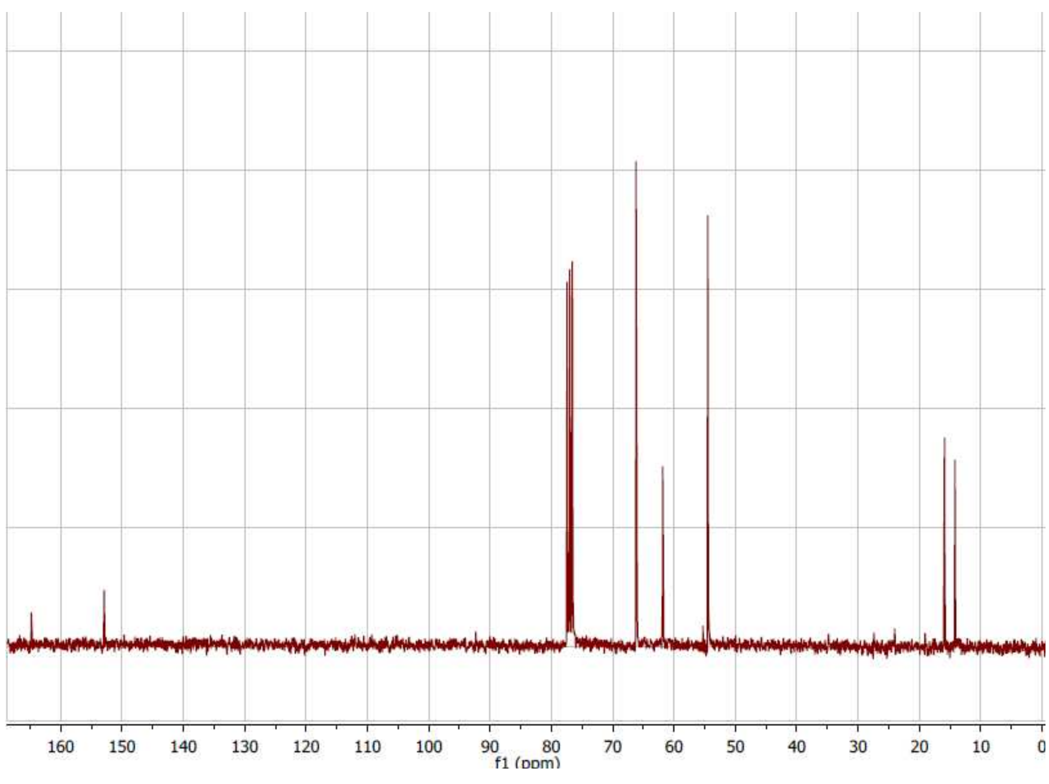
[1]H and [13]C Spectra of  **2k**

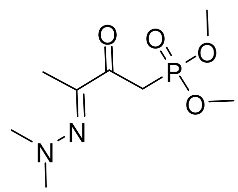


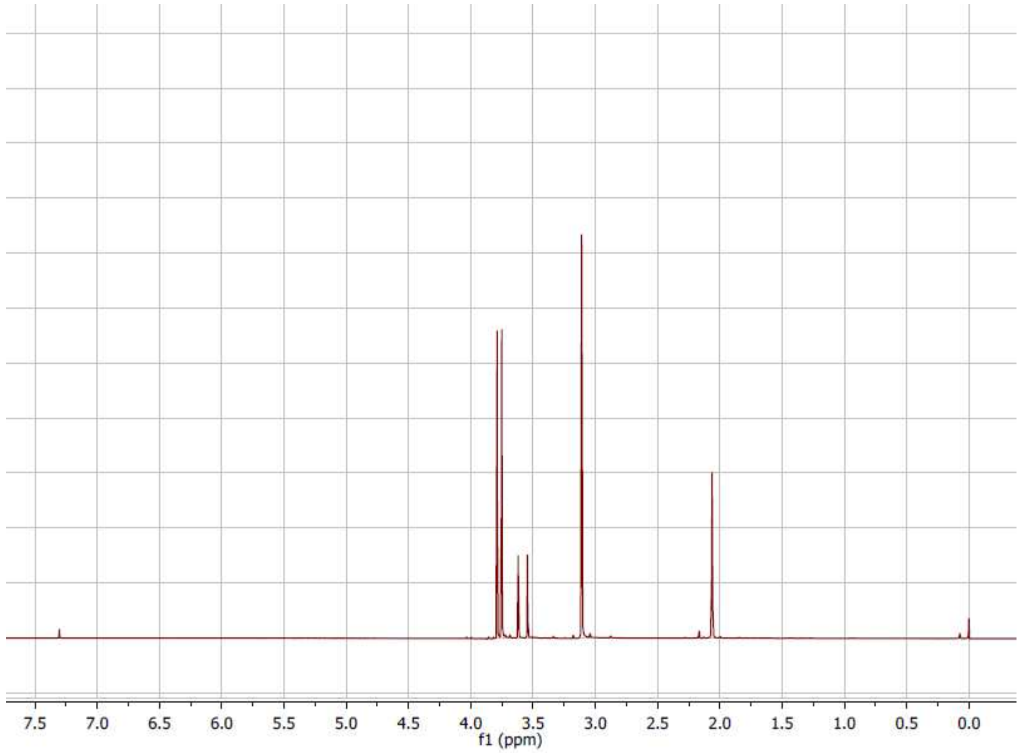


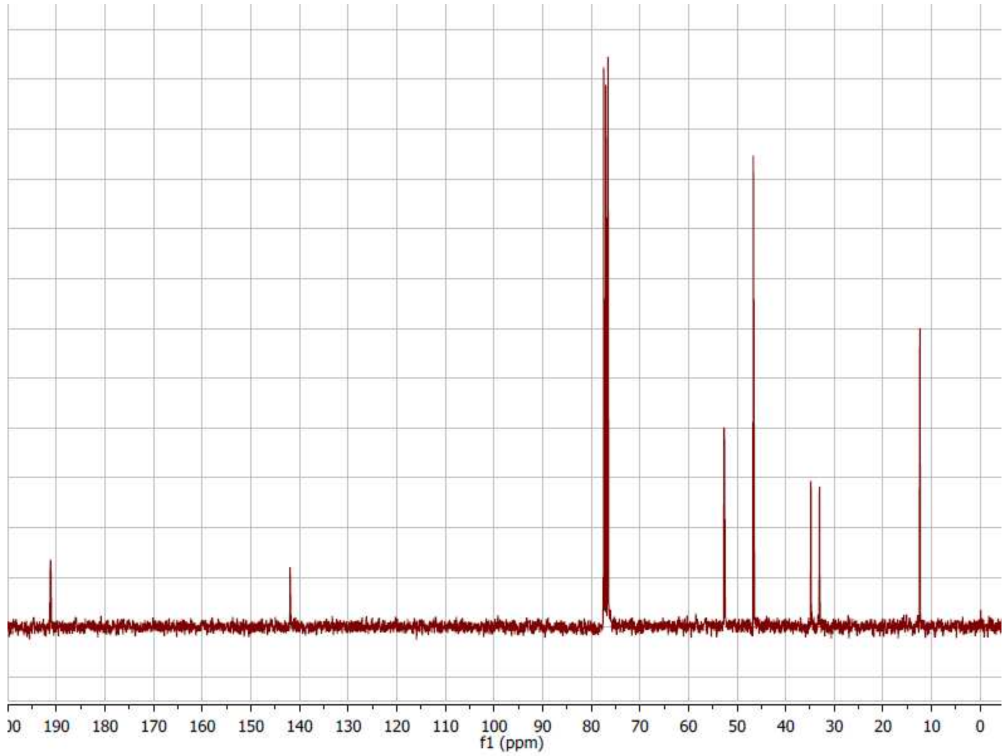
^{1}H and ^{13}C Spectra of  **2l**

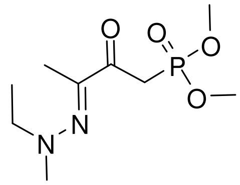


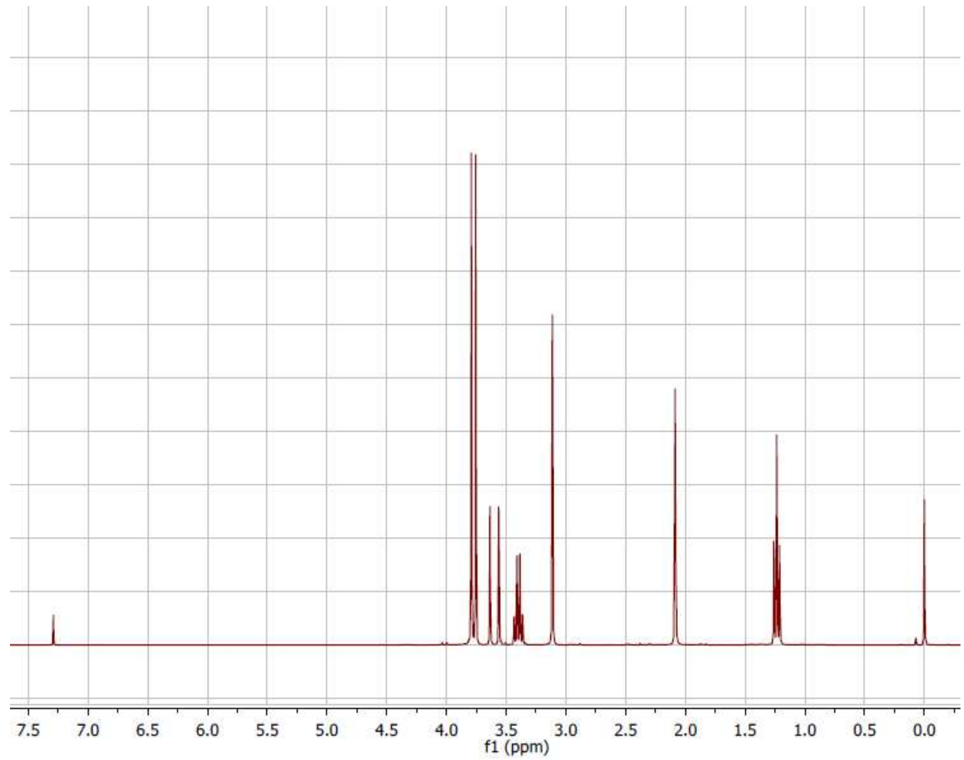


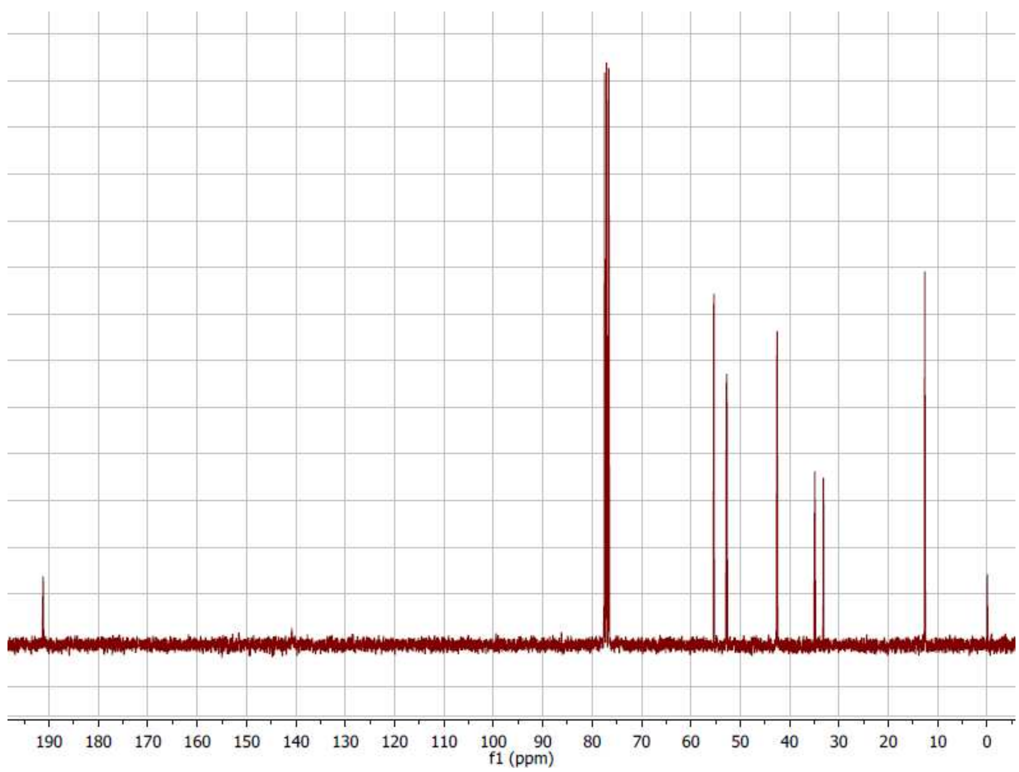
^{1}H and ^{13}C Spectra of  **3a**

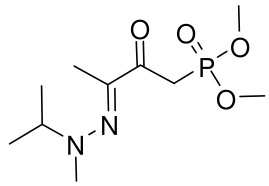


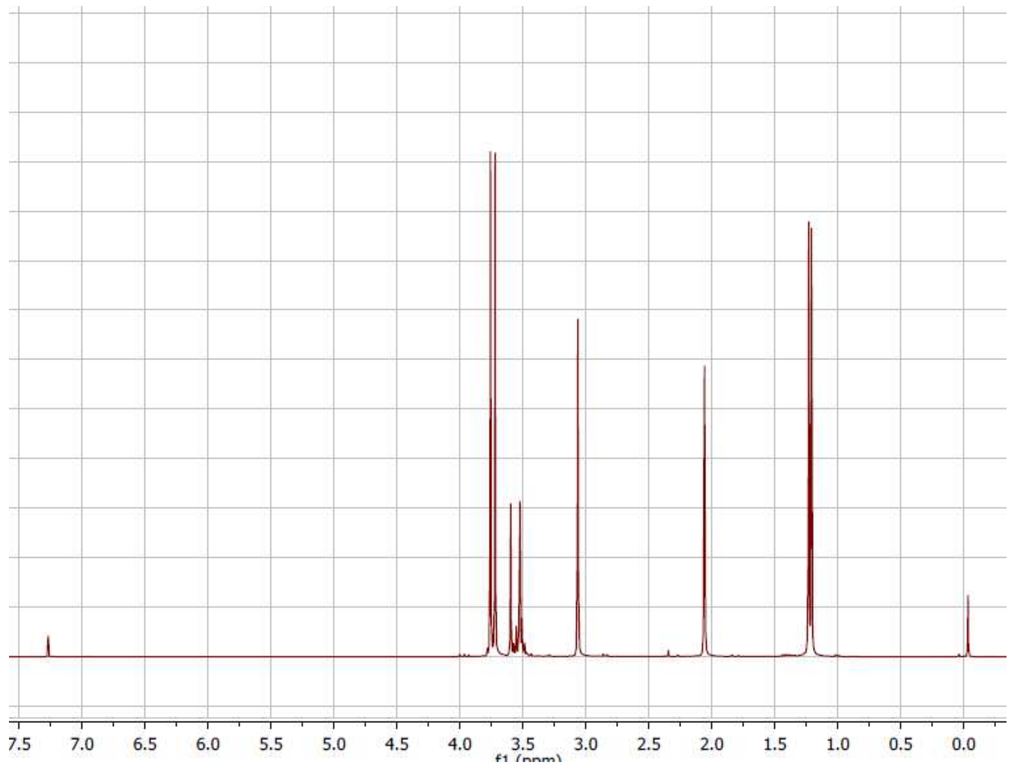


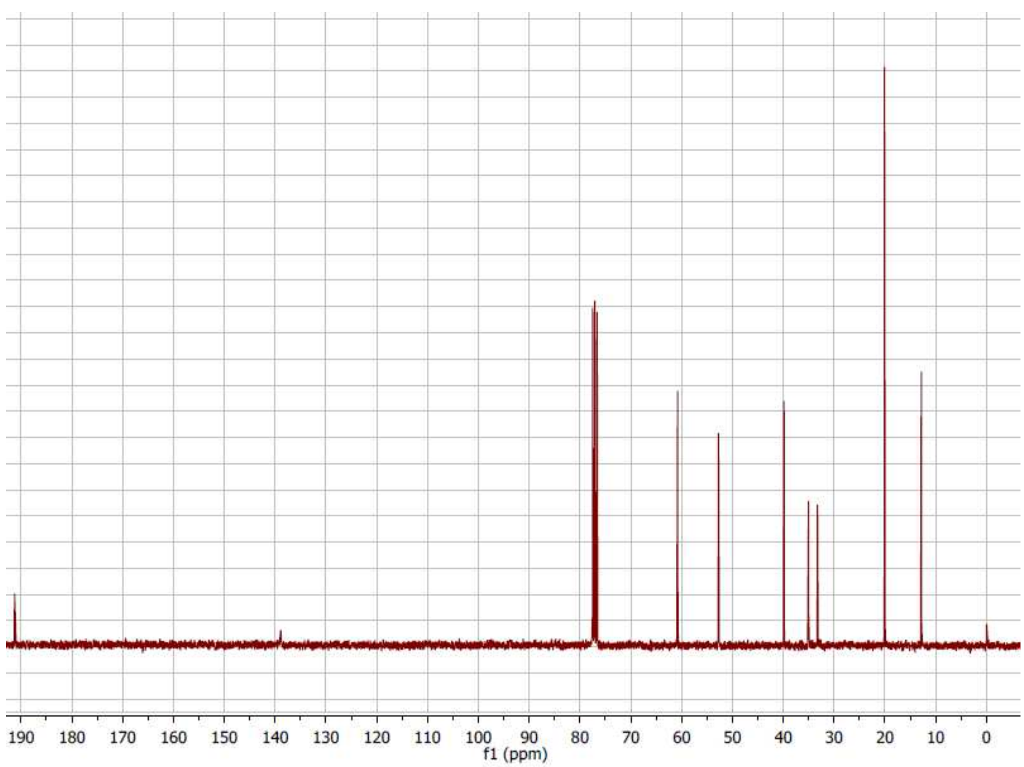
^{1}H and ^{13}C Spectra of  **3b**

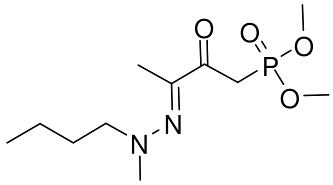


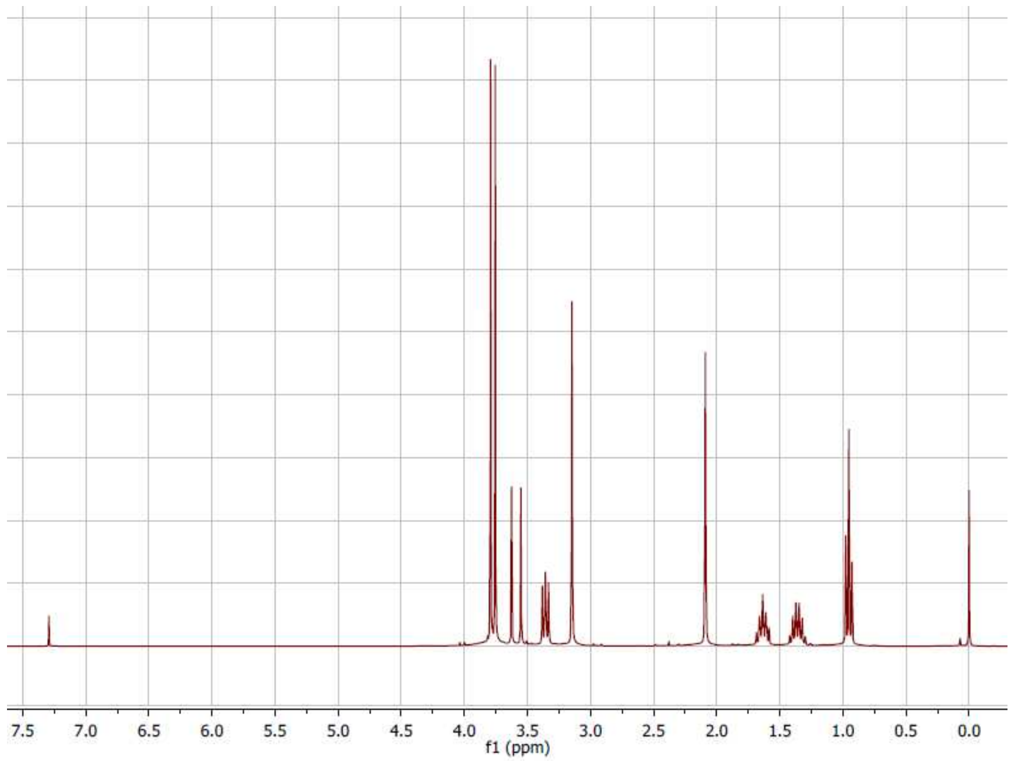


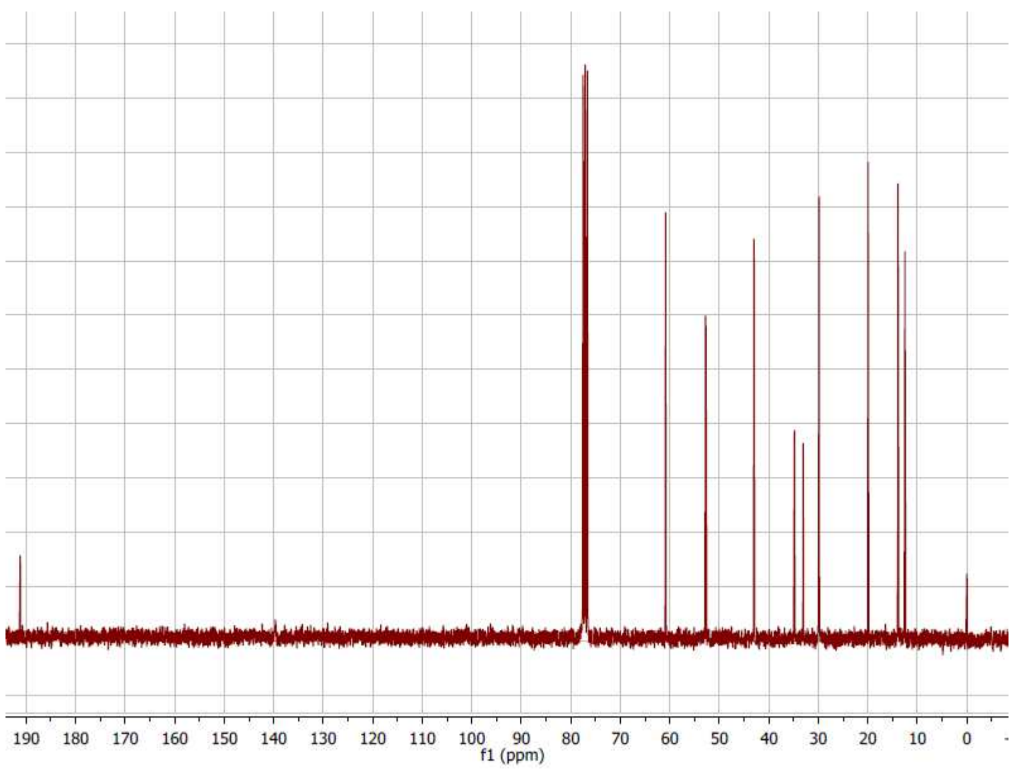
[1]H and [13]C Spectra of  **3c**

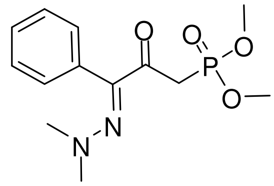


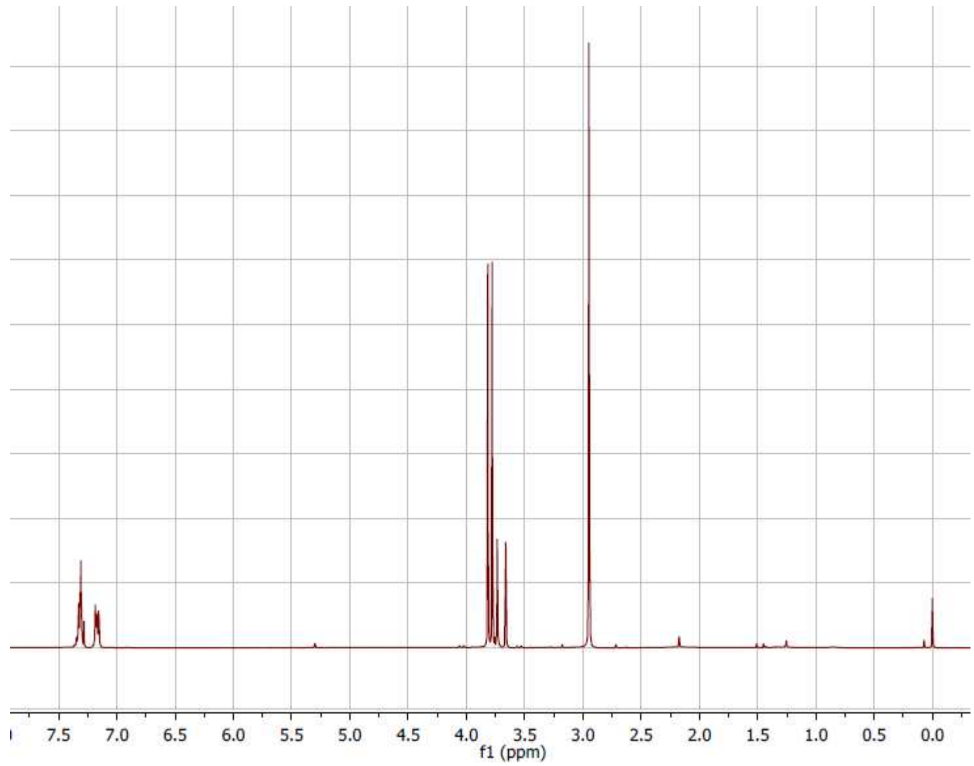


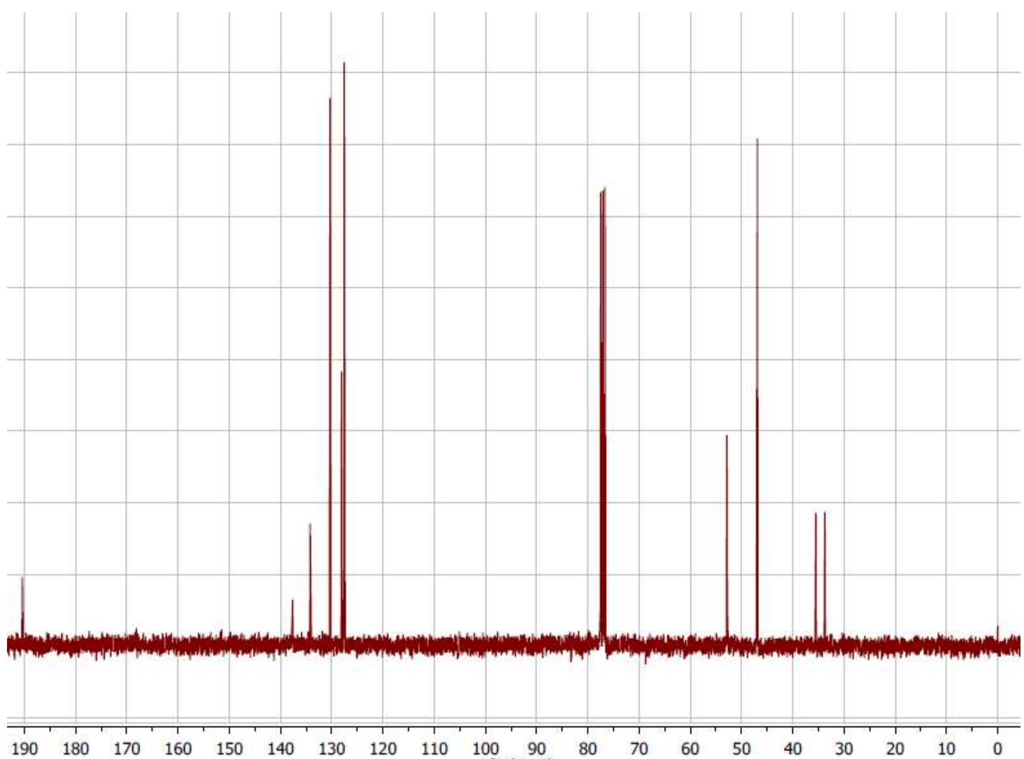
[1]H and [13]C Spectra of  **3d**

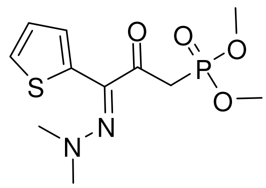


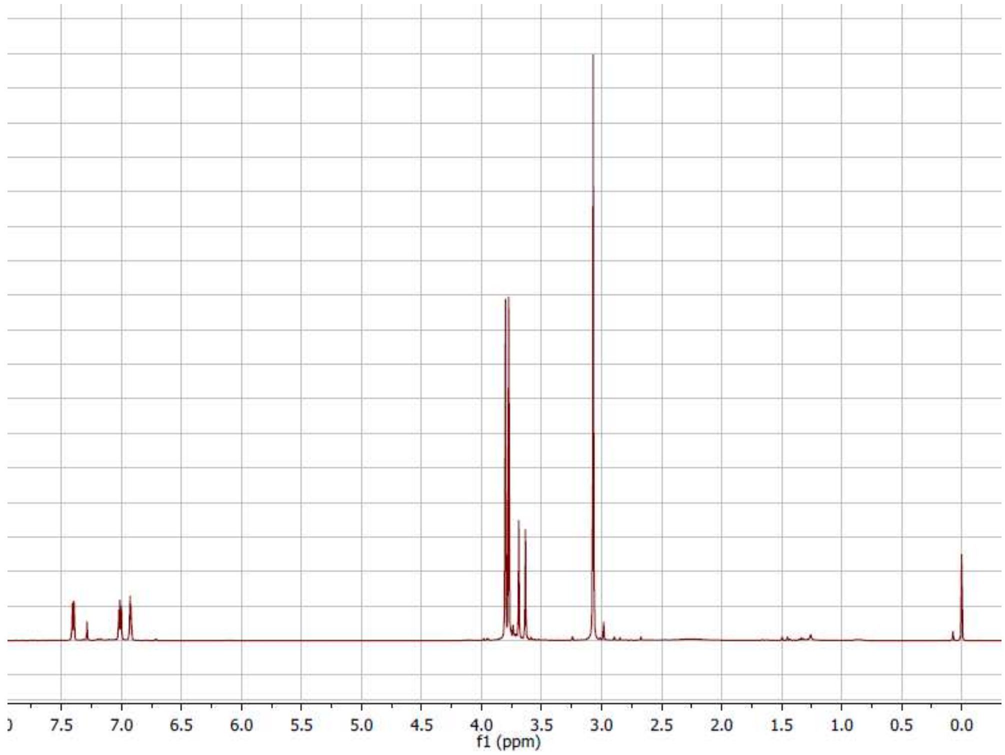


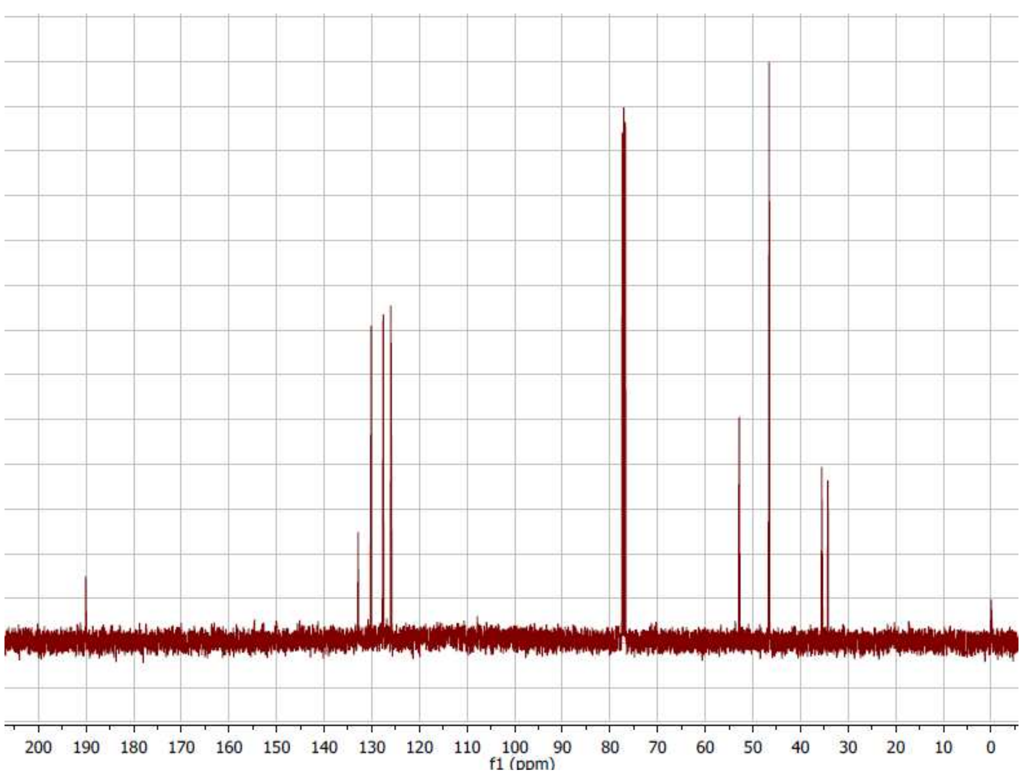
^{1}H and ^{13}C Spectra of  **3e**

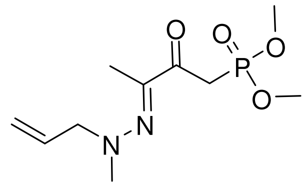


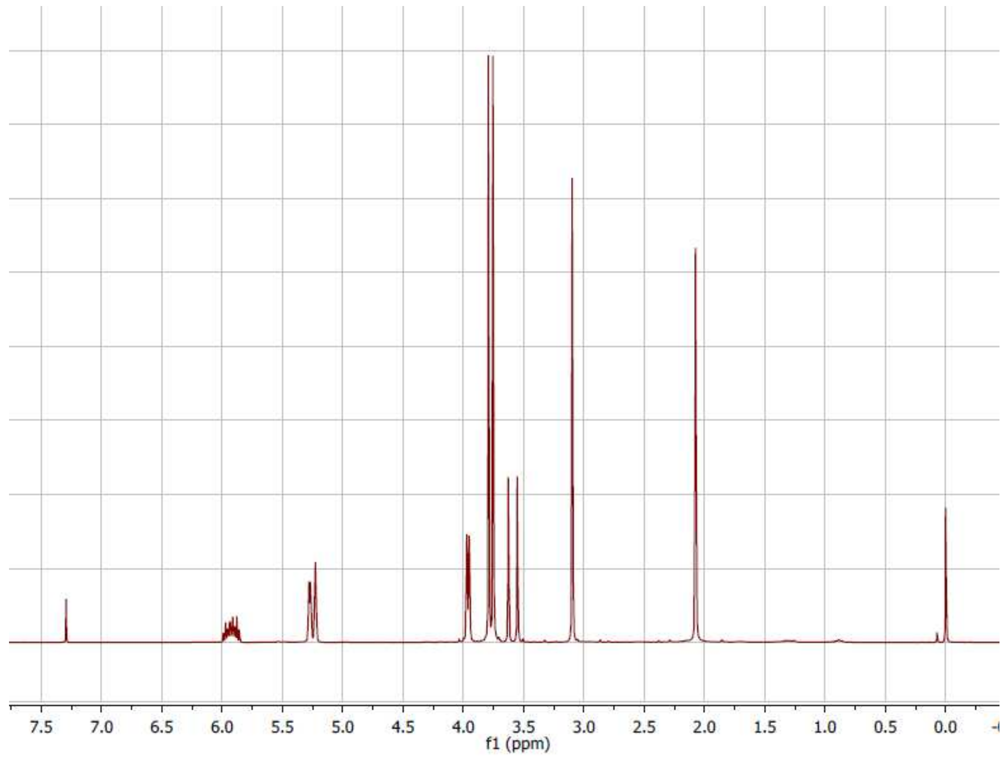


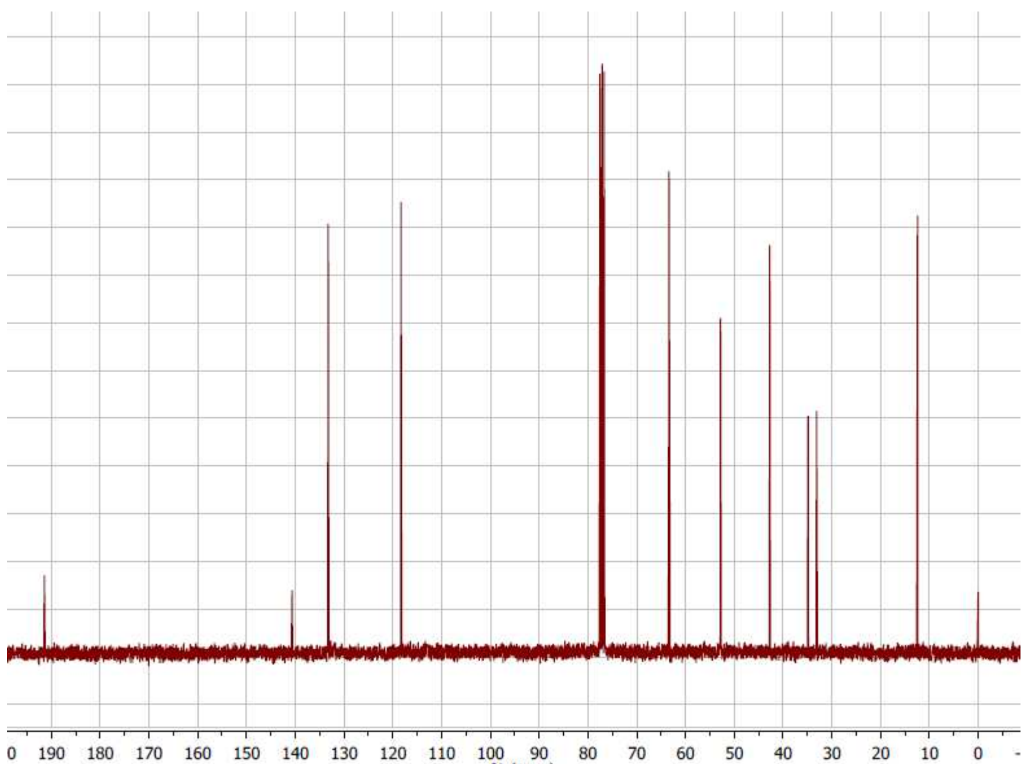
[1]H and [13]C Spectra of  **3f**

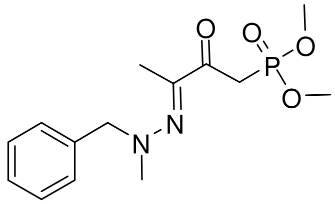




[1]H and [13]C Spectra of  **3g**





^{1}H and ^{13}C Spectra of 

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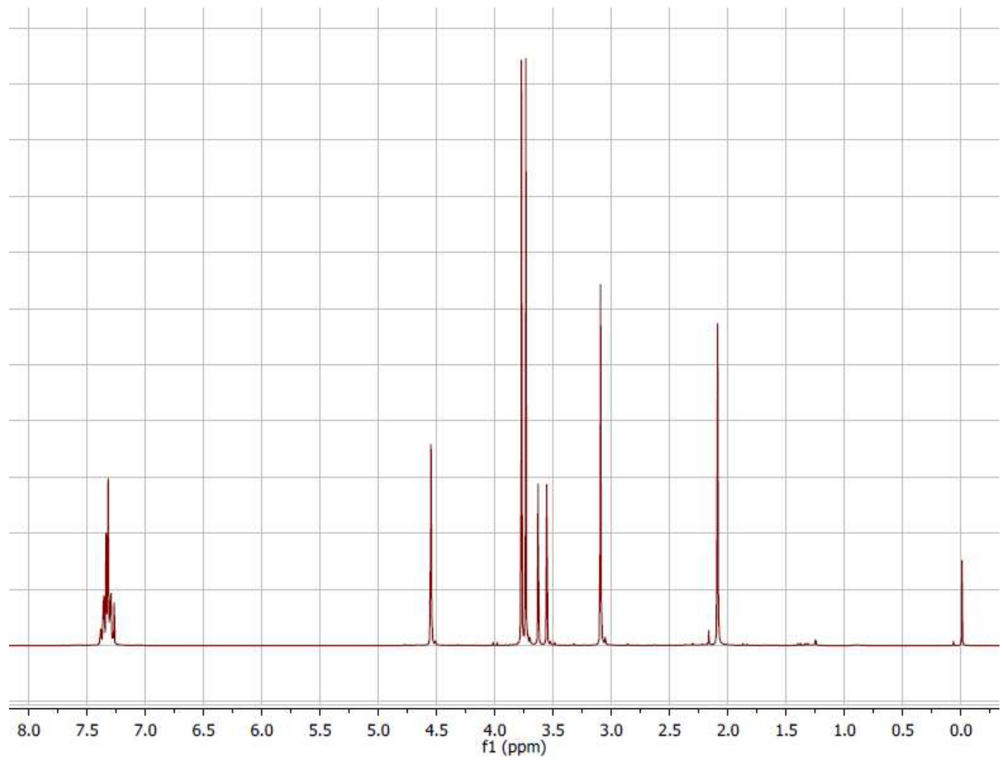
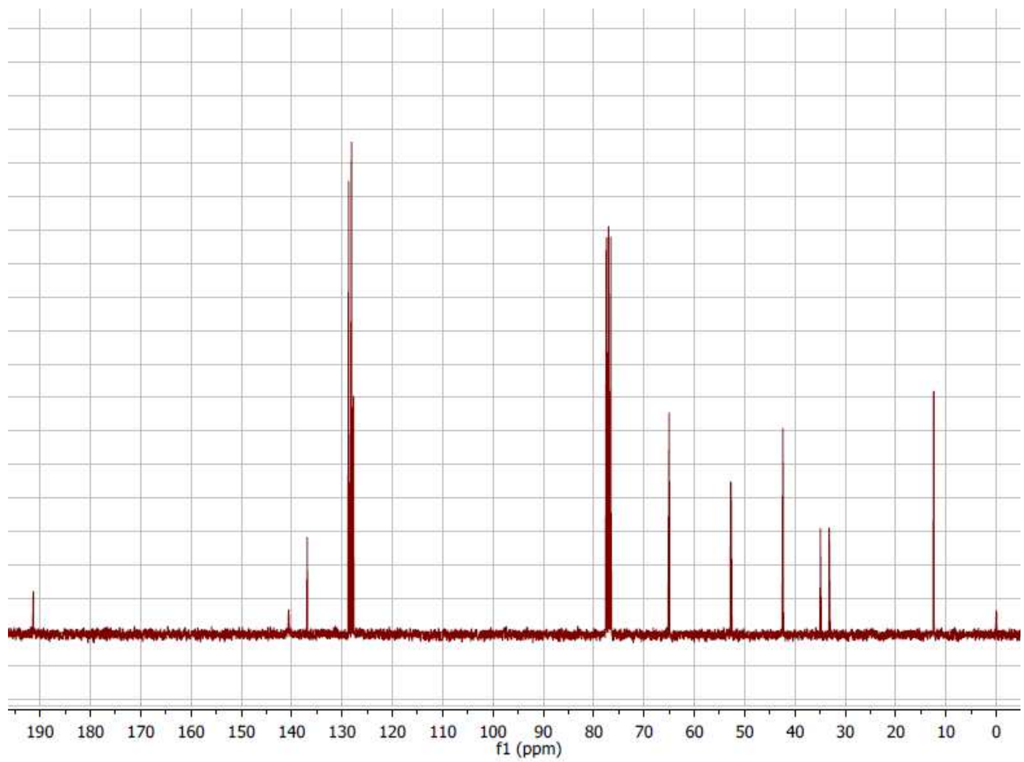
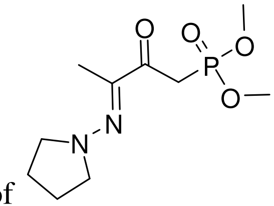
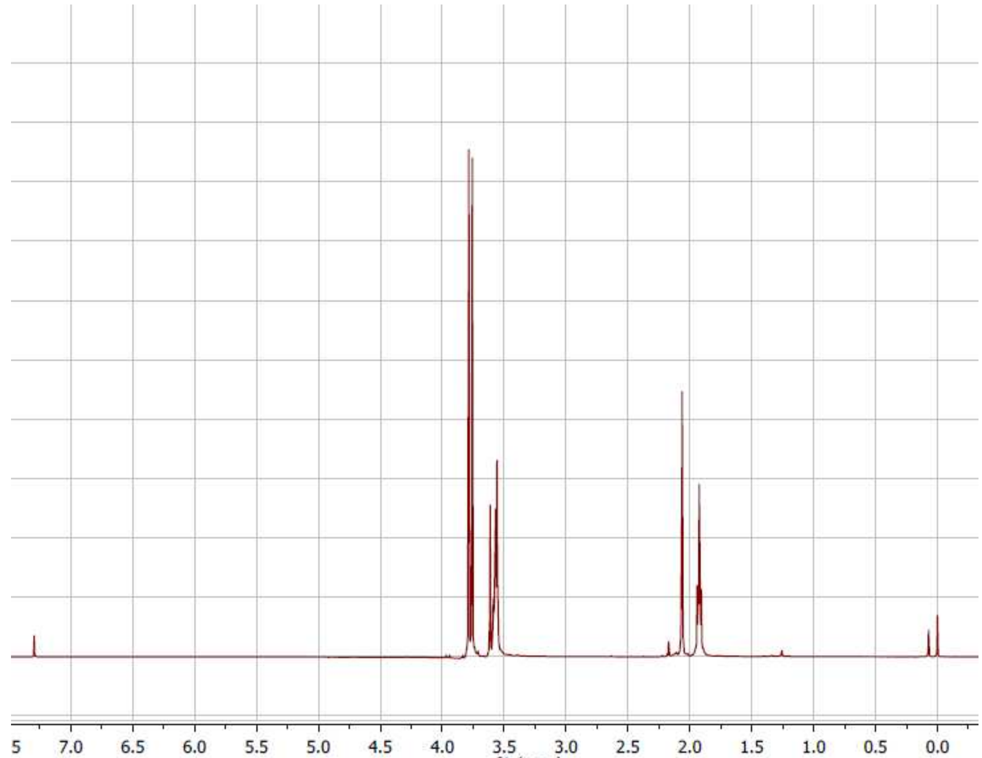
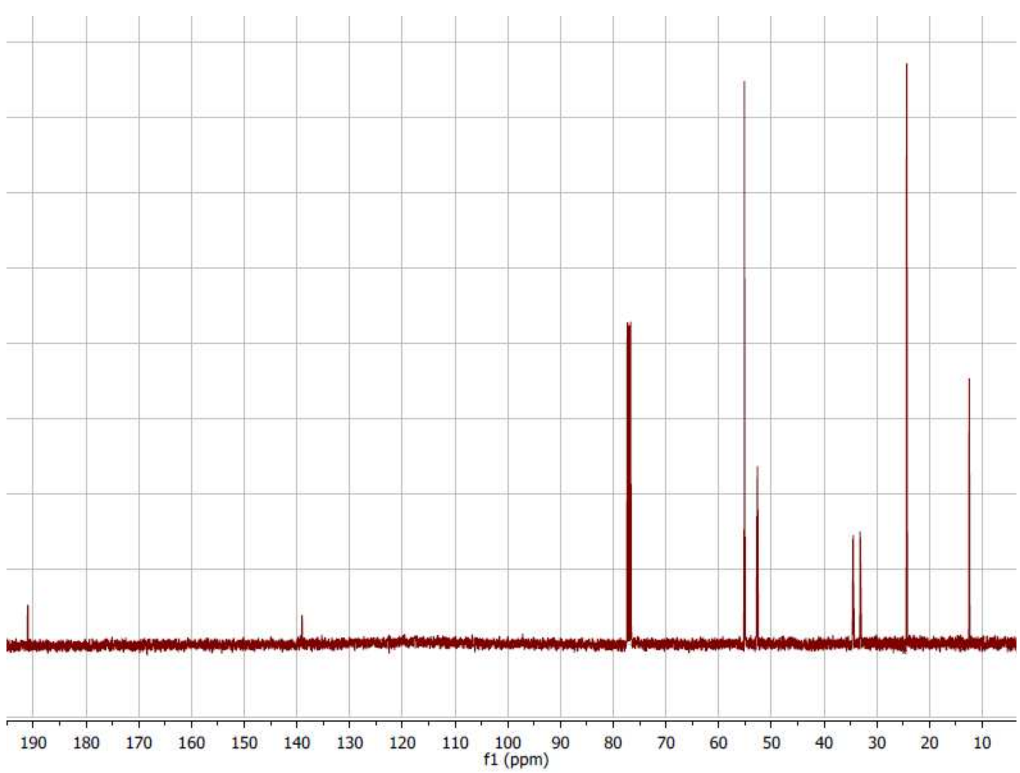
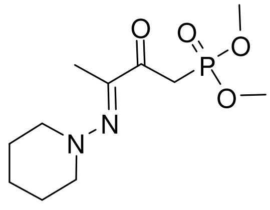


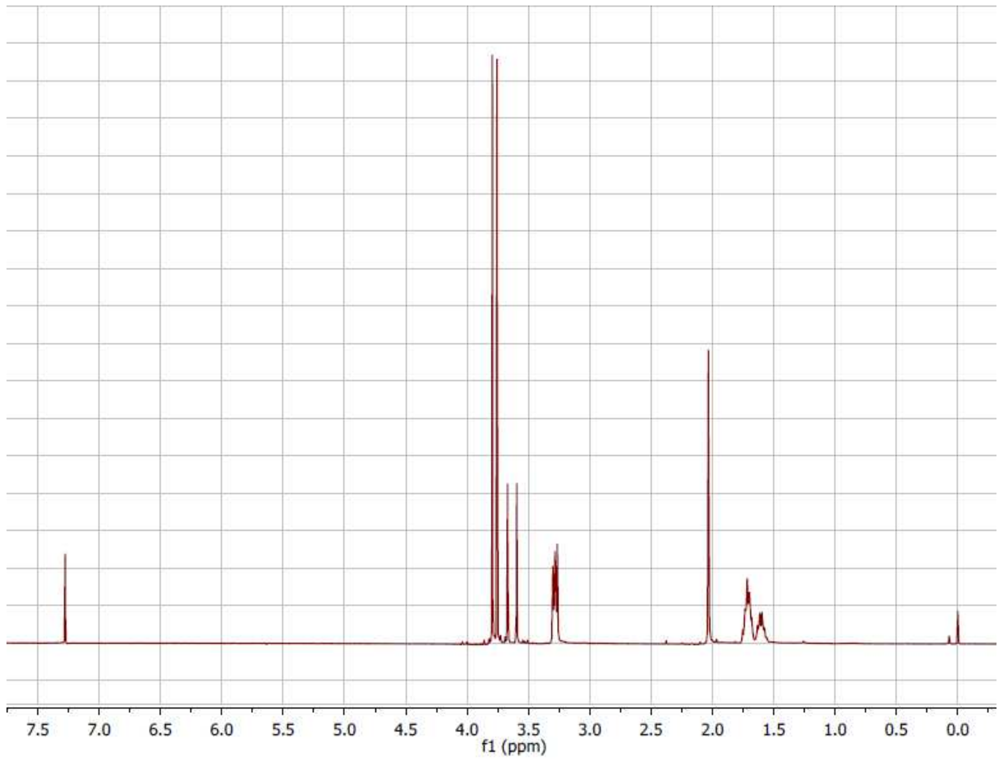


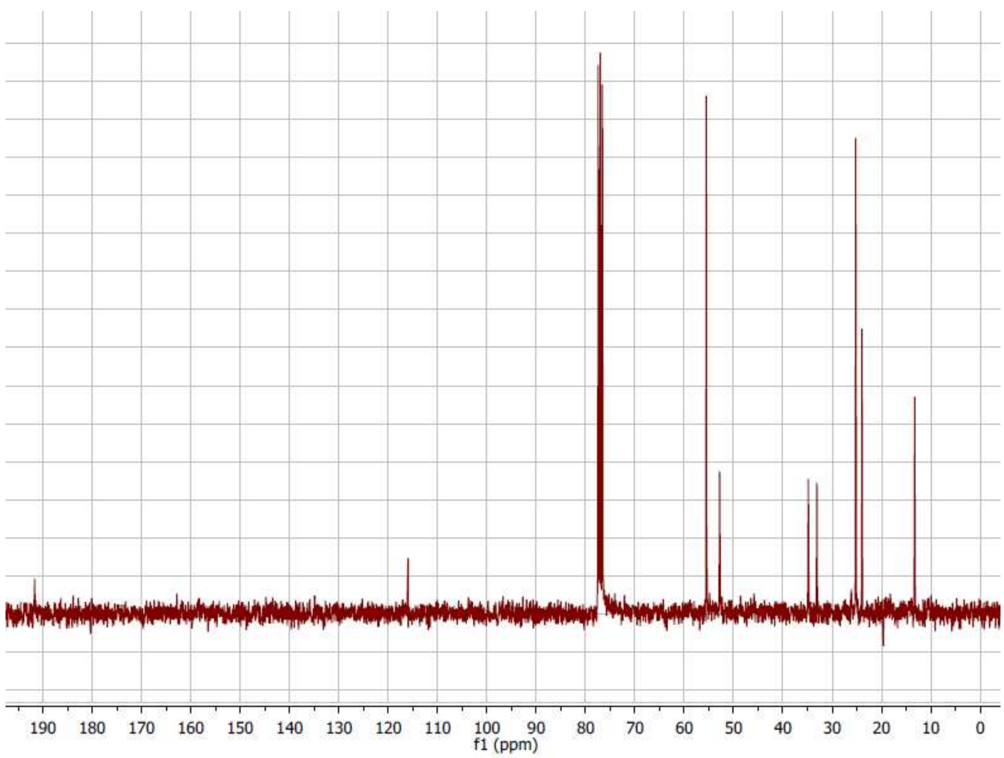
[1]H and [13]C Spectra of  **3i**

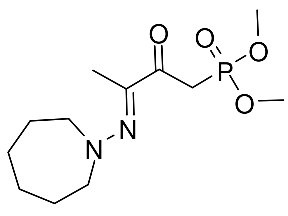


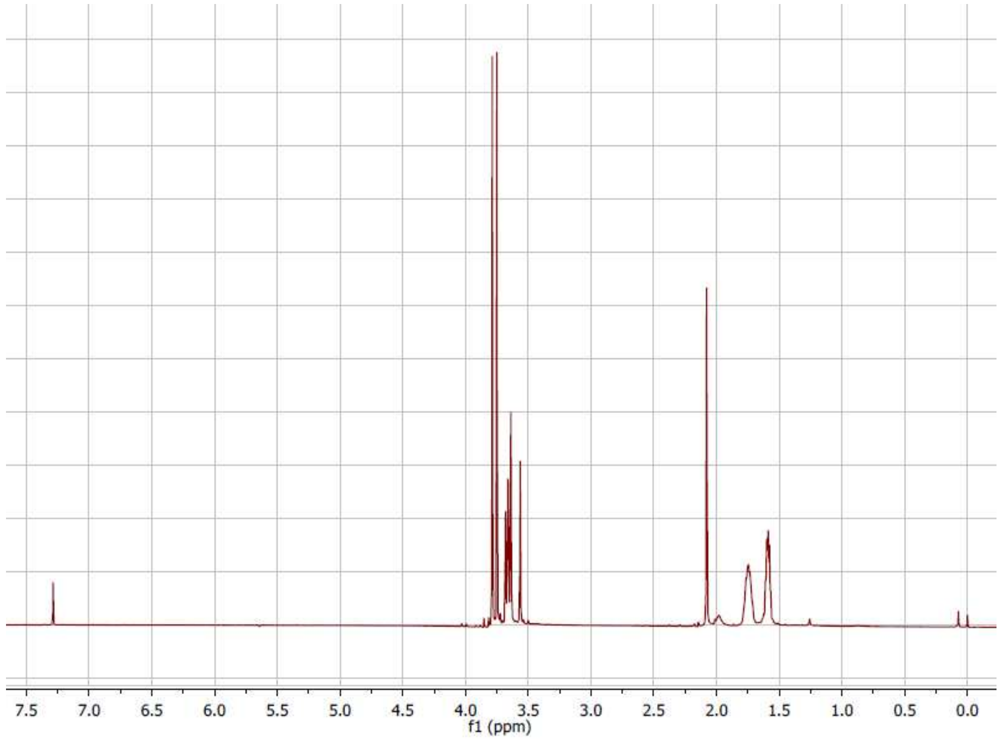


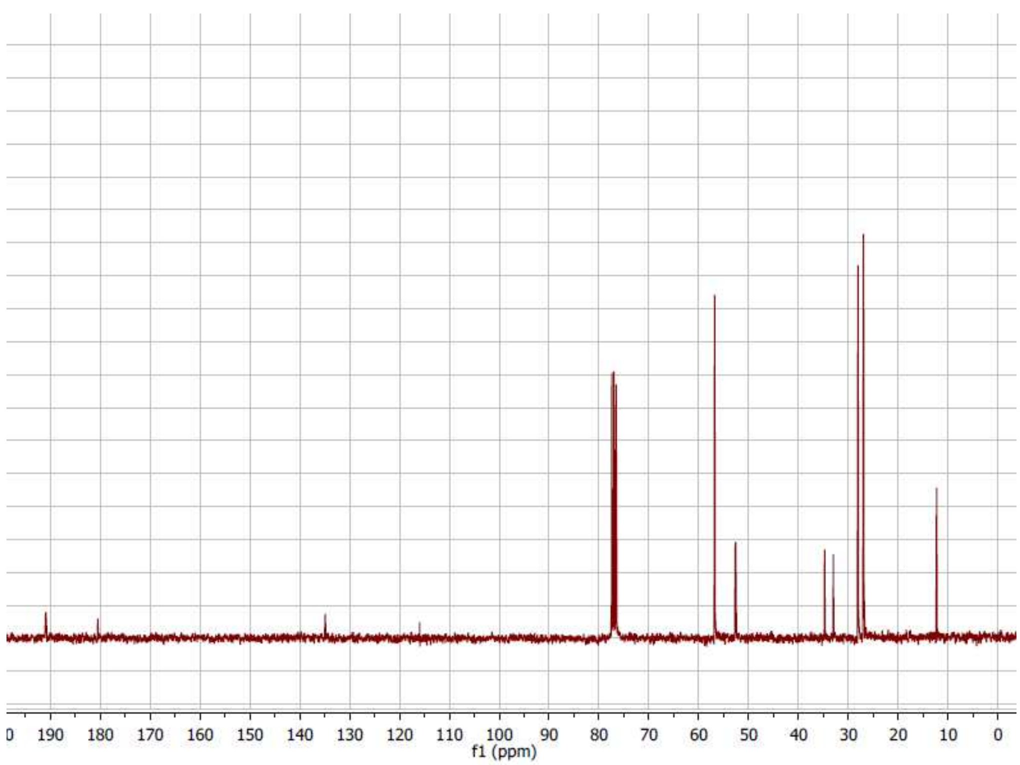
[1]H and [13]C Spectra of  **3j**

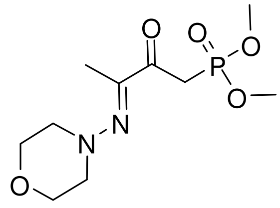


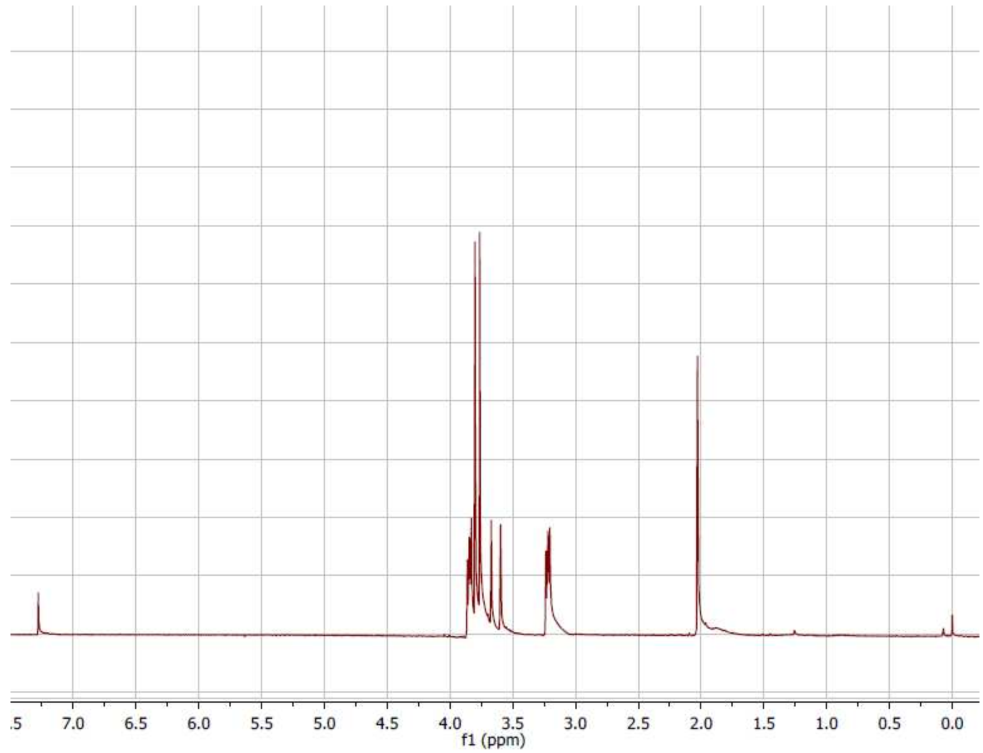


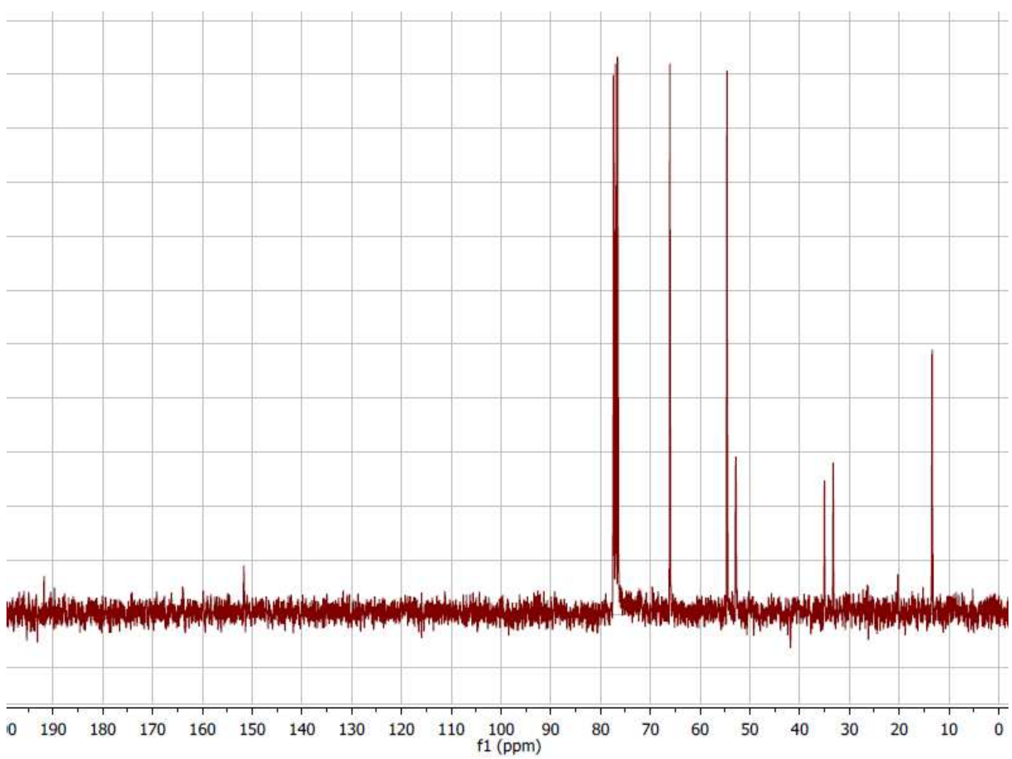
^{1}H and ^{13}C Spectra of  **3k**

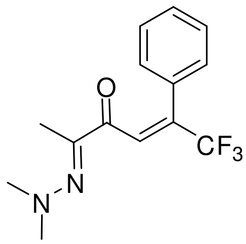


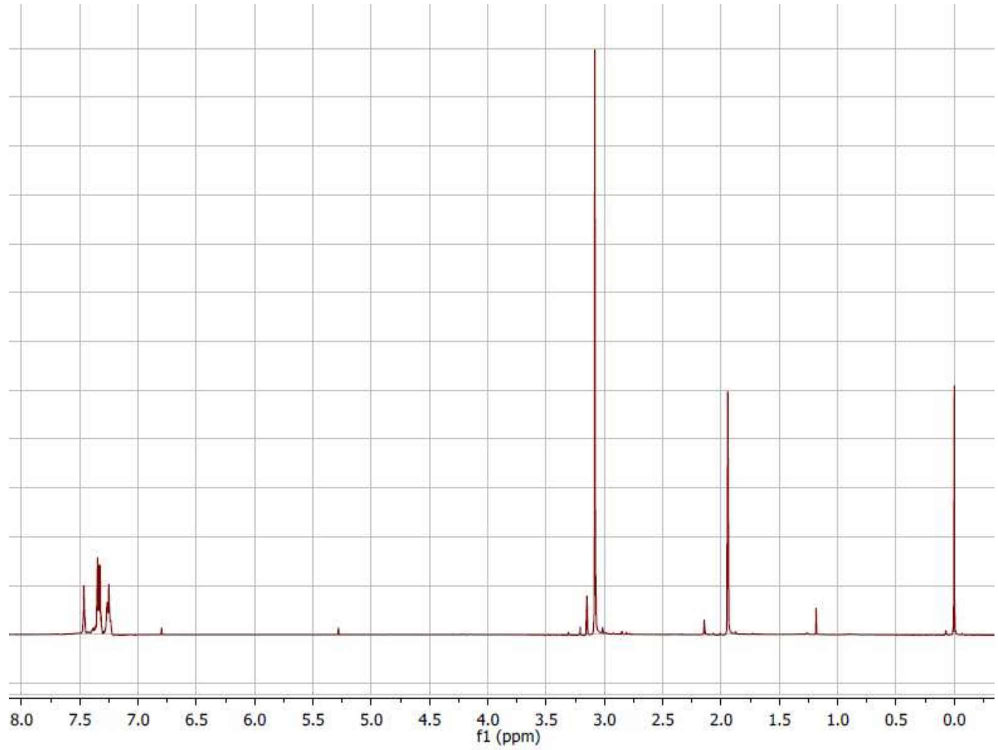


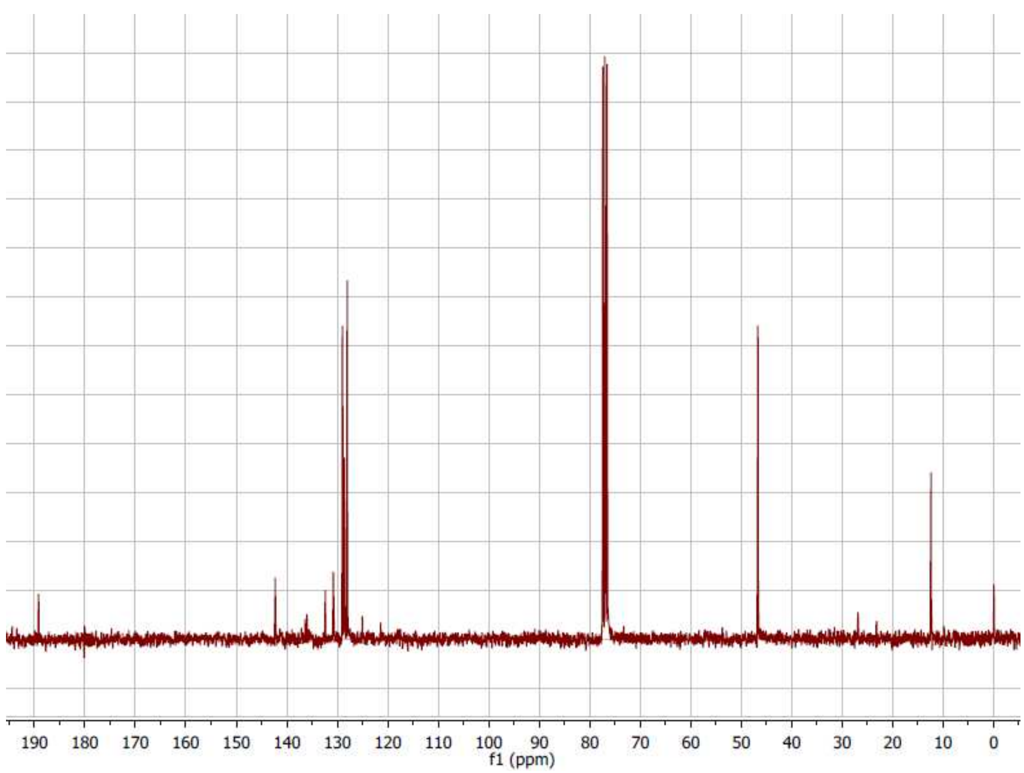
[1]H and [13]C Spectra of  **3l**

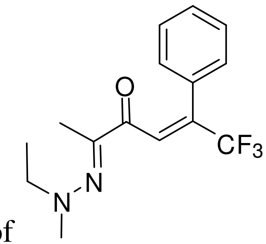


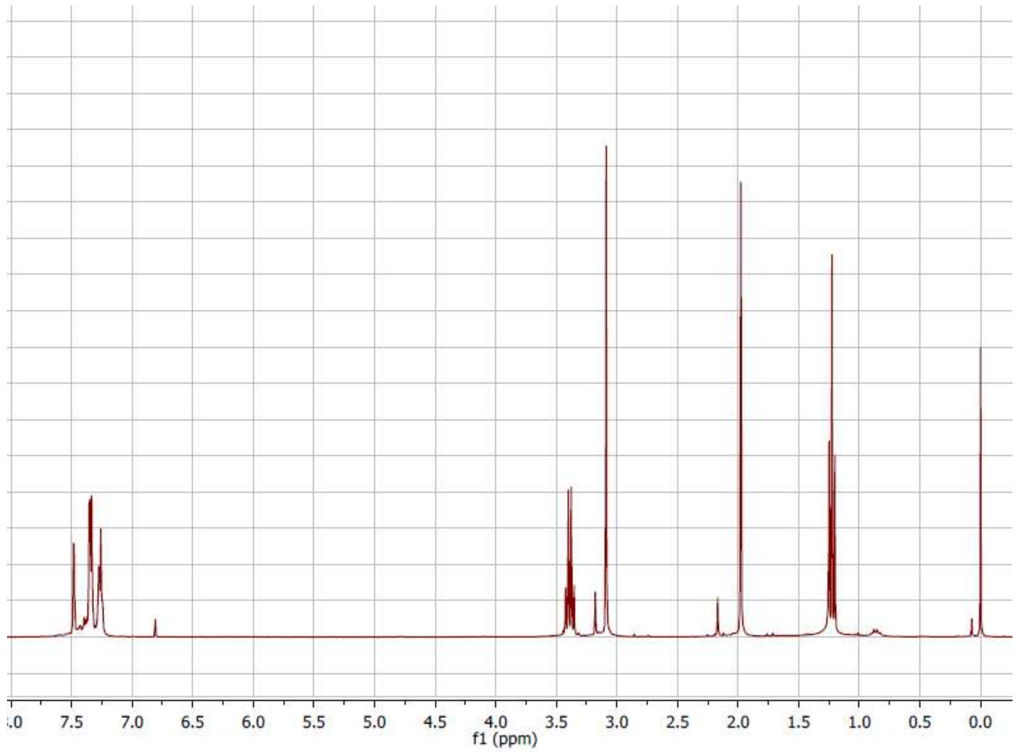


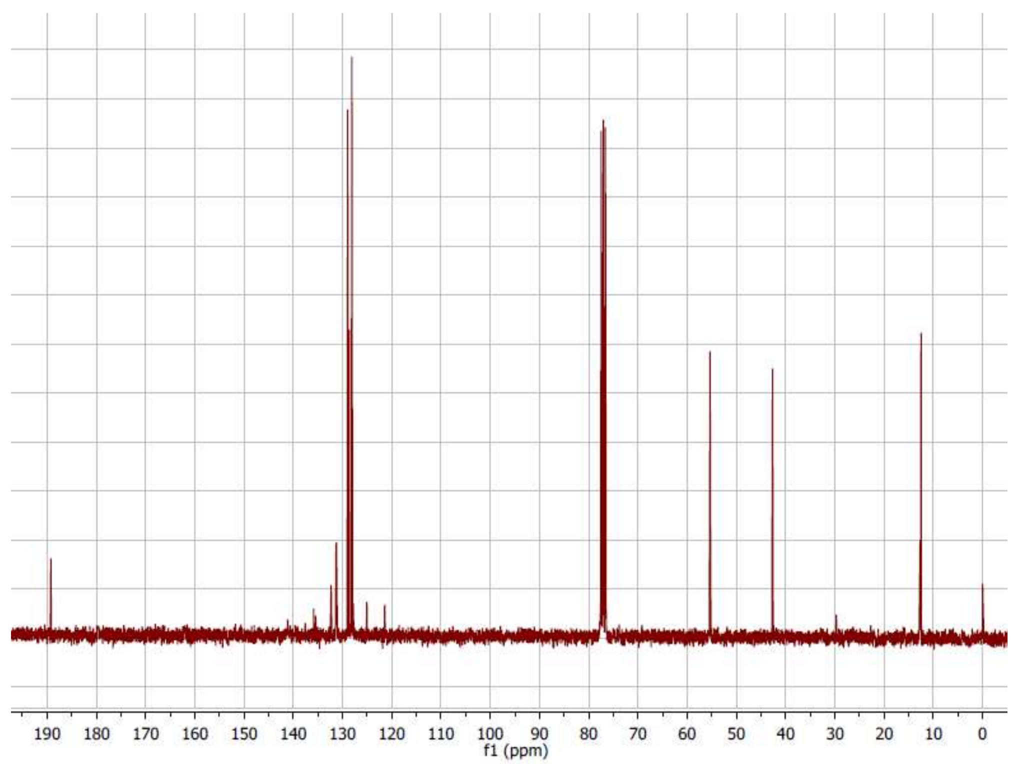
^{1}H and ^{13}C Spectra of  **4a**

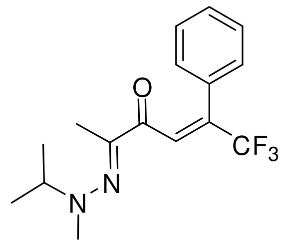


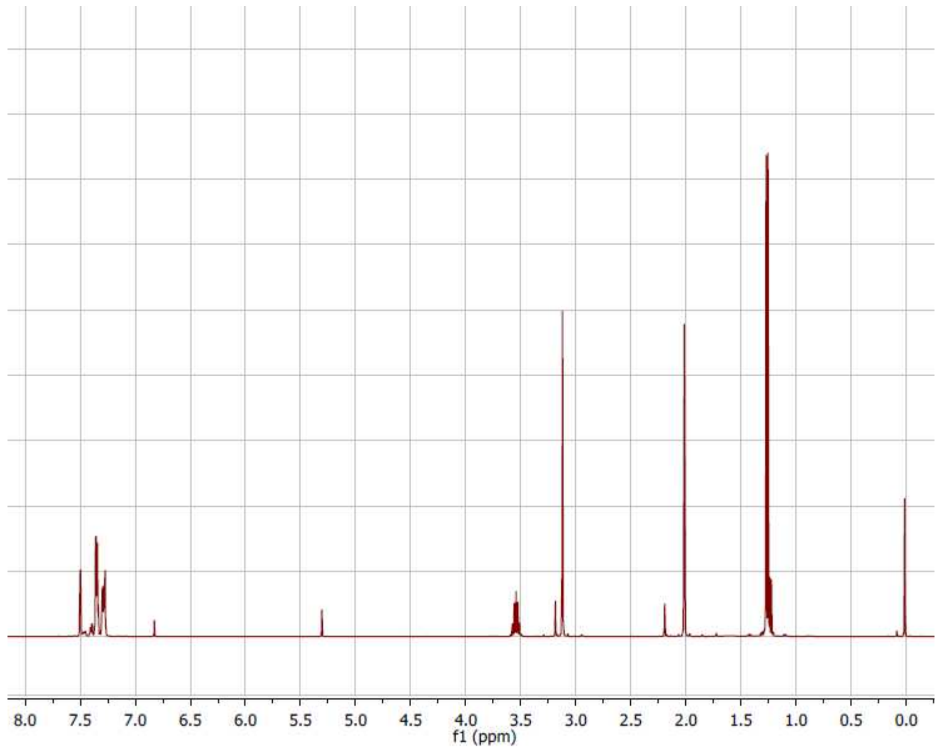


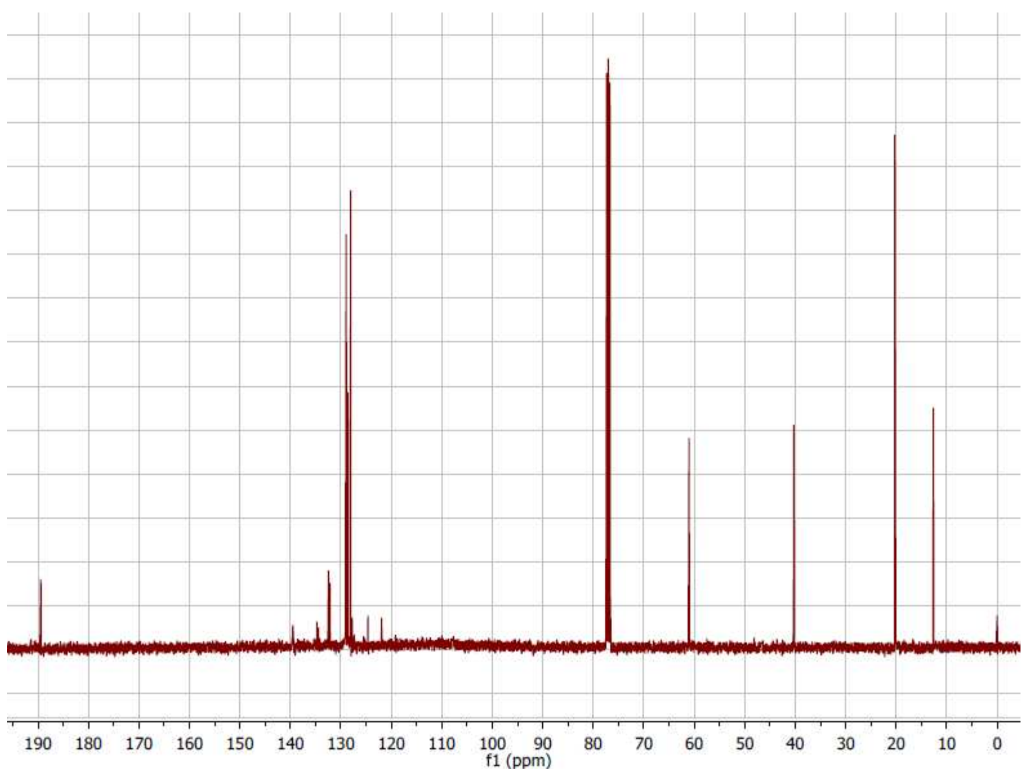
^{1}H and ^{13}C Spectra of  **4b**

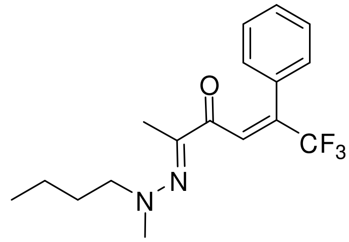


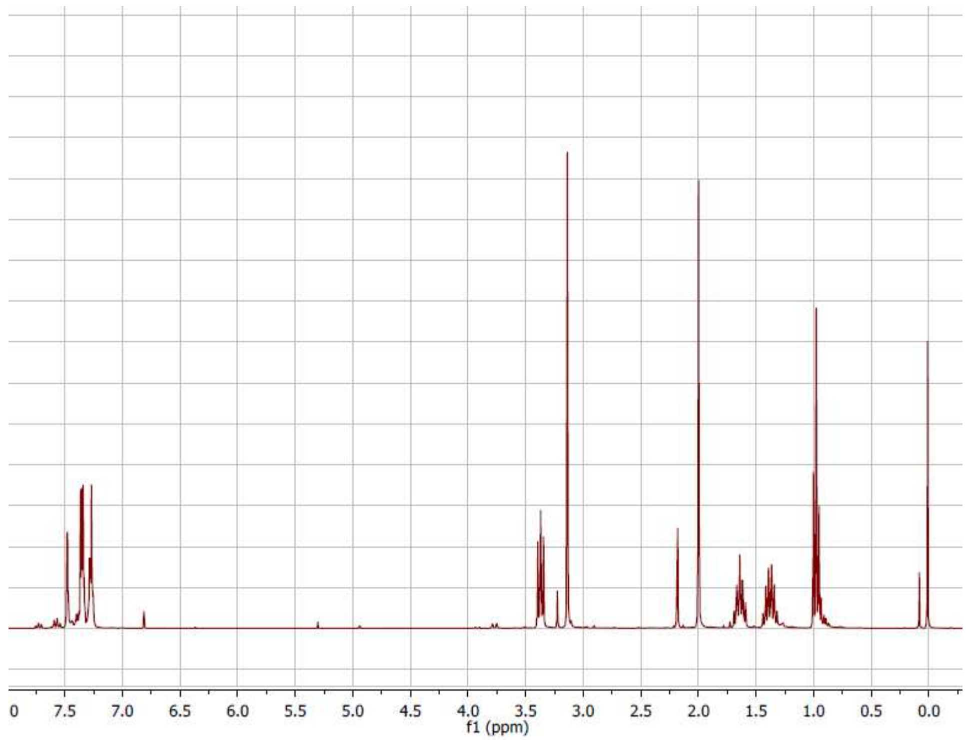


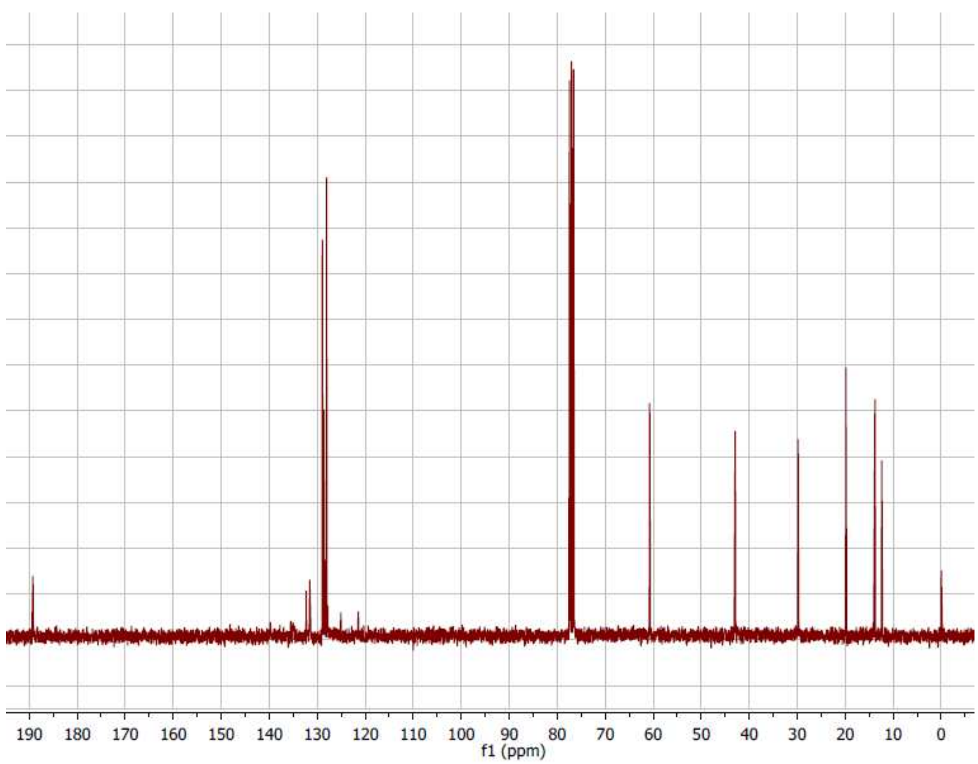
^{1}H and ^{13}C Spectra of  **4c**

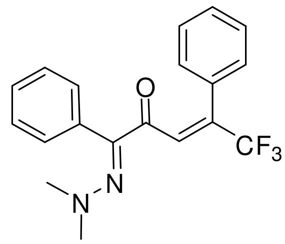




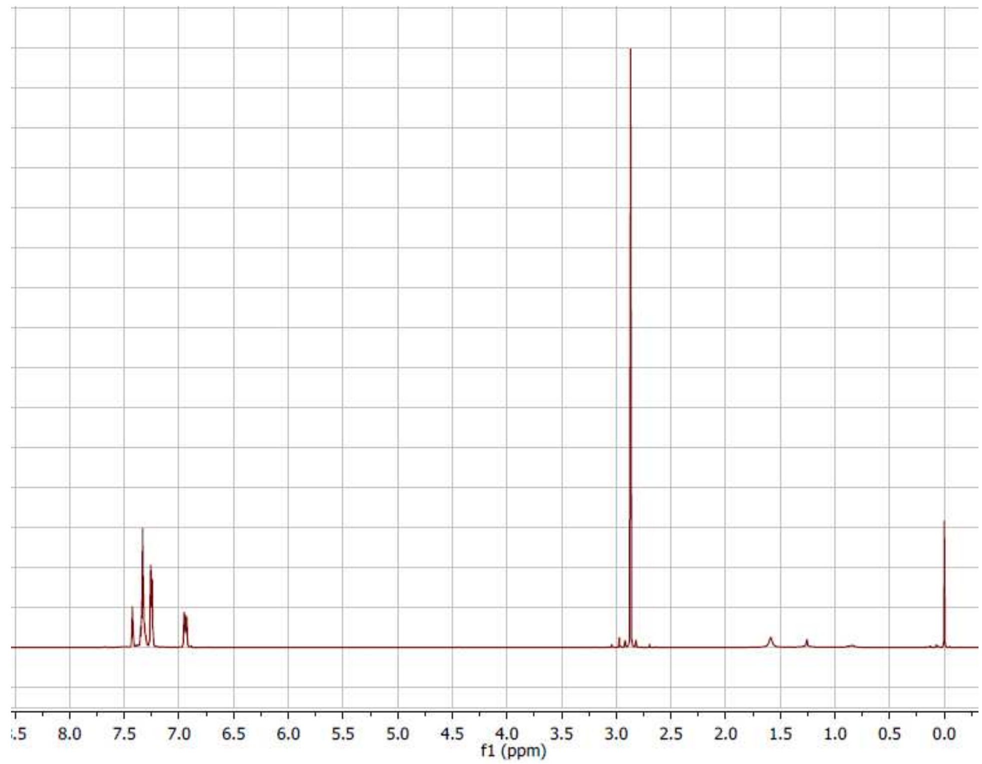
[1]H and [13]C Spectra of  **4d**

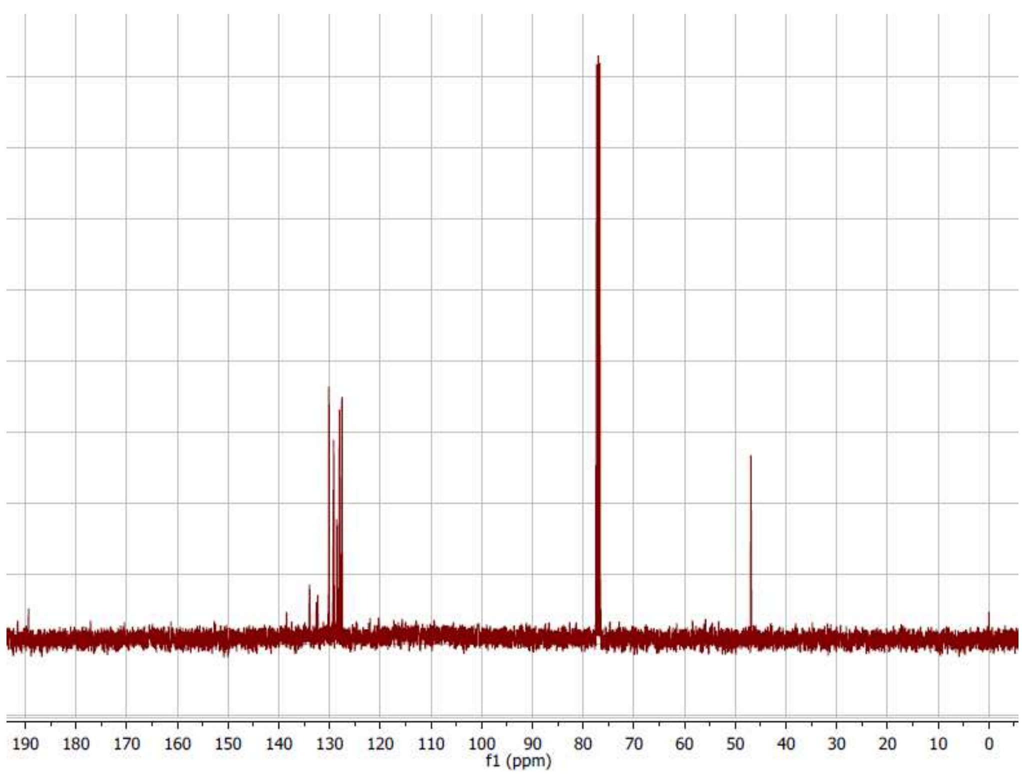


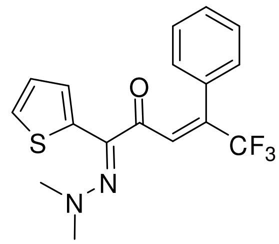


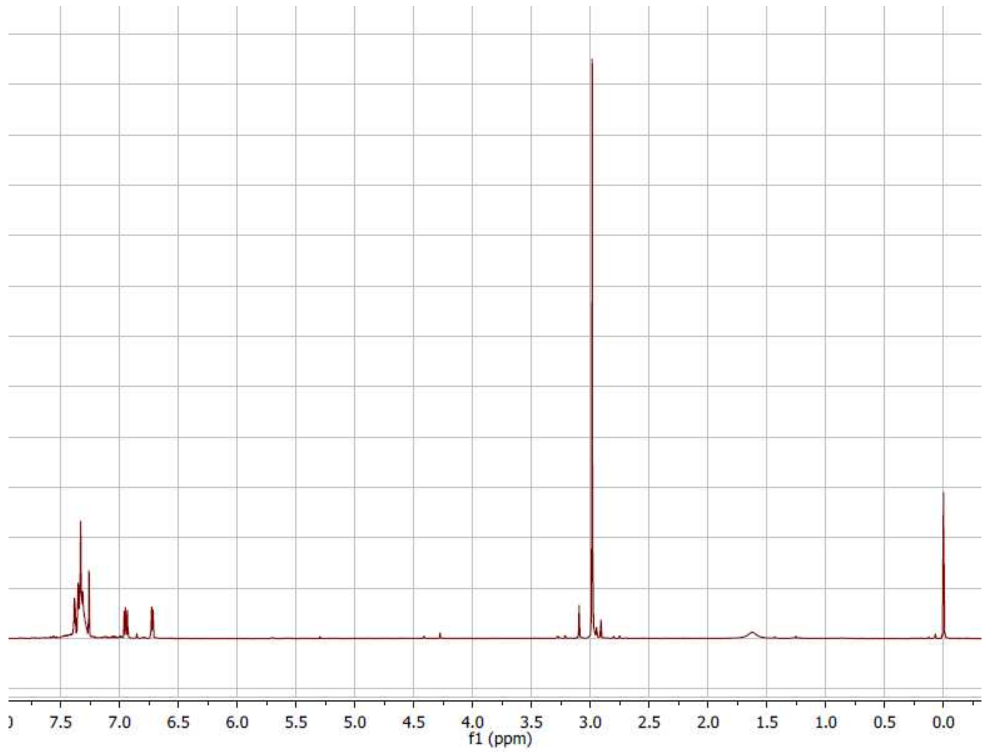
[1]H and [13]C Spectra of 

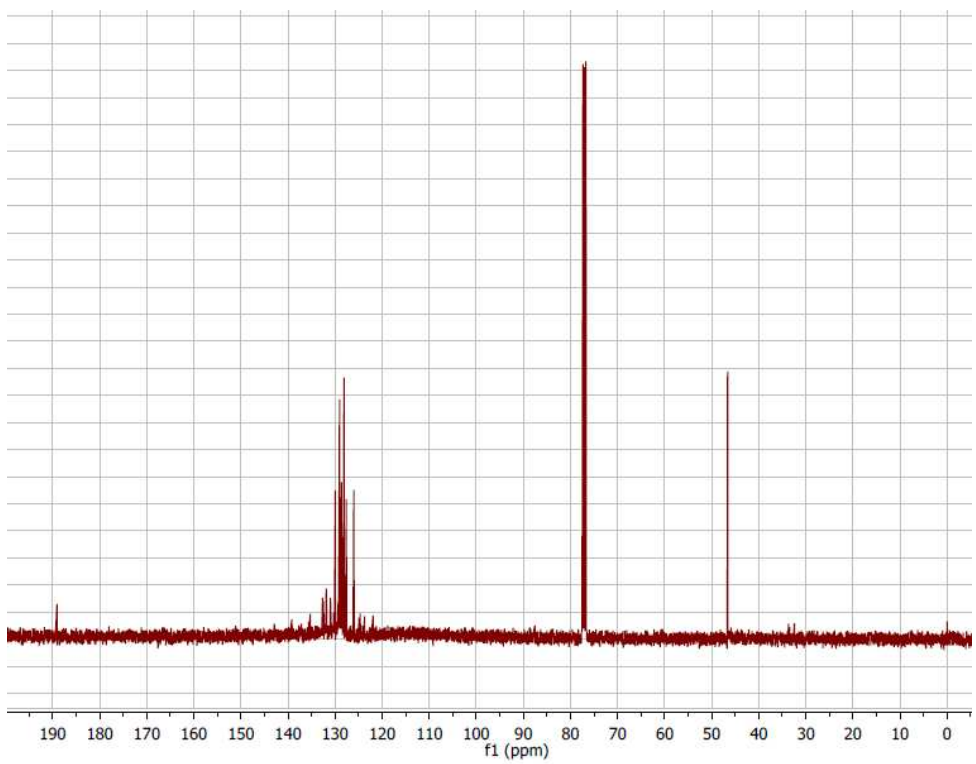
4e





^{1}H and ^{13}C Spectra of  **4f**





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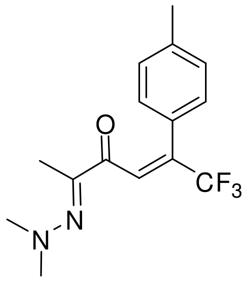

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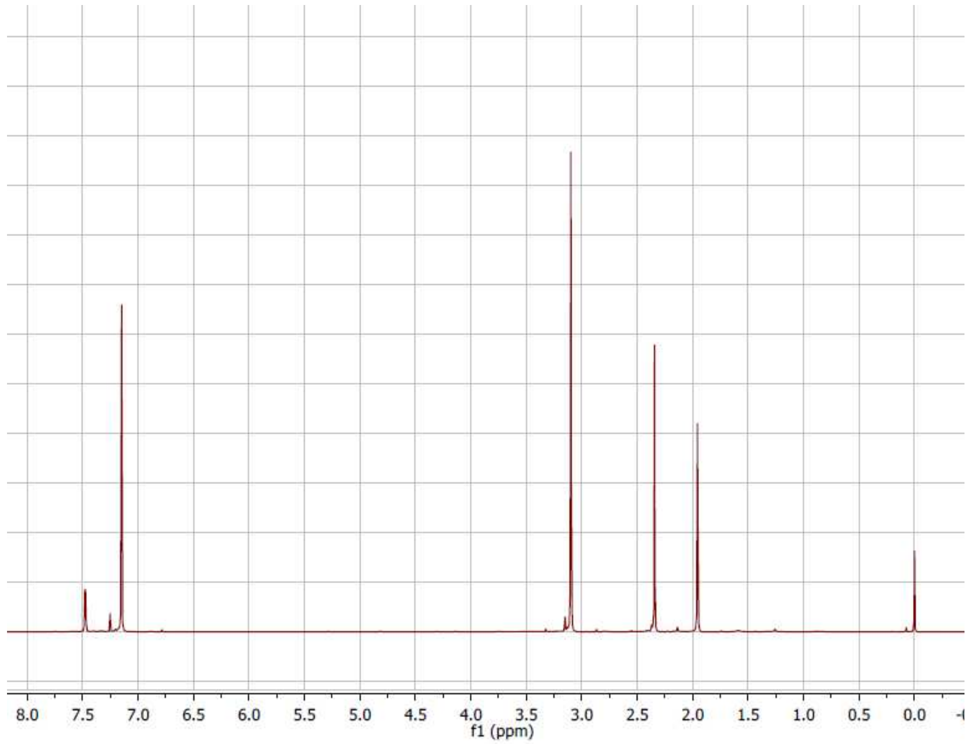

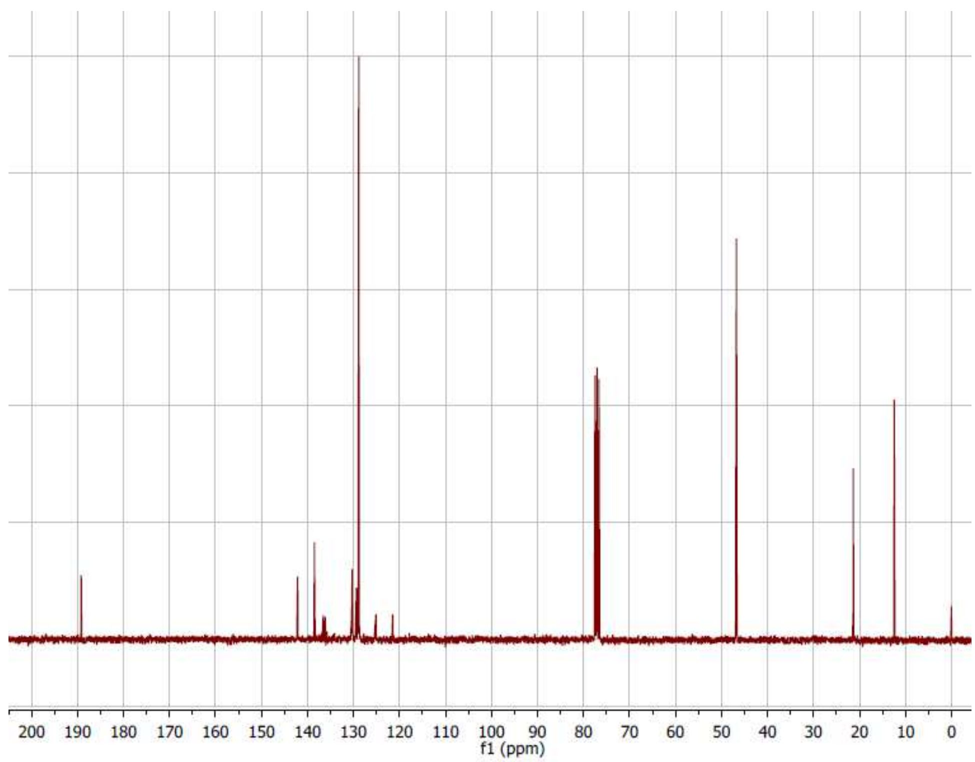

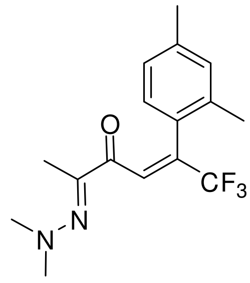

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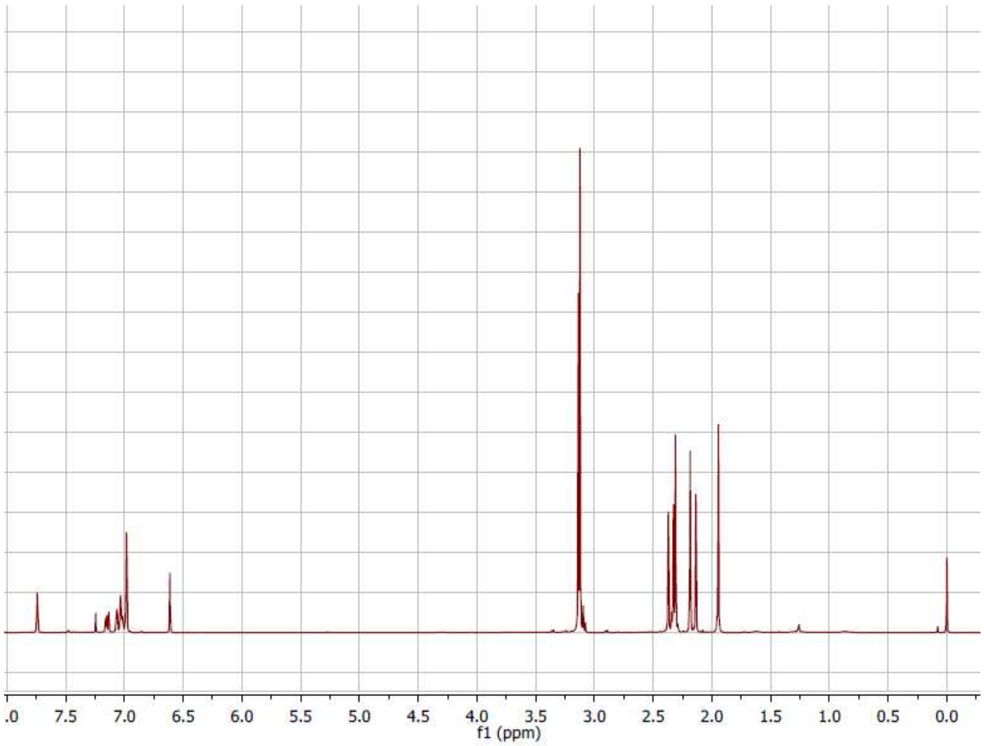
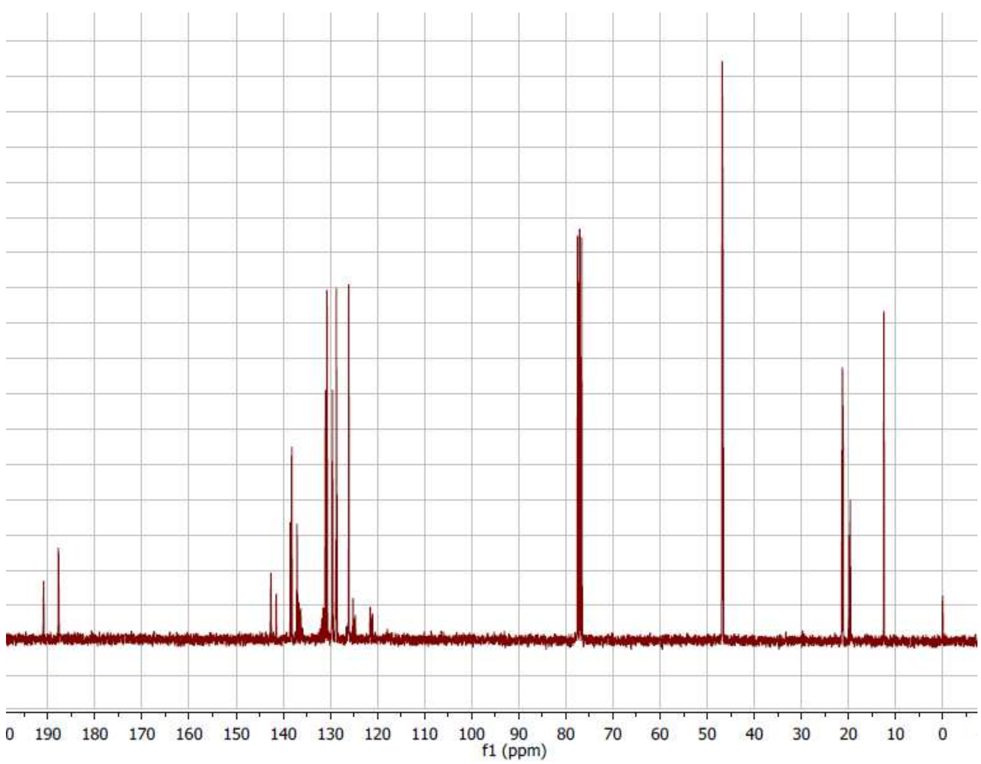
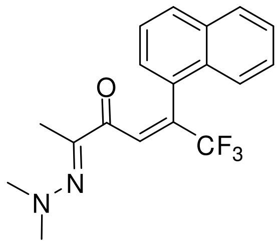




[1]H and [13]C Spectra of 

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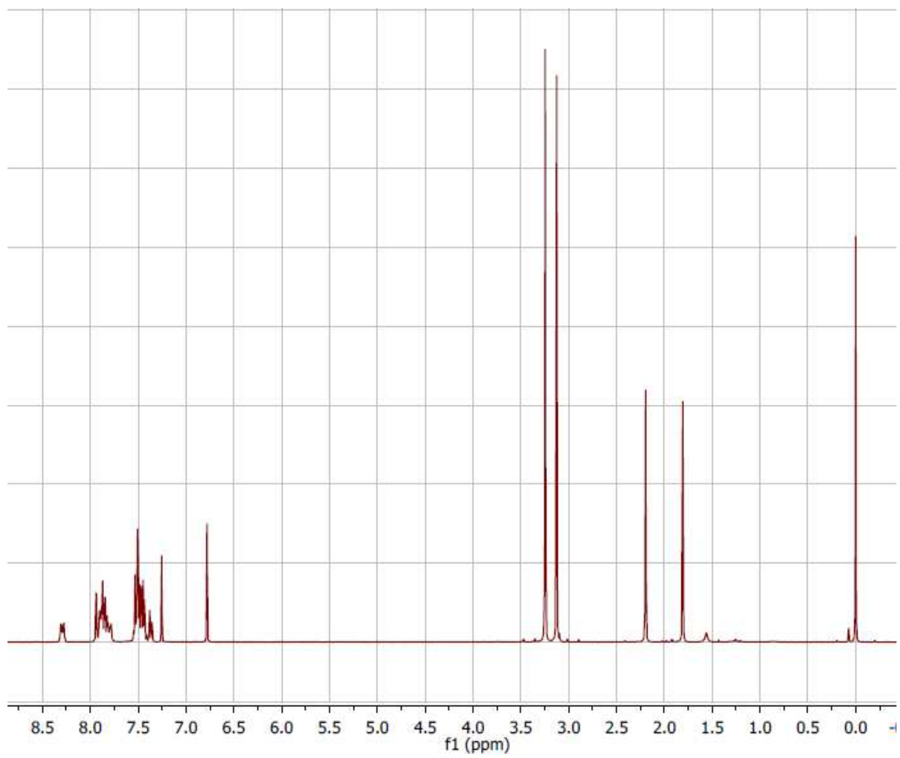
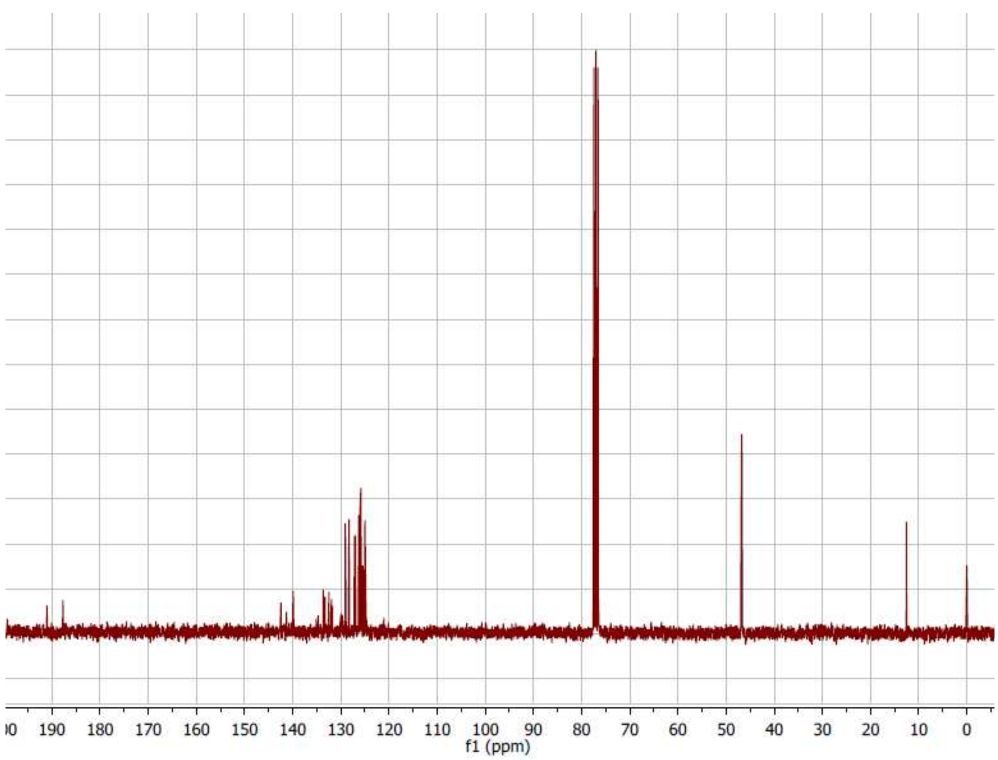
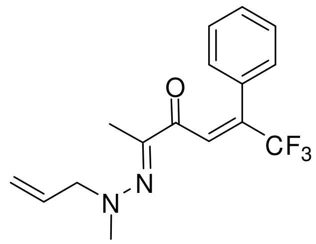
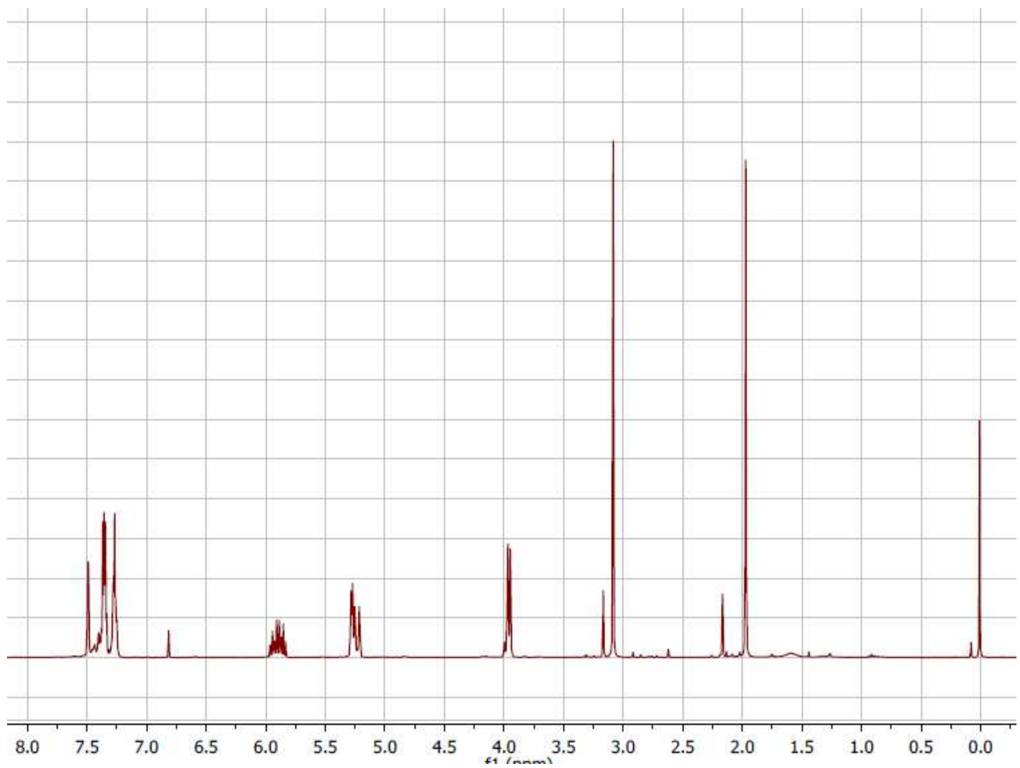
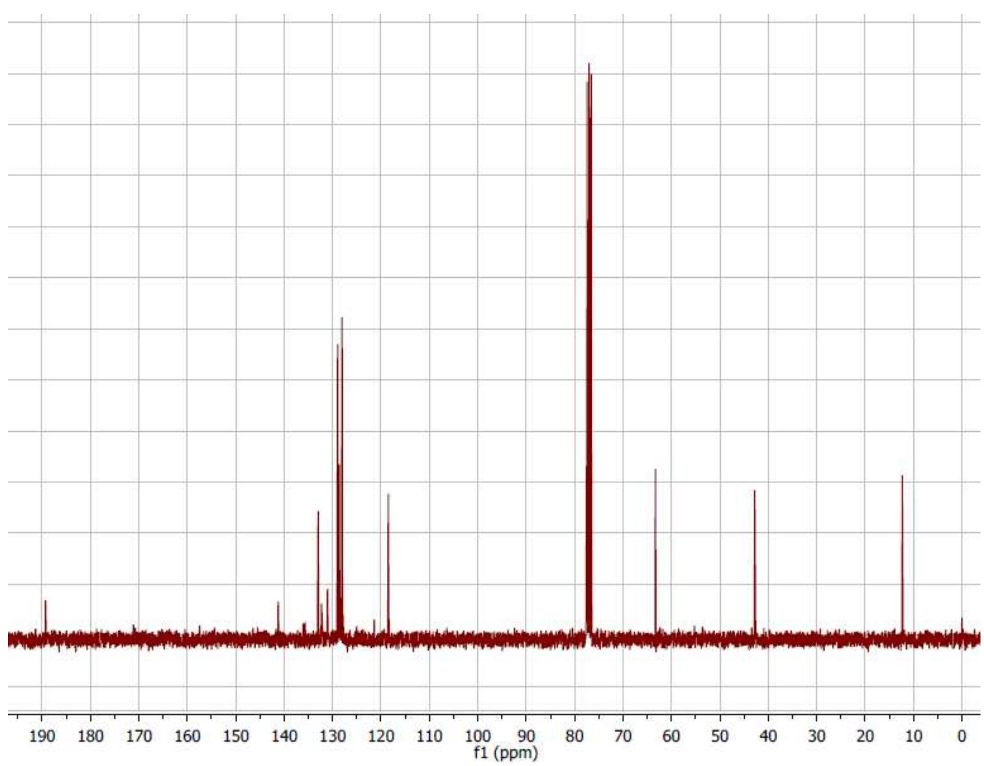
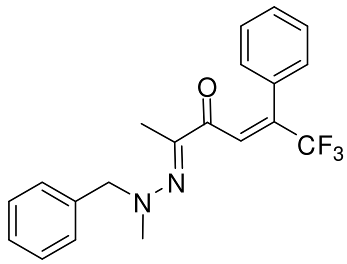




^{1}H and ^{13}C Spectra of  **4j**





^{1}H and ^{13}C Spectra of 

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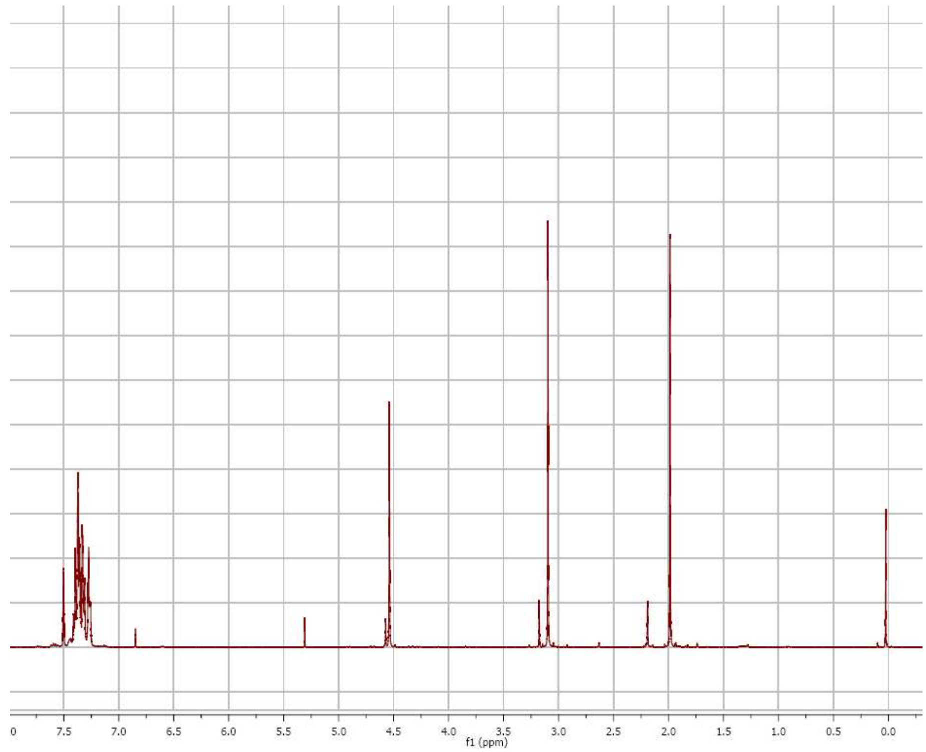
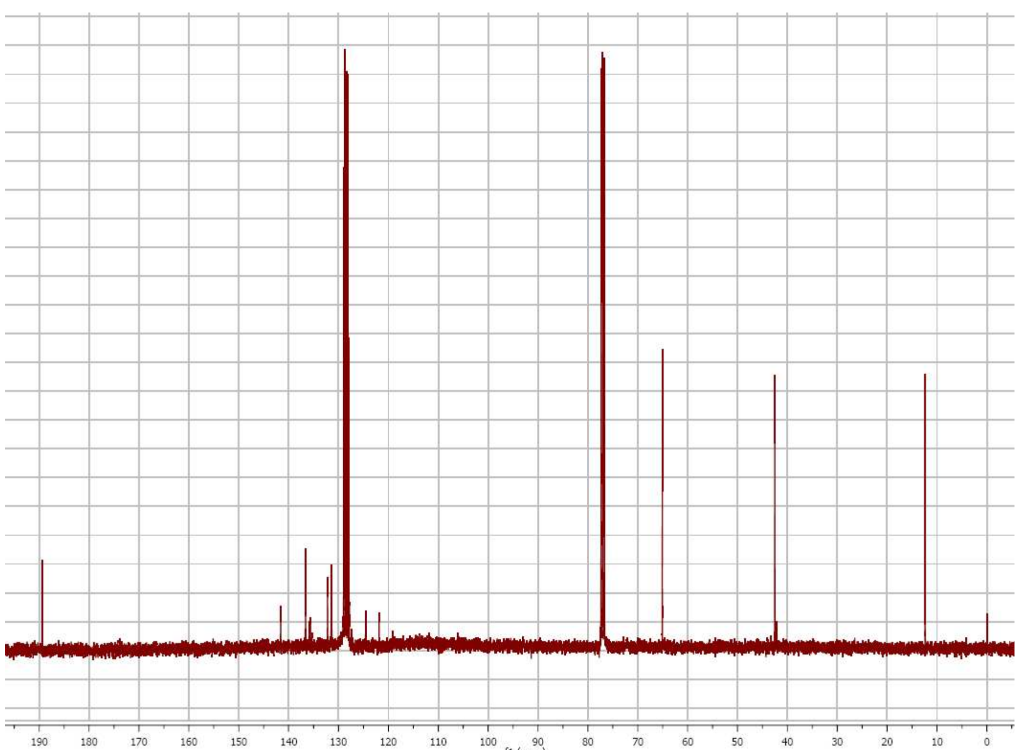
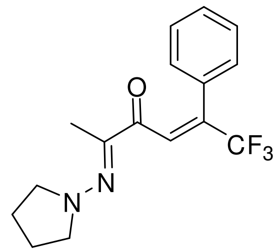
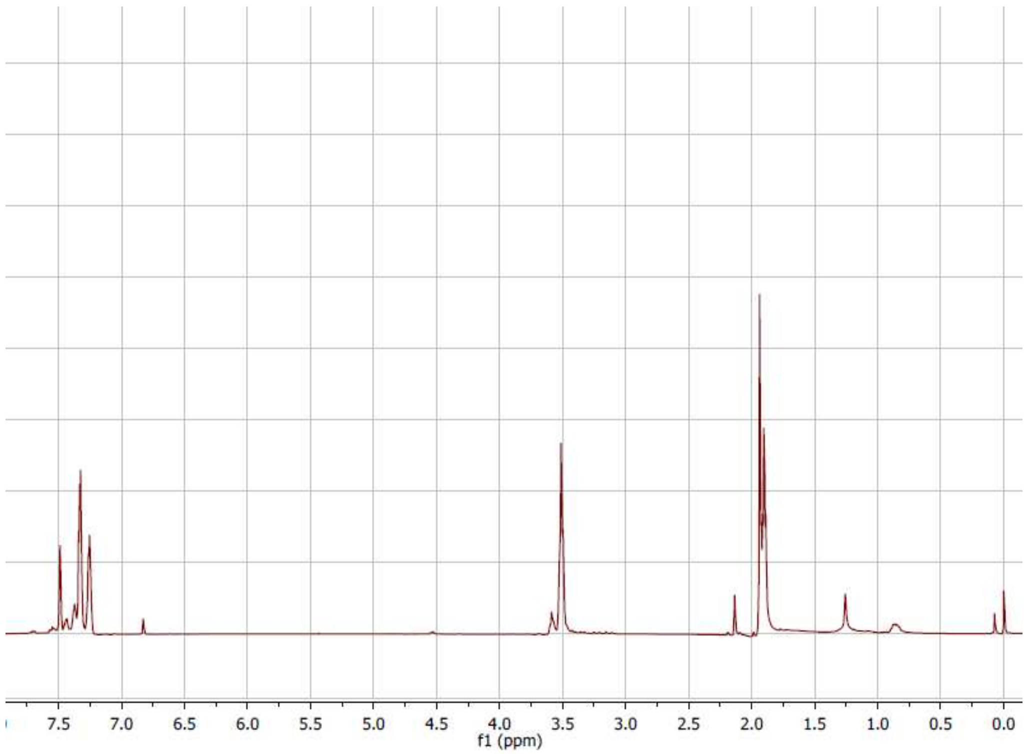
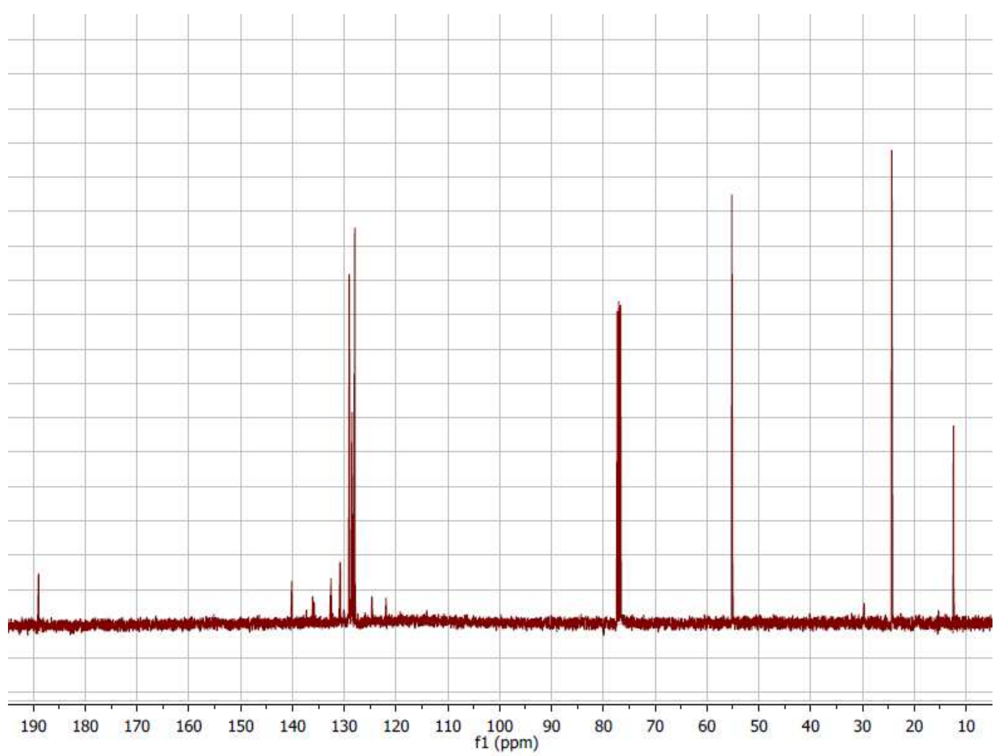
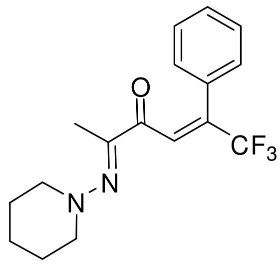




^{1}H and ^{13}C Spectra of  **4l**





[1]H and [13]C Spectra of 

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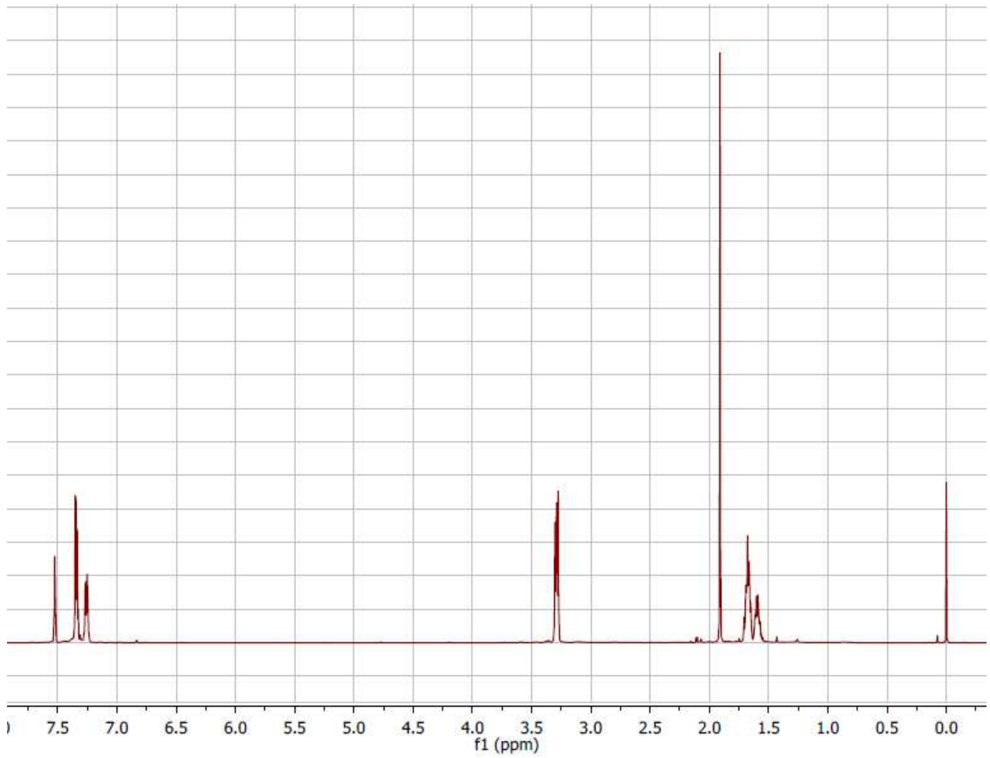
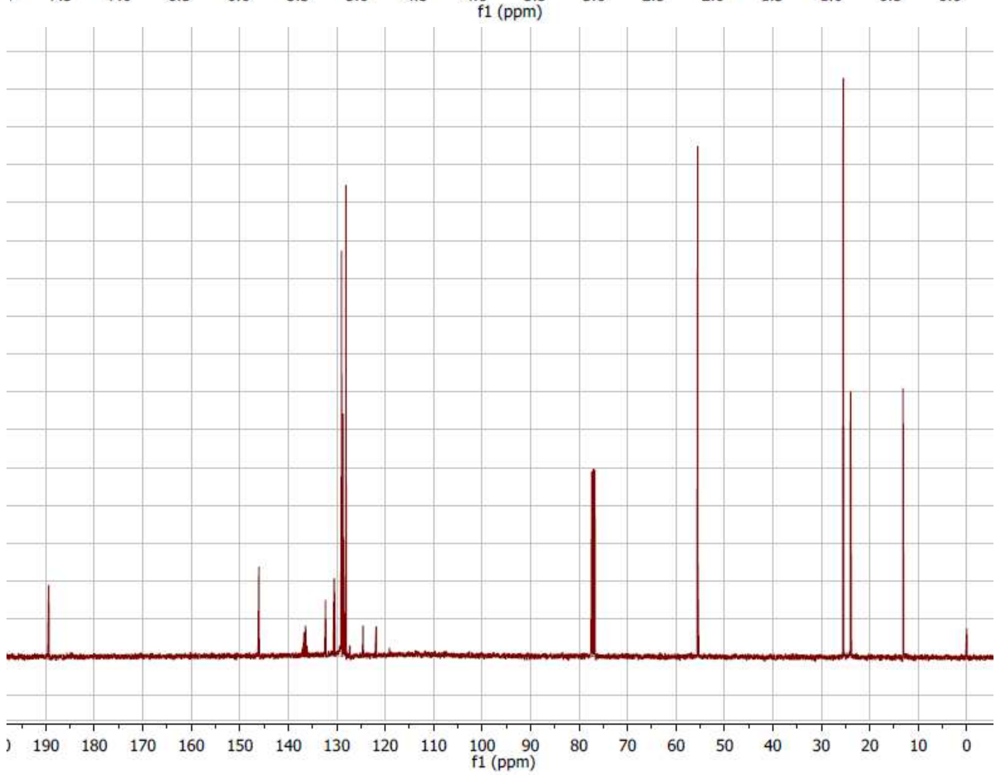
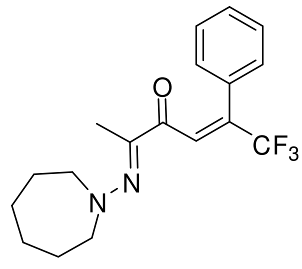




^{1}H and ^{13}C Spectra of 

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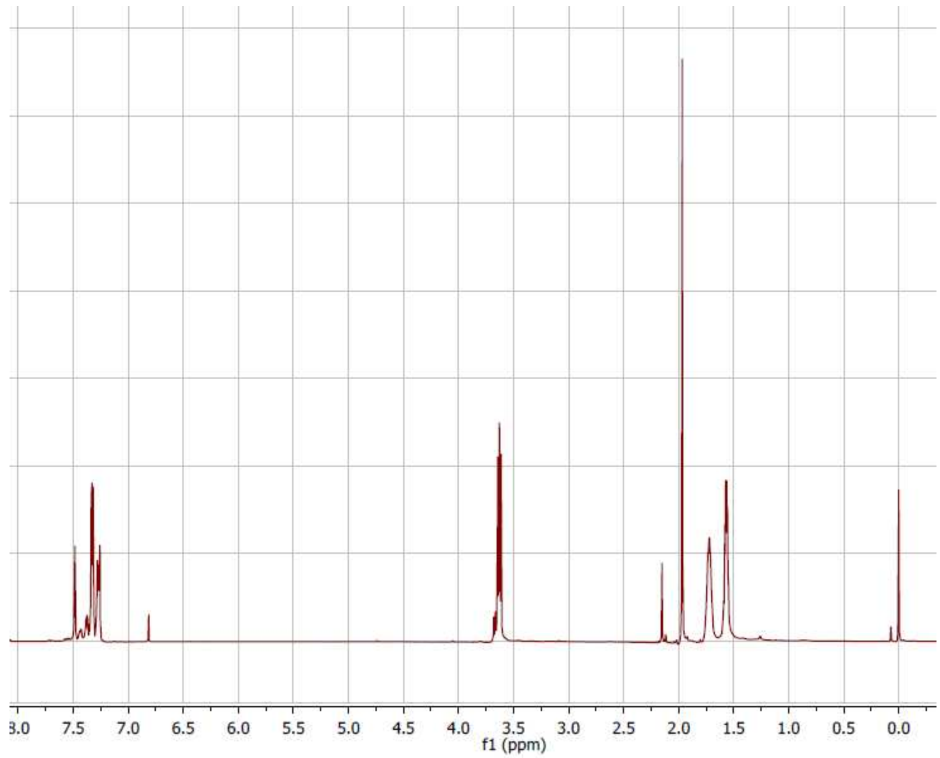
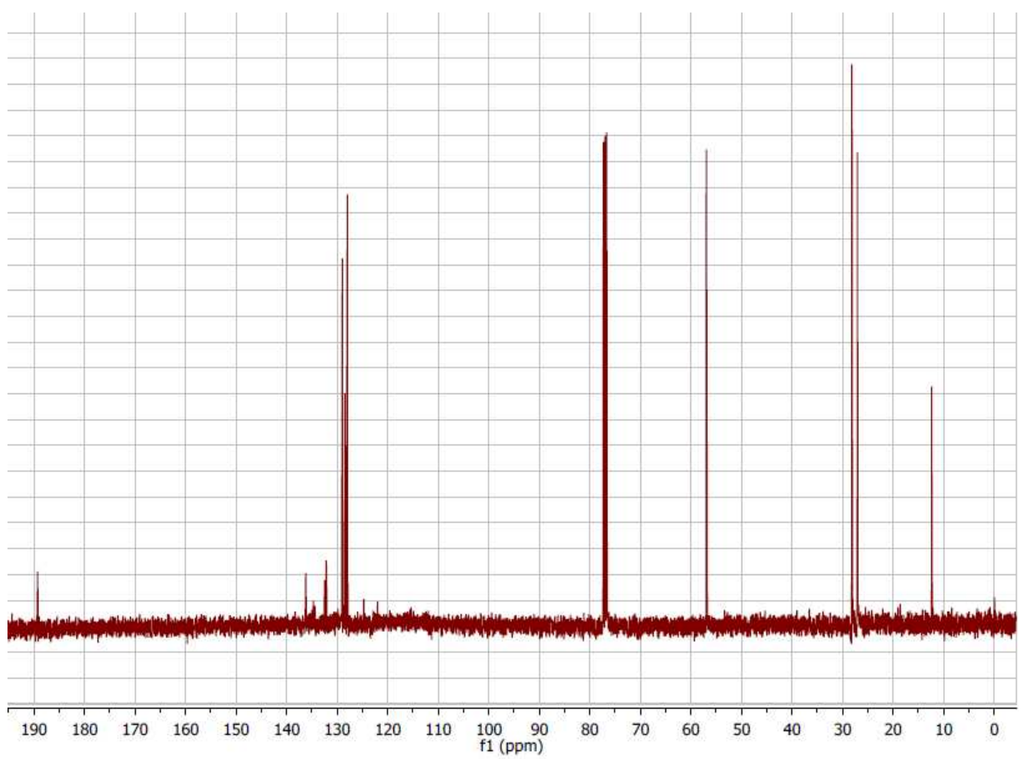
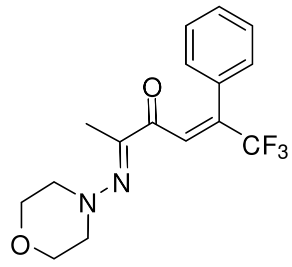




^{1}H and ^{13}C Spectra of 

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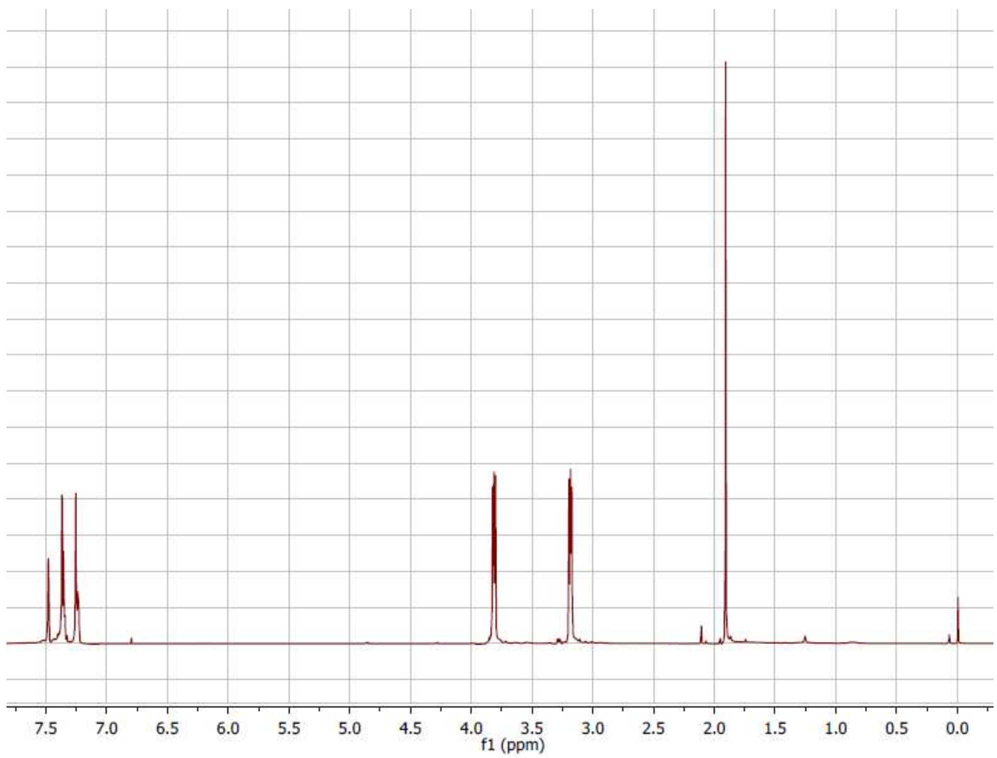
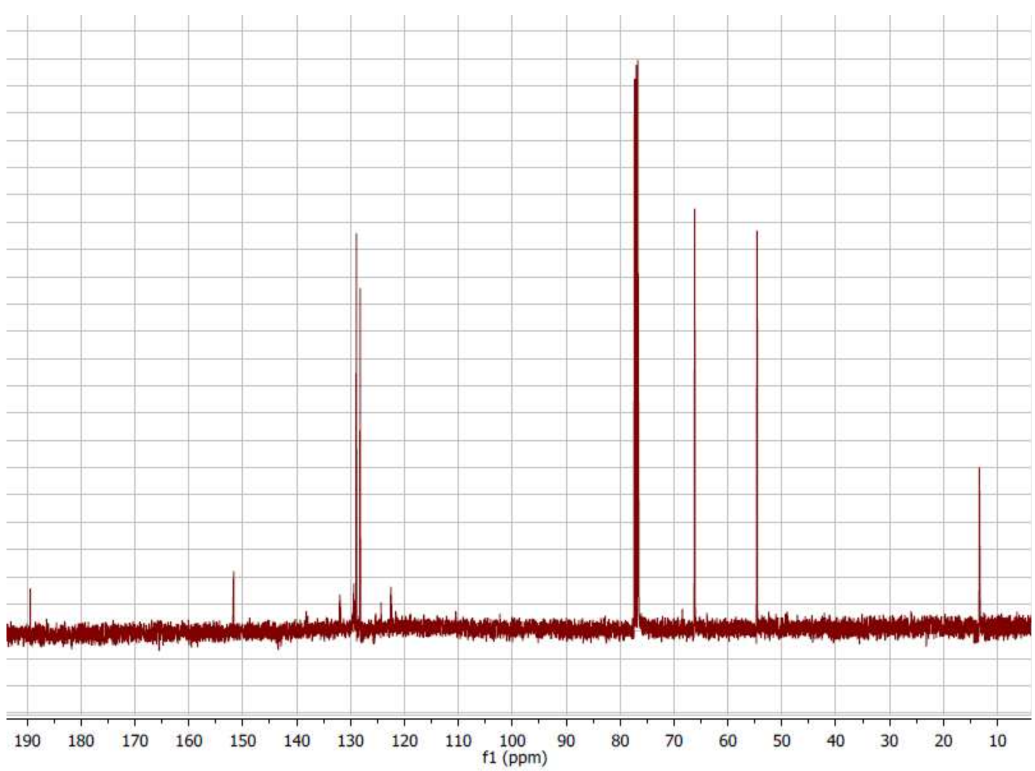
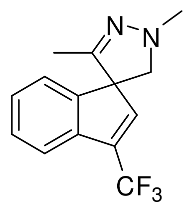
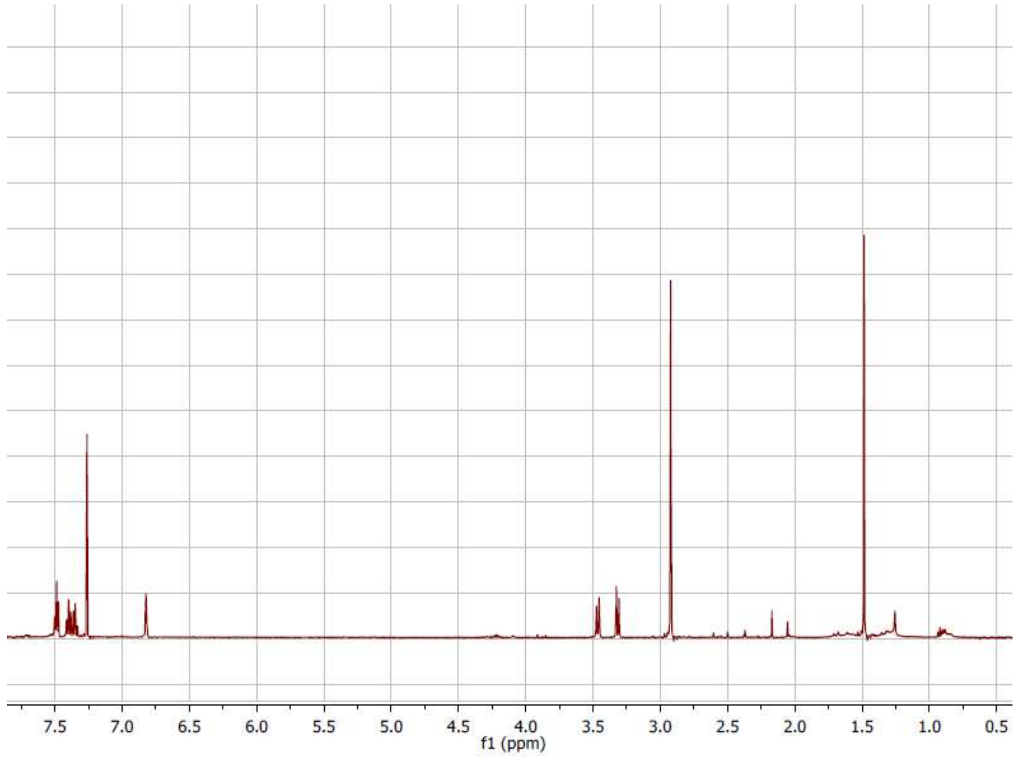
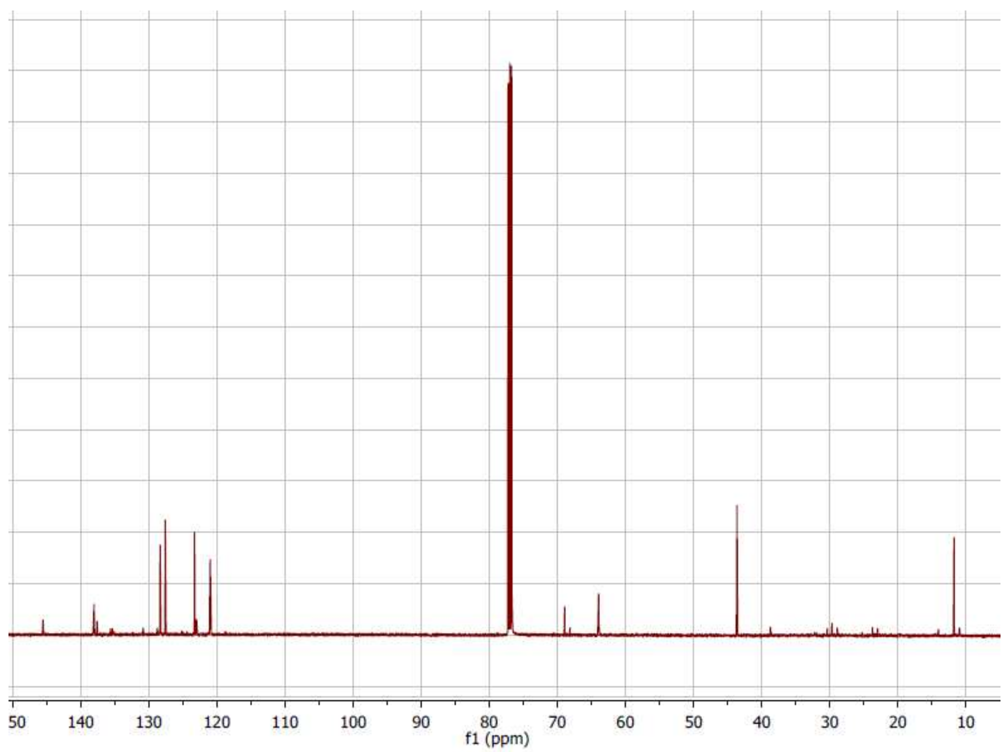
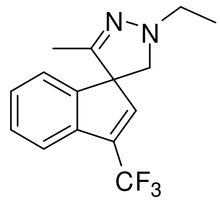


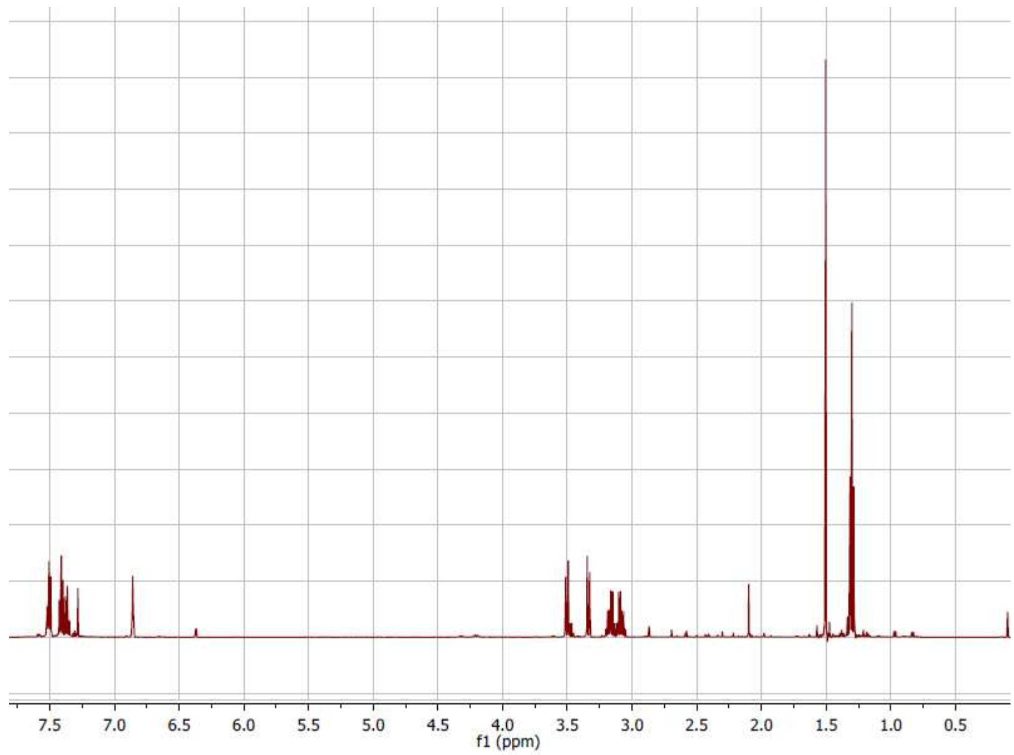


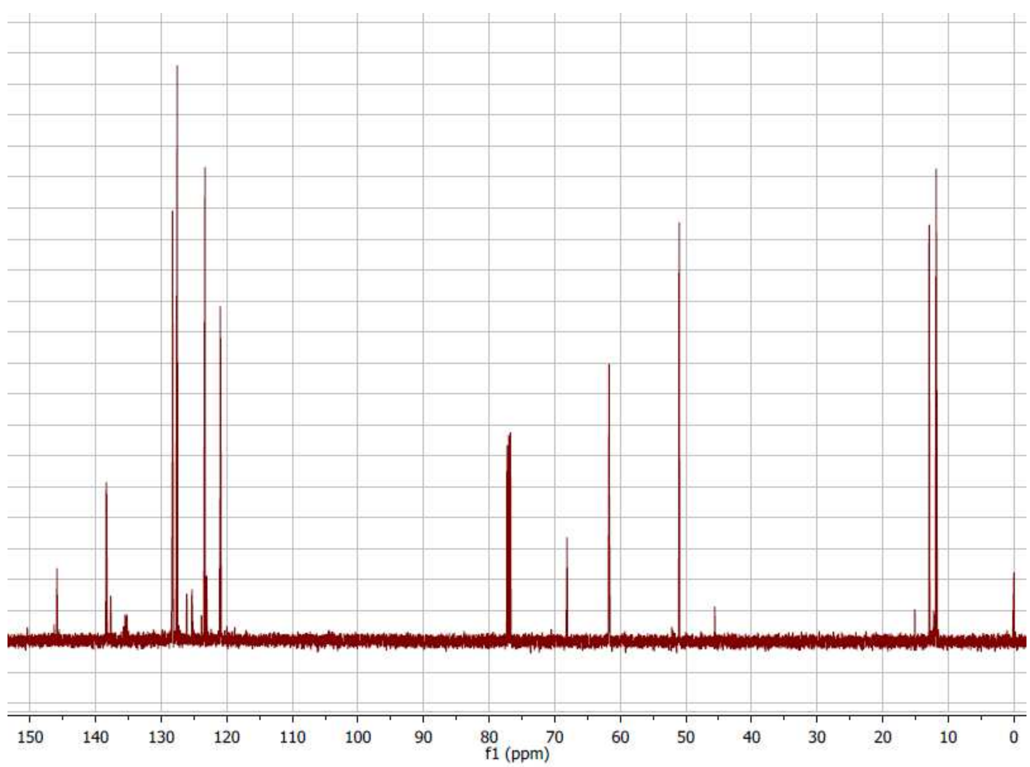
[1]H and [13]C Spectra of  **5a**

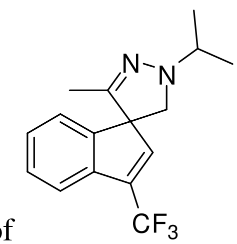




[1]H and [13]C Spectra of  **5b**





^{1}H and ^{13}C Spectra of 

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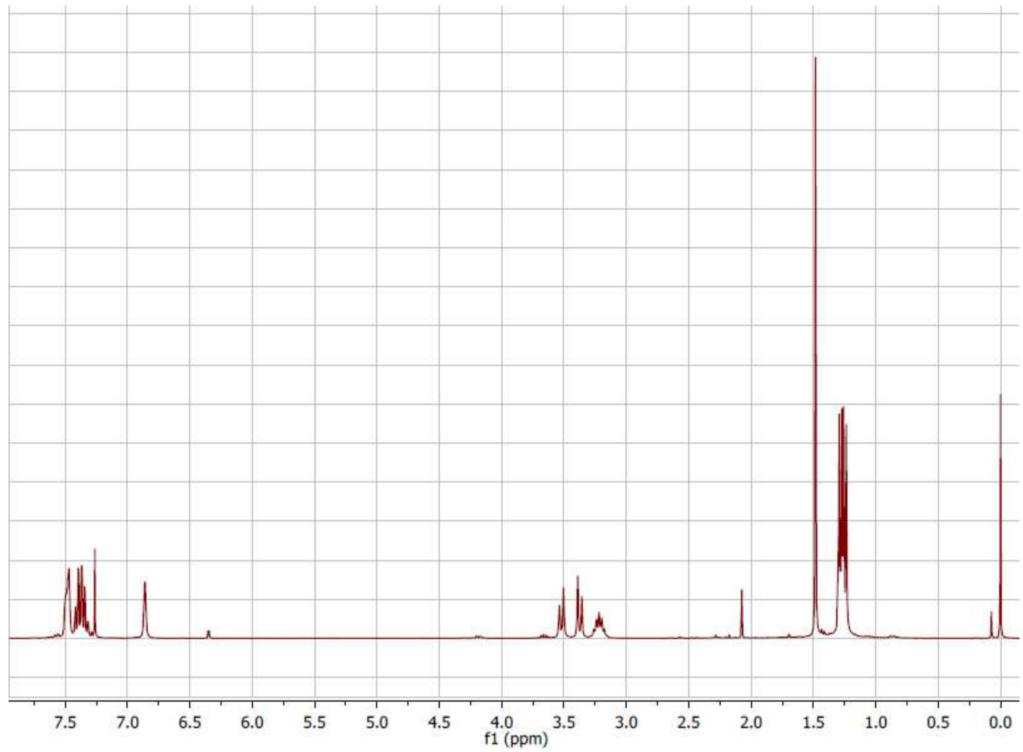
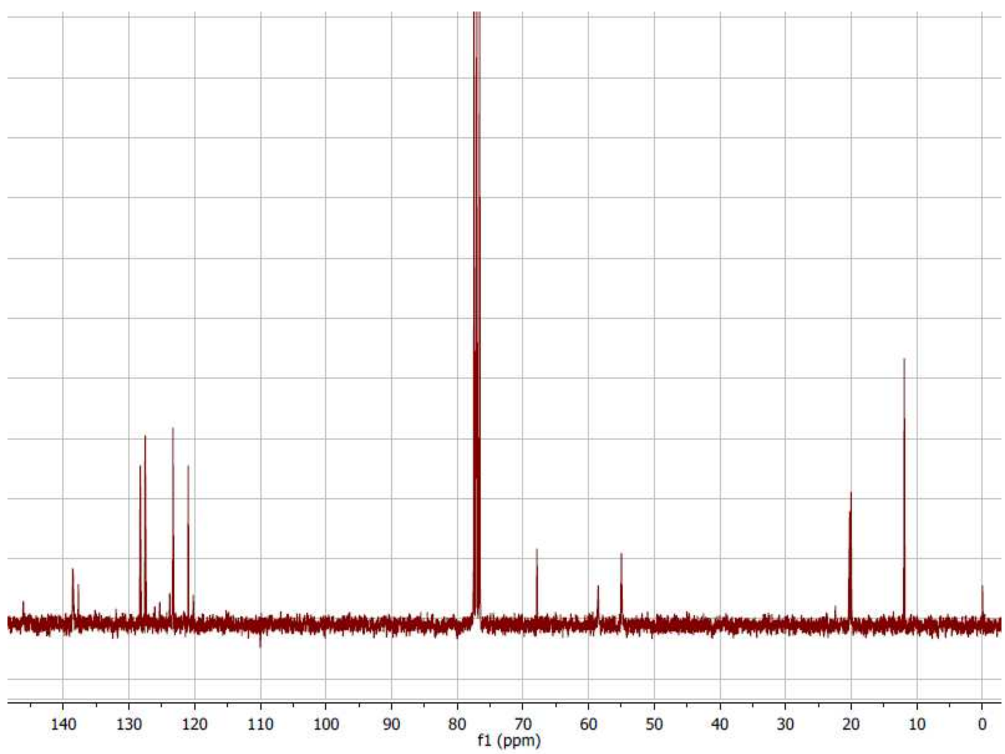
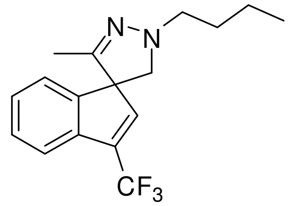
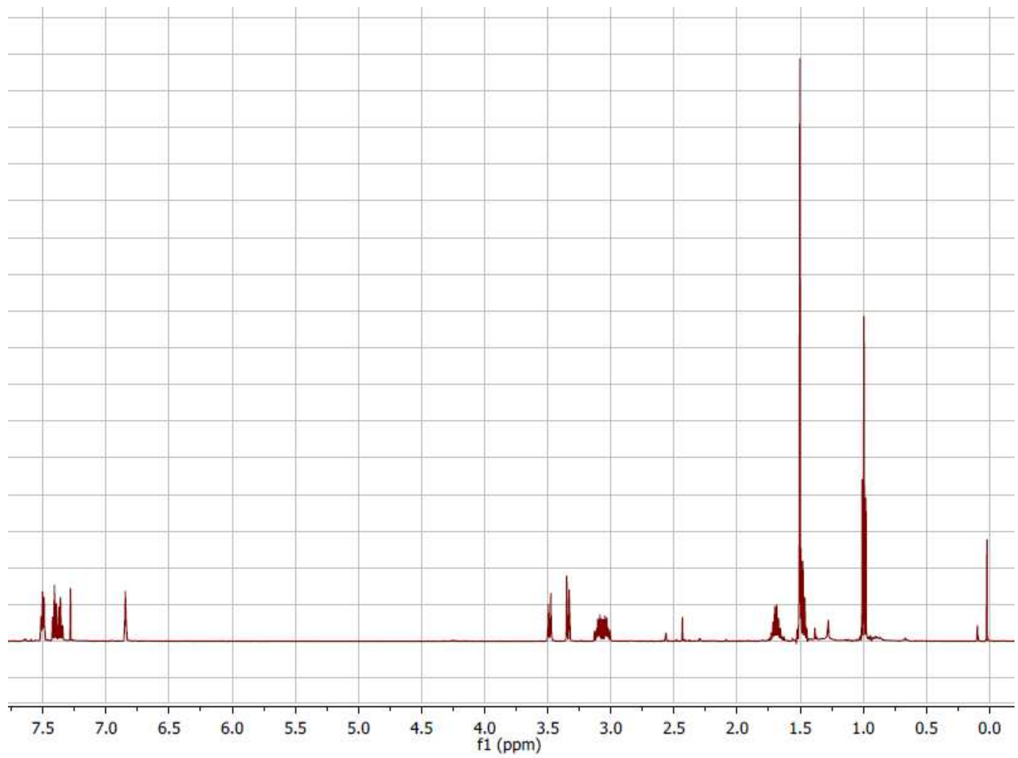
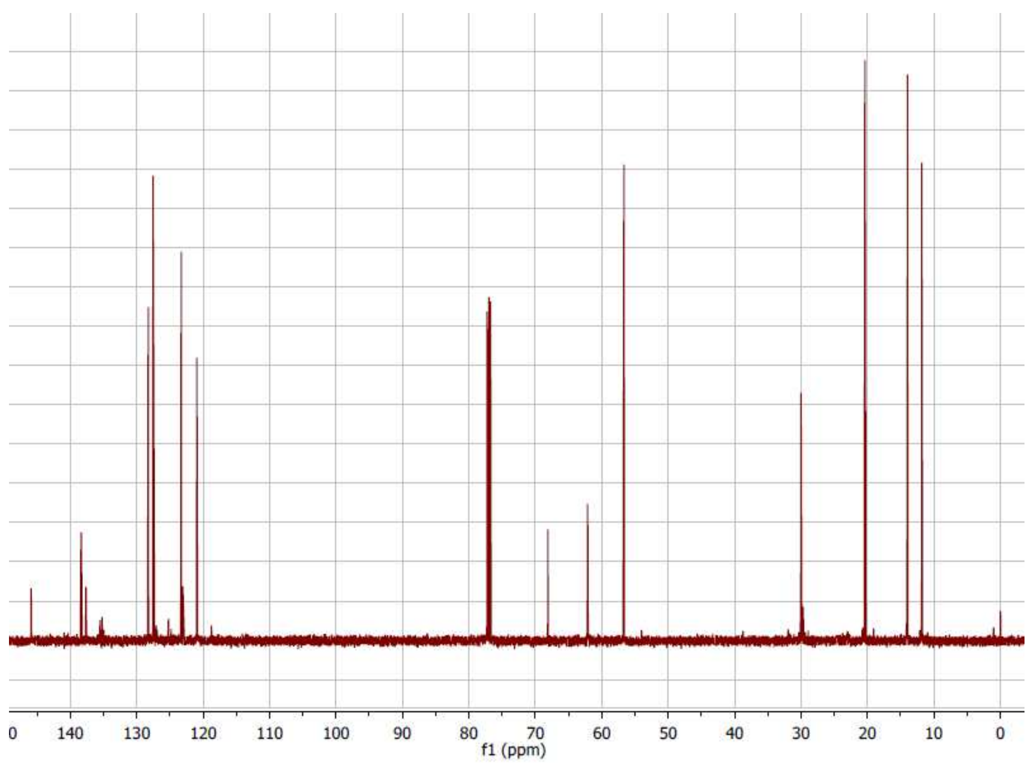
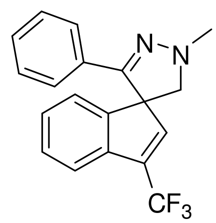


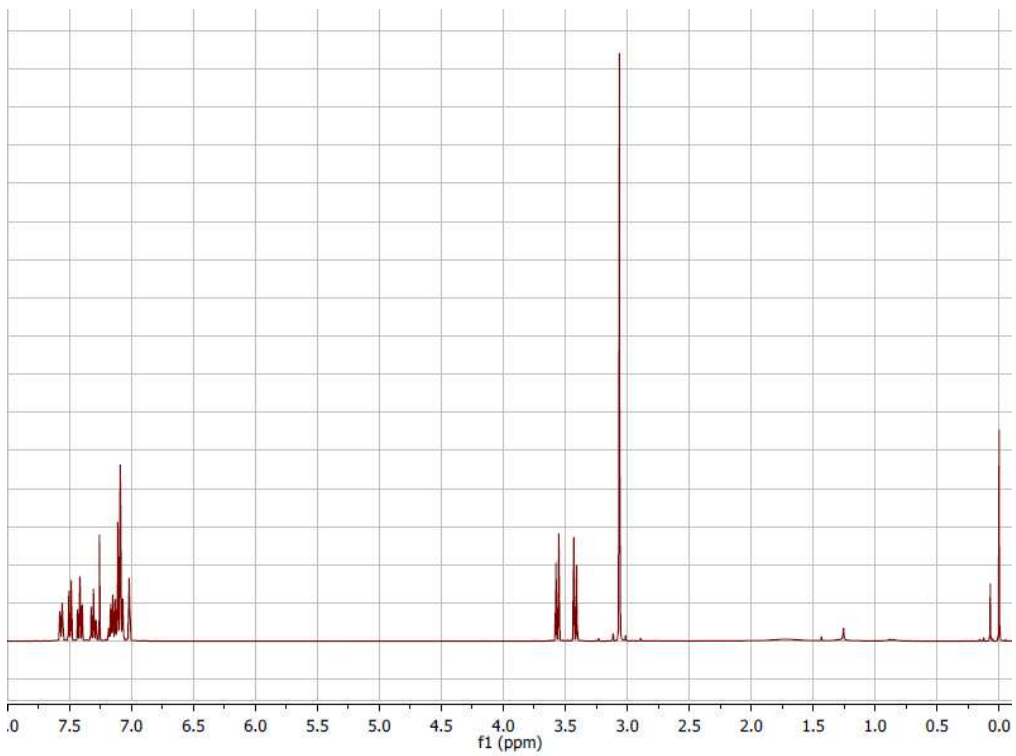


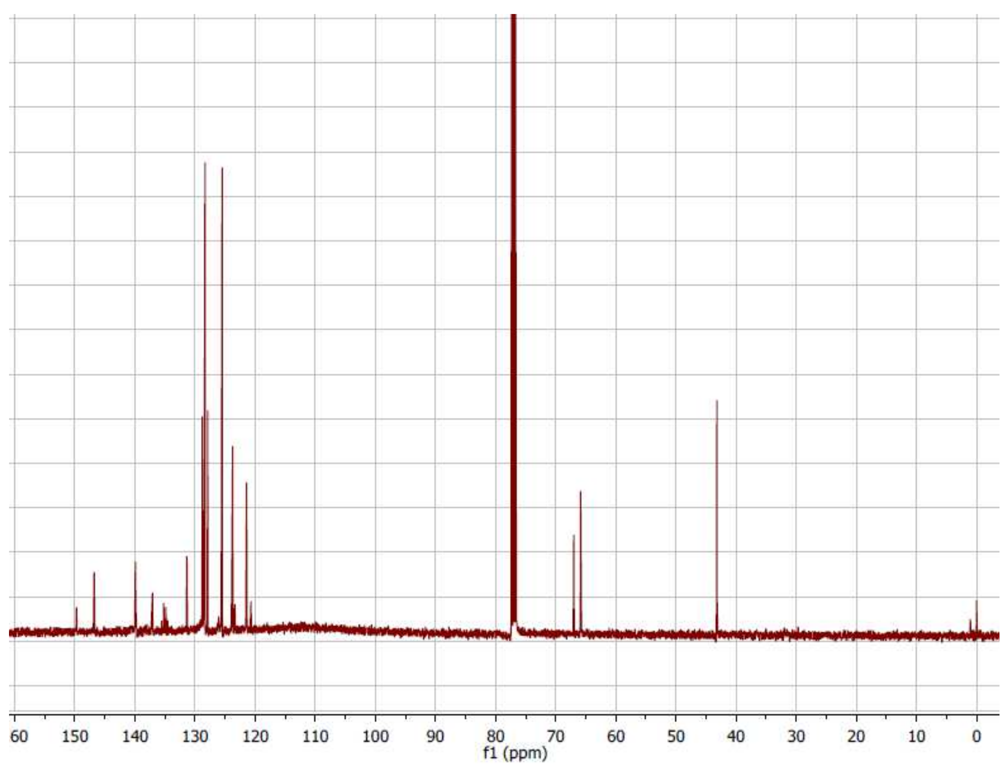
[1]H and [13]C Spectra of  **5d**

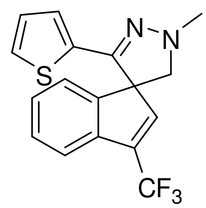




[1]H and [13]C Spectra of  **5e**





^{1}H and ^{13}C Spectra of 

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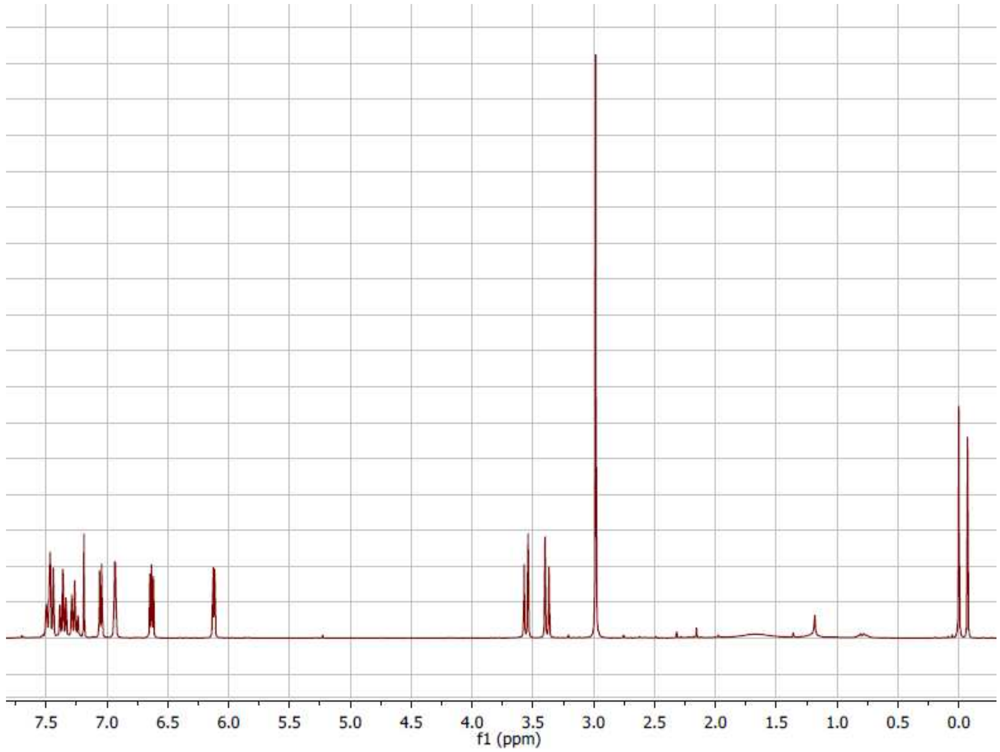
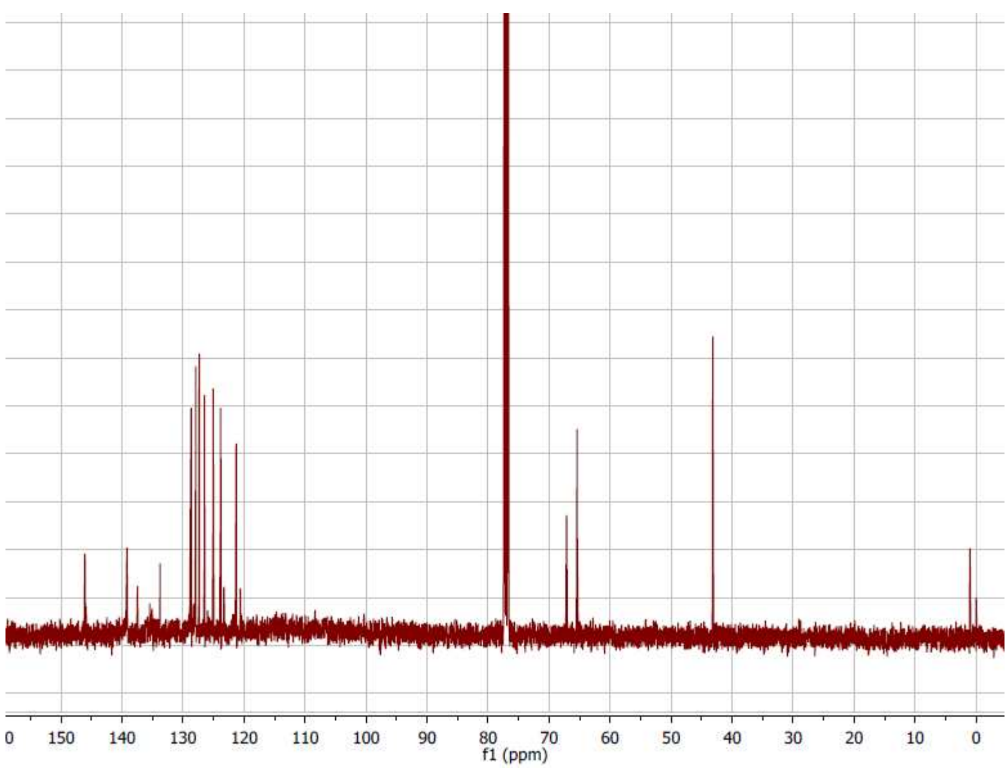
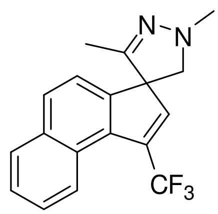




^{1}H and ^{13}C Spectra of 

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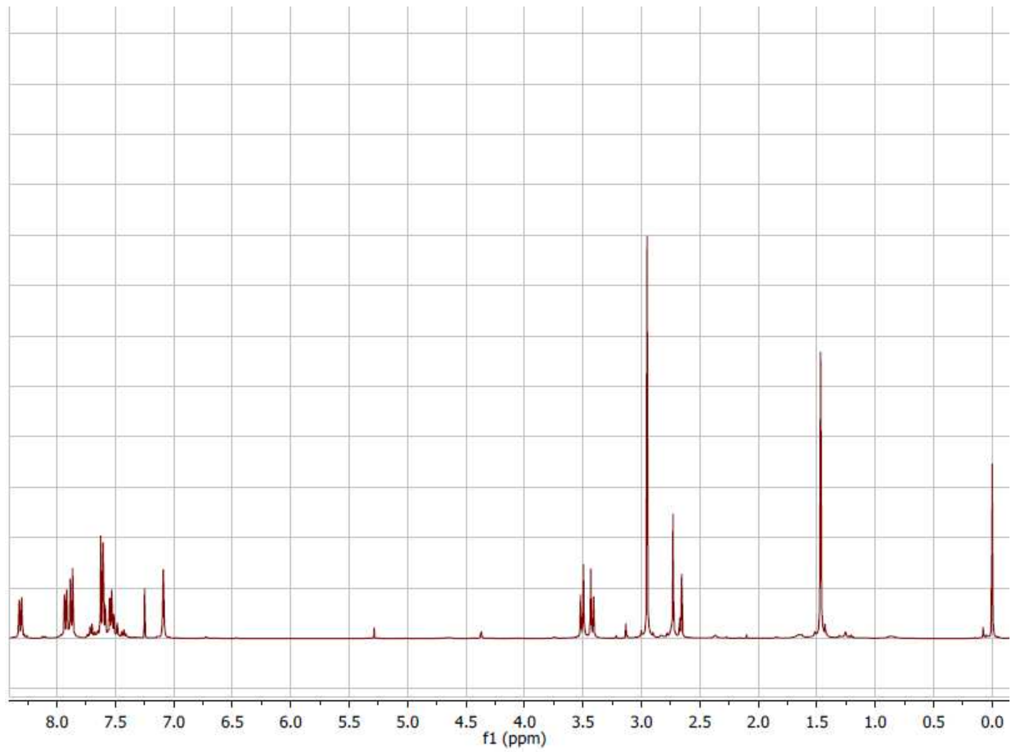
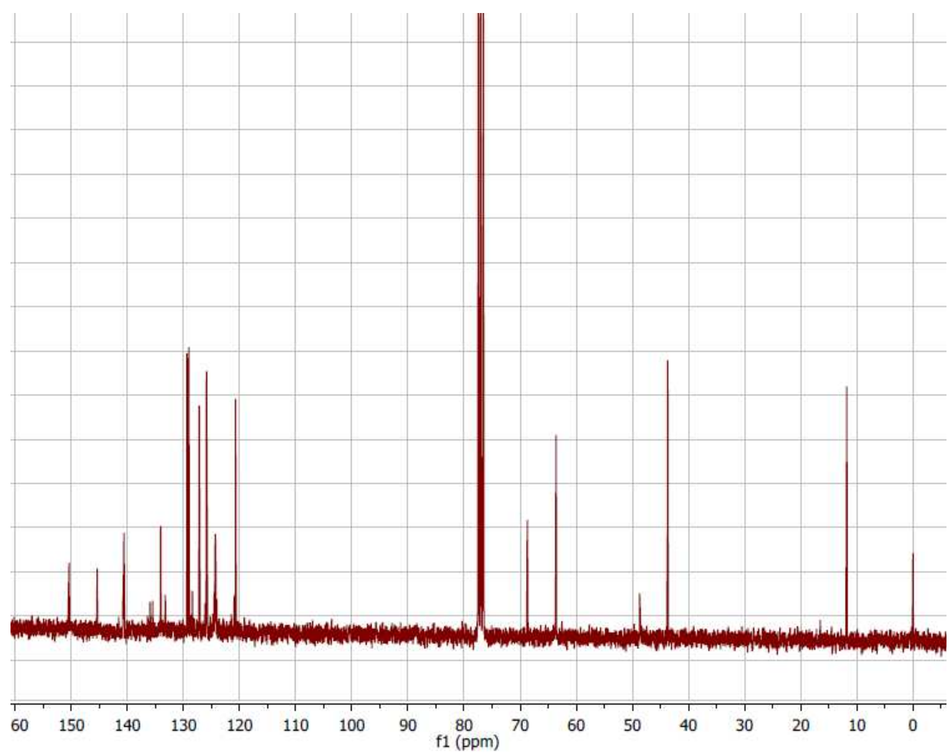
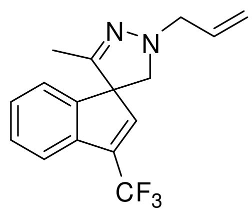




^{1}H and ^{13}C Spectra of 

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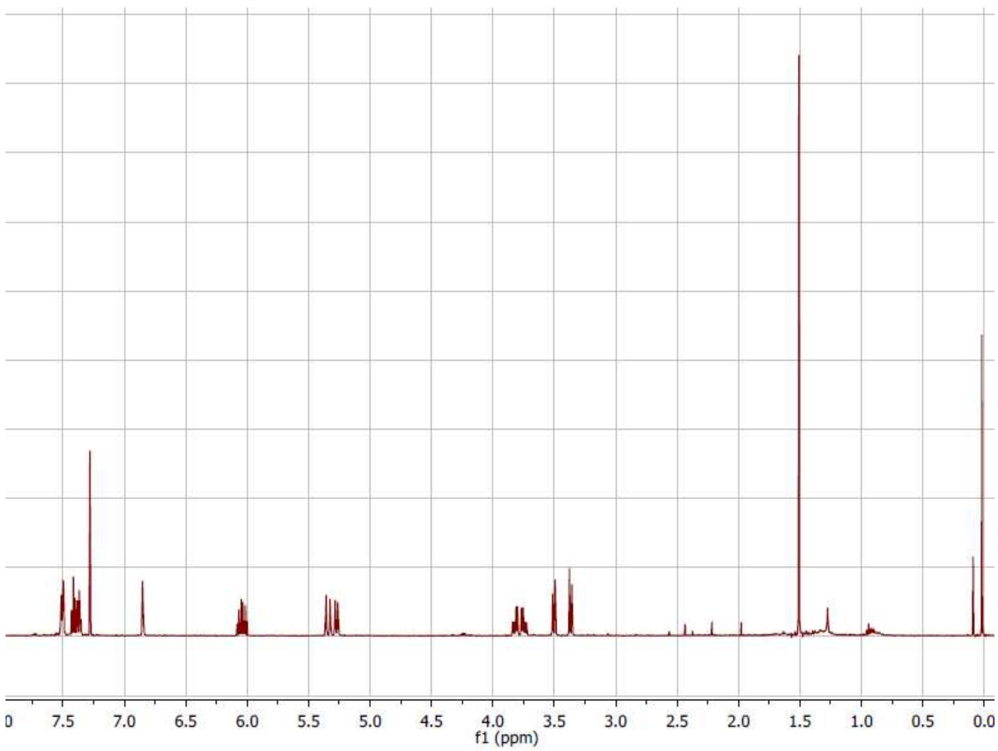
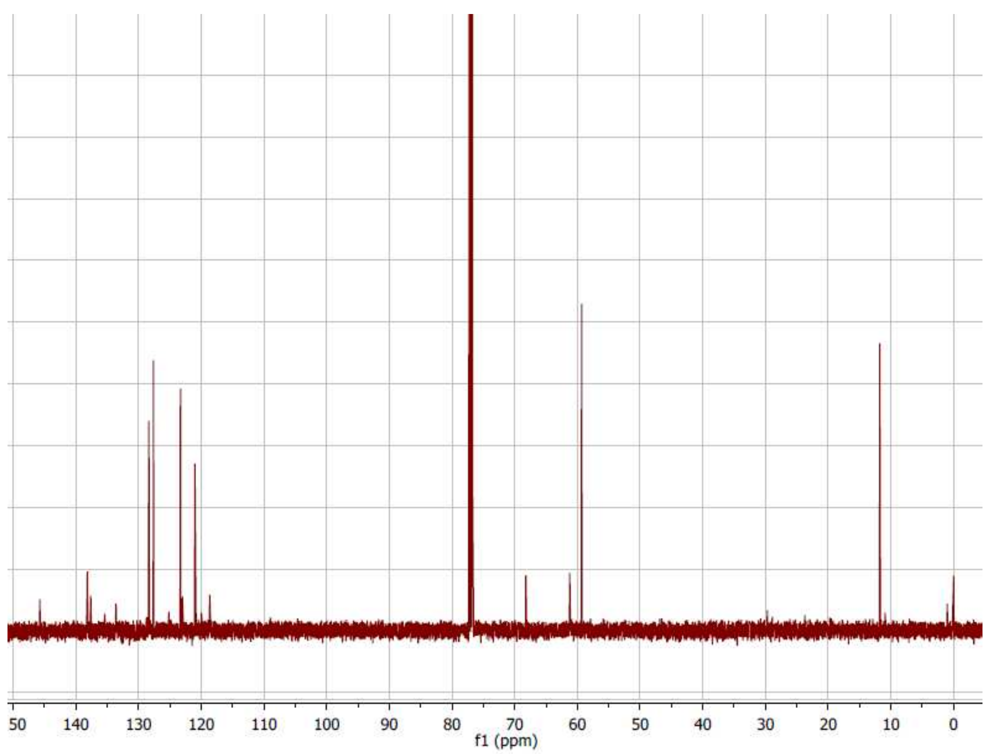
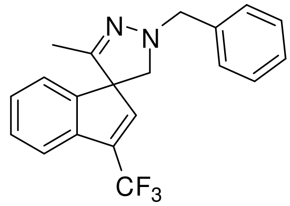
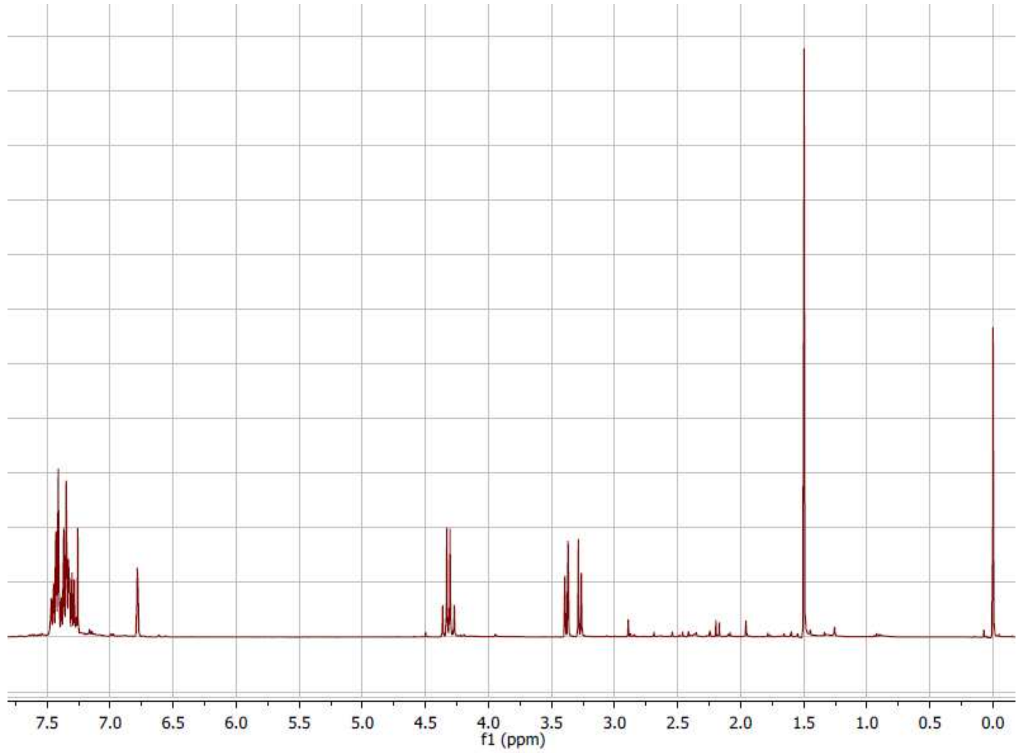
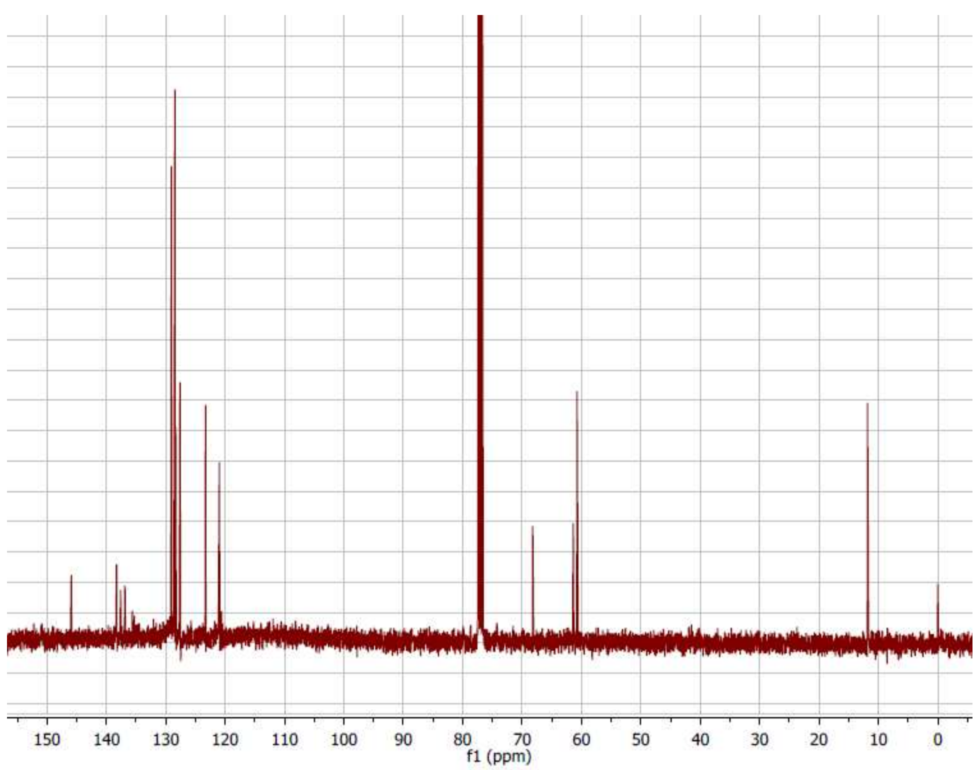
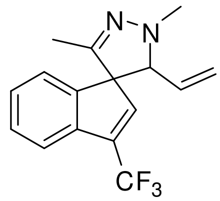


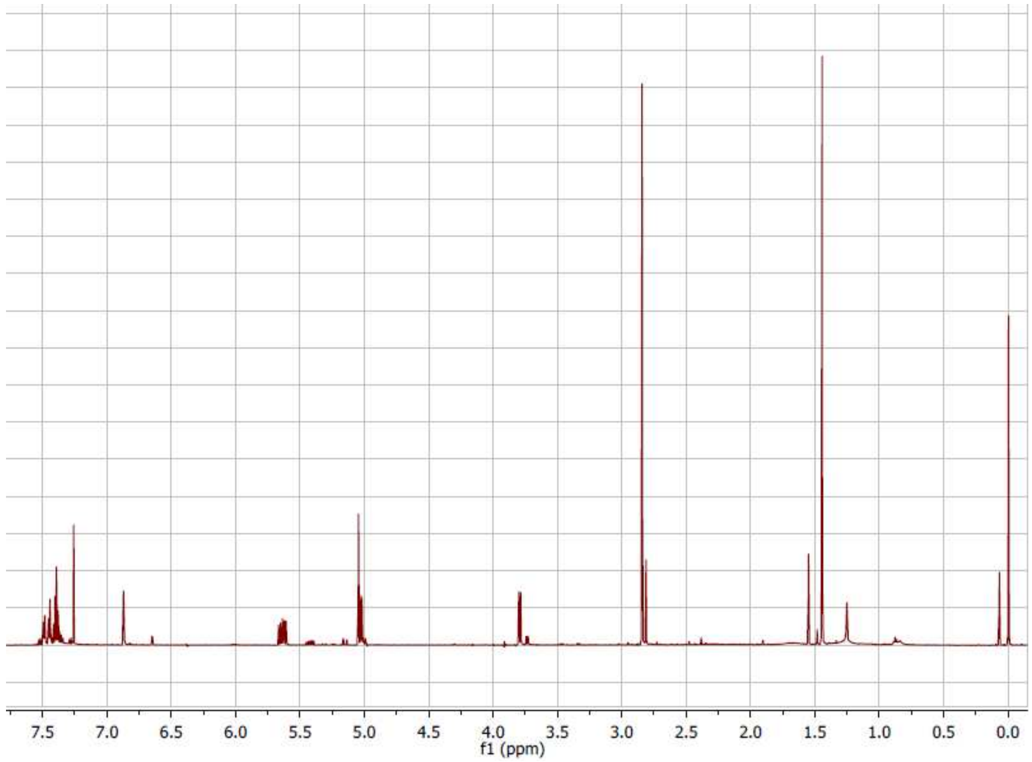


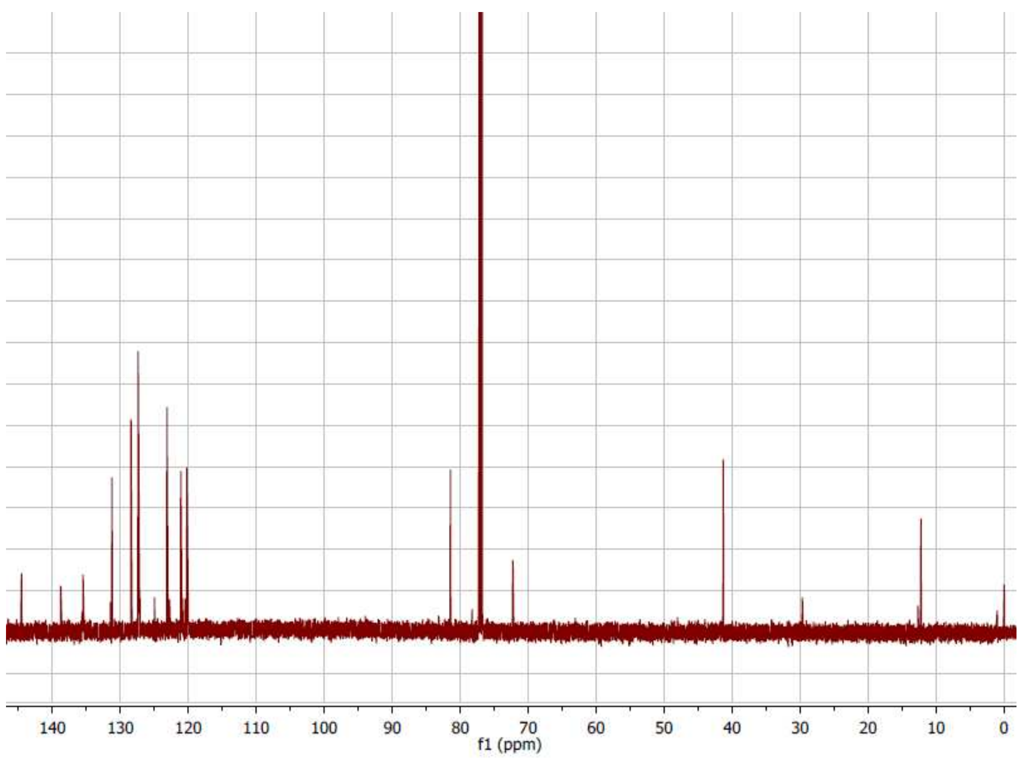
[1]H and [13]C Spectra of  **5i**

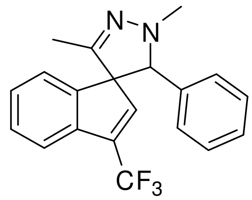




^1H and ^{13}C Spectra of  **5j**





^{1}H and ^{13}C Spectra of 

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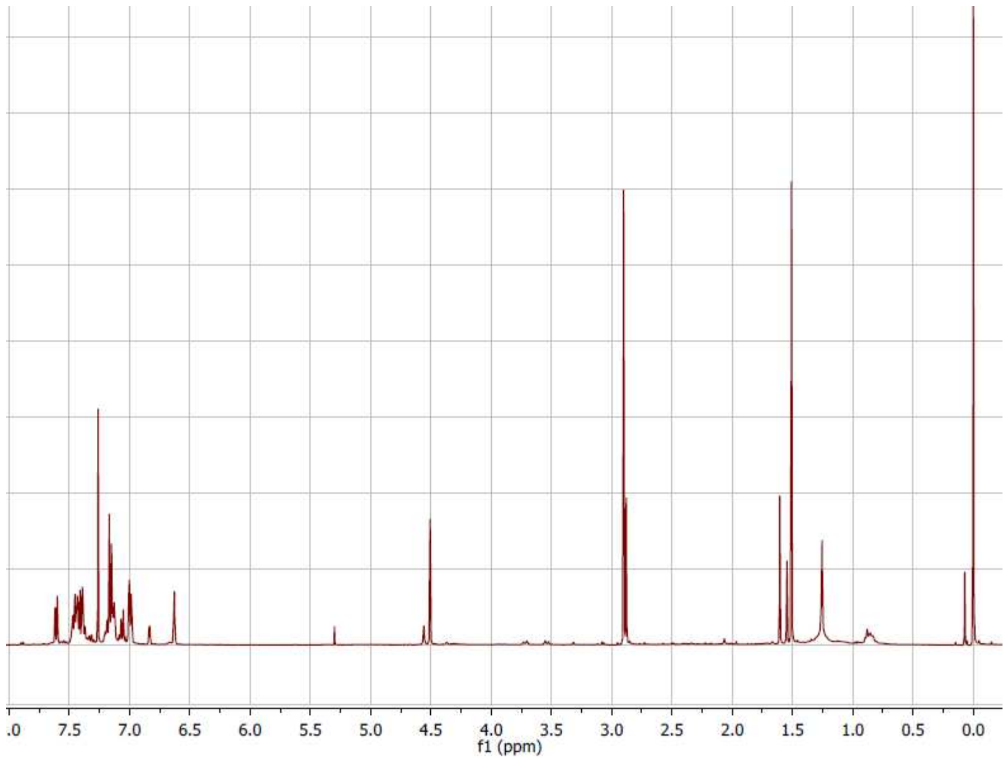
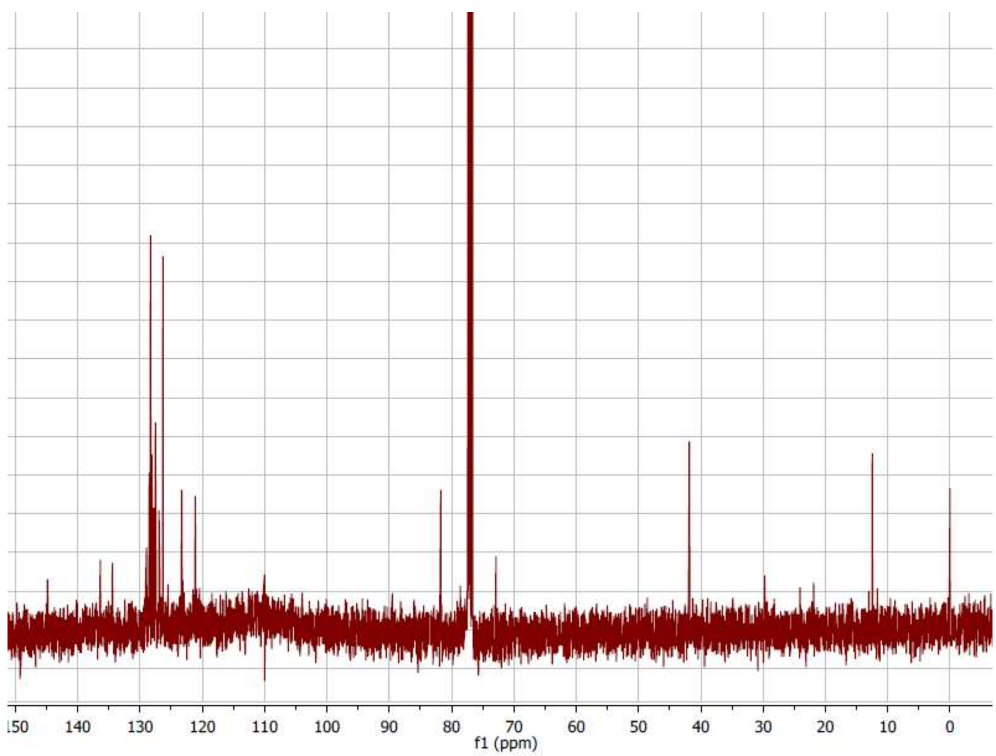
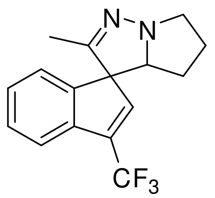




^{1}H and ^{13}C Spectra of 

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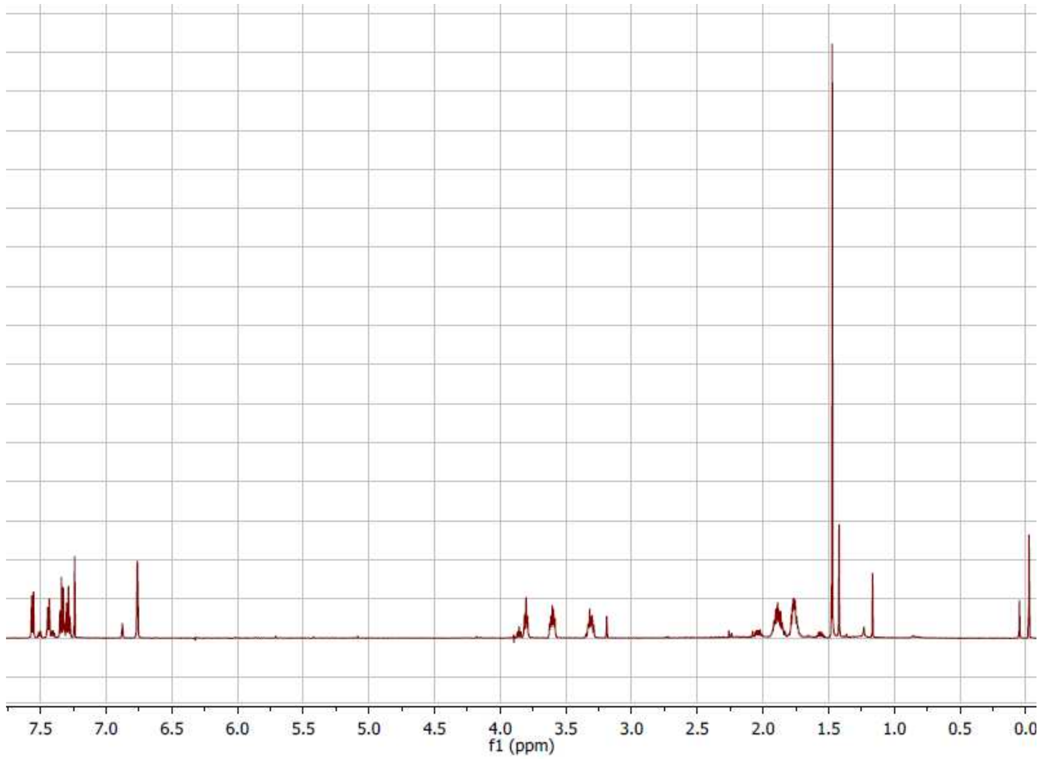
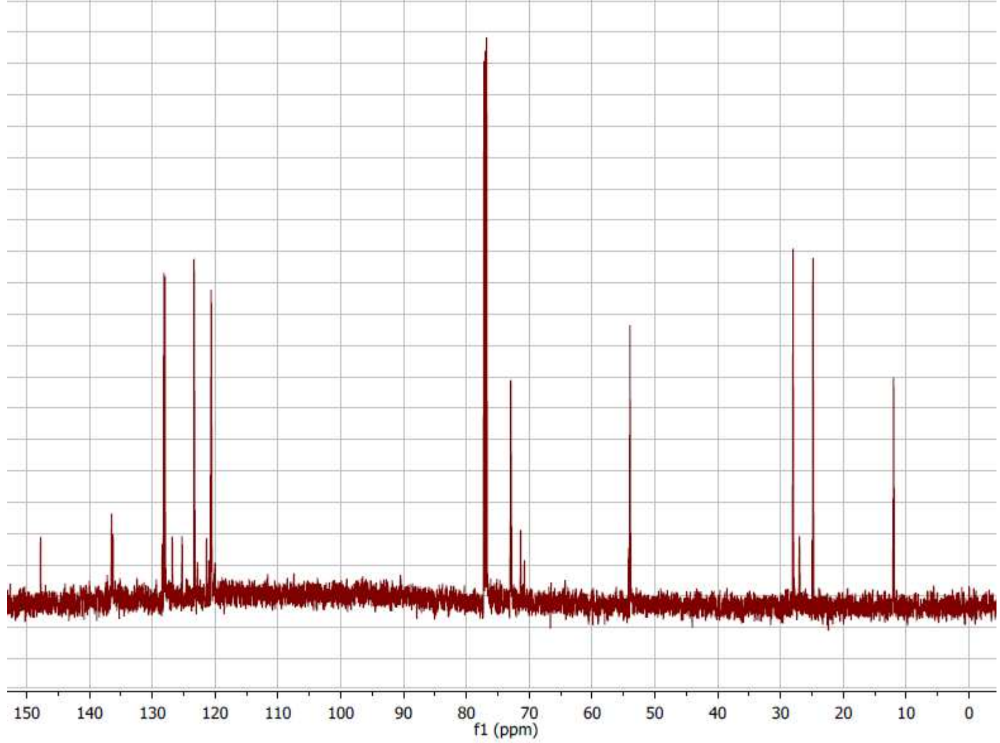
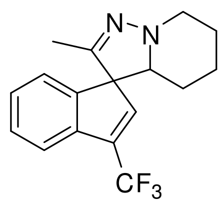
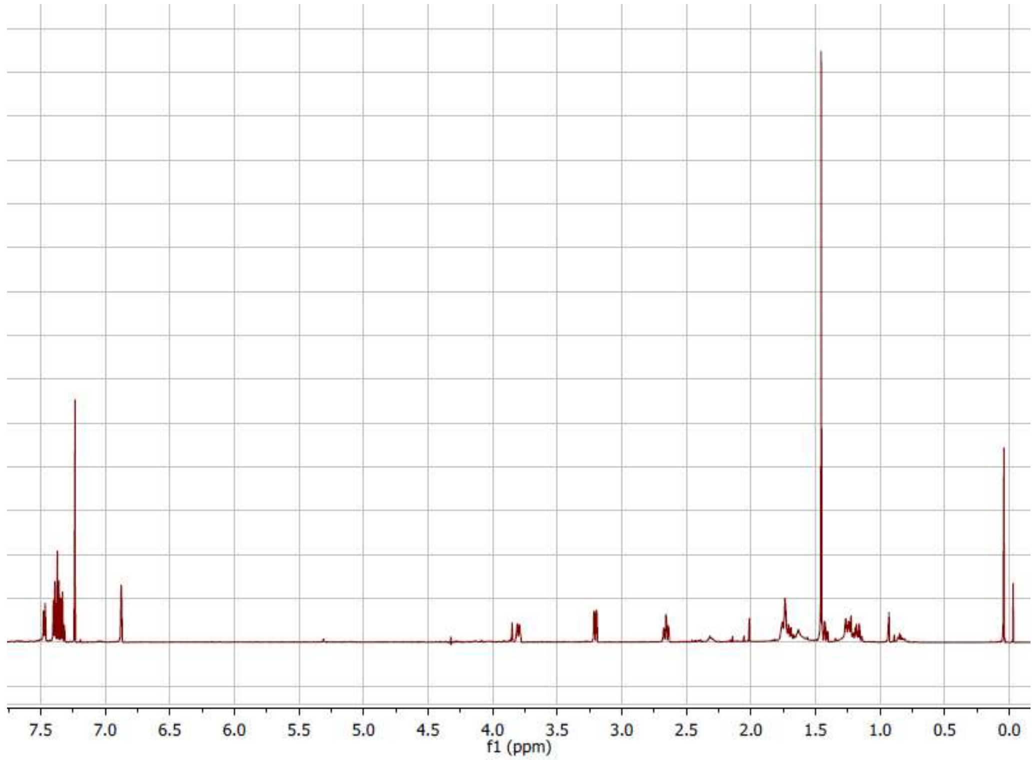
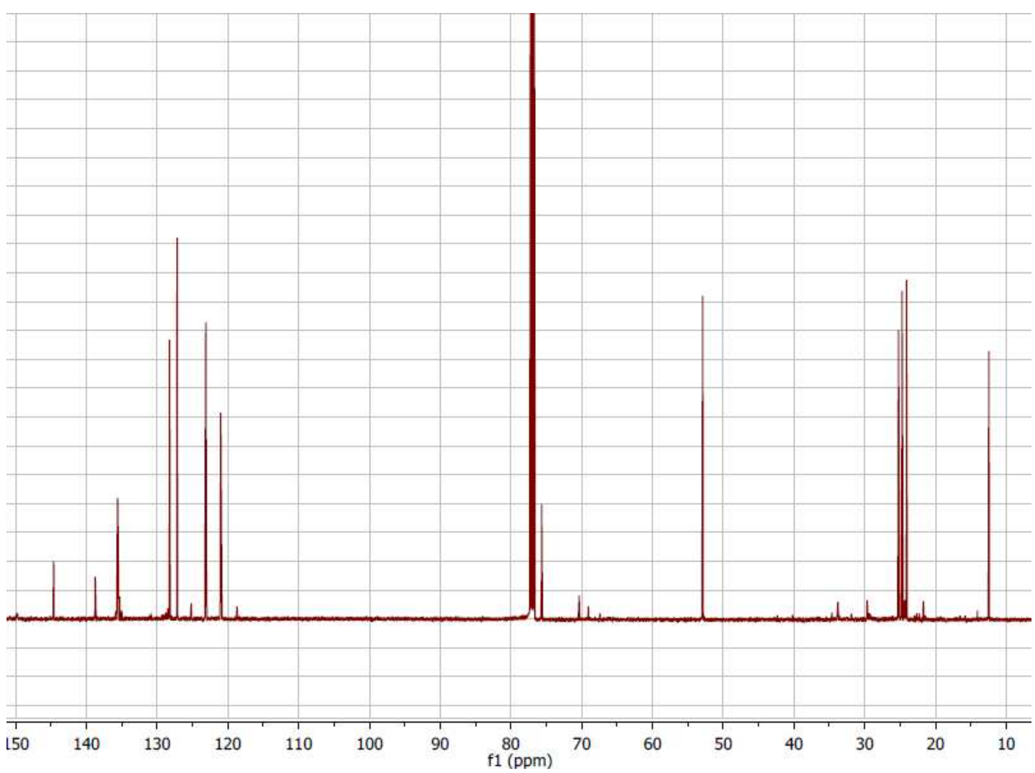
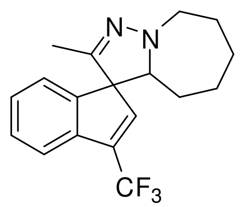


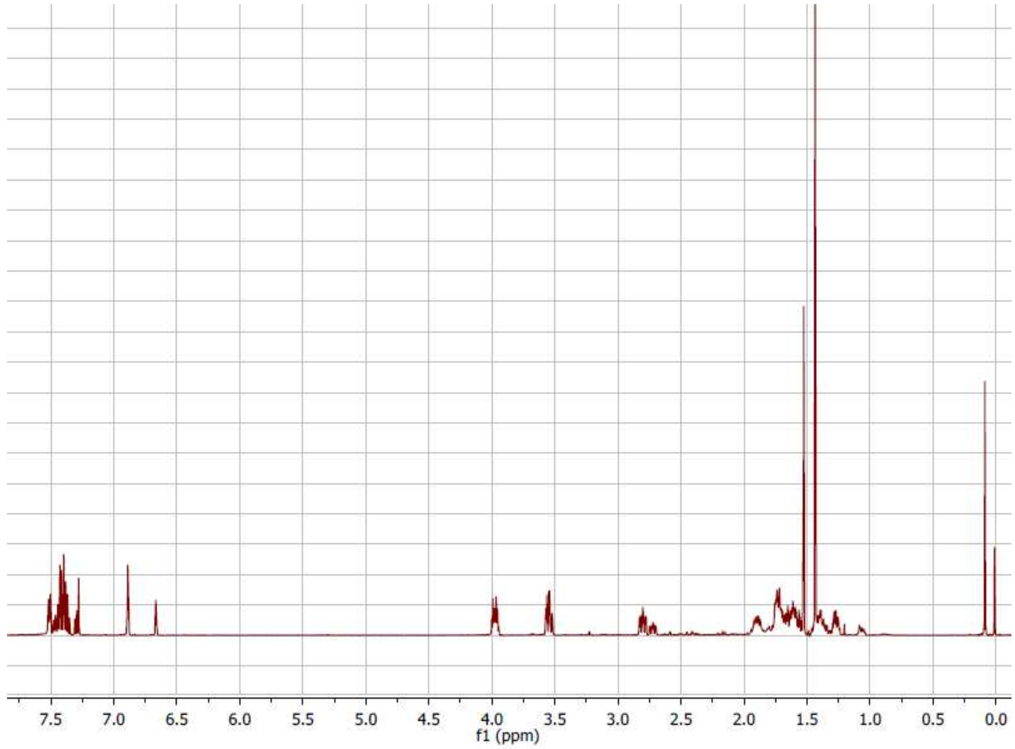


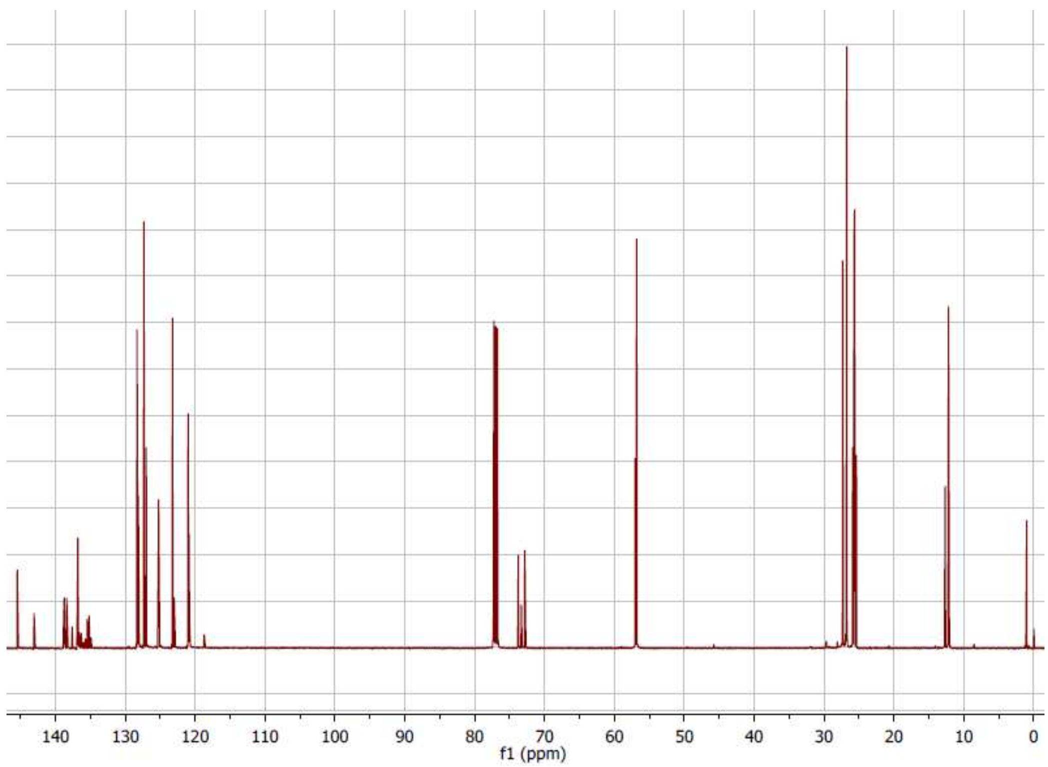
[1]H and [13]C Spectra of  **5m**

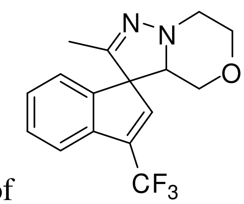




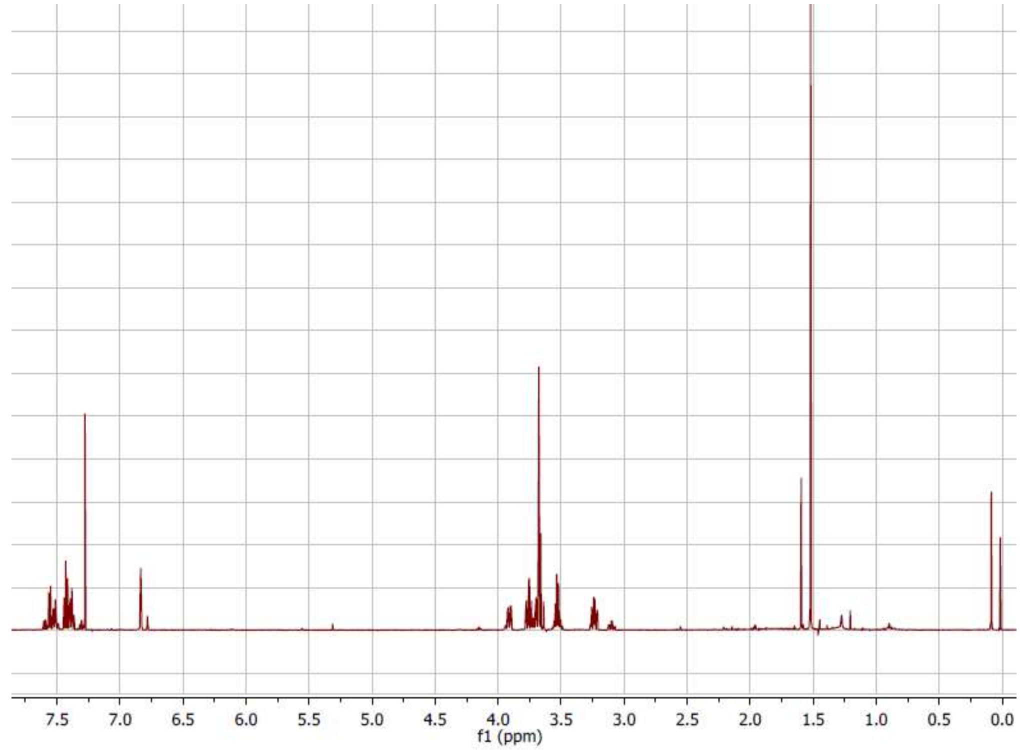
^{1}H and ^{13}C Spectra of  **5n**

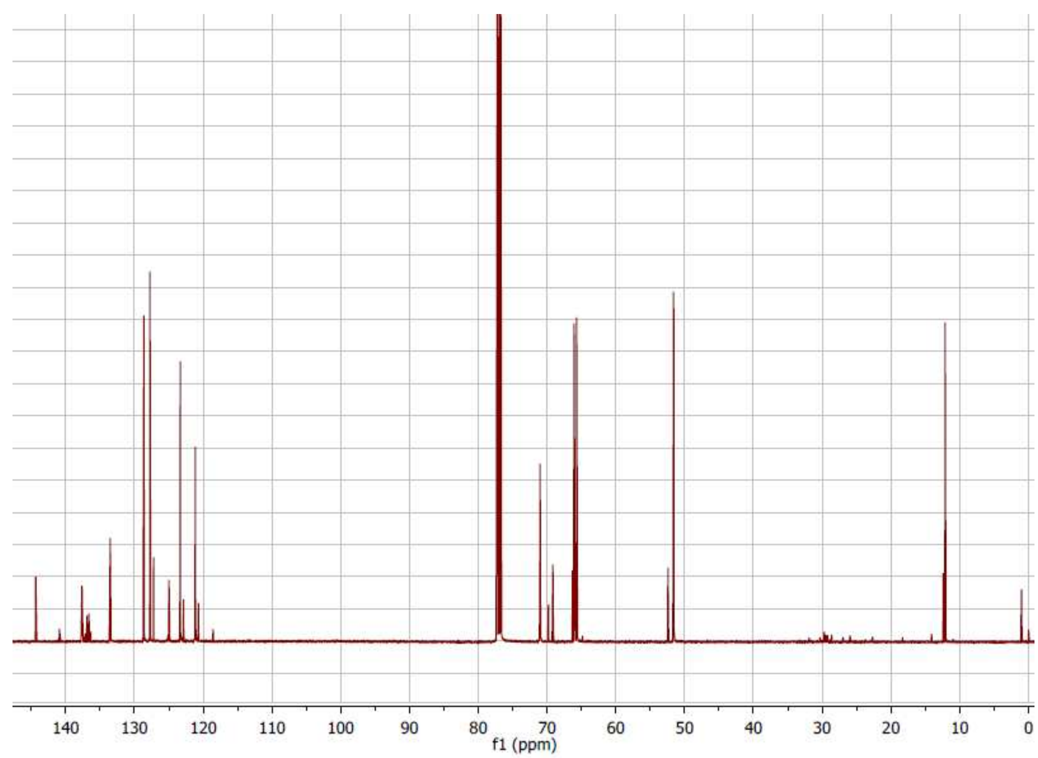


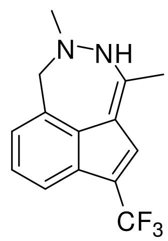


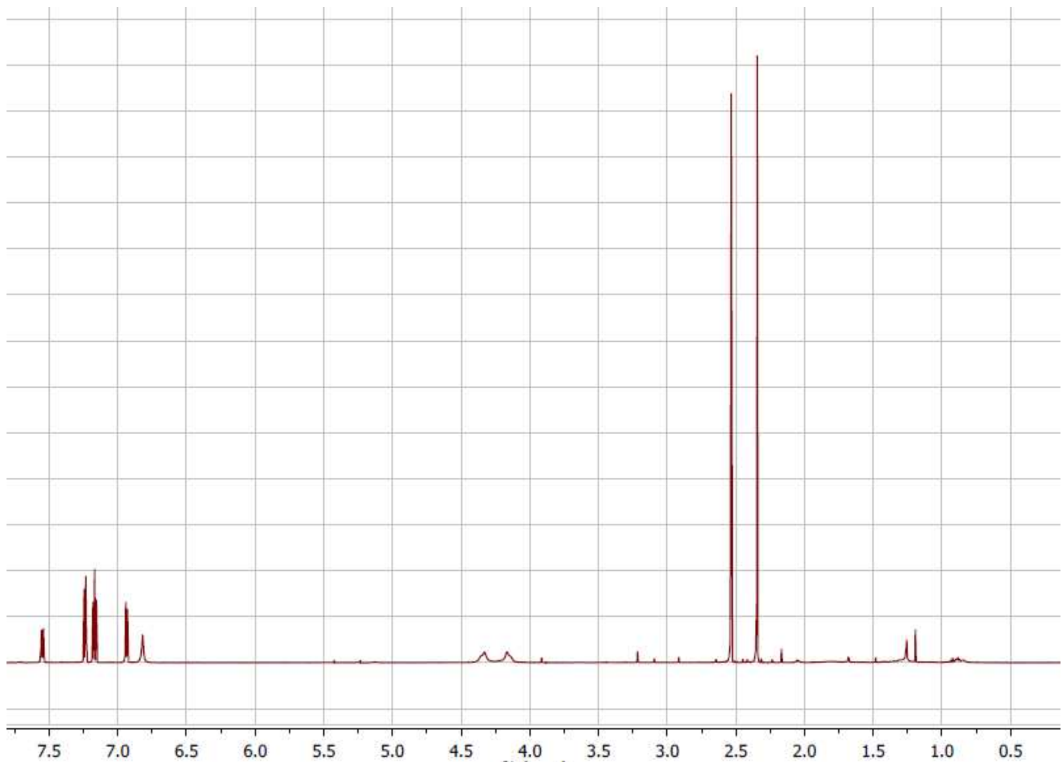
^{1}H and ^{13}C Spectra of 

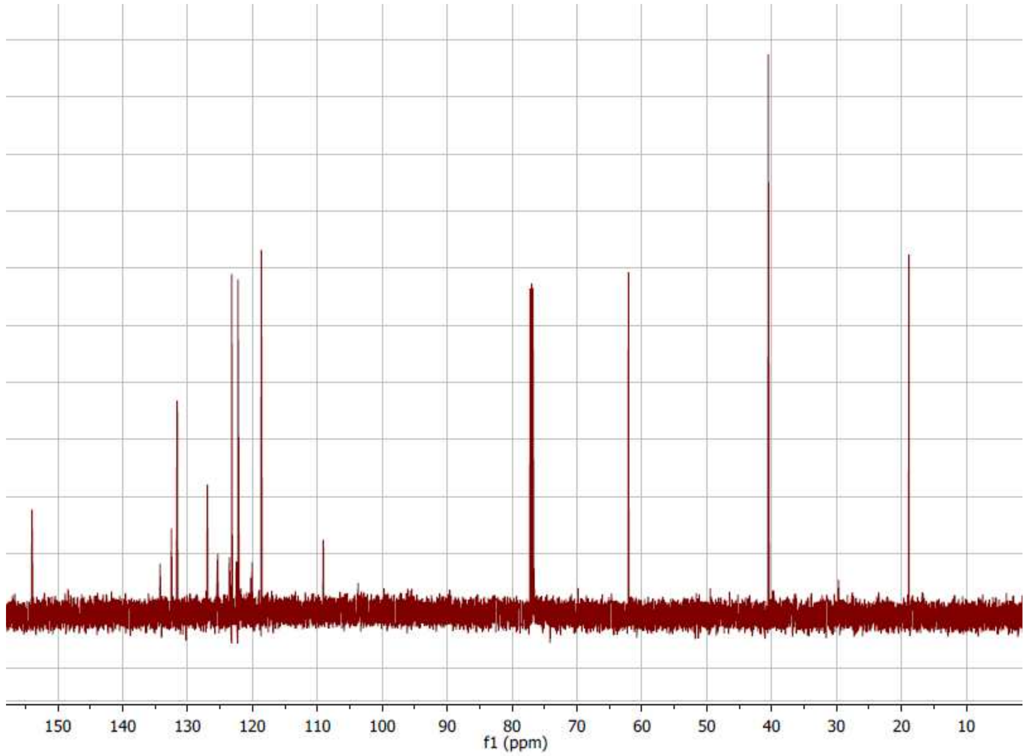
5o

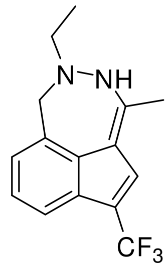


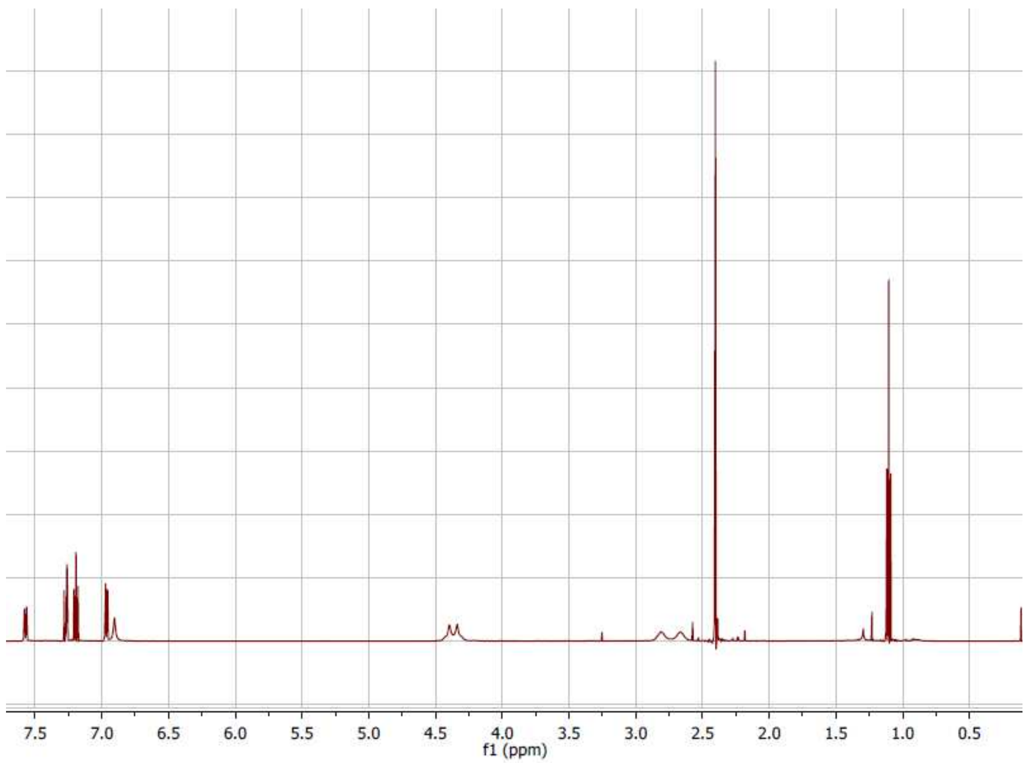


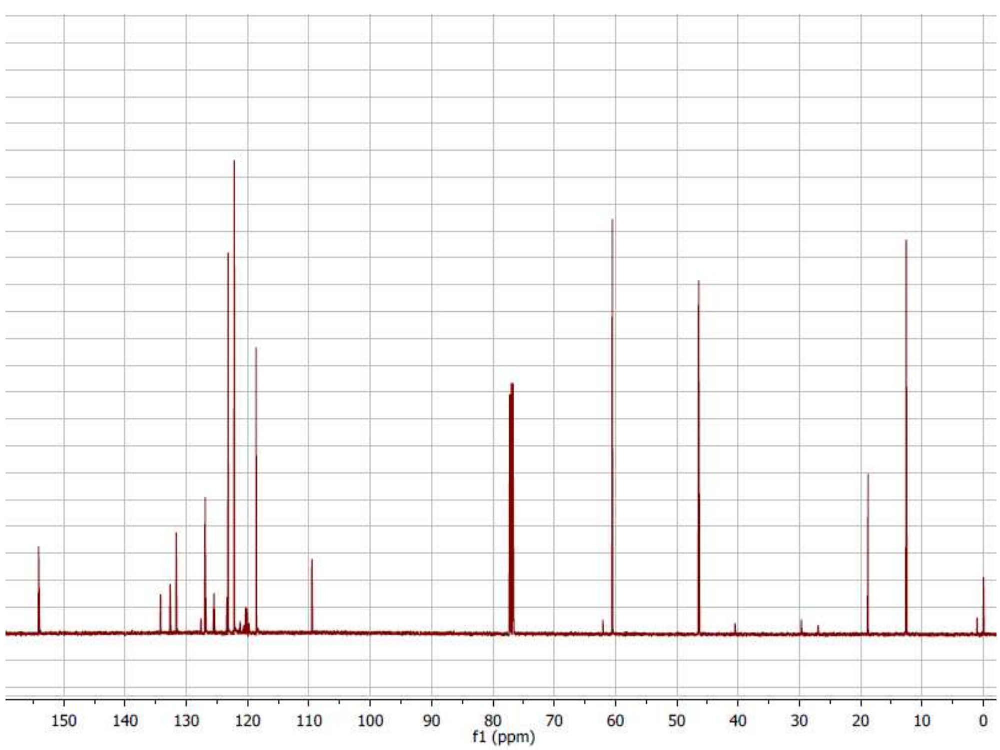
[1]H and [13]C Spectra of  **6a**

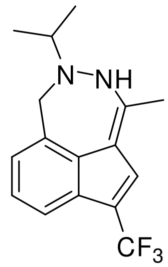


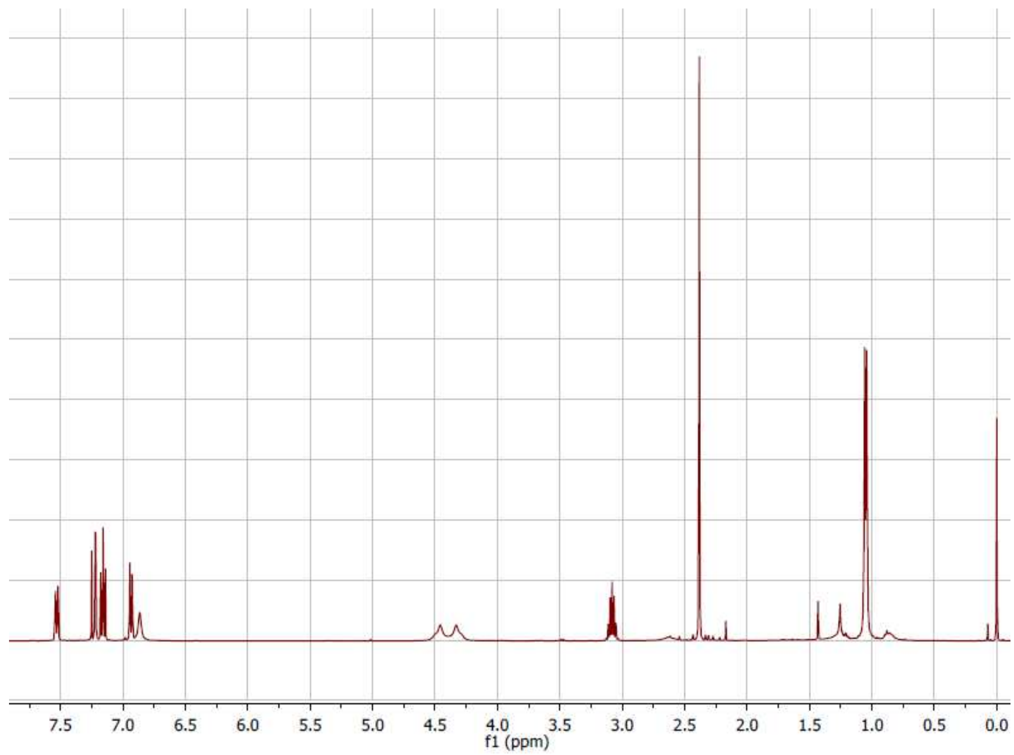


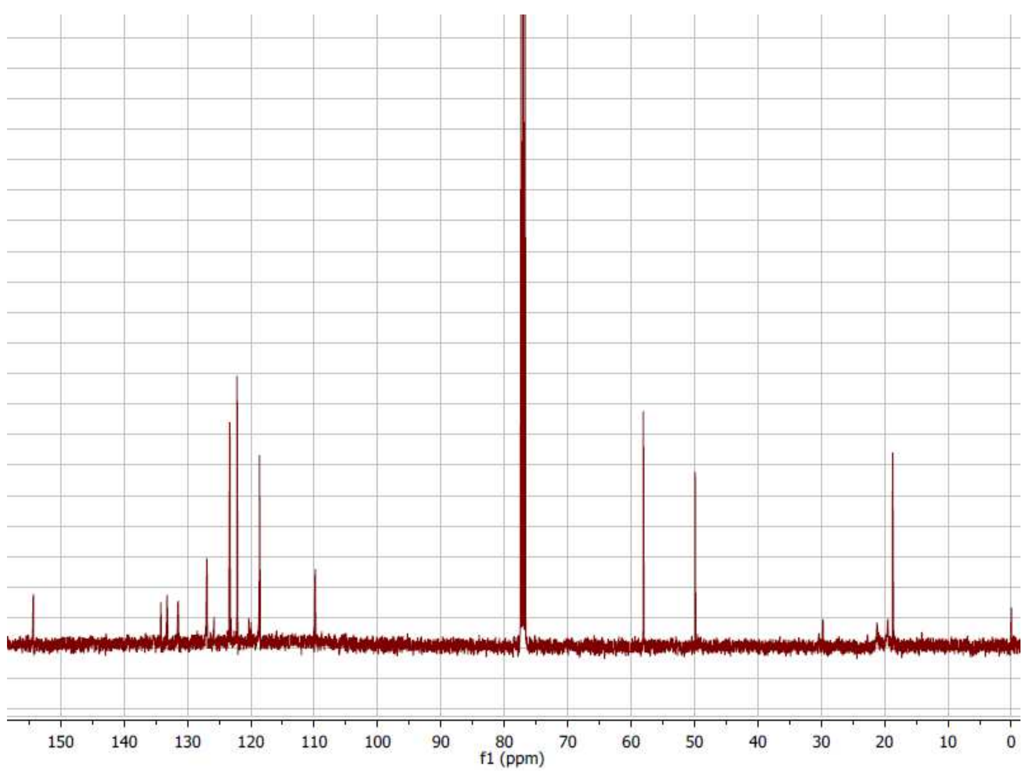
^{1}H and ^{13}C Spectra of  **6b**

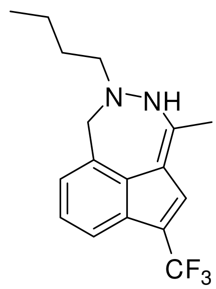


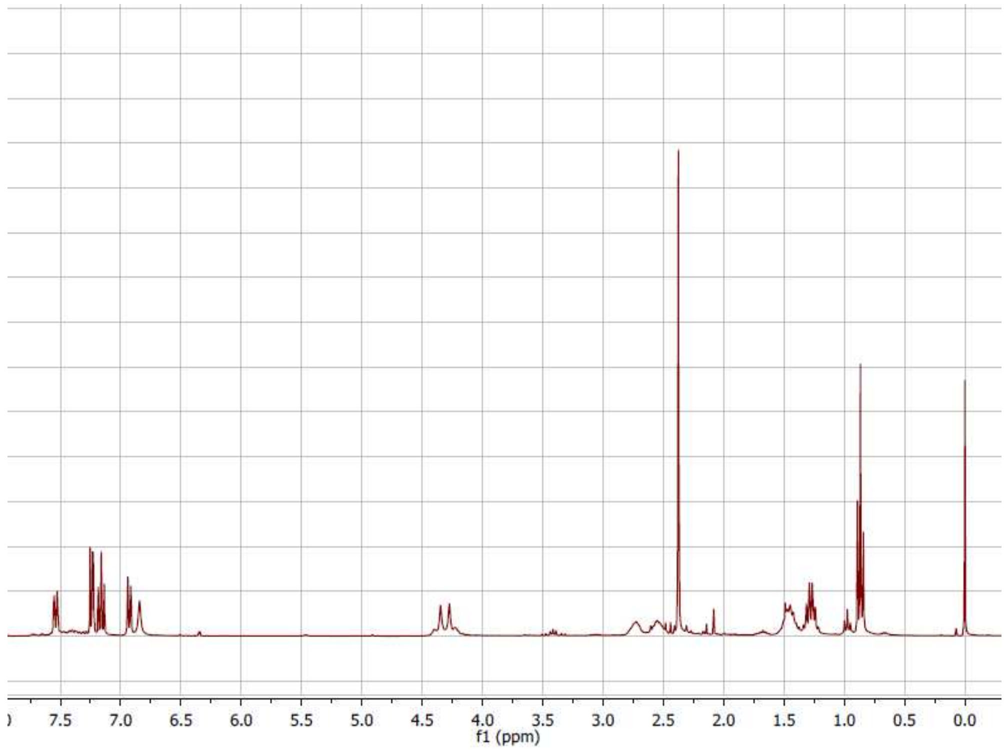


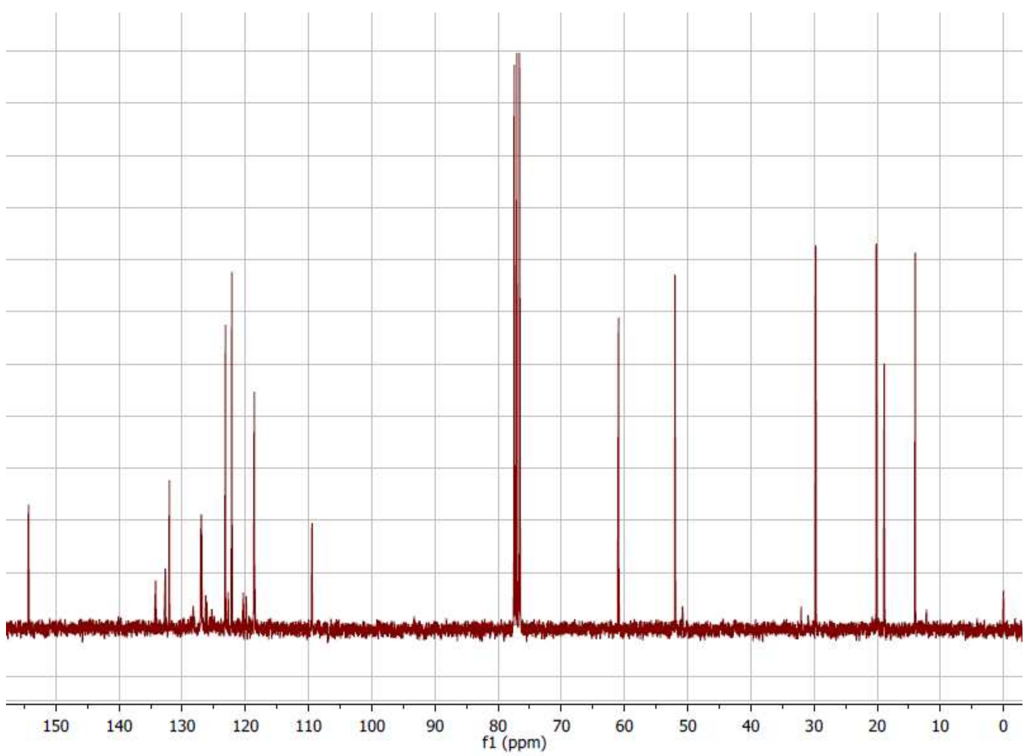
^{1}H and ^{13}C Spectra of  **6c**

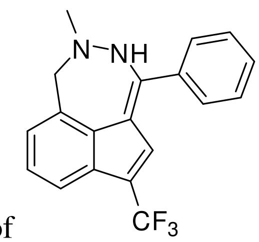


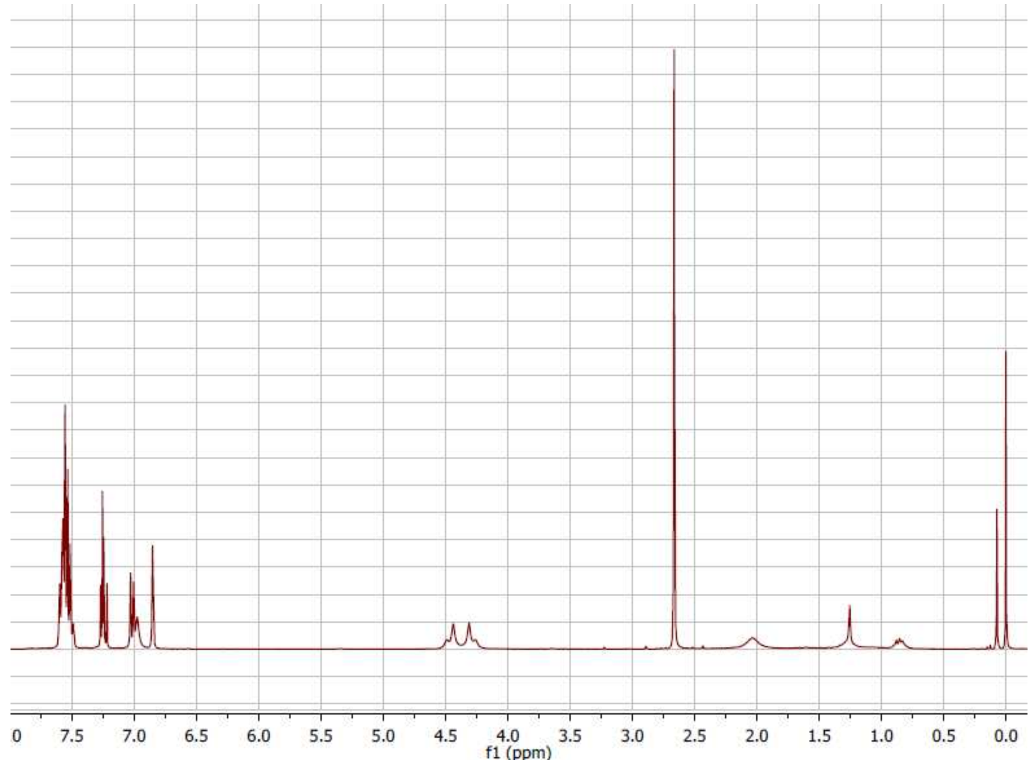


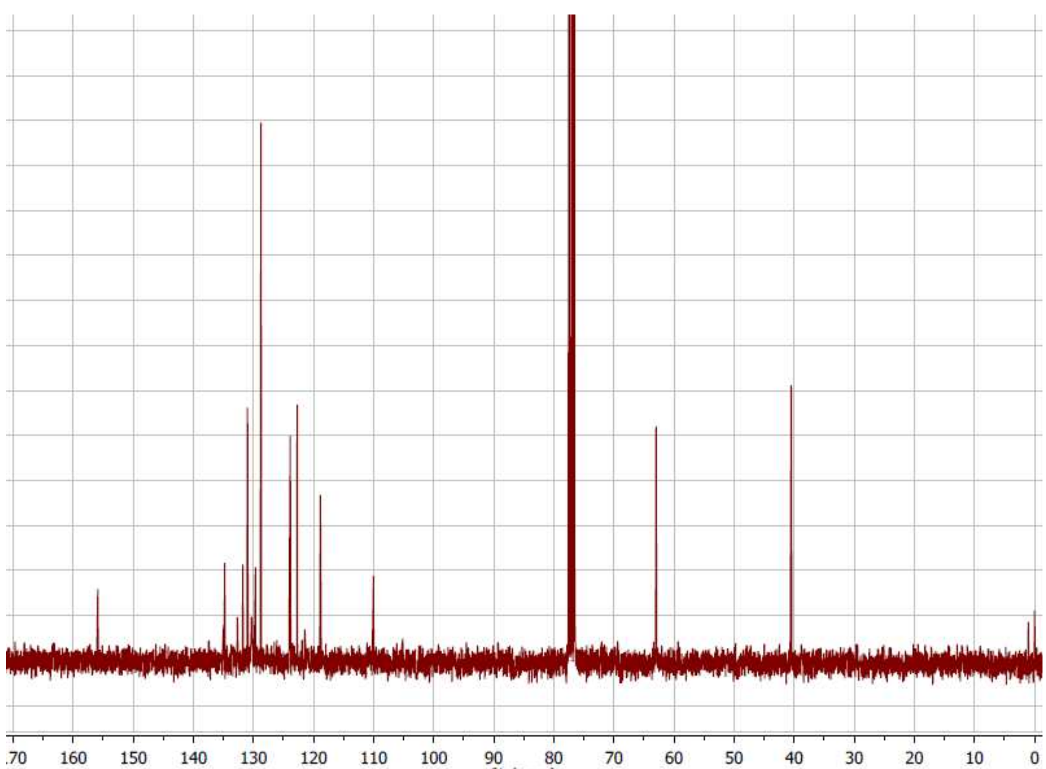
[1]H and [13]C Spectra of  **6d**

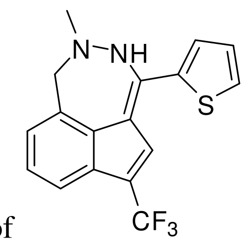


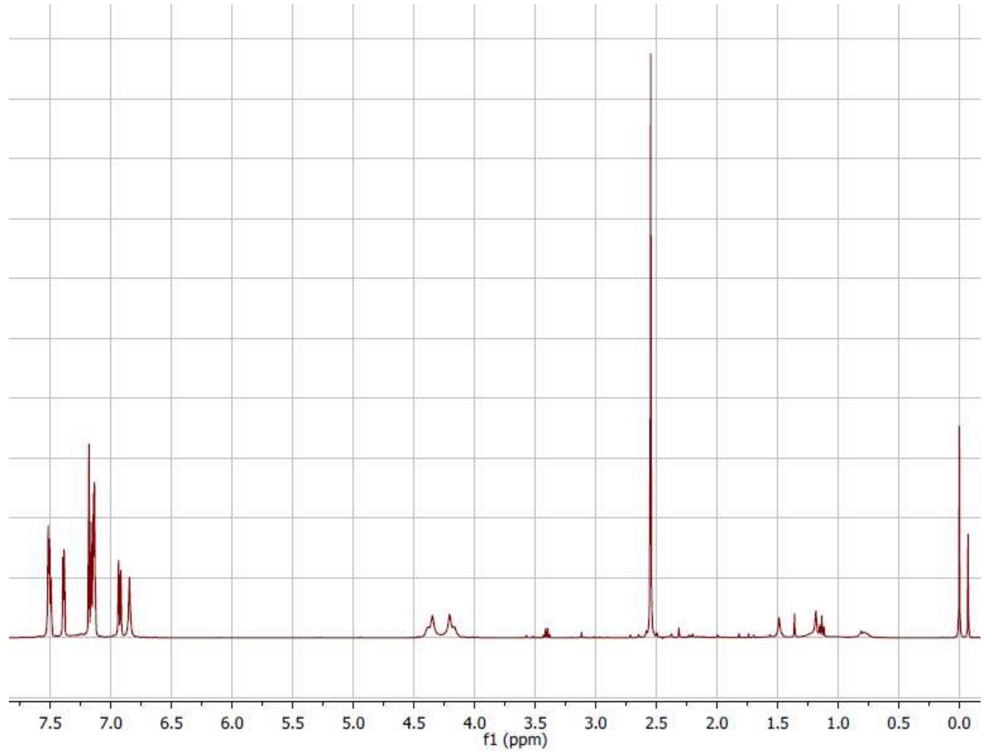


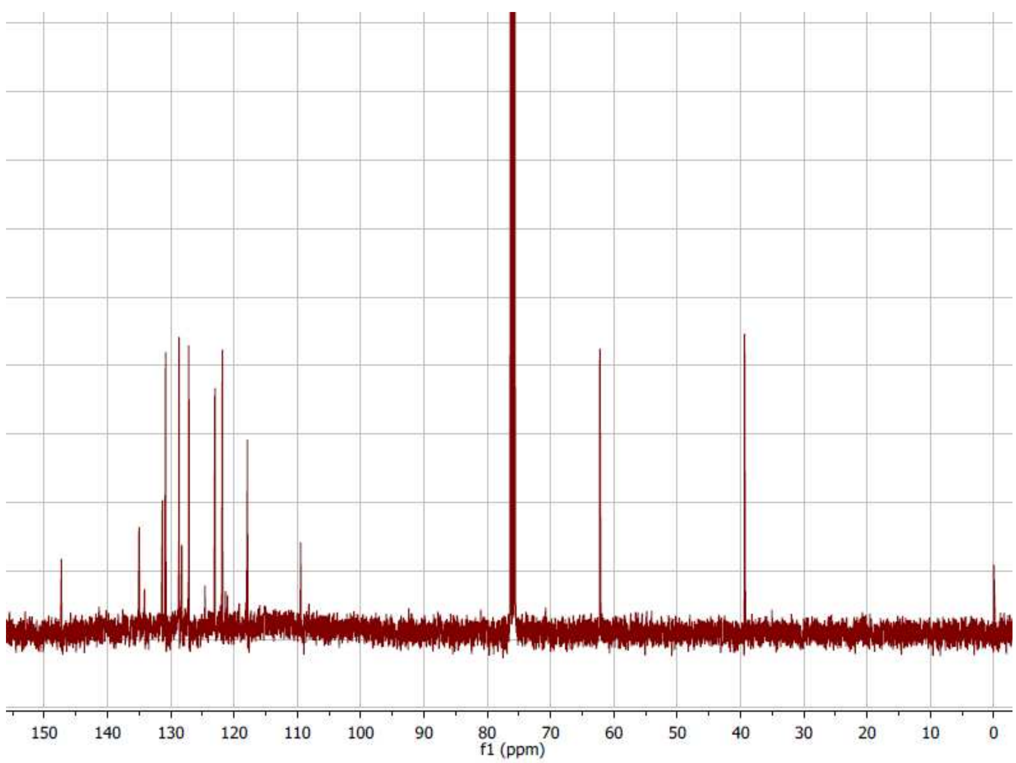
[1]H and [13]C Spectra of  **6e**

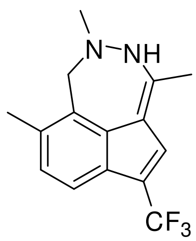




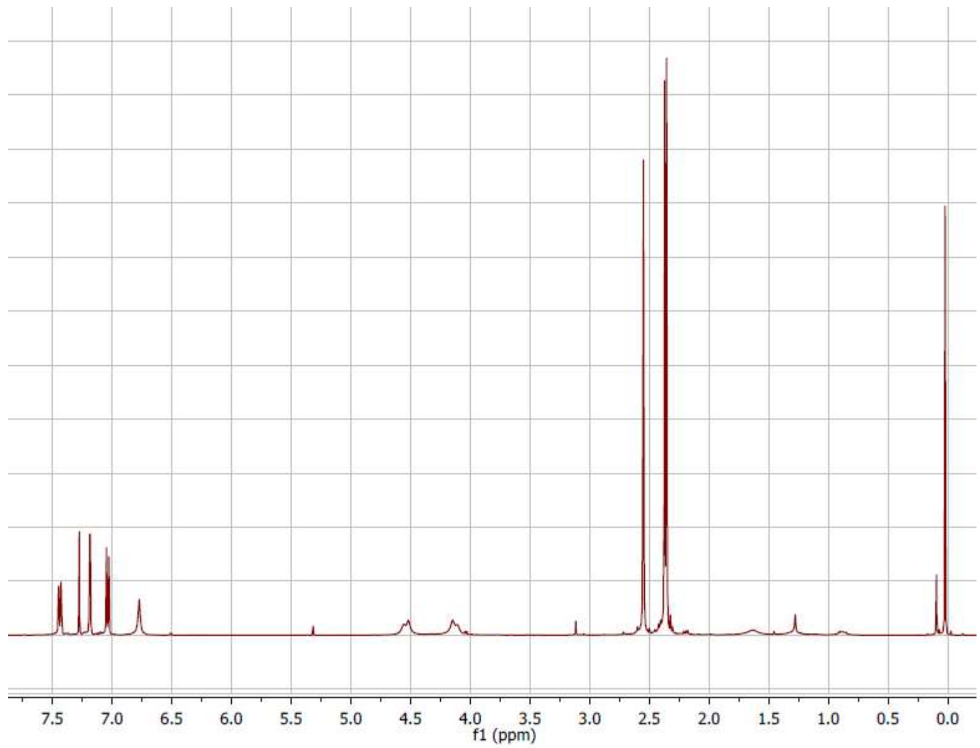
[1]H and [13]C Spectra of  **6f**

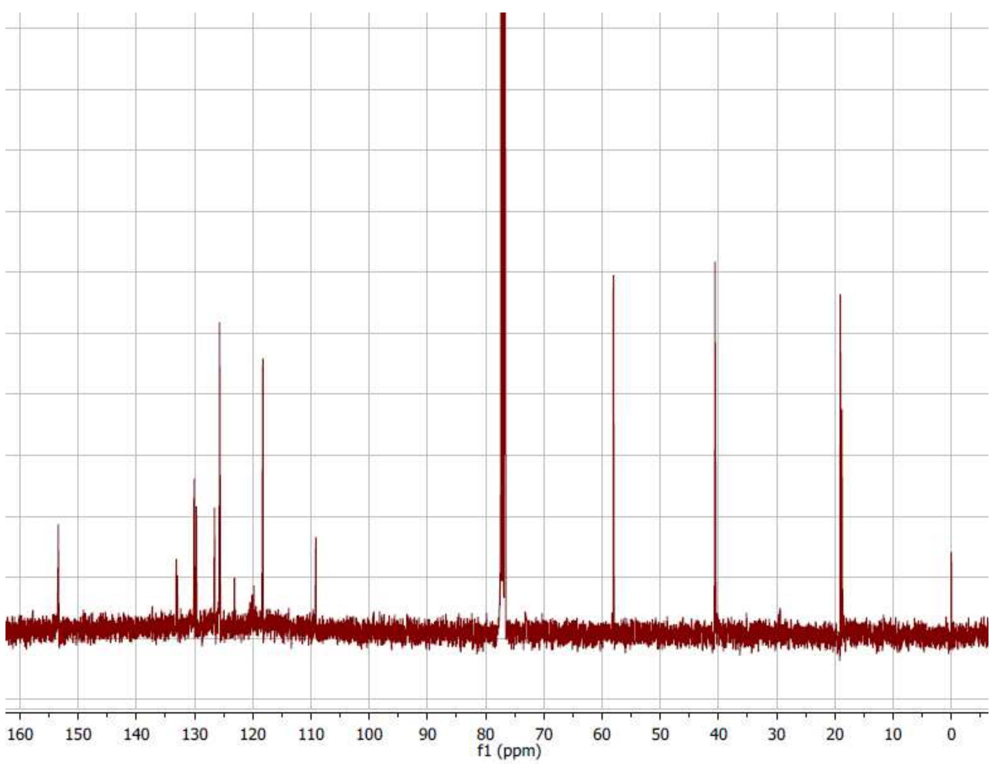


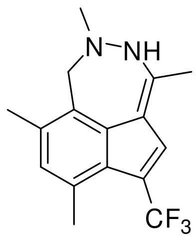


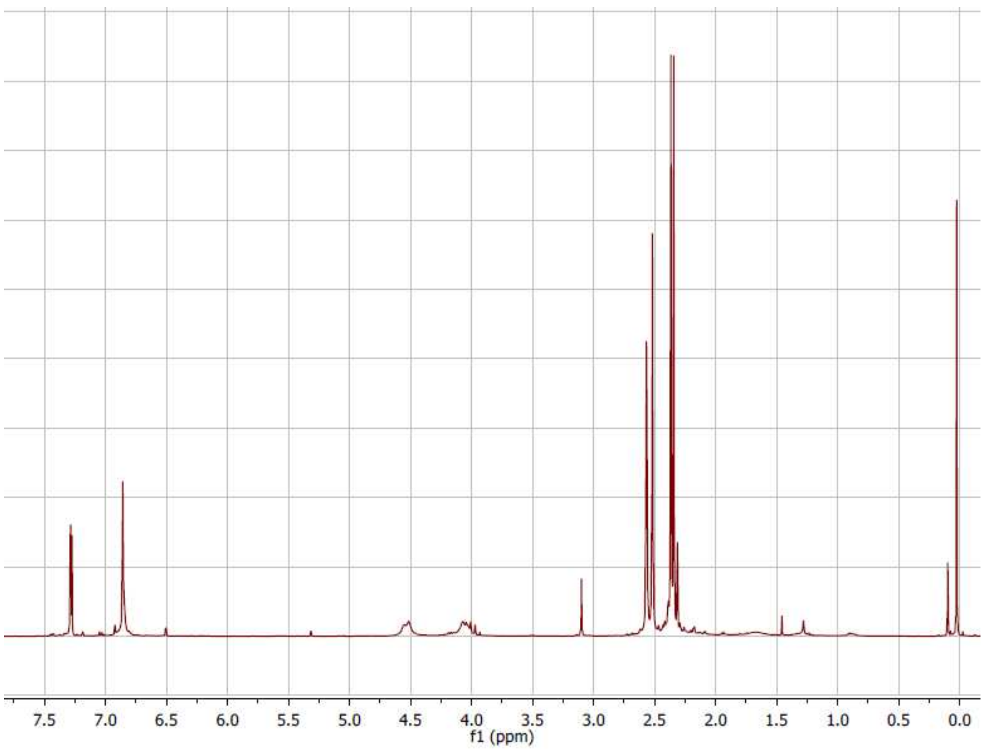
^{1}H and ^{13}C Spectra of 

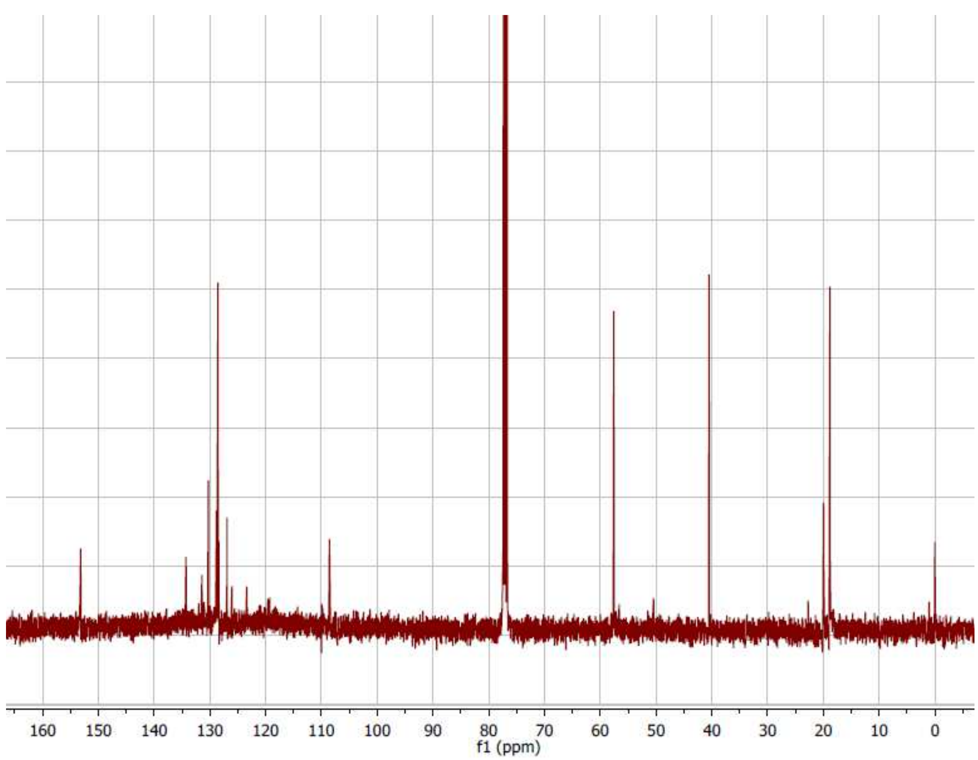
6g

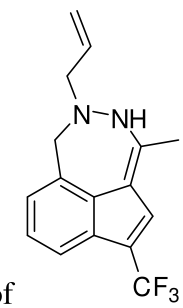




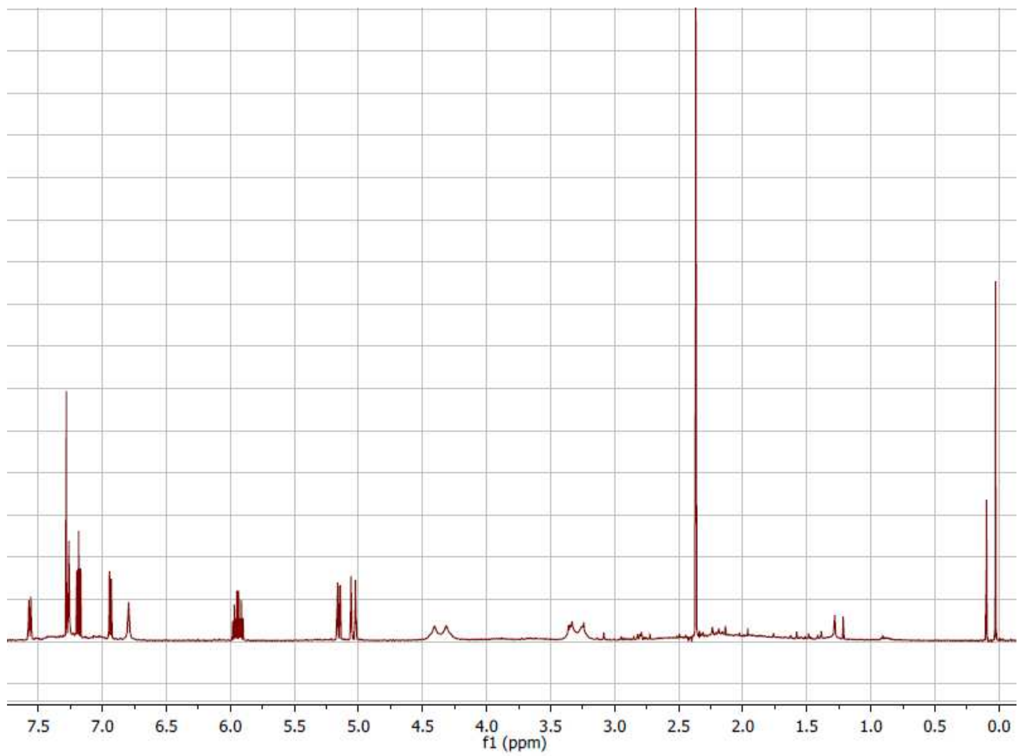
[1]H and [13]C Spectra of  **6h**

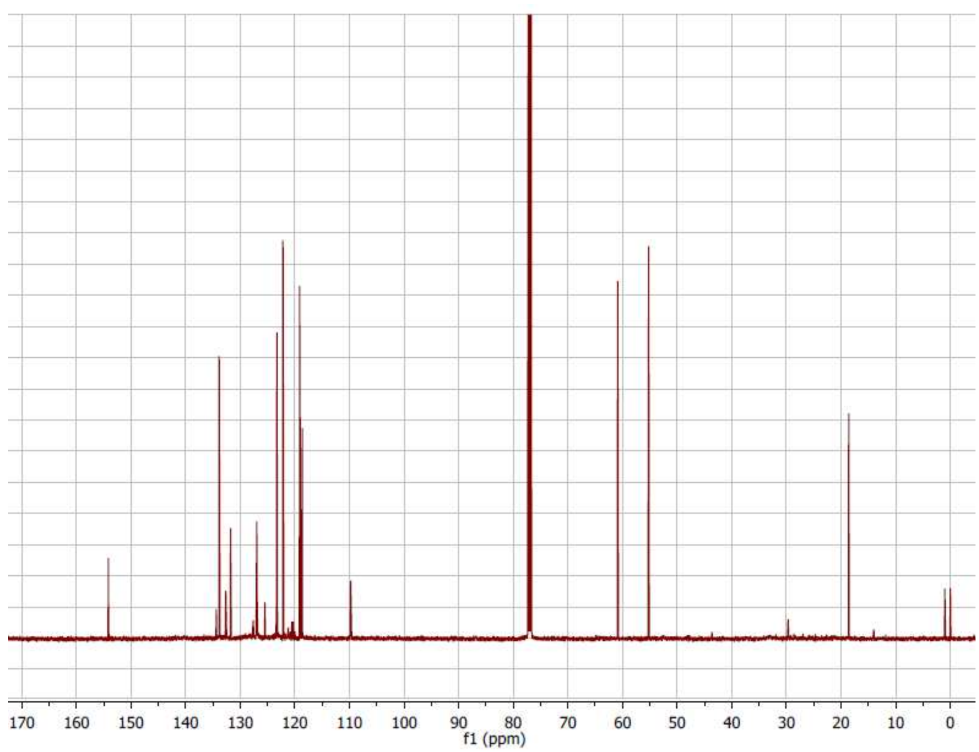


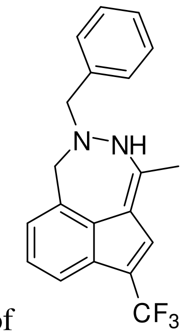




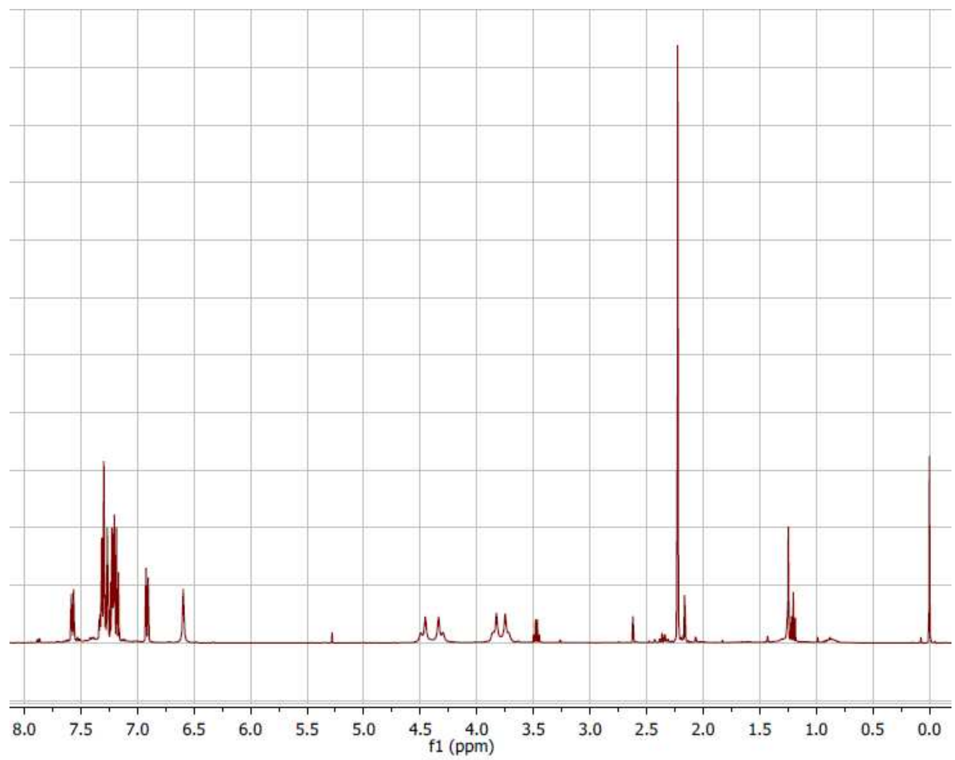
^{1}H and ^{13}C Spectra of **6i**

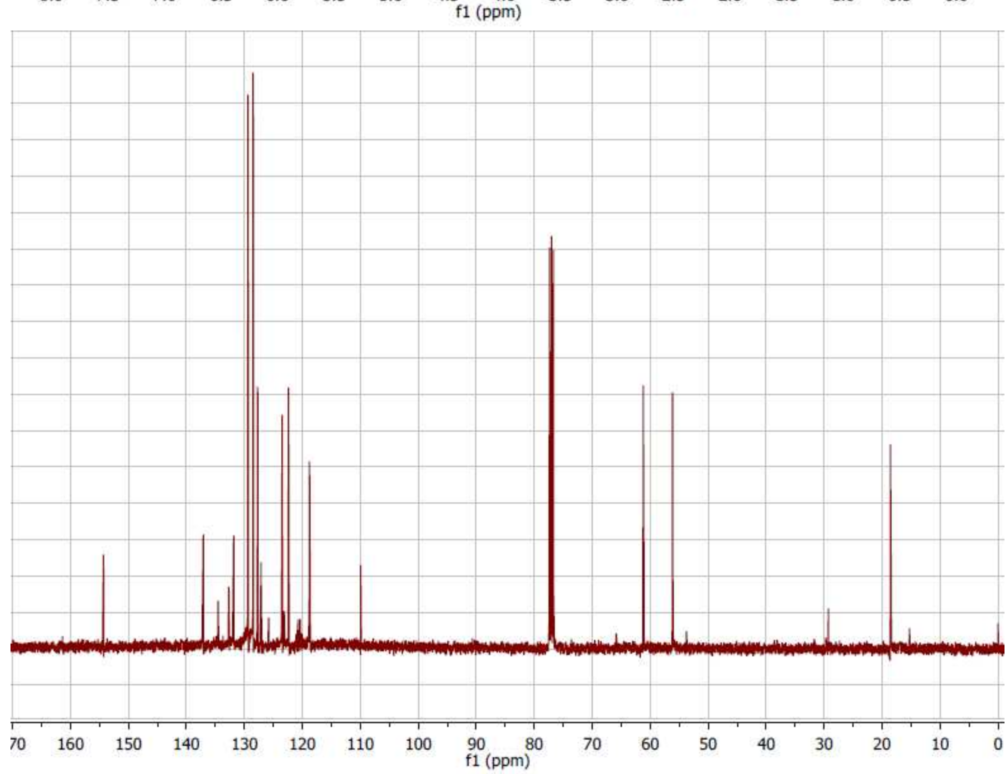






^{1}H and ^{13}C Spectra of **6j**





Assignment of diastereomers based on NOE-experiments

The stereochemistry of the diastereomers was determined by means of the NOE NMR technique. It was easy to find out the ^{1}H-NMR shifts of H_a and H_b atoms (Figure 1,2). In one of the diastereomers (*R,S; S,R* in case of **5j, k, l-n**, and *R,R; S,S* in case of **5o**) this hydrogen atoms are close to each other (Figure 2a) and very strong NOE is detected after irradiation of the H_b atom (Figure 4a), in case of another diastereomer (*R,R; S,S* in case of **5j, k, l-n**, and *R,S; S,R* in case of **5o**) H_a and H_b atoms are far apart from each other (Figure 2b) and NOE is weak if again H_b atom is subjected to irradiation (Figure 4b).

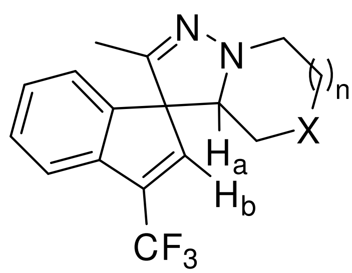
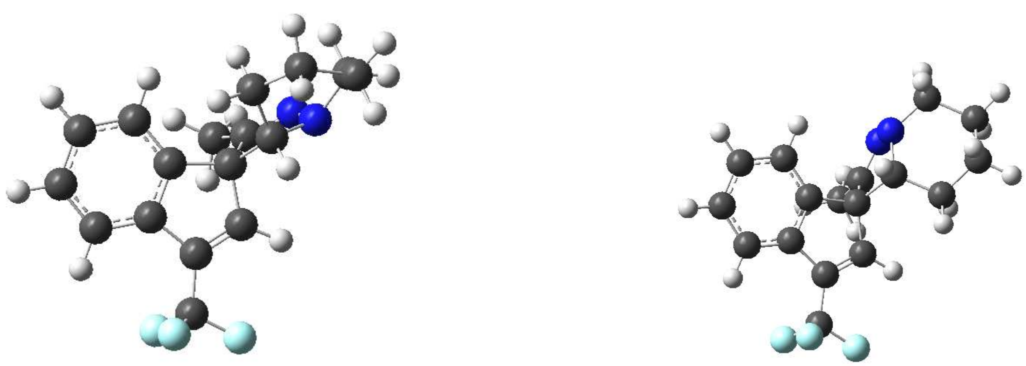


Figure 1.



a) R,S-diastereomer b) R,R-diastereomer

Figure 2. Computed B3LYP/6-311G(d,p) geometries of *R,S*- and *R,R*-diastereomers of compound **5m**.

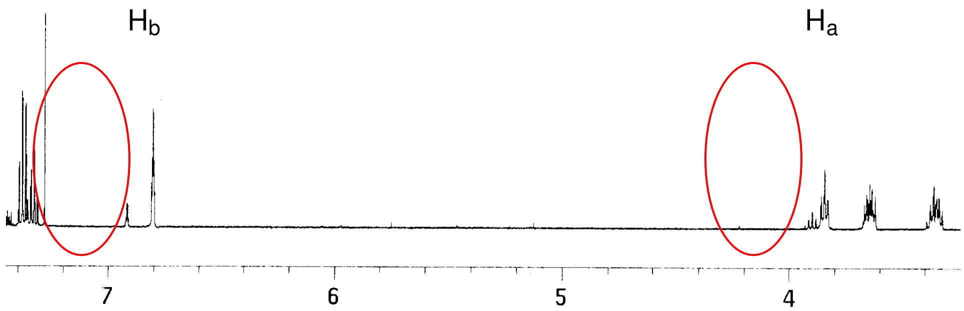


Figure 3. H_a and H_b signals (δ [ppm]) of the compound **5l** in ^{1}H NMR spectrum.

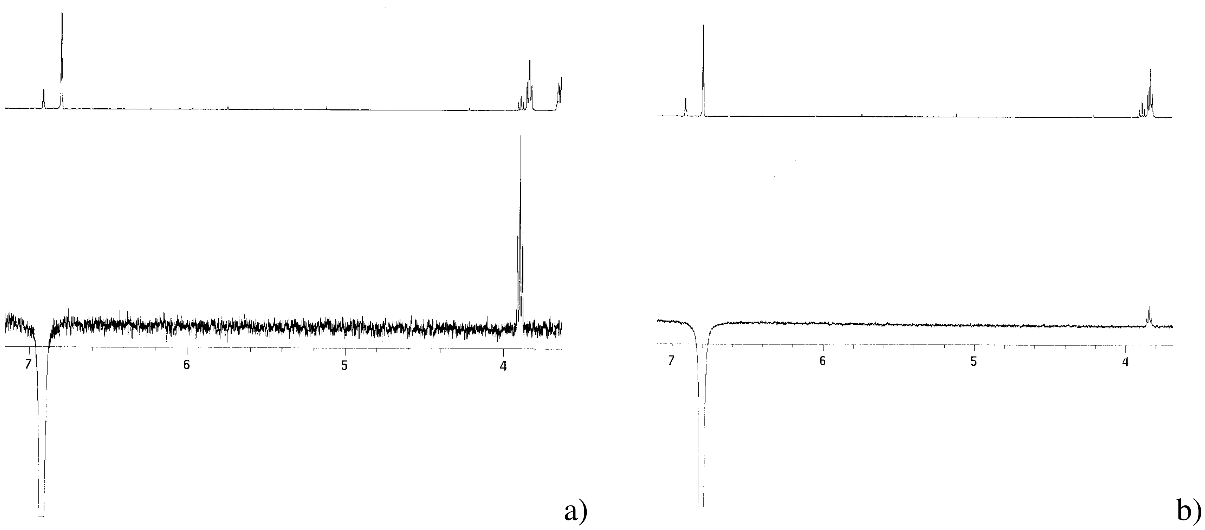
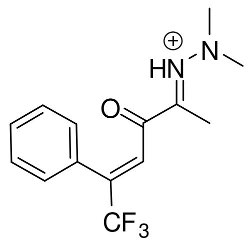
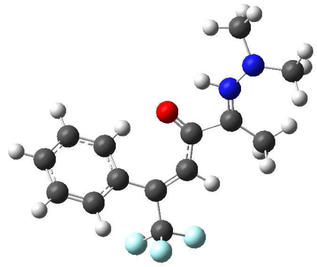


Figure 4. Result of NOE experiments for compound **5l**: a) Irradiation of H_b atom of the minor (*R,S;S,R)* diastereomer; b) Irradiation of H_b atom of the major (*R,R;S,S*) diastereomer.

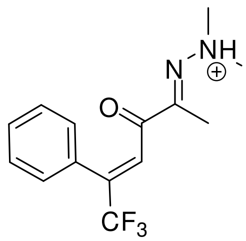
Cartesian coordinates, SCS-MP2/6-311G(d,p)//B3LYP/6-311G(d,p)+ZPE energies and numbers of imaginary frequencies (in parenthesis) for the calculated structures

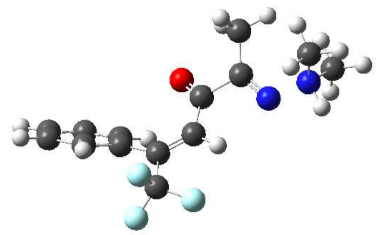




E = -1024.236193 (0)

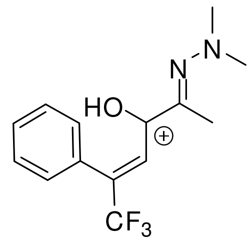
C	-2.921162	-0.700827	0.450234
C	0.338099	-0.080117	0.502629
C	-0.385113	1.116730	0.875587
C	-1.668195	1.450258	0.550595
C	-2.724027	0.613798	-0.015332
C	-3.962983	-1.472832	-0.040166
C	-4.810556	-0.962096	-1.023010
C	-4.626967	0.337295	-1.497488
C	-3.610511	1.128932	-0.986608
C	-2.034064	2.922437	0.799738
F	-3.265415	3.045587	1.301891
F	-1.980305	3.614136	-0.359679
F	-1.185330	3.523309	1.655483
O	-0.116141	-1.104219	0.004057
C	1.870856	-0.046698	0.696272
C	2.597554	1.083761	1.343511
N	2.356551	-1.154446	0.214693
N	3.568966	-1.673466	-0.038076
C	4.793017	-0.996817	0.376098
C	3.585561	-3.138561	-0.141203
H	-2.278084	-1.099247	1.221273
H	0.201318	1.891382	1.345091
H	-4.117934	-2.473020	0.345684
H	-5.618518	-1.570868	-1.411531
H	-5.285506	0.736845	-2.258893
H	-3.486239	2.136585	-1.358487
H	2.604139	1.960842	0.688100
H	2.075594	1.370744	2.258893
H	3.620668	0.845113	1.611320
H	4.938942	-1.015229	1.461969
H	5.618518	-1.529945	-0.092234
H	4.803394	0.027479	0.006602
H	2.686691	-3.481131	-0.656350
H	3.645998	-3.614137	0.843611
H	4.449852	-3.425453	-0.737530
H	1.562513	-1.737014	-0.135009

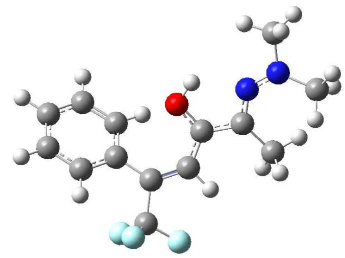




E = -1024.233334 (0)

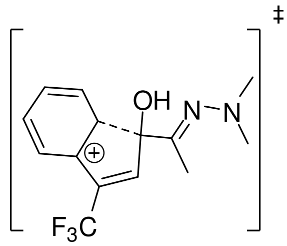
C	2.828925	-1.322962	-0.870468
C	-0.349740	-0.744313	-0.065132
C	0.341127	0.528605	-0.237593
C	1.674093	0.761100	-0.126650
C	2.774287	-0.206479	-0.017822
C	3.896626	-2.207811	-0.804973
C	4.914891	-2.009261	0.125140
C	4.873333	-0.906378	0.978196
C	3.825767	-0.000549	0.897978
C	2.075967	2.240144	-0.081440
F	3.174519	2.474169	-0.806421
F	2.327567	2.620759	1.192669
F	1.105436	3.053169	-0.544246
O	0.113144	-1.864706	-0.076675
C	-1.887753	-0.660141	0.212445
C	-2.417441	-1.817739	0.998547
N	-2.446754	0.359775	-0.316507
N	-3.925644	0.545180	-0.199672
C	-4.721655	-0.401154	-1.058150
C	-4.444062	0.724318	1.202275
H	2.048561	-1.479638	-1.600798
H	-0.307844	1.384816	-0.343296
H	3.934114	-3.053169	-1.481350
H	5.743023	-2.706085	0.180244
H	5.664621	-0.746866	1.700606
H	3.812030	0.854530	1.559977
H	-1.909318	-2.716494	0.646050
H	-2.118925	-1.692666	2.045607
H	-3.492887	-1.960043	0.954038
H	-4.711570	-1.393908	-0.620022
H	-5.743023	-0.025903	-1.117598
H	-4.264717	-0.416201	-2.045607
H	-3.789687	1.428712	1.712470
H	-4.456141	-0.229567	1.718416
H	-5.454093	1.128477	1.136477
H	-4.011297	1.459889	-0.645292

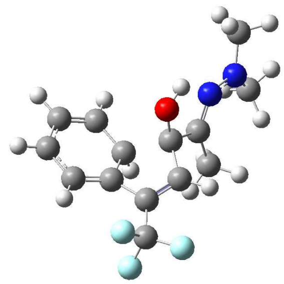




E = -1024.242614 (0)

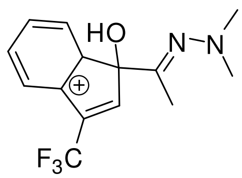
C	2.303747	1.314209	0.935913
C	0.180070	-1.163186	0.160902
C	1.484241	-1.669547	0.449833
C	2.697631	-1.054037	0.299757
C	2.991076	0.366692	0.150872
C	2.616706	2.660649	0.848599
C	3.603513	3.092834	-0.039465
C	4.294103	2.167578	-0.822408
C	4.011499	0.814357	-0.715746
C	3.911168	-1.997048	0.313217
F	4.926912	-1.482130	1.011289
F	4.333516	-2.209600	-0.951644
F	3.620117	-3.198360	0.842956
O	0.058710	0.044957	-0.338381
C	-1.000765	-1.980822	0.312962
C	-0.937253	-3.335921	0.981607
N	-2.057900	-1.331966	-0.158437
N	-3.273525	-1.730615	-0.296094
C	-3.801036	-3.090267	-0.084908
C	-4.240500	-0.728415	-0.762150
H	-0.891896	0.168642	-0.542434
H	1.558034	0.980941	1.645646
H	1.510953	-2.719496	0.695621
H	2.101528	3.375749	1.478341
H	3.843063	4.147251	-0.110453
H	5.062379	2.501593	-1.508788
H	4.557787	0.106634	-1.324088
H	-0.734921	-4.147251	0.276472
H	-0.150546	-3.348200	1.734936
H	-1.861279	-3.560065	1.508039
H	-4.078241	-3.248620	0.960095
H	-4.694449	-3.191181	-0.699256
H	-3.074476	-3.833953	-0.400089
H	-3.740383	0.232314	-0.842190
H	-5.062379	-0.655420	-0.045745
H	-4.641371	-1.024235	-1.734936

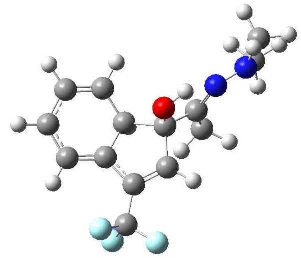




E = -1024.196520 (1)

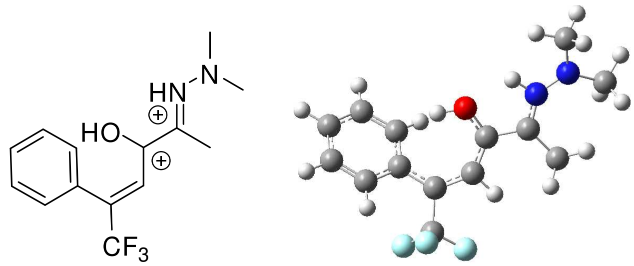
C	-1.220264	0.249572	-0.404558
C	0.484301	0.212180	-0.320804
C	0.710563	1.714955	-0.334799
C	-0.333034	2.405758	-0.829539
C	-1.416225	1.498379	-1.155398
C	-1.927832	-0.925933	-0.892476
C	-2.812710	-0.818026	-1.927306
C	-3.053810	0.443690	-2.527775
C	-2.371531	1.600977	-2.152280
C	-0.363369	3.888603	-1.081072
F	-1.336236	4.467762	-0.354183
F	-0.621526	4.145083	-2.379734
F	0.801145	4.464002	-0.761742
O	0.945508	-0.340614	-1.502107
C	0.978144	-0.500591	0.915110
C	0.690723	0.144691	2.251557
N	1.639229	-1.576157	0.618181
N	2.256658	-2.429937	1.406420
C	2.087039	-2.525970	2.858720
C	2.807096	-3.608600	0.735334
H	1.413926	-1.153563	-1.227144
H	-1.471596	0.411042	0.652082
H	1.650975	2.147846	-0.017044
H	-1.779783	-1.873381	-0.386266
H	-3.356392	-1.684088	-2.283475
H	-3.766172	0.501552	-3.343790
H	-2.519104	2.525885	-2.694211
H	1.595854	0.565393	2.699088
H	0.000811	0.984346	2.127202
H	0.245364	-0.539113	2.974245
H	1.089195	-2.894173	3.123454
H	2.823539	-3.235639	3.231783
H	2.266733	-1.569666	3.343790
H	2.959286	-3.374706	-0.315285
H	2.131184	-4.467762	0.822303
H	3.766172	-3.869351	1.186011





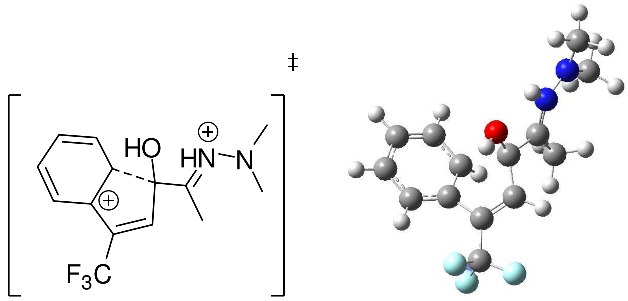
E = -1024.198340 (0)

C	1.294720	0.244564	0.345428
C	0.458061	-0.868858	-0.449828
C	1.493087	-1.985353	-0.494870
C	2.737903	-1.556740	-0.187860
C	2.705419	-0.145077	0.102012
C	0.972957	1.666670	0.154690
C	1.976060	2.577909	0.017707
C	3.331786	2.148719	-0.003007
C	3.709780	0.807180	0.034491
C	3.993544	-2.384896	-0.228871
F	4.558624	-2.438150	0.991697
F	4.896709	-1.838942	-1.067914
F	3.742099	-3.634190	-0.633317
O	0.251181	-0.397256	-1.751720
C	-0.843489	-1.281717	0.230086
C	-0.750068	-1.881367	1.613830
N	-1.860106	-1.152282	-0.555250
N	-3.132982	-1.455014	-0.330208
C	-3.733832	-1.480677	1.006644
C	-4.031231	-1.061681	-1.419205
H	-0.706009	-0.532335	-1.907139
H	1.112452	0.043036	1.417877
H	1.235924	-2.993090	-0.796523
H	-0.065131	1.975462	0.201800
H	1.757757	3.634190	-0.076225
H	4.106615	2.900918	-0.109355
H	4.746690	0.525895	-0.094869
H	-1.106644	-2.914897	1.620504
H	0.290774	-1.917102	1.947104
H	-1.317317	-1.328124	2.364486
H	-3.660248	-0.500395	1.494538
H	-4.787398	-1.728836	0.892328
H	-3.280306	-2.238432	1.640637
H	-3.503242	-1.162794	-2.364486
H	-4.377562	-0.026595	-1.304957
H	-4.896709	-1.725006	-1.425553



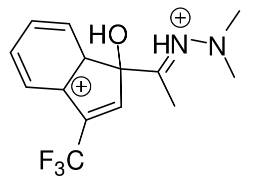
E = -1024.448698 (0)

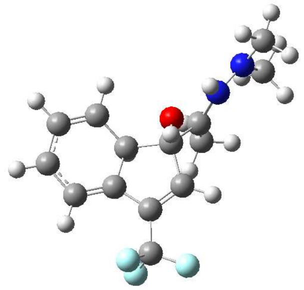
C	2.100700	1.302234	0.720290
C	0.066399	-1.243373	0.129405
C	1.307861	-1.680092	0.596065
C	2.570650	-1.109188	0.398138
C	2.888741	0.261783	0.139091
C	2.436329	2.626419	0.523789
C	3.546419	2.958616	-0.271706
C	4.337866	1.956922	-0.842152
C	4.037278	0.624817	-0.625246
C	3.746876	-2.115343	0.467380
F	4.791666	-1.587072	1.095490
F	4.102728	-2.435670	-0.788099
F	3.391160	-3.236667	1.102581
C	-1.128216	-2.077833	0.288860
C	-1.077489	-3.401776	0.988826
N	-2.205166	-1.542829	-0.279846
N	-3.491529	-1.842056	-0.299723
C	-4.320702	-1.145854	-1.298810
C	-4.121696	-2.847229	0.562230
O	-0.161932	-0.127082	-0.553753
H	-2.006790	-0.686697	-0.808060
H	0.627932	0.433779	-0.660995
H	1.306636	1.050933	1.414623
H	1.310457	-2.669795	1.026159
H	1.868863	3.409198	1.012033
H	3.803993	4.000563	-0.423323
H	5.196794	2.222130	-1.445975
H	4.653530	-0.140125	-1.077178
H	-0.231917	-3.981197	0.613082
H	-1.962457	-4.000563	0.810449
H	-0.949661	-3.281939	2.068650
H	-5.196794	-0.727810	-0.802013
H	-4.638432	-1.854412	-2.068650
H	-3.753270	-0.341699	-1.768592
H	-5.175334	-2.579774	0.628166
H	-4.047082	-3.850450	0.134135
H	-3.690959	-2.815984	1.561561



E = -1024.423670 (1)

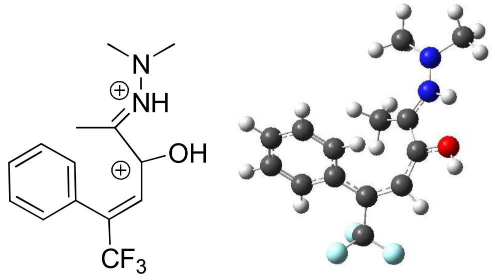
C	-1.790825	0.067124	-0.262752
C	0.251423	0.119981	-0.379729
C	0.253660	1.604341	-0.544382
C	-0.857891	2.117750	-1.103658
C	-1.913632	1.122555	-1.249668
C	-2.493179	-1.158007	-0.475074
C	-3.301766	-1.297790	-1.581225
C	-3.475618	-0.216795	-2.473466
C	-2.792055	0.993297	-2.315169
C	-1.009114	3.568675	-1.523426
F	-2.052028	4.115341	-0.895193
F	-1.226798	3.626611	-2.848512
F	0.092060	4.263592	-1.236220
C	0.811111	-0.459210	0.869330
C	0.553445	0.212994	2.181248
N	1.525841	-1.551044	0.670208
N	2.117483	-2.443790	1.456886
C	3.142924	-3.284309	0.813646
C	2.070187	-2.391804	2.921611
O	0.571987	-0.639156	-1.461567
H	1.625139	-1.791274	-0.323026
H	0.561350	-0.131739	-2.286383
H	-1.740037	0.399182	0.771506
H	1.113169	2.190070	-0.235589
H	-2.454830	-1.940928	0.273781
H	-3.858118	-2.213209	-1.742746
H	-4.135287	-0.339165	-3.325770
H	-2.891899	1.778795	-3.053825
H	0.260570	1.249333	2.007205
H	1.439074	0.231492	2.813760
H	-0.258010	-0.264462	2.739633
H	3.127593	-4.263593	1.289265
H	4.135287	-2.837378	0.925488
H	2.914135	-3.408762	-0.246402
H	2.317298	-3.391742	3.274723
H	2.805142	-1.689741	3.325770
H	1.069179	-2.148058	3.266759





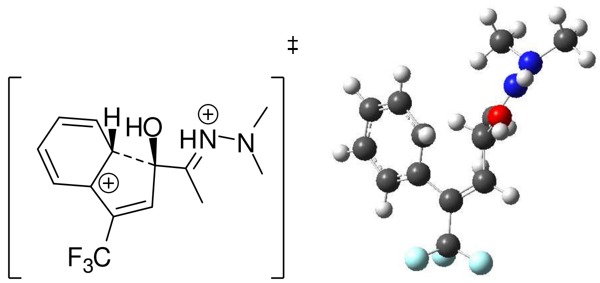
E = -1024.437637 (0)

C	1.460483	0.355817	0.288971
C	0.559536	-0.734362	-0.434547
C	1.517301	-1.919223	-0.476458
C	2.786745	-1.554425	-0.206182
C	2.849173	-0.130901	0.064710
C	1.234888	1.802395	0.087172
C	2.306668	2.641161	-0.011432
C	3.628134	2.117757	-0.003339
C	3.913743	0.743597	0.023427
C	3.993999	-2.470606	-0.227408
F	4.571015	-2.475704	0.979624
F	4.885125	-2.017133	-1.122644
F	3.639935	-3.712297	-0.553026
C	-0.742634	-1.068215	0.304124
C	-0.677112	-1.478683	1.741383
N	-1.811598	-0.943074	-0.435584
N	-3.137414	-1.031373	-0.229710
C	-3.933692	-1.095493	-1.469783
C	-3.690760	-1.690489	0.958076
O	0.213424	-0.274004	-1.733014
H	-1.583820	-0.632823	-1.389876
H	0.828828	-0.589665	-2.407730
H	1.311035	0.230450	1.381794
H	1.193194	-2.923201	-0.724799
H	0.224051	2.193591	0.128075
H	2.165232	3.712297	-0.088877
H	4.457437	2.815807	-0.069691
H	4.934391	0.396092	-0.080037
H	0.341010	-1.776313	1.998744
H	-1.318868	-2.329072	1.963562
H	-0.965428	-0.658249	2.407729
H	-4.934391	-0.733308	-1.242057
H	-3.994308	-2.117453	-1.856983
H	-3.501585	-0.434569	-2.223280
H	-4.766254	-1.528377	0.927723
H	-3.501500	-2.768953	0.951454
H	-3.315016	-1.235221	1.871009



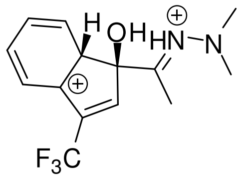
E = -1024.441896 (0)

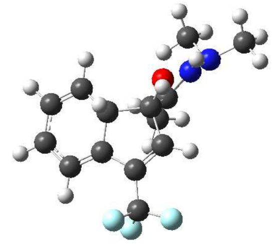
C	-1.936602	2.763052	0.640233
C	-1.215813	1.882237	1.459741
C	-1.422009	0.522376	1.353429
C	-2.368266	-0.000267	0.418588
C	-3.112547	0.920144	-0.379354
C	-2.876795	2.276175	-0.279071
C	-0.344765	-2.481919	0.806752
C	-1.741248	-2.420724	0.763212
C	-2.610780	-1.405080	0.362079
C	-4.001001	-1.888476	-0.112891
F	-4.977202	-1.158343	0.416048
F	-4.039233	-1.768820	-1.454227
F	-4.208520	-3.169803	0.198583
C	0.613958	-1.798959	-0.061303
C	0.208592	-1.009498	-1.268801
N	1.874923	-2.107890	0.238957
N	3.051037	-1.741411	-0.232431
C	3.263521	-0.633383	-1.171094
C	4.217955	-2.538565	0.186191
O	0.239421	-3.404566	1.579471
H	1.963164	-2.787755	1.001717
H	-0.362653	-3.832353	2.207667
H	-1.788507	3.832352	0.740334
H	-0.538907	2.274462	2.208755
H	-3.837756	0.559803	-1.095402
H	-3.431718	2.966476	-0.902288
H	-2.221717	-3.346941	1.071254
H	0.871111	-1.224749	-2.105361
H	-0.793141	-1.305656	-1.572416
H	0.198933	0.067640	-1.092190
H	3.209715	-0.971919	-2.208755
H	4.267701	-0.255435	-0.981693
H	2.549806	0.164944	-0.986996
H	3.928959	-3.267872	0.943483
H	4.623755	-3.068161	-0.679896
H	4.977202	-1.870527	0.595043
H	-0.945502	-0.145735	2.059654



E = -1024.426112 (1)

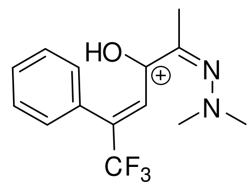
C	-1.948249	-1.563144	-2.491031
C	-0.581539	-1.714887	-2.528819
C	0.256478	-0.552663	-2.518408
C	-0.359686	0.755252	-2.370228
C	-1.744899	0.886562	-2.398513
C	-2.523532	-0.268518	-2.462780
C	1.743763	-0.173815	-1.177073
C	1.725972	1.278787	-1.458424
C	0.605697	1.776978	-2.020984
C	0.357978	3.261637	-2.229586
F	-0.007712	3.498152	-3.489018
F	-0.642230	3.645044	-1.412350
F	1.447321	3.970098	-1.941225
C	1.173353	-0.672554	0.118434
C	-0.002422	-0.066684	0.790834
N	1.850763	-1.643762	0.679001
N	1.587745	-2.239454	1.881217
C	0.349459	-3.043642	1.975497
C	2.789368	-2.863924	2.462957
O	2.872557	-0.848257	-1.471425
H	2.730369	-1.912853	0.224691
H	3.415428	-0.423497	-2.153210
H	-2.597041	-2.428812	-2.554665
H	-0.139601	-2.693084	-2.682652
H	-2.213628	1.858335	-2.305978
H	-3.604307	-0.174881	-2.463803
H	2.615210	1.864922	-1.243653
H	0.140844	-0.132173	1.873165
H	-0.123076	0.976434	0.507284
H	-0.930699	-0.594584	0.548641
H	-0.516647	-2.479935	1.639556
H	0.206094	-3.285812	3.026843
H	0.440865	-3.970098	1.398096
H	3.604307	-2.141075	2.490921
H	2.550283	-3.138448	3.489019
H	3.088598	-3.767005	1.916332
H	1.072315	-0.608075	-3.235741

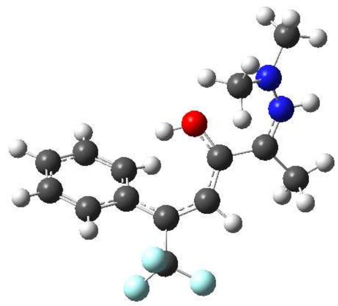




E = -1024.441017 (0)

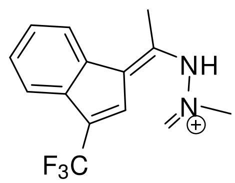
C	-1.246065	2.582764	0.129481
C	-0.506954	1.590016	0.703694
C	-1.072929	0.228590	0.797261
C	-2.308546	-0.036124	0.017222
C	-3.048486	0.999086	-0.520635
C	-2.514639	2.292144	-0.447869
C	-0.239243	-1.132009	0.676575
C	-1.337545	-2.100993	0.262882
C	-2.471423	-1.471451	-0.103076
C	-3.730614	-2.136724	-0.622178
F	-4.778703	-1.769695	0.120673
F	-3.943395	-1.731018	-1.887030
F	-3.610588	-3.460826	-0.601781
C	0.828727	-1.064065	-0.429819
C	0.537958	-0.597091	-1.806800
N	2.002617	-1.505054	-0.100888
N	3.096896	-1.604846	-0.949432
C	3.763754	-0.312254	-1.231857
C	4.012202	-2.663571	-0.484178
O	0.433041	-1.498159	1.848227
H	2.102278	-1.870055	0.855339
H	-0.154766	-1.891265	2.507991
H	-0.888539	3.605508	0.125359
H	0.427178	1.808217	1.211600
H	-3.978524	0.818950	-1.045870
H	-3.080465	3.110837	-0.882622
H	-1.185413	-3.174331	0.285737
H	1.173465	-1.146596	-2.507991
H	-0.509000	-0.740678	-2.069942
H	0.775877	0.466359	-1.925001
H	3.064173	0.399766	-1.665258
H	4.537149	-0.511375	-1.971661
H	4.224225	0.111965	-0.332712
H	3.471342	-3.605508	-0.396633
H	4.778703	-2.787987	-1.247432
H	4.498874	-2.407331	0.465928
H	-1.403773	0.196908	1.856516

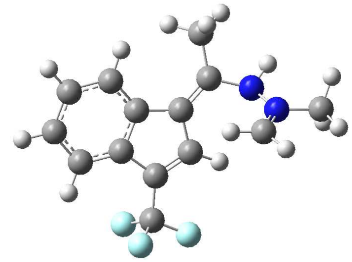




E = -1024.441999 (0)

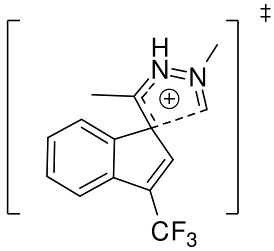
C	1.342004	-0.808100	0.173104
C	2.773669	-0.592311	0.348687
N	3.427866	0.433845	-0.189559
N	3.057228	1.649894	-0.572053
C	3.627334	-1.612228	1.051867
C	0.670642	-1.665128	1.054886
O	0.810763	-0.150396	-0.843619
C	-0.691494	-1.976389	1.109879
C	-1.641493	-1.954199	0.038878
C	-1.202215	-2.388084	2.513183
C	-1.228066	-2.274912	-1.290720
C	-3.024761	-1.700840	0.277811
C	-2.146720	-2.311482	-2.319957
C	-3.926517	-1.709724	-0.770406
C	-3.496625	-2.013591	-2.066017
C	3.948057	2.339315	-1.516012
C	1.861663	2.301884	-0.052342
H	4.441224	0.306528	-0.260919
H	3.555135	-1.493125	2.138830
H	4.681917	-1.486384	0.793737
H	3.333745	-2.629409	0.793958
H	3.929572	3.404959	-1.294902
H	3.615527	2.170742	-2.544105
H	4.970644	1.968820	-1.404987
H	2.095834	3.361598	0.050899
H	1.007032	2.183647	-0.721277
H	1.620539	1.885417	0.927821
H	1.258052	-1.986664	1.903044
H	-0.116551	-0.409100	-1.005835
F	-2.053217	-3.404959	2.430137
F	-1.827962	-1.332858	3.063019
F	-0.193155	-2.741398	3.314932
H	-0.211467	-2.605574	-1.473017
H	-3.368964	-1.459028	1.273817
H	-4.970644	-1.492457	-0.582411
H	-1.837154	-2.606981	-3.314932
H	-4.213960	-2.044675	-2.878115

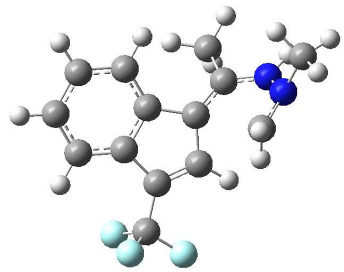




E = -947.9998455 (0)

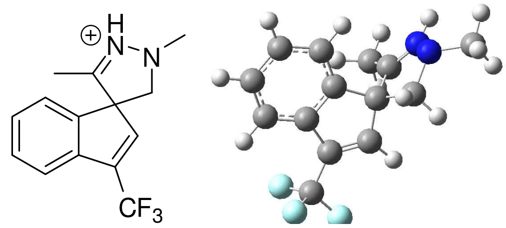
C	0.037414	-0.401576	0.761295
C	-1.904045	-1.748910	-1.380596
N	-2.460975	-2.021162	-0.252008
N	-2.089334	-1.477895	0.963180
C	-3.495595	-3.073874	-0.118059
C	1.070493	0.654801	0.629983
C	0.722479	-1.676619	0.507350
C	-1.283019	-0.291127	1.048107
C	2.030209	-1.436385	0.271896
C	2.294372	0.006866	0.329161
C	3.069149	-2.484535	0.015720
C	-2.019125	0.928745	1.519329
C	1.026394	2.042197	0.694389
C	3.463207	0.724812	0.130350
C	3.409498	2.120770	0.224623
C	2.208946	2.768055	0.497041
H	2.183177	3.849285	0.556372
H	0.108072	2.581425	0.882994
H	4.395647	0.223887	-0.097439
H	4.311642	2.701519	0.075761
H	0.267900	-2.652149	0.587717
H	-2.530085	1.446397	0.699117
H	-2.784370	0.655124	2.253431
H	-1.346728	1.631858	2.005428
H	-2.881583	-1.503407	1.595251
H	-4.395647	-2.624703	0.304257
H	-3.111834	-3.849285	0.544082
H	-3.713574	-3.483159	-1.099877
H	-1.130638	-0.997532	-1.434334
H	-2.228748	-2.294597	-2.253430
F	4.044399	-2.439676	0.940713
F	3.647053	-2.299902	-1.189260
F	2.539031	-3.722055	0.030375





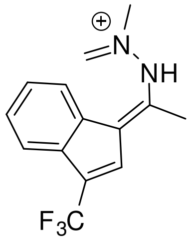
E = -947.9613474 (1)

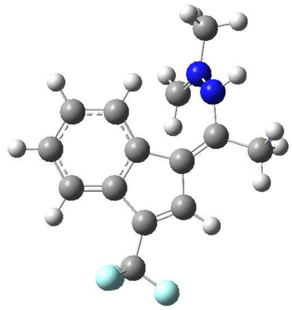
C	-0.607047	0.491150	-0.567993
C	1.847140	0.716165	-0.649561
N	1.750649	2.051866	-0.645809
N	0.538022	2.555758	-1.012042
C	2.502304	2.904218	0.293738
C	-1.450939	-0.186007	0.429280
C	-0.477306	-0.475297	-1.688828
C	-0.617190	1.895669	-0.762916
C	-1.148364	-1.605405	-1.380677
C	-1.745912	-1.485114	-0.049661
C	-1.281553	-2.794725	-2.277945
C	-1.850901	2.747989	-0.717580
C	-1.877327	0.214295	1.693976
C	-2.478104	-2.377624	0.723428
C	-2.919759	-1.958161	1.981175
C	-2.625085	-0.679936	2.461297
H	-2.971671	-0.383805	3.443822
H	-1.630112	1.192423	2.093112
H	-2.702668	-3.374510	0.365541
H	-3.493761	-2.639358	2.597658
H	-0.011954	-0.263046	-2.640449
H	-1.658455	3.769545	-0.382723
H	-2.301290	2.782248	-1.716596
H	-2.588134	2.287209	-0.062433
H	0.530128	3.546959	-1.227612
H	1.981355	2.969622	1.252376
H	2.612152	3.899156	-0.140843
H	3.493761	2.476012	0.420081
H	1.629816	0.177187	-1.550606
H	2.540737	0.278556	0.056889
F	-2.573325	-3.051852	-2.558918
F	-0.773245	-3.899156	-1.693315
F	-0.633281	-2.611123	-3.443821



E = -948.0399032 (0)

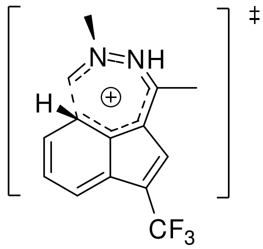
C	-2.500207	-2.421580	-0.513192
C	-1.108527	-2.282705	-0.547021
C	-0.579313	-1.001576	-0.513950
C	-1.412116	0.130367	-0.441549
C	-2.795664	-0.010683	-0.407586
C	-3.328392	-1.300914	-0.441678
C	0.879957	-0.533059	-0.549529
C	0.741600	0.975418	-0.507810
C	-0.552522	1.322353	-0.443628
C	-1.064726	2.732597	-0.383695
F	-1.902063	2.981857	-1.406278
F	-1.748319	2.935390	0.760051
F	-0.064046	3.626153	-0.433930
C	1.594773	-1.123258	0.651410
C	1.394356	-0.782549	2.079314
N	2.376994	-2.063904	0.230940
N	2.347103	-2.324840	-1.146482
C	1.742444	-1.094941	-1.710289
C	3.651207	-2.718181	-1.693331
H	2.893441	-2.706645	0.826044
H	-2.939274	-3.411103	-0.549273
H	-0.474223	-3.159516	-0.615898
H	-3.445563	0.853792	-0.359619
H	-4.403263	-1.433270	-0.418047
H	1.585453	1.650573	-0.533206
H	1.766894	0.228202	2.270444
H	0.325990	-0.778197	2.309710
H	1.903754	-1.479075	2.746109
H	1.151596	-1.337935	-2.590656
H	2.531626	-0.380787	-1.980942
H	3.999363	-3.626153	-1.197865
H	3.501607	-2.954078	-2.746109
H	4.403263	-1.924490	-1.601012

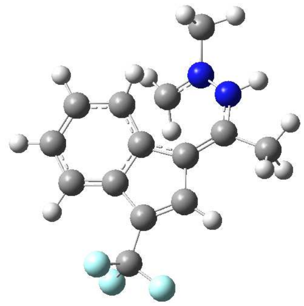




E = -948.0025404 (0)

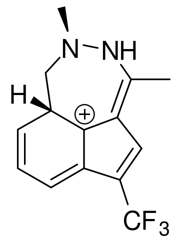
C	-0.445775	1.282758	-1.206481
C	0.432218	0.256084	-0.868229
C	0.268129	-1.208160	-0.754392
C	1.611407	-1.746248	-0.482152
C	-0.854488	-1.969971	-0.821726
N	-2.149756	-1.380109	-0.922681
C	-0.893120	-3.471375	-0.874588
C	0.035694	2.597899	-1.264397
C	-2.068350	-0.094732	1.061511
C	1.797855	0.549325	-0.628275
C	2.272329	1.849955	-0.685238
C	2.487569	-0.725760	-0.387620
C	1.371427	2.877482	-0.995877
C	3.946975	-0.854867	-0.083338
N	-2.720042	-0.625495	0.083709
F	4.262034	-0.181211	1.043266
F	4.309801	-2.136715	0.086657
F	4.695277	-0.337968	-1.078020
H	-2.854968	-1.991025	-1.318938
C	-4.150743	-0.332133	-0.160521
H	-1.472336	1.081913	-1.485547
H	1.852221	-2.787687	-0.339449
H	-1.368022	-3.892569	0.017987
H	-1.472665	-3.805439	-1.743869
H	0.100746	-3.899709	-0.973968
H	-0.637217	3.401868	-1.536842
H	-1.019455	-0.305647	1.194553
H	-2.609633	0.542900	1.743869
H	3.317060	2.072248	-0.507980
H	1.726334	3.899709	-1.046593
H	-4.695278	-1.275537	-0.222061
H	-4.534637	0.258190	0.666090
H	-4.239807	0.217238	-1.097519

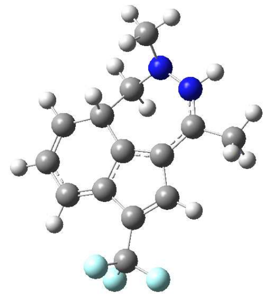




E = -947.991445 (1)

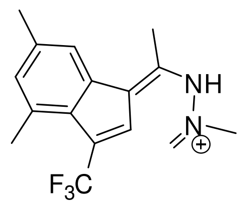
C	-1.890893	-0.481254	0.463809
C	-0.472534	-0.500122	0.527766
C	0.500318	0.556753	0.518926
C	1.814894	-0.094637	0.635907
C	0.345615	1.903616	0.244820
N	-0.809682	2.518470	-0.164769
C	1.493852	2.877934	0.342742
C	-2.568848	-1.735613	0.336868
C	-1.952440	0.754969	-1.277395
C	0.228132	-1.740877	0.504358
C	-0.456948	-2.932406	0.367000
C	1.653474	-1.436939	0.605040
C	-1.868044	-2.916490	0.257297
C	2.740534	-2.459188	0.652990
N	-1.928720	1.998099	-0.786932
F	2.711337	-3.248542	-0.445241
F	3.955057	-1.891084	0.720901
F	2.600168	-3.273420	1.720060
H	-0.773086	3.525496	-0.259453
C	-3.168630	2.700250	-0.426082
H	-2.443233	0.313053	0.951266
H	2.765062	0.413796	0.686114
H	2.017392	2.960935	-0.614621
H	1.138434	3.875913	0.614359
H	2.207167	2.568724	1.102931
H	-3.652538	-1.749494	0.341618
H	-1.042006	0.367545	-1.706392
H	-2.892469	0.460135	-1.720061
H	0.074887	-3.875913	0.338069
H	-2.399773	-3.854637	0.156533
H	-3.016823	3.775340	-0.535334
H	-3.955058	2.390053	-1.110434
H	-3.450263	2.479600	0.607400

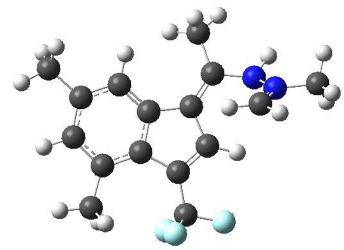




E = -948.0065917 (0)

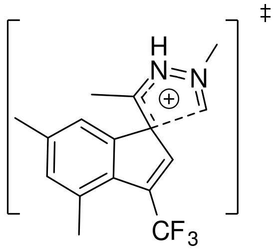
C	-2.391072	-1.396214	-0.246447
C	-0.899057	-1.390807	-0.171213
C	-0.309729	-0.040018	-0.197949
C	-1.109066	1.120863	-0.473978
C	-2.469670	1.007754	-0.601964
C	-3.109688	-0.273037	-0.474107
C	-0.226091	2.276187	-0.412826
C	1.011705	1.846298	-0.069024
C	0.989230	0.385199	0.097218
C	-0.638598	3.686320	-0.674373
F	-1.650067	4.056334	0.145084
F	0.377829	4.542468	-0.490302
F	-1.089480	3.837922	-1.937673
C	-0.279575	-2.211419	1.024849
N	1.083769	-2.633029	0.810129
N	2.093929	-1.680480	0.806830
C	2.090907	-0.370476	0.566881
C	3.394624	0.315937	0.877730
C	1.317904	-3.703194	-0.161798
H	2.971310	-2.074995	1.127848
H	-2.888313	-2.358243	-0.180124
H	-0.581231	-1.938884	-1.076596
H	-3.081362	1.887953	-0.765771
H	-4.187531	-0.324976	-0.565976
H	1.870816	2.483408	0.074596
H	-0.335282	-1.618469	1.937673
H	-0.854949	-3.124587	1.178240
H	3.715465	0.918470	0.026717
H	4.187531	-0.396261	1.111436
H	3.277261	0.983422	1.735518
H	0.669544	-4.542468	0.087955
H	1.128091	-3.383624	-1.195888
H	2.353093	-4.042059	-0.091344

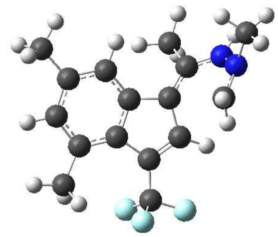




E = -1026.343032 (0)

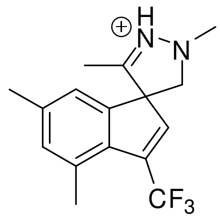
C	-0.149071	0.580095	-0.618353
C	2.855863	0.578455	0.374857
N	2.951728	0.930311	-0.861152
N	1.885175	1.271654	-1.669788
C	4.234396	0.867098	-1.599736
C	-1.431753	0.624811	0.121076
C	0.215925	-0.831958	-0.707509
C	0.592385	1.592258	-1.136365
C	-0.744552	-1.582818	-0.118842
C	-1.804208	-0.713744	0.430018
C	-0.671269	-3.083216	-0.103863
C	0.194793	3.031591	-1.292773
C	-2.198235	1.694188	0.552612
C	-2.976524	-0.977472	1.146600
C	-3.741935	0.137145	1.540836
C	-3.384946	1.453559	1.269295
H	-1.905348	2.718512	0.363599
H	-4.655540	-0.047360	2.095630
H	1.063750	-1.222125	-1.248325
H	0.514433	3.645180	-0.442311
H	0.652297	3.462640	-2.189183
H	-0.883384	3.131262	-1.401881
H	2.209741	1.884185	-2.409136
H	4.448847	1.854996	-2.010066
H	4.133902	0.137327	-2.402457
H	5.023365	0.574663	-0.913491
H	1.898078	0.604518	0.871585
H	3.752282	0.257264	0.882900
F	-1.729936	-3.645180	-0.715612
F	-0.620975	-3.563204	1.156549
F	0.436199	-3.521842	-0.736848
C	-3.456975	-2.356555	1.519817
H	-3.620799	-2.975164	0.635702
H	-2.732189	-2.877444	2.148423
H	-4.396735	-2.295671	2.068305
C	-4.248753	2.605967	1.714674
H	-3.655092	3.379660	2.209220
H	-4.745592	3.074239	0.858881
H	-5.023365	2.279150	2.409136

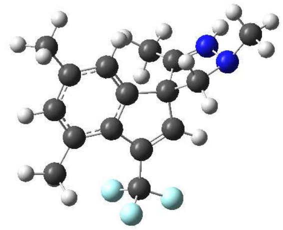




E = -1026.305613 (1)

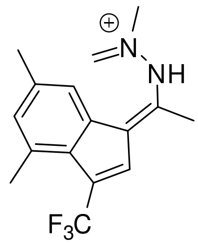
C	0.683111	-1.058368	-0.223472
C	0.680477	-1.034617	2.242209
N	2.020526	-1.046464	2.270616
N	2.632714	-1.451644	1.122115
C	2.809055	-0.093756	3.073147
C	0.080466	-0.106769	-1.165933
C	-0.275931	-2.182248	-0.141019
C	2.082798	-1.243926	-0.097147
C	-1.340270	-1.922264	-0.932934
C	-1.181353	-0.605265	-1.576590
C	-2.460187	-2.906677	-1.091614
C	3.046401	-1.243399	-1.247571
C	0.545444	1.139557	-1.576329
C	-1.990452	0.158042	-2.432649
C	-1.478340	1.397769	-2.842851
C	-0.237195	1.907576	-2.441663
H	1.494443	1.528612	-1.220631
H	-2.090226	2.001977	-3.505084
H	-0.098903	-3.112269	0.378383
H	4.032296	-0.853176	-0.985088
H	3.161228	-2.268459	-1.619700
H	2.633651	-0.659063	-2.067549
H	3.619298	-1.668644	1.213395
H	2.935621	0.849919	2.536294
H	3.784092	-0.533865	3.288910
H	2.290863	0.064268	4.015913
H	0.151046	-1.937508	2.009135
H	0.191253	-0.299118	2.867798
F	-2.629487	-3.272511	-2.377750
F	-3.633891	-2.402919	-0.655439
F	-2.223869	-4.030333	-0.383700
C	-3.349087	-0.276299	-2.920114
H	-3.288199	-1.201772	-3.496145
H	-4.032296	-0.459478	-2.088614
H	-3.788723	0.490562	-3.557745
C	0.226311	3.256328	-2.932445
H	1.167617	3.552373	-2.466156
H	0.377677	3.248077	-4.015913
H	-0.514885	4.030333	-2.716419

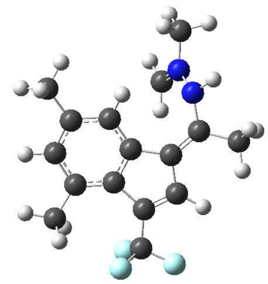




E = -1026.383396 (0)

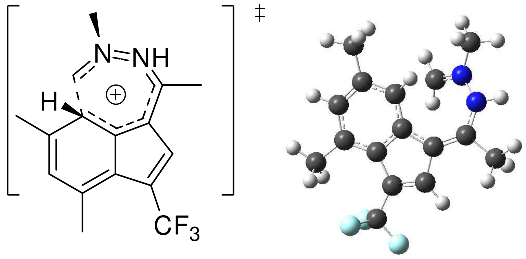
C	-0.616439	-1.132332	-0.585331
C	-1.641101	-1.268750	-1.740206
N	-2.833353	-1.857791	-1.087321
N	-2.721018	-1.413525	0.237916
C	-4.130899	-1.547774	-1.697520
C	0.407822	-0.020116	-0.703644
C	0.253466	-2.361980	-0.373287
C	-1.543936	-1.022835	0.608693
C	1.550379	-2.010295	-0.362350
C	1.705778	-0.552158	-0.561712
C	2.638339	-3.036280	-0.184994
C	-1.191384	-0.633726	1.993554
C	0.176399	1.329453	-0.904133
C	2.821844	0.302634	-0.628863
C	2.556126	1.661979	-0.836722
C	1.271793	2.198877	-0.979525
H	-0.830620	1.720946	-1.011893
H	3.402480	2.338798	-0.892783
H	-0.142042	-3.361660	-0.268873
H	-2.008097	-0.810017	2.694430
H	-0.308800	-1.190882	2.318411
H	-0.923704	0.426768	2.014872
H	-3.515569	-1.553621	0.856622
H	-4.313514	-0.468333	-1.774653
H	-4.929672	-2.024551	-1.126705
H	-4.132005	-1.986634	-2.694429
H	-1.291160	-1.919723	-2.538576
H	-1.885023	-0.280351	-2.151432
F	3.368514	-2.783438	0.920345
F	3.474941	-3.058762	-1.238225
F	2.124110	-4.271618	-0.051036
C	4.252178	-0.154054	-0.493130
H	4.427789	-0.646516	0.465000
H	4.519507	-0.866319	-1.275917
H	4.929672	0.696466	-0.565048
C	1.083157	3.672924	-1.231856
H	0.045772	3.977842	-1.084230
H	1.711855	4.271618	-0.568801
H	1.361955	3.928123	-2.259123





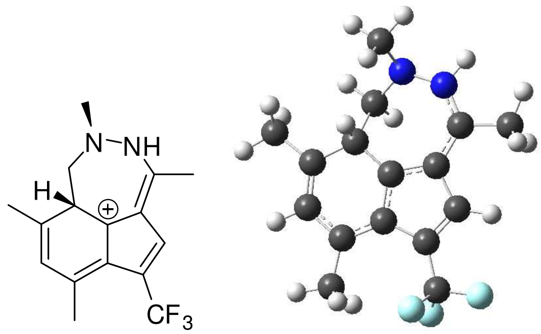
E = -1026.346310 (0)

C	−0.632612	0.953580	−0.785649
C	0.340651	−0.012705	−0.554725
C	0.253635	−1.485240	−0.550111
C	1.626101	−1.966261	−0.372396
C	−0.828109	−2.306708	−0.627117
N	−2.160969	−1.807929	−0.614400
C	−0.775716	−3.798772	−0.805539
C	−0.279707	2.313769	−0.764162
C	−2.041546	−0.591411	1.410482
C	1.696107	0.350738	−0.331783
C	2.067734	1.699558	−0.295530
C	2.457250	−0.912933	−0.219219
C	1.045602	2.647294	−0.501408
C	3.926232	−1.088886	0.026876
N	−2.717517	−1.127625	0.450144
F	4.303646	−0.527660	1.196427
F	4.259068	−2.391140	0.084266
F	4.667838	−0.528017	−0.949749
H	−2.848182	−2.447975	−0.995502
C	−4.170743	−0.901465	0.287950
H	−1.643098	0.677652	−1.061490
H	1.925649	−3.000237	−0.320216
H	−1.154519	−4.322660	0.078550
H	−1.396921	−4.100420	−1.657719
H	0.232579	−4.147651	−1.011509
H	−0.979267	−0.755232	1.486543
H	−2.579652	−0.009990	2.143497
H	1.318387	3.697029	−0.474319
H	−4.667837	−1.868640	0.198940
H	−4.544635	−0.379471	1.163720
H	−4.336057	−0.308519	−0.611465
C	3.474316	2.189184	−0.064945
H	3.877220	1.821978	0.880306
H	4.147022	1.847796	−0.854275
H	3.500691	3.278596	−0.046328
C	−1.301331	3.381309	−1.067352
H	−1.347381	3.578491	−2.143497
H	−2.303311	3.085646	−0.746882
H	−1.053204	4.322660	−0.574385



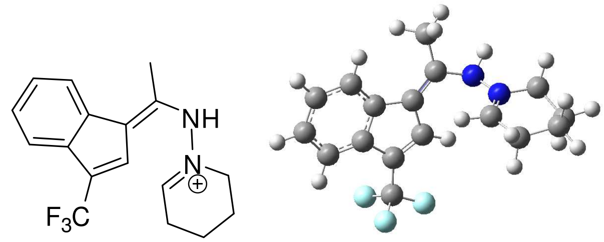
E = -1026.339623 (1)

C	0.106134	0.655139	-1.605480
C	0.087996	0.611501	-0.194880
C	1.180553	0.620135	0.751156
C	0.562394	0.634462	2.077812
C	2.534945	0.448032	0.557728
N	3.157248	0.136133	-0.634004
C	3.534850	0.578142	1.680621
C	-1.127209	0.527772	-2.313880
C	1.482734	-1.134935	-1.729042
C	-1.133260	0.484251	0.524834
C	-2.339945	0.348314	-0.168669
C	-0.781750	0.527679	1.953772
C	-2.286819	0.345468	-1.587444
C	-1.696381	0.457472	3.136169
N	2.669903	-0.546816	-1.732533
F	-2.387130	-0.706405	3.167166
F	-1.010196	0.543283	4.289270
F	-2.605734	1.456776	3.134002
H	4.168785	0.114002	-0.613410
C	3.346756	-0.178500	-2.984945
H	0.921090	1.147856	-2.120711
H	1.090527	0.664675	3.017316
H	3.764342	-0.398465	2.118089
H	4.472937	1.007289	1.315497
H	3.165194	1.233464	2.464923
H	1.103112	-1.528774	-0.801199
H	1.174670	-1.581457	-2.662372
H	-3.224573	0.243892	-2.122489
H	4.426311	-0.245937	-2.840583
H	3.054308	-0.884781	-3.758302
H	3.082760	0.841397	-3.275302
C	-3.679579	0.212386	0.497911
H	-3.704906	-0.654008	1.161732
H	-3.896729	1.087034	1.114935
H	-4.472937	0.105427	-0.240997
C	-1.147532	0.639492	-3.815112
H	-0.697393	1.581457	-4.143682
H	-0.583981	-0.171585	-4.289270
H	-2.165076	0.602224	-4.203696



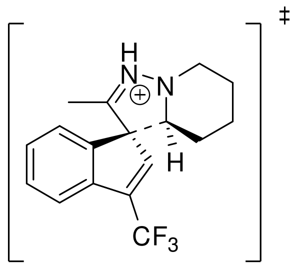
E = -1026.357772 (0)

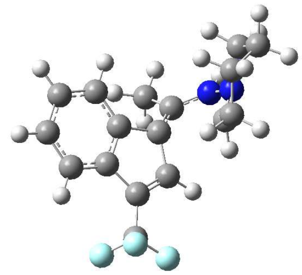
C	-0.979470	0.906653	-0.148877
C	0.160381	-0.033103	-0.179607
C	0.137432	-1.439242	-0.151052
C	1.525811	-1.883451	-0.203256
C	-0.952127	-2.326438	-0.006952
N	-2.234309	-1.986022	0.121441
C	-0.709234	-3.812769	0.056459
C	-0.588655	2.341209	0.068406
C	-2.091690	0.344538	0.817269
C	1.521144	0.402613	-0.192196
C	1.812485	1.759727	-0.077971
C	2.348252	-0.803491	-0.232973
C	0.723068	2.689656	0.066092
C	3.837236	-0.917112	-0.280286
N	-2.856305	-0.752319	0.273133
F	4.423426	-0.380870	0.817205
F	4.224923	-2.201530	-0.349791
F	4.361444	-0.278832	-1.352642
H	-2.895327	-2.747627	0.222206
C	-3.779023	-0.452361	-0.822952
H	-1.452274	0.914328	-1.146351
H	1.860992	-2.908612	-0.206063
H	-0.166149	-4.071302	0.968946
H	-1.641792	-4.379078	0.047110
H	-0.106913	-4.133694	-0.794339
H	-1.632902	0.031287	1.755332
H	-2.817870	1.124344	1.042266
H	0.984439	3.737005	0.166797
H	-4.410420	-1.321167	-1.017238
H	-4.423426	0.370477	-0.514094
H	-3.261279	-0.186317	-1.755332
C	3.202166	2.313047	-0.071750
H	3.767959	1.917529	0.776108
H	3.744412	2.006397	-0.969162
H	3.198054	3.400212	-0.013174
C	-1.672018	3.369654	0.195171
H	-2.442132	3.239574	-0.571818
H	-2.173334	3.297947	1.167789
H	-1.271193	4.379078	0.107986



E = -1064.348881 (0)

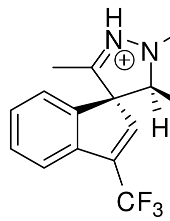
C	-0.547565	-0.192946	-0.507187
C	1.649567	1.907861	0.573709
N	1.551469	2.189180	-0.680440
N	0.579103	1.643028	-1.539549
C	2.541251	3.039709	-1.413362
C	2.739000	2.416289	1.454459
C	3.604683	3.503536	0.812181
C	3.858020	3.159234	-0.656198
C	-1.558782	-0.996587	0.221723
C	0.646077	-1.044971	-0.619769
C	-0.623418	1.068920	-0.996737
C	0.391546	-2.241101	-0.049453
C	-0.971193	-2.256401	0.498472
C	1.341446	-3.396235	-0.001363
C	-1.845669	1.934273	-1.097426
C	-2.842583	-0.723499	0.680451
C	-1.661965	-3.240181	1.189429
C	-2.962912	-2.959857	1.622003
C	-3.541333	-1.718548	1.375465
H	-3.521391	-3.715537	2.161012
H	-4.545705	-1.514765	1.726278
H	-3.316633	0.236192	0.526059
H	-1.208803	-4.201388	1.396939
H	1.546318	-0.775889	-1.150046
F	0.837715	-4.471601	-0.633934
F	2.522488	-3.094123	-0.574678
F	1.589312	-3.761335	1.275058
H	0.399319	2.331557	-2.263129
H	0.890443	1.249205	0.979689
H	-1.826027	2.515407	-2.025510
H	-2.755574	1.338734	-1.111179
H	-1.914856	2.651337	-0.270565
H	3.340959	1.542267	1.741921
H	2.275642	2.756867	2.386504
H	3.099520	4.471601	0.885918
H	4.545704	3.595401	1.355453
H	4.413046	2.219597	-0.737739
H	4.458447	3.927866	-1.146690
H	2.064201	4.013958	-1.556113
H	2.675318	2.566667	-2.386505

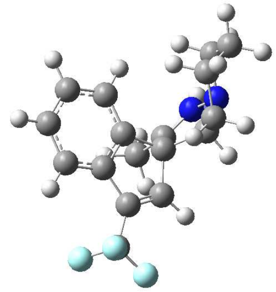




E = -1064.309811 (1)

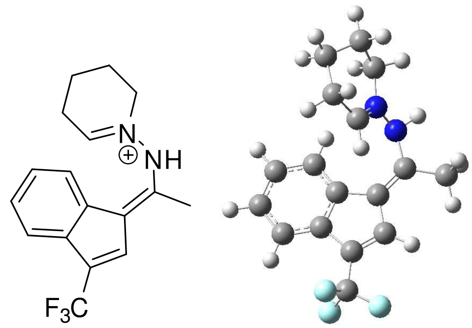
C	-0.613335	0.435909	-0.604824
C	1.774969	0.564487	-0.333462
N	1.835221	1.665645	-1.107798
N	0.801817	1.766810	-2.003906
C	2.321938	2.986753	-0.619079
C	2.408955	0.520247	1.015453
C	2.703511	1.903186	1.604311
C	3.313669	2.802385	0.524912
C	-1.662914	0.614237	0.410412
C	-0.447172	-1.030897	-0.731624
C	-0.439467	1.349212	-1.686454
C	-1.262018	-1.653711	0.150299
C	-2.021364	-0.662891	0.908477
C	-1.376533	-3.133873	0.312029
C	-1.559425	1.919092	-2.500291
C	-2.225783	1.768078	0.957386
C	-2.947035	-0.787520	1.940503
C	-3.519959	0.372314	2.462645
C	-3.166392	1.635634	1.977324
H	-4.246807	0.293777	3.262160
H	-3.622260	2.520111	2.405518
H	-1.941374	2.756382	0.610458
H	-3.220710	-1.760051	2.330144
H	0.164811	-1.526571	-1.471135
F	-2.640091	-3.556643	0.112120
F	-0.579509	-3.791934	-0.552836
F	-1.026015	-3.514703	1.560552
H	0.961691	2.394148	-2.785103
H	1.689314	-0.360264	-0.875792
H	-1.858806	1.190463	-3.262160
H	-2.428903	2.069239	-1.860712
H	-1.303725	2.860520	-2.991148
H	3.336728	-0.060945	0.916972
H	1.763709	-0.080580	1.665313
H	1.782265	2.353951	1.986776
H	3.382639	1.802278	2.451818
H	4.246807	2.371989	0.148202
H	3.554175	3.791934	0.919032
H	1.450439	3.562213	-0.287854
H	2.776438	3.497900	-1.471739





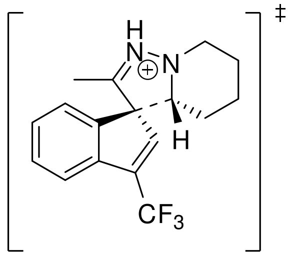
E = -1064.371654 (0)

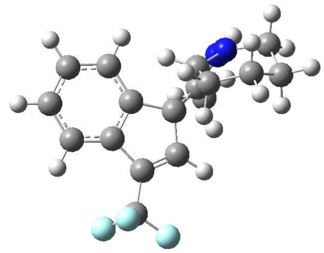
C	-0.137171	-0.973054	0.410639
C	-1.318416	-1.844906	-0.162700
N	-2.563211	-1.252871	0.417196
N	-2.091652	-0.568629	1.536822
C	-3.465343	-0.406990	-0.409405
C	-1.380202	-2.128837	-1.670350
C	-2.271007	-1.172286	-2.472193
C	-3.634828	-1.023256	-1.793907
C	0.475507	0.173266	-0.402180
C	1.074257	-1.842863	0.695993
C	-0.807584	-0.422035	1.651874
C	2.167983	-1.340213	0.107249
C	1.849471	-0.083274	-0.581988
C	3.531610	-1.965335	0.139041
C	-0.153315	0.191860	2.831080
C	-0.089496	1.341543	-0.893192
C	2.655153	0.800355	-1.292616
C	2.072855	1.959645	-1.807306
C	0.720184	2.232483	-1.605272
H	2.682456	2.661466	-2.363400
H	0.290861	3.143990	-2.002986
H	-1.135573	1.579687	-0.740021
H	3.709505	0.601807	-1.437446
H	1.017063	-2.763591	1.259887
F	4.422508	-1.128126	0.706455
F	3.536505	-3.111967	0.836904
F	3.964197	-2.231715	-1.107620
H	-2.774220	-0.256142	2.223338
H	-1.220017	-2.804105	0.354369
H	0.363577	-0.580427	3.410059
H	0.606796	0.901503	2.496857
H	-0.864924	0.700956	3.482601
H	-1.766277	-3.143990	-1.795858
H	-0.359185	-2.137348	-2.059638
H	-1.798074	-0.191239	-2.573715
H	-2.390584	-1.568571	-3.482602
H	-4.131448	-1.995214	-1.710540
H	-4.295196	-0.374577	-2.373652
H	-3.059826	0.608590	-0.508319
H	-4.422507	-0.343001	0.114977



E = -1064.352126 (0)

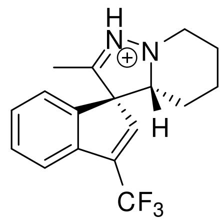
C	-1.316276	-0.055938	-1.079280
C	1.661489	0.664261	-0.272535
N	1.340301	1.666181	-1.021805
N	0.169478	1.730437	-1.789544
C	2.079071	2.964923	-1.016667
C	2.834800	0.659634	0.646013
C	3.458681	2.040818	0.862246
C	3.488452	2.806553	-0.461040
C	-1.462204	0.291844	0.349898
C	-2.026187	-1.332431	-1.258494
C	-0.633522	0.583839	-2.063496
C	-2.507509	-1.745137	-0.067766
C	-2.186894	-0.756432	0.969844
C	-3.249838	-3.019829	0.176975
C	-0.687354	0.238176	-3.525068
C	-1.099130	1.412755	1.092045
C	-2.509430	-0.706958	2.317611
C	-2.111805	0.412154	3.058877
C	-1.428093	1.462557	2.452751
H	-2.358648	0.469435	4.112177
H	-1.162721	2.336580	3.035514
H	-0.623866	2.267090	0.627513
H	-3.069497	-1.506112	2.786629
H	-2.115098	-1.875776	-2.185801
F	-4.464418	-2.781538	0.711930
F	-3.425988	-3.721055	-0.955588
F	-2.580384	-3.804882	1.049478
H	0.373292	2.277945	-2.618004
H	1.037938	-0.216874	-0.353787
H	-1.431360	-0.525172	-3.737143
H	-0.961258	1.123210	-4.112177
H	0.284976	-0.108975	-3.891406
H	3.563322	-0.044298	0.218576
H	2.513545	0.200589	1.586311
H	2.874418	2.597819	1.601025
H	4.464418	1.932960	1.269511
H	4.116950	2.284600	-1.189281
H	3.911478	3.804882	-0.333070
H	1.476179	3.661335	-0.428879
H	2.095717	3.317822	-2.050161

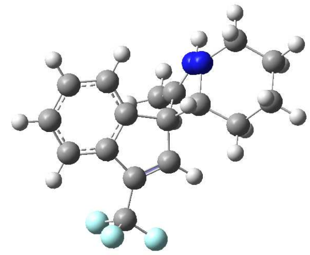




E = -1064.305924 (1)

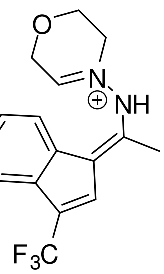
C	-1.069930	0.442151	-0.623686
C	1.290442	0.489722	-0.611796
N	1.327559	1.842826	-0.602918
N	0.164077	2.432437	-0.179427
C	2.157134	2.666938	-1.535537
C	2.095362	-0.302995	-1.598192
C	3.079660	0.521519	-2.441684
C	2.481471	1.881969	-2.805681
C	-1.085708	-0.609115	0.435179
C	-1.871671	-0.098935	-1.716914
C	-1.026195	1.845375	-0.359462
C	-2.197533	-1.390209	-1.444192
C	-1.751823	-1.737967	-0.101494
C	-2.885296	-2.324585	-2.387598
C	-2.229991	2.730832	-0.341237
C	-0.632738	-0.619334	1.751054
C	-1.918067	-2.890892	0.662847
C	-1.432404	-2.904543	1.970303
C	-0.805917	-1.781060	2.510825
H	-1.557729	-3.791858	2.578551
H	-0.456524	-1.802636	3.536066
H	-0.170093	0.251068	2.206346
H	-2.431664	-3.753750	0.257379
H	-2.091135	0.420616	-2.638566
F	-4.008079	-2.831998	-1.841187
F	-3.225274	-1.710993	-3.536067
F	-2.088989	-3.369451	-2.701408
H	0.237635	3.410686	0.079904
H	1.047162	0.025824	0.329108
H	-2.792413	2.570921	-1.266327
H	-2.895604	2.447633	0.478599
H	-1.985001	3.791858	-0.262719
H	1.368174	-0.808096	-2.248641
H	2.608255	-1.105464	-1.062593
H	4.008079	0.671995	-1.881577
H	3.343311	-0.034584	-3.342292
H	1.574878	1.756598	-3.406495
H	3.183007	2.472195	-3.399419
H	3.071306	2.941637	-1.004002
H	1.598513	3.575593	-1.762978

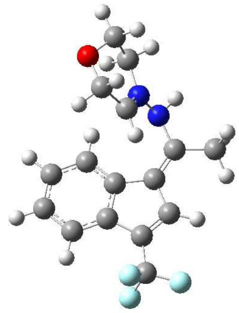




E = -1064.377640 (0)

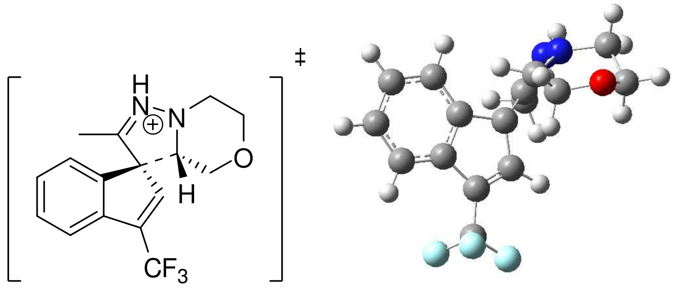
C	0.403023	-0.828931	-0.447104
C	-0.852158	-1.011973	-1.363043
N	-1.840881	-0.117556	-0.684840
N	-1.480363	-0.194590	0.661679
C	-3.277450	-0.296628	-0.984164
C	-1.350884	-2.465554	-1.461546
C	-2.793858	-2.548098	-1.976130
C	-3.729753	-1.756324	-1.056004
C	1.289963	0.376596	-0.794601
C	1.404396	-1.966964	-0.411041
C	-0.255647	-0.542738	0.891743
C	2.639172	-1.510971	-0.668375
C	2.620890	-0.063054	-0.914665
C	3.879010	-2.356044	-0.699636
C	0.374443	-0.549710	2.232615
C	0.956755	1.709149	-0.988090
C	3.637255	0.830373	-1.237878
C	3.300432	2.171023	-1.433346
C	1.980255	2.605764	-1.313094
H	4.075997	2.883339	-1.687383
H	1.742605	3.649563	-1.478735
H	-0.067543	2.054264	-0.909874
H	4.662684	0.498173	-1.338831
H	1.144556	-2.991893	-0.193129
F	4.759176	-1.939151	0.232410
F	3.605501	-3.649563	-0.461884
F	4.487079	-2.270685	-1.896969
H	-2.127883	0.166599	1.357413
H	-0.662924	-0.600618	-2.354531
H	0.630446	-1.574539	2.517533
H	1.309757	0.015426	2.201083
H	-0.276376	-0.123201	2.997010
H	-1.301961	-2.948768	-0.478577
H	-0.670366	-3.015107	-2.116227
H	-2.854273	-2.152887	-2.997010
H	-3.103733	-3.593661	-2.028030
H	-3.737949	-2.204589	-0.055295
H	-4.759176	-1.785352	-1.421701
H	-3.425922	0.192656	-1.950129
H	-3.845074	0.287184	-0.254004





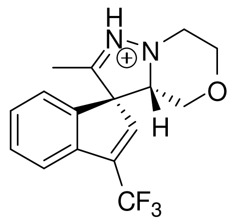
E = -1100.215341 (0)

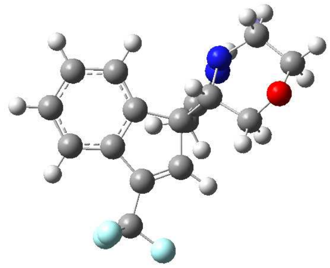
C	-1.534693	0.235144	-0.997781
C	1.557480	0.795205	-1.292808
N	1.042030	1.883583	-1.757338
N	-0.316036	2.074699	-2.016423
C	1.844178	3.133490	-1.875666
C	2.994436	0.710947	-0.883334
O	3.638107	1.955562	-0.806554
C	3.325541	2.779636	-1.915636
C	-1.083722	0.374836	0.402482
C	-2.350221	-0.989659	-1.039433
C	-1.246217	0.996075	-2.085462
C	-2.354308	-1.563018	0.181419
C	-1.580209	-0.741393	1.121266
C	-3.033453	-2.846676	0.539149
C	-1.893013	0.866292	-3.435846
C	-0.376830	1.369341	1.074457
C	-1.341287	-0.884540	2.479260
C	-0.601509	0.107071	3.135954
C	-0.136986	1.223726	2.447229
H	-0.407604	0.012595	4.197582
H	0.402187	1.997604	2.980176
H	-0.065167	2.278086	0.575972
H	-1.728211	-1.734555	3.027028
H	-2.835117	-1.390652	-1.915267
F	-3.921570	-2.665292	1.536918
F	-3.687972	-3.374150	-0.508734
F	-2.135375	-3.759860	0.968889
H	-0.401713	2.731157	-2.784295
H	0.925619	-0.080547	-1.227419
H	-2.301074	1.833371	-3.753848
H	-1.172970	0.548034	-4.197583
H	-2.720845	0.162236	-3.424514
H	3.500887	0.025015	-1.584592
H	3.044935	0.250571	0.107176
H	3.584448	2.284799	-2.860993
H	3.921570	3.686464	-1.824250
H	1.600085	3.759860	-1.016284
H	1.531337	3.639828	-2.791863



E = -1100.169767 (1)

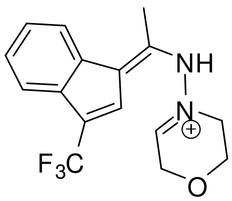
C	-0.977740	0.759905	-1.037058
C	1.201472	1.073536	-0.154042
N	1.535965	1.956420	-1.120912
N	0.467754	2.502756	-1.787938
C	2.771209	1.770436	-1.940185
C	2.130944	-0.059159	0.180625
O	3.306455	-0.138724	-0.596696
C	3.136678	0.287266	-1.934086
C	-1.576788	0.926797	0.320194
C	-1.501055	-0.508522	-1.537488
C	-0.693157	1.845615	-1.918117
C	-2.200224	-1.130421	-0.552459
C	-2.294171	-0.258869	0.612050
C	-2.768331	-2.511944	-0.637119
C	-1.588719	2.270204	-3.036826
C	-1.571144	1.986466	1.222154
C	-2.962885	-0.400178	1.825577
C	-2.925335	0.654096	2.738907
C	-2.246421	1.834952	2.438538
H	-3.442911	0.560386	3.685618
H	-2.248125	2.651368	3.150572
H	-1.077863	2.928190	1.001064
H	-3.517217	-1.303047	2.049641
H	-1.288332	-0.923581	-2.512110
F	-4.091374	-2.510466	-0.381155
F	-2.582521	-3.050928	-1.855442
F	-2.188195	-3.329106	0.267197
H	0.675330	3.329106	-2.339180
H	0.561115	1.425575	0.637720
H	-2.536731	2.644109	-2.640635
H	-1.140800	3.025315	-3.685617
H	-1.830796	1.390759	-3.641396
H	1.543083	-0.989139	0.111628
H	2.448950	0.034959	1.222665
H	2.369191	-0.304105	-2.451499
H	4.091374	0.137299	-2.437291
H	3.569410	2.360582	-1.488691
H	2.575917	2.128644	-2.951609

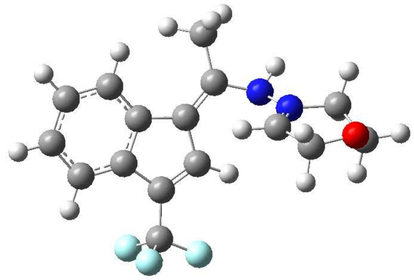




E = -1100.243874 (0)

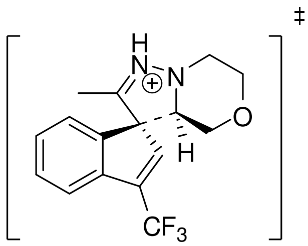
C	0.320091	-0.804913	-0.760930
C	-0.925246	-0.974389	-1.685603
N	-1.941073	-0.115037	-1.002961
N	-1.576184	-0.191063	0.345755
C	-3.364152	-0.384895	-1.307373
C	-1.424511	-2.429249	-1.797728
O	-2.737707	-2.473207	-2.316797
C	-3.668572	-1.875624	-1.425948
C	1.221395	0.390580	-1.100297
C	1.309695	-1.955581	-0.721122
C	-0.345175	-0.518680	0.574697
C	2.550232	-1.511038	-0.971930
C	2.547973	-0.062994	-1.215525
C	3.782150	-2.369205	-0.997469
C	0.285911	-0.508054	1.914998
C	0.900649	1.726068	-1.293789
C	3.574462	0.821011	-1.532698
C	3.250992	2.165051	-1.727245
C	1.934432	2.612886	-1.612603
H	4.034421	2.870203	-1.977006
H	1.708077	3.659133	-1.778266
H	-0.120871	2.080976	-1.220623
H	4.596960	0.479081	-1.630571
H	1.040854	-2.978240	-0.501651
F	4.660916	-1.960207	-0.061140
F	3.493318	-3.659133	-0.760503
F	4.395367	-2.289521	-2.191788
H	-2.224312	0.169070	1.041622
H	-0.746059	-0.559280	-2.676282
H	1.216906	0.063560	1.877542
H	-0.367574	-0.080253	2.676282
H	0.549799	-1.528721	2.208050
H	-1.393005	-2.932800	-0.819343
H	-0.787753	-2.982846	-2.488064
H	-3.630741	-2.374058	-0.445443
H	-4.660916	-2.027785	-1.850593
H	-3.551234	0.106211	-2.263988
H	-3.984387	0.114100	-0.557457

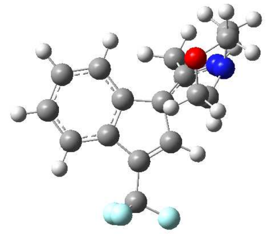




E = -1100.212445 (0)

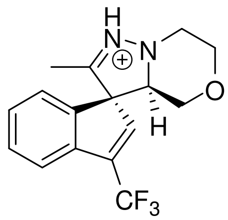
C	-1.029560	0.608197	-0.550440
C	1.953721	1.013877	0.557254
N	1.999646	1.509770	-0.630553
N	0.887319	1.705344	-1.462015
C	3.299660	1.811560	-1.299237
C	3.192458	0.748938	1.353383
O	4.360988	1.278698	0.786317
C	4.419730	1.041457	-0.609876
C	-2.303839	0.364564	0.168168
C	-0.471932	-0.718752	-0.852971
C	-0.432875	1.776057	-0.894350
C	-1.316263	-1.667825	-0.396742
C	-2.471584	-1.039996	0.257412
C	-1.124983	-3.143929	-0.555411
C	-1.013349	3.157360	-0.810673
C	-3.239771	1.205959	0.758750
C	-3.570202	-1.597947	0.892994
C	-4.517788	-0.737915	1.459672
C	-4.351442	0.642098	1.397645
H	-5.385384	-1.152789	1.958235
H	-5.089422	1.292937	1.850511
H	-3.133295	2.282135	0.749162
H	-3.694315	-2.671619	0.957308
H	0.423987	-0.894736	-1.428042
F	-2.130157	-3.694672	-1.258921
F	0.029628	-3.430285	-1.187637
F	-1.093894	-3.754987	0.648121
H	1.103205	2.482749	-2.077858
H	0.982490	0.767620	0.969217
H	-2.100584	3.132517	-0.814557
H	-0.682214	3.692230	0.087432
H	-0.701497	3.754987	-1.673939
H	3.263243	-0.342612	1.502257
H	3.071219	1.196442	2.344340
H	4.344508	-0.031051	-0.831458
H	5.385383	1.402686	-0.960171
H	3.456401	2.890123	-1.229128
H	3.192449	1.517607	-2.344340

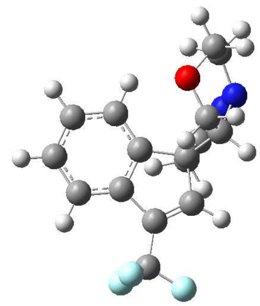




E = -1100.174375 (1)

C	0.605686	0.424424	-0.349716
C	2.414241	0.541679	1.262290
N	3.122862	1.350215	0.451826
N	2.770672	1.294900	-0.870604
C	3.588853	2.693285	0.891572
C	2.225631	0.917129	2.701473
O	2.446253	2.283926	2.951799
C	3.689128	2.702248	2.412627
C	-0.796419	0.829832	-0.168919
C	0.611539	-1.046868	-0.154569
C	1.493393	1.073423	-1.249312
C	-0.638414	-1.462236	0.148317
C	-1.548544	-0.318449	0.181161
C	-1.031517	-2.883176	0.393927
C	1.117846	1.549757	-2.618791
C	-1.400399	2.086308	-0.201536
C	-2.903344	-0.216109	0.478871
C	-3.502433	1.043246	0.417798
C	-2.762406	2.180802	0.082131
H	-4.557567	1.142066	0.642641
H	-3.250557	3.147319	0.053169
H	-0.832075	2.982303	-0.428120
H	-3.483337	-1.088991	0.751100
H	1.461475	-1.692123	-0.324900
F	-1.991405	-3.282913	-0.461962
F	0.017226	-3.718268	0.258451
F	-1.521863	-3.041245	1.642241
H	3.444037	1.699743	-1.512335
H	2.412993	-0.506519	1.023024
H	0.090026	1.911665	-2.604426
H	1.771877	2.337939	-2.997146
H	1.137739	0.704252	-3.315604
H	2.890706	0.286036	3.315604
H	1.199337	0.681991	2.995822
H	4.506765	2.058296	2.761802
H	3.873400	3.718269	2.759120
H	2.860920	3.438159	0.558750
H	4.557567	2.886977	0.422677

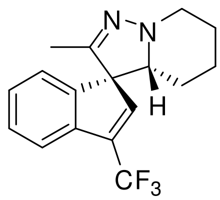


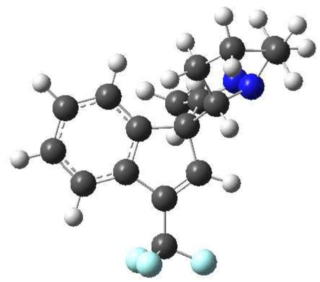


E = -1100.242114 (0)

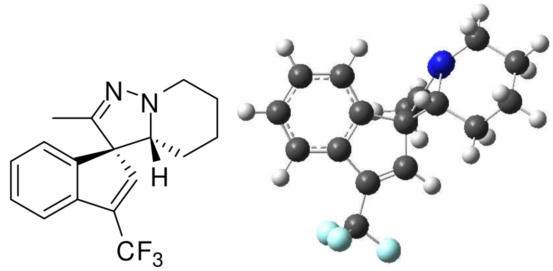
C	1.223450	0.023393	0.305582
C	2.373734	0.872307	0.957052
N	2.364823	2.186347	0.240582
N	1.672522	1.896501	-0.939940
C	1.789454	3.383223	0.914949
C	2.398893	1.022897	2.485969
O	1.622729	2.110103	2.941544
C	2.111332	3.327188	2.403298
C	-0.139092	-0.119509	0.992903
C	1.637159	-1.426949	0.110418
C	1.066058	0.752920	-1.012200
C	0.700193	-2.253856	0.594599
C	-0.426200	-1.491155	1.146474
C	0.784573	-3.752519	0.584851
C	0.362856	0.274943	-2.225866
C	-1.042574	0.841259	1.421748
C	-1.610684	-1.911437	1.741977
C	-2.512070	-0.938809	2.177147
C	-2.233446	0.418707	2.020237
H	-3.439906	-1.243179	2.646086
H	-2.943571	1.156273	2.373617
H	-0.838757	1.899904	1.328412
H	-1.831700	-2.963954	1.865960
H	2.575100	-1.715473	-0.343582
F	-0.237886	-4.276709	-0.119556
F	1.931333	-4.181497	0.033981
F	0.710398	-4.244278	1.834773
H	1.707644	2.584548	-1.688173
H	3.308794	0.390842	0.656372
H	-0.593993	-0.167507	-1.941173
H	0.193902	1.074840	-2.948047
H	0.950624	-0.514185	-2.705907
H	3.439905	1.145566	2.811077
H	2.000747	0.119392	2.948047
H	3.191074	3.422919	2.577274
H	1.602186	4.141788	2.917248
H	0.700934	3.411062	0.790292
H	2.222030	4.276709	0.456937

The following two diastereomeric structures of **5m** were calculated for the assignement of the diastereomers based on NMR-NOE-experiments





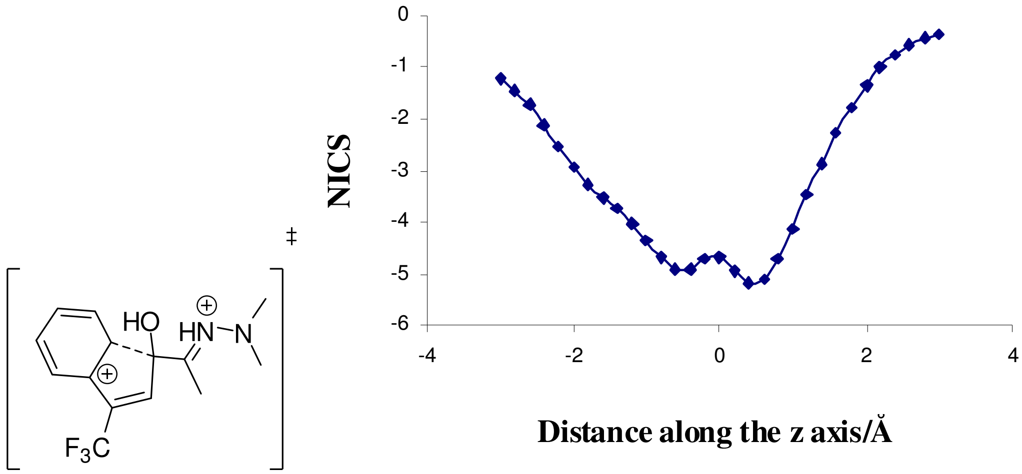
C	-1.988711	-2.466549	0.629202
C	-0.605832	-2.615305	0.524578
C	0.229799	-1.496293	0.452173
C	-0.336629	-0.228932	0.474467
C	-1.732561	-0.085823	0.601728
C	-2.567019	-1.197957	0.675506
C	0.312818	1.144077	0.447040
C	-0.892467	2.060509	0.580499
C	-2.028987	1.353185	0.662690
C	-3.399232	1.922898	0.804691
F	-3.993196	1.510570	1.950733
F	-3.396441	3.270103	0.818289
F	-4.210311	1.531600	-0.207710
C	1.307016	1.443713	1.581800
N	2.278006	2.182572	1.196620
N	2.155240	2.497659	-0.147777
C	1.177643	1.561397	-0.787896
C	1.117543	1.024924	3.002513
C	1.914858	0.465885	-1.563491
C	2.743169	1.105422	-2.703438
C	3.266868	2.510823	-2.322935
C	3.460712	2.637037	-0.813629
H	-2.620606	-3.345628	0.684580
H	-0.172666	-3.608833	0.503315
H	1.303262	-1.627218	0.386386
H	-3.639735	-1.084280	0.773142
H	-0.801797	3.137597	0.597531
H	0.552194	2.123273	-1.486067
H	0.168274	1.399002	3.401086
H	1.095495	-0.064668	3.097331
H	1.932616	1.419135	3.609470
H	1.208678	-0.264252	-1.963887
H	2.577765	-0.073700	-0.879900
H	3.581780	0.445908	-2.945154
H	2.134265	1.176158	-3.609470
H	2.560036	3.281116	-2.647815
H	4.210311	2.720538	-2.832432
H	4.162583	1.867675	-0.460012
H	3.881032	3.608833	-0.544719



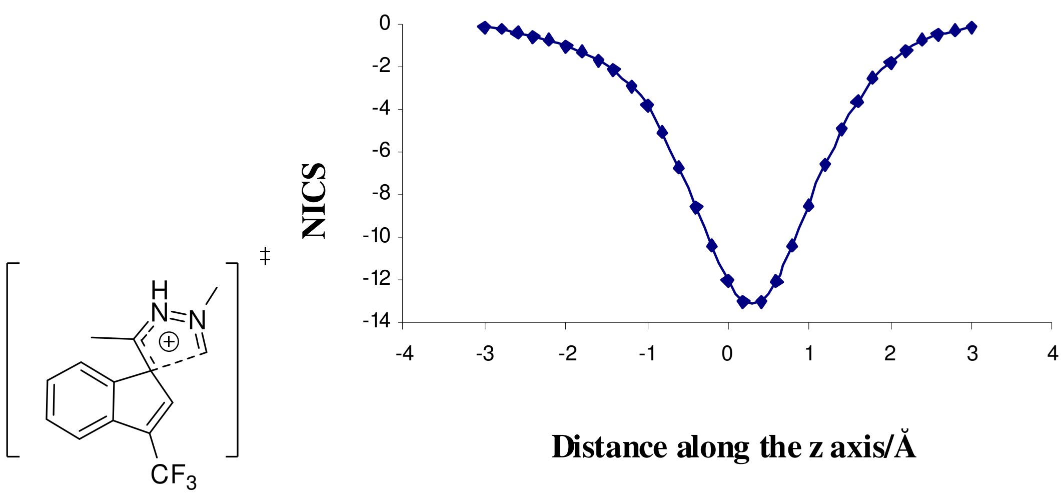
C	-1.476398	-3.106288	0.440447
C	-0.087341	-2.990426	0.365456
C	0.523140	-1.736381	0.265337
C	-0.282556	-0.607517	0.233742
C	-1.681680	-0.725257	0.311829
C	-2.290716	-1.973537	0.415755
C	0.100156	0.866742	0.135058
C	-1.251874	1.538893	0.147285
C	-2.238440	0.634218	0.257961
C	-3.694603	0.948892	0.324748
F	-4.245383	0.518174	1.484487
F	-3.938950	2.272116	0.233663
F	-4.381151	0.344151	-0.673668
C	1.046436	1.262894	1.292633
N	2.269045	1.310460	0.917621
N	2.361123	0.976206	-0.430015
C	1.038581	1.206336	-1.060636
C	0.617208	1.446164	2.709799
C	0.892712	2.648434	-1.588176
C	2.101479	3.060714	-2.440372
C	3.396009	2.922374	-1.629458
C	3.544218	1.482574	-1.121345
H	-1.928975	-4.088154	0.519975
H	0.526471	-3.883827	0.387211
H	1.601420	-1.643666	0.210235
H	-3.368227	-2.066657	0.476731
H	-1.392911	2.608401	0.094975
H	0.902045	0.497117	-1.881200
H	-0.077663	2.285548	2.814645
H	0.099898	0.554479	3.080012
H	1.490514	1.631021	3.335589
H	0.809372	3.340929	-0.743140
H	-0.034100	2.728983	-2.163877
H	2.158831	2.427333	-3.335588
H	1.972811	4.088155	-2.792948
H	3.372523	3.609298	-0.775820
H	4.267728	3.189373	-2.235581
H	3.733688	0.814930	-1.970530
H	4.381151	1.381661	-0.429368

NICS vs distance along the z axis diagrams of the transition states

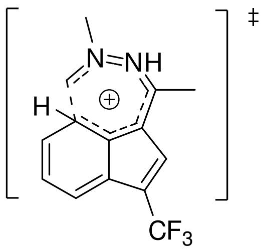
NICS values were determined at B3LYP/6-311+G(d,p) level with respect to an axis perpendicular to the centre of the formed cyclic system)

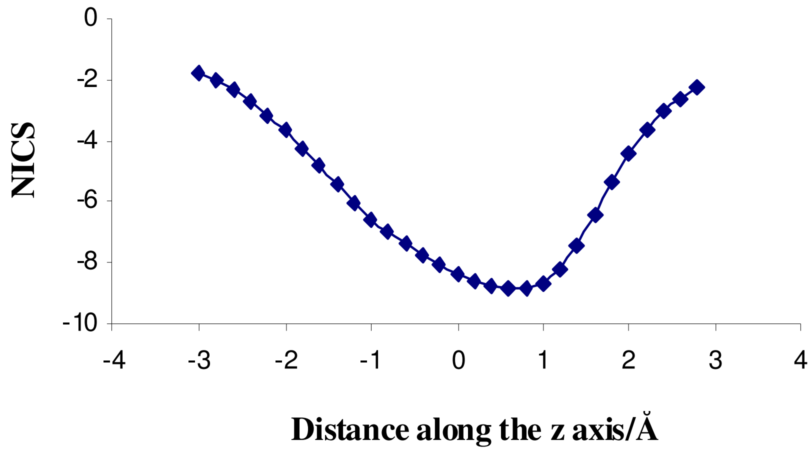


Representation of the dependence of the NICS value on the distance along the z axis for the transition structure of dicationic 1,5-electrocyclization, which affords the indenole intermediate.



Representation of the dependence of the NICS value on the distance along the z axis for the transition structure of 1,5-electrocyclization.

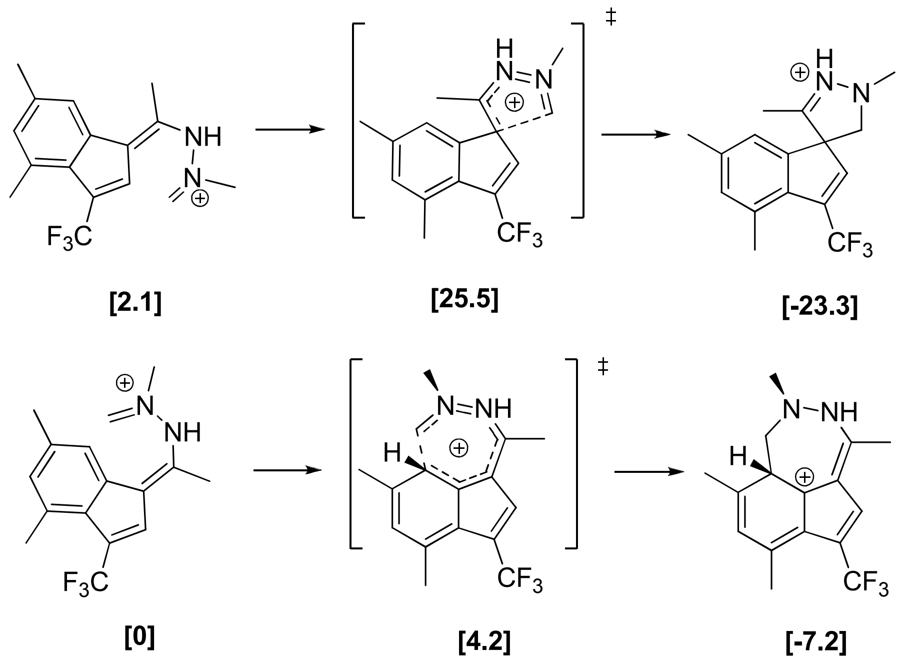




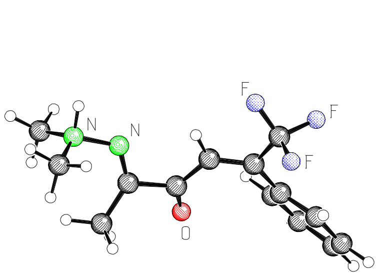
Representation of the dependence of the NICS value on the distance along the z axis for the transition structure of 1,7-electrocyclization.

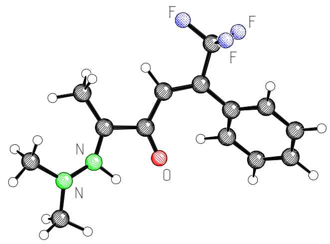
Quantum chemical results obtained for cyclization reactions of dimethyl-substituted intermediates (see Table 1, compound 4h).

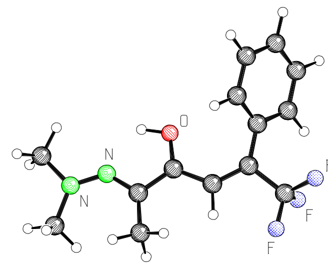
The formation of the seven-membered ring is kinetically favored. In comparison to the system without dimethyl substitution (see Scheme 7) the seven-membered system is stabilized by 4.7 kcal/mol.



Quantum chemical results concerning the preferred protonation site of azadienones 4, displayed in Scheme 5 (relative energies [kcal/mol])



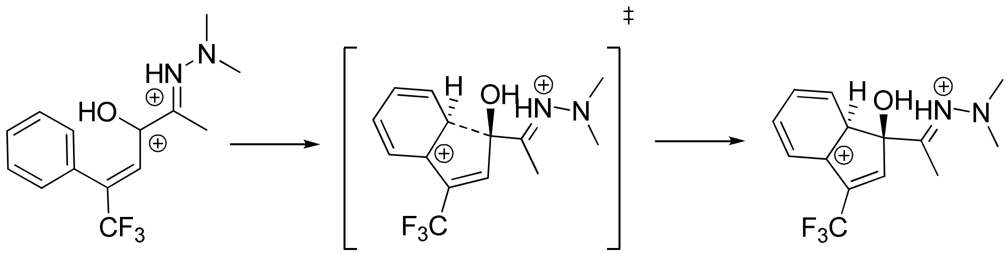




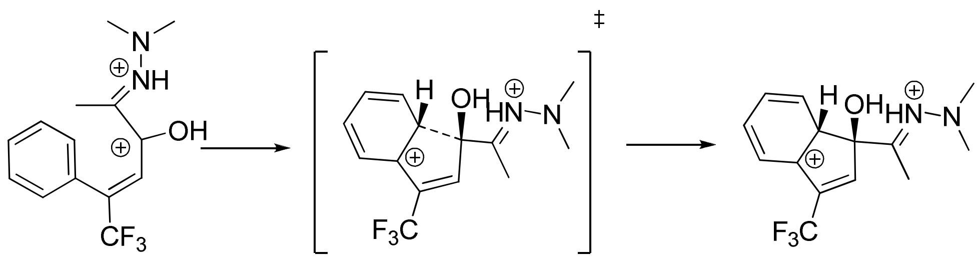
[5.8] **[4.0]** **[0.0]**

N2-protonation N1-protonation O-protonation

Quantum chemical results for two different cyclization modes leading to diasteromeric intermediates (Compare Scheme 6)

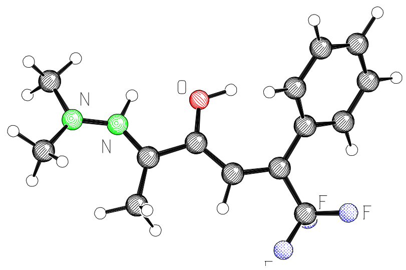


[0] **[15.7]** **[6.9]**

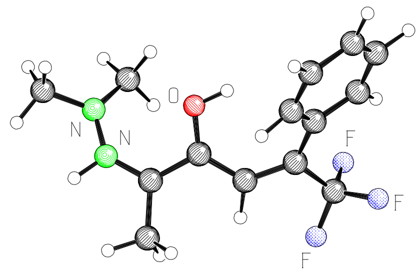


[4.3] **[14.2]** **[4.8]**

Quantum chemical results for two conformations of the diprotonated azadienone 4a

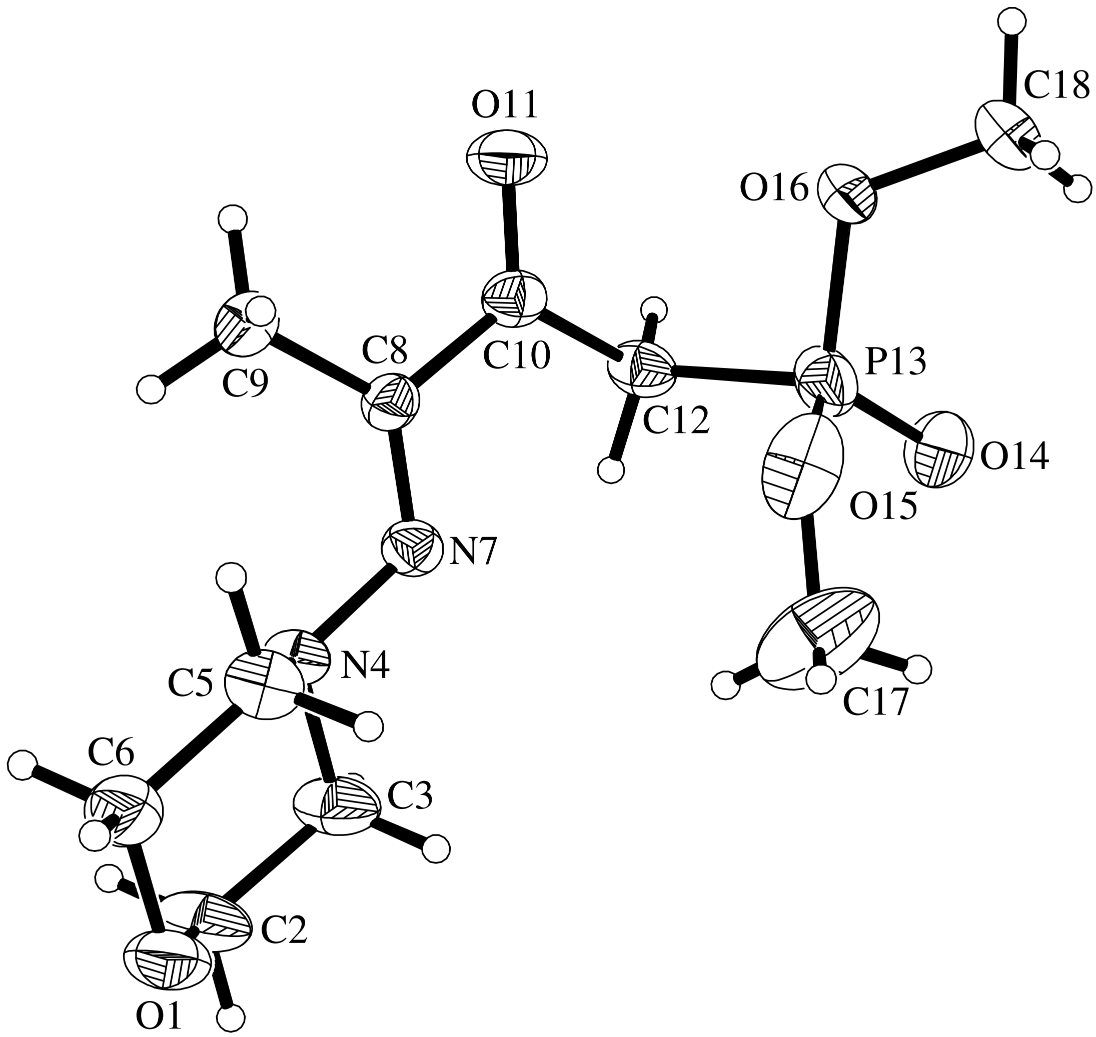


[0.0]

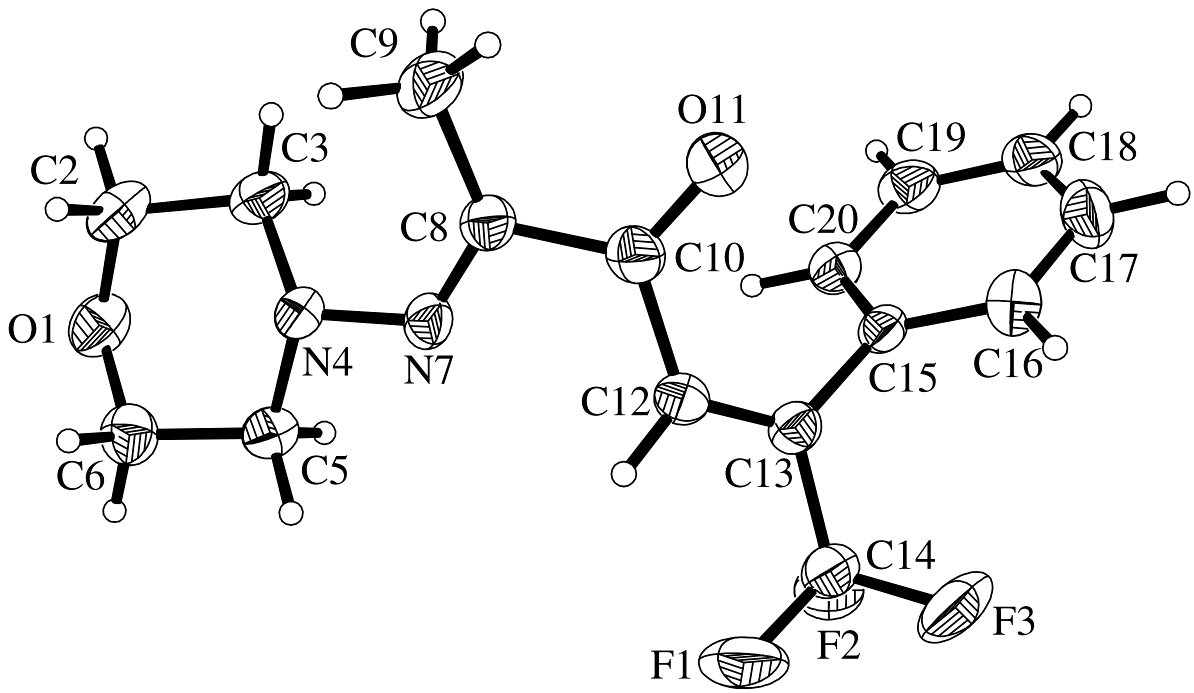


[4.2]

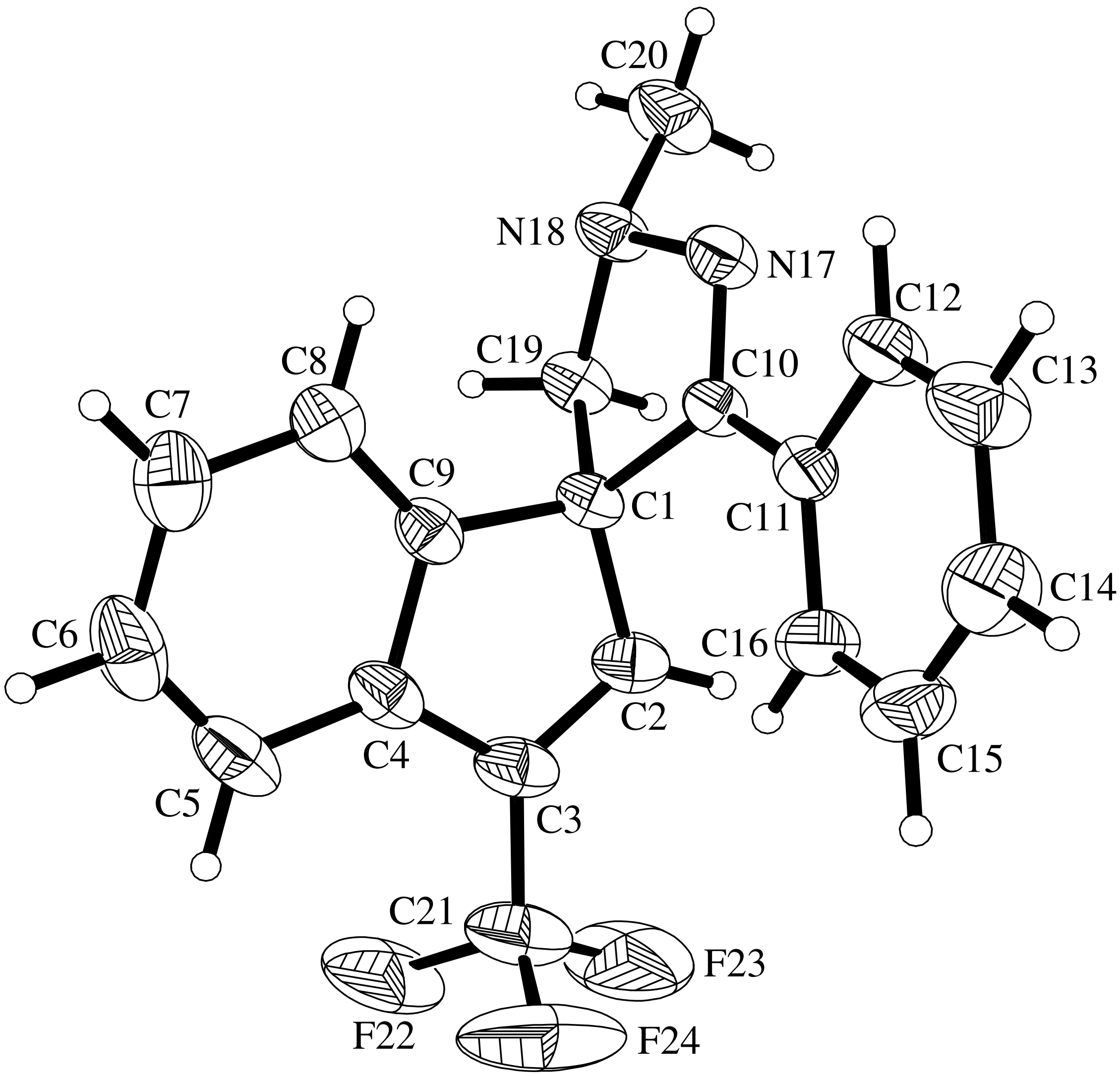
Thermal Ellipsoid Plots for the Crystal Structures (Ellipsoid Probability Contours 50 %)



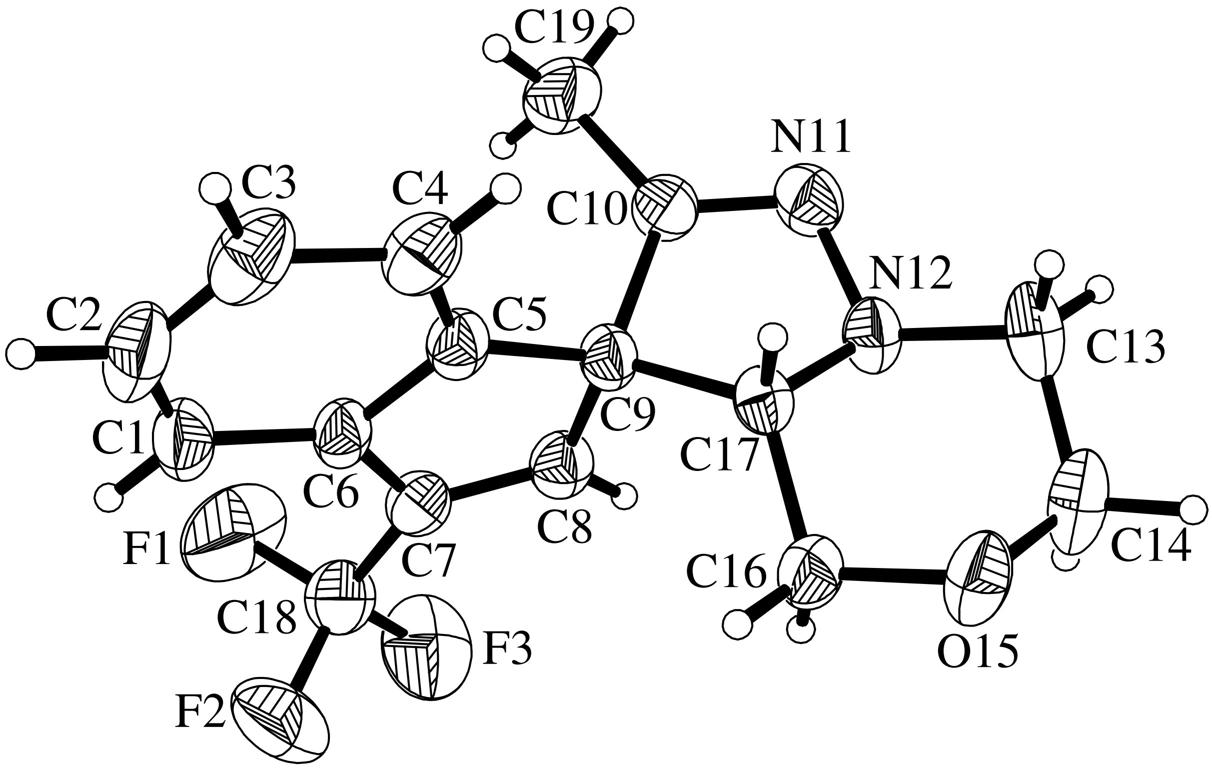
3l


C9
O11
C2
C3
C19
C18
C8
C20
C10
C17
O1
N4
N7
C16
C15
C12
C5
C6
C13
C14
F3
F2
F1

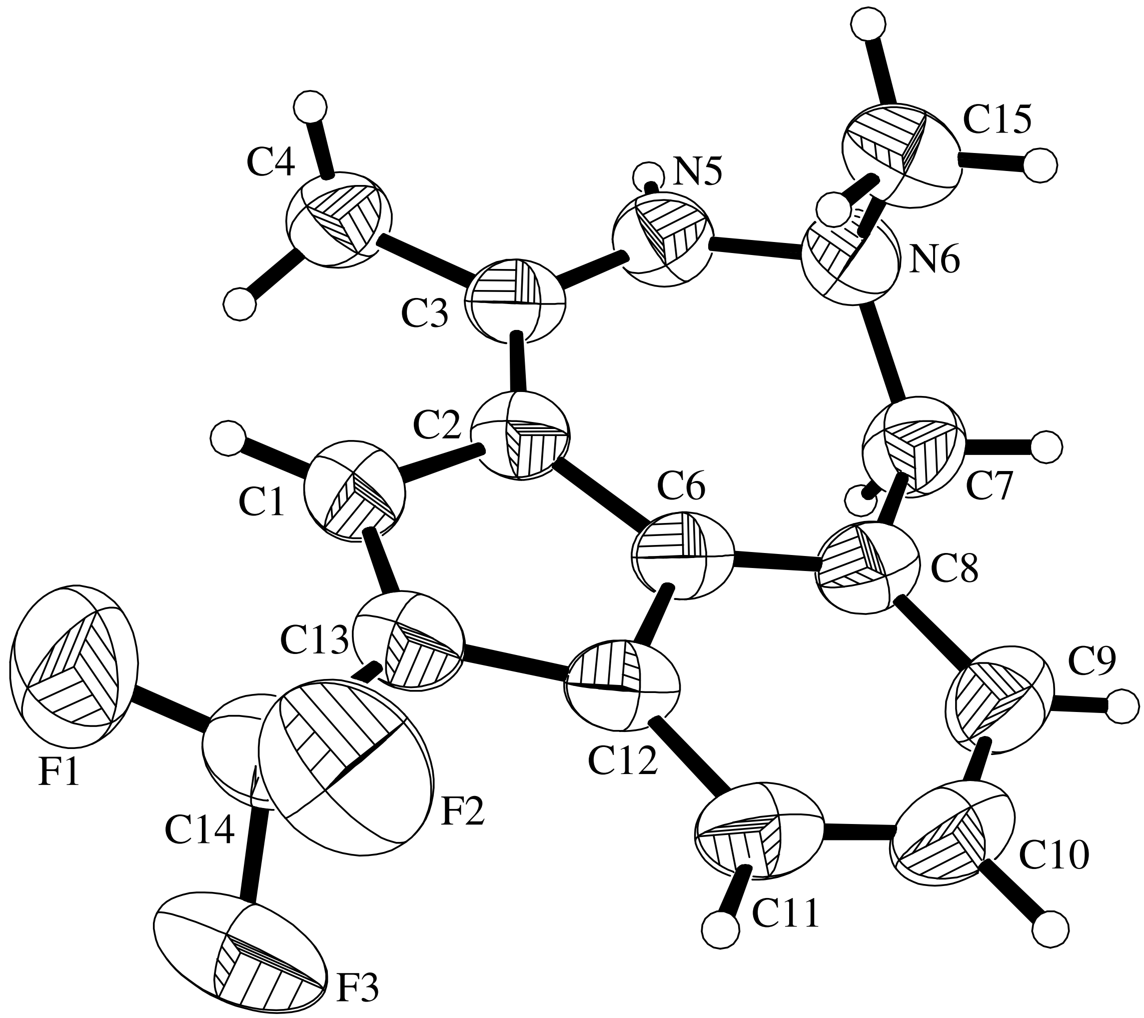
4o


C20
N18
N17
C12
C13
C19
C10
C8
C7
C9
C1
C11
C14
C6
C16
C2
C4
C15
C3
C5
C21
F23
F22
F24

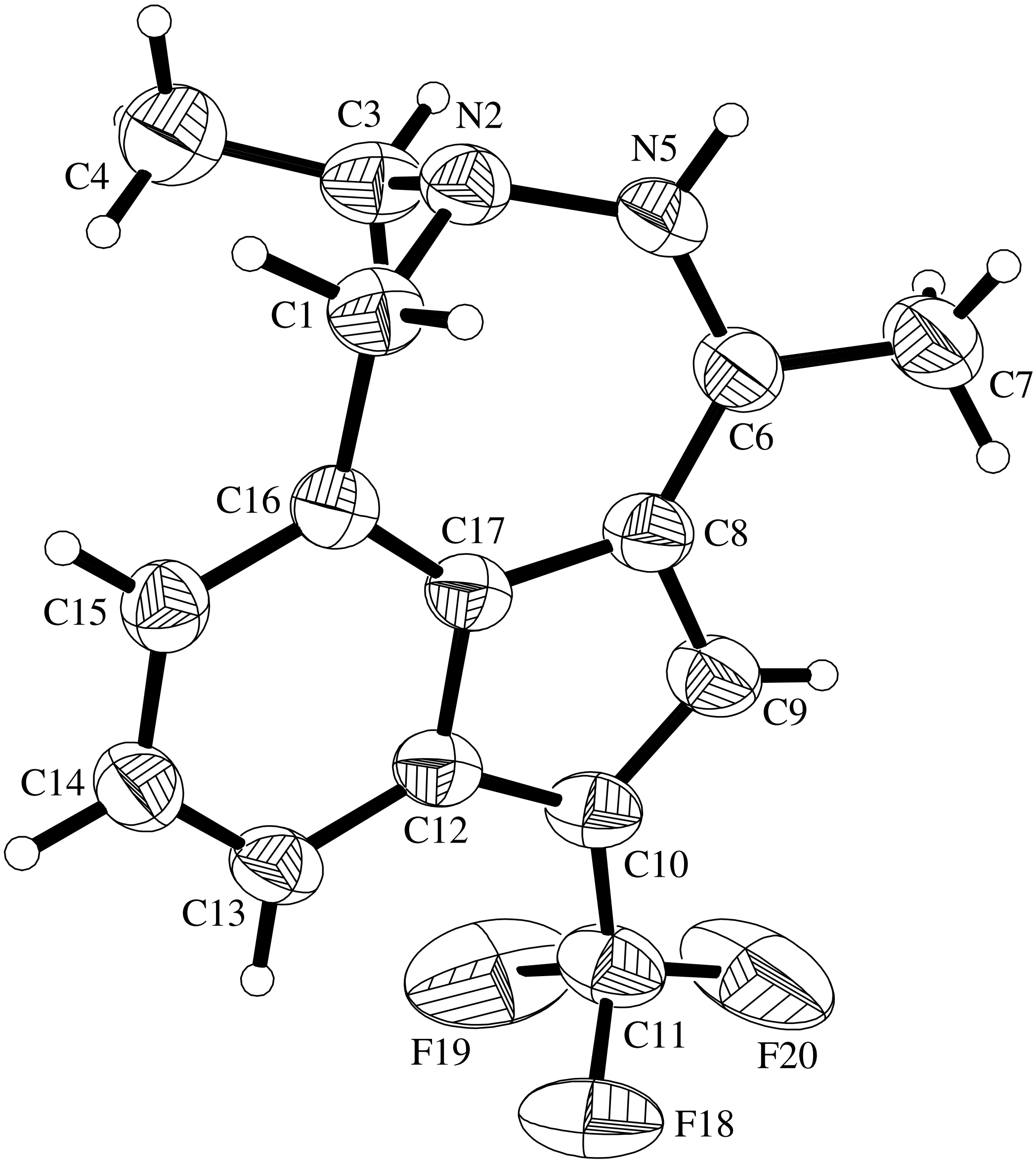
5e


C19
C3
C4
C10
N11
C2
C5
N12
C9
C13
C17
C1
C6
C8
C7
F1
C16
C14
C18
F3
O15
F2

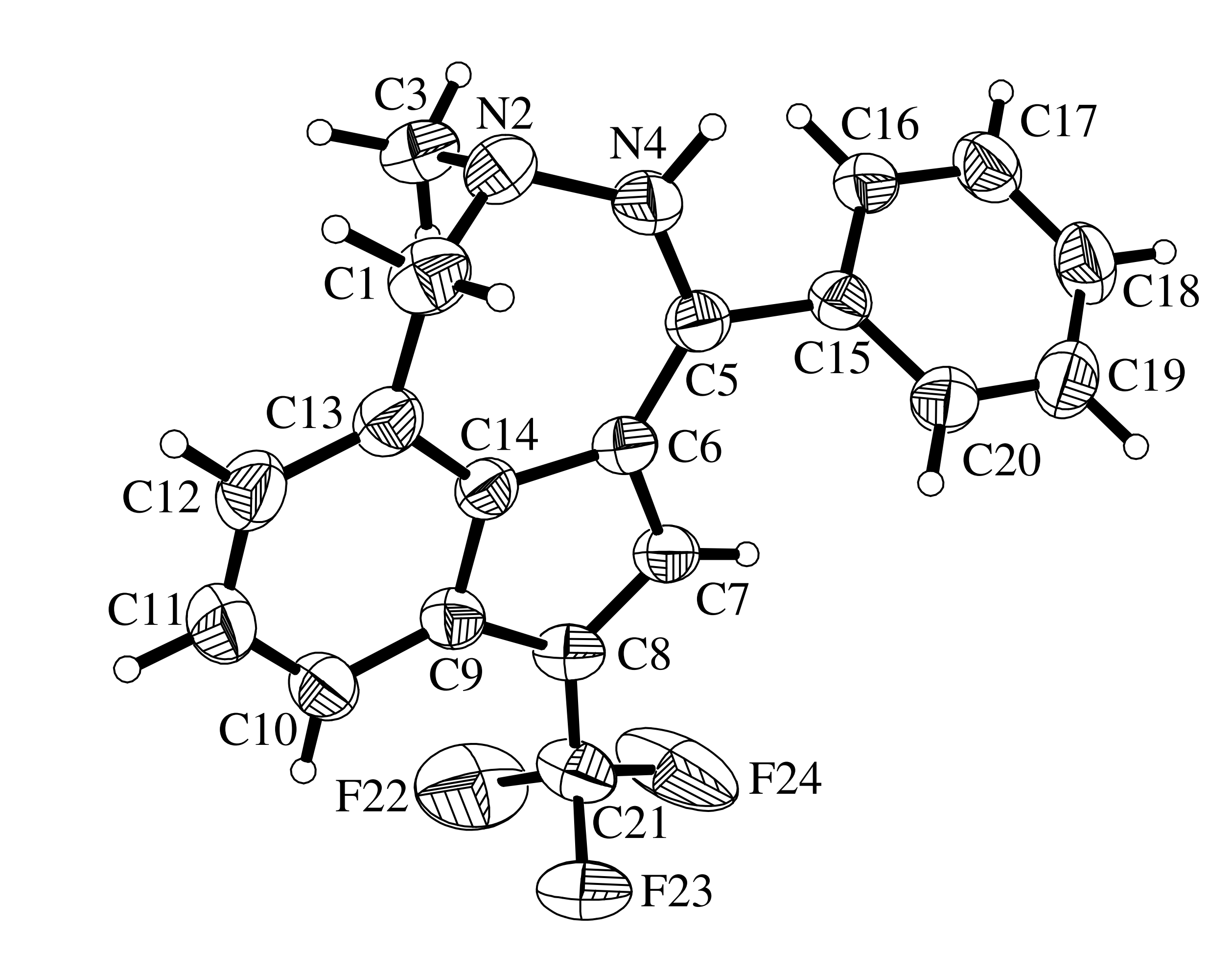
5o



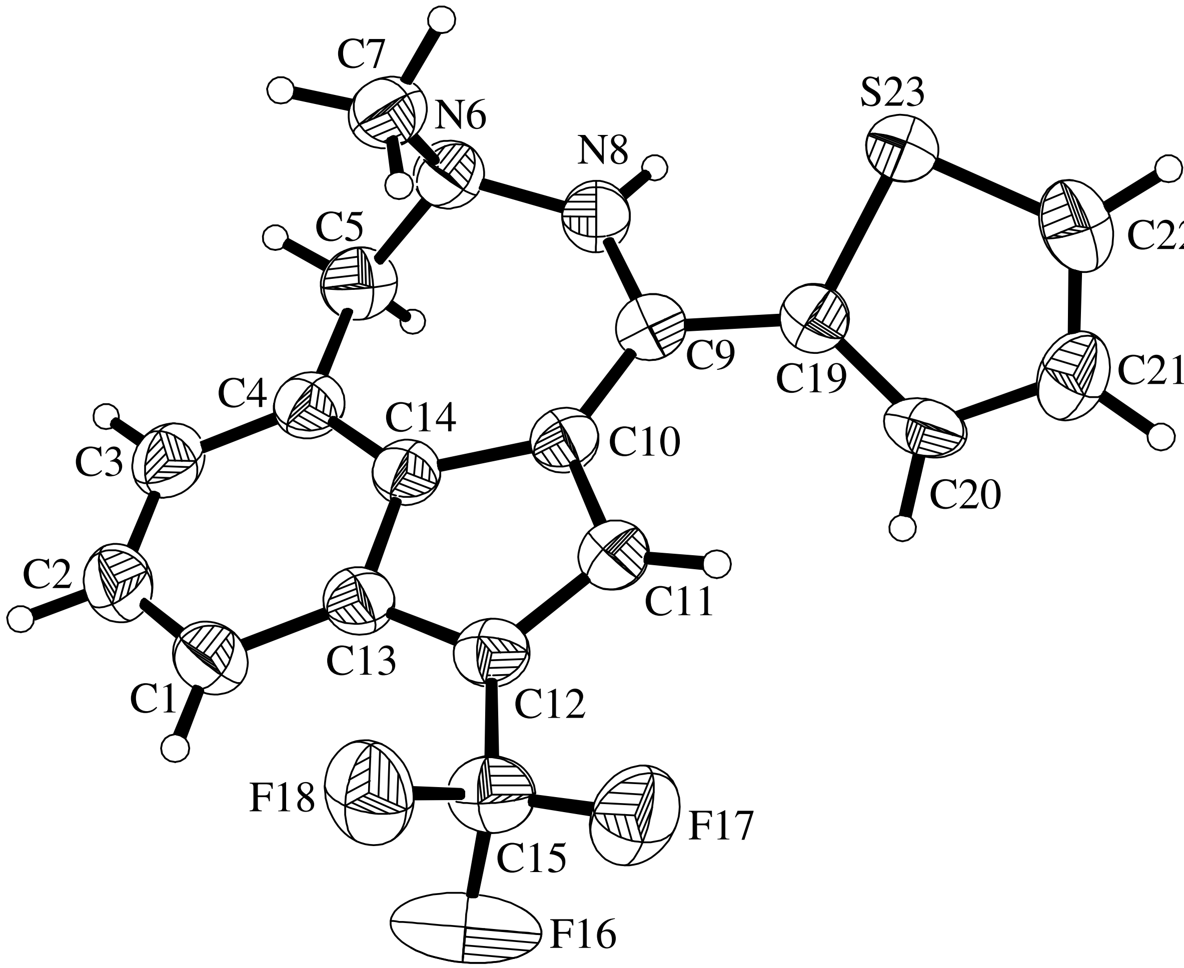
6a


C3
N2
N5
C4
C1
C7
C6
C16
C17
C8
C15
C9
C14
C12
C10
C13
F19
C11
F20
F18

6b


C3
N2
N4
C16
C17
C1
C18
C5
C15
C19
C13
C14
C6
C20
C12
C7
C11
C8
C9
C10
F22
F24
C21
F23

6e



6f

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[1] Severin, T.; Supp, W.; Manninger, G. *Chem. Ber*. **1979,** *112*, 3013.

[2] Data sets were collected with Enraf-Nonius CAD4- and Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998), data reduction MolEN (Fair, K. Enraf-Nonius B.V., 1990) and Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods in Enzymology*, **1997**, *276*, 307.), absorption correction for CCD-data SORTAV (Blessing, R.H. *Acta Cryst.* **1995**, *A51*, 33; Blessing, R.H. *J. Appl. Cryst.* **1997**, *30*, 421) and Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Cryst.* **2003**, *A59*, 228), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Cryst.* **1990**, *A46*, 467), structure refinement SHELXL-97 (Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122), graphics

SCHAKAL (Keller, E. 1997). CCDC-693648 (**6a**), -693649 (**3l**), -693650 (**5**o), -693651 (**4o**), -693652 (**6b**), -693653 (**6f**), -693654 (**6e**) and -693655 (**5e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

[3] Ghavtadze, N.; Fröhlich, R.; Würthwein, E-U. *Eur. J. Org. Chem.* **2008**, 3656.