Supporting Information

Evgeniya A. Varaksina[a*], Alexey I. Ferulev[a,b], Vladislav M. Korshunov[a,b], Tatyana S. Stankevich[a,d], Victoria E. Gontcharenko[a,e], Ilya V. Taydakov[a,e]

a *P. N. Lebedev Physical Institute of the Russian Academy of Sciences, 53 Leninskiy Prospect, 119991 Moscow, Russia*

b *Bauman Moscow State Technical University, 5/1 2-ya Baumanskaya str., 105005 Moscow, Russia*

c *Chemistry Department, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russia*

d *N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences, 47 Leninskiy Prospect, 119991 Moscow, Russia*

e *Faculty of Chemistry, National Research University Higher School of Economics, 20 Miasnitskaya Str., Moscow 101000, Russia*

Synthesis of starting compounds and ketones 4a-c

2-(4-Bromophenyl)-2-methyl-1,3-dioxolane (2)

This compound was obtained according published procedure [24] with some modifications.

4-Bromoacetophenone (**1**) (80.0 g, 0.402 mol), ethylene glycol (23.2 mL, 25.7 g, 0.415 mol), and p-toluenesulfonic acid (0.15 g) were dissolved in toluene (100 mL). The resulting solution was refluxed for 24 hours using a Dean-Stark apparatus; the reaction progress was monitored by the amount of water collected (15 mL). The resulting yellow solution was washed with 50mL of saturated aqueous $KHCO_3$ solution, 50 mL of water, and 50 mL of brine. The organic solution was dried over $MgSO_4$, 2 drops of Et_3N and 2 drops of triethyl orthoformate were added, and solution was concentrated on a rotary evaporator. Upon concentration, the product crystallized as yellowish crystals. The yield of the target product was 90.7 g (93%).

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.56 (d, J = 8.3 Hz 2H). 7.38 (d, J = 8.3 Hz 2H, Ar), 3.97–4.02 (m, 2H), 3.67–3.72 (m, 2H), 1.55 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 142.67, 131.08, 127.37, 121.02, 107.65, 64.10, 27.07.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{10}H_{11}O_2Br$+Na 243.0015; Found 243.0022.

M.p. = 39–42 °C (lit. 40–42 °C [25]). FTIR spectrum of freshly prepared compound contains virtually no bands at 1670 and 1585 cm^{-1} corresponding to vibrations of free C=O group (see SI, Fig. S1).

1-Bromo-4-(1,1-diethoxyethyl)benzene (3)

A mixture of 4-bromoacetophenone **(1)** (54.6 g, 0.274 mol), triethyl orthoformate (90 mL, 80.2 g, 0.541 mol) and 0.1 g of p-toluenesulfonic acid were left in a closed flask at 25 °C (room temperature) for 3 days. Piperidine (0.3 mL) and solid NaOMe (60 mg) were added and mixture were evaporated at diminished pressure (10 torr). Resulted oil was distilled at 5 torr and fraction b.p. 119-121 °C (lit. 108-109.5 /5 torr [26]) was collected. Yield was 67.7 g (90%) of slightly viscous water-clear liquid.

It can be stored in a fridge at -18 °C for at least 2 years without any signs of decomposition. Sufficient vacuum level (at least 5 torr or better) is mandatory for the distillation, at lower vacuum decomposition may occur. NMR spectra should be made in non-acidic solvents like DMSO-d_6, as traces of acids causes full decomposition of sample.

^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.57 (d, J = 8.3 Hz 2H), 7.41 (d, J = 8.3 Hz, 2H), 3.58 – 3.08 (m, 5H), 1.47 (s, 3H), 1.15 (t, J = 7.0 Hz, 5H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 143.2, 131.3, 128.3, 121.7, 101.1, 56.9, 27.3, 15.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{12}H_{17}BrO_2$ +Na 295.0304; Found: 295.0313.

Chlorotriphenylgermane

Title compound was obtained by modified published procedure [27]. In 50 mL round bottom flack, equipped with Ar inlet, magnetic stirring bar and reflux condenser, 8 g of Ph_4Ge (21 mmol), 0.28 g (2.1 mmol, 10% mol.) anhydrous $AlCl_3$ and 1.4 g (0.75 mL, 6.5 mmol) $GeCl_4$ were mixed, and resulted mixture were heated on an old bath at 135-140 °C for 4h. Sample was taken from the mixture, quenched by 1 mL of anhydrous EtOH, evaporated and analyzed by GC-

MS. The reaction mixture was found to consist from Ph_4Ge and Ph_3GeCl in 55:45 ratio. More $GeCl_4$ (0.4 mL, 0.75 g, 3.5 mmol) was added, and heated was continued for additional 2h. At the end of the reaction brown homogenous liquid was obtained. It was cooled to a room temperature, poured into 10 mL of conc. HCl and extracted 3 times by CH_2Cl_2 (each portion of 40 mL). Combined organic phases were dried for 0.5h over $CaCl_2$ and evaporated, afforded brown solid (9.5 g). It was recrystallized from hot hexane (40 mL). Yield was 5.4 g (57%) of tan crystals. Less pure compound can be isolated from mother liquor.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.79-7.37 (m, 15H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 134.97, 134.16, 130.59, 128.81.

M.p. 113-114 °C (lit. 114 °C [28])

HRMS (ESI) m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{15}ClGe$ 340.0068; Found: 340.0083.

1-(4-(Triphenylsilyl)phenyl)ethan-1-one (4a).

In Ar atmosphere, solution of 1-bromo-4-(1,1-diethoxyethyl)benzene (7.1 g, 26 mmol) in 60 mL of dry THF was cooled to -70 °C (internal temperature, dry ice- 2-propanole bath) and 12.2 mL (27.3 mmol) of n-BuLi (2.24 M) was added dropwise with stirring during 20min. The resulted solution was kept at -70 °C for 1h, then solution of chlorotriphenylsilane (7.7 g, 26 mmol) in 50 mL was added slowly over 30min at the same temperature. Resulted mixture was stirred for additional 30min at -70 °C, then left to warm slowly to a room temperature with the cooling bath and left overnight. Next day clear orange solution was cooled to 0 °C, 10% HCl was added slowly to achieve pH~1, solution was stirred for 30min and evaporated. Resulted slurry was dissolved in 150 mL of EtOAc and 20 mL of water was added. Organic phase was separated, aqueous – extracted with EtOAc (50 mL). Combined organic extracts were washed with saturated $KHCO_3$ solution (50 mL), 50 mL of brine and dried over $MgSO_4$. Solvent was evaporated, and resulted solid was triturated by 50 mL of hot hexane. After cooling to a room temperature solid was collected, washed with 10 mL of cold hexane and dried in air to a constant weight. Yield was 5.7 g (58%) of light yellow powder.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.92 (d, J= 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.59 – 7.50 (m, 6H), 7.40-7.35 (m, 9H), 2.60 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 197.83, 140.65, 136.15, 137.31, 135.88, 132.91, 129.43, 127.59, 126.81, 26.20.

^{29}Si NMR (99 MHz, $CDCl_3$) δ (ppm): -14.23.

HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{26}H_{22}OSi$: 379.1513; Found: 379.1512.

M.p. 104-105 °C

1-(4-(Triphenylgermyl)phenyl)ethan-1-one (4b).

It was obtained in a same manner as silyl compound from 2.4 g (8.8 mmol) of 1-bromo-4-(1,1-diethoxyethyl)benzene and Ph_3GeCl (3.0 g, 8.8 mmol). Yield was 2.6 g of gray powder (69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.98 (d, J = 7.9 Hz, 2H), 7.71 (d, J= 7.7 Hz, 2H), 7.57 (dd, J_1 = 7.6, J_2 =1.8 Hz, 6H), 7.47 (d, J= 7.1 Hz, 2H), 7.46 – 7.39 (m, 7H), 2.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): 197.89, 142.81, 137.00, 135.15, 134.82, 134.79, 134.46, 133.57, 128.90, 128.16, 127.95, 127.64, 127.16, 26.18.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{22}OGe$ +H: 425.0955; Found: 425.0941.

M.p. 136-137 °C

1-(4-(Triphenylstannyl)phenyl)ethan-1-one (4c).

It was obtained from 4.3 g (15.6 mmol) of 1-bromo-4-(1,1-diethoxyethyl)benzene and Ph_3SnCl (6.0 g, 15.6 mmol) in a manner described above.

The isolation of this ketone is quite laborious and differs greatly from the isolation of silicon and germanium analogues. After adding all the reagents and slowly increasing the temperature, the reaction mixture does not remain transparent, but a copious white precipitate forms. Ignoring this, an acid solution was added, after which the precipitate was filtered off and washed with 5 mL of EtOAc and 5 mL of water. After drying in air, it weighs 1.1 g (16.5%) and has been identified by mass-spectrum as Ph_4Sn. Combined solutions were evaporated, and treated as it was described for silicon analog. Solid after evaporation of solvents was dissolved in 100 mL of hot hexane-EtOAc (20% by volume) and cooled to a room temperature. The cloudy solution is filtered and stirred vigorously for 1 hour with a saturated aqueous solution of NaF (4.5 g in 100 mL of water). A thick white suspension is formed. To this, 100 ml of acetone is added and the precipitate is filtered through a porous glass filter G3. The precipitate was washed with 30 mL of acetone and 50 ml of water, and then dried in air. According to mass spectrometry data, it was identified as Ph_3SnF and weighs 2.35 g (41%). Volatile solvents are distilled off from the combined filtrate on a rotary evaporator at 45 °C and 100 torr, and the remaining aqueous phase is extracted in three portions with 50 mL of hexane- EtOAc mixture (1:1 by volume). Organic phase was washed with 50 mL of brine, dried over $MgSO_4$. Solvent was evaporated, and resulted solid was extracted by two 70 mL of hot hexane. Hexane solution was slow evaporated, and semisolid triturated by 15 mL of cyclohexane to remove acetophenone (acetophenon is not mixable with hexane, but soluble in cyclohexane). Crystalline powder thus obtained was washed on filter by 5 mL of cyclohexane and 10 mL hexane and dried in air, afforded 1.96 g (23%) of target keton of 85% purity. It was finally purified by column chromatography on silica, eluent – hexane-EtOAc (4:1 by volume) afforded 1.20 g of analytically pure ketone (yield – 16.4%) as white crystalline solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.05 – 7.95 (m, 2H), 7.84 – 7.75 (m, 2H), 7.65 (ddt, J_1 = 5.0, J_2 = 3.7, J_3 = 2.0 Hz, 5H), 7.46 (m, 9H), 2.65 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 198.44, 145.68, 137.50, 137.26, 137.01, 129.48, 129.40, 129.24, 128.90, 128.56, 127.85, 26.68.

^{119}Sn NMR (112 MHz, $CDCl_3$) δ (ppm): -130.12.

HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{22}OSn$ +H: 471.0758; Found: 471.0760.

M.p. 130-131 °C

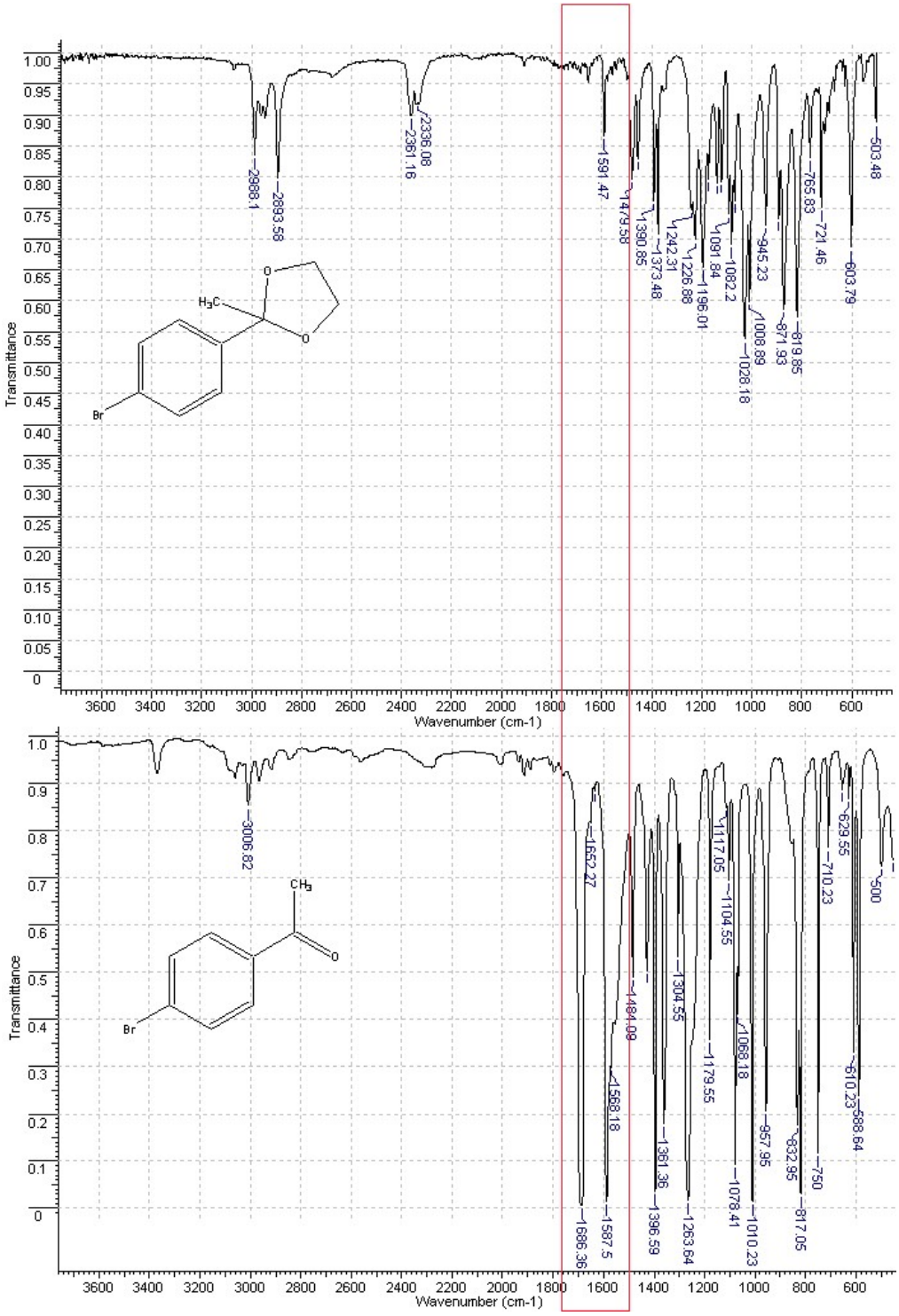

Figure S1. FTIR spectra of as-prepared 2-(4-bromophenyl)-2-methyl-1,3-dioxolane and starting 4-bromoacetophenone. Characteristic absorption bands of C=O group is marked by red frame.

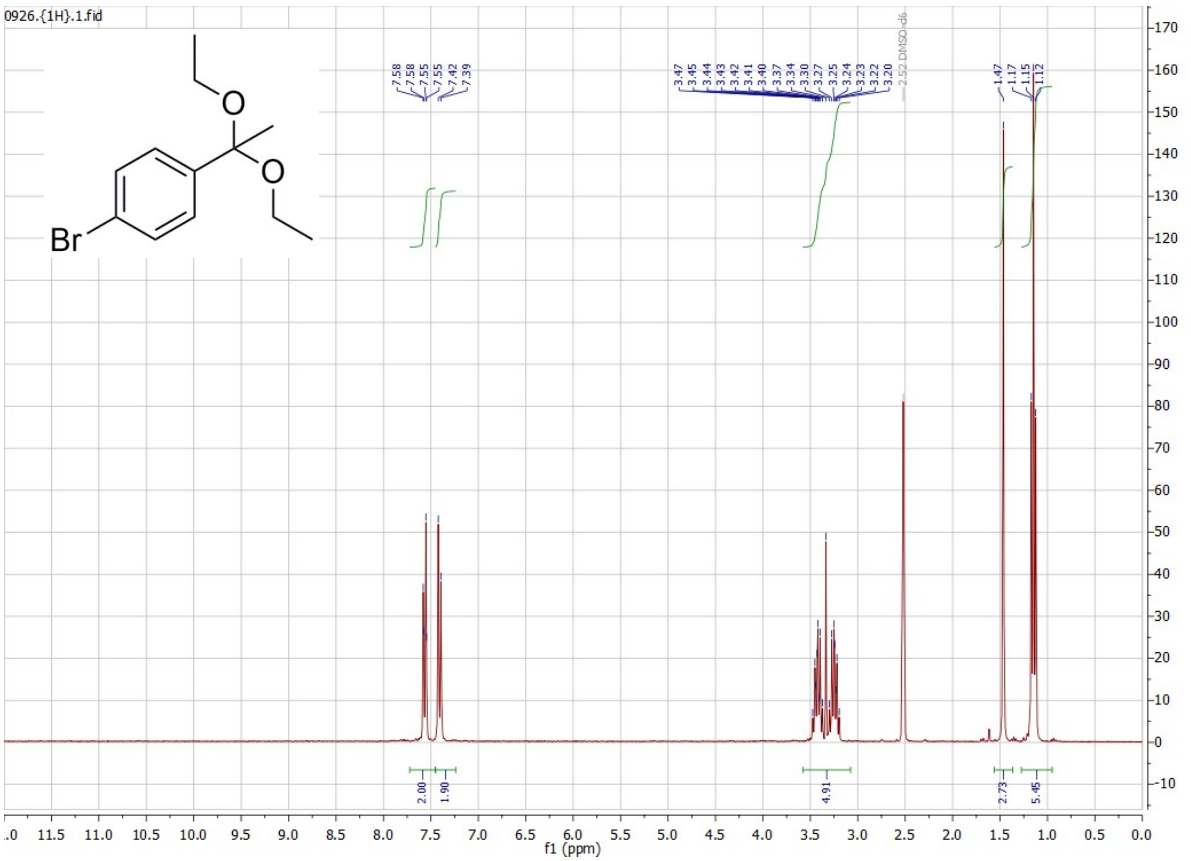

Figure S2. ^{1}H–NMR spectrum of 1-bromo-4-(1,1-diethoxyethyl)benzene in DMSO-d_6

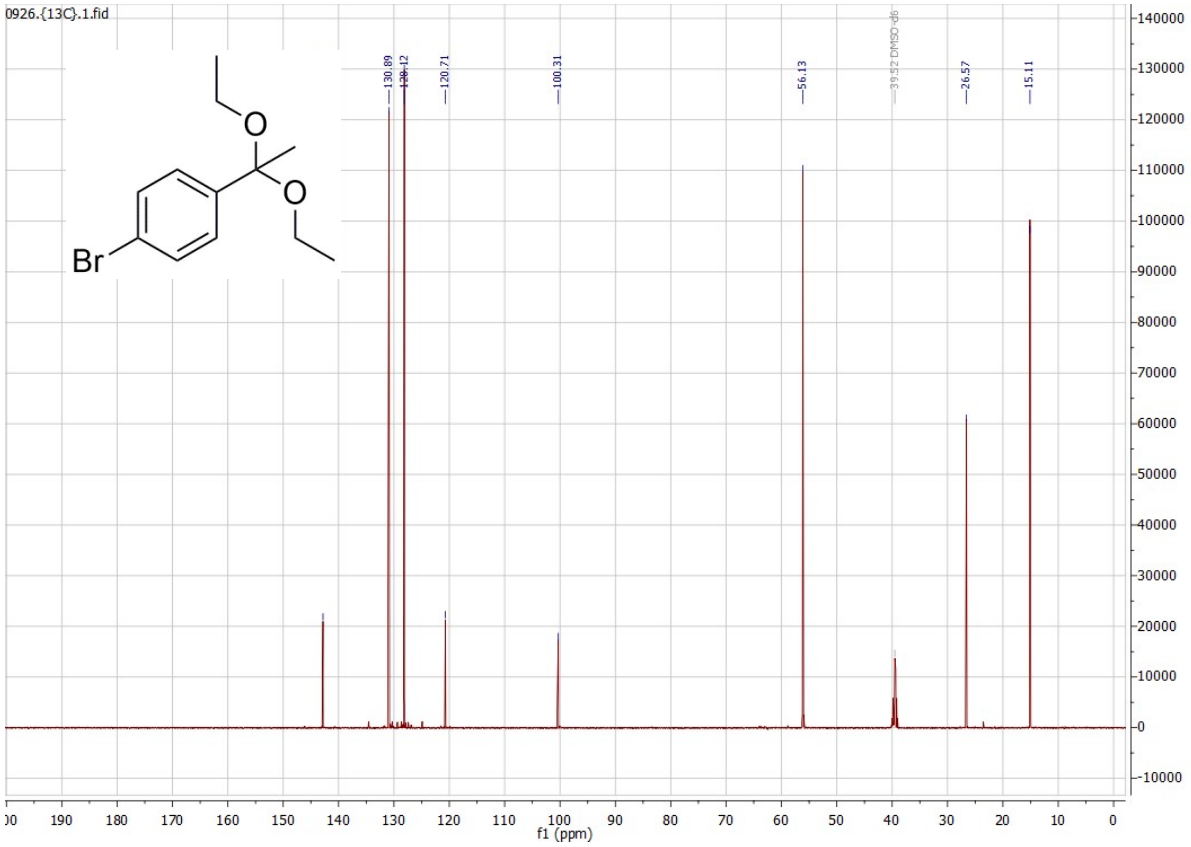

Figure S3. ^{13}C–NMR spectrum of 1-bromo-4-(1,1-diethoxyethyl)benzene in DMSO-d_6

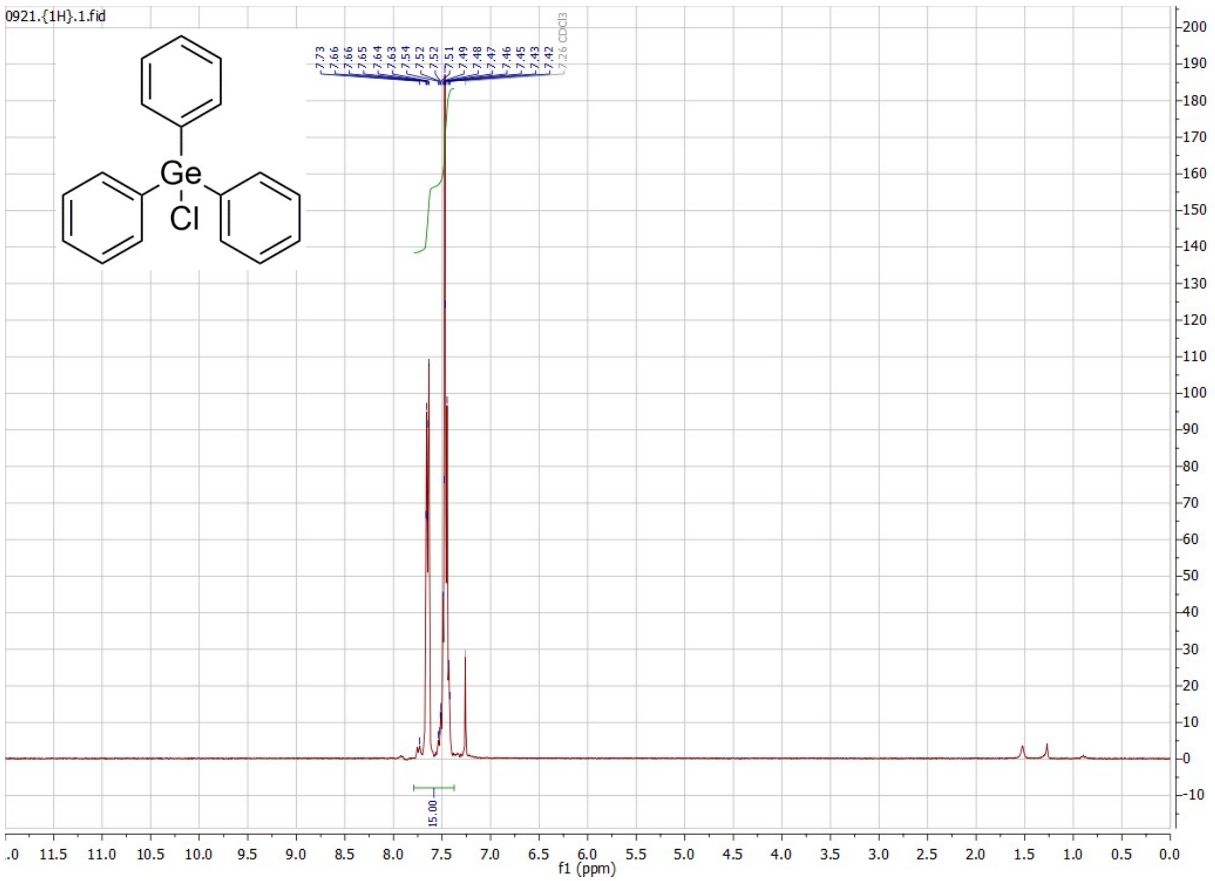

Figure S4. ^{1}H–NMR spectrum of Ph_3GeCl in $CDCl_3$.

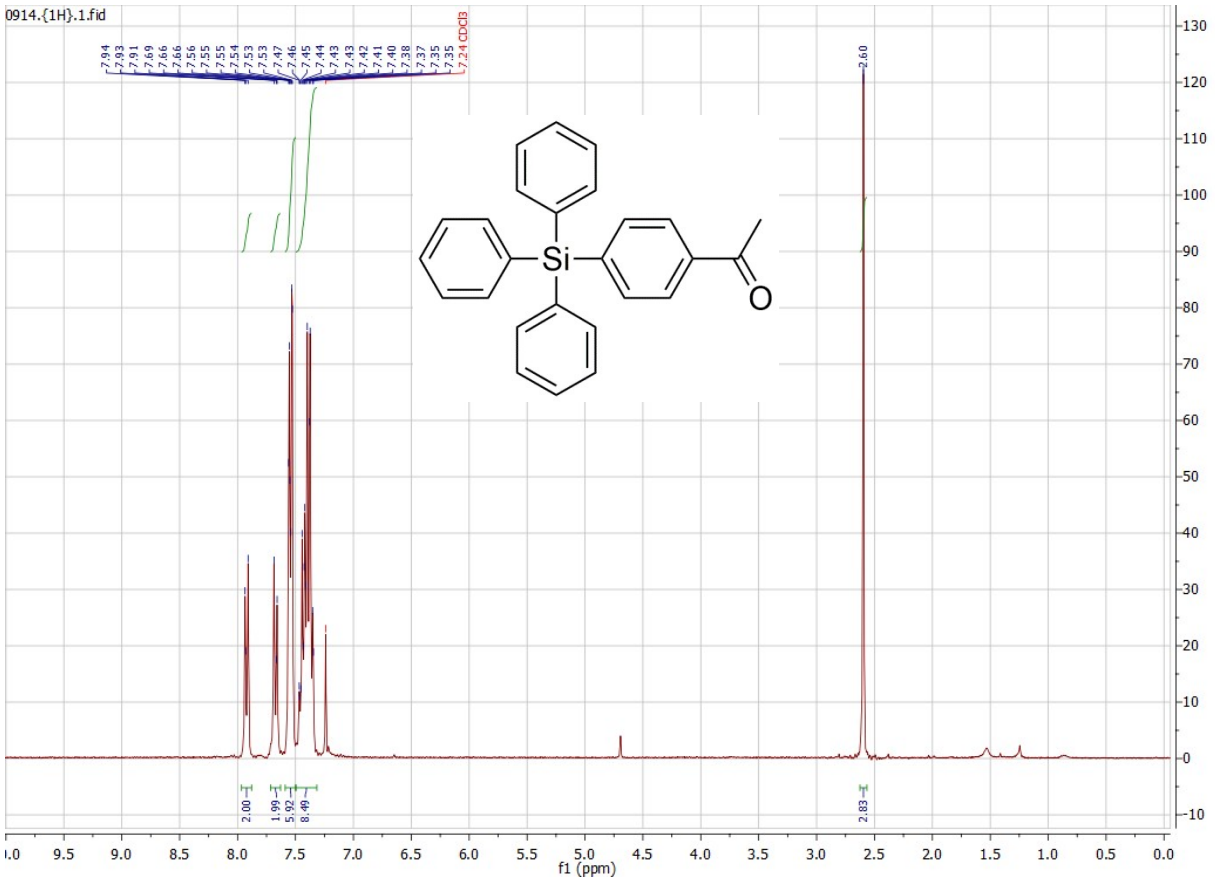

Figure S5. ^{1}H–NMR spectrum of 1-(4-(triphenylsilyl)phenyl)ethan-1-one in $CDCl_3$.

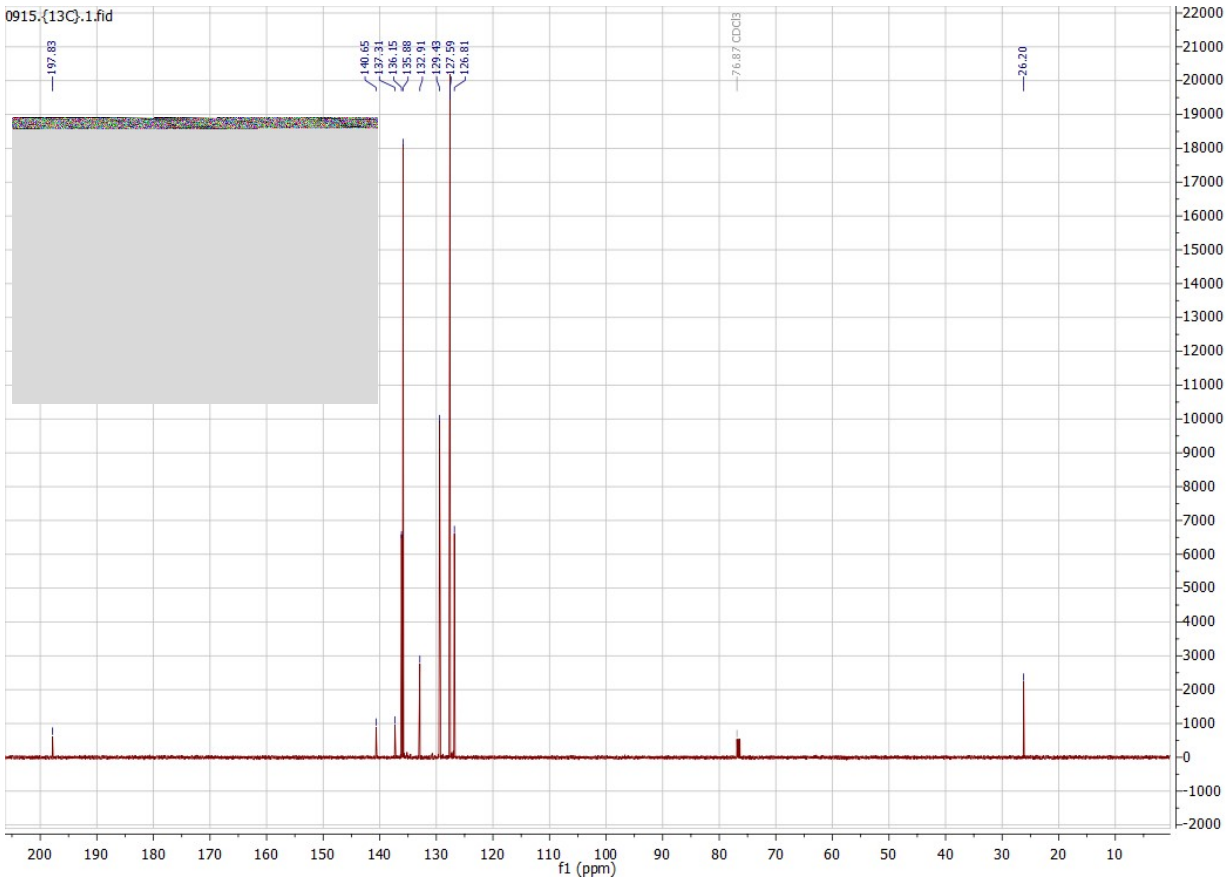

Figure S6. ^{13}C–NMR spectrum of 1-(4-(triphenylsilyl)phenyl)ethan-1-one in $CDCl_3$.

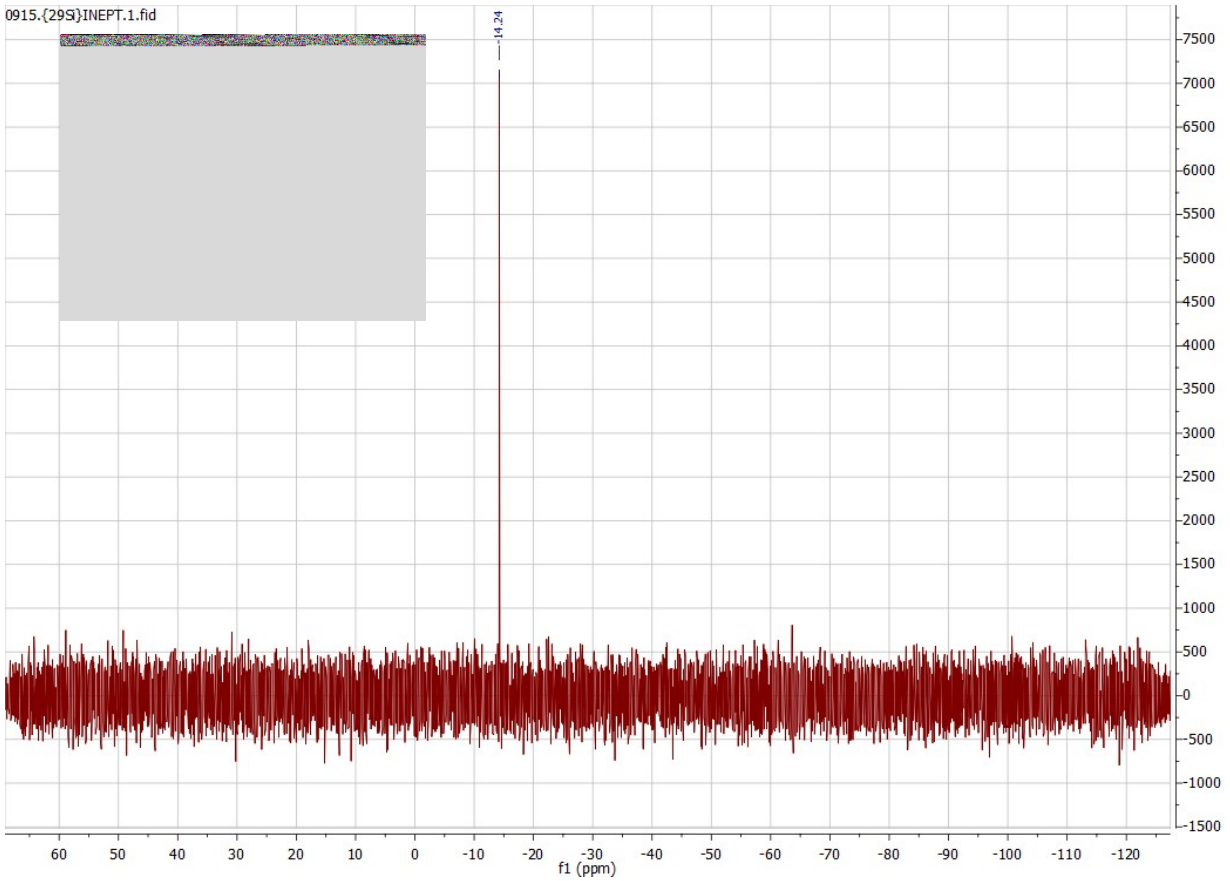

Figure S7. ^{29}Si–NMR spectrum of 1-(4-(triphenylsilyl)phenyl)ethan-1-one in $CDCl_3$.

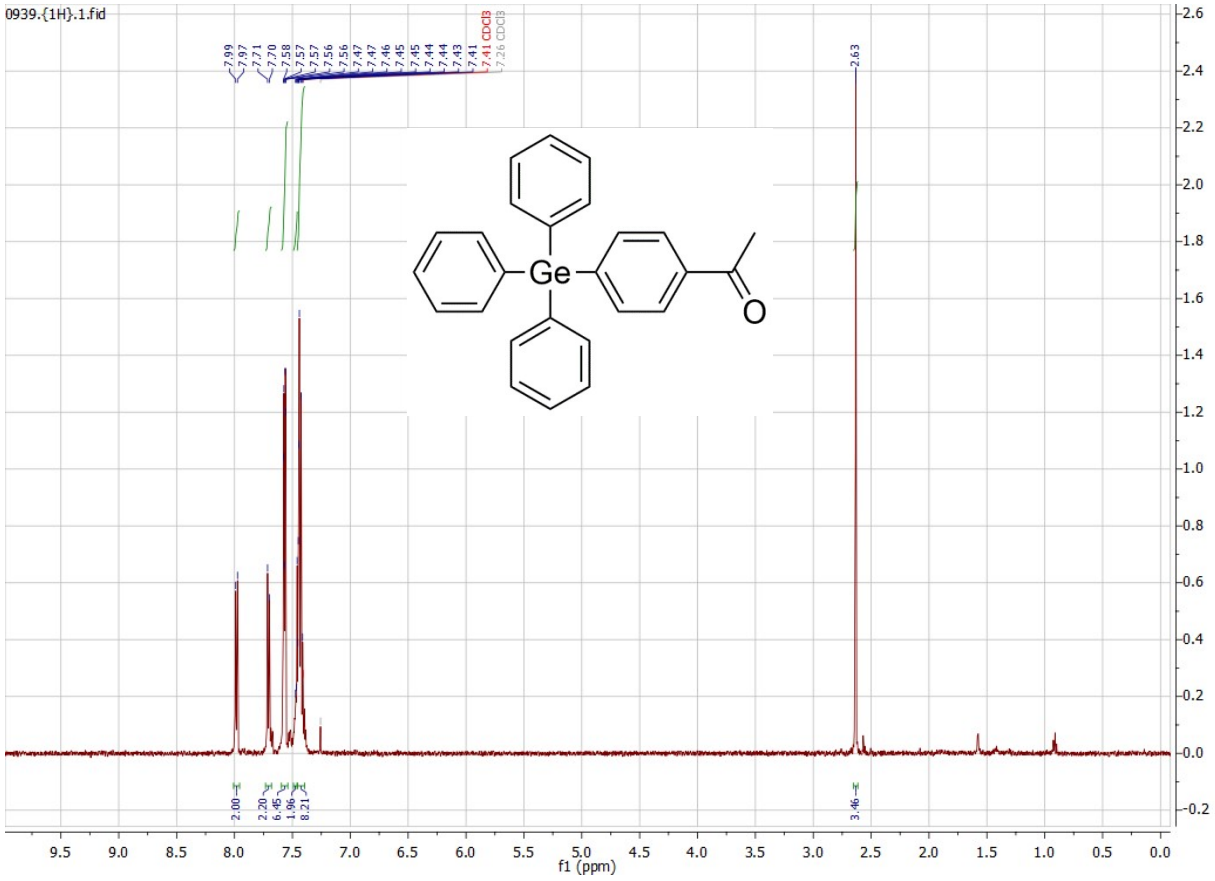

Figure S8. ^{1}H–NMR spectrum of 1-(4-(triphenylgermyl)phenyl)ethan-1-one in $CDCl_3$.

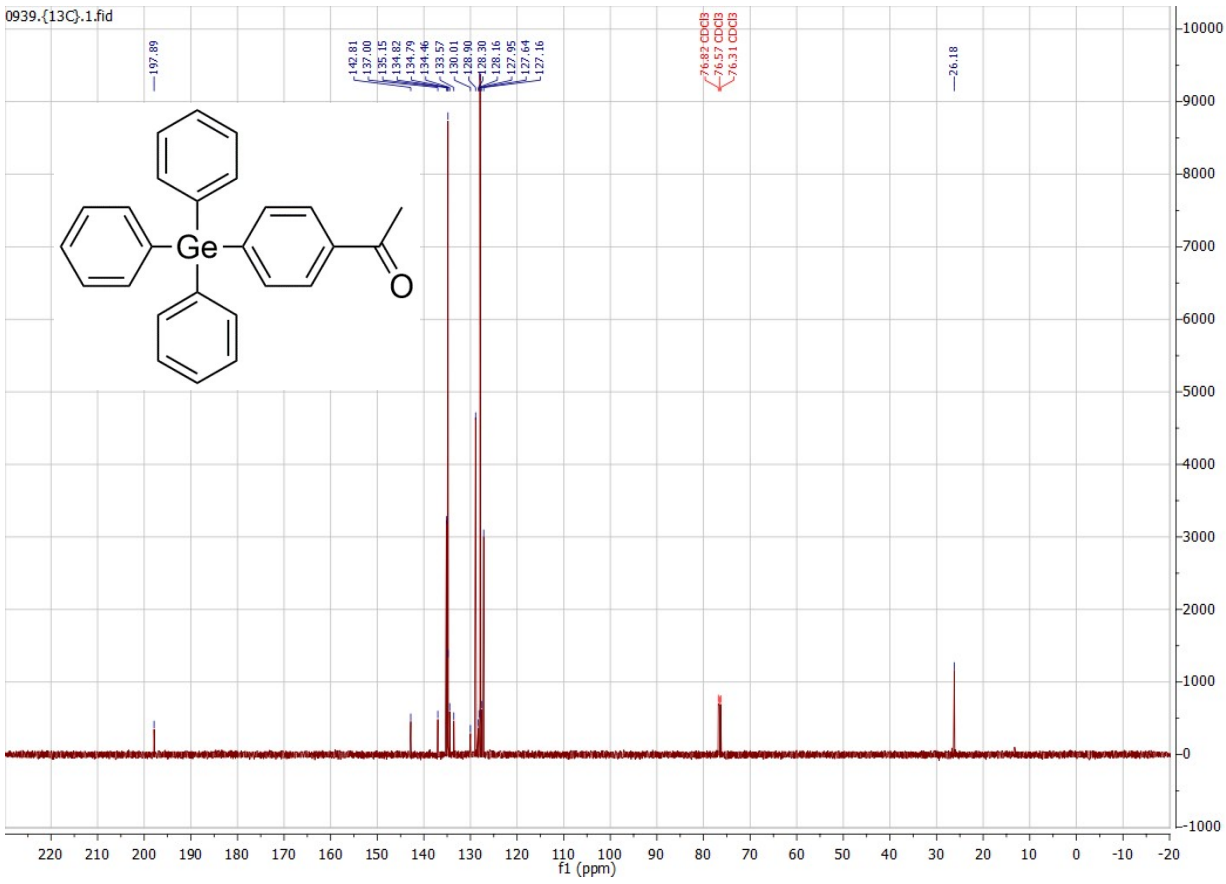

Figure S9. ^{13}C–NMR spectrum of 1-(4-(triphenylgermyl)phenyl)ethan-1-one in $CDCl_3$.

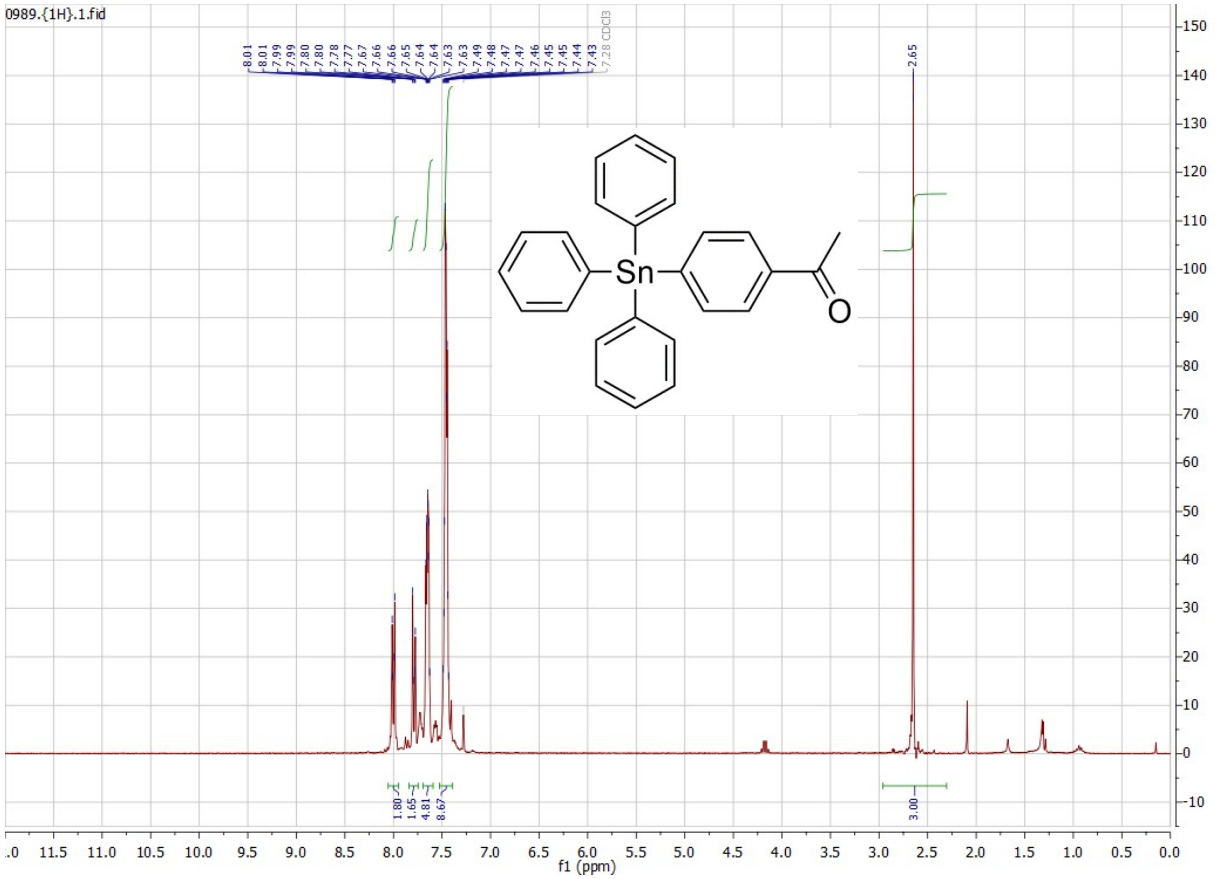

Figure S10. ^{1}H–NMR spectrum of 1-(4-(triphenylstannyl)phenyl)ethan-1-one in $CDCl_3$.

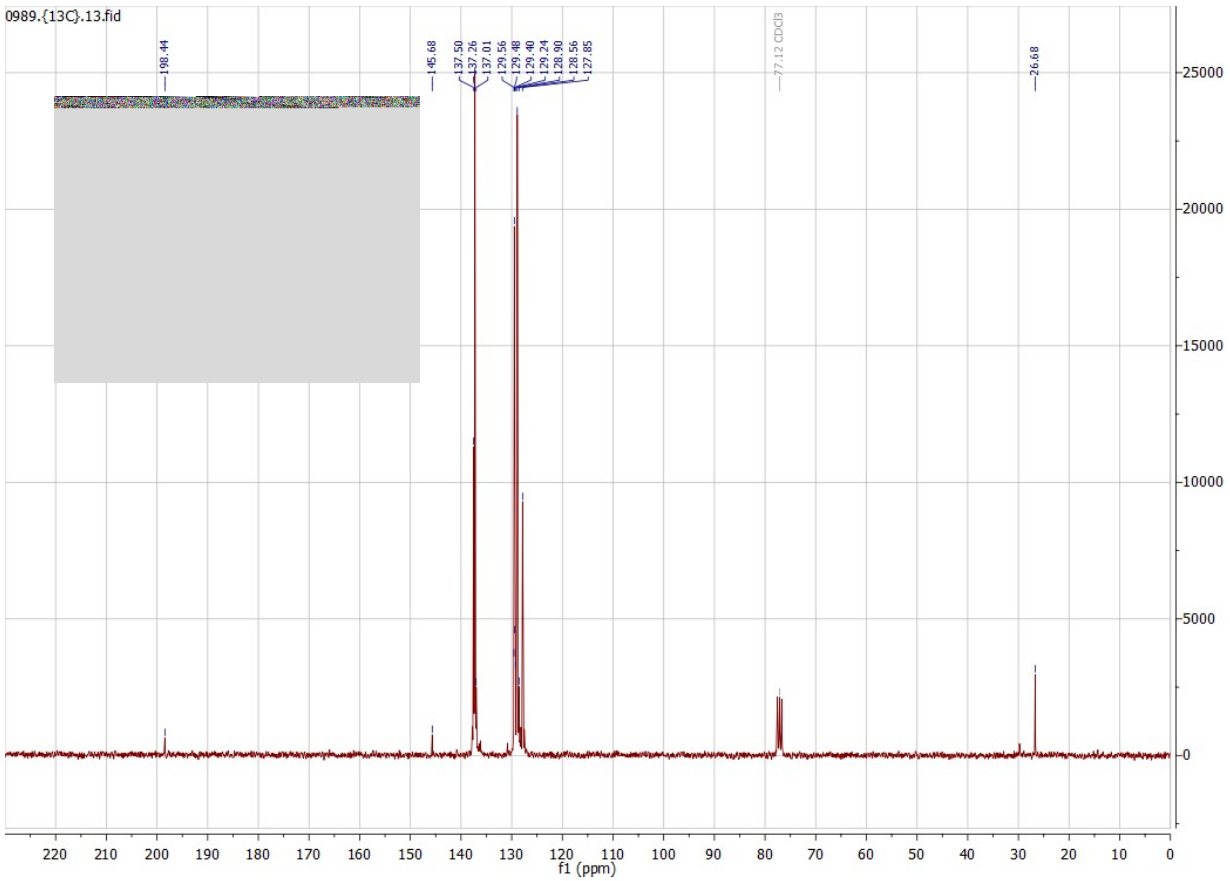

Figure S11. ^{13}C–NMR spectrum of 1-(4-(triphenylstannyl)phenyl)ethan-1-one in $CDCl_3$.

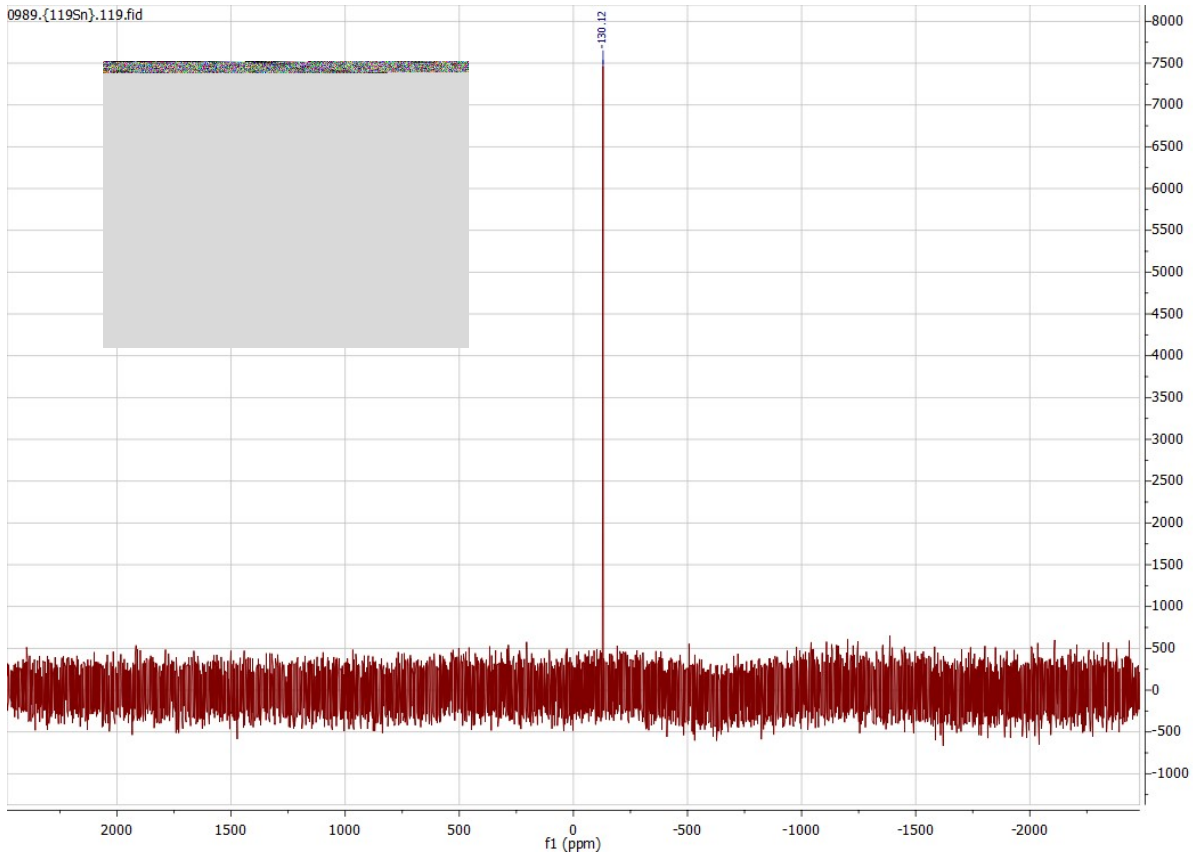

Figure S12. ^{119}Sn–NMR spectrum of 1-(4-(triphenylstannyl)phenyl)ethan-1-one in $CDCl_3$.

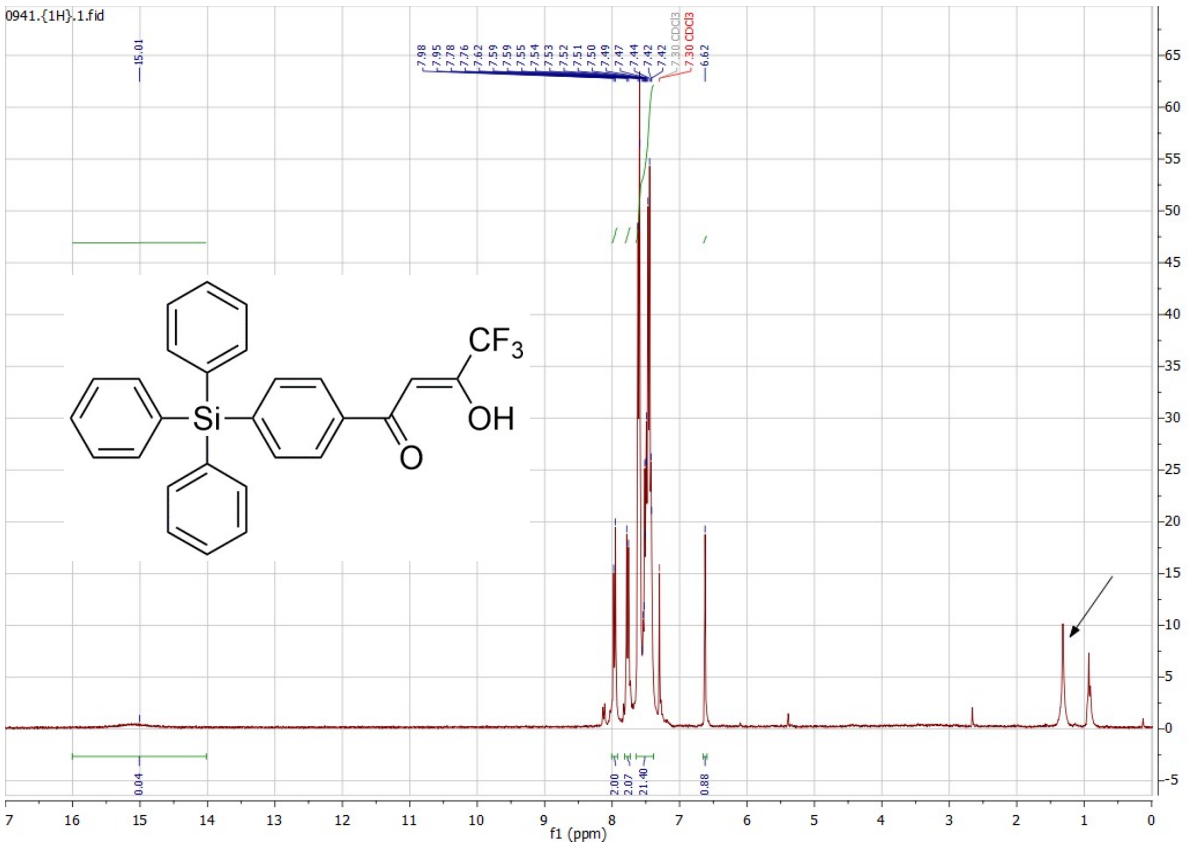

Figure S13. ^{1}H–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylsilyl)phenyl)butane-1,3-dione in $CDCl_3$. Only enol form is detected. Arrow mark solvent impurity.

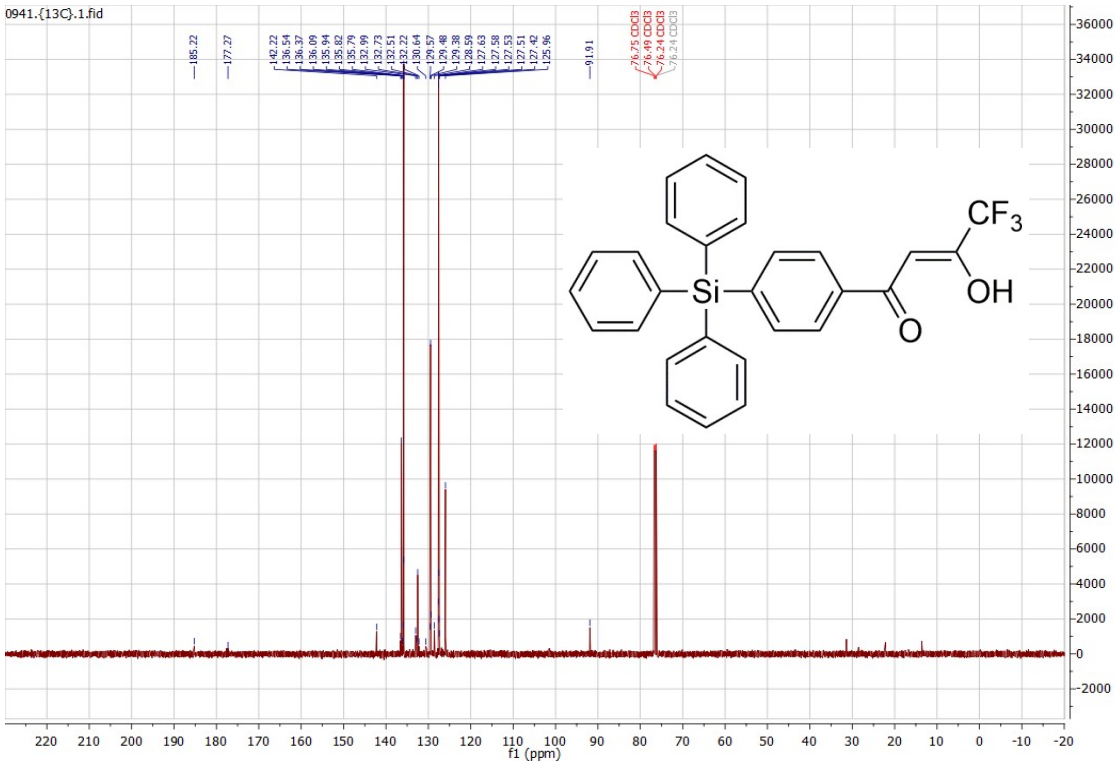

Figure S14. ^{13}C–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylsilyl)phenyl)butane-1,3-dione in $CDCl_3$.

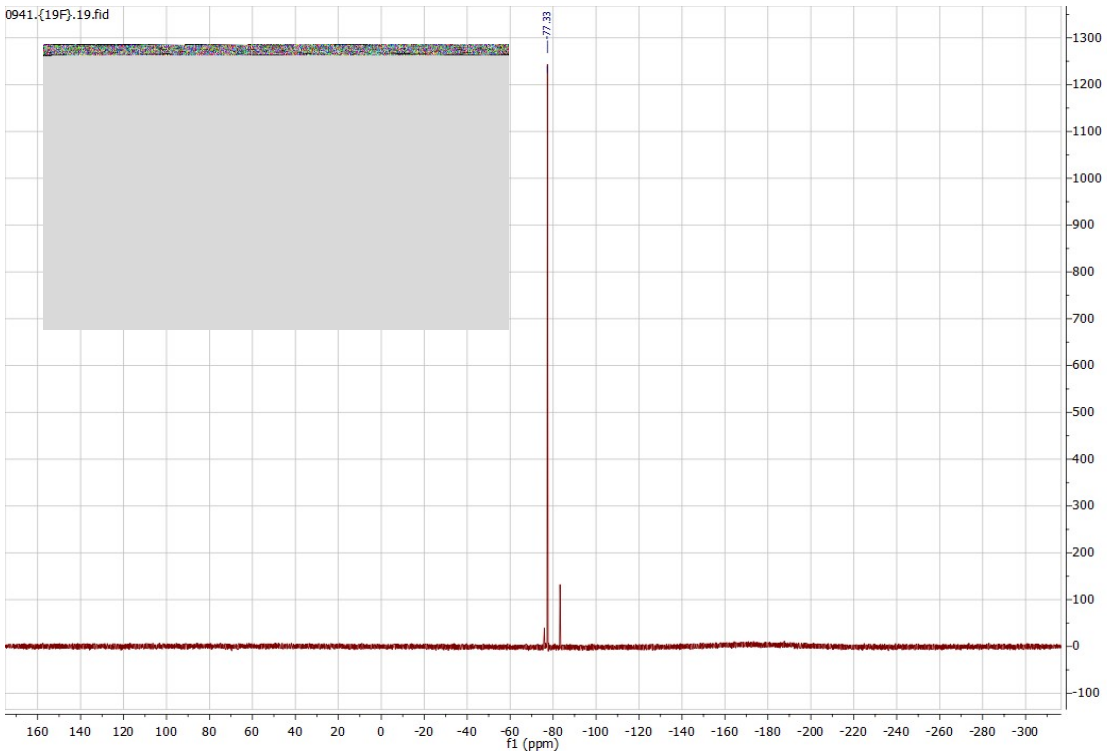

Figure S15. ^{19}F–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylsilyl)phenyl)butane-1,3-dione in $CDCl_3$.

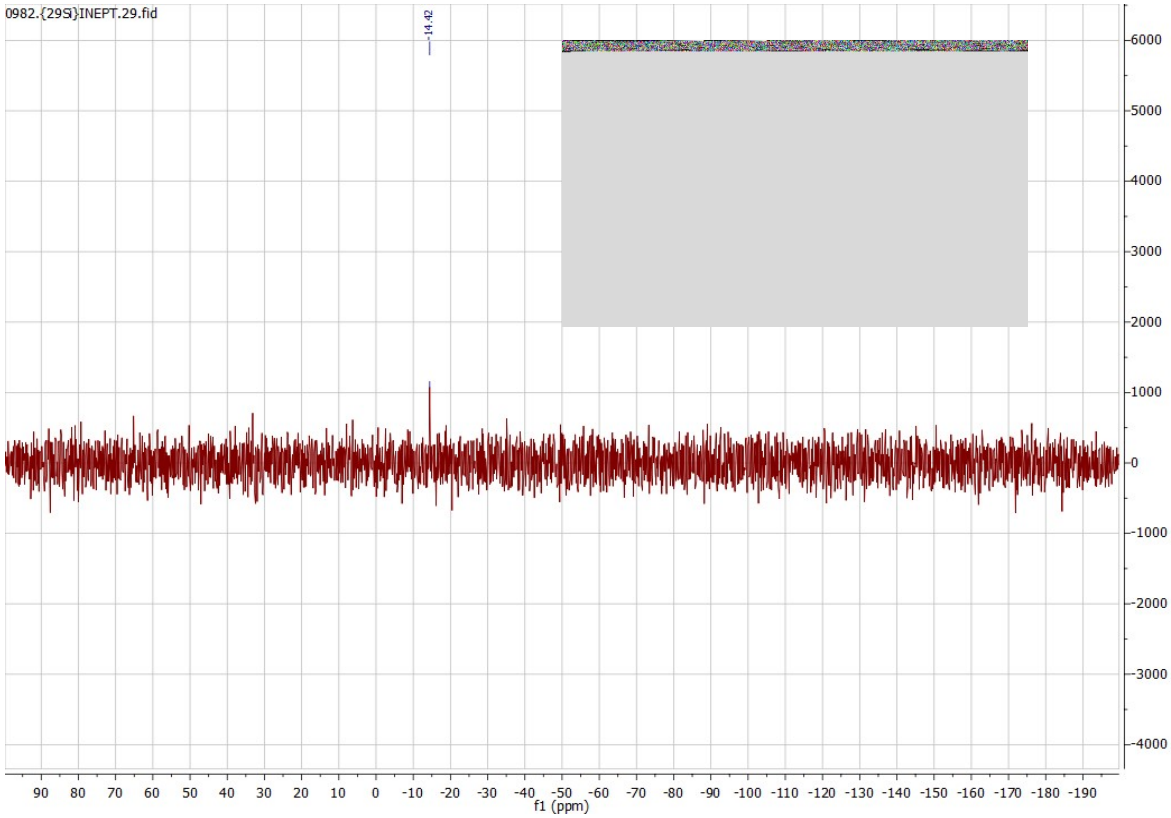

Figure S16. ^{29}Si–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylsilyl)phenyl)butane-1,3-dione in $CDCl_3$.

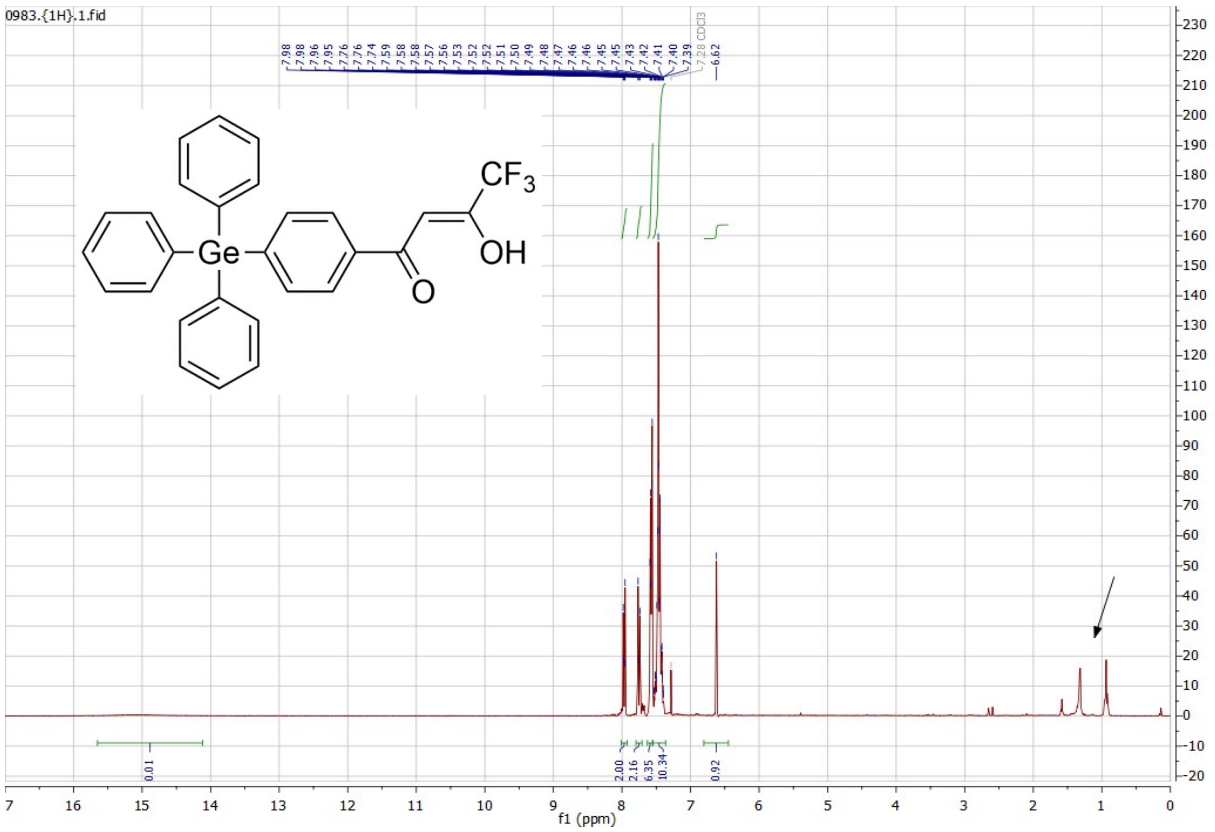

Figure S17. ^{1}H–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylgermyl)phenyl)butane-1,3-dione in $CDCl_3$. Only enol form is detected. Arrow mark solvent impurity.

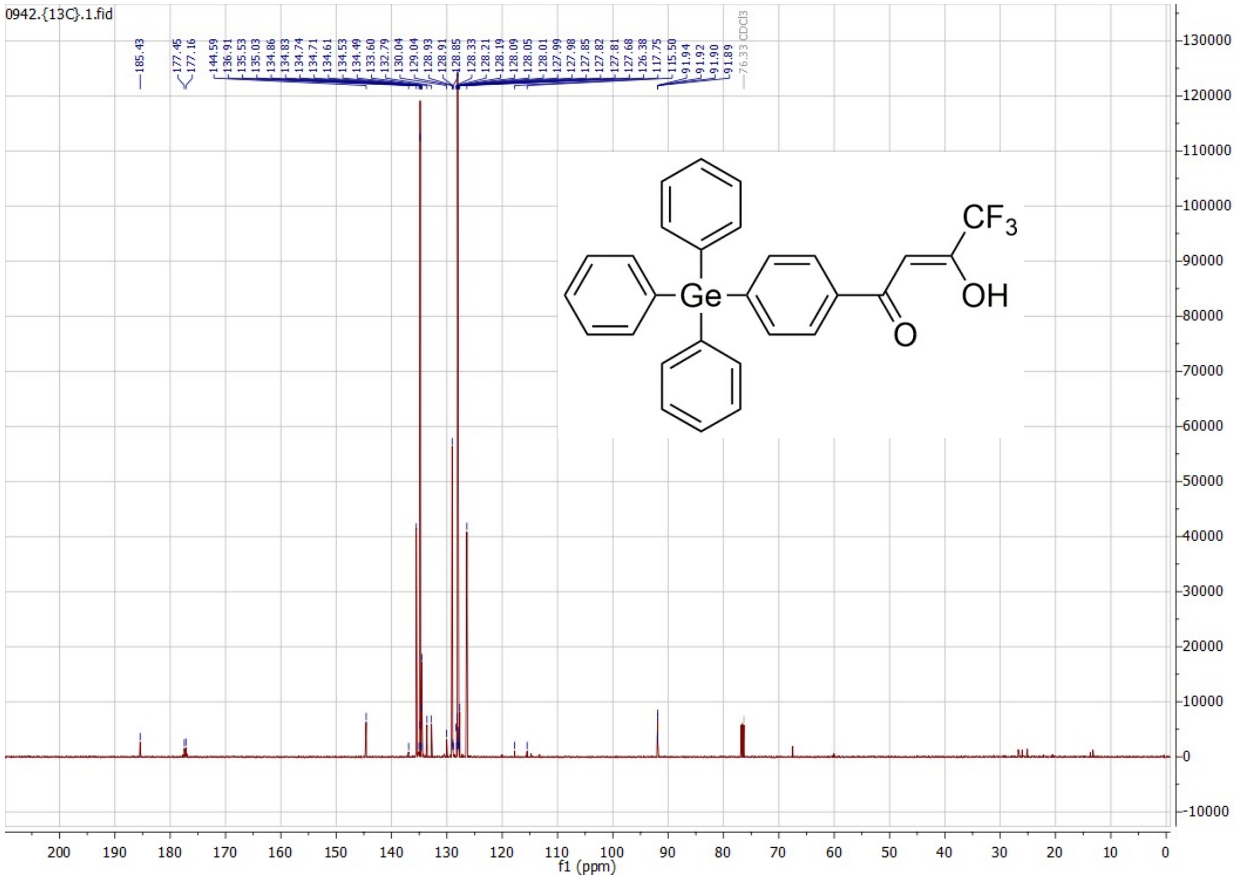

Figure S18. ^{13}C–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylgermyl)phenyl)butane-1,3-dione in $CDCl_3$.

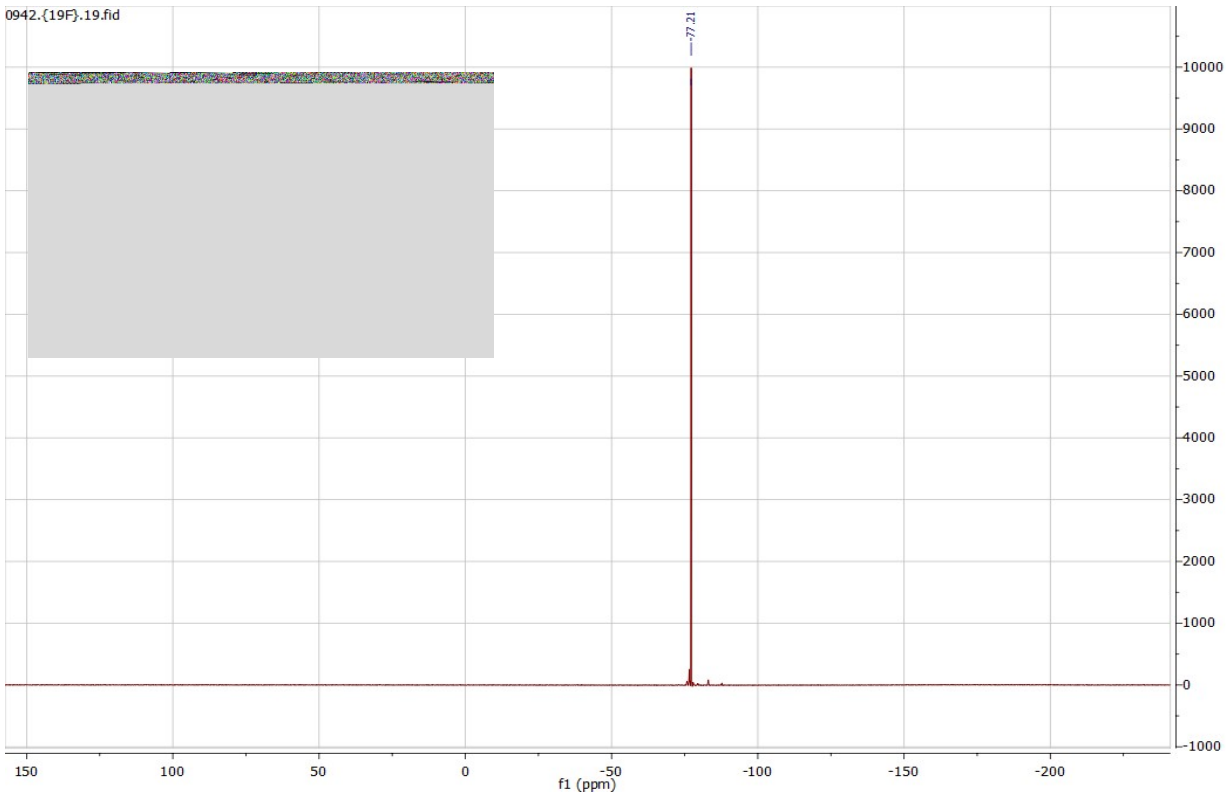

Figure S19. ^{19}F–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylgermyl)phenyl)butane-1,3-dione in $CDCl_3$.

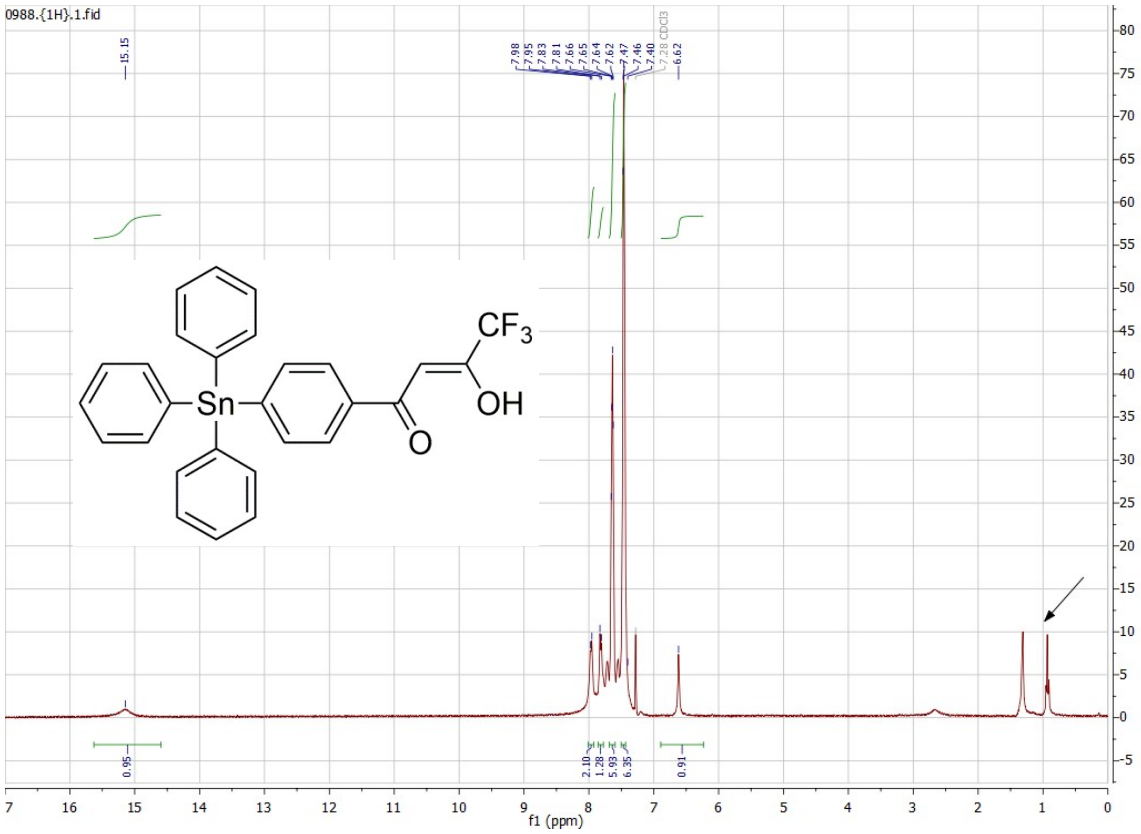

Figure S20. ^{1}H–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylstannyl)phenyl)butane-1,3-dione in $CDCl_3$. Only enol form is detected. Arrow mark solvent impurity.

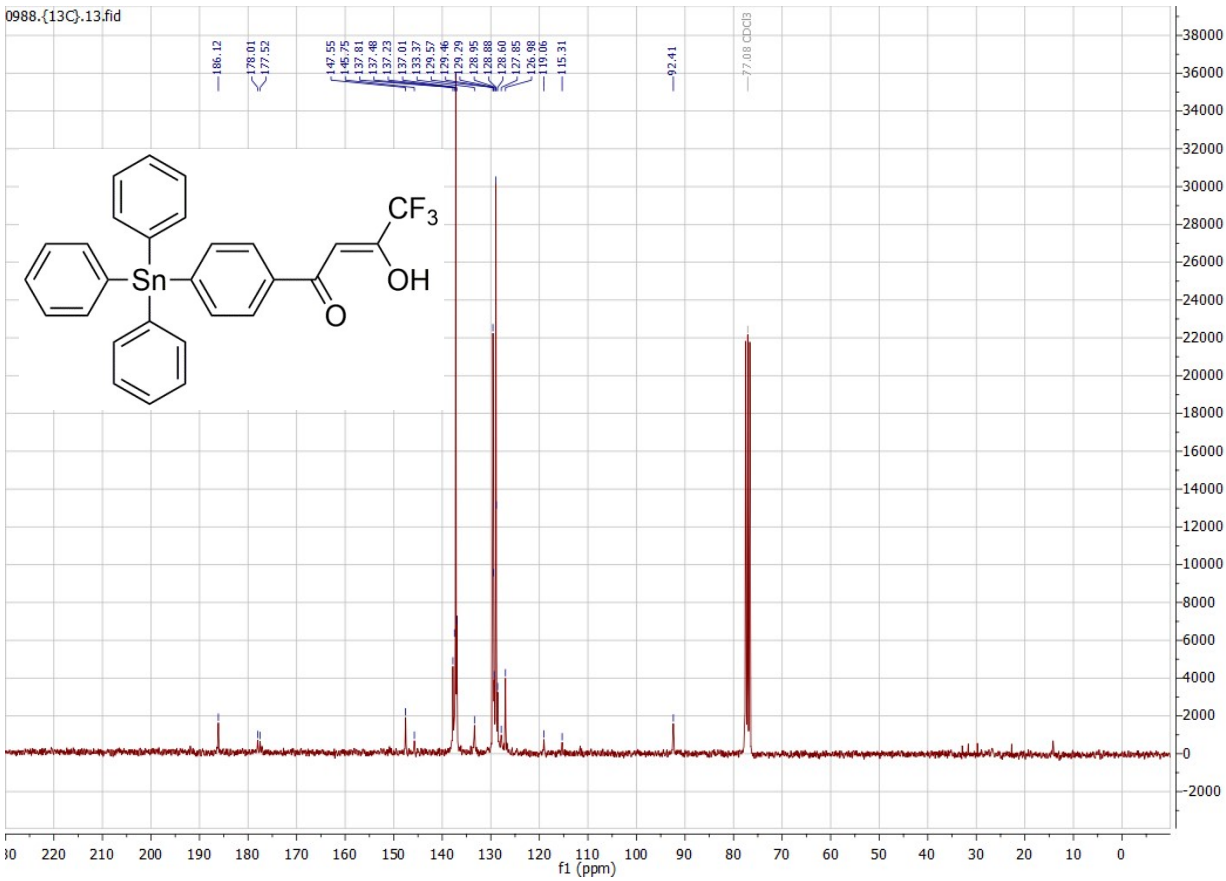

Figure S21. ^{13}C–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylstannyl)phenyl)butane-1,3-dione in $CDCl_3$.

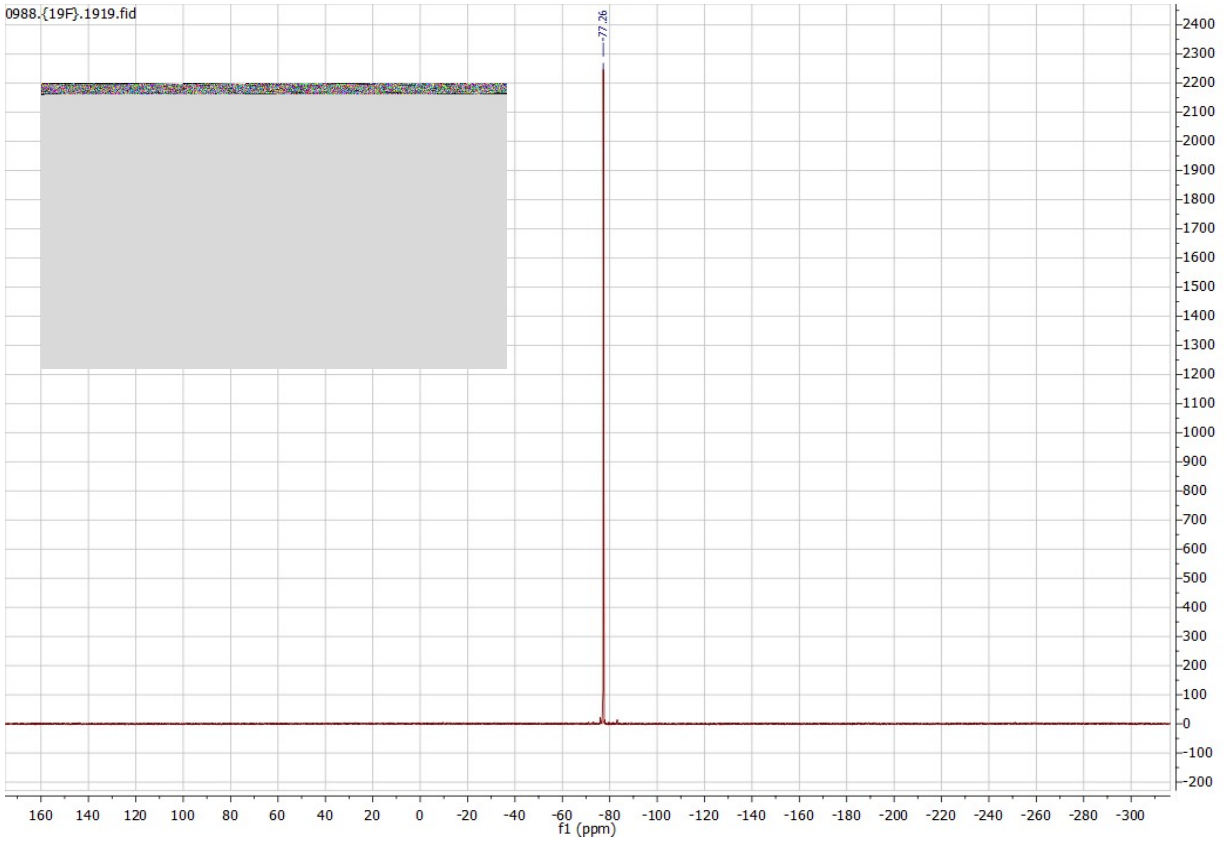

Figure S22. ^{19}F–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylstannyl)phenyl)butane-1,3-dione in $CDCl_3$.

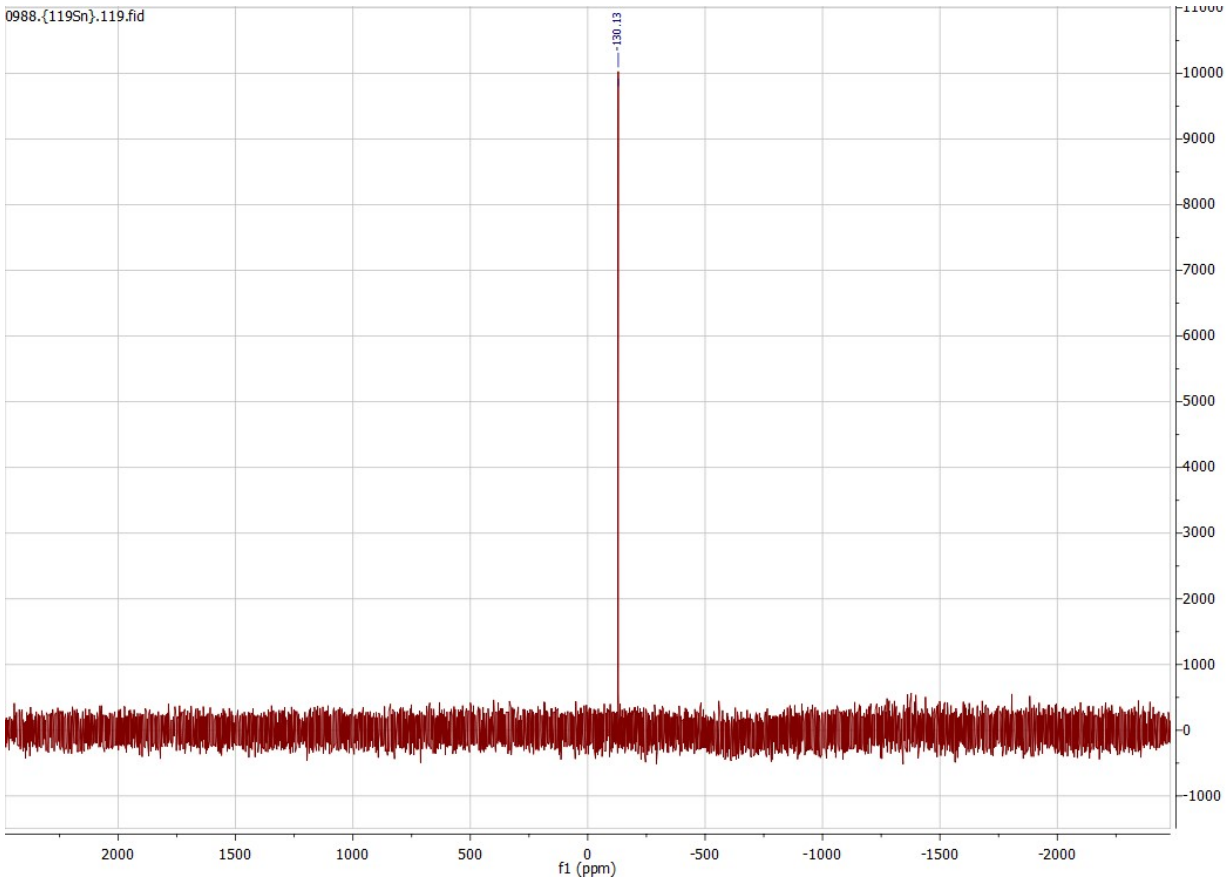

Figure S23. ^{119}Sn–NMR spectrum of 4,4,4-trifluoro-1-(4-(triphenylstannyl)phenyl)butane-1,3-dione in $CDCl_3$.

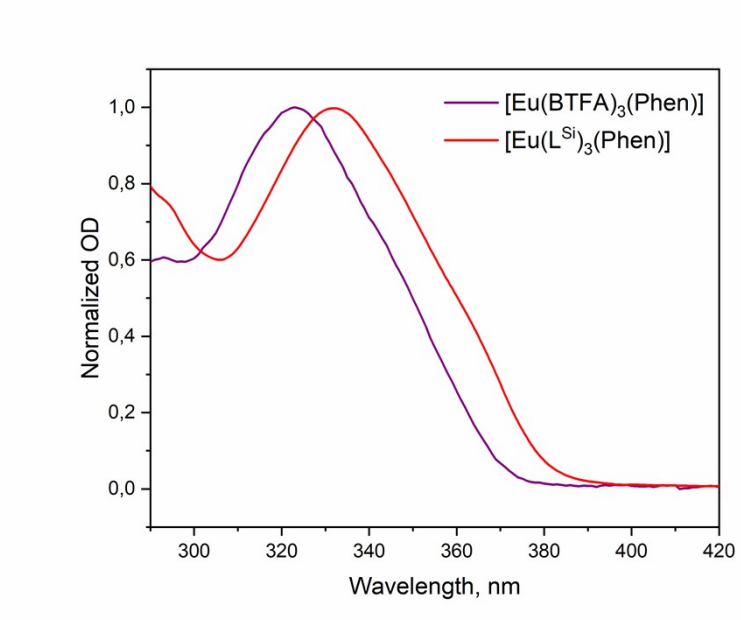

Figure S24. UV-Vis spectra of $[Eu(BTFA)_3(Phen)]$ and $[Eu(L^{Si})_3(Phen)]$ in toulene.

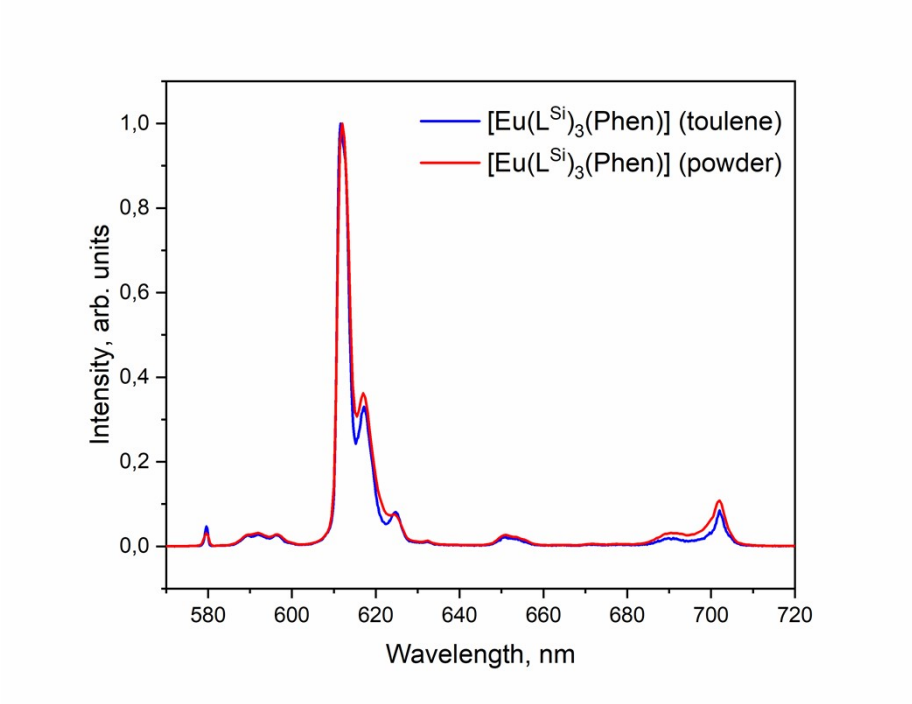

Figure S25. Emission spectra of $[Eu(L^{Si})_3(Phen)]$ in the solid state and in toluene solution at 300 K. The spectra are normalized to the maximum intensity of the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition.

Table S1. The energies of first excited singlet (S_1) and triplet (T_1) states for β-diketone and Phen ligands

Ligand	T_1, cm^{-1}	S_1, cm^{-1}
L^{Si}	21370	26900
L^{Ge}	21480	26900
L^{Sn}	21570	26900
BTFA	22350	27200
Phen	22100	28000