Electronic Supplementary Information for:

Site selectivity in divergently activated dienes

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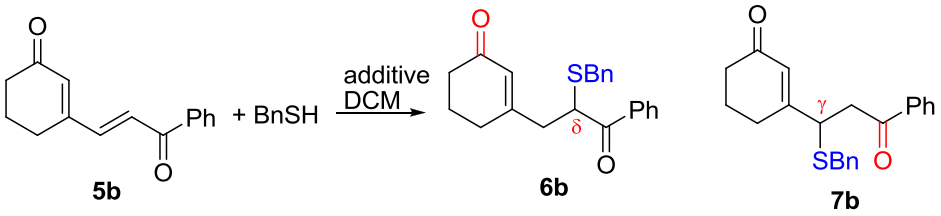
S1. Supplementary tables

Table S1. Regioselectivity of the addition of benzyl mercaptans to **5b**[a]

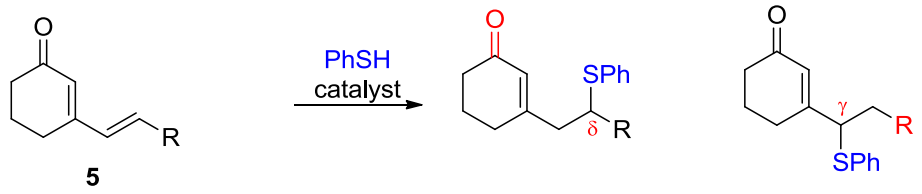


5b **6b** **7b**

Entry	Additive	**6b** to **7b** ratio	Conversion, %
1	DABCO	0:100	>98
2	DBN	12:88	60
3	Ph_2PCH_3	0:100	98
4	Quinine	0:100[b]	70[c]
5	Pyrrolidine	6:94	>98
6	L-Proline	0:100	89
7	(*S*)-α-Methylbenzylamine/**11a**	0:100[d]	85[c]
8	(*R*,*R*)-Diaminocyclohexane/**11a**	0:100[d]	45[c]
9	Cyclohexylamine/**11a**	0:100	60[c]
10	$PhNH_2 \cdot HCl$	0:100	>98
11	DMAP/TFA	0:100	>98
12	TFA	2:98	51
13	*rac*-1,1'-Binaphthalene-2,2'-diyl hydrogen phosphate	50:50	54
14	$Sc(OTf)_3$	2:98	91
15	$Zn(OTf)_2$	62:38	62
16	$Zn(CH_3)_2$	0:100	49
17	$Ti(O\textit{i}Pr)_4$	2:98	49
18	$Na(OCH_3)$	0:100	88
19	$Mg(OEt)_2$	0:100	>98
20	**10a** / **11b**	77:23	50[c]
21	**10d** / **11a**	73:27	51[c]

[a] Reactions were performed in a 0.3 mmol scale in dichloromethane (1.5mL) at rt for 20h applying GP2 for the Sulfa-Michael addition (entries 7-9) or general procedure for preparation of racemates (GP3, others; for details see: Section S5). [b] 22 %*ee*, [c] isolated yield, [d] <1 %*ee*

Table S2. Site selectivity in the addition of thiophenol to ketoesters **5d** and **5c**[a]



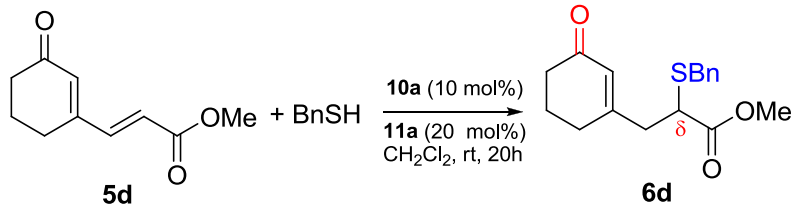
5

catalyst **A**: DABCO
catalyst **B**: *epi*-aminoquinine (**10a**) + (*S*)-*O*-acetylmandelic acid (**11b**)

Entry	**5**, R	Catalyst, **δ:γ** product ratio[b]	
		A: DABCO	**B**: **10a**/**11b**
1	**5c**, CO_2Ph	17:83	100:0
2	**5d**, CO_2CH_3	100:0	100:0

[a] Reactions were performed in a 0.3 mmol scale in dichloromethane (1.5mL) at rt for 20h applying GP2 for the Sulfa-Michael addition.

Table S3. Solvent screening in the reaction of **5d** with benzyl mercaptan catalyzed by the **10a** / **11a** system[a]

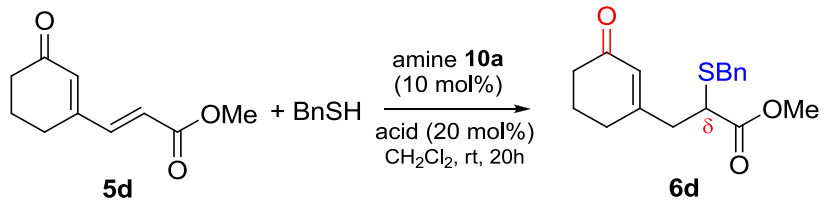


5d **6d**

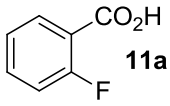
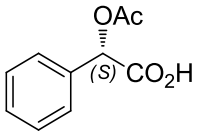
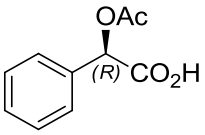
Entry	Solvent	Conversion, %	*ee*, %
1	$PhCH_3$	98	54
2	$PhCF_3$	83	52
3	AcOEt	92	24
4	MTBE	96	60 (53)[b]
6	CH_2Cl_2	48[c]	79

[a] Performed according to GP for the Sulfa-Michael addition, for details see: Section S5
[b] Obtained with **10f** / **11b** catalyst system
[c] Isolated yield

Table S4. Influence of acid on the *ee* in the reaction of **5d** with benzyl mercaptan catalyzed by **10a** / acid[a]

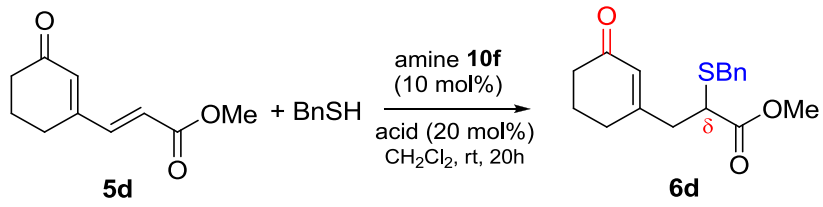


5d **6d**

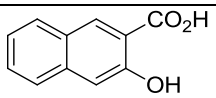
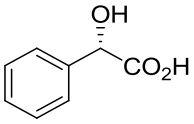
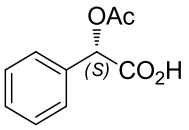
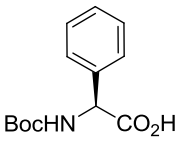
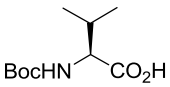
Entry	Acid	Yield, %	*ee*, %, (absolute configuration)
1	 **11a**	33	79 (*R*)
2	 (*S*)-(+)-*O*-Acetyl-Mandelic acid, **11b**	55	83 (*R*)
3	 (*R*)-(-)-*O*-Acetyl-Mandelic acid, *ent*-**11b**	59	79 (*R*)

[a] Performed according to GP2 for the Sulfa-Michael addition, for details see: Section S5

Table S5. Influence of acid on the *ee* in the reaction of **5d** with benzyl mercaptan catalyzed by **10f** / acid



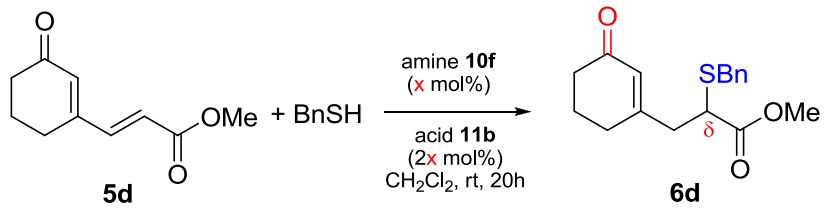
5d **6d**

Entry	Acid	Conversion, %	*ee*, %, (absolute configuration)
1		51	78 (*R*)
2	 L-(+)-Mandelic acid	76	79 (*R*)
3	 (*S*)-(+)-*O*-Acetyl-Mandelic acid	48[b]	87 (*R*)
4		96	85 (*R*)
5		97	85 (*R*)

[a] Performed according to GP2 for the Sulfa-Michael addition, for details see: Section S5

[b] Isolated yield

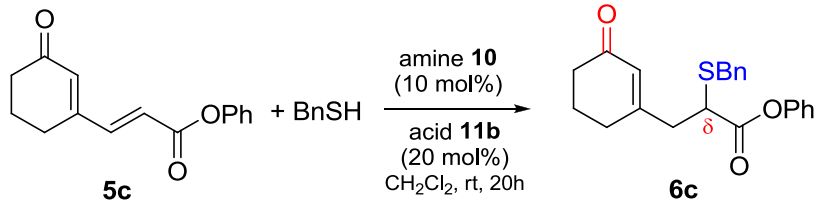
Table S6. Influence of catalyst loading in the reaction of **5d** with benzyl mercaptan catalyzed by **10f** / **11b**[a]



Entry	**10f** / **11b**, mol%	Yield, %	*ee*, %, (absolute configuration)
1	20 / 30	71	88 (*R*)
2	10 / 20	48	87 (*R*)
3[b]	10 / 20	50	86 (*R*)
4[ec]	10 / 20	71	87 (*R*)
5	5 / 10	(66)[d]	89 (*R*)
6	1 / 2	(8)[d]	n.d.[e]
7	0.5 / 1	-	n.d.[e]

[a] Unless otherwise stated, reaction was performed in dichloromethane (1.5 mL) using 10 mol% of **10h**, 20 mol% of **11b** and 1.5 equiv. of benzyl mercaptan for 20h at rt.
[b] Performed at 0°C
[c] 3 Equiv of benzyl mercaptan was used
[d] Conversion instead of yield is given in parenthesis
[e] Not determined

Table S7: Influence of catalyst structure in the reaction of **5c** with benzyl mercaptan[a]



Entry	Amine **10**	Yield, %	*ee*, %, (absolute configuration)
1	**10a**	53	73 (*R*)
2[b]	**10d**	58	60 (*S*)
3	**10f**	74	80 (*R*)
4	**10h**	60	67 (*R*)

[a] Unless otherwise stated, reaction was performed in dichloromethane (1.5 mL) using 10 mol% of **10**, 20 mol% of **11b** and 1.5 equiv. of benzyl mercaptan for 20h at rt.
[b] Regioisomer ratio was 96:4

S2. General experimental procedures

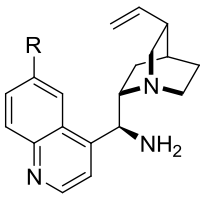
Catalytic reactions were performed in standard reaction tubes with PTFE stopper without any precautions of moisture or air. Heck reactions were performed in reaction tubes with inert gas inlet. Tubes were heated to 550°C for 3–5 min., under high vacuum, cooled down and then flushed with argon.

^{1}H and ^{13}C NMR spectra (600 and 151 MHz, respectively) were recorded in $CDCl_3$ on a Bruker Avance II 600 instrument. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) and $CDCl_3$ (δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, etc.), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) and $CDCl_3$ (δ 77.16 ppm). ESI-TOF HRMS spectra were recorded on Waters LCT Premier XE apparatus. HPLC analysis was performed on Thermo Scientific System (SCM 1000, Spectra System P4000 pump and Spectra System UV 2000 detector) using 4.6 × 250 mm Chiralpak AD-H column (Amylose tris(3,5-dimethylphenylcarbamate)coated on 5 μm silica-gel) without guard column. Each HPLC analysis has been controlled by comparison with the purified sample and the racemate. Optical rotations were measured on an automatic polarimeter at λ = 589 nm (c, g/100 mL).

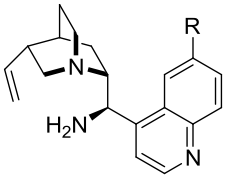
Flash chromatography was performed using silica gel 35–70 μm. Thin layer chromatography was performed using silica gel on aluminum foil with fluorescent indicator. Chromatograms were visualized using UV-lamp and $KMnO_4$ dip.

S3. Materials and catalysts

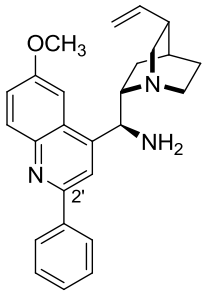
Commercially available starting materials were used without further purification. Xylene, toluene, *tert*-butyl-methyl ether, 1,2-dichloroethane, dichloromethane and chloroform were used as received. Dimethyl acetamide and dimethyl formamide used in Heck reaction were stored over 4Å MS under argon. Commercially available acrylates were distilled before use. Phenyl acrylate, cyclohexyl acrylate and benzyl acrylate were prepared following the literature procedure.[S1]



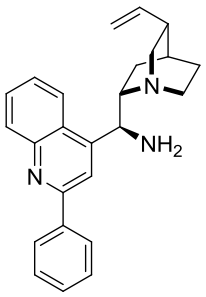
10a, R = OCH_3
10b, R = H
10c, R = OH



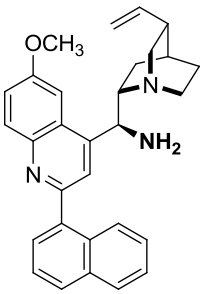
10d, R = OCH_3
10e, R = H



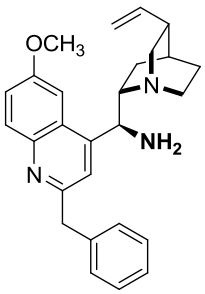
10f



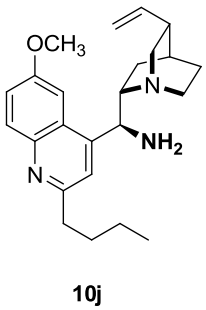
10g



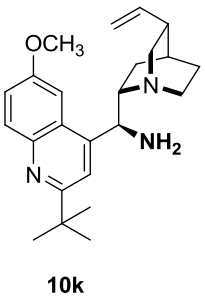
10h



10i



10j



10k

[S1] S. Chanthamath, S. Takaki, K. Shibatomi, and S. Iwasa, *Angew. Chem. Int. Ed.*, 2013, **52**, 5818.

Amines **10a**-**10k** were prepared following the literature precedents:[S2-S6] 9-(*epi*)-Amino-deoxy quinine (**10a**) is commercially available. Cinchonidine, quinidine and cinchonine derivatives **10b**, **10d**, and **10e**, respectively are known to form in Mitsunobu reaction – Staudinger reduction sequence,[S2] although they were synthesized stepwise from the corresponding mesylates.[S3]

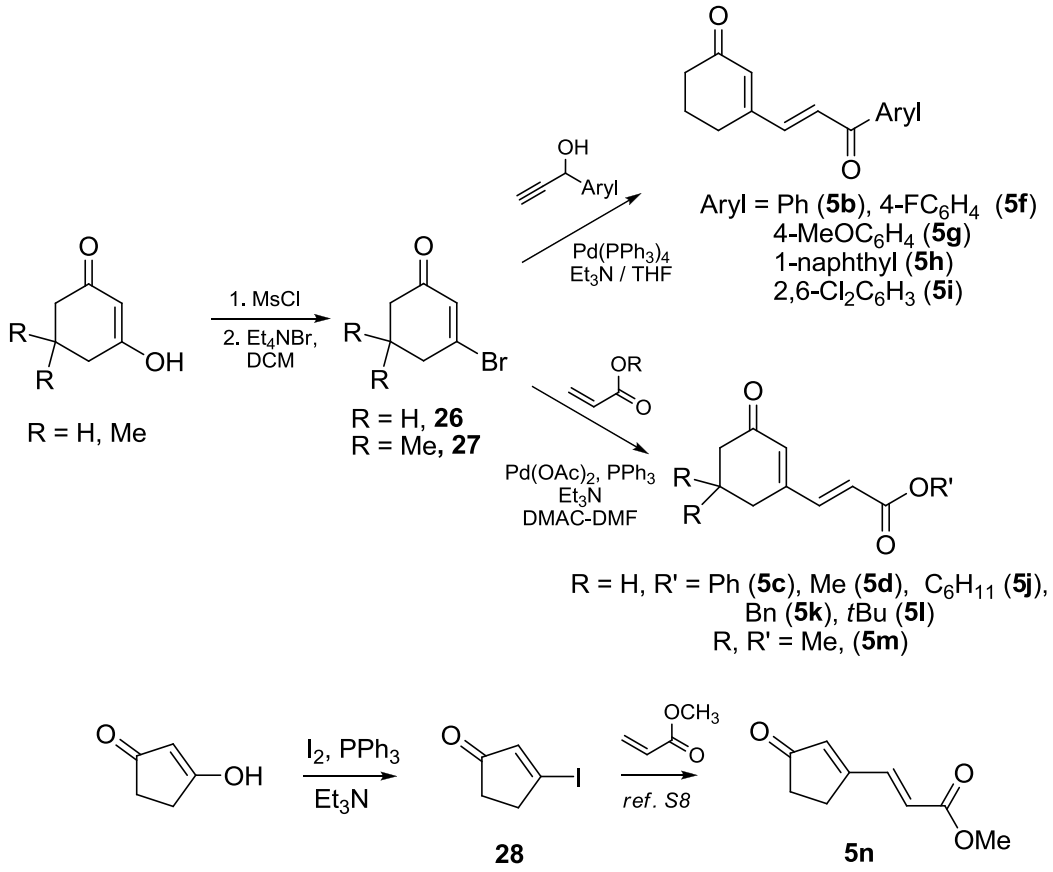
Cupreine derivative **10c** was obtained by demethylation of **10a** with boron tribromide as described in the literature.[S4] 2'-Substituted derivatives **10f**, **10h**, **10i**, **10j**, **10k** were obtained in a reaction of **10a** with an excess of the corresponding organolithium or Grignard reagents.[S5] Compound **10g** was obtained by 2'-arylation of cinchonidine followed by its transformation to the corresponding 9-amine.[S6]

S4. Synthesis of Michael acceptors

Synthesis of Michael acceptors were performed applying Heck (**5c**, **5d**, **5j-n**) or Sonogashira (followed by rearrangement, **5b**, **5f-i**)[S7] reactions of corresponding alkene or acetylene, respectively, as presented below. In contrast to reported procedure[S8] for synthesis **5d** vinyl bromide was used instead of corresponding tosylate. Vinyl bromide **26** can be purified using column chromatography on silica gel and kept in a refrigerator without notable decomposition. Application of analogous vinyl iodide led to similar results. Both vinyl halides were prepared using simple ammonium halides with slight modifications of the original procedure[S9] (however, cheaper Et_4NBr was used instead of BuN_4Br leading to comparable results). Although synthesis of dimedone derivative **5m** was reported using stable nosylate as a reactant in Heck reaction,[S10] but in our hand conversion was incomplete and we were not able to isolate the product from resulted mixture. Application of vinyl bromide **27** gave desired ester **5m** with good yield (82 %) and shorter time (3h vs 16h).

3-Iodocyclopent-3-enone (**28**)[S11] and dienes **5e**, **5n** were prepared following literature precedents.[S8]

[S2] H. Brunner, J. Bügler, B. Nuber, *Tetrahedron: Asymmetry*, 1995, **6**, 1699.
[S3] K. Kacprzak, B. Gierczyk, *Tetrahedron: Asymmetry*, 2010, **21**, 2740.
[S4] W. Chen, Y.-Z. Duan, Y. Wu, S.-Y. Yang, Y.-C. Chen, *Angew. Chem., Int. Ed.*, 2007, **46**, 7667.
[S5] A. Lee, A. Michrowska, S. Sulzer-Mosse, B. List, *Angew. Chem., Int. Ed.*, 2001, **50**, 1707.
[S6] A. Gualdani, D. Petruzziello, E.; Emer, P. G. Cozzi, *Chem. Commun.*, 2012, **48**, 3614.
[S7] R. U. Braun, M. Ansorge, T. J. J. Mueller, *Chem. Eur. J.*, 2006, **12**, 9081.
[S8] D. Duvvuru, J.-F. Betzer, P. Retailleau, G. Frison, A. Marinetti, *Adv. Synth. Catal*., 2011, **353**, 483.
[S9] C. J. Kowalski, K. W. Fields, *J. Org. Chem.*, 1981, **46**, 197.
[S10] N. P. Cheval, A. Dikova, A. Blanc, J.-M. Weibel, P. Pale, *Chem. Eur. J*. 2013, **19**, 8765.
[S11] G. Lemière, V. Gandon, K. Cariou, A. Hours, T. Fukuyama, A.-L. Dhimane, L. Fensterbank, M. Malacria, *J. Am. Chem. Soc*., 2009, **131**, 2993.

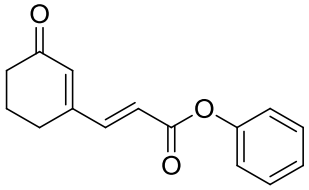


Scheme S1. General synthesis of Michael acceptors **5b**-**n**

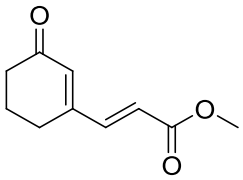
General procedure for synthesis of esters 5c, 5d, 5j-m (GP1):

Under positive pressure of argon, DMAC (11 mL/10 mmol) and DMF (5 mL/10 mmol) were added to the modified Schlenk tube. Mixture of solvent was degassed for 45 min. Then, vinyl bromide (1.0 equiv), corresponding acrylate (1.5 equiv.), $Pd(OAc)_2$ (2 mol %), PPh_3 (2 mol %) and Et_3N (1.6 equiv.) were added subsequently. Resulted mixture was put into warmed silicon-oil bath (85 °C) and stirred vigorously. After 0.5h of stirring, a solid material appeared together with colour changing from reddish to brown. Reaction was performed for 3h at 85 °C (oil bath), then cooled to rt and diluted with diethyl ether (25 mL/10 mmol of vinyl bromide). After treatment with 1 % HCl solution (25 mL), phases were separated. Remained layer was washed with ether (25 mL). Combined organic extracts were washed with $NaHCO_3$ (satd., aq., 25 mL), brine (25 mL) and dried (Na_2SO_4). Purification on silica gel (100 g, hexanes/AcOEt 3:1, v/v) gave the desired ester.

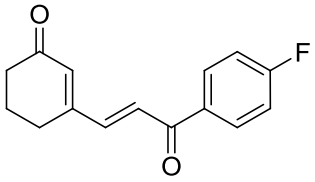
Phenyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (5c): According to GP1 product was obtained as a light yellow crystals, 56%, mp 92.0–93.0°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.53 (d, J = 15.9 Hz, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 15.9 Hz, 1H), 6.21 (s, 1H), 2.53 (t, J = 5.6 Hz, 2H), 2.45-2.48 (m, 2H), 2.10 (quint., J = 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6, 164.3, 153.4, 150.6, 146.2, 133.2, 129.6, 126.1, 123.3, 121.5, 37.8, 24.8, 22.1 ppm; HRMS (ESI): $[C_{15}H_{14}O_3+Na]^+$) requires: 265.0835; found: 265.0837.



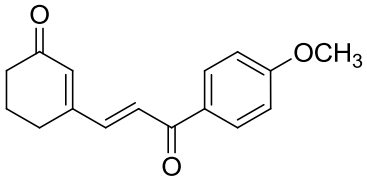
Methyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (5d): According to GP1 product was obtained a light yellow crystals, 84%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.32 (d, J = 15.9 Hz, 1H), 6.23 (d, J = 15.9 Hz, 1H), 6.12 (s, 1H), 3.75 (s, 3H), 2.45 (t, J = 6.0 Hz, 2H), 2.41 (t, J = 6.7 Hz, 2H), 2.04 (quint., J = 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.7, 166.3, 153.7, 144.6, 132.6, 123.7, 52.0, 37.7, 24.8, 22.1 ppm. Recorded spectra are in accordance with the previously reported.[S12]



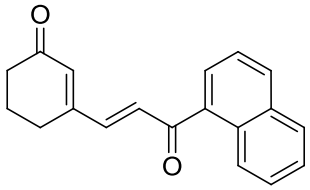
3-((1*E*)-3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)cyclohex-2-en-1-one (5f): Product was obtained as a waxy brown solid, 43%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.97 (dd, J = 8.5, 5.5 Hz, 2H), 7.40 (d, J = 15.7 Hz, 1H), 7.26 (d, J = 15.7 Hz, 1H), 7.16 (t, J = 8.5 Hz, 2H), 6.20 (s, 1H), 2.57 (t, J = 5.9 Hz, 2H), 2.44 (t, J = 6.9 Hz, 2H), 2.09 (quint., J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6, 188.1, 165.8 (d, $J_{C\text{-}F}$ = 256.1Hz), 154.1, 144.3, 133.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.3, 131.2 (d, $J_{C\text{-}F}$ = 9.3 Hz), 126.8, 116.0 (d, $J_{C\text{-}F}$ = 21.9 Hz), 37.2, 25.0, 22.1 ppm. HRMS (ESI): $[C_{15}H_{13}FO_2+H]^+$ requires: 245.0972; found: 245.0987.



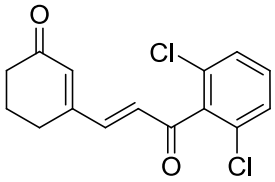
3-((1*E*)-3-(4-methoxyphenyl)-3-oxoprop-1-en-1-yl)cyclohex-2-en-1-one (**5g**): Product was obtained as a light brown solid, 43%, mp 151.9–154.0 °C; ^{1}H NMR (CDCl3, 600 MHz): δ 7.97 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 15.6 Hz, 1H), 7.31 (d, J = 15.6 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 6.23 (s, 1H), 3.88 (s, 3H), 2.60 (t, J = 5.8 Hz, 2H), 2.45-2.48 (m, 2H), 2.11 (quint., J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.8, 188.1, 163.9, 154.5, 143.4, 132.9, 131.1, 130.5, 127.3, 114.1, 55.7, 37.8, 25.2, 22.2 ppm. HRMS (ESI): $[C_{16}H_{16}O_3+H]^+$ requires: 257.1172; found: 257.1176.



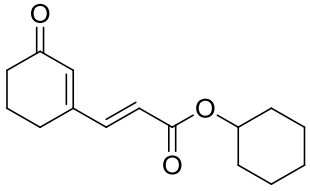
3-((1*E*)-3-(naphthalen-2-yl)-3-oxoprop-1-en-1-yl)cyclohex-2-en-1-one (**5h**): Product was obtained as a light brown solid, 63%, mp 120.5–122.5 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.34 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.0 Hz, 1H), 7.50-7.59 (m, 3H), 7.29 (d, J = 15.9 Hz, 1H), 7. 10 (d, J = 15.9 Hz, 1H), 6.17 (s, 1H), 2.56 (t, J = 6.0 Hz, 2H), 2.46 (t, J = 6.6 Hz, 2H), 2.10 (quint., J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6, 194.5, 154.2, 144.9, 136.1, 134.0, 133.4, 132.6, 131.9, 130.5, 128.7, 127.91, 127.87, 126.8, 125.5, 124.5, 37.8, 25.0, 22.2 ppm. HRMS (ESI): $[C_{19}H_{16}O_2+H]^+$ requires: 277.1223; found: 277.1235.



3-((1*E*)-3-(2,6-dichlorophenyl)-3-oxoprop-1-en-1-yl)cyclohex-2-en-1-one (**5i**): Product was obtained as a light brown solid, 32%, mp 164.0–165.5 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31-7.38 (m, 3H), 6.94 (d, J = 16.2 Hz, 1H), 6.72 (d, J = 16.2 Hz, 1H), 6.12 (s, 1H), 2.54 (t, J = 5.9 Hz, 2H), 2.46 (t, J = 6.7 Hz, 2H), 2.10 (quint., J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.4, 192.2, 157.7, 146.7, 137.3, 134.1, 131.8, 131.24, 131.18, 128.4, 37.8, 24.9, 22.1 ppm. HRMS (ESI): $[C_{15}H_{12}Cl_2O_2+H]^+$ requires: 295.0287; found: 295.0299.



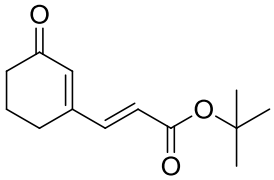
Cyclohexyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (5j): According to GP1 product was obtained as a light yellow crystals, 87%, mp 72.6–73.5°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31 (d, J = 16.0 Hz, 1H), 6.23 (d, J = 16.0 Hz, 1H), 6.13 (s, 1H), 4.83 (sept., J = 4.3 Hz, 1H), 2.46 (t, J = 5.8 Hz, 2H), 2.42 (t, J = 6.6 Hz, 2H), 2.05 (quint., J = 6.4 Hz, 2H), 1.84-1.89 (m, 2H), 1.69-1.75 (m, 2H), 1.51-1.56 (m, 1H), 1.40-1.47 (m, 2H), 1.32-1.40 (m, 2H), 1.22-1.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.7, 165.4, 154.0, 144.0,



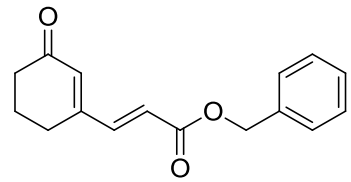
[S12] X. Fu, X.; S. Zhang, J. Yin, T. L. McAllister, S. A. Jiang, C.-H. Tann, T. K. Thiruvengadam, F. Zhang, *Tetrahedron Lett.*, 2002, **43**, 573.

132.4, 124.9, 73.4, 37.8, 31.7, 25.4, 24.9, 23.8, 22.2; HRMS (ESI): $[C_{15}H_{20}O_3+H]^+$ requires: 249.1485; found: 249.1483.

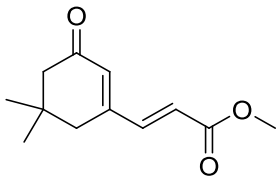
***tert*-Butyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (5l)**: According to GP1 product was obtained as a light yellow crystals, 81%, mp 108–109.5°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24 (d, J = 15.9 Hz, 1H), 6.18 (d, J = 15.9 Hz, 1H), 6.12 (s, 1H), 2.41-2.47 (m, 4H), 2.05 (quint., J = 6.5 Hz, 2H), 1.49 (s, 9H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.8, 165.2, 154.1, 143.3, 132.1, 126.2, 81.3, 37.7, 28.1, 24.9, 22.1 ppm. HRMS (ESI): $[C_{13}H_{18}O_3+H]^+$ requires: 223.1329; found: 223.1325.



Benzyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (5k)[S13]: According to GP1 product was obtained as a yellow oil, 93%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.31-7.41 (m, 6H), 6.30 (d, J = 16 Hz, 1H), 6.15 (s, 1H), 5.22 (s, 2H), 2.42-2.47 (m, 4H), 2.06 (quint., J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.7, 165.7, 153.7, 144.9, 135.6, 132.7, 128.7, 128.5, 128.4, 123.8, 66.8, 37.7, 24.8, 22.1 ppm. HRMS (ESI): $[C_{16}H_{16}O_3+H]^+$ requires: 257.1172; found: 257.1169.



Methyl (*E*)-3-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)acrylate (5m): According to GP1 product was obtained as a light yellow solid, 82%; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.39 (d, J = 15.9 Hz, 1H) 6.25 (d, J = 15.9 Hz, 1H), 6.17 (s, 1H), 3.79 (s, 3H), 2.34 (s, 2H), 2.30 (s, 2H), 1.07 (s, 6H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.9, 166.4, 151.6, 144.8, 131.7, 123.6, 52.1, 51.5, 38.9, 33.4, 28.4 ppm. Spectra match the previously reported data.[S12]



S5. General procedures for sulfa-Michael reactions

General procedure for catalytic Sulfa-Michael reactions (GP2):

(*S*)-*O*-Acetyl mandelic acid (0.06 mmol, 20 mol%) was added to solution of catalyst **10f** (0.03 mmol, 10 mol%) in dichloromethane (1.0 mL) at rt. After 15 minutes diene **5** (0.3 mmol, 1.0 equiv.) was added and resulted solution was stirred for another 15 min. followed by slow addition of thiol (0.45 mmol, 1.5 equiv.) in dichloromethane (0.5 mL). Reaction was performed for 20h at rt, diluted with about 2 mL of AcOEt and finally filtered through a plug of silica gel (5–10 g). Elution by total volume 100 mL of AcOEt afforded crude product, which was further purified using column chromatography (silica gel, hexanes / AcOEt, 3:1, v/v). Enantiomeric excess was determined using HPLC on chiral stationary phase (AD-H).

In reactions with allyl, lauryl and 4-*tert*-Butyl-benzyl mercaptans as well as in case of esters **5d** and **5l**, 3.0 equiv of thiol was used. Amount of thiol had no impact on *ee* in reaction of **5d** and **5l** with benzyl mercaptan.

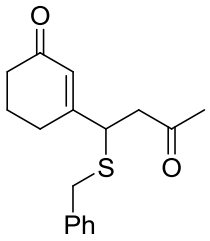
General procedure for preparation of racemates (GP3):

DABCO (10 to 20 mol%) was added to solution of thiol (1.5 equiv) in dichloromethane (2.5 mL) and resulted solution was stirred for 15 minutes at r.t. followed by addition of Michael acceptor (0.3 or 0.5 mmol). After 18–21 h whole reaction mixture was loaded onto a plug of silica gel, and purified as described above.

[S13] Compound **5e** is known from: H. Jo, M. E. Fitzgerald, J. D. Winkler, *Org. Lett.*, 2009, **11**, 1685. However, it was not isolated and no spectra were provided.

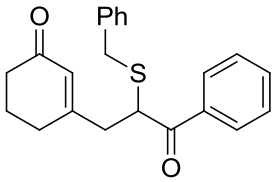
S7. Characterization of sulfa-Michael adducts

3-(1-(Benzylsulfanyl)-2-oxopropyl)cyclohex-2-enone (7a): According to GP3 the product was obtained as a light brown oil, 87 %. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24-7.30 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.80 (s, 1H), 3.69 (t, *J* = 7.4 Hz, 1H), 3.65 (d, *J* = 13.7 Hz, 1H), 3.61 (d, *J* = 13.7 Hz, 1H), 2.78 (dd, *J* = 17.2, 7.2 Hz, 1H) 2.74 (dd, *J* = 17.2, 7.9 Hz, 1H), 2.38-2.49 (m, 1H), 2.22-2.36 (m, 3H), 2.08 (s, 3H), 1.84-1.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 204.5, 199.5, 162.7, 137.4, 129.0, 128.7, 127.4, 126.3, 46.1, 45.7, 37.6, 36.0, 30.3, 26.6, 22.8 ppm. HRMS: (ESI): $[C_{17}H_{20}O_2S+Na]^+$ requires: 311.1076; found: 311.1075.



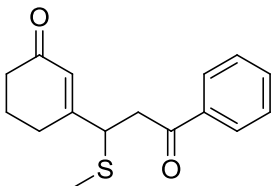
Using conditions specified in GP2, products **6a** and **7a** were not separated.

3-(2-(Benzylsulfanyl)-3-oxo-3-phenylpropyl)cyclohex-2-enone (6b): According to GP2 (reaction catalyzed by **10a**) the product eluted in second fraction and derived as a light brown oil, 50%, $[\alpha]_D$ -10.5 (*c* 0.7, CH_2Cl_2), 67% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.20-7.30 (m, 5H), 5.77 (s, 1H), 4.37 (dd, *J*= 8.6, 6.1 Hz, 1H), 3.73 (d, *J* = 13.1 Hz, 1H), 3.63 (d, *J* = 13.1 Hz, 1H), 3.04 (dd, *J* = 15.6, 8.6 Hz, 1H), 2.71 (dd, *J* = 15.6, 6.1 Hz, 1H), 2.28-2.32 (m, 2H), 2.19-2.28 (m, 2H), 1.90-1.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.4, 194.3, 162.4, 136.9, 135.5, 133.6, 129.3, 128.84, 128.76, 128.63, 127.6, 127.1, 44.6, 38.6, 37.3, 34.6, 30.2, 22.6 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 9:1 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 18.82 (minor), 25.30 min (major). HRMS (ESI): $[C_{22}H_{22}O_2S+Na]^+$ requires: 373.1233; found: 373.1230.



For reaction catalyzed by amine **10d**: light brown oil, 49%, $[\alpha]_D$ = +13.4 (*c* 0.3, CH_2Cl_2), 49% *ee*. HPLC (Chiralpak AD-H, hexane/*i*PrOH 9:1 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 18.48 (major), 24.95 min (minor).

3-(1-(Benzylsulfanyl)-3-oxo-3-phenylpropyl)cyclohex-2-enone (7b): According to GP3 the product was obtained as a light brown oil, 93 %. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.57 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.27-7.31 (m, 4H), 7.21-7.25 (m, 1H), 5.84 (s, 1H), 3.90 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.67 (d, *J* = 13.6 Hz, 1H), 3.35 (dd, *J* = 17.1, 6.4 Hz, 1H), 3.30 (dd, *J* = 17.1, 8.3 Hz, 1H), 2.49 (dt, *J* = 17.8, 5.6 Hz, 1H), 2.29-2.38 (m, 3H), 1.87-1.99 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6, 196.3, 162.9, 137.6, 136.3, 133.6, 129.1, 128.85, 128.73, 128.1, 127.4, 126.4, 46.2, 41.6, 37.7, 36.2, 26.8, 22.9 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 9:1 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 29.77, 32.63 min. HRMS (ESI): $[C_{22}H_{22}O_2S+Na]^+$ requires: 373.1233; found: 373.1232.

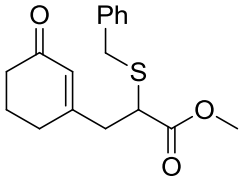


Phenyl 2-(benzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (6c): According to GP2, product was obtained as a colorless solid, 74%, mp 51-52°C; °C; $[\alpha]_D$ +189 (*c* 0.2, CH_2Cl_2), 80% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.39 (t, *J* = 7.9, 2H), 7.31-7.37 (m, 4H), 7.23-7.29 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 5.85 (s, 1H), 3.98 (d, *J*= 13.5 Hz, 1H), 3.88 (d, *J* =

13.5 Hz, 1H), 3.52 (dd, *J* = 8.3, 7.4 Hz, 1H), 2.84 (dd, *J* = 15.4, 8.3 Hz, 1H) 2.57 (dd, *J* = 15.4 Hz, 7.4 Hz, 1H) 2.27-2.53 (m, 2H), 2.15 (dt, *J* = 18.1, 6.0 Hz, 1H), 2.02 (dt, *J* = 18.1, 6.2 Hz, 1H), 1.85-1.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.0, 170.0, 160.6, 150.3, 136.8, 129.5, 129.1, 128.6, 127.44, 127.36, 126.1, 121.1, 42.6, 38.6, 37.1, 36.1, 29.2, 22.4. HPLC (Chiralpak AD-H, hexane/iPrOH 95:5 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 29.13 (major), 30.50 min (minor). HRMS (ESI): $[C_{22}H_{22}O_3S+Na]^+$ requires: 389.1182; found: 389.1178.

For reaction catalyzed by **10d**: colorless solid, 58%, $[\alpha]_D$ -94 (*c* 0.2, CH_2Cl_2), 60% *ee*. HPLC (Chiralpak AD-H, hexane/iPrOH 95:5 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 31.51 (minor), 32.74 min (major).

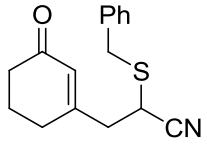
Methyl 2-(benzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (6d): According to GP2, product was



obtained as a colorless oil, 71%, $[\alpha]_D$ +156 (*c* 0.9, CH_2Cl_2), 87% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.29-7.33 (m, 4H), 7.23-7.27 (m, 1H), 5.74 (s, 1H), 3.84 (d, *J* = 13.6 Hz, 1H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.71 (s, 3H), 3.33 (t, *J* = 7.9 Hz, 1H), 2.72 (dd, *J* = 15.3, 8.2 Hz, 1H), 2.46 (dd, *J* = 15.3, 7.5 Hz, 1H), 2.24-2.32 (m, 2H), 2.09 (dt, *J* = 18.1, 5.8 Hz, 1H), 1.97 (dt, *J* = 18.1, 6.0 Hz, 1H), 1.84-1.89 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.4, 172.2, 161.1, 137.2, 129.2, 128.7, 127.5, 127.4, 52.6, 42.8, 38.9, 37.2, 36.2, 29.3, 22.5. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 21.12 (minor), 22.95 min (major). HRMS (ESI): $[C_{17}H_{20}O_3S+H]^+$ requires: 305.1206; found: 305.1212.

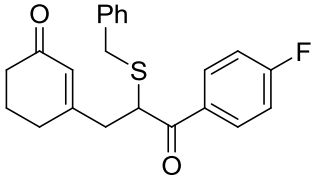
For reaction catalyzed by **10e**: colorless oil, 58%, 69% *ee*. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* = 220 nm): t_R 19.24 (major), 20.85 min (minor).

2-(Benzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanenitrile (6e): According to GP3 the product was



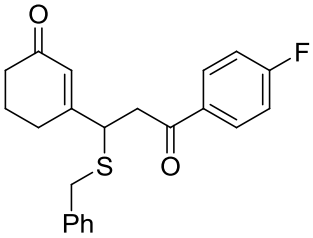
obtained as a yellowish oil, 55 %. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33-7.36 (m, 4H), 7.28-7.31 (m, 1H), 5.84 (s, 1H), 3.97 (d, *J* = 13.7 Hz, 1H), 3.94 (d, *J* = 13.7 Hz, 1H), 3.45 (dd, *J* = 8.0, 7.1 Hz, 1H), 2.66 (dd, *J* = 15.0, 8.0 Hz, 1H), 2.58 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.33-2.35 (m, 2H), 2.13-2.23 (m, 2H), 1.94-1.98 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 198.8, 157.9, 135.9, 129.04, 129.01, 128.7, 128.0, 118.1, 39.5, 37.2, 36.3, 29.7, 29.2, 22.5 ppm. HPLC (Chiralpak OD-H, hexane/*i*PrOH 9:1 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 33.37 (minor), 37.39 min (major). HRMS (ESI): $[C_{16}H_{17}NOS+Na]^+$ requires: 294.0923; found: 294.0930.

3-(2-(Benzylsulfanyl)-3-(4-fluorophenyl)-3-oxopropyl)cyclohex-2-enone (**6f**): According to GP2, product

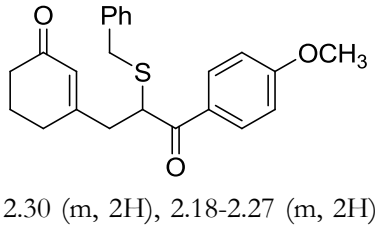


was obtained as a brown oil, 49%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.84 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.21-7.31 (m, 5H), 7.08 (t, *J* = 8.7 Hz, 2H), 5.75 (s, 1H), 4.31 (dd, *J* = 8.7, 6.2 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.63 (d, *J* = 13.2 Hz, 1H), 3.04 (dd, *J* = 15.7, 8.7 Hz, 1H), 2.71 (dd, *J* = 15.7, 6.2 Hz, 1H), 2.19-2.32 (m, 4H), 1.90-1.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 192.7, 165.9 (d, J_{C-F} = 256.1 Hz), 162.3, 136.8, 131.7 (d, J_{C-F} = 3.0 Hz), 131.3 (d, J_{C-F} = 9.3 Hz), 129.3, 128.8, 127.6, 127.0, 116.0 (d, J_{C-F} = 21.9 Hz), 44.6, 38.5, 37.3, 34.6, 30.3, 22.6 ppm. HRMS (ESI): $[C_{22}H_{21}FO_2S+Na]^+$ requires: 391.1138; found: 391.1152.

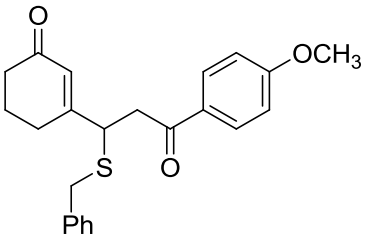
3-(1-(Benzylsulfanyl)-3-(4-fluorophenyl)-3-oxopropyl)cyclohex-2-enone (**7f**): According to GP3, product was obtained as a brown oil, 81%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.86 (dd, *J* = 8.0, 5.4 Hz, 2H), 7.26-7.31 (m, 4H), 7.22-7.25 (m, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 5.83 (s, 1H), 3.88 (dd, *J* = 8.2, 6.6 Hz, 1H), 3.70 (d, *J* = 13.7 Hz, 1H), 3.67 (d, *J* = 13.7 Hz, 1H), 3.31 (dd, *J* = 16.9, 6.6 Hz, 1H), 3.27 (dd, *J* = 16.9, 8.2 Hz, 1H), 2.49 (dt, *J* = 17.8, 5.8 Hz, 1H), 2.30-2.39 (m, 3H), 1.89-2.00 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6, 194.7, 166.1 (d, $J_{C\text{-}F}$ = 256.0 Hz), 162.8, 137.6, 132.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.9 (d, $J_{C\text{-}F}$ = 9.4 Hz), 129.1, 128.8, 127.5, 126.4, 116.0 (d, $J_{C\text{-}F}$ = 22.0 Hz), 46.2, 41.5, 37.7, 36.2, 26.9, 22.9 ppm. HRMS (ESI): $[C_{22}H_{21}FO_2S+H]^+$ requires: 369.1319; found: 369.1301.



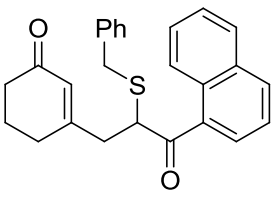
3-(2-(Benzylsulfanyl)-3-(4-methoxyphenyl)-3-oxopropyl)cyclohex-2-enone (**6g**): According to GP2, product was obtained as a brown oil, 46%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.23-7.30 (m, 5H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.76 (s, 1H), 4.33 (dd, *J* = 8.7, 6.0 Hz, 1H), 3.86 (s, 3H), 3.73 (d, *J* = 13.0 Hz, 1H), 3.63 (d, *J* = 13.0 Hz, 1H), 3.03 (dd, *J* = 15.6, 8.7 Hz, 1H), 2.69 (dd, *J* = 15.6, 6.0 Hz, 1H), 2.27-2.30 (m, 2H), 2.18-2.27 (m, 2H), 1.89-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.4, 193.1, 163.9, 162.7, 137.1, 131.0, 129.3, 128.7, 128.2, 127.5, 127.0, 114.0, 55.6, 44.3, 38.8, 37.3, 34.6, 30.3, 22.6 ppm. HRMS (ESI): $[C_{23}H_{24}O_3S+Na]^+$ requires: 403.1338; found: 403.1334.



3-(1-(Benzylsulfanyl)-3-(4-methoxyphenyl)-3-oxopropyl)cyclohex-2-enone (**7g**): According to GP3, product was obtained as a brown oil, 74%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.82 (d, *J* = 9.1 Hz, 2H), 7.27-7.30 (m, 4H), 7.21-7.25 (m, 1H), 6.91 (d, *J* = 9.1 Hz, 2H), 5.86 (s, 1H), 3.90 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.87 (s, 3H), 3.70 (d, *J* = 13.6 Hz, 1H), 3.67 (d, *J* = 13.6 Hz, 1H), 3.29 (dd, *J* = 16.9, 6.4 Hz, 1H), 3.25 (dd, *J* = 16.9, 8.4 Hz, 1H), 2.49 (dt, *J* = 17.9, 5.5 Hz, 1H), 2.29-2.38 (m, 3H), 1.87-1.99 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.7, 194.8, 164.0, 163.1, 137.7, 130.5, 129.5, 129.1, 128.7, 127.4, 126.4, 114.0, 55.7, 46.5, 41.2, 37.7, 36.2, 26.8, 22.9 ppm. HRMS (ESI): $[C_{23}H_{24}O_3S+H]^+$ requires: 381.1519; found: 381.1521.



3-(2-(Benzylsulfanyl)-3-(2-naphtyl)-3-oxopropyl)cyclohex-2-enone (**6h**): According to GP2, product was obtained as a brown oil, 30%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.58-7.62 (m, 1H), 7.54-7.57 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.22-7.27 (m, 3H), 7.12-7.14 (m, 2H), 5.88 (s, 1H), 4.24 (t, *J* = 7.6 Hz, 1H), 3.66 (d, *J* = 13.3 Hz, 1H), 3.51 (d, *J* = 13.3 Hz, 1H), 3.04 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.70 (dd, *J* = 15.1, 6.9 Hz, 1H), 2.26-2.29 (m, 2H), 2.16-2.24 (m, 2H), 1.89 (quint., *J* = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 197.9, 162.2, 136.7,



135.8, 134.0, 132.8, 130.9, 129.2, 128.7, 128.6, 128.2, 127.68, 127.62, 126.8, 126.5, 125.5, 124.3, 48.3, 38.6, 37.2, 35.5, 30.2, 22.6 ppm. HRMS (ESI): $[C_{26}H_{24}O_2S+Na]^+$ requires: 423.1389; found: 423.1398.

3-(1-(Benzylsulfanyl)-3-(2-naphtyl)-3-oxopropyl)cyclohex-2-enone (**7h**): According to GP3, product was obtained as a brown oil, 73%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.50 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.56-7.59 (m, 1H), 7.52-7.54 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.18-7.25 (m, 5H), 5.86 (s, 1H), 3.94 (t, *J* = 7.6 Hz, 1H), 3.68 (d, *J* = 13.7 Hz, 1H), 3.65 (d, *J* = 13.7 Hz, 1H), 3.42 (dd, *J* = 16.5, 7.2 Hz, 1H), 3.36 (dd, *J* = 16.5, 8.0 Hz, 1H), 2.49 (dt, *J* = 17.8, 5.5 Hz, 1H), 2.27-2.37 (m, 3H), 1.85-1.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 200.2, 199.5, 162.6, 137.4, 135.2, 134.0, 133.2, 130.1, 129.0, 128.6, 128.5, 128.2, 127.7, 127.3, 126.7, 126.6, 125.6, 124.3, 46.9, 44.6, 37.7, 36.1, 26.6, 22.8 ppm. HRMS (ESI): $[C_{26}H_{24}O_2S+H]^+$ requires: 401.1570; found: 401.1595.

3-(1-(Benzylsulfanyl)-3-(2,6-dichlorophenyl)-3-oxopropyl)cyclohex-2-enone (**7i**): According to GP3, product was obtained as a brown oil, 69%, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.22-7.32 (m, 8H), 5.91 (s, 1H), 3.88-3.91 (m, 1H), 3.71 (d, *J* = 13.5 Hz, 1H), 3.68 (d, *J* = 13.5 Hz, 1H), 3.27 (dd, *J* =19.1, 7.6 Hz, 1H), 3.23 (dd, *J* =19.1, 6.3 Hz, 1H), 2.46-2.53 (m, 1H), 2.30-2.41 (m, 3H), 1.87-2.01 (m, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6, 198.0, 162.1, 138.7, 137.2, 131.1, 130.7, 129.1, 128.7, 128.4, 127.4, 127.0, 46.4, 45.0, 37.7, 36.3, 26.6, 22.9 ppm. HRMS (ESI): $[C_{22}H_{20}Cl_2O_2S+Na]^+$ requires: 441.0453; found: 441.0461.

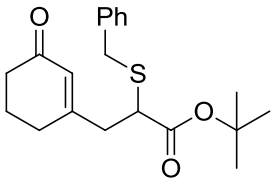
Using conditions specified in GP2, products **6i** and **7i** were not separated.

Cyclohexyl 2-(benzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (6j): According to GP2, product was obtained as a colorless solid, 61%, mp 83-85°C; $[\alpha]_D$ +153 (*c* 0.25, CH_2Cl_2), 82% *ee*. Recrystallization from CH_2Cl_2/cyclohexane gave an analytical sample of product with 90% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.28-7.32 (m, 4H), 7.22-7.26 (m, 1H), 5.74 (s, 1H), 4.77-4.82 (m, 1H), 3.86 (d, *J* = 13.5 Hz, 1H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.28 (dd, *J* = 8.6, 7.3 Hz, 1H), 2.70 (dd, *J* = 15.4, 8.6 Hz, 1H), 2.44 (dd, *J* = 15.4, 7.3 Hz, 1H), 2.27-2.31 (m, 2H), 2.10 (dt, *J* = 18.2, 5.8 Hz, 1H), 1.97 (dt, *J* = 18.2, 6.0 Hz, 1H), 1.82-1.88 (m, 4H), 1.70-1.75 (m, 2H), 1.51-1.56 (m, 1H), 1.42-1.50 (m, 2H), 1.33-1.41 (m, 2H), 1.23-1.30 (m, 1H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 171.1, 161.3, 137.2, 129.2, 128.6, 127.4, 127.3, 74.0, 43.0, 38.9, 37.2, 36.1, 31.6, 31.5, 29.3, 25.3, 23.76, 23.73, 22.5. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 14.45 (minor), 16.32 min (major). HRMS (ESI): $[C_{22}H_{28}O_3S+Na]^+$ requires: 395.1651; found: 395.1653.

Benzyl 2-(benzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (6k): According to GP2, product was obtained as a colorless oil, 81%, $[\alpha]_D$ +136 (*c* 0.3, CH_2Cl_2), 87% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.23-7.41 (m, 10H), 5.75 (s, 1H), 5.20 (d, *J* = 12.1 Hz, 1H),

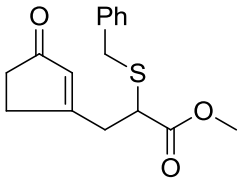
5.13 (d, *J* = 12.1 Hz, 1H), 3,79 (d, *J* = 13.5 Hz, 1H), 3,73 (d, *J* = 13.5 Hz, 1H), 3.37 (t, *J* = 7.9 Hz, 1H), 2.74 (dd, *J* = 15.2, 8.4 Hz, 1H), 2.49 (dd, *J* = 15.2, 7.5 Hz, 1H), 2.24-2.26 (m, 2H), 2.07 (dt, *J* = 17.9, 5.9 Hz, 1H), 1.95 (dt, *J* = 17.9, 6.1 Hz, 1H), 1.83 (quint., *J* = 6.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 171.5, 160.9, 137.1, 135.5, 129.2, 128.8, 128.68, 128.66, 128.62, 128.5, 127.5, 67.3, 43.0, 38.9, 37.3, 36.1, 29.4, 22.5 ppm. HPLC (Chiralpak AD-H, hexane/iPrOH 9:1 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 17.83 (minor), 22.21 min (major). HRMS (ESI): $[C_{23}H_{24}O_3S+Na]^+$ requires: 403.1338; found: 403.1343.

***tert*-Butyl 2-(benzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (6l):** According to GP2, product was



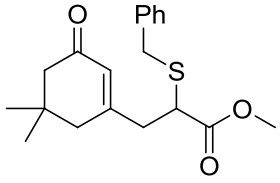
obtained as a colorless oil, 68%, $[\alpha]_D$ +138 (*c* 0.8, CH_2Cl_2), 87% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.29-7.32 (m, 4H), 7.23-7.27 (m, 1H), 5.76 (s, 1H), 3.87 (d, *J* = 13.3 Hz, 1H), 3.78 (d, *J* = 13.3 Hz, 1H), 3.21 (dd, *J* = 8.6, 7.3 Hz, 1H), 2.67 (dd, *J* =15.2, 8.6 Hz, 1H), 2.40 (dd, *J* = 15.2, 7.3 Hz, 1H), 2.44-2.32 (m, 2H), 2.11 (dt, *J* = 18.0, 5.9 Hz, 1H), 1.99 (dt, *J* = 18.0, 6.0 Hz, 1H), 1.87 (quint., *J* = 6.4 Hz, 2H), 1.49 (s, 9H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.4, 170.9, 161.5, 137.4, 129.2, 128.7, 127.4, 127.3, 82.1, 43.7, 39.0, 37.3, 36.1, 29.4, 28.1, 22.6. HPLC (Chiralpak AD-H, hexane/*i*PrOH 97:3 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 9.91 (minor), 11.53 min (major). HRMS (ESI): $[C_{20}H_{26}O_3S+Na]^+$ requires: 369.1495; found: 369.1507.

Methyl 2-(benzylsulfanyl)-3-(3-oxocyclopent-1-en-1-yl)propanoate (8): According to GP2, product was



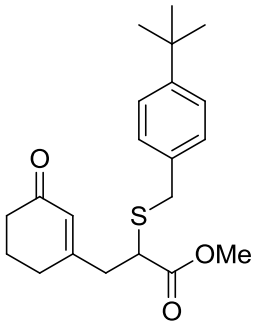
obtained as a colorless oil, 47%, $[\alpha]_D$ +44 (*c* 0.2, CH_2Cl_2), 40% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.29-7.32 (m, 4H), 7.24-7.27 (m, 1H), 5.78 (s, 1H), 3.86 (d, *J* = 13.6 Hz, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.73 (s, 3H), 3.38 (t, *J* = 7.7 Hz, 1H), 2.91 (dd, *J* = 16.5, 8.2 Hz, 1H), 2.66 (dd, *J* = 16.5, 7.3 Hz, 1H), 2.36-2.42 (m, 1H), 2.26-2.33 (m, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 209.4, 177.3, 172.2, 137.1, 130.9, 129.2, 128.7, 127.6, 52.6, 42.7, 36.2, 35.2, 34.7, 31.3. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 20.49 (minor), 22.88 min (major). HRMS (ESI): $[C_{16}H_{18}O_3S+Na]^+$ requires: 313.0869; found: 313.0869.

Methyl 2-(benzylsulfanyl)-3-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)propanoate (9): According to GP2,

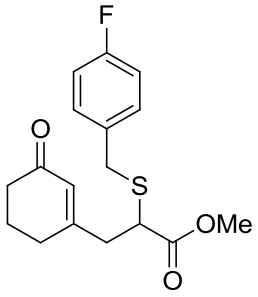


product was obtained as a colorless oil, 63%, $[\alpha]_D$ +76 (*c* 0.4, CH_2Cl_2), 57% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.28-7.33 (m, 4H), 7.23-7.27 (m, 1H), 5.75 (s, 1H), 3.84 (d, *J* = 13.6 Hz, 1H), 3.78 (d, *J* = 13.6 Hz, 1H), 3.71 (s, 3H), 3.37 (t, *J* = 7.9 Hz, 1H), 2.70 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.44 (dd, *J* = 15.1, 7.5 Hz, 1H), 2.13 (s, 2H), 1.94 (d, *J* = 18.0 Hz, 1H), 1.89 (d, *J* = 18.0 Hz, 1H), 0.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.6 172.1, 158.6, 137.2, 129.2, 128.7, 127.5, 126.4, 52.6, 51.0, 43.5, 42.8, 39.0, 36.2, 33.6, 28.6, 27.9. HPLC (Chiralpak AD-H, hexane/*i*PrOH 97:3 v/v, flow rate: 0.8 mL/min, *λ* 220 nm): t_R 20.48 (minor), 24.37 min (major). HRMS (ESI): $[C_{19}H_{24}O_3S+Na]^+$ requires: 355.1338; found: 355.1331.

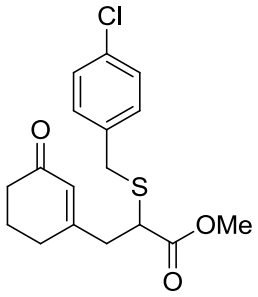
Methyl 2-(4-*tert*-butylbenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (12): According to GP2, product was obtained as a colorless oil, 67%, $[\alpha]_D$ +146 (*c* 1.2, $CHCl_3$), 86% *ee*. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.74 (s, 1H), 3.81 (d, *J* = 13.5 Hz, 1H), 3.74 (d, *J* = 13.5 Hz, 1H), 3.71 (s, 3H), 3.34 (t, *J* = 7.9 Hz, 1H), 2.72 (dd, *J* = 15.4, 8.0 Hz, 1H), 2.46 (dd, *J* = 15.4, 7.8 Hz, 1H), 2.23-2.32 (m, 2H), 2.06 (dt, *J* = 18.0, 5.7 Hz, 1H), 1.92 (dt, *J* = 18.0, 6.1 Hz, 1H), 1.82-1.87 (m, 2H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.3, 161.1, 150.5, 134.1, 128.9, 127.4, 125.6, 52.5, 42.7, 38.9, 37.2, 35.8, 34.6, 31.4, 29.2, 22.6 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 12.86 (minor), 15.31 min (major). HRMS (ESI): $[C_{21}H_{28}O_3S+Na]^+$ requires: 383.1651; found: 383.1671.



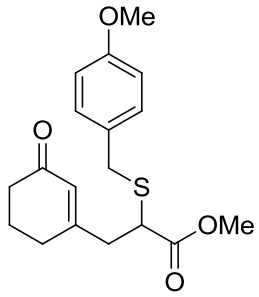
Methyl 2-(4-fluorobenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (13): According to GP2, product was obtained as a colorless oil, 78%, $[\alpha]_D$ +121 (*c* 0.3, CH_2Cl_2), 87% *ee*. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.25-7.29 (m, 2H), 6.99 (t, *J* = 8.5 Hz, 2H), 5.74 (s, 1H), 3.81 (d, *J* = 13.6 Hz, 1H), 3.74 (d, *J* = 13.6 Hz, 1H), 3.71 (s, 3H), 3.32 (t, *J* = 7.9 Hz, 1H), 2.73 (dd, *J* = 15.4, 8.4 Hz, 1H), 2.47 (dd, *J* = 15.4, 7.3 Hz, 1H), 2.24-2.33 (m, 2H), 2.13 (dt, *J* = 18.2, 5.7 Hz, 1H), 2.03 (dt, *J* = 18.2, 6.1 Hz, 1H), 1.89 (quint., *J* = 6.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.0, 162.1 (d, J_{C-F} = 246.5 Hz), 160.9, 132.9 (d, J_{C-F} = 3.3 Hz), 130.7 (d, J_{C-F} = 8.1 Hz), 127.3, 115.5 (d, J_{C-F} = 21.5 Hz), 52.6, 42.9, 38.8, 37.2, 35.4, 29.4, 22.5 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 21.29 (minor), 22.69 min (major). HRMS (ESI): $[C_{17}H_{19}FO_3S+Na]^+$ requires: 345.0931; found: 345.0941.



Methyl 2-(4-chlorobenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (14): According to GP2, product was obtained as a colorless oil, 57%, $[\alpha]_D$ +135 (*c* 1.4, CH_2Cl_2), 86% *ee*. ^1H NMR ($CDCl_3$, 600 MHz): δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.73 (s, 1H), 3.79 (d, *J* = 13.7 Hz, 1H), 3.72 (d, *J* = 13.7 Hz, 1H), 3.69 (s, 3H), 3.30 (dd, *J* = 8.4, 7.4 Hz, 1H), 2.72 (dd, *J* = 15.4, 8.4 Hz, 1H), 2.46 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.24-2.32 (m, 2H), 2.11 (dt, *J* = 18.2, 5.8 Hz, 1H), 2.02 (dt, *J* = 18.2, 6.0 Hz, 1H), 1.85-1.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.2, 171.9, 160.8, 135.7, 133.3, 130.5, 128.7, 127.3, 52.6, 42.9, 38.8, 37.2, 35.4, 29.4, 22.5. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, λ 220 nm): t_R 20.89 (minor), 22.70 min (major). HRMS (ESI): $[C_{17}H_{19}ClO_3S+Na]^+$ requires: 361.0636; found: 361.0648.

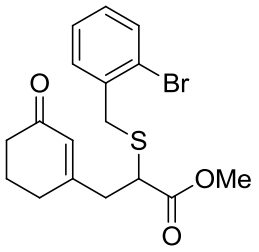


Methyl 2-(4-methoxybenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (15): According to GP2,



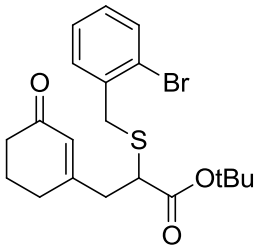
product was obtained as a colorless oil, 45%, $[\alpha]_D$ +127 (*c* 1.2, CH_2Cl_2), 84% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.84 (d, J= 8.6 Hz, 2H), 5.73 (s, 1H), 3.79 (d, *J* = 13.5 Hz, 1H), 3.78 (s, 3H), 3.73 (d, *J* = 13.5 Hz, 1H), 3.72 (s, 3H), 3.32 (t, *J* = 7.9 Hz, 1H), 2.73 (dd, *J* = 15.4, 8.2 Hz, 1H), 2.46 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.24-2.33 (m, 2H), 2.11 (dt, *J* = 18.1, 5.8 Hz, 1H), 2.02 (dt, *J* = 18.1, 6.0 Hz, 1H), 1.86-1.91 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.2, 161.2, 159.0, 130.3, 129.0, 127.3, 114.1, 55.4, 52.6, 42.8, 38.9, 37.3, 35.7, 29.4, 22.5 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 28.22 (minor), 29.92 min (major). HRMS (ESI): $[C_{18}H_{22}O_4S+Na]^+$ requires: 357.1131; found: 357.1123

Methyl 2-(2-bromobenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (16): According to GP2, product



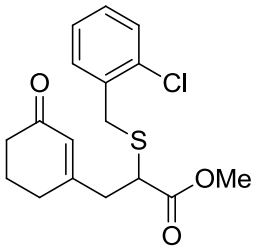
was obtained as a colorless oil, 70%, $[\alpha]_D$ +169 (*c* 0.3, CH_2Cl_2), 88% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.11 (td, *J* = 7.7, 1.2 Hz, 1H), 5.73 (s, 1H), 3.94 (d, *J* = 13.5 Hz, 1H), 3.91 (d, *J* = 13.5 Hz, 1H), 3.71 (s, 3H), 3.40 (t, *J* = 7.9 Hz, 1H), 2.75 (dd, *J* = 15.4, 8.4 Hz, 1H). 2.49 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.26-2.29 (m, 2H), 2.14 (dt, *J* = 18.2, 5.8 Hz, 1H), 2.04 (dt, *J* = 18.2, 6.1 Hz, 1H), 1.85-1.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.0, 161.0, 136.4, 133.4, 131.1, 129.2, 127.5, 127.3, 124.7, 52.6, 43.3, 38.8, 37.2, 36.4, 29.5, 22.5 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 97:3 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 40.83 (minor), 43.13 (major). HRMS (ESI): $[C_{17}H_{19}BrO_3S+Na]^+$ requires: 405.0130; found: 405.0144.

***tert*-Butyl 2-(2-bromobenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (17):** According to GP2,



product was obtained as a colorless oil, 72%, $[\alpha]_D$ +178 (*c* 0.3, CH_2Cl_2), 85% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.10 (td, *J* = 7.7, 1.2 Hz, 1H), 5.75 (s, 1H), 3.97 (d, *J* = 13.3 Hz, 1H), 3.92 (d, *J* = 13.3 Hz, 1H), 3.28 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.69 (dd, *J* = 15.3, 8.8 Hz, 1H). 2.43 (dd, *J* = 15.3, 7.0 Hz, 1H), 2.26-2.29 (m, 2H), 2.16 (dt, *J* = 18.2, 5.8 Hz, 1H), 2.05 (dt, *J* = 18.2, 6.1 Hz, 1H), 1.85-1.90 (m, 2H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 170.7, 161.5, 136.7, 133.4, 131.1, 129.1, 127.5, 127.3, 124.7, 82.2, 44.3, 39.0, 37.3, 36.4, 29.6, 28.1, 22.5 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 97:3 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R =16.68 (minor), 17.87 min (major). HRMS (ESI): $[C_{20}H_{25}BrO_3S+Na]^+$ requires: 447.0600; found: 447.0606.

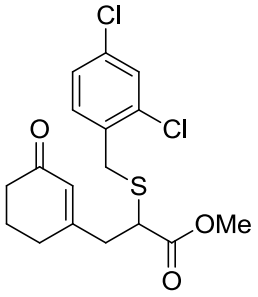
Methyl 2-(2-chlorobenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (18): According to GP2, product



was obtained as a colorless oil, 81%, $[\alpha]_D$ +179 (*c* 0.3, CH_2Cl_2), 90% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33-7.37 (m, 2H), 7.18-7.22 (m, 2H), 5.73 (s, 1H), 3.94 (d, *J* = 13.9 Hz, 1H), 3.92 (d, *J* = 13.9 Hz, 1H), 3.71 (s, 3H), 3.40 (t, *J* = 8.0 Hz, 1H), 2.76 (dd, *J* = 15.5,

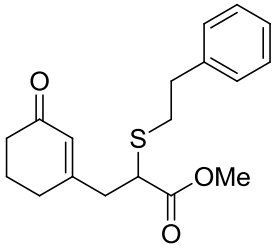
8.4 Hz, 1H). 2.49 (dd, *J* = 15.5, 7.3 Hz, 1H), 2.26-2.30 (m, 2H), 2.15 (dt, *J* = 18.1, 5.9 Hz, 1H), 2.04 (dt, *J* = 18.1, 6.0 Hz, 1H), 1.88 (quint., *J* = 6.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.0, 161.0, 134.8, 134.3, 131.1, 130.0, 129.0, 127.3, 126.9, 52.6, 43.4, 38.8, 37.2, 33.8, 29.5, 22.5. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R =33.16 (minor), 34.89 min (major). HRMS (ESI): $[C_{17}H_{19}ClO_3S+Na]^+$ requires: 361.0636; found: 361.0641.

Methyl 2-(2,4-dichlorobenzylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (19): According to GP2, product was obtained as a colorless oil, 76%, $[\alpha]_D$ +163 (*c* 0.3, CH_2Cl_2), 84% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.39 (d, *J* = 2.2 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.20 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.76 (s, 1H), 3.91 (d, *J* = 13.7 Hz, 1H), 3.88 (d, *J* = 13.7 Hz, 1H), 3.72 (s, 3H), 3.40 (dd, *J* = 8.7, 7.1 Hz, 1H), 2.77 (dd, *J* = 15.3, 8.7 Hz, 1H). 2.51 (dd, *J* = 15.3, 7.1 Hz, 1H), 2.27-2.35 (m, 2H), 2.19 (dt, *J* = 18.1, 5.9 Hz, 1H), 2.11 (dt, *J* = 18.1, 6.0 Hz, 1H), 1.92 (quint., *J* = 6.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 171.9, 160.8, 135.0, 134.1, 133.5, 131.8, 129.9, 127.3, 127.2, 52.7, 43.4, 38.8, 37.3, 33.2, 29.6, 22.6 ppm



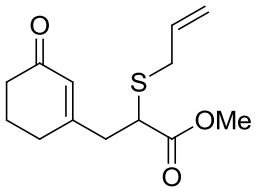
HPLC (Chiralpak AD-H, hexane/*i*PrOH = 90:10 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 15.26 (minor), 18.50 min (major). HRMS (ESI): $[C_{17}H_{18}Cl_2O_3S+Na]^+$ requires: 395.0246; found: 395.0256.

Methyl 3-(3-oxocyclohex-1-en-1-yl)-2-(phenethylsulfanyl)propanoate (20): According to GP2, product was obtained as a colorless oil, 59%, $[\alpha]_D$ +67 (*c* 0.2, CH_2Cl_2), 86% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 5.83 (s, 1H), 3.72 (s, 3H), 3.48 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.83-2.93 (m, 4H), 2.78 (dd, *J* = 15.4, 9.1 Hz, 1H), 2.53 (dd, *J* = 15.4, 6.6 Hz, 1H), 2.32-2.35 (m, 2H), 2.25 (t, *J* = 5.8 Hz, 2H), 1.93-1.98 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.0, 161.2, 139.9, 128.59, 128.57, 127.2, 126.6, 52.6, 43.9, 39.2, 37.3, 35.8, 32.9, 29.7, 22.6 ppm. HPLC



(Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 21.04 (minor), 23.44 min (major). HRMS (ESI): $[C_{18}H_{22}O_3S+Na]^+$ requires: 341.1182; found: 341.1179.

Methyl 2-allylsulfanyl-3-(3-oxocyclohex-1-en-1-yl)propanoate (21): According to GP2, product was obtained as a colorless oil, 73%, $[\alpha]_D$ +93 (*c* 0.2, CH_2Cl_2), 88% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.80 (s, 1H), 5.68-5.75 (m, 1H), 5.14 (d, *J* = 18 Hz, 1H), 5.11 (d, *J* = 10 Hz, 1H), 3.69 (s, 3H), 3.41-3.44 (m, 1H), 3.25 (dd, *J* = 13.7, 8.4 Hz, 1H), 3.16 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.75 (dd, *J* = 15.4, 8.9 Hz, 1H), 2.51 (dd, *J* = 15.4, 6.8 Hz, 1H), 2.29-2.32 (m, 2H), 2.24 (t, *J* = 5.9 Hz, 2H), 1.91-1.97 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 172.2, 161.2, 133.1, 127.2, 118.5, 52.5, 42.6, 39.1, 37.3, 34.8, 29.7, 22.6. HPLC (Chiralpak AD-H, hexane/*i*PrOH 97:3 v/v, flow rate: 0.8 mL/min, *λ* 220 nm): t_R 20.10 (minor), 21.30 min (major). HRMS (ESI): $[C_{13}H_{18}O_3S+Na]^+$ requires: 277.0869; found: 277.0879.



Methyl 2-(dodecylsulfanyl)-3-(3-oxocyclohex-1-en-1-yl)propanoate (22): According to GP2 product was obtained as a colorless oil, 39%, $[\alpha]_D$ +77 (*c* 0.2, CH_2Cl_2), 86% *ee*. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.84 (s, 1H), 3.71 (s, 3H), 3.47 (dd, *J* = 8.9, 6.6 Hz, 1H), 2.79 (dd, *J* = 15.5, 9.1 Hz, 1H), 2.53-2.64 (m, 3H), 2.32-2.35 (m, 2H), 2.29 (t, *J* = 5.8 Hz, 2H), 1.93-2.01 (m, 2H), 1.47-1.60 (m, 2H), 1.30-1.36 (m, 2H), 1.18-1.30 (m, 16H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.4, 172.2, 161.4, 127.2, 52.5., 44.0, 39.4, 37.3, 32.0, 31.6, 29.8, 29.72, 29.70, 29.65, 29.56, 29.4, 29.2 (2C, overlapped), 28.9, 22.7, 22.6, 14.2 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 97:3 v/v, flow rate: 0.8 mL/min, *λ* 220 nm): t_R 10.29 (minor), 11.13 min (major). HRMS (ESI): $[C_{22}H_{38}O_3S+Na]^+$ requires: 405.2434; found: 405.2441.

Phenyl 3-(3-oxocyclohex-1-en-1-yl)-2-(phenylsulfanyl)propanoate (23): According to GP2 product was obtained as a colorless oil, 39%, racemate. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55-7.57 (m, 2H), 7.32-7.37 (m, 5H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.01 (s, 1H), 4.08 (dd, *J* = 9.2, 6.5 Hz, 1H), 2.92 (dd, *J* = 15.4, 9.2 Hz, 1H), 2.77 (dd, *J* = 15.4, 6.5 Hz, 1H), 2.32-2.41 (m, 4H), 1.97-2.04 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.2, 169.8, 160.7, 150.4, 134.0, 132.0, 129.6, 129.4, 129.0, 127.8, 126.2, 121.2, 48.4, 39.5, 37.4, 29.8, 22.7 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 32.36, 43.93 min. HRMS (ESI): $[C_{21}H_{20}O_3S+Na]^+$ requires: 375.1025; found: 375.1019.

Phenyl 3-(3-oxocyclohex-1-en-1-yl)-3-(phenylsulfanyl)propanoate (24): According to GP3 the product was obtained as a colorless oil, 68%, racemate. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.30-7.35 (m, 3H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.58 (s, 1H), 4.13 (t, *J* = 8.0 Hz, 1H), 3.03 (dd, *J* = 15.8, 7.6 Hz, 1H), 2.96 (dd, *J* = 15.8, 8.2 Hz, 1H), 2.52-2.61 (m, 2H), 2.32-2.39 (m, 2H), 1.95-2.07 (m, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.2, 168.9, 161.3, 150.5, 134.8, 131.6, 129.7, 129.3, 129.2, 126.5, 126.3, 121.5, 51.2, 37.68, 37.63, 27.2, 22.8 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 37.03, 38.56 min. HRMS (ESI): $[C_{21}H_{20}O_3S+Na]^+$ requires: 375.1025; found: 375.1022.

Methyl 3-(3-oxocyclohex-1-en-1-yl)-2-(phenylsulfanyl)propanoate (25): According to GP2 product was obtained as a yellowish oil, 49%, racemate. ^{1}HNMR ($CDCl_3$, 600 MHz): δ 7.43-7.45 (m, 2H), 7.31-7.33 (m, 3H), 5.86 (s, 1H), 3.86 (dd, *J* = 8.8, 6.6 Hz, 1H), 3.65 (s, 3H), 2.79 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.64 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.31-2.35 (m, 2H), 2.25-2.28 (m, 2H), 1.96 (quint., *J* = 6.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 199.3, 171.6, 160.9, 133.7, 132.3, 129.2, 128.7, 127.6, 52.6, 48.3, 39.7, 37.3, 29.7, 22.6 ppm. HPLC (Chiralpak AD-H, hexane/*i*PrOH 95:5 v/v, flow rate: 1.0 mL/min, *λ* 220 nm): t_R 19.84, 21.83 min. HRMS (ESI): $[C_{16}H_{18}O_3S+Na]^+$ requires: 313.0869; found: 313.0863.

S6. X-ray structural data for 6j

A sample of **6j** obtained in the reaction of acceptor **5j** with benzyl mercaptan was recrystallized from CH_2Cl_2/hexane giving material of ca. 90 %*ee*. A sample was dissolved in 2-propanol and the solvent was allowed to slowly partially evaporate forming needle-like crystals suitable for X-ray diffraction study (Figure S1).

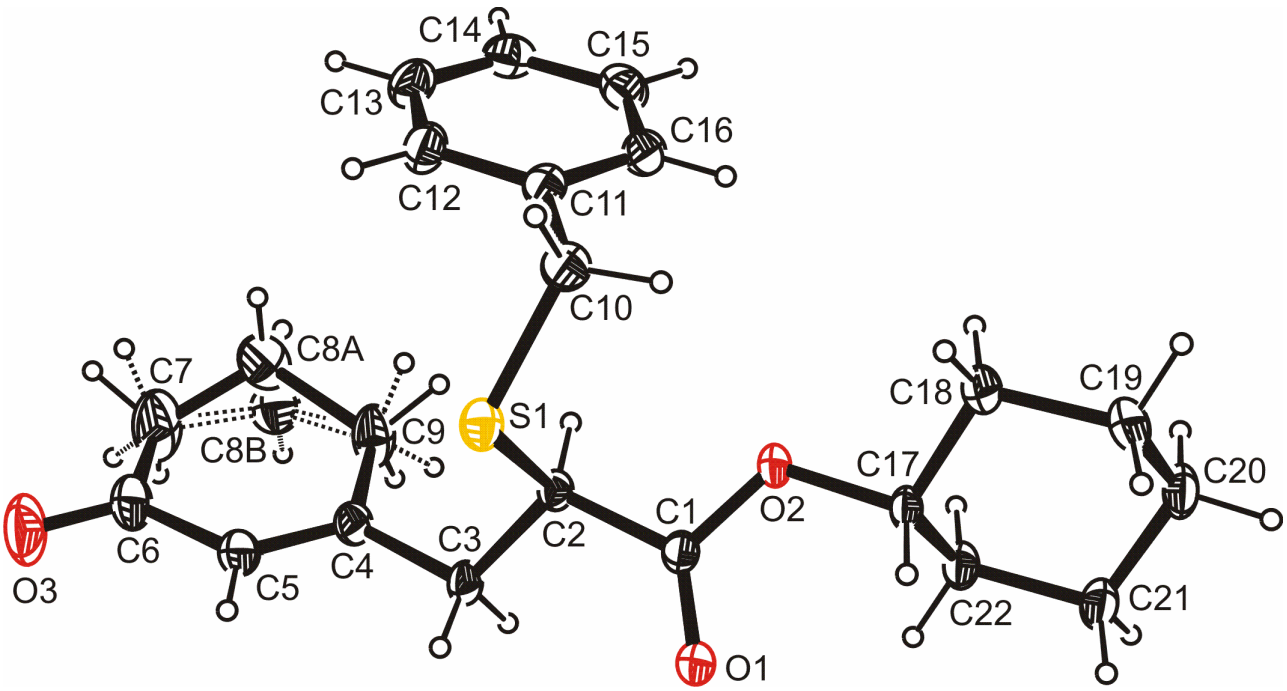


Figure S1. The molecular structure and atom-numbering scheme for compound **6j**, with displacement ellipsoids drawn at the 20% probability level. The methylene group labelled C8 is disordered over two sites, with refined occupancies of 0.69(3) and 0.31(3). The major and minor disordered components are drawn with solid and dashed bonds, respectively.

Crystal data. $C_{22}H_{28}O_3S$, M_r = 372.50, monoclinic, a = 14.4387(11) Å, b = 5.4586(3) Å, c = 14.5272(13) Å, β = 117.943(11)°, V = 1011.48(16) Å^3, space group $P2_1$, Z = 2, no. of measured, independent and observed [$I > 2\sigma(I)$] reflections: 7106, 3983 and 2825, R_{int} = 0.046, $R[F^2 > 2\sigma(F^2)]$ = 0.061, $wR(F^2)$ = 0.122, S = 1.06 . Flack parameter was -0.04(8).

S7. Computational details

Vacuum-phase geometries of the structures were calculated using Gaussian code[S14] at the DFT/B3LYP/CC-pVDZ level of theory. All the geometries converged to local energy minima, as evidenced by no imaginary vibrational frequencies. The solvent and the presence of counterions were not included in the calculations. The

[S14] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

structures of intermediate iminium positively charged species were derived from diketones **5b**, and **5i** and *epi*-aminoquinine. The calculations were carried for imine at the cyclohexenone (**A**), and at the phenome units (**B**), both *Z*, and *E* configurations of imine were considered, as well as *syn* and *anti* orientation of the quinoline ring (Figure S2). In all the optimized structures for the cyclohexenone imines **A** derived from **5b**, the π-system including the terminal phenyl group was planar. However, in all of the studied conformations of phenome imine **B**, some parts of the π-system were out of plane (corresponding dihedral angles of at least 32°, Table S8, Figure S3). As a result, the structures of type **5b-B** were estimated to be more than 8.5 kcal/mol higher in energy than those of type **5b-A**. On the other hand, the structures optimized for **5i** with 2,6-dichlorophenyl residue, showed out-of plane arrangement of the terminal dichlorophenyl ring, regardless of the site of iminium ion formation. The structures of **5i-A** and **5i-B** differed only slightly in the extent of the aryl group twist (for imine of type **A** the corresponding dihedral was ca. 63°, while 69° for the lowest energy conformation of type **B**, Table S8) All the structures of type **5i-A** were lower in energy than these of type **5i-B** , although the energy difference was 6.3 kcal/mol. Thus, the energy difference between the regioisomeric imines was lower by 2.2 kcal/mol for **5i** compared to **5b**, which is in qualitative agreement with the lower regioselectivity achieved for **5i**.

In all the structures an internal hydrogen bond N···H of 1.88-1.96 Å was present, corresponding to interatomic N-N distance of 2.59-2.62 Å. For iminium cations of type **A**, the alternative geometries were marginally (< 1 kcal/mol) higher in energy (Table S8). For the lowest energy geometry, the calculated electrostatic potential was not noticeably differentiated at the *Re* and *Si* faces of the π-system (Figure S4).

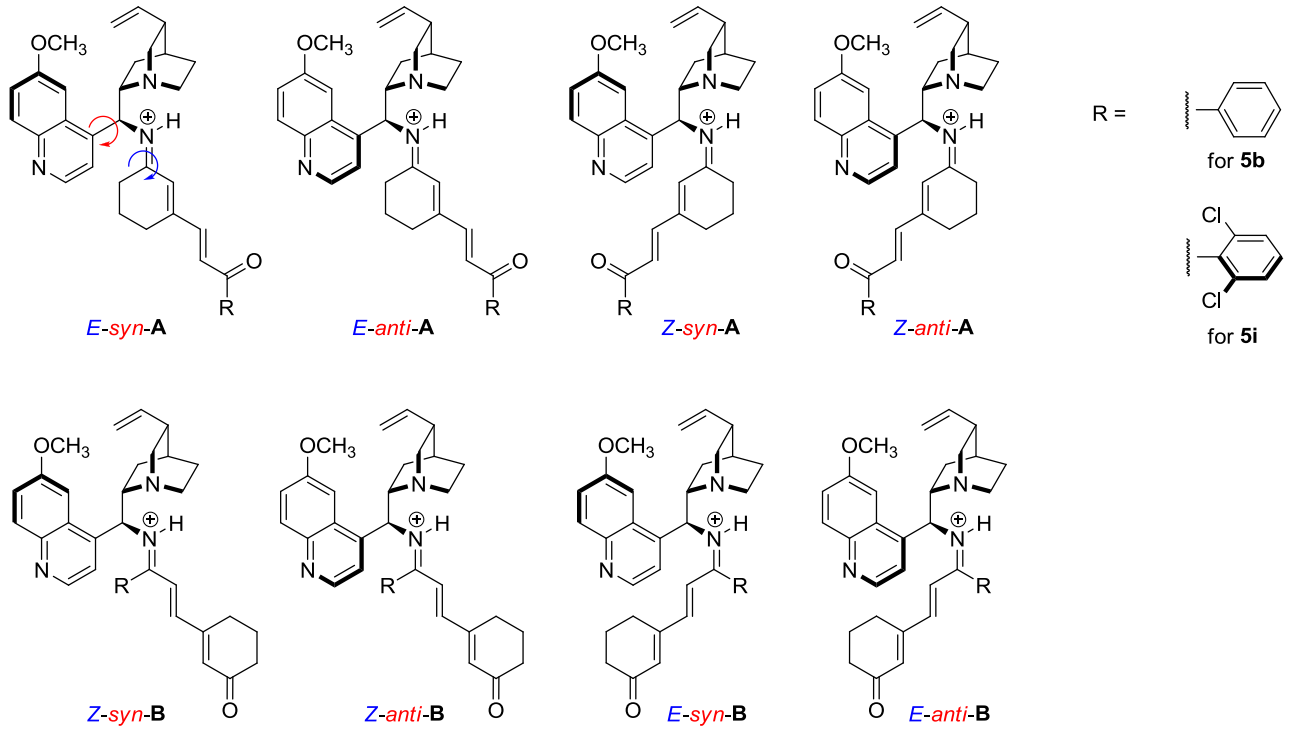
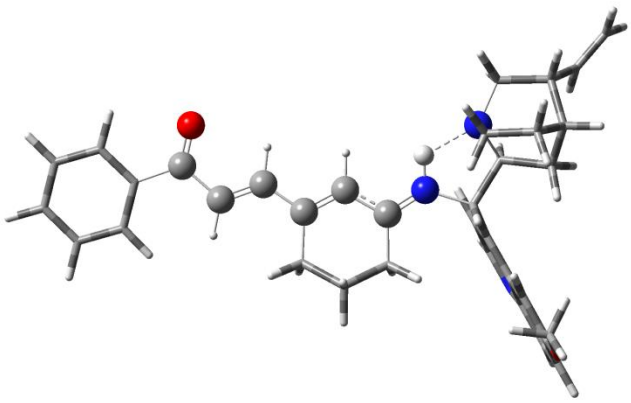
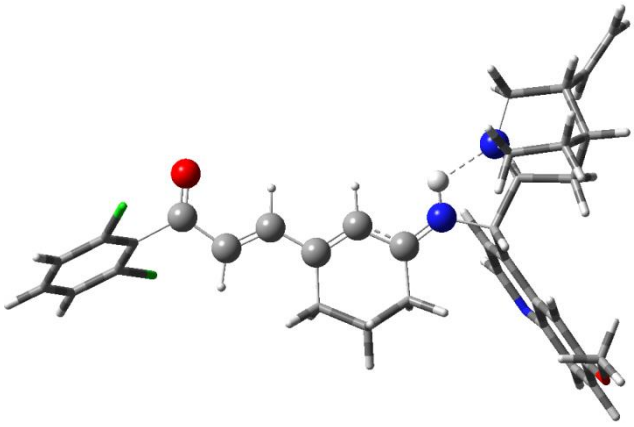


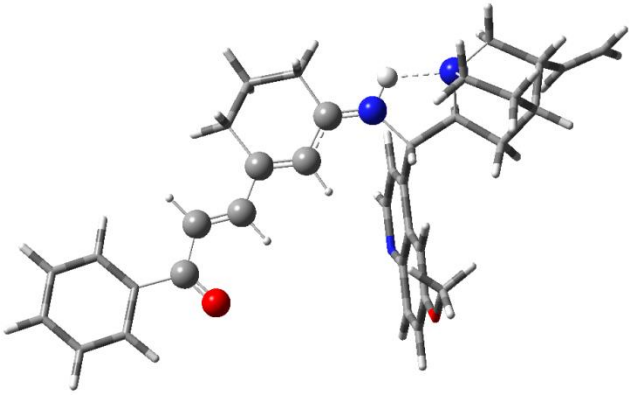
Figure S2. Summary of initial geometries studied for iminium cations **A** and **B** from diketones **5b** and **5i**.



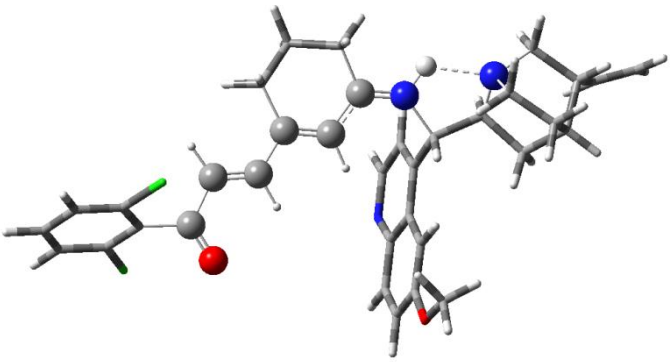
5b: *E-anti*-**A** (ΔE = 0.06 kcal/mol)



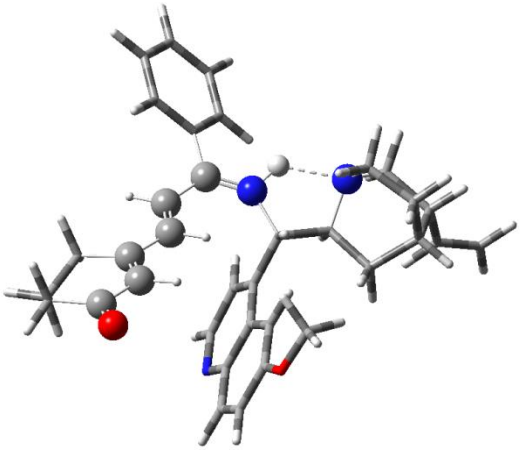
5i: *E-anti*-**A** (ΔE = 0)



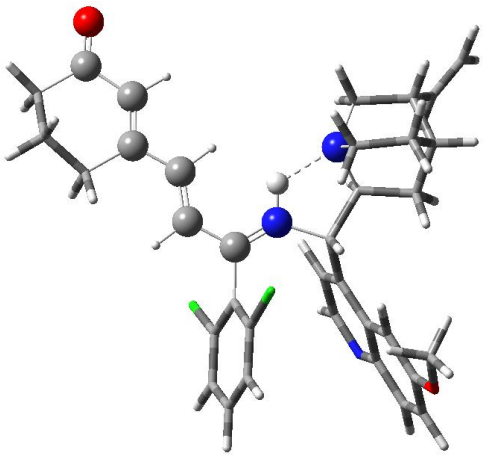
5b: *Z-anti*-**A** (ΔE = 0)



5i: *Z-anti*-**A** (ΔE = 0.05 kcal/mol)



5b: *E-anti*-**B** (ΔE = 8.3 kcal/mol)



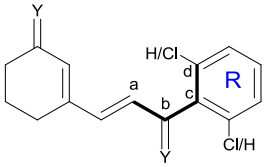
5i: *Z-anti*-**B** (ΔE = 6.4 kcal/mol)

Figure S3. Low energy DFT/B3LYP/CC-pVDZ optimized structures of iminium ions of type **A** and **B** derived from **5b** (left) and **5i** (right)

Table S8. Calculated energies, energies after ZPE[a] correction and relative energies for the studied geometries of iminium ions of type **A** and **B**.

Structure	Phenyl out-of-plane angle[c]	Energy		
		Total electronic energy (Hartree)	Total energy after ZPE correction[a] (Hartree)	Relative energy after ZPE correction (kcal/mol)[b]
5b: R = Ph,				
E-anti-**A**	-0.8	-1671.1456344	-1670.484764	+0.06
E-syn-**A**	-1.4	-1671.1448968	-1670.484075	+0.50
Z-anti-**A**	3.3	-1671.1456503	-1670.484867	0
Z-syn-**A**	-0.3	-1671.1445114	-1670.483815	+0.66
E-anti-**B**	32.6	-1671.1312545	-1670.471220	+8.56
E-syn-**B**	-39.1	-1671.1272175	-1670.467013	+11.57
Z-anti-**B**	39.6	-1671.1302398	-1670.470213	+9.20
Z-sym-**B**	45.8	-1671.1289338	-1670.468782	+10.09
5i: R = 2,6-$Cl_2C_6H_3$,				
E-anti-**A**	-63.0	-2590.3644879	-2589.723818	0
E-syn-**A**	-63.1	-2590.3637562	-2589.722963	+0.54
Z-anti-**A**	-62.8	-2590.3646291	-2589.723738	+0.05
Z-syn-**A**	-62.6	-2590.3635789	-2589.722423	+0.88
E-anti-**B**	-80.8	-2590.3516226	-2589.711257	+7.88
E-syn-**B**	-73.7	-2590.3478999	-2589.707381	+10.31
Z-anti-**B**	69.4	-2590.3540820	-2589.713706	+6.35
Z-sym-**B**	71.2	-2590.3523465	-2589.712002	+7.41

[a]Zero point vibrational energy; [b]Assumed 1 Hartree = 627.51 kcal/mol [c] abcd dihedral for:



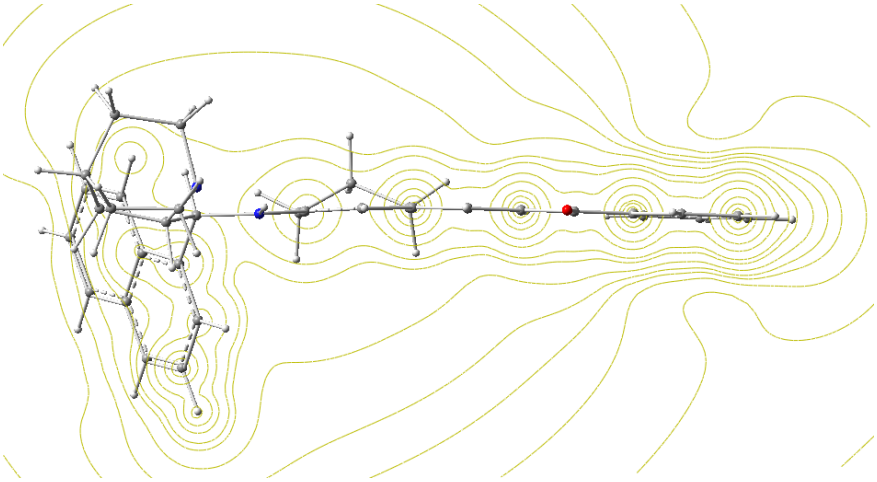


Figure S4. Electrostatic potential (ESP) map for structure of iminium ion of type **A** at the plane perpendicular to the π-system and intersecting at the β, δ, and ζ-atoms. The structure of Cinchona alkaloid residue was simplified to facilitate calculation.

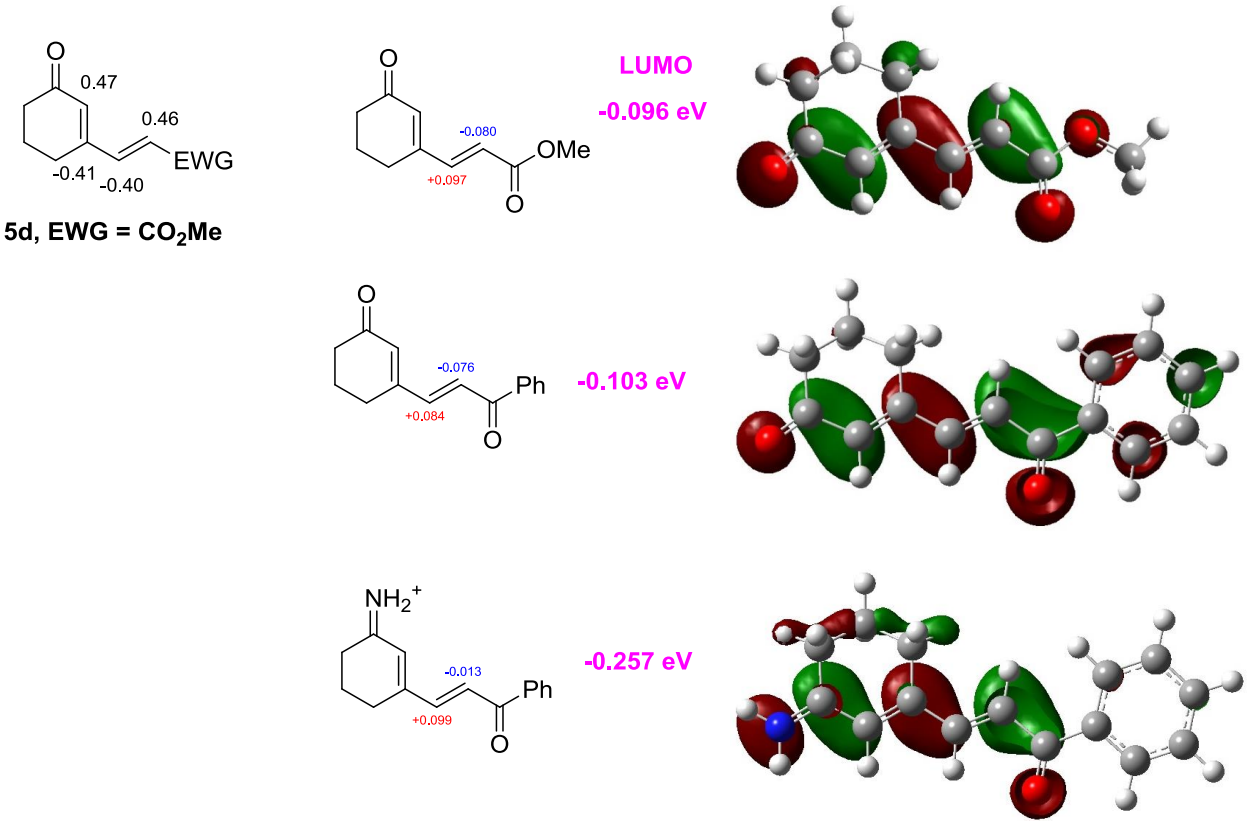


Figure S5. Mulliken partial atomic charges (with hydrogens summed with the carbon atoms), LUMO orbital energy and LUMO orbital isosurface calculated at the DFT/B3LYP/CC-pVDZ level of theory for **5b**, **5d**, and **5b**-derived iminium ion. On the left LUMO-coefficients taken from ref. S8

S8. ^{1}H and ^{13}C NMR spectra

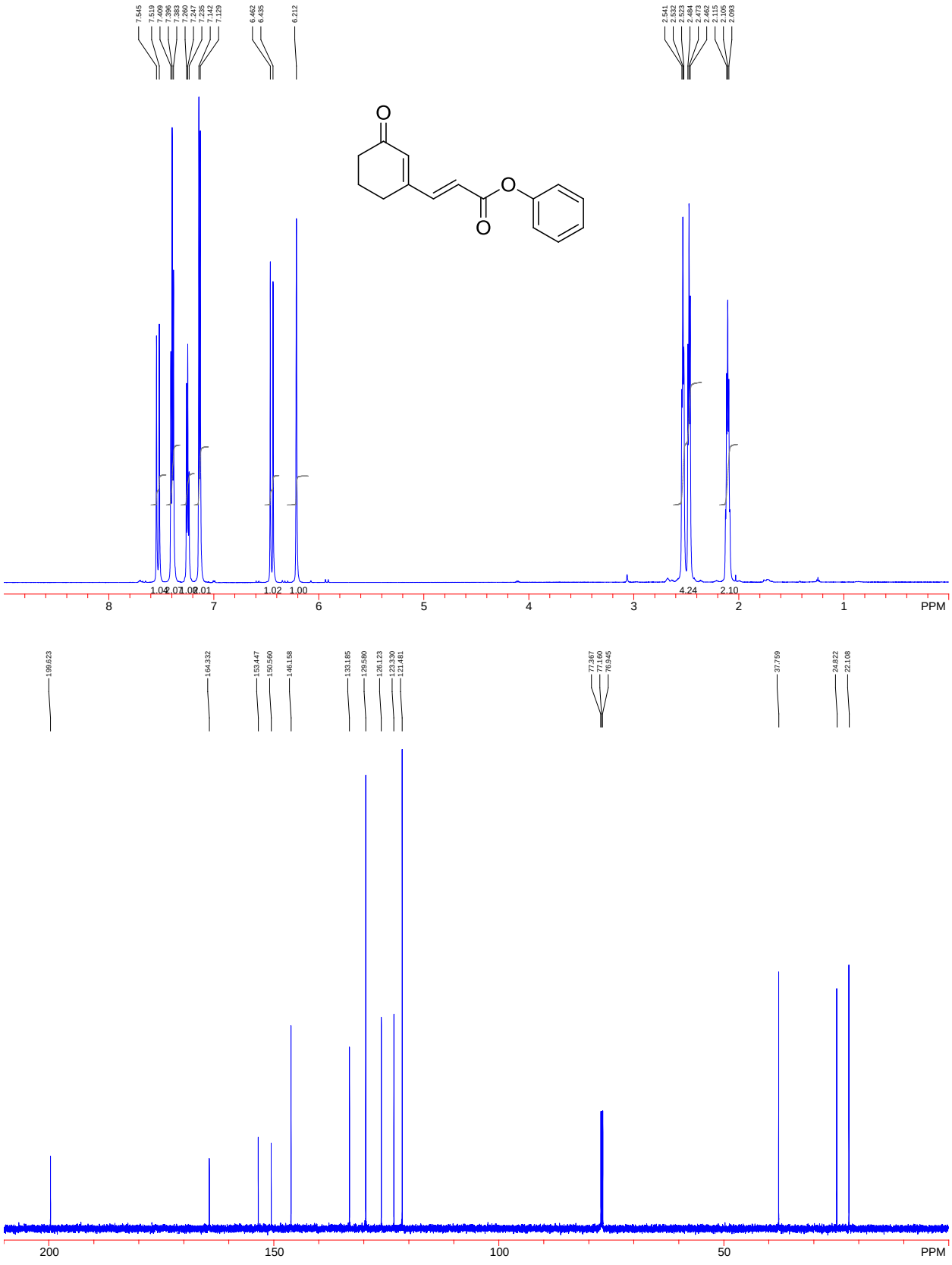


Figure S6. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for phenyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (**5c**) in $CDCl_3$

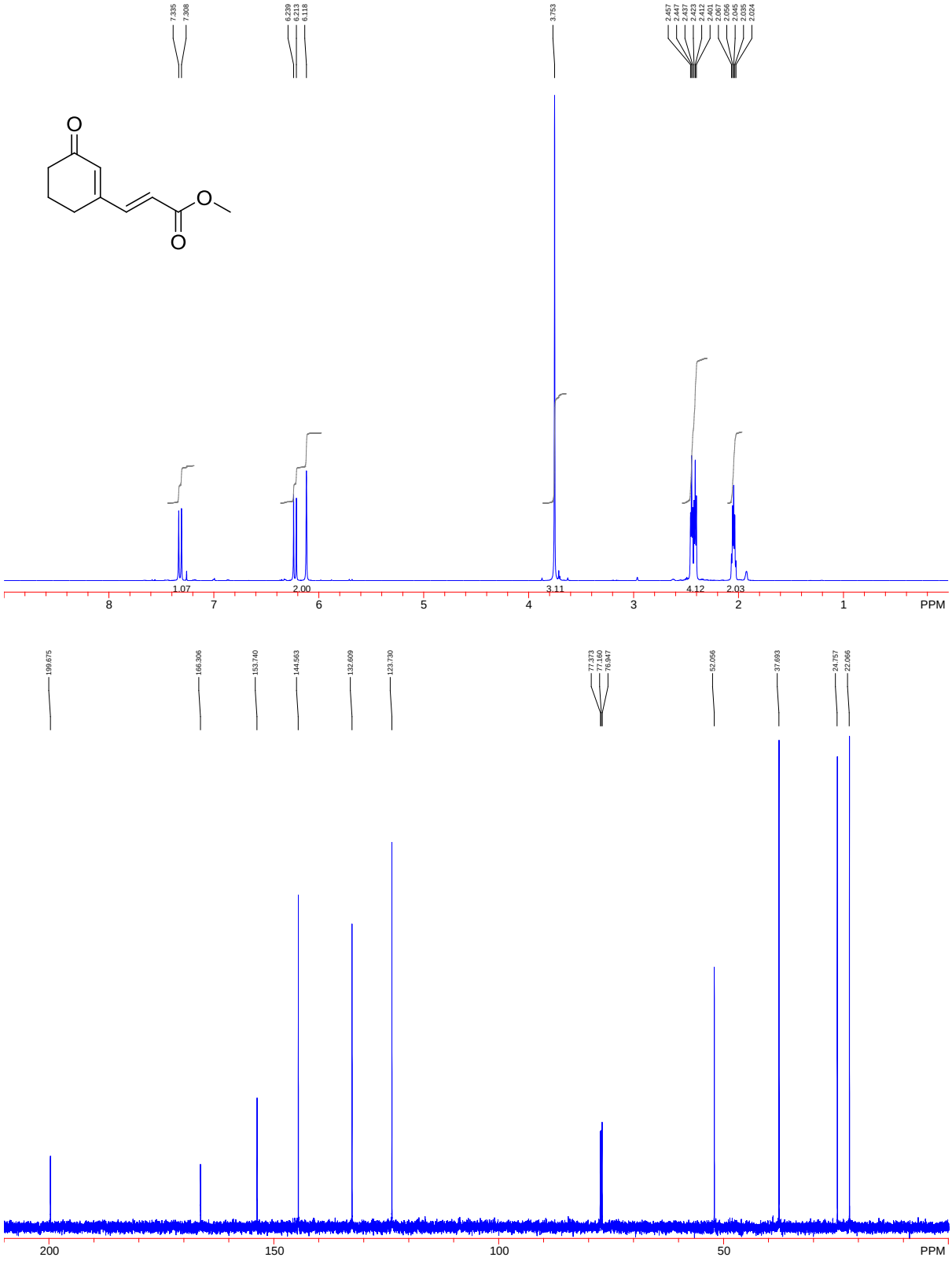


Figure S7. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for methyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (**5d**) in $CDCl_3$

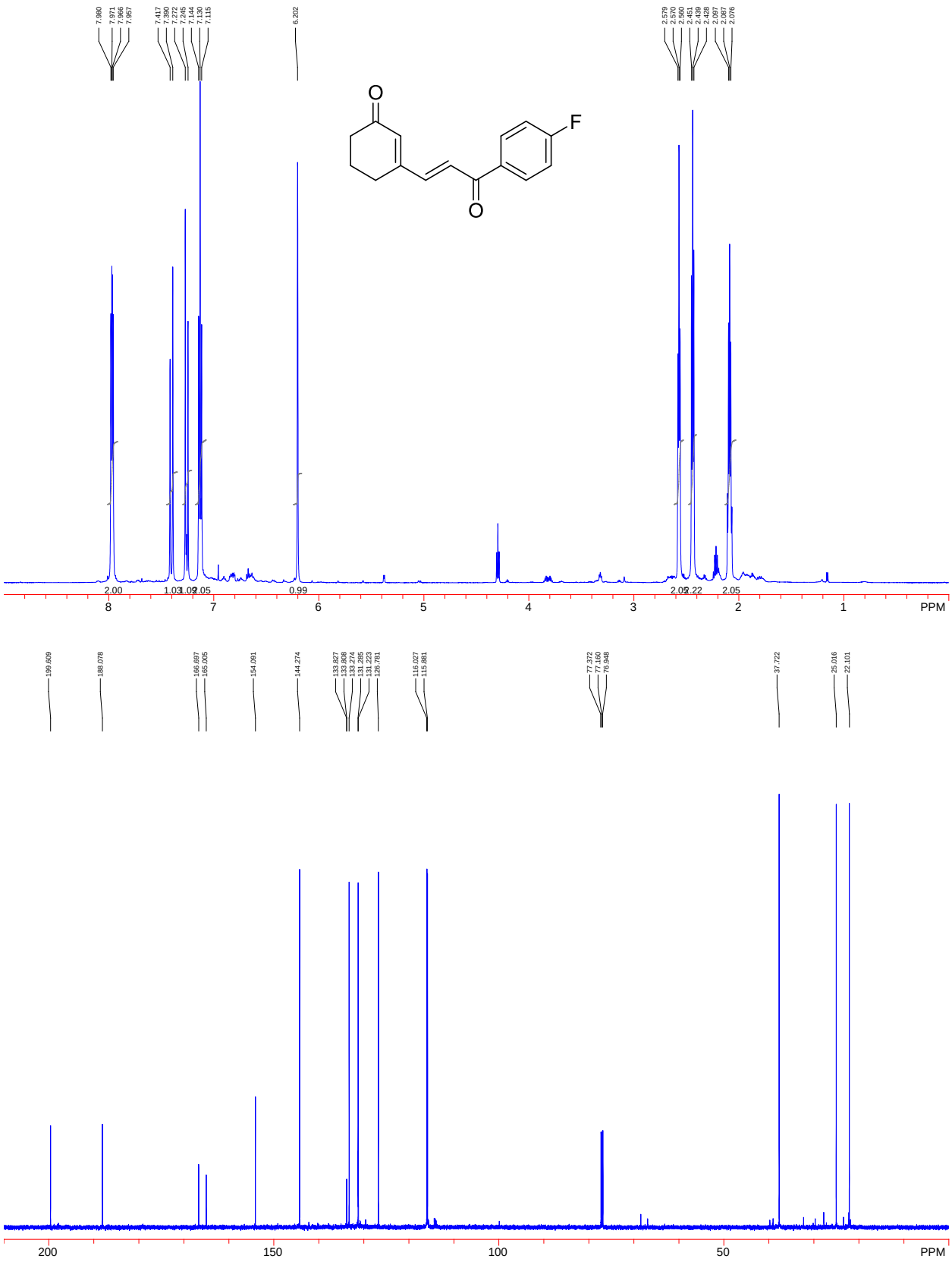


Figure S8. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for diene **5f** in $CDCl_3$

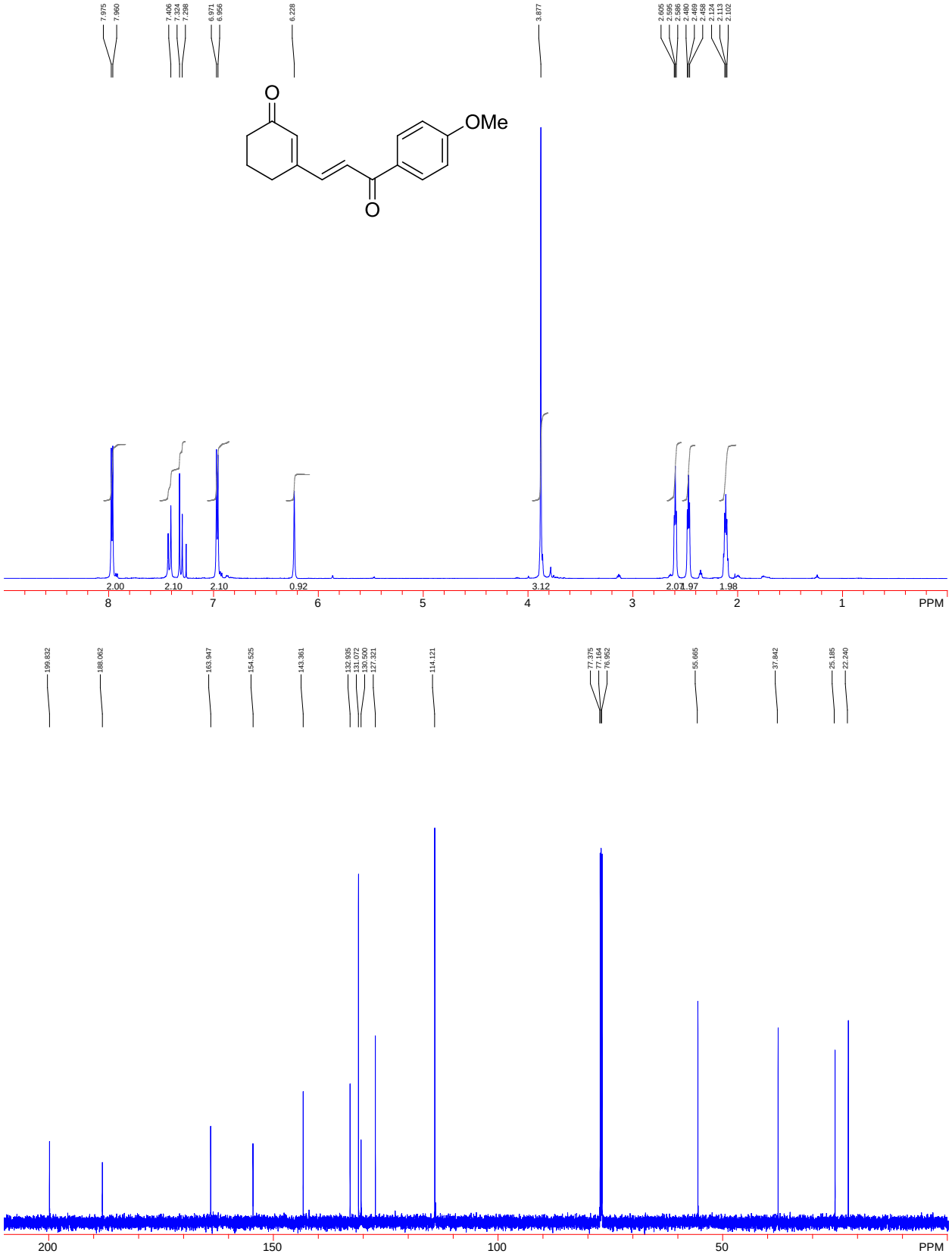


Figure S9. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for diene **5g** in $CDCl_3$

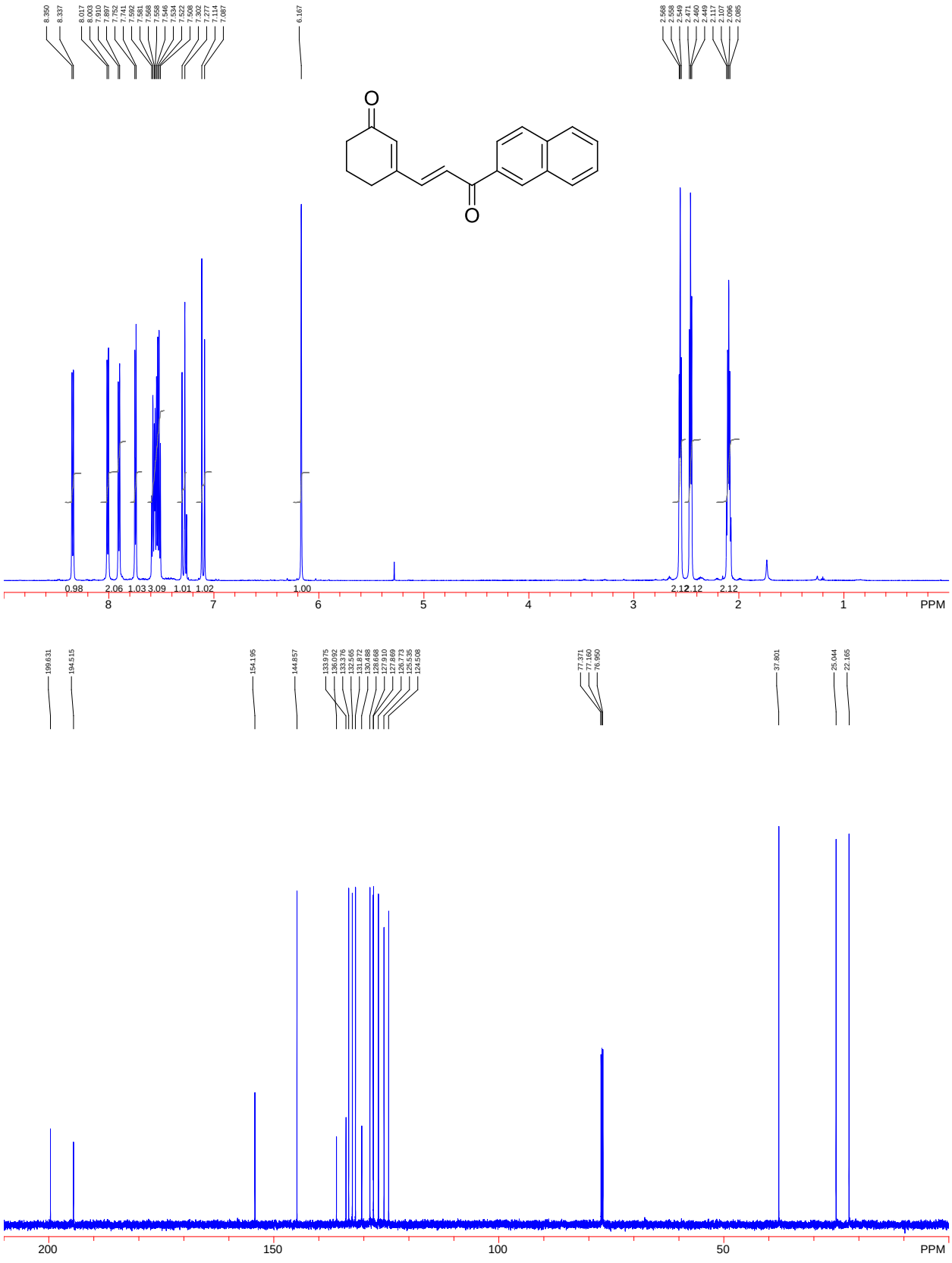


Figure S10. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for diene **5h** in $CDCl_3$

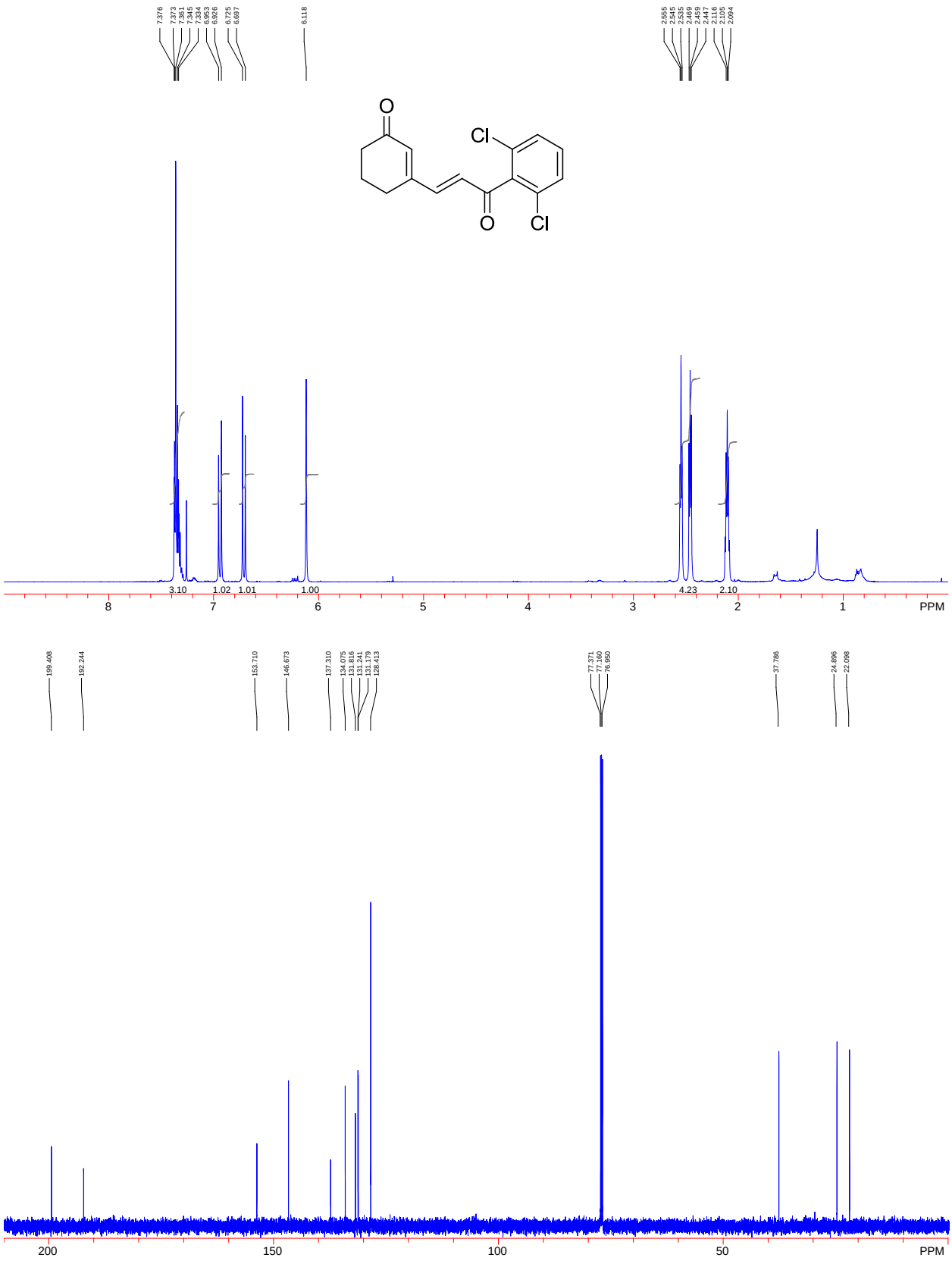


Figure S11. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for diene **5i** in $CDCl_3$

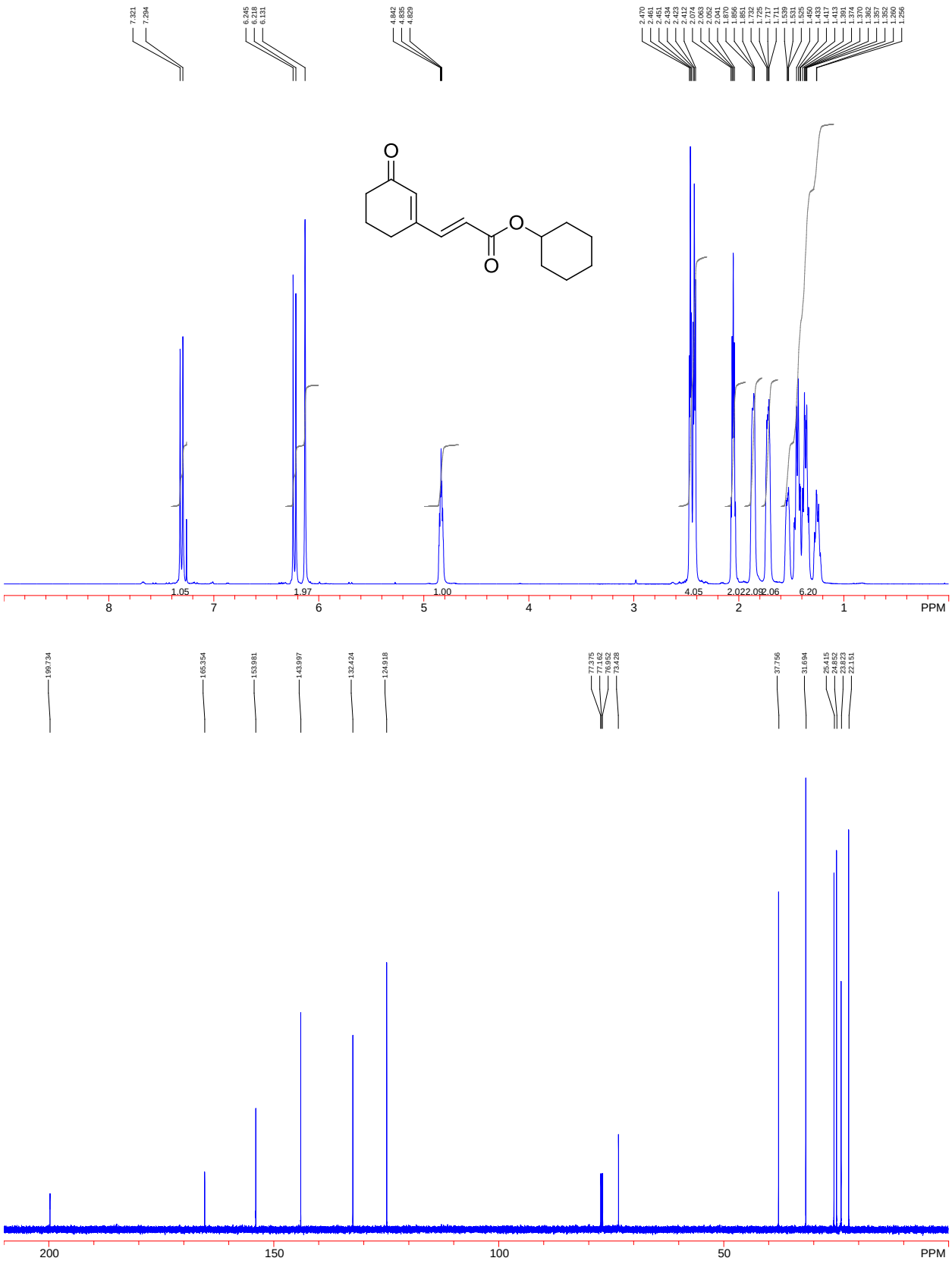


Figure S12. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for Cyclohexyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (**5j**) in $CDCl_3$

Figure S13. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for Benzyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (**5k**) in $CDCl_3$

Figure S14. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for *tert*-Butyl (*E*)-3-(3-oxocyclohex-1-enyl)prop-2-enoate (**5l**) in $CDCl_3$

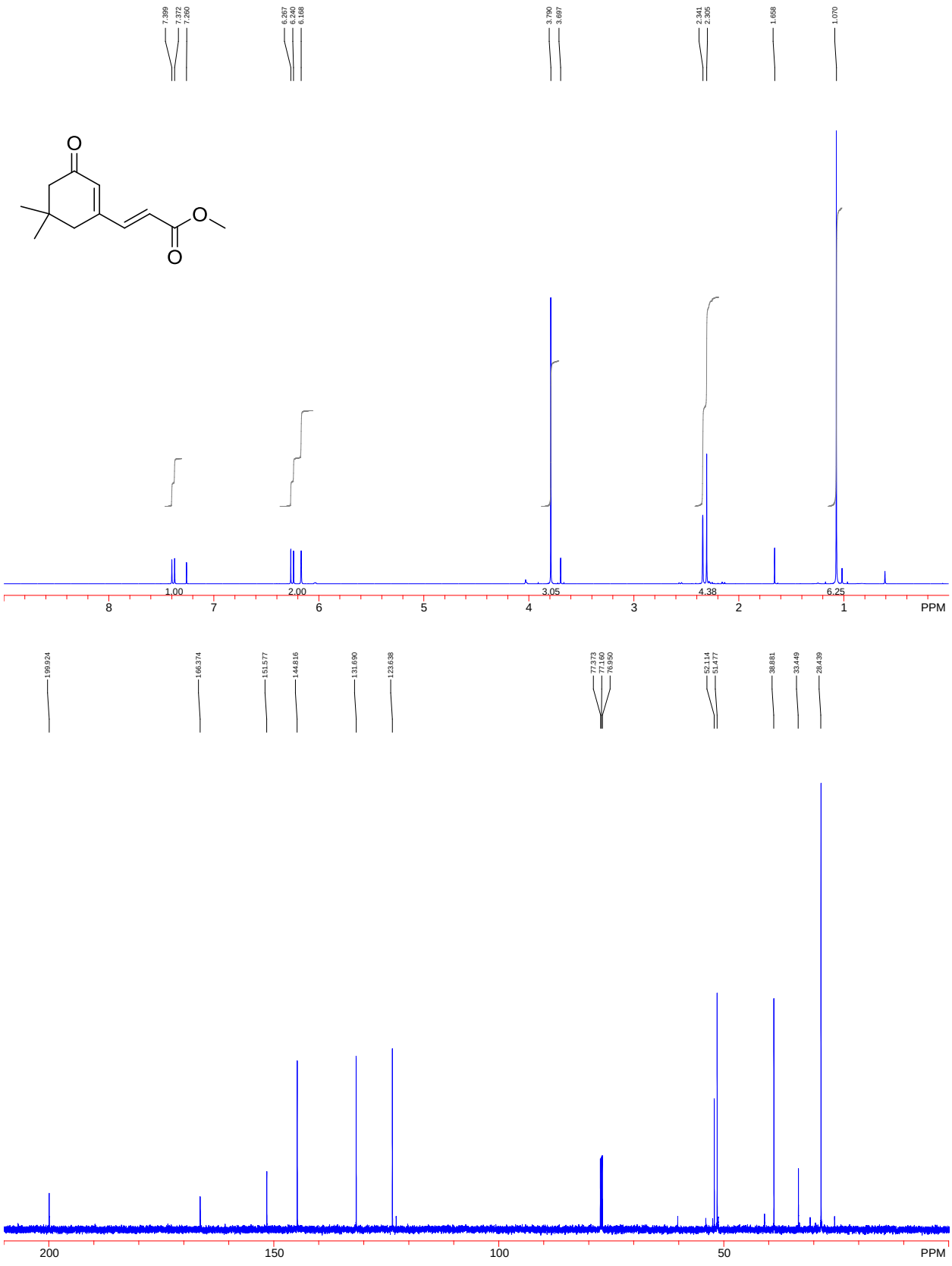


Figure S15. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for Methyl (*E*)-3-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)-acrylate (**5m**) in $CDCl_3$

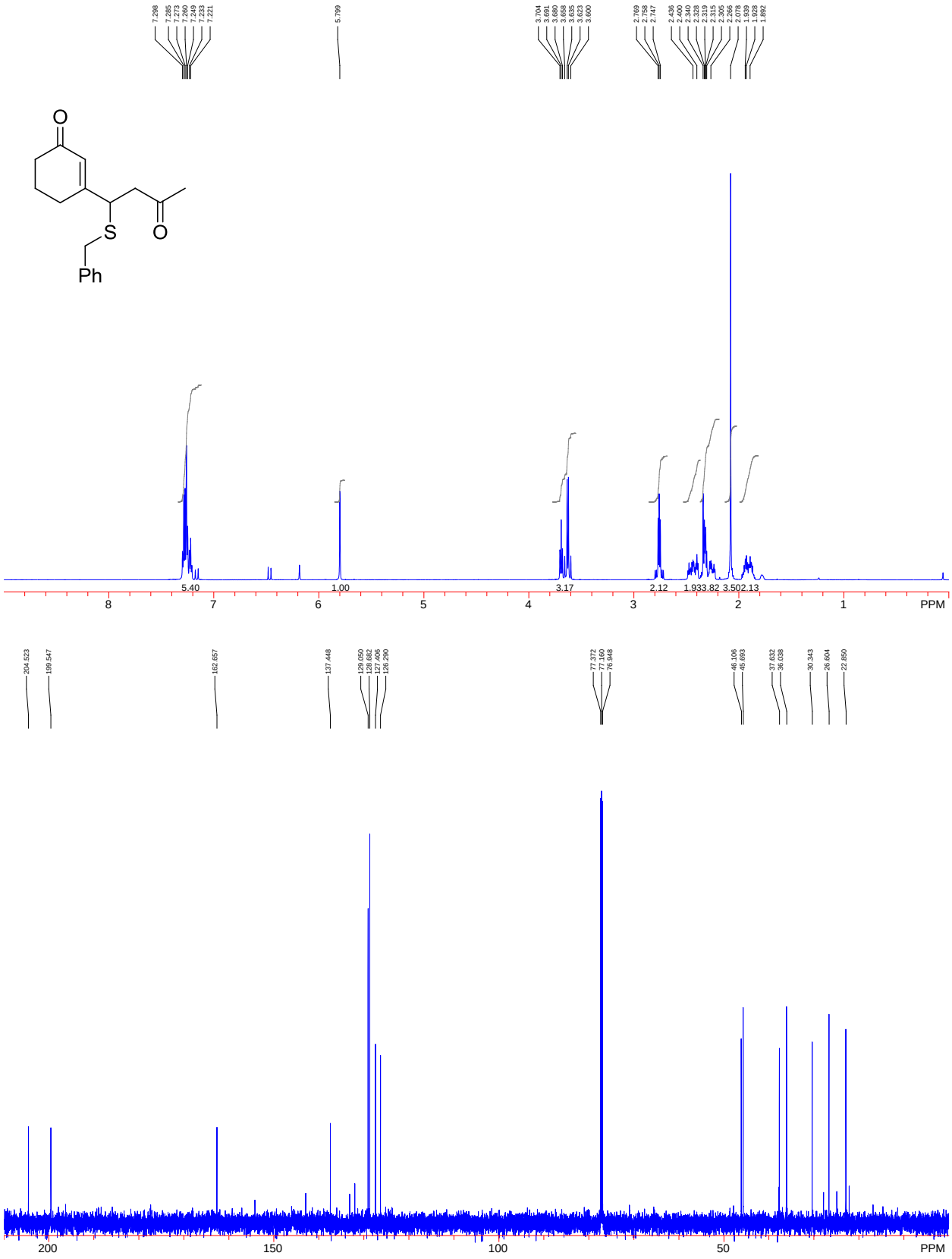


Figure S16. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **7a** in $CDCl_3$

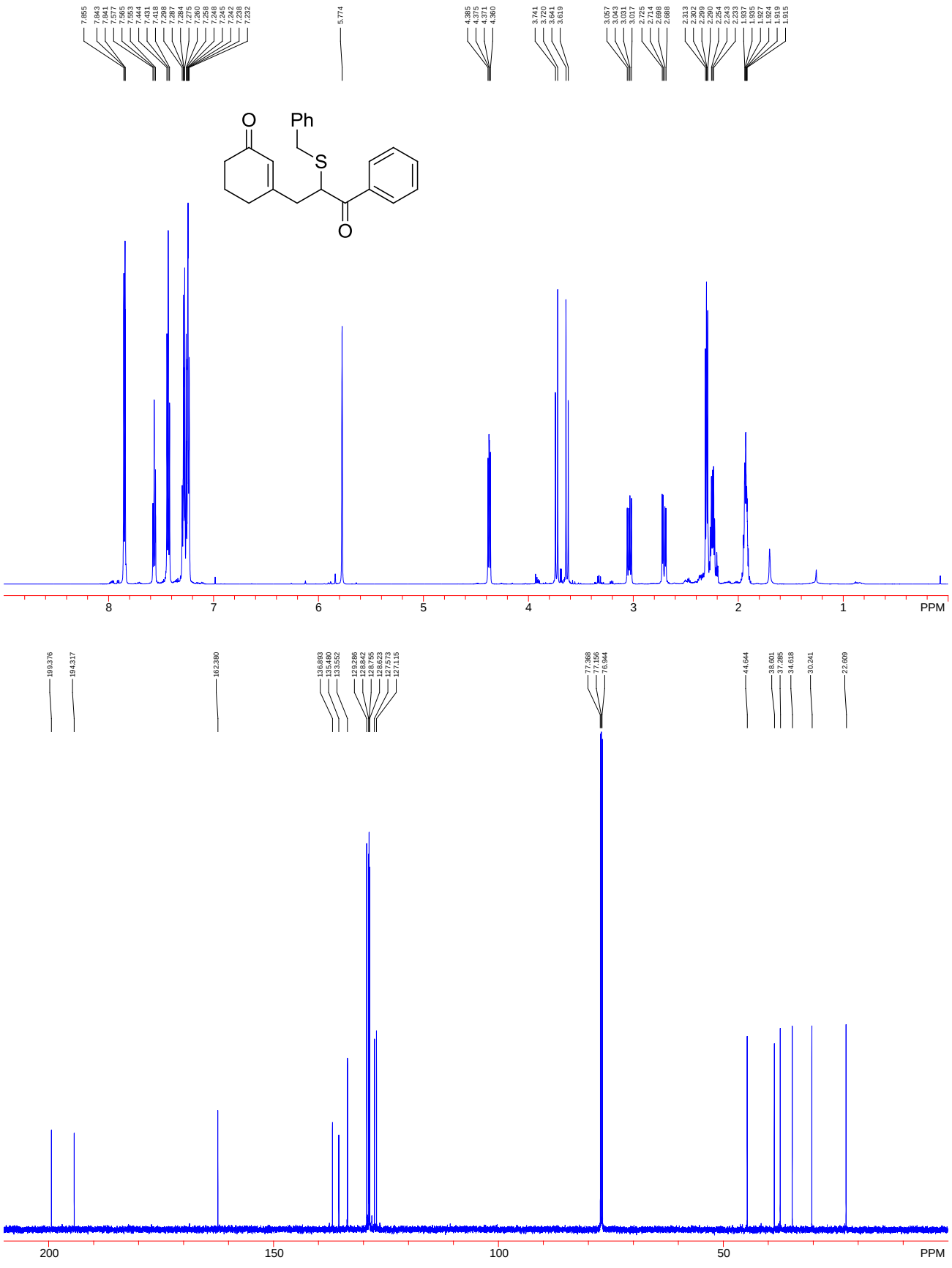


Figure S17. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6b** in $CDCl_3$

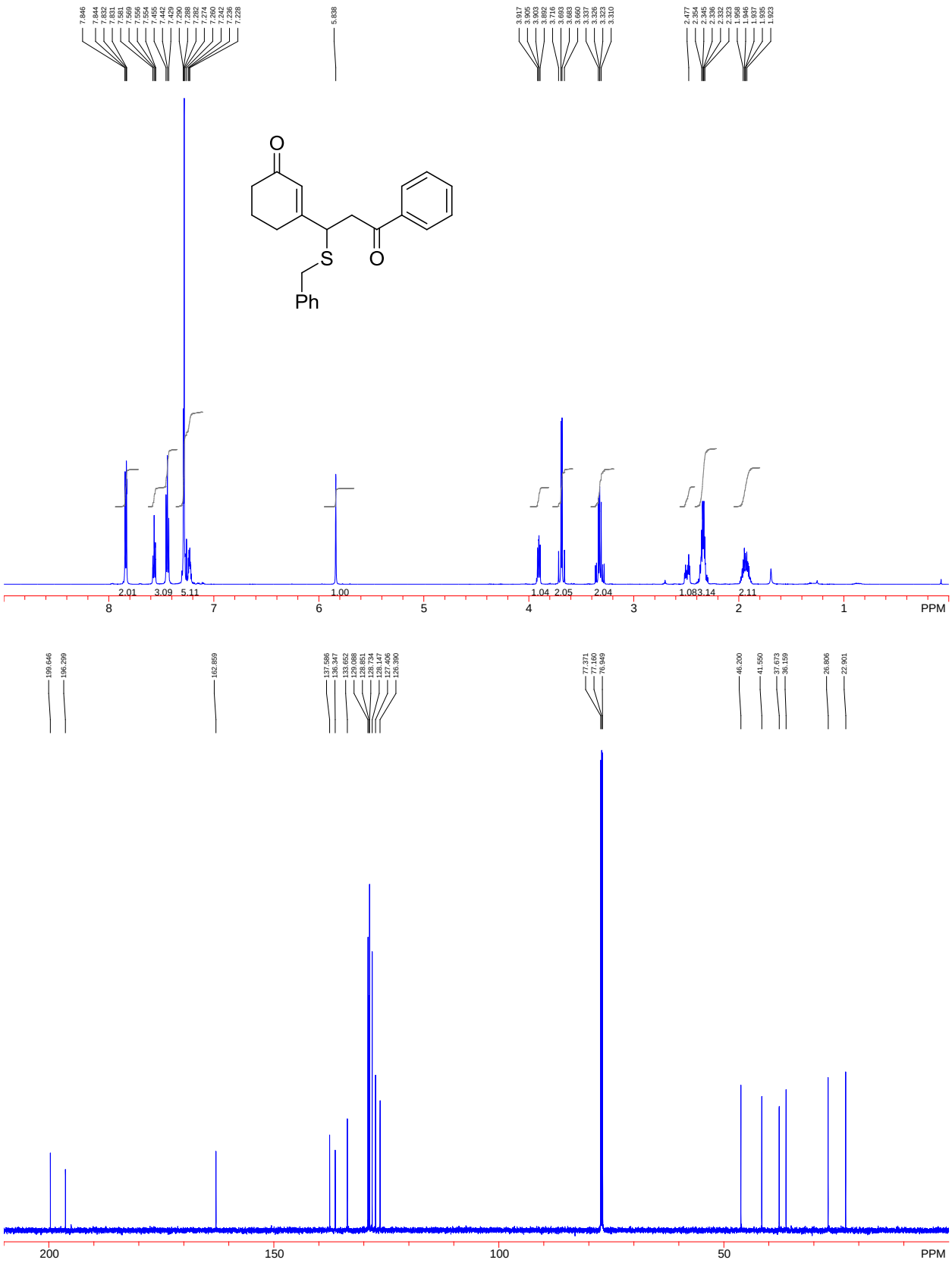


Figure S18. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **7b** in $CDCl_3$

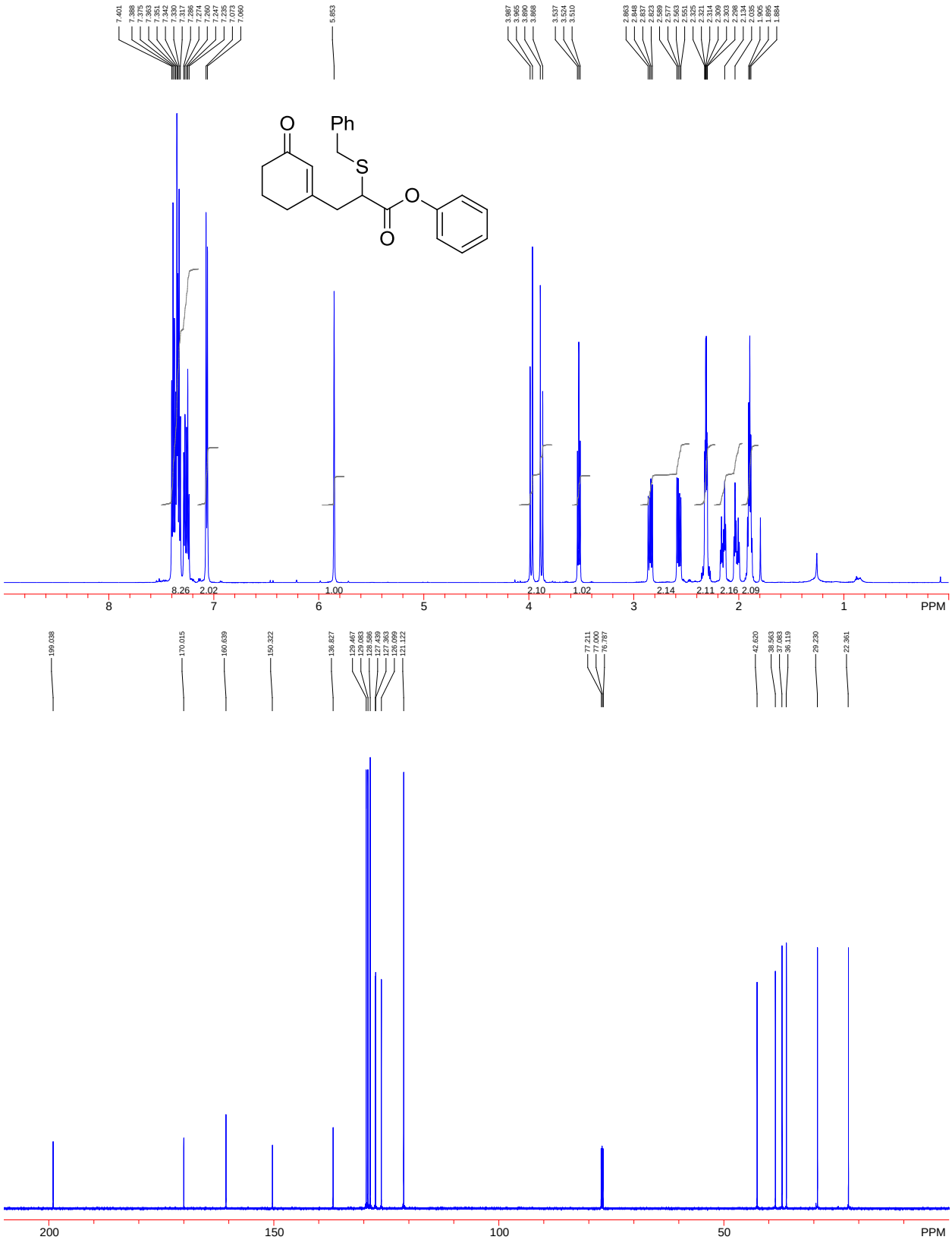


Figure S19. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6c** in $CDCl_3$

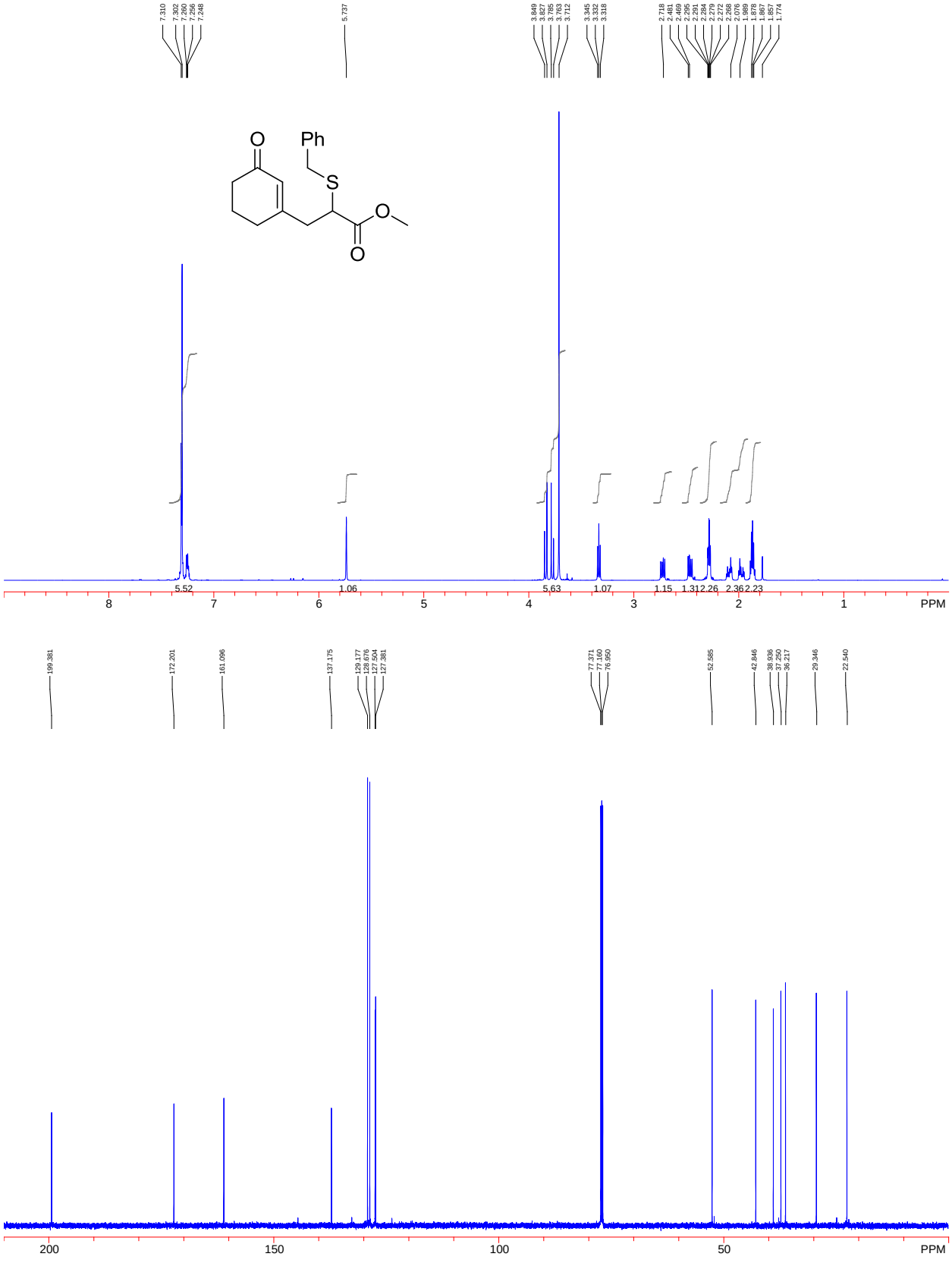


Figure S20. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6d** in $CDCl_3$

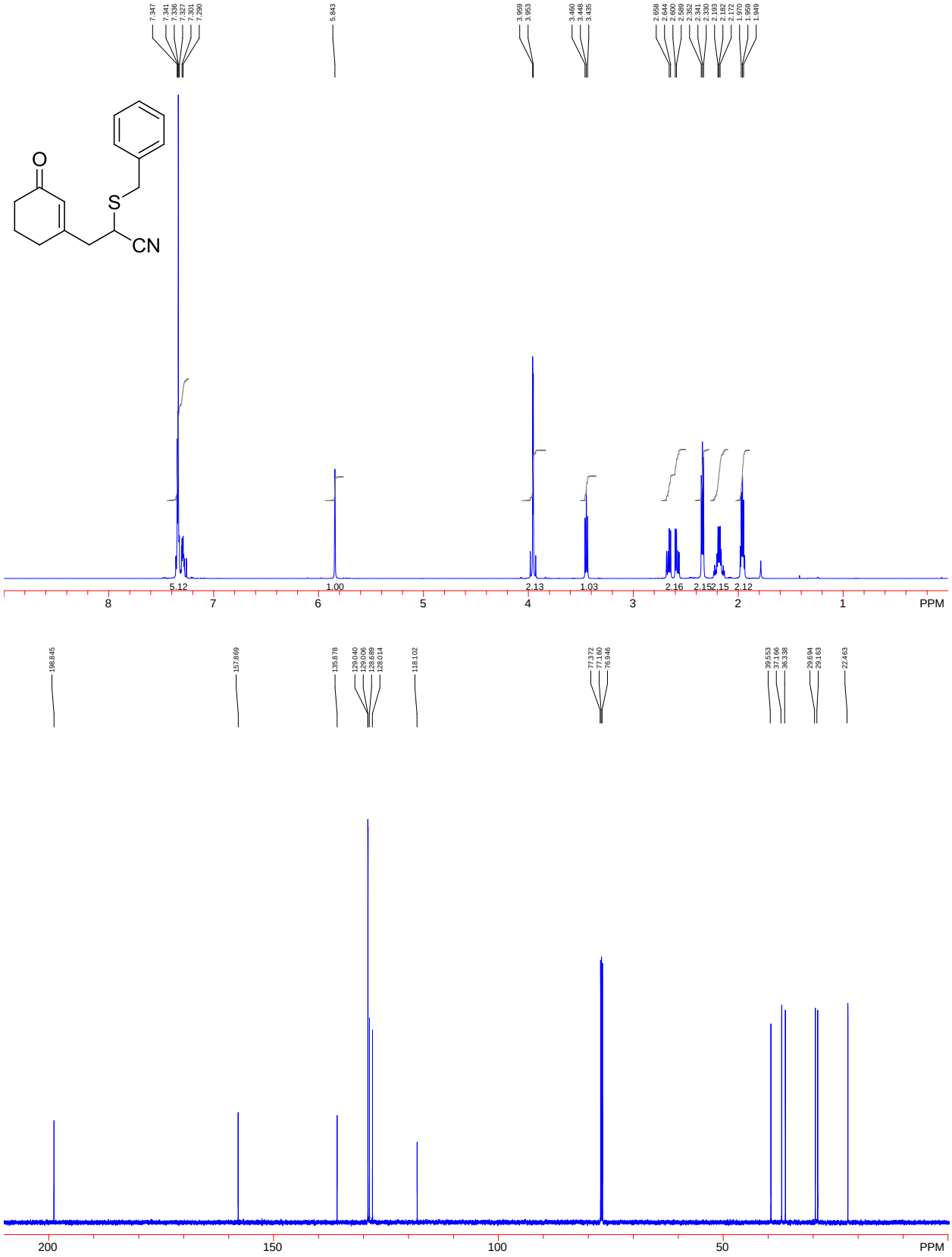


Figure S21. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6e** in $CDCl_3$

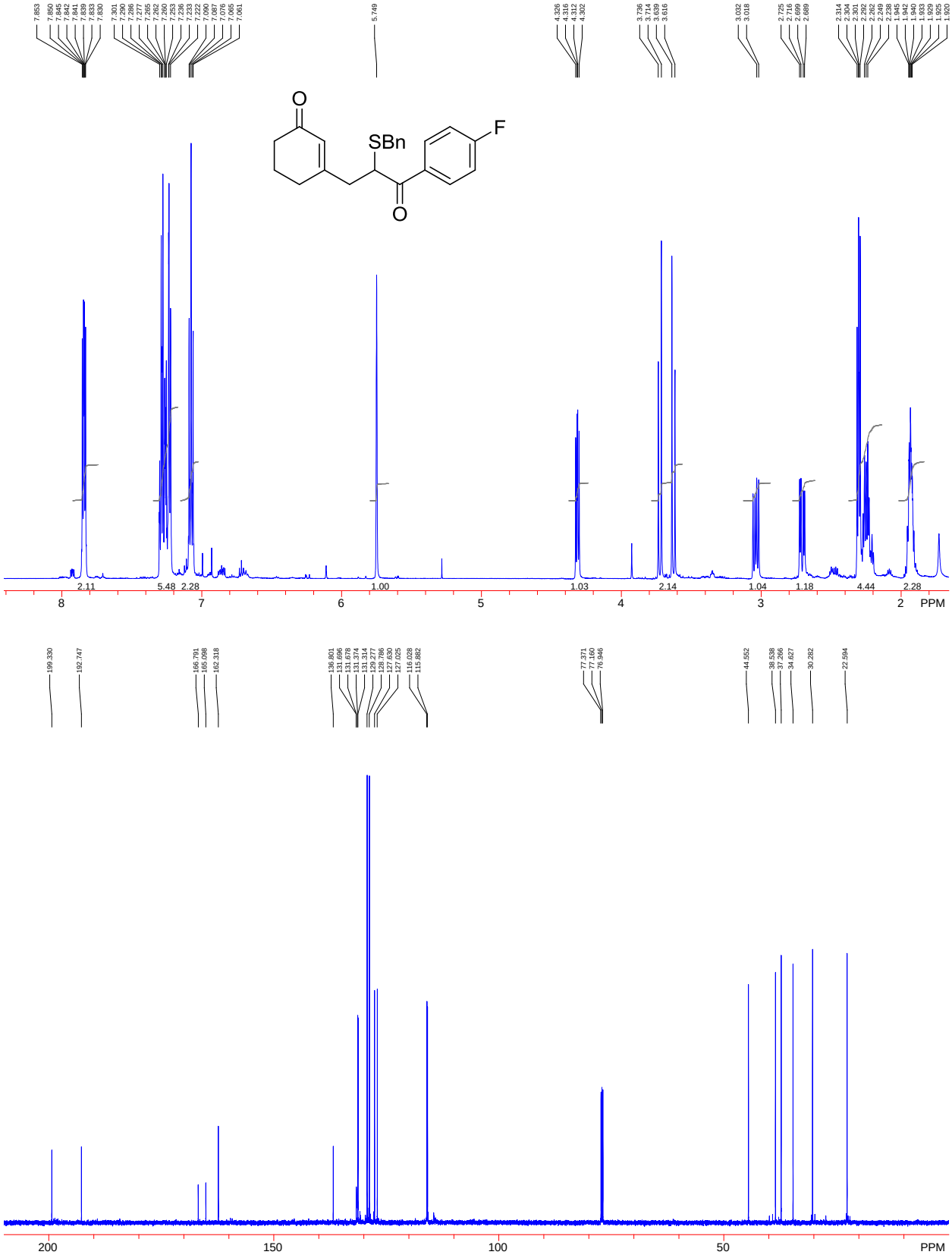


Figure S22. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6f** in $CDCl_3$

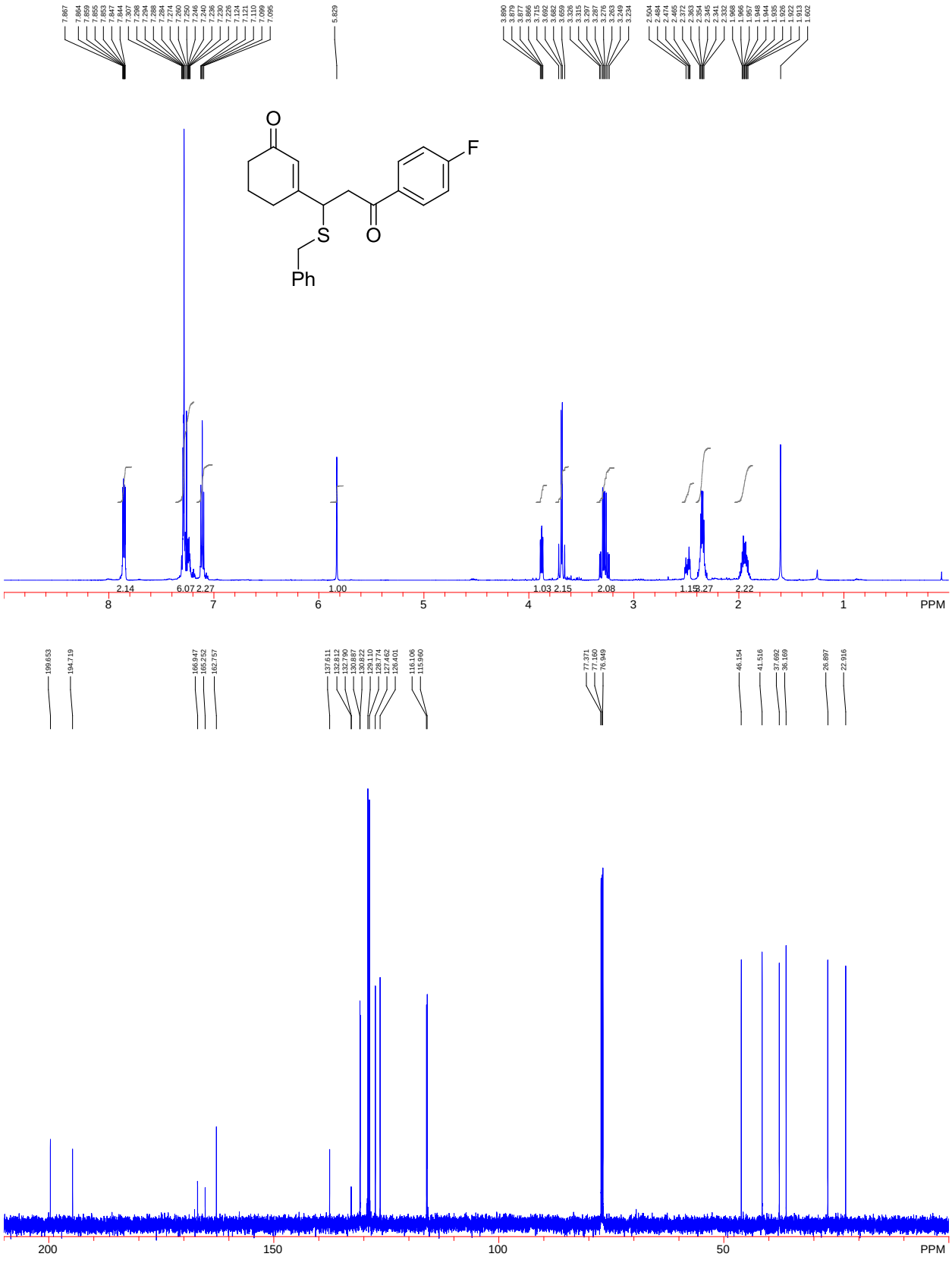


Figure S23. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **7f** in $CDCl_3$

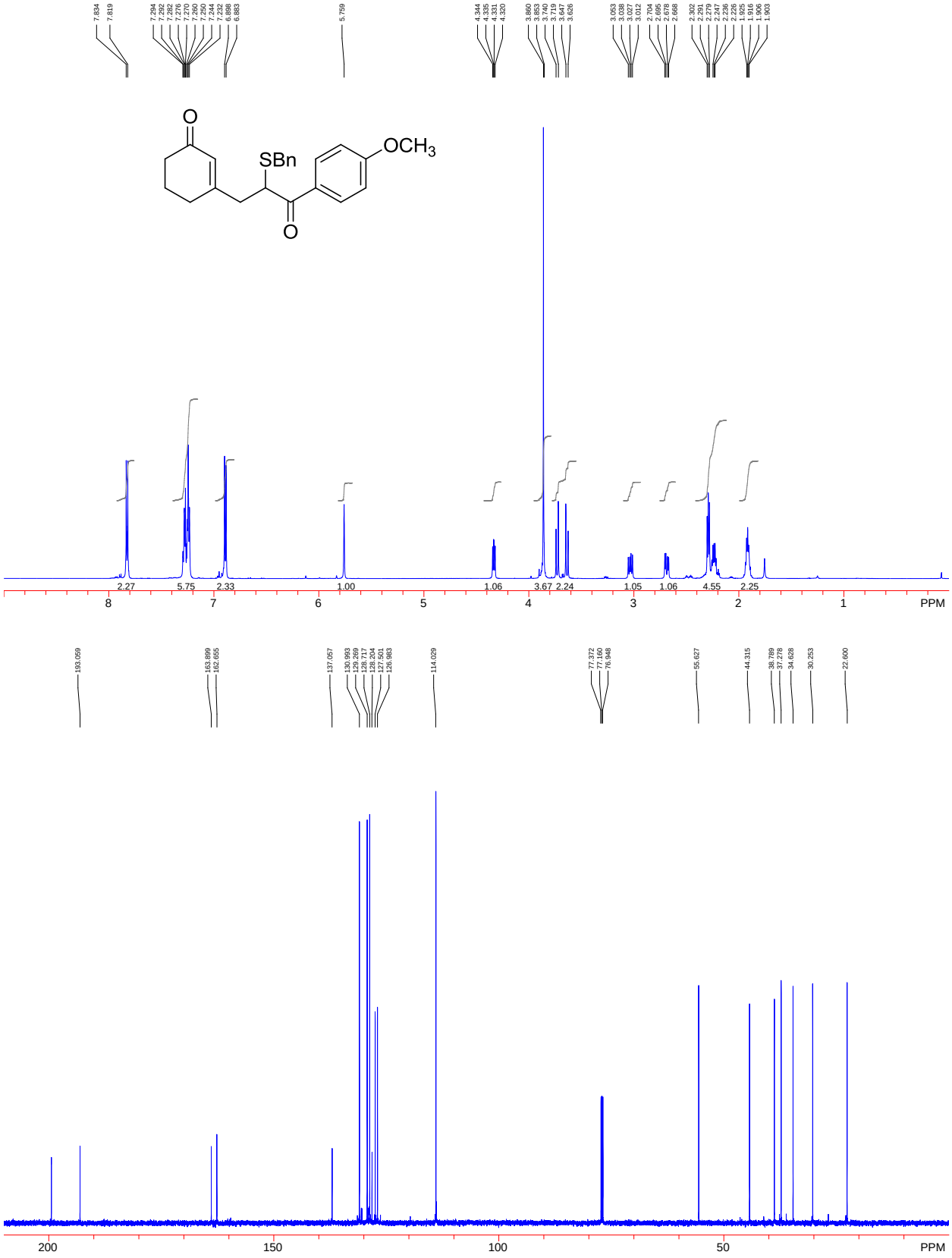


Figure S24. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6g** in $CDCl_3$

Figure S25. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **7g** in $CDCl_3$

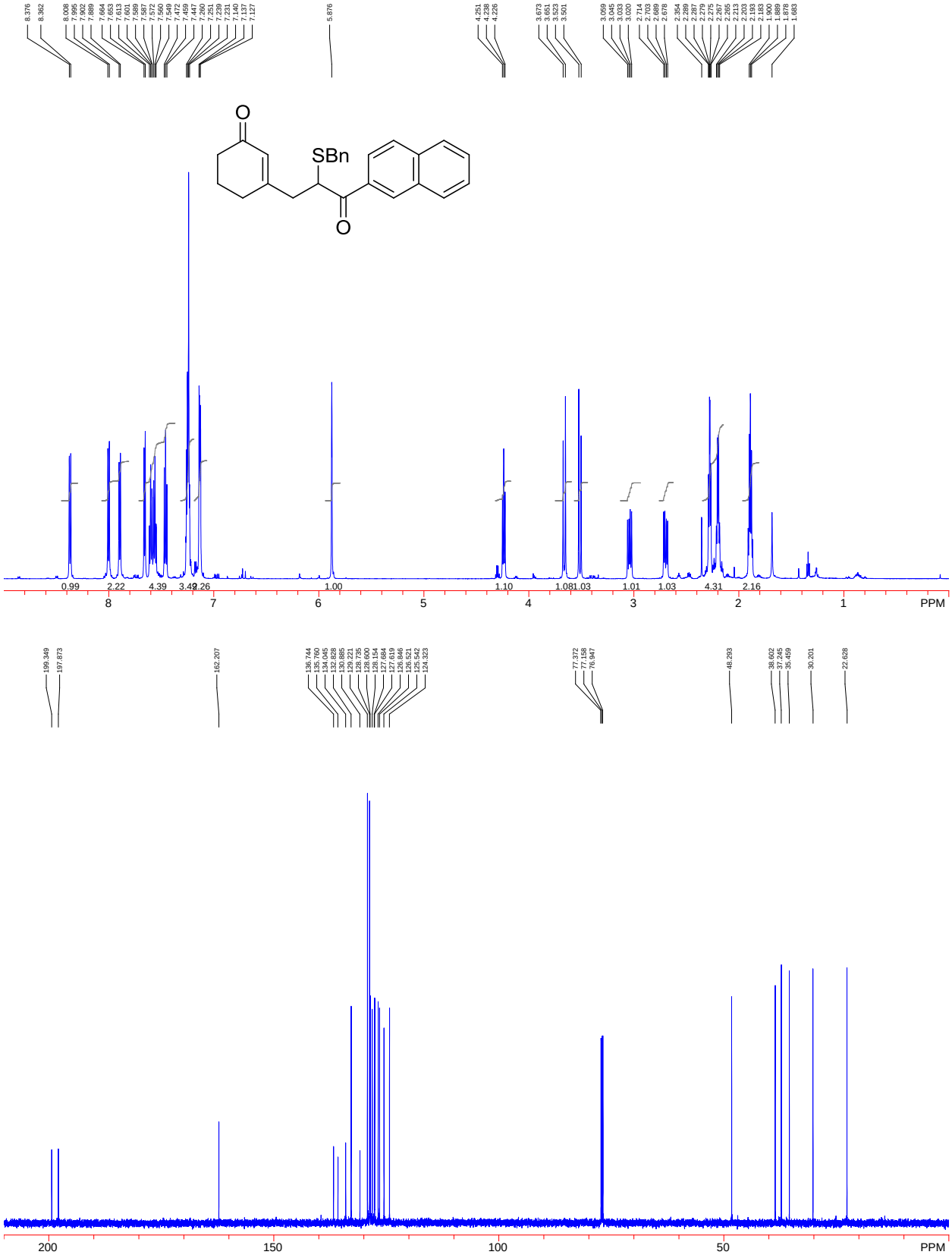


Figure S26. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6h** in $CDCl_3$

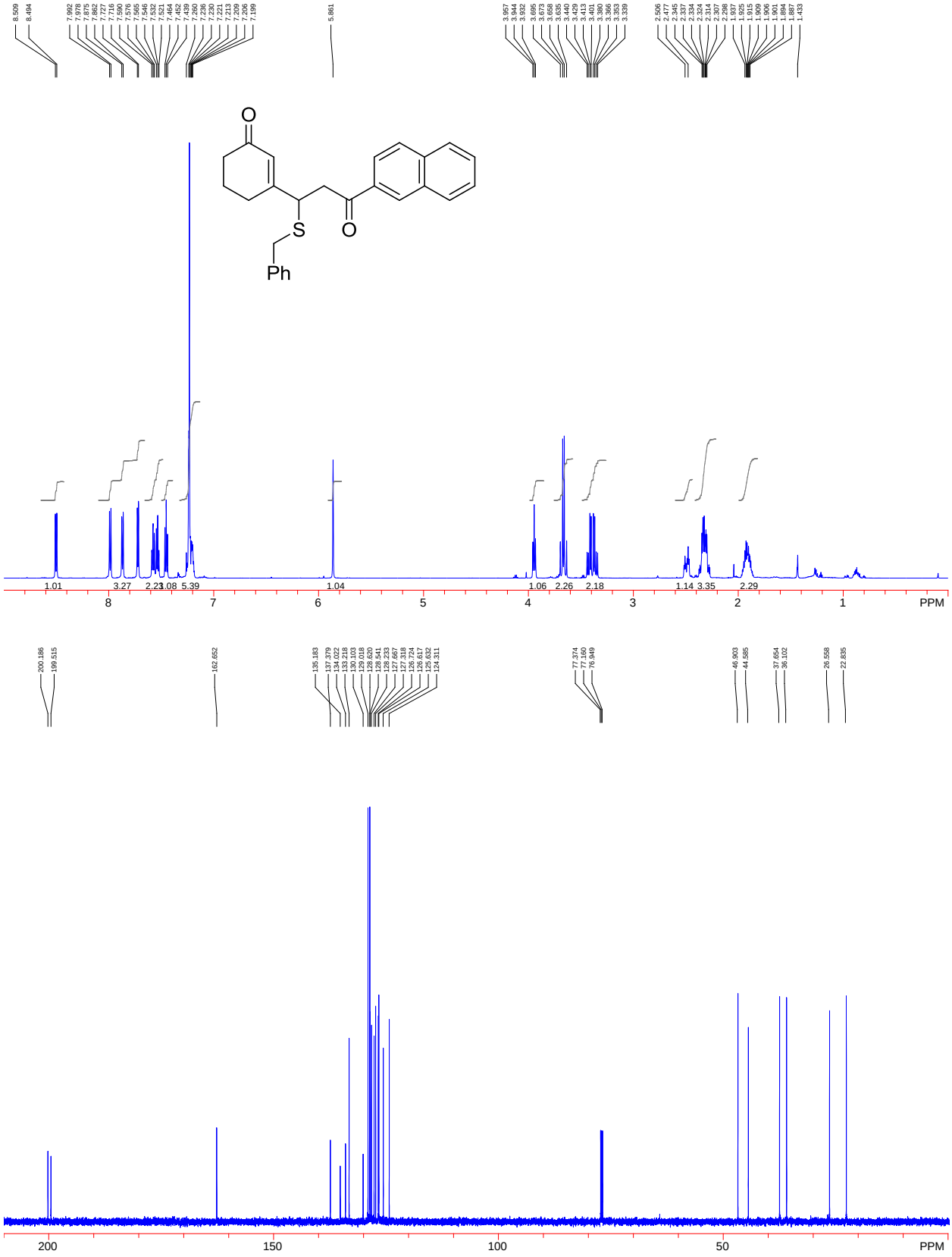


Figure S27. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **7h** in $CDCl_3$

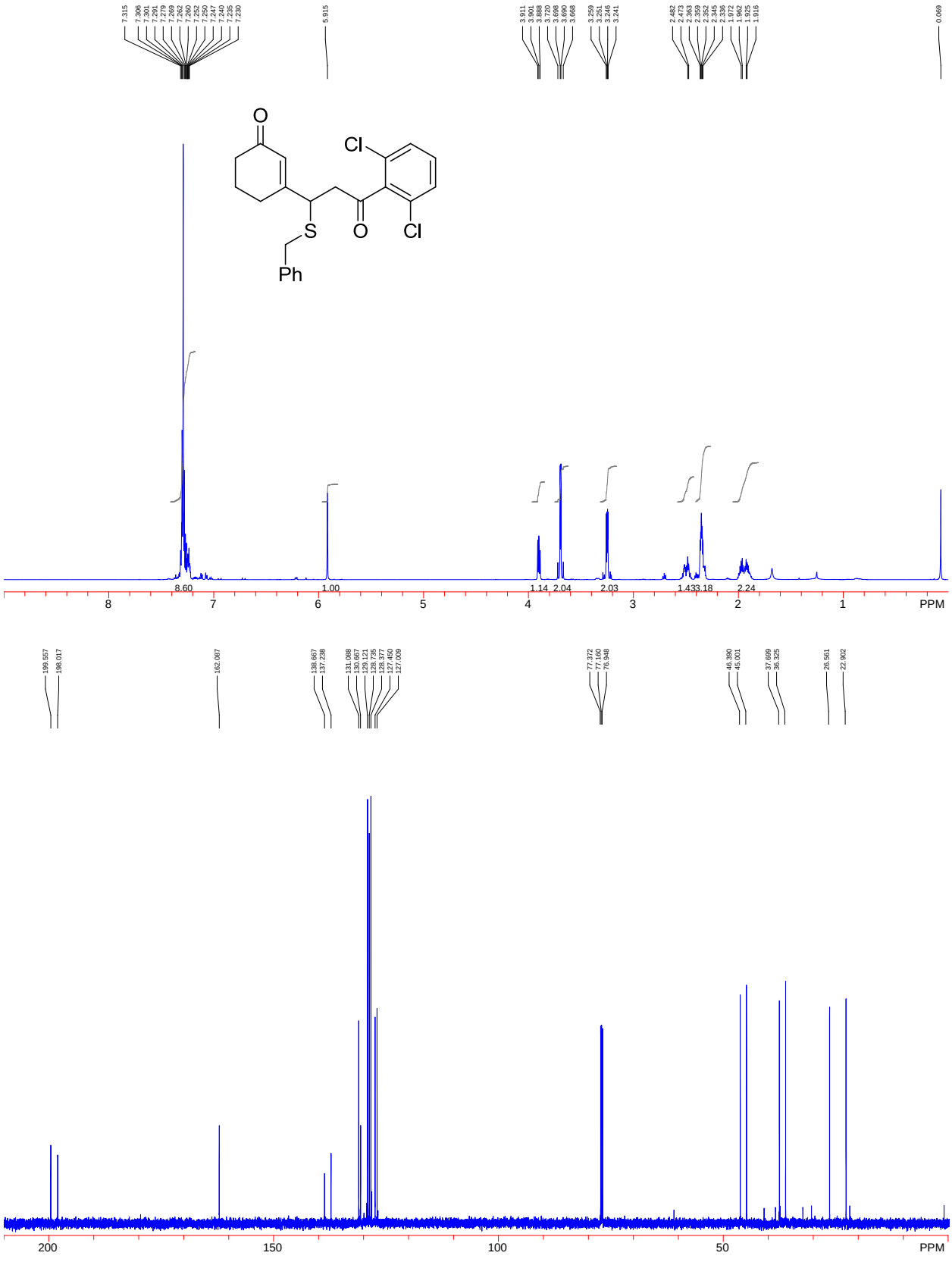


Figure S28. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **7i** in $CDCl_3$

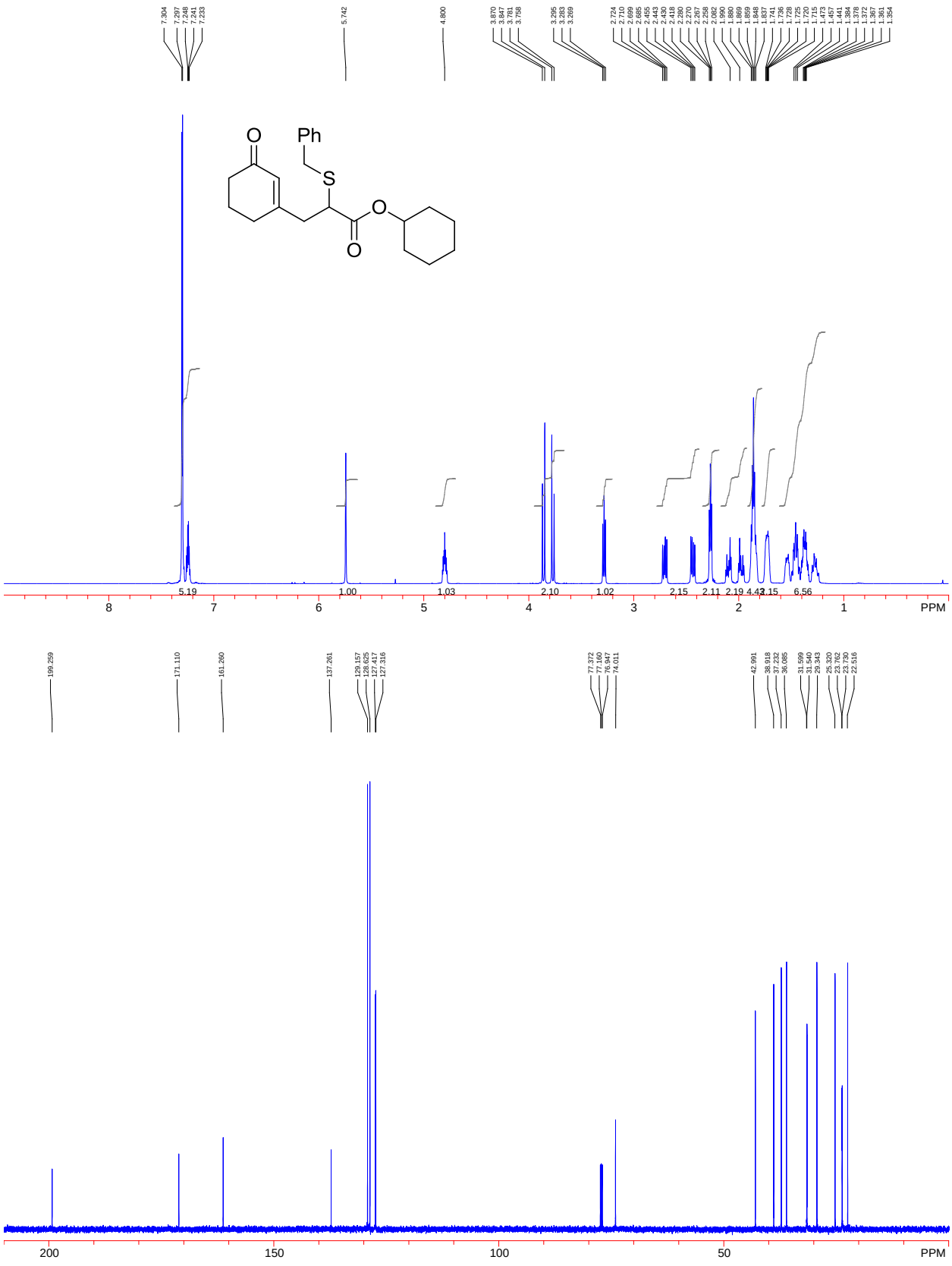


Figure S29. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6j** in $CDCl_3$

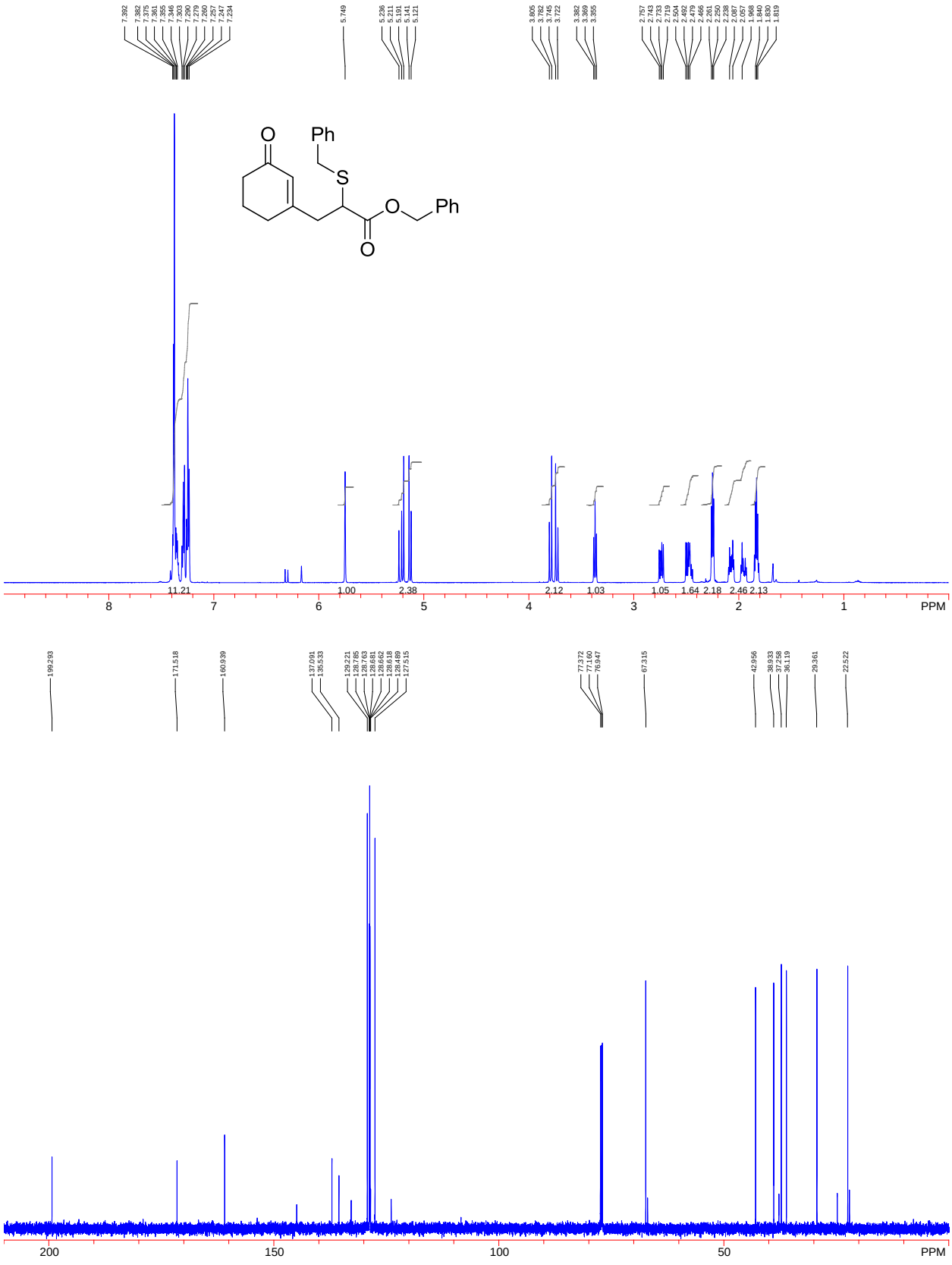


Figure S30. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6k** in $CDCl_3$

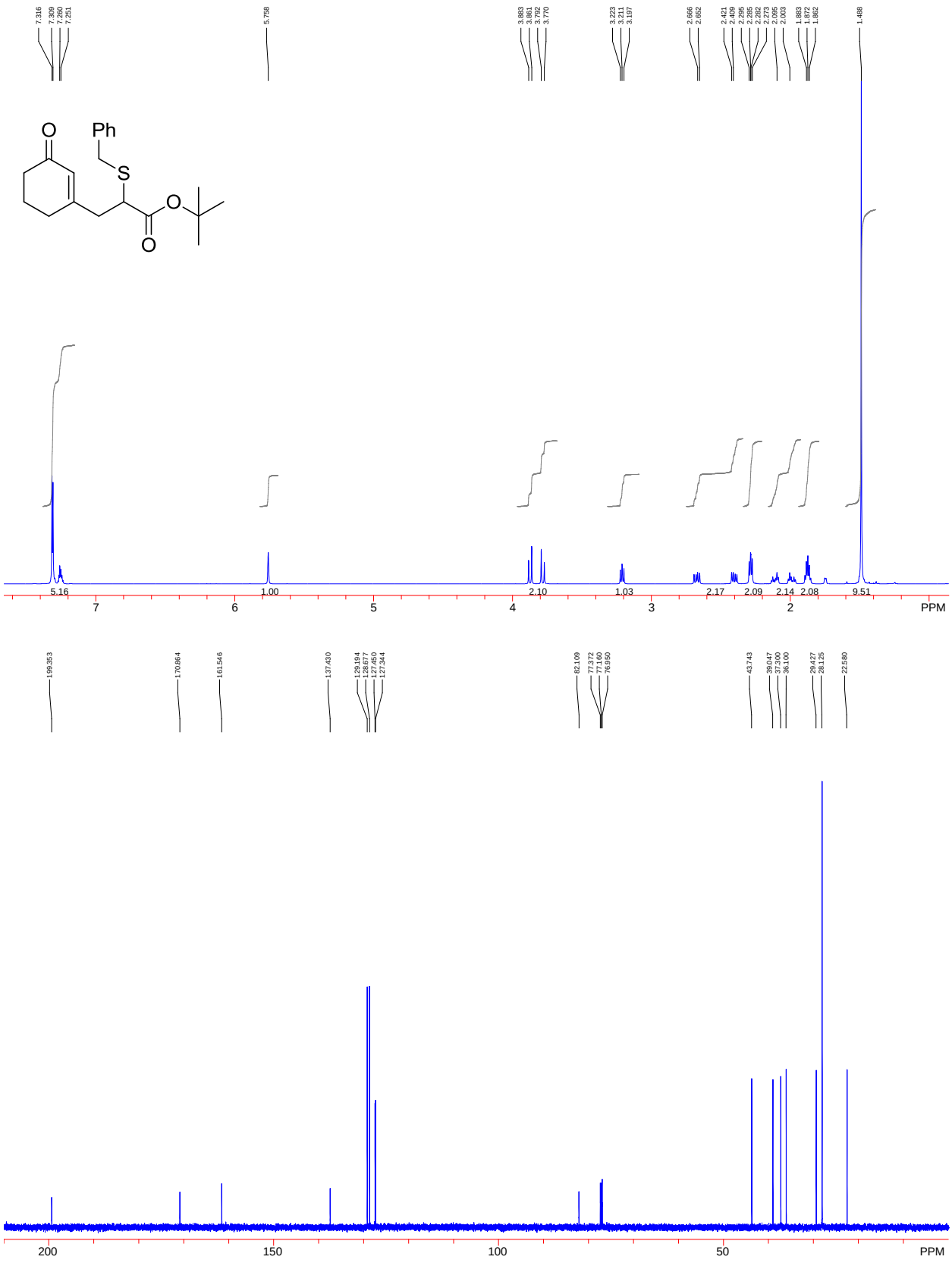


Figure S31. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **6l** in $CDCl_3$

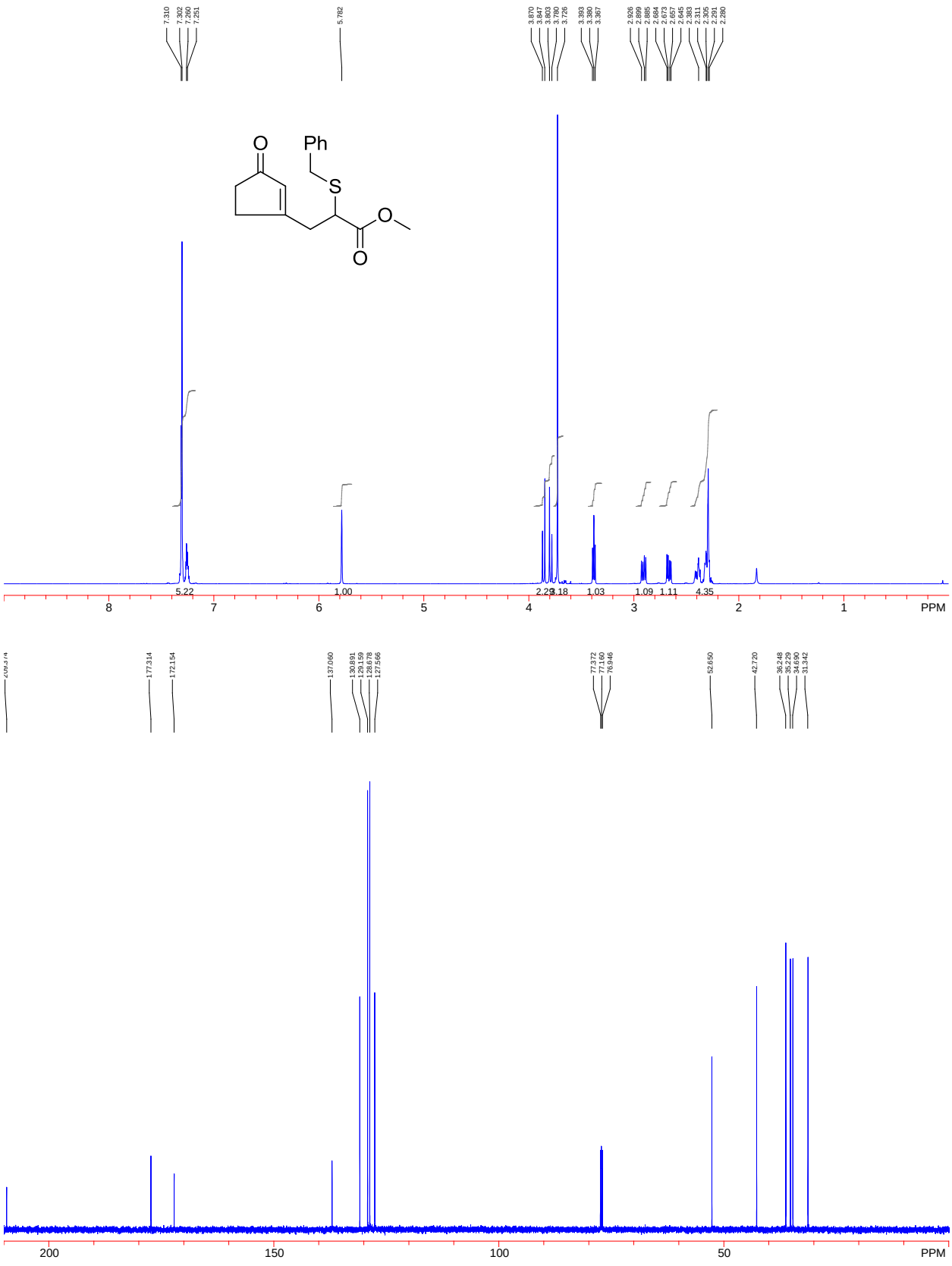


Figure S32. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **8** in $CDCl_3$

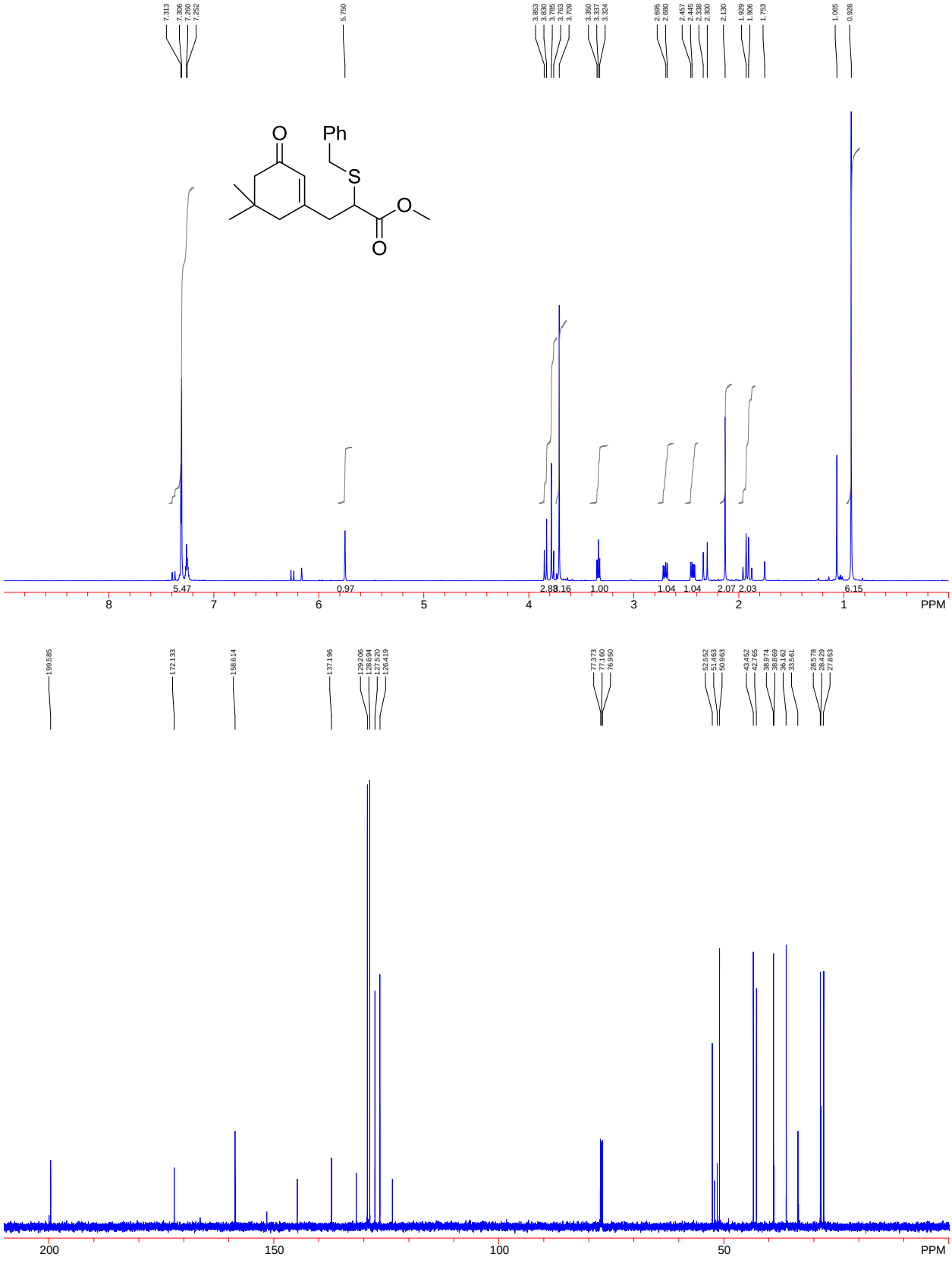


Figure S33. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **9** in $CDCl_3$

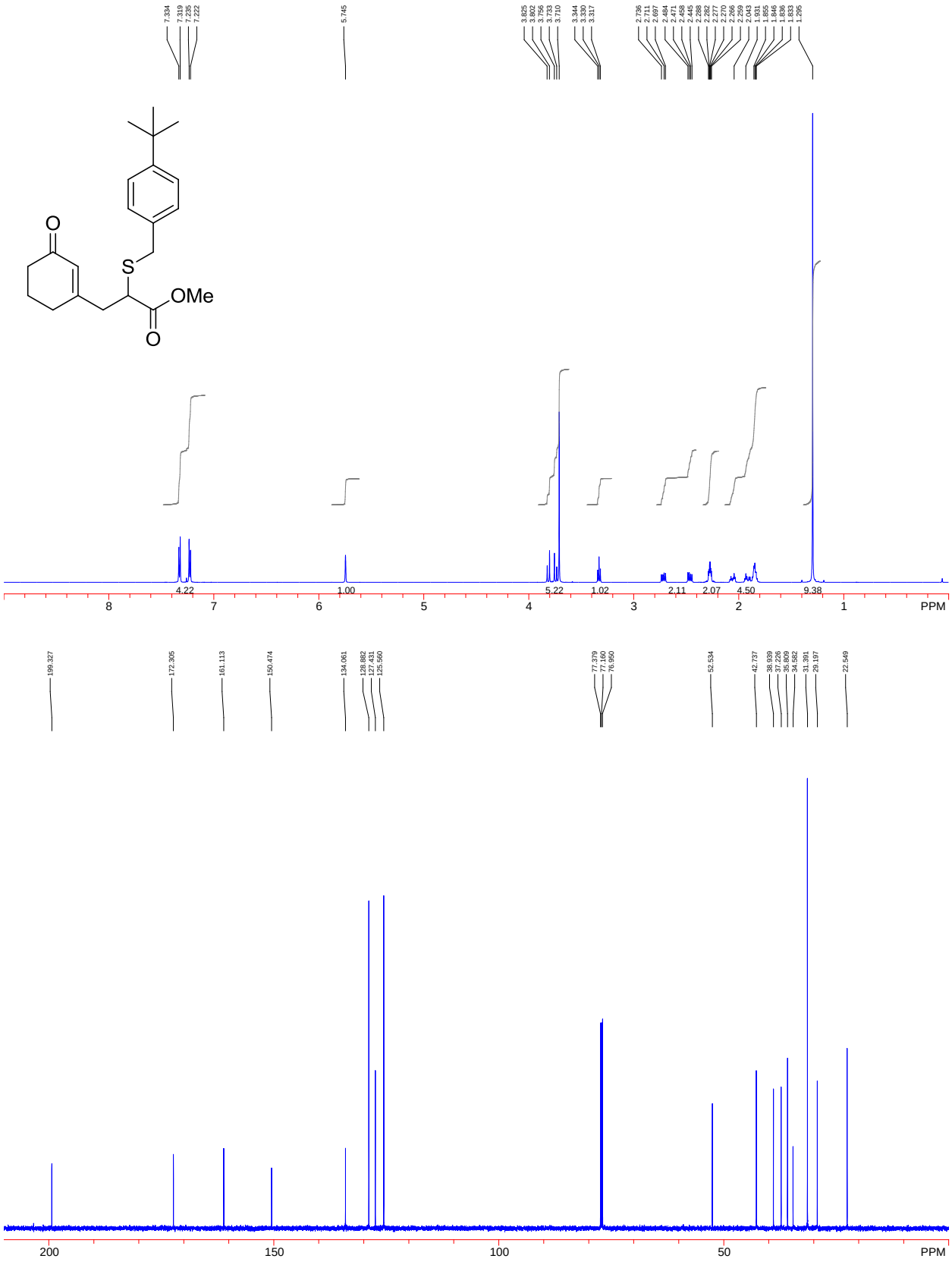


Figure S34. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **12** in $CDCl_3$

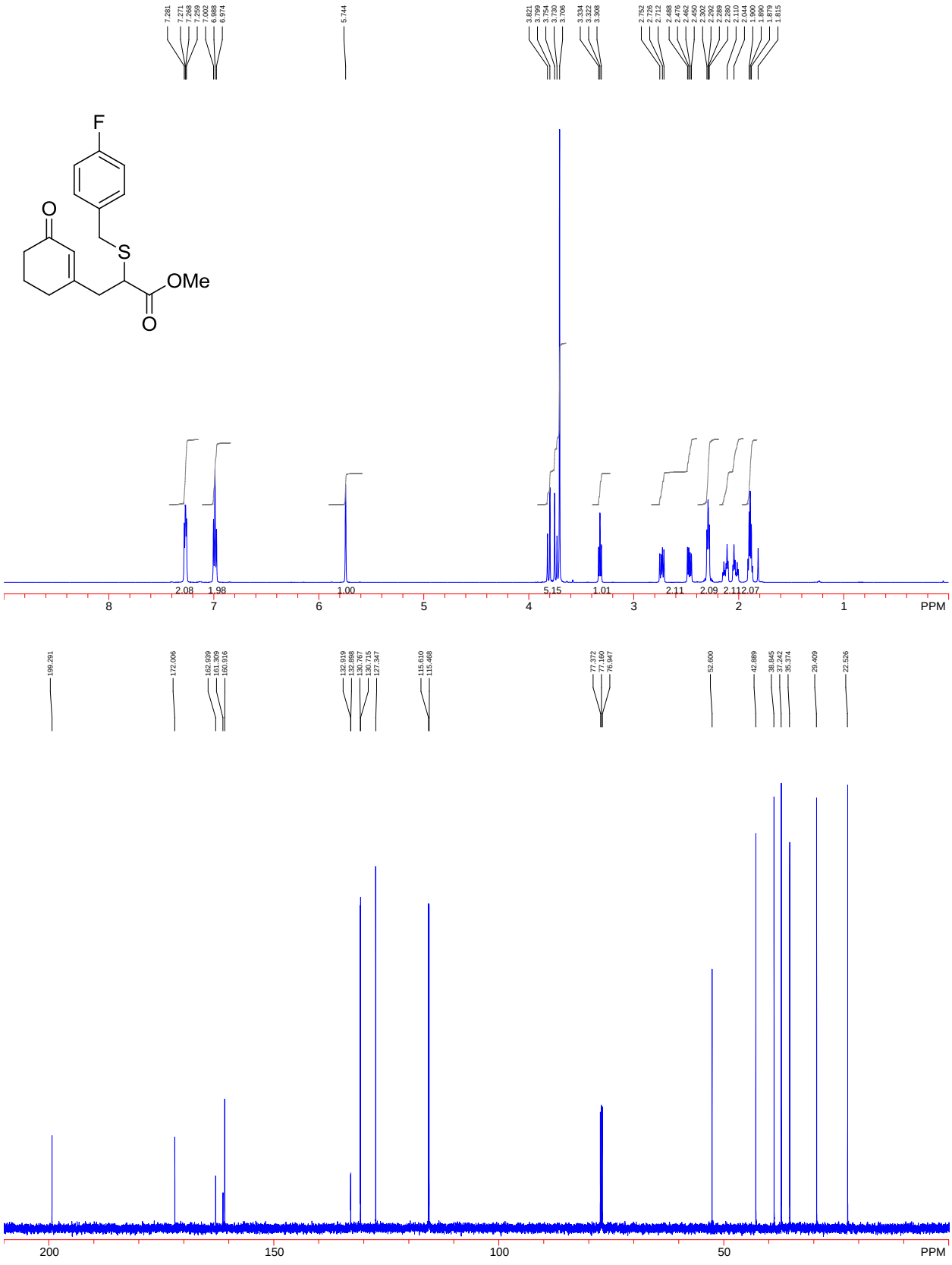


Figure S35. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **13** in $CDCl_3$

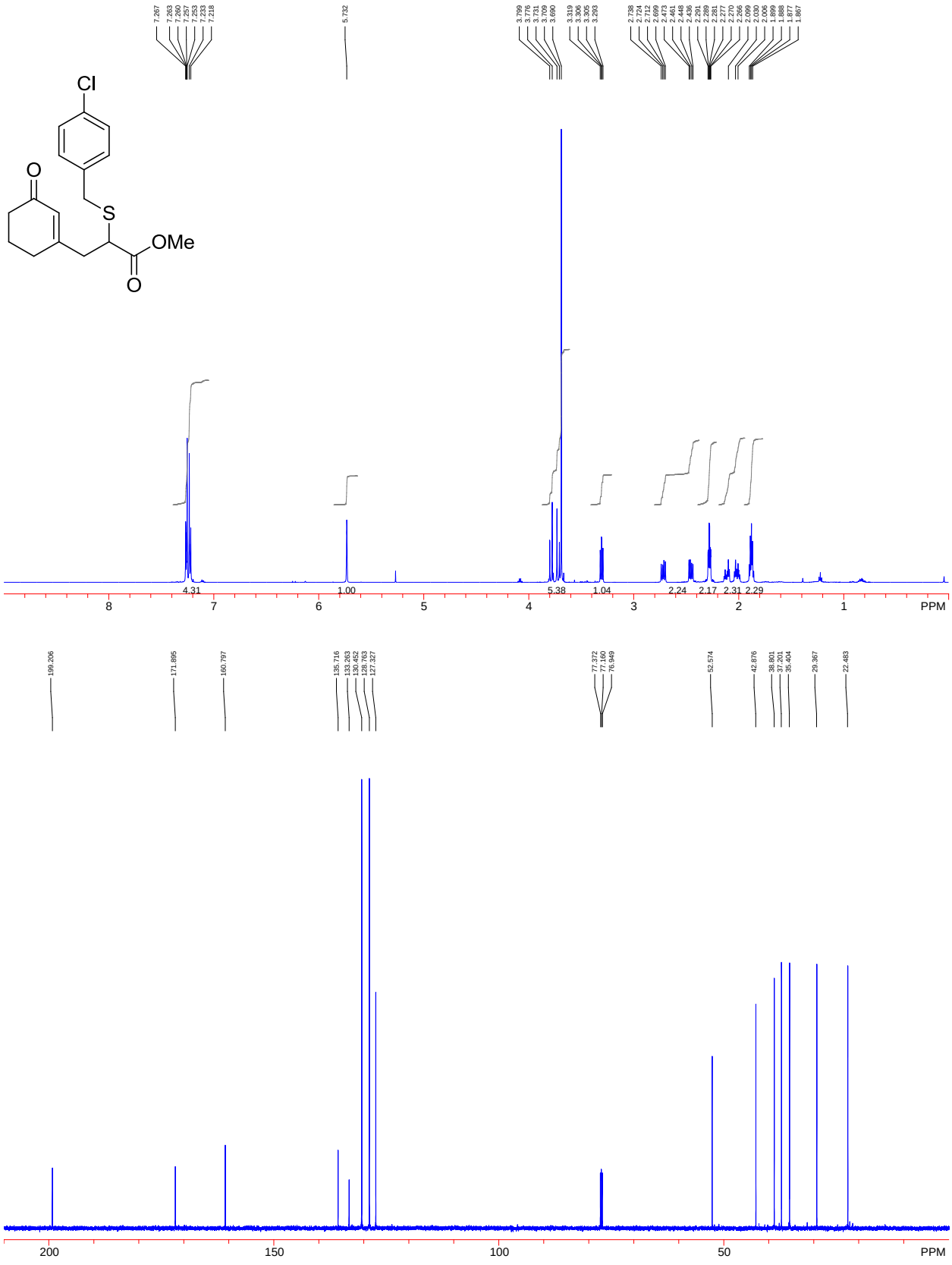


Figure S36. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **14** in $CDCl_3$

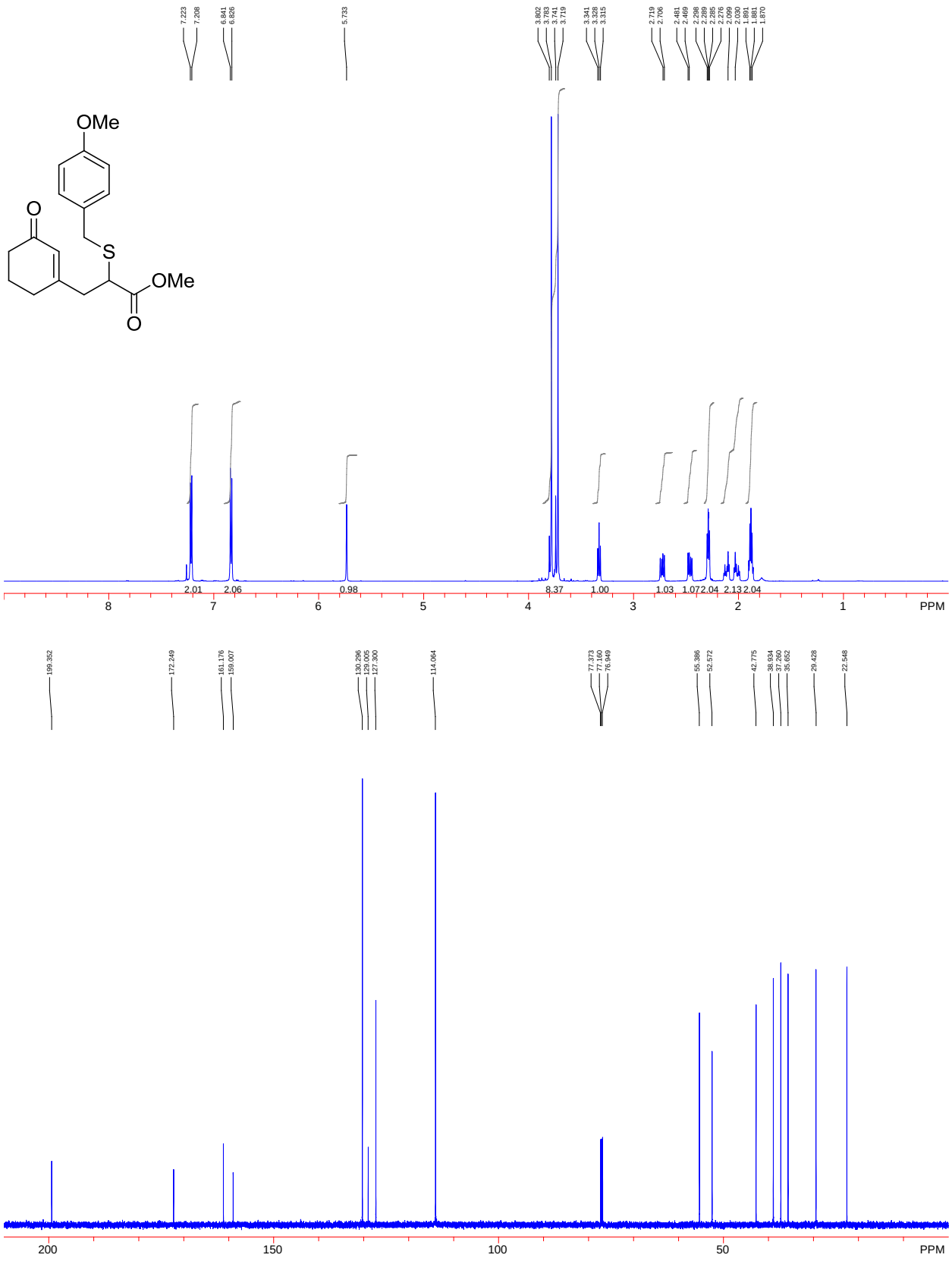


Figure S37. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **15** in $CDCl_3$

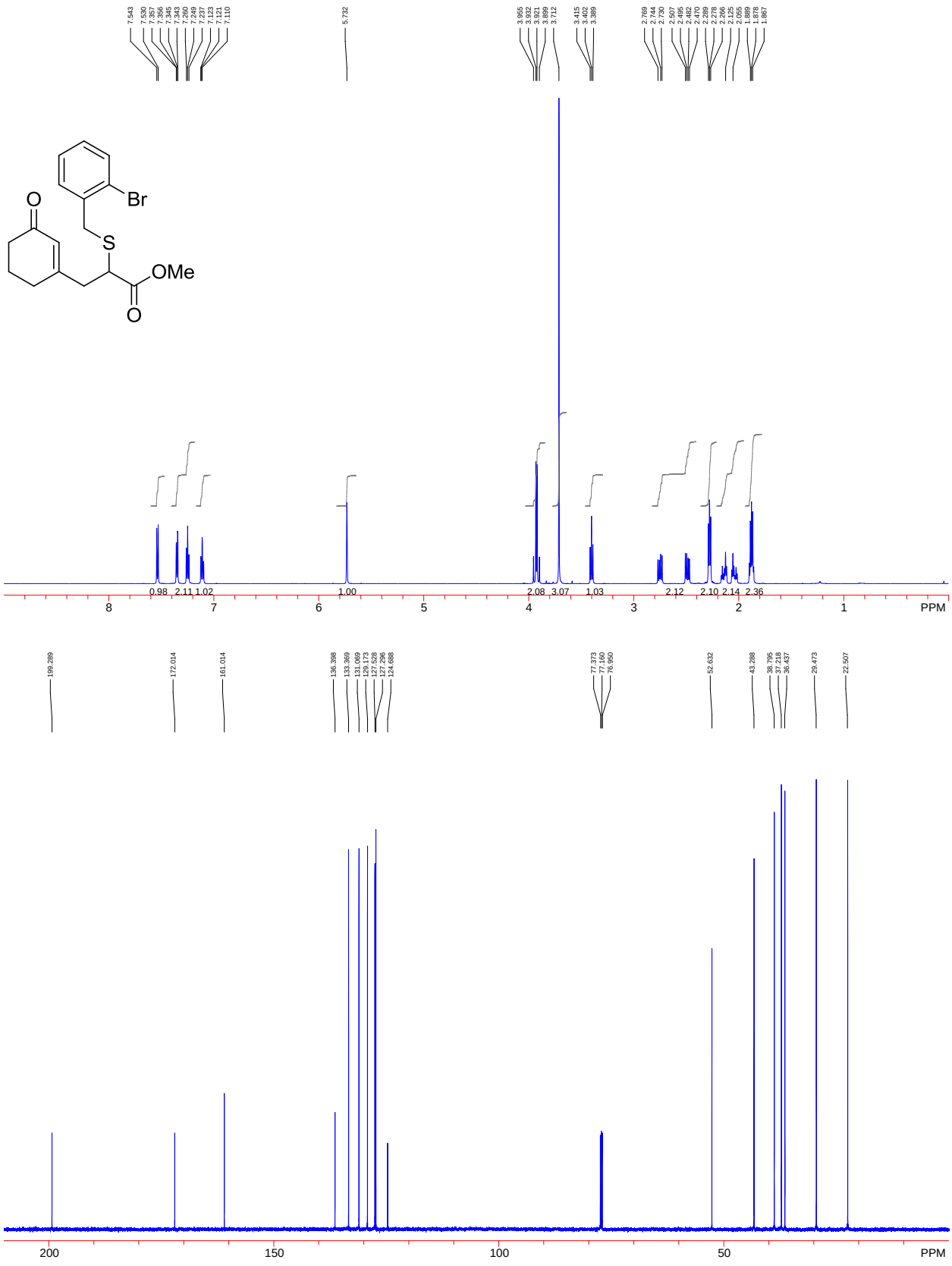


Figure S38. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **16** in $CDCl_3$

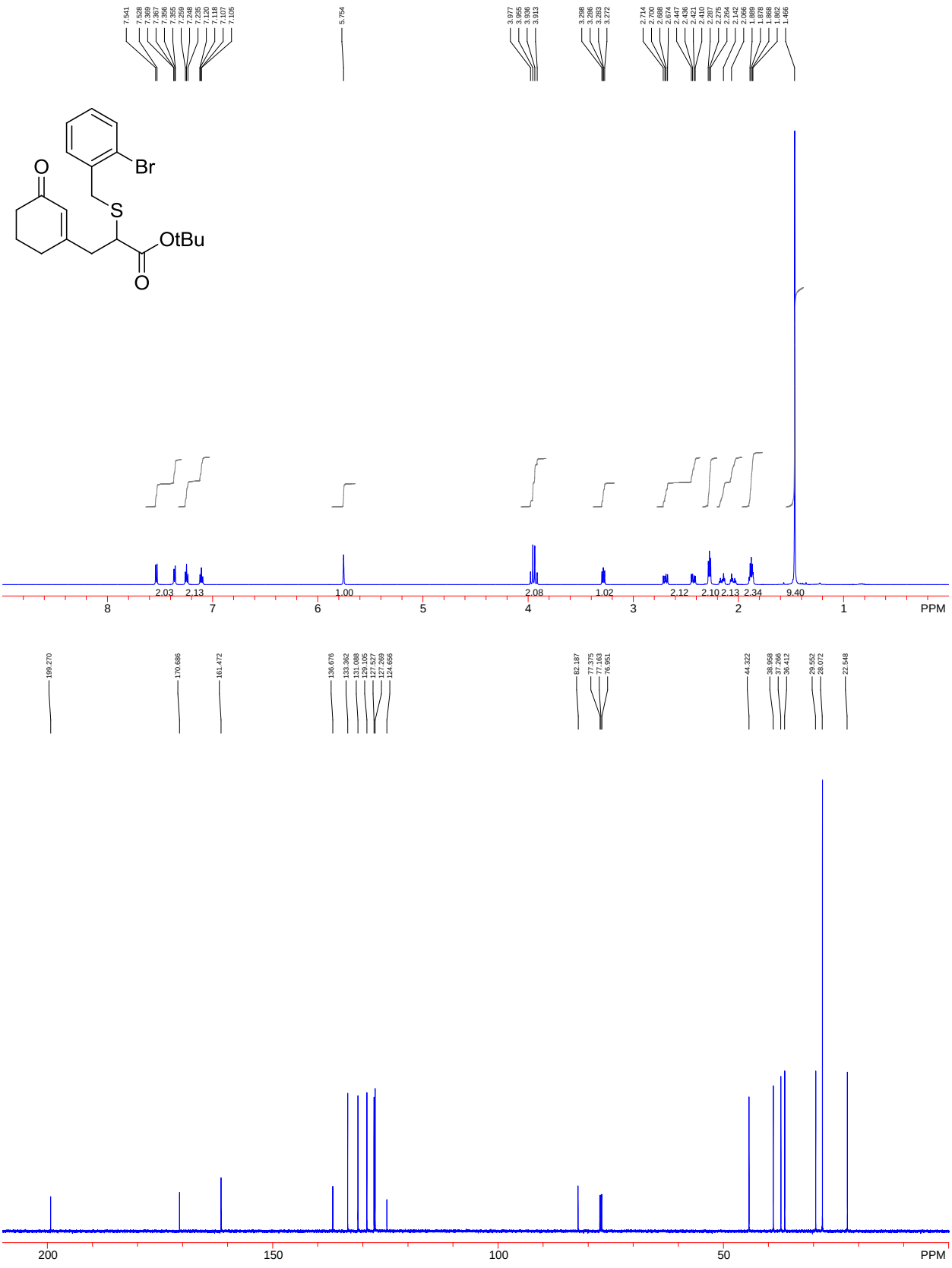


Figure S39. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **17** in $CDCl_3$

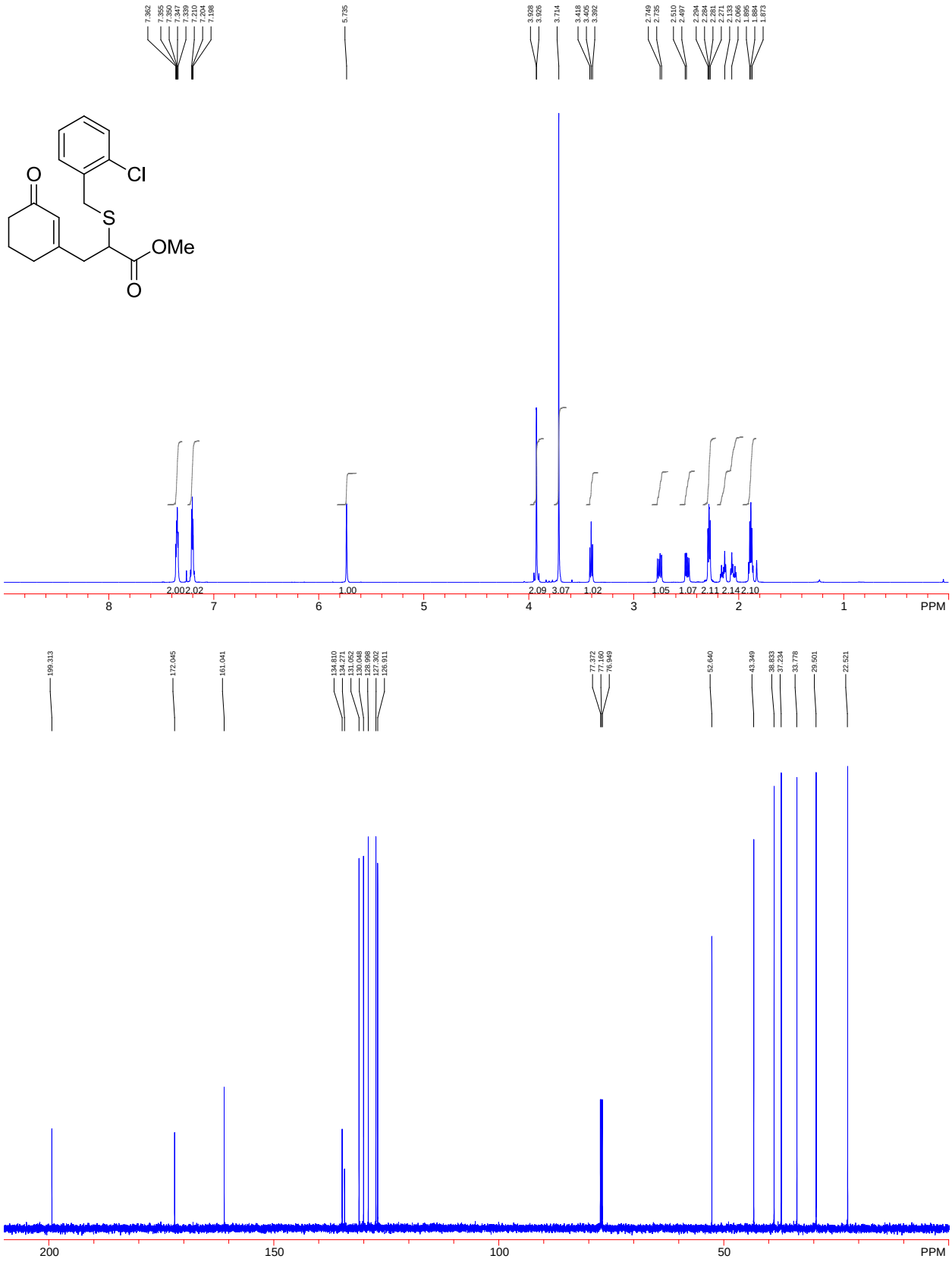


Figure S40. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **18** in $CDCl_3$

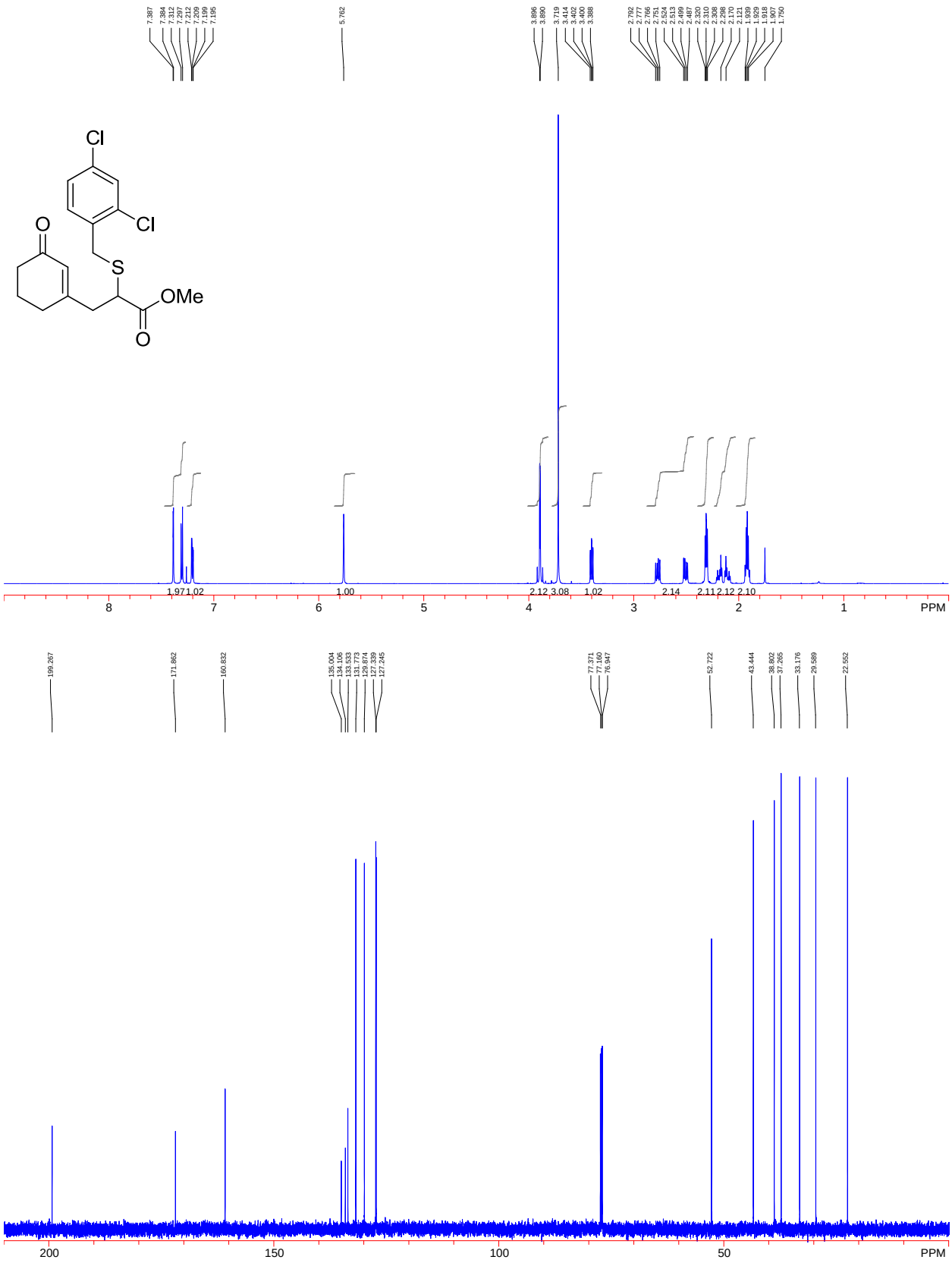


Figure S41. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **19** in $CDCl_3$

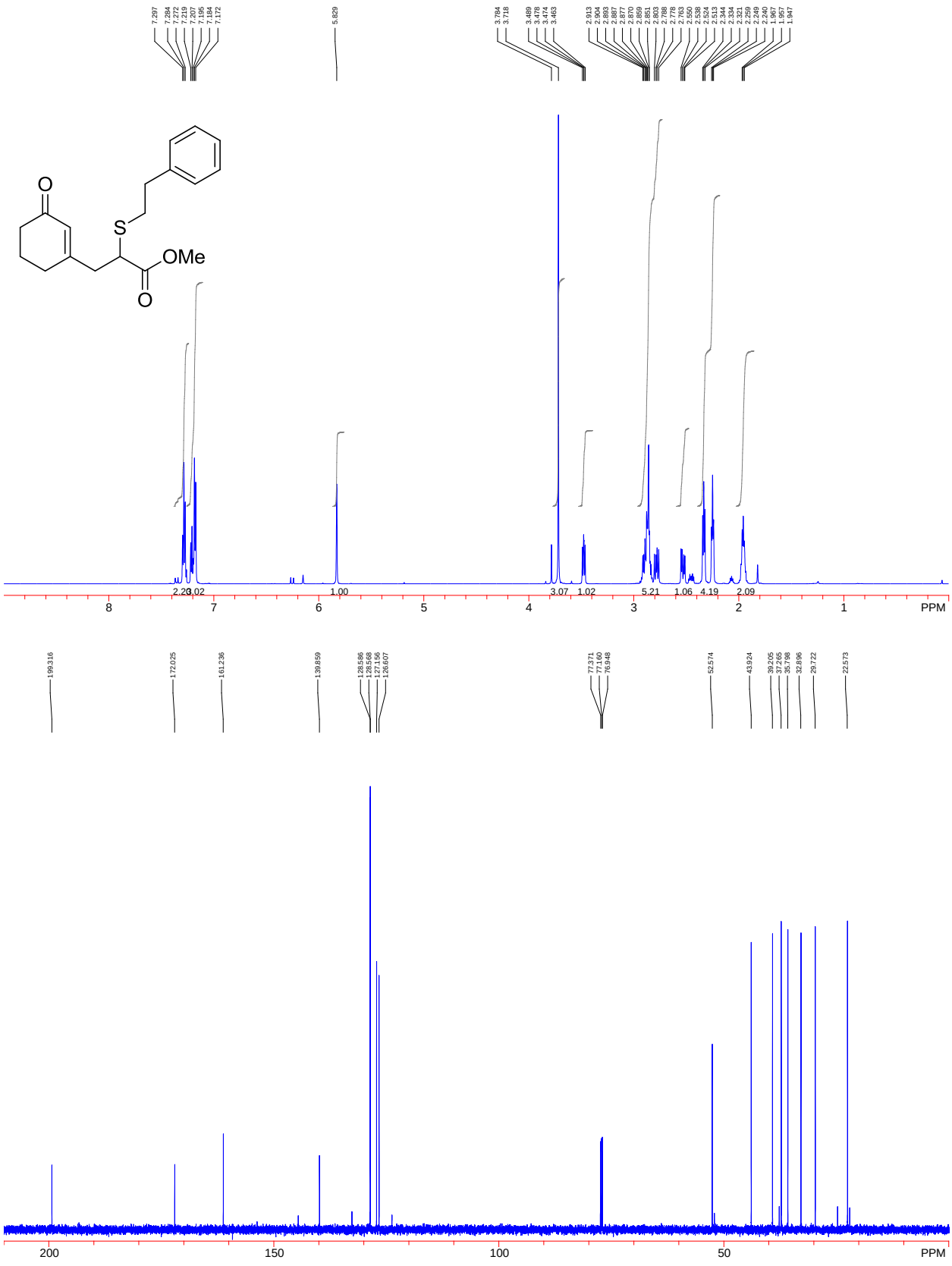


Figure S42. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **20** in $CDCl_3$

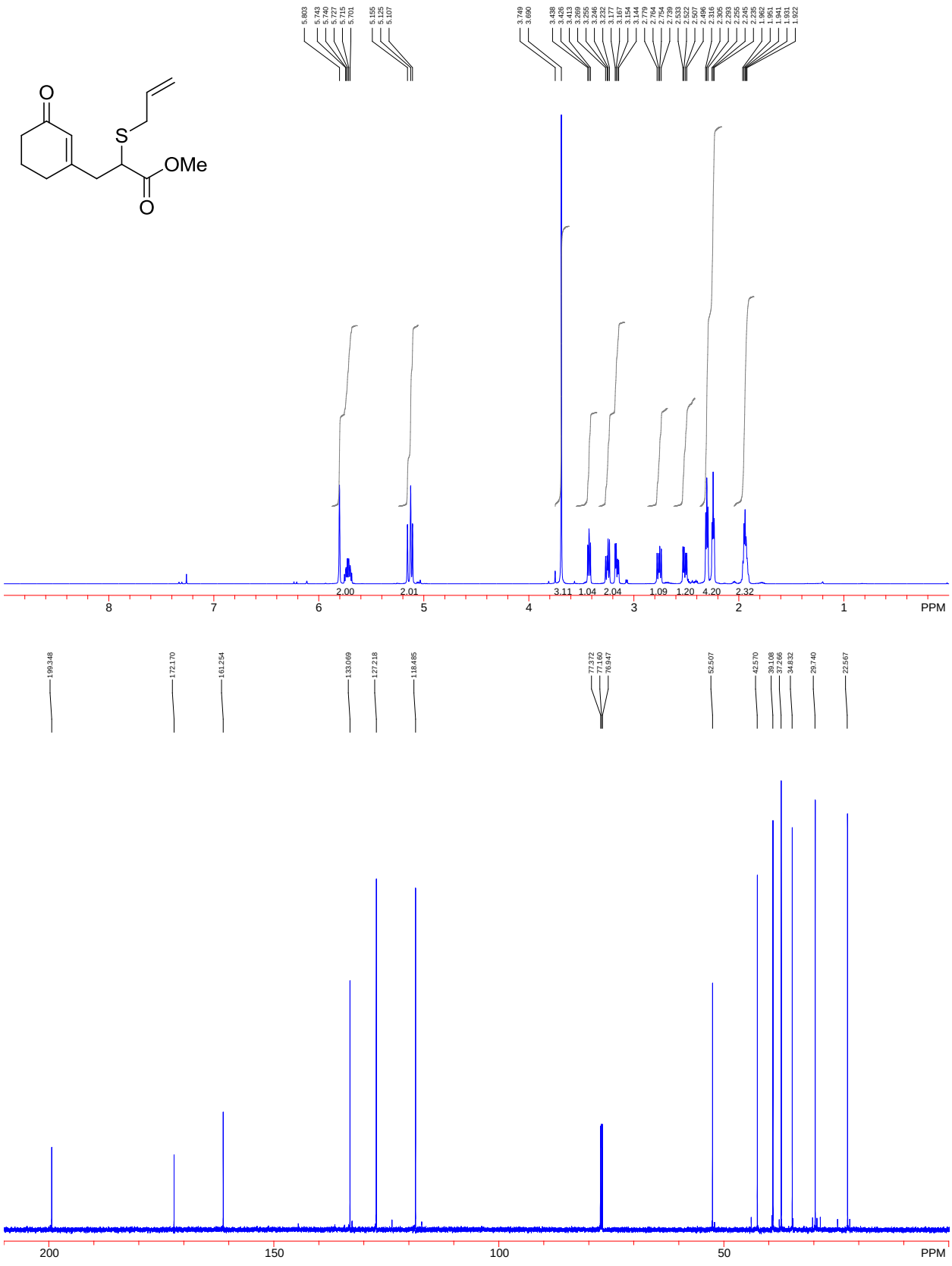


Figure S43. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **21** in $CDCl_3$

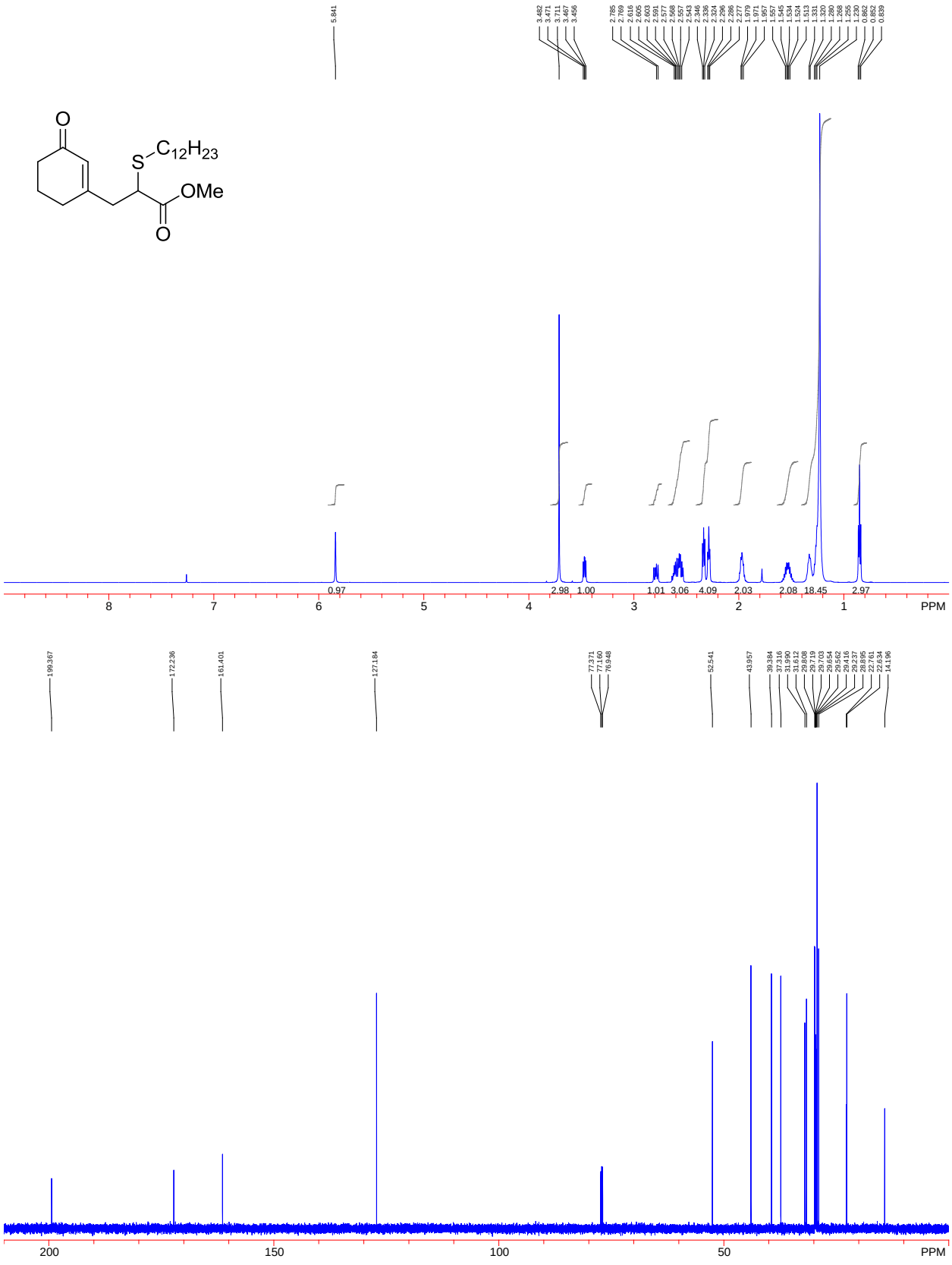


Figure S44. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **22** in $CDCl_3$

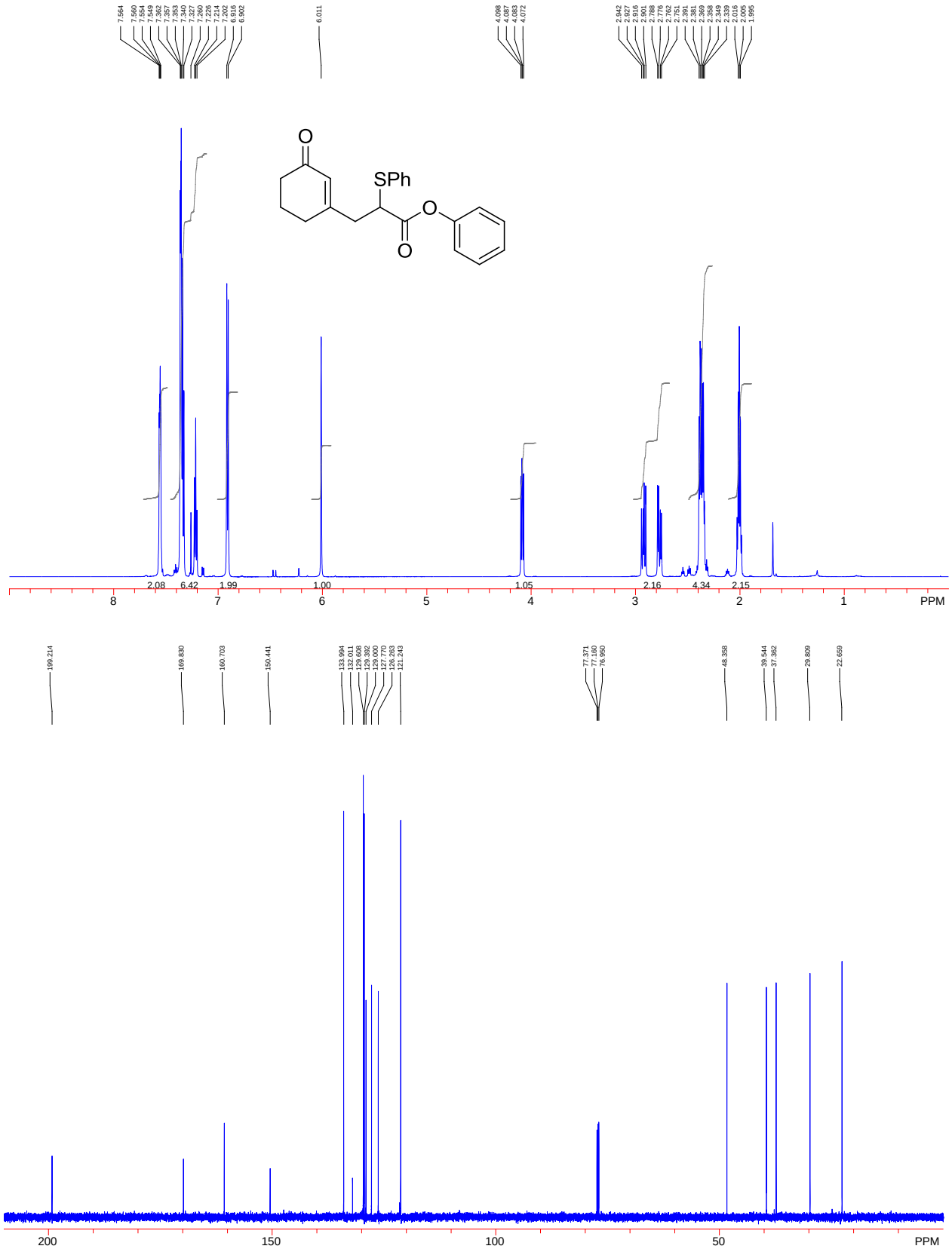


Figure S45. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **23** in $CDCl_3$

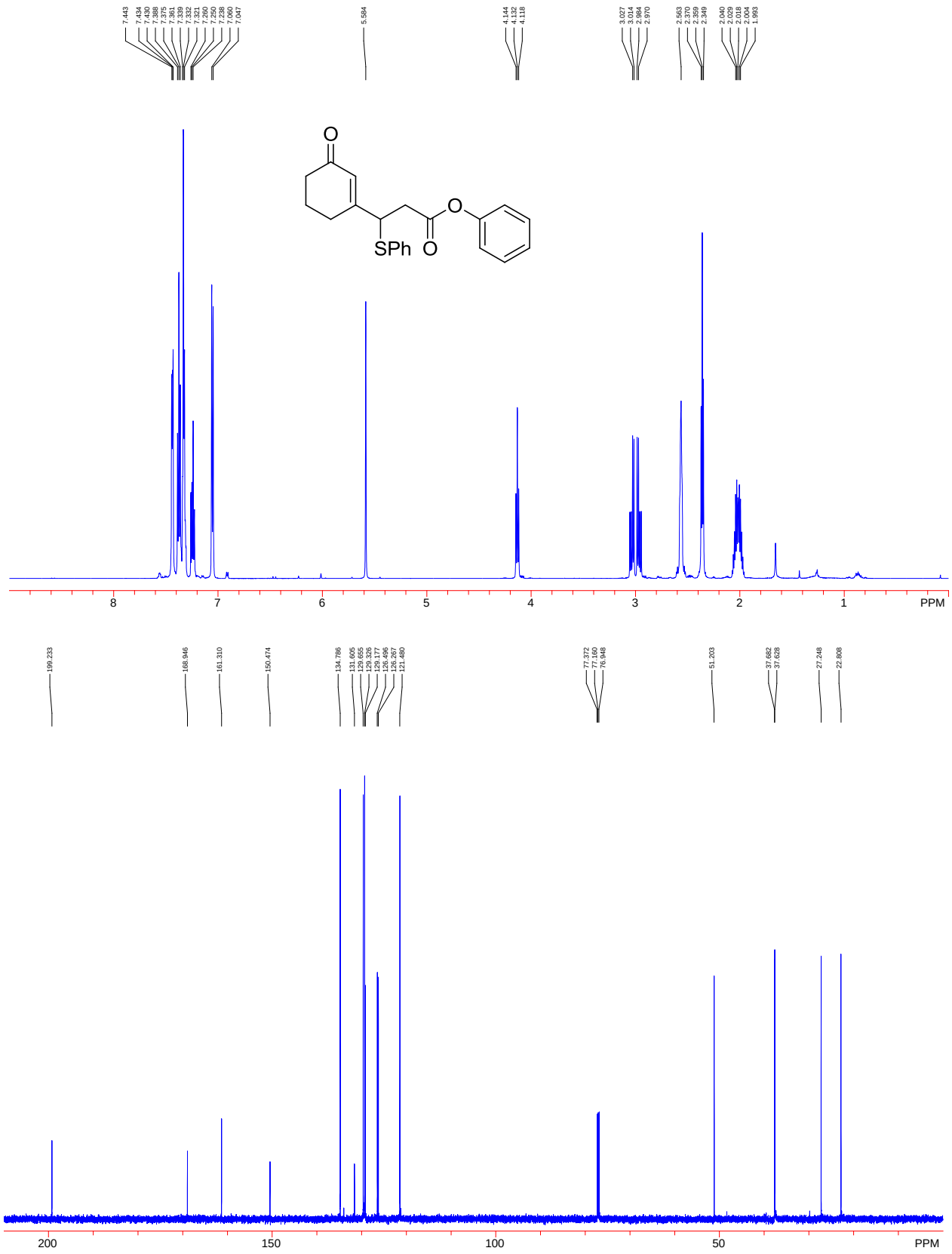


Figure S46. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **24** in $CDCl_3$

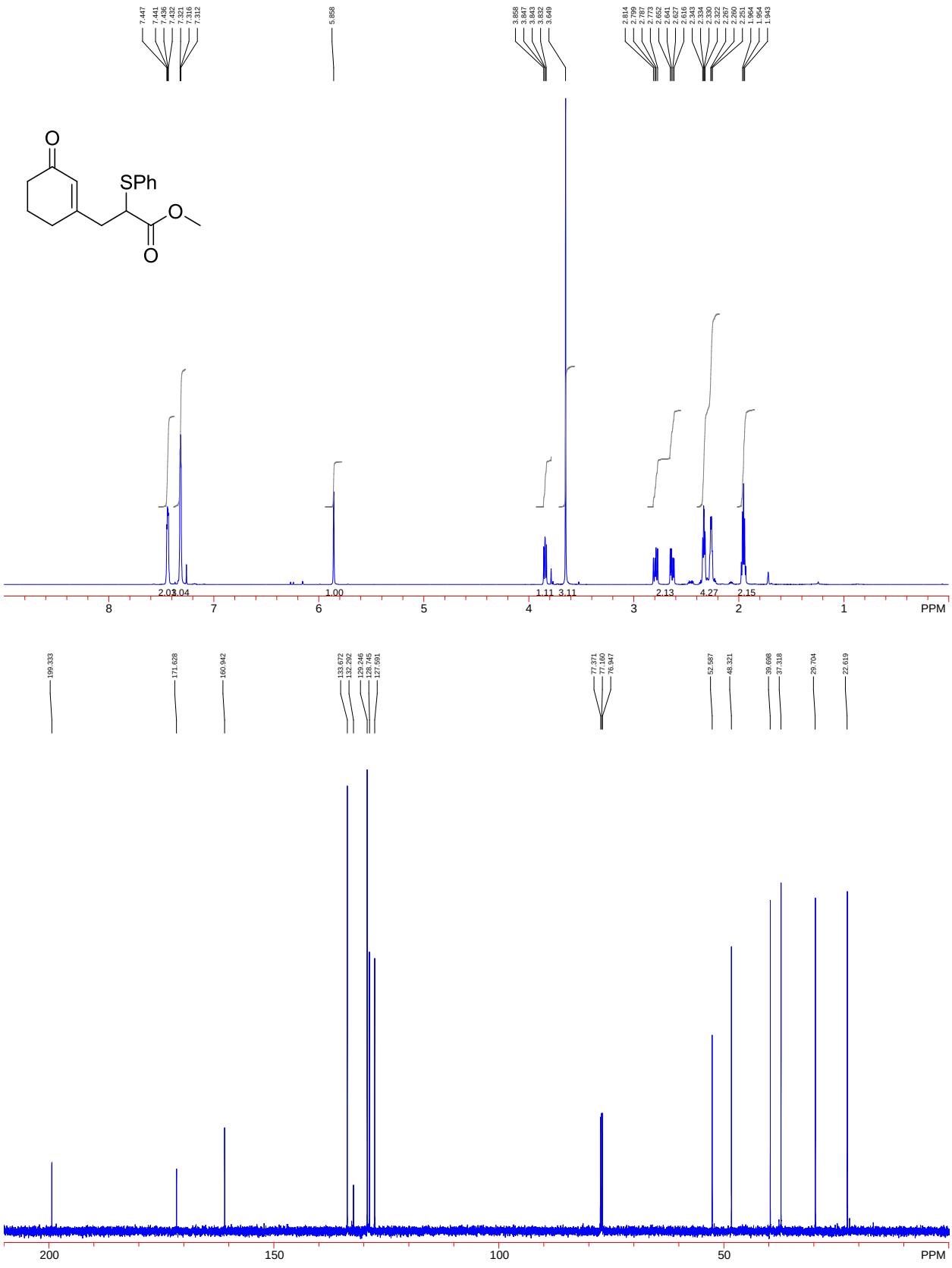


Figure S47. ^{1}H (600 MHz) and ^{13}C (151 MHz) spectra for adduct **25** in $CDCl_3$

S9. Two-dimensional NMR experiments and spectral assignment

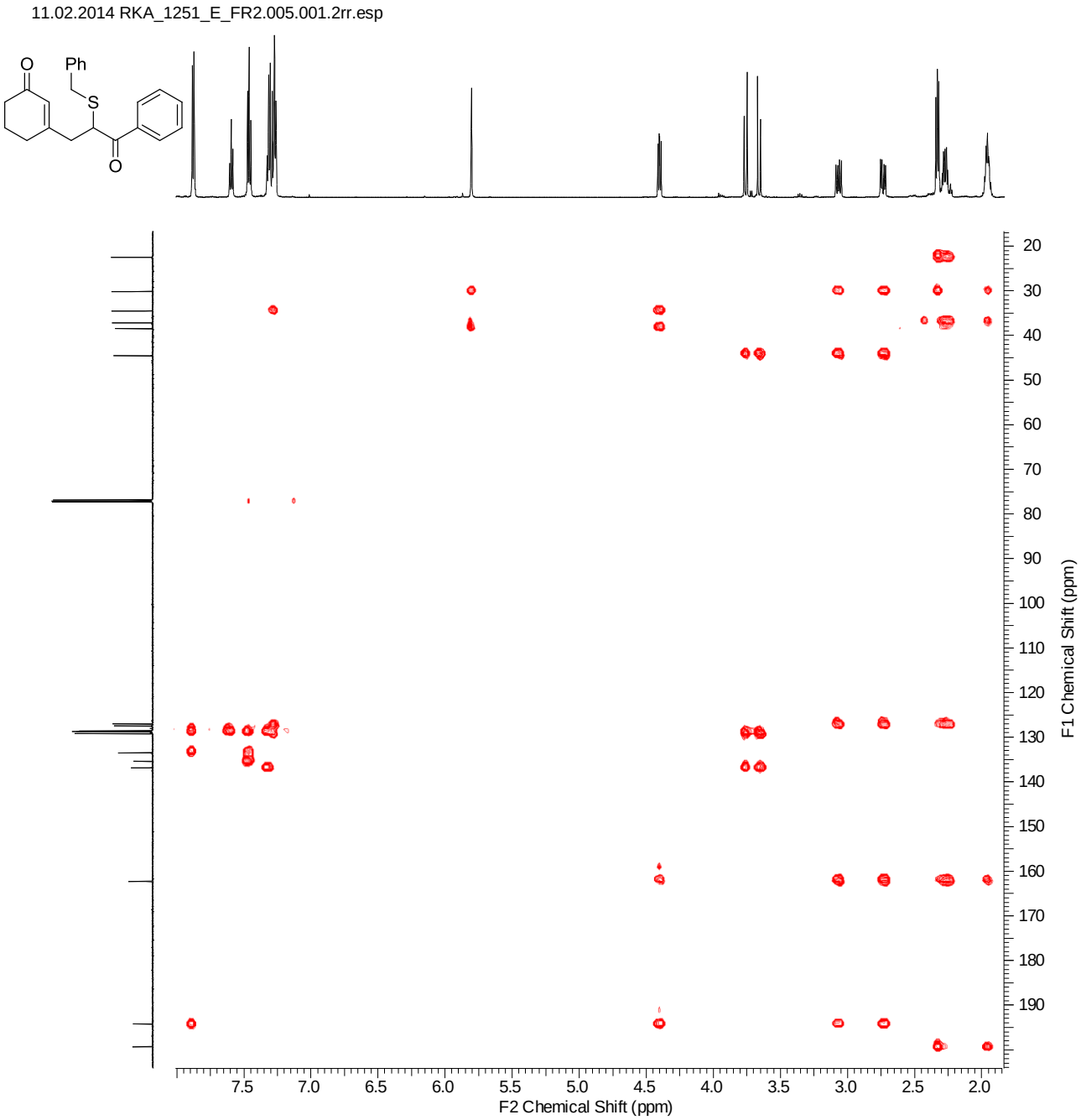


Figure S48. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6b**

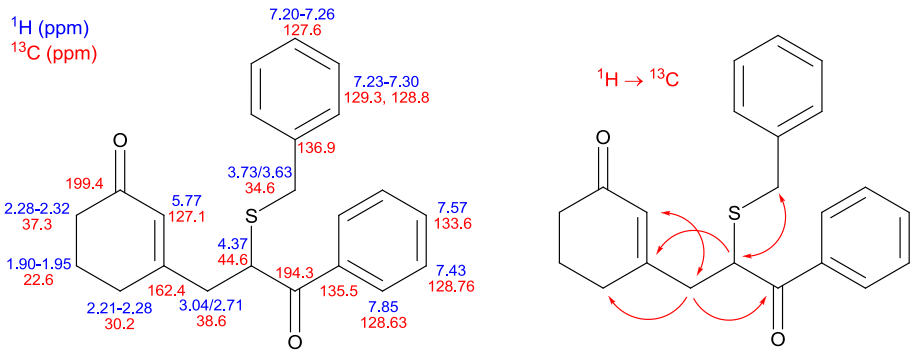


Figure S49. Spectral assignment and selected ^{1}H,^{13}C HMBC correlations for adduct **6b**

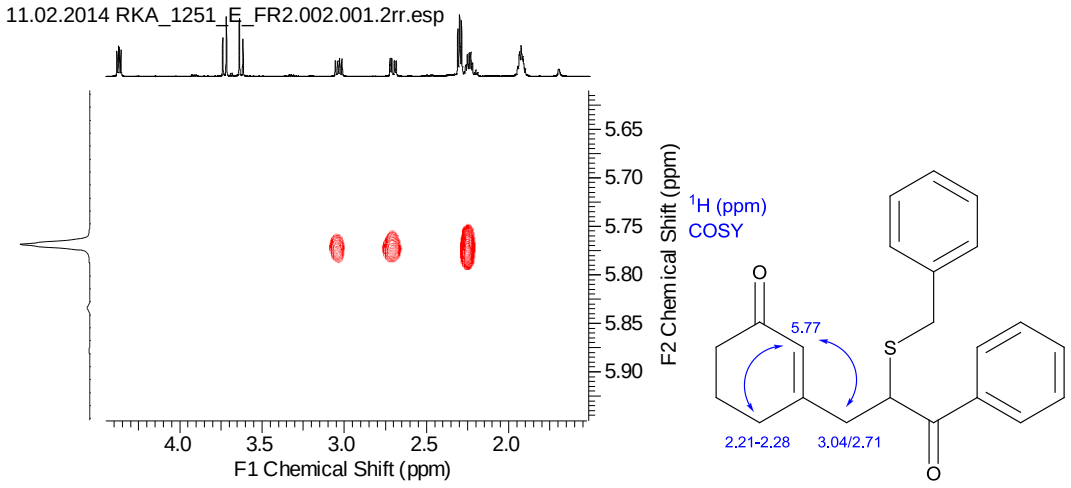


Figure S50. Section of COSY spectra for **6b** showing allylic ^{4}J couplings to 5.77 ppm resonance

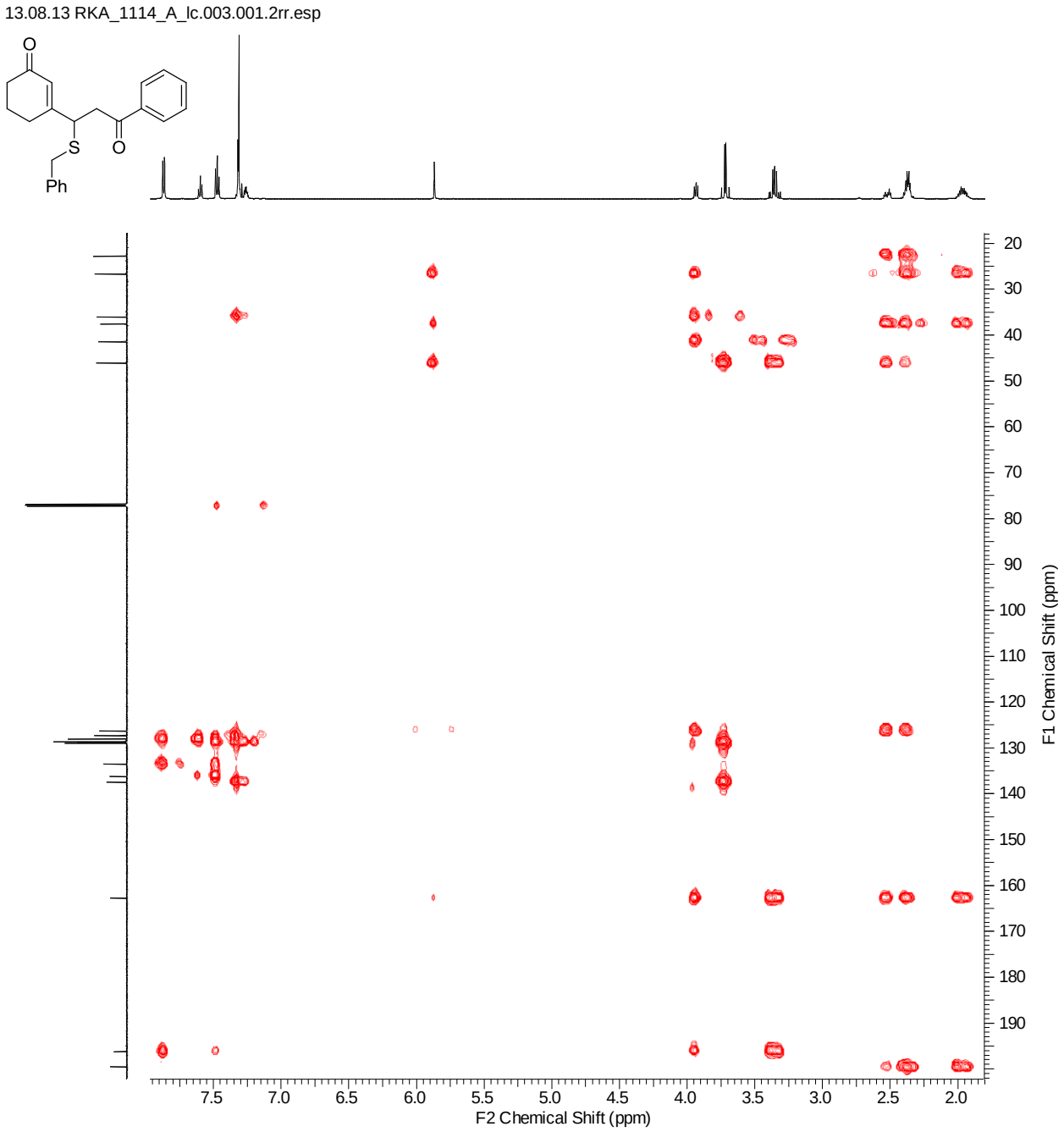


Figure S51. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **7b**

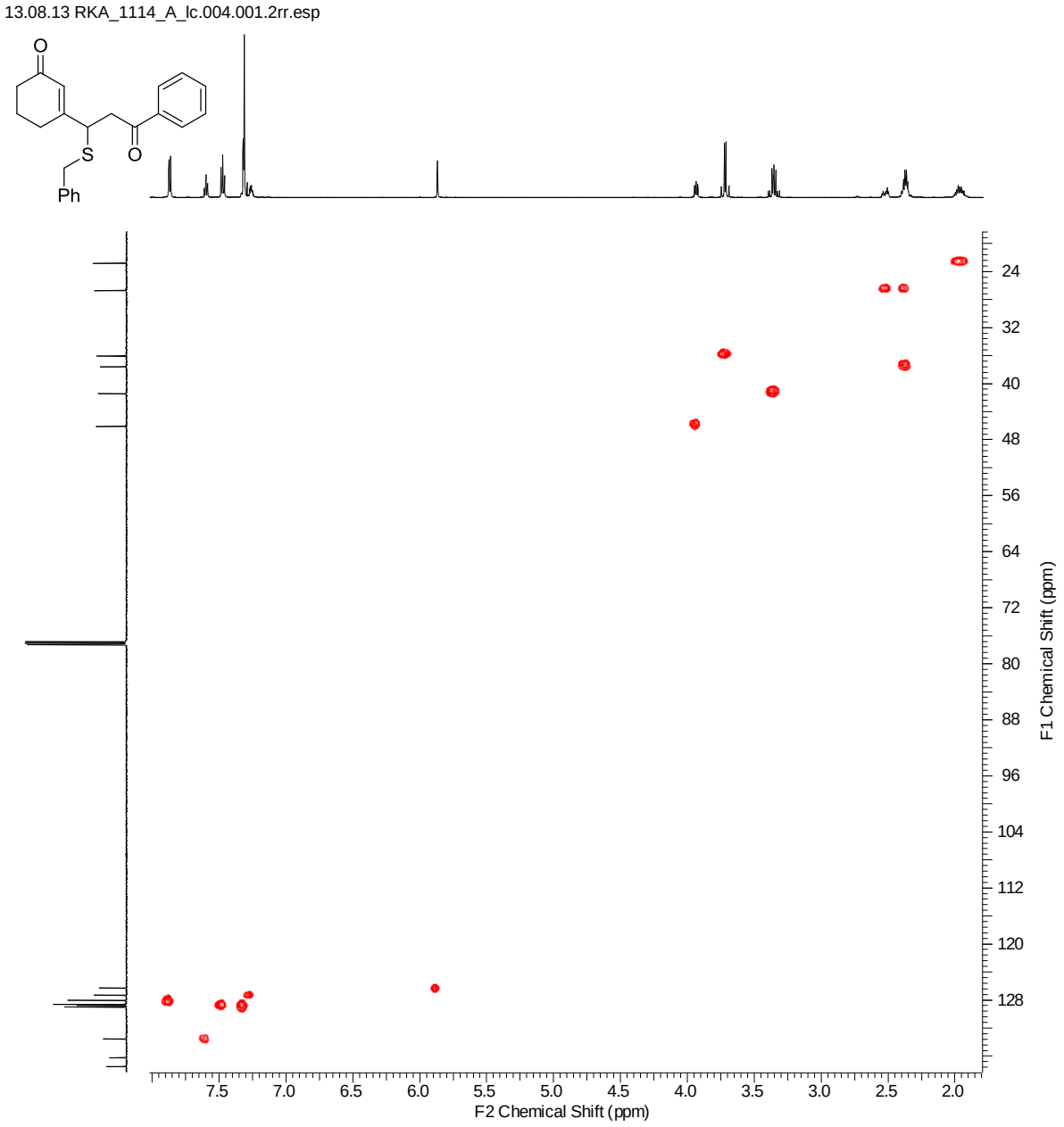


Figure S52. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **7b**

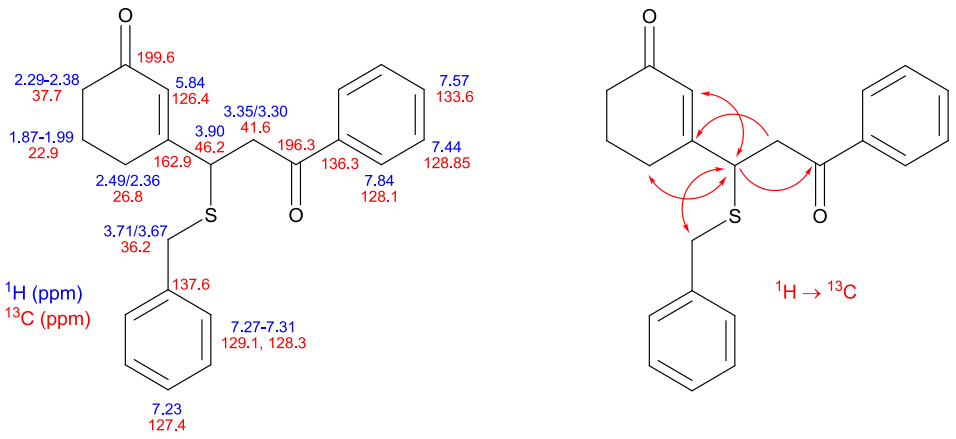


Figure S53. Spectral assignment and selected $^{1}H,^{13}C$ HMBC correlations for adduct **7b**

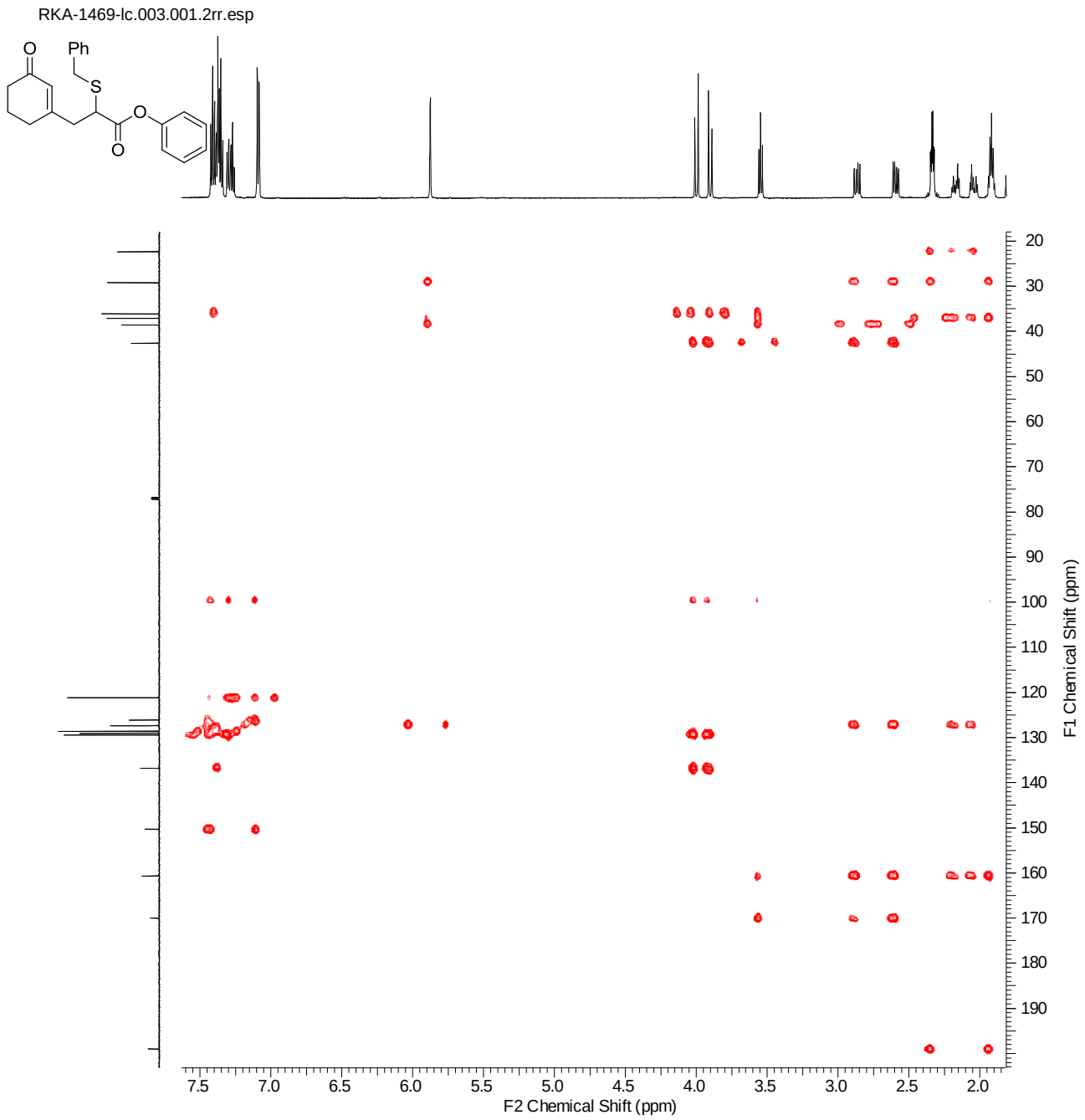


Figure S54. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6c**

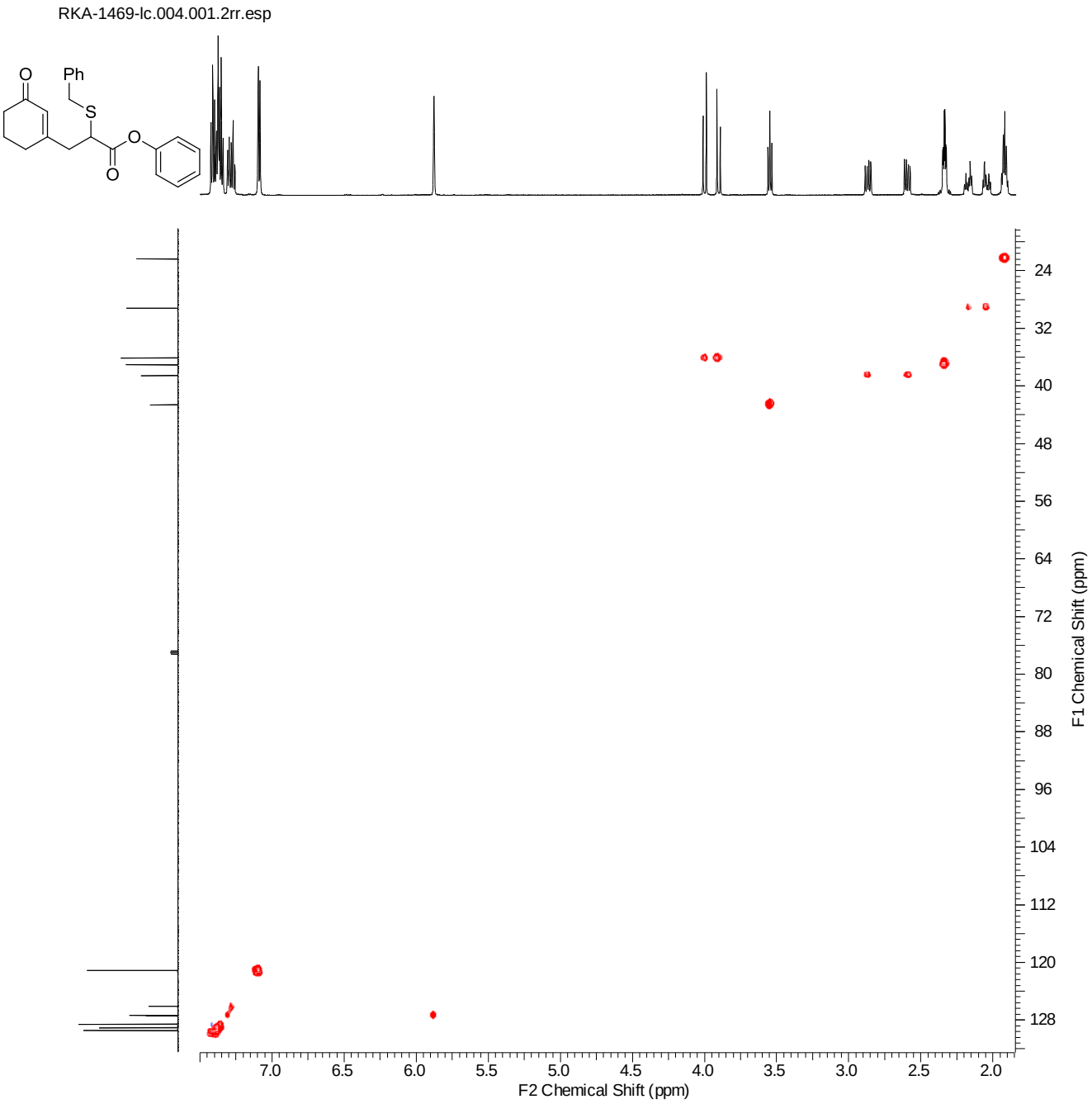


Figure S55. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6c**

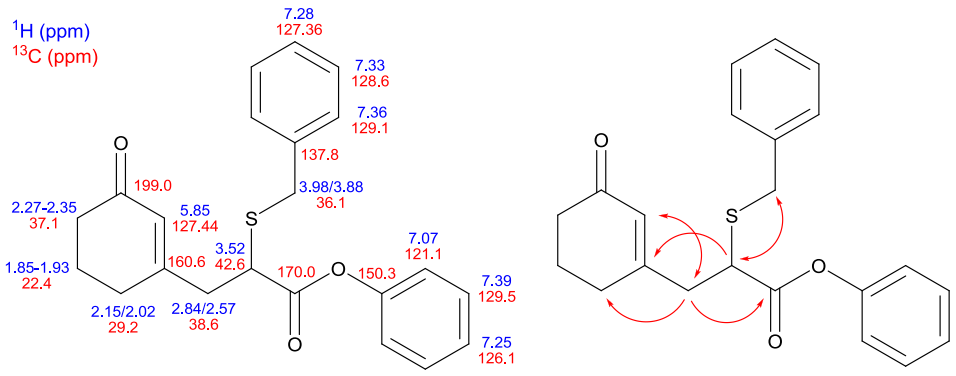


Figure S56. Spectral assignment and selected ^{1}H,^{13}C HMBC correlations for adduct **6c**

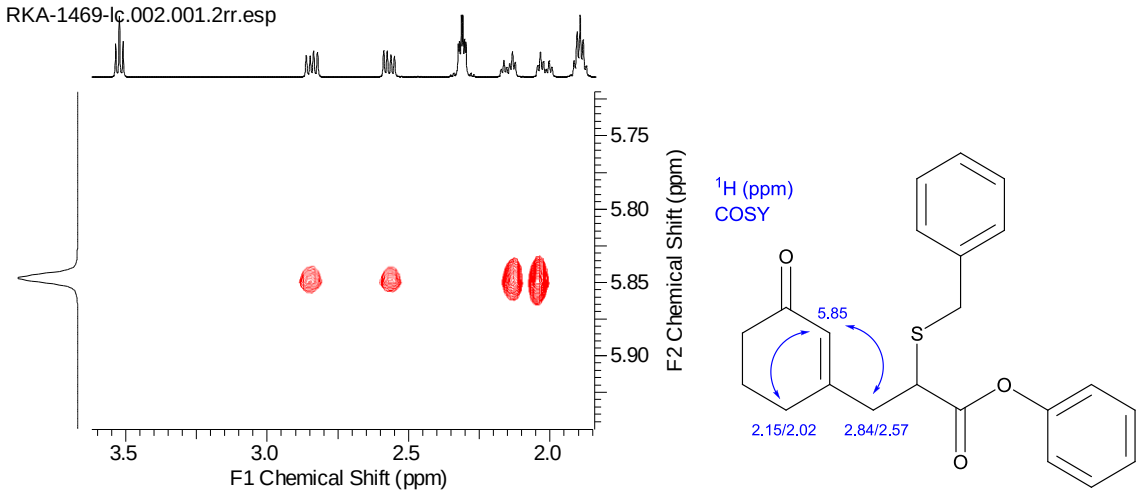


Figure S57. Section of COSY spectra for **6c** showing allylic ^{4}J couplings to 5.85 ppm resonance

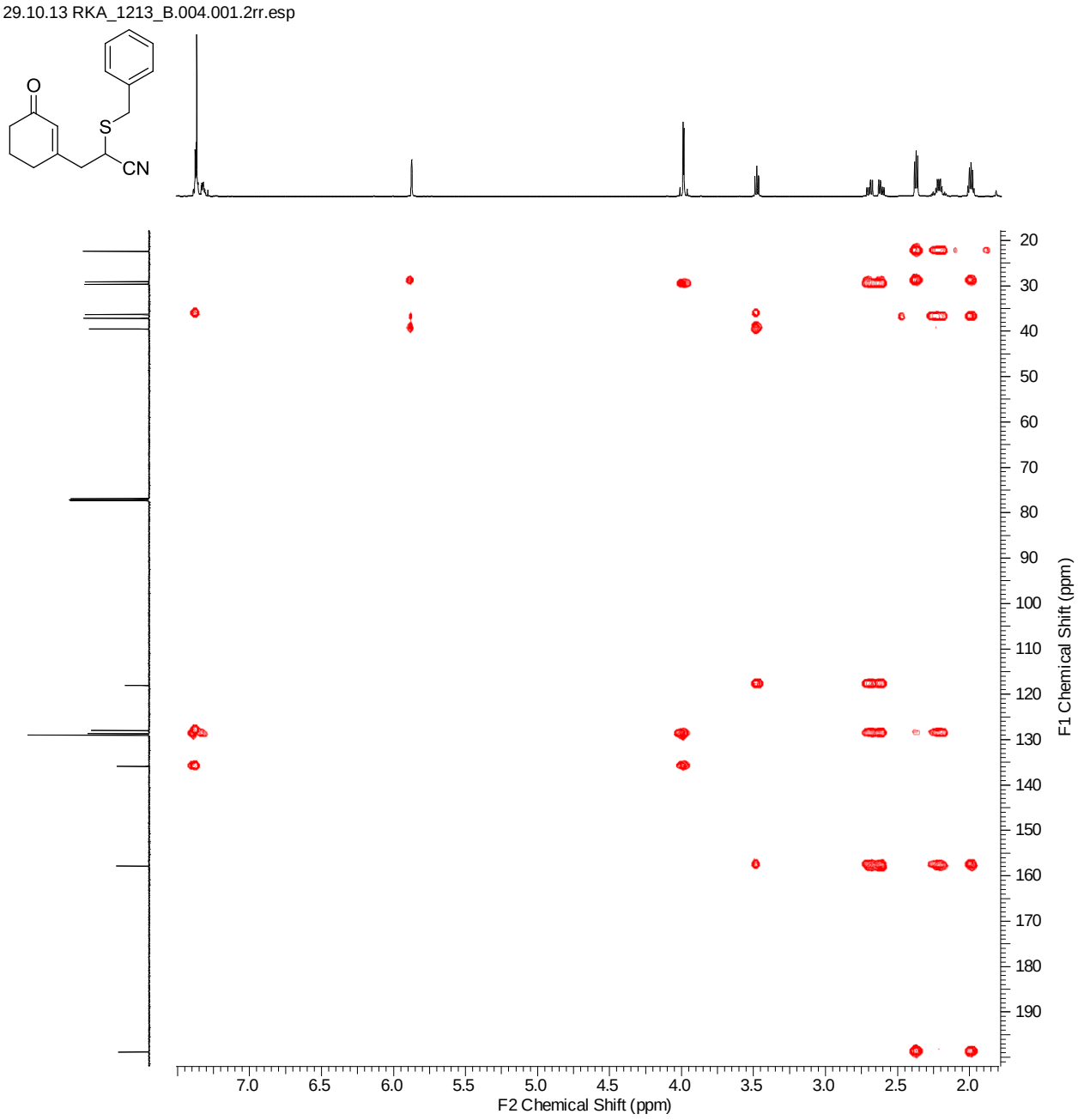


Figure S58. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6e**

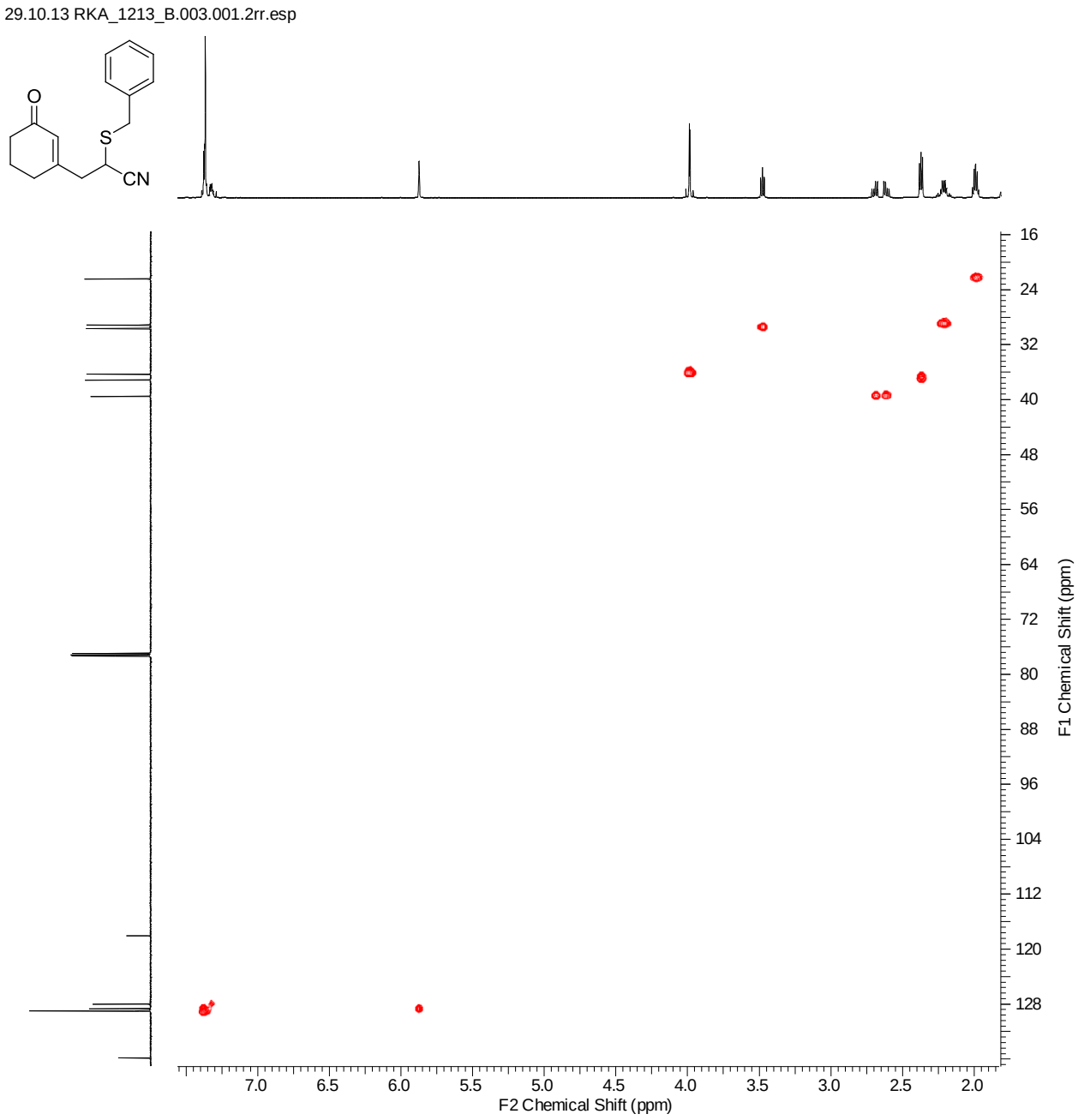


Figure S59. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6e**

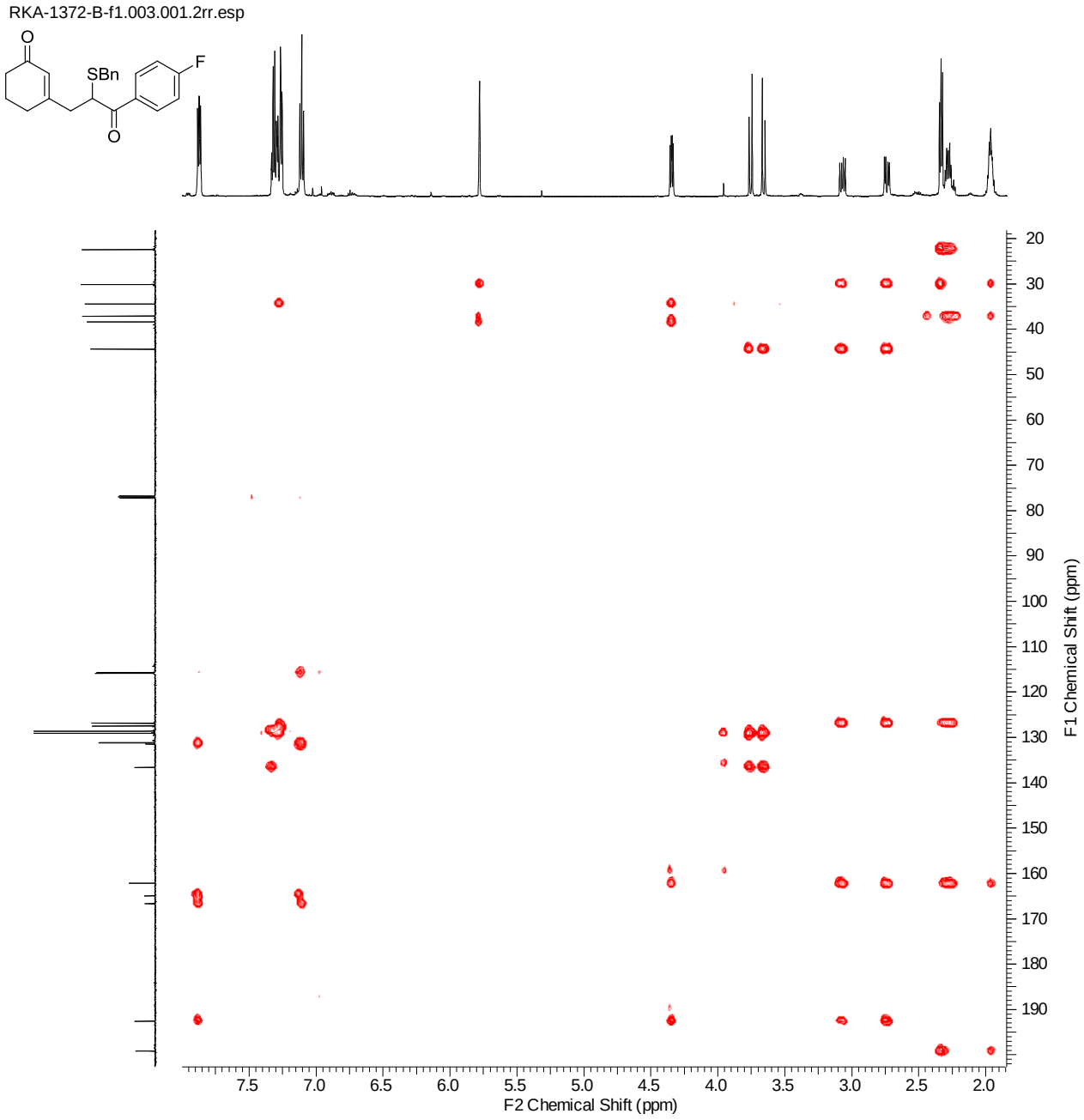


Figure S60. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6f**

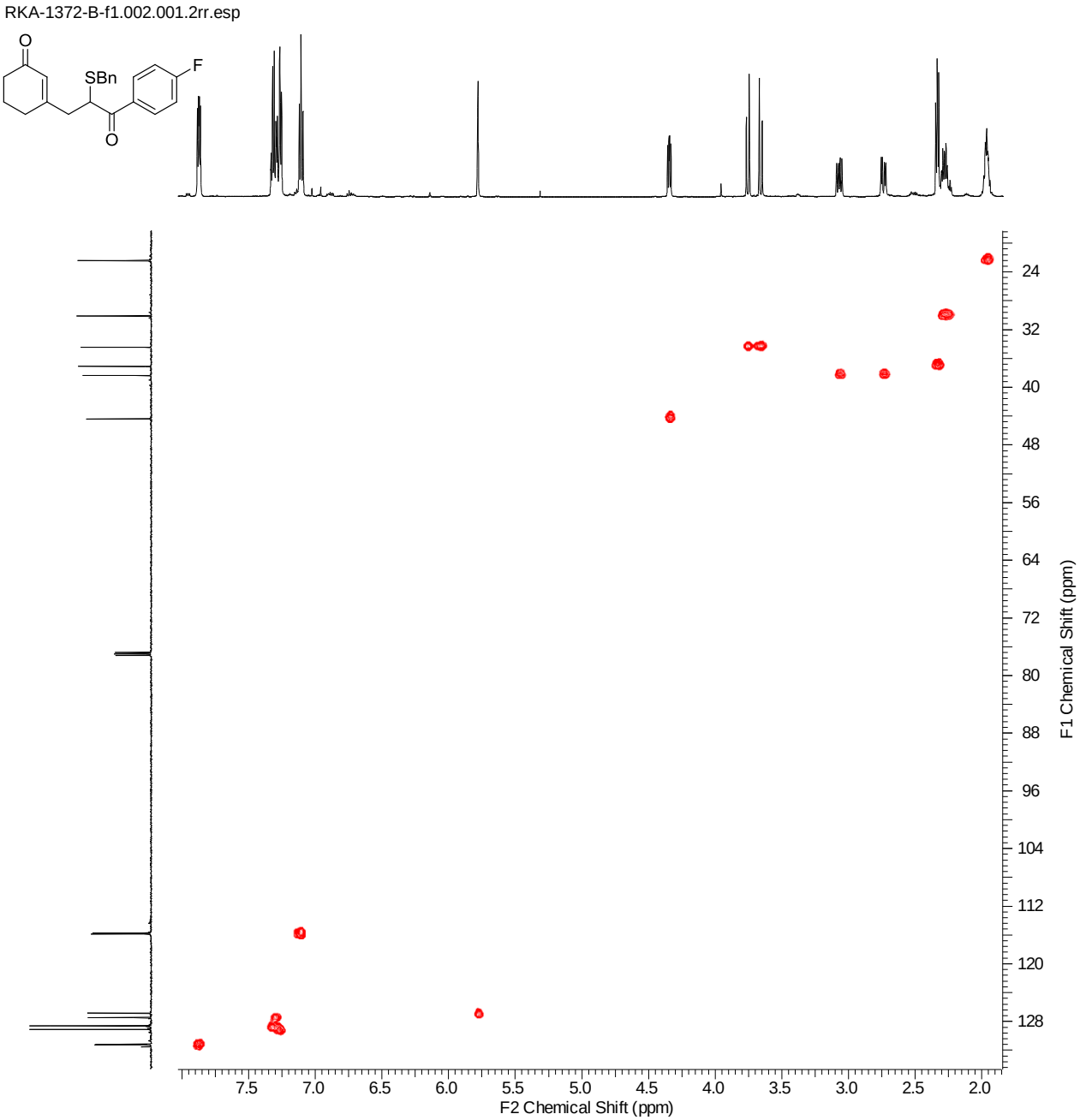


Figure S61. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6f**

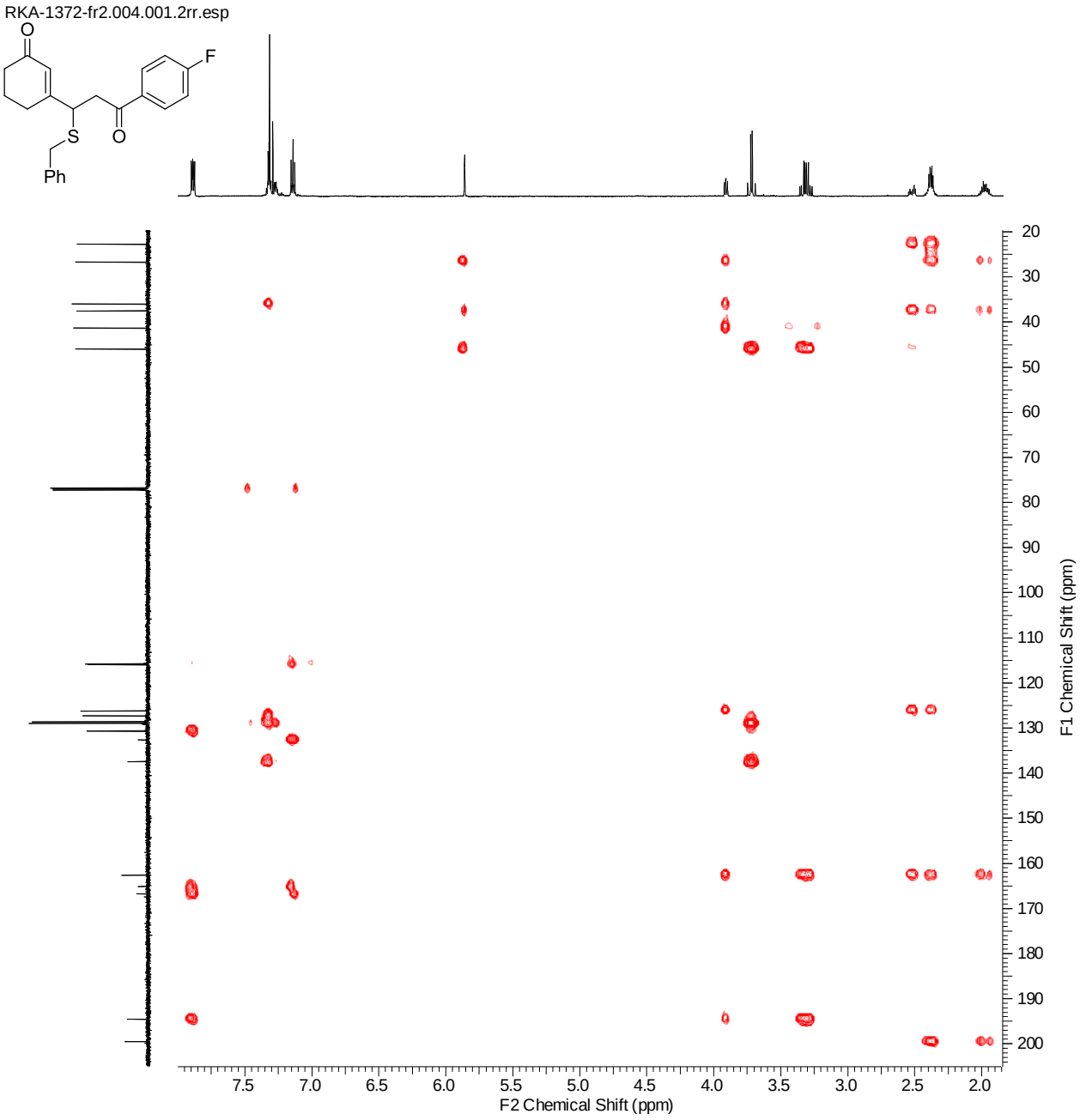


Figure S62. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **7f**

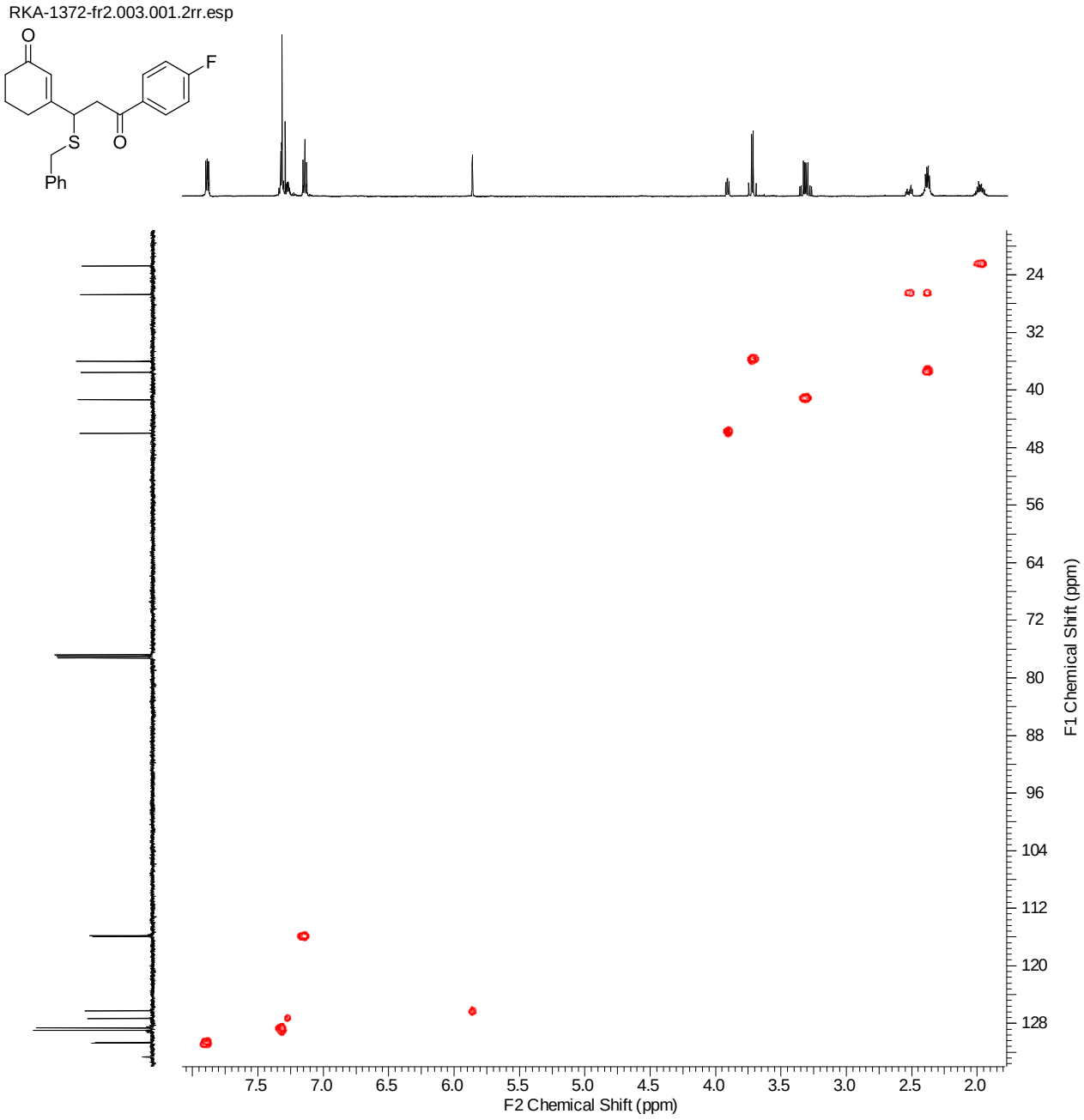


Figure S63. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **7f**

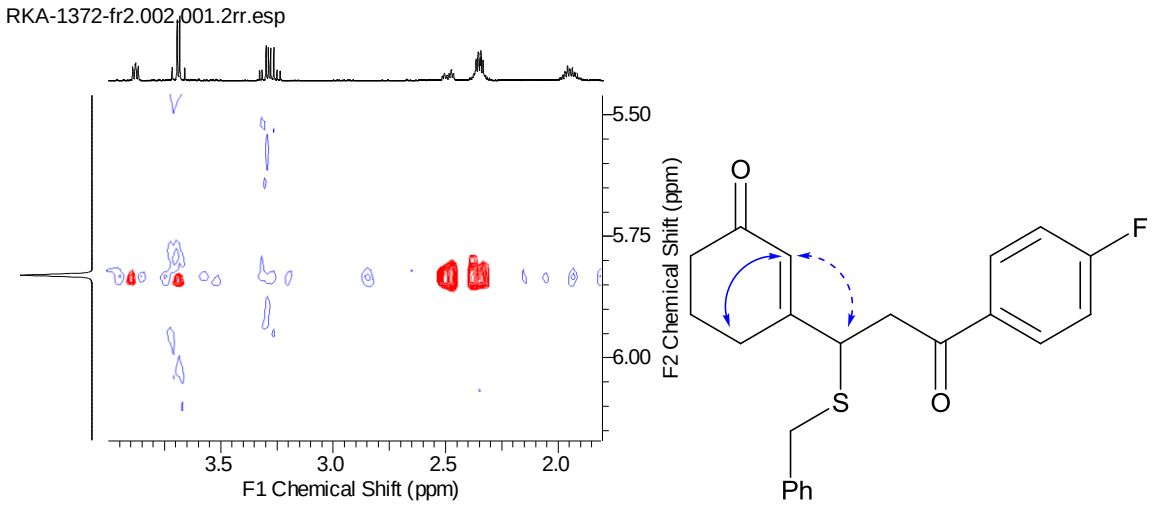


Figure S64. Section of COSY spectra for **7f** showing allylic ^{4}J couplings to 5.77 ppm resonance

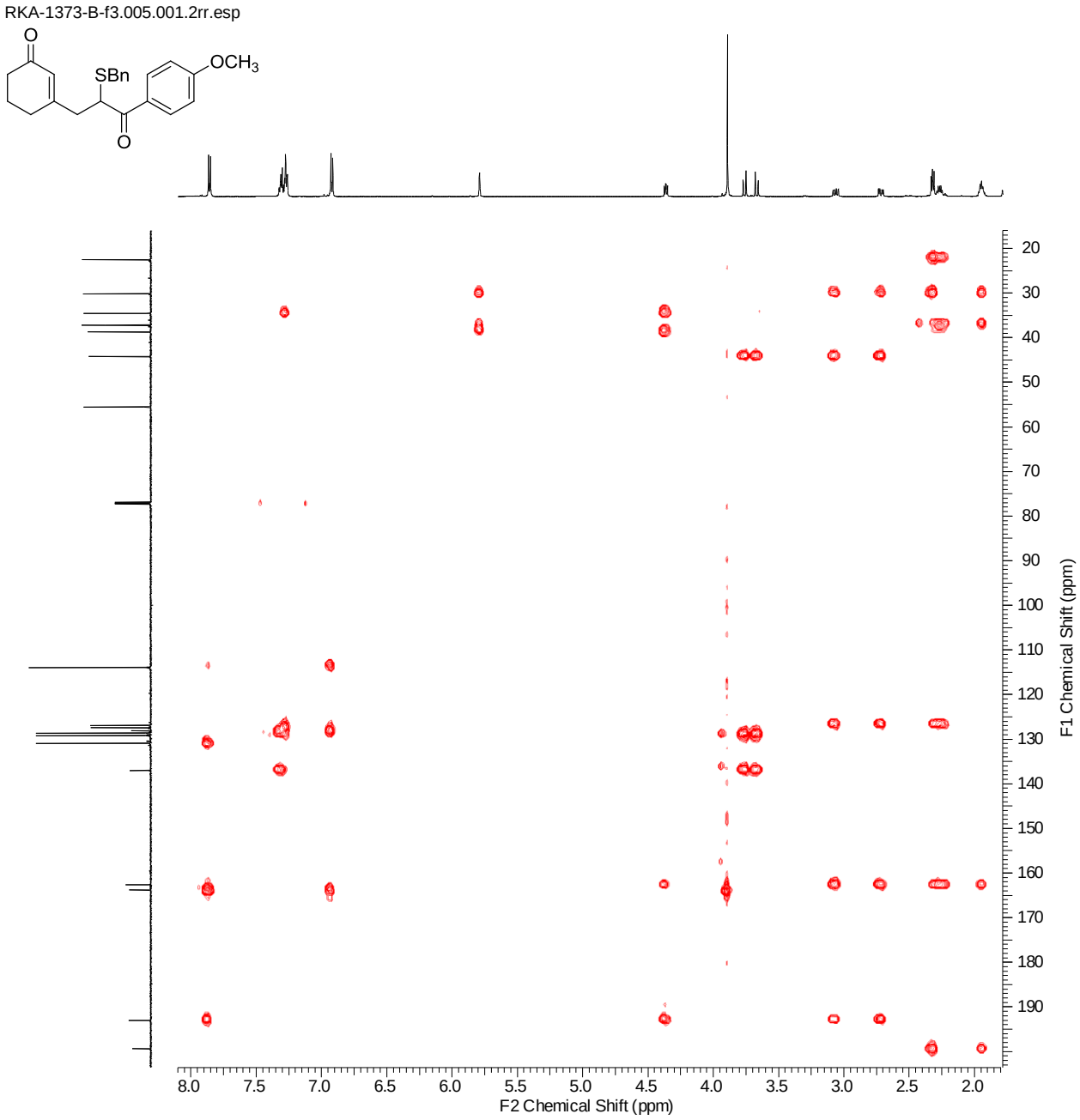


Figure S65. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6g**

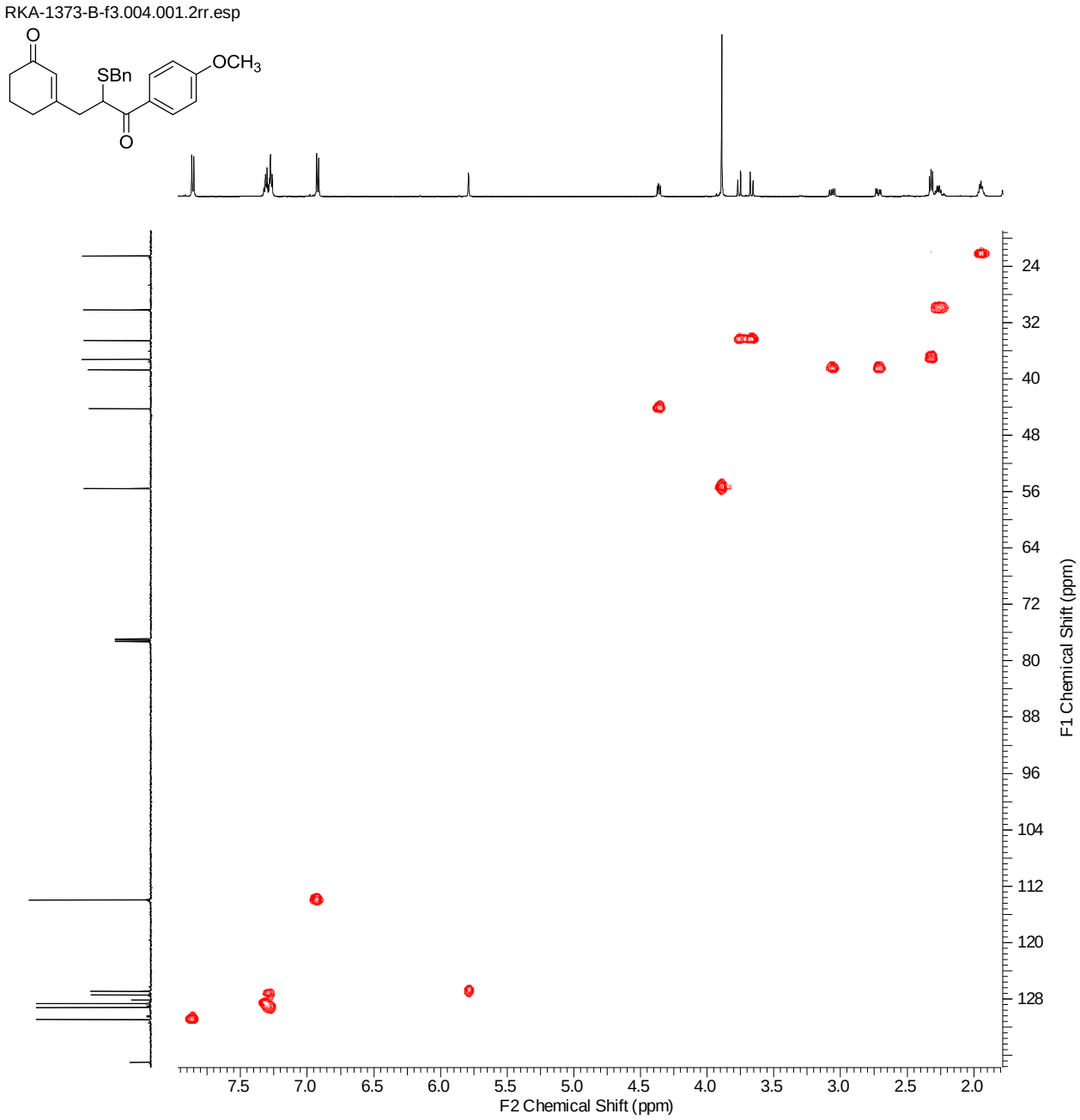


Figure S66. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6g**

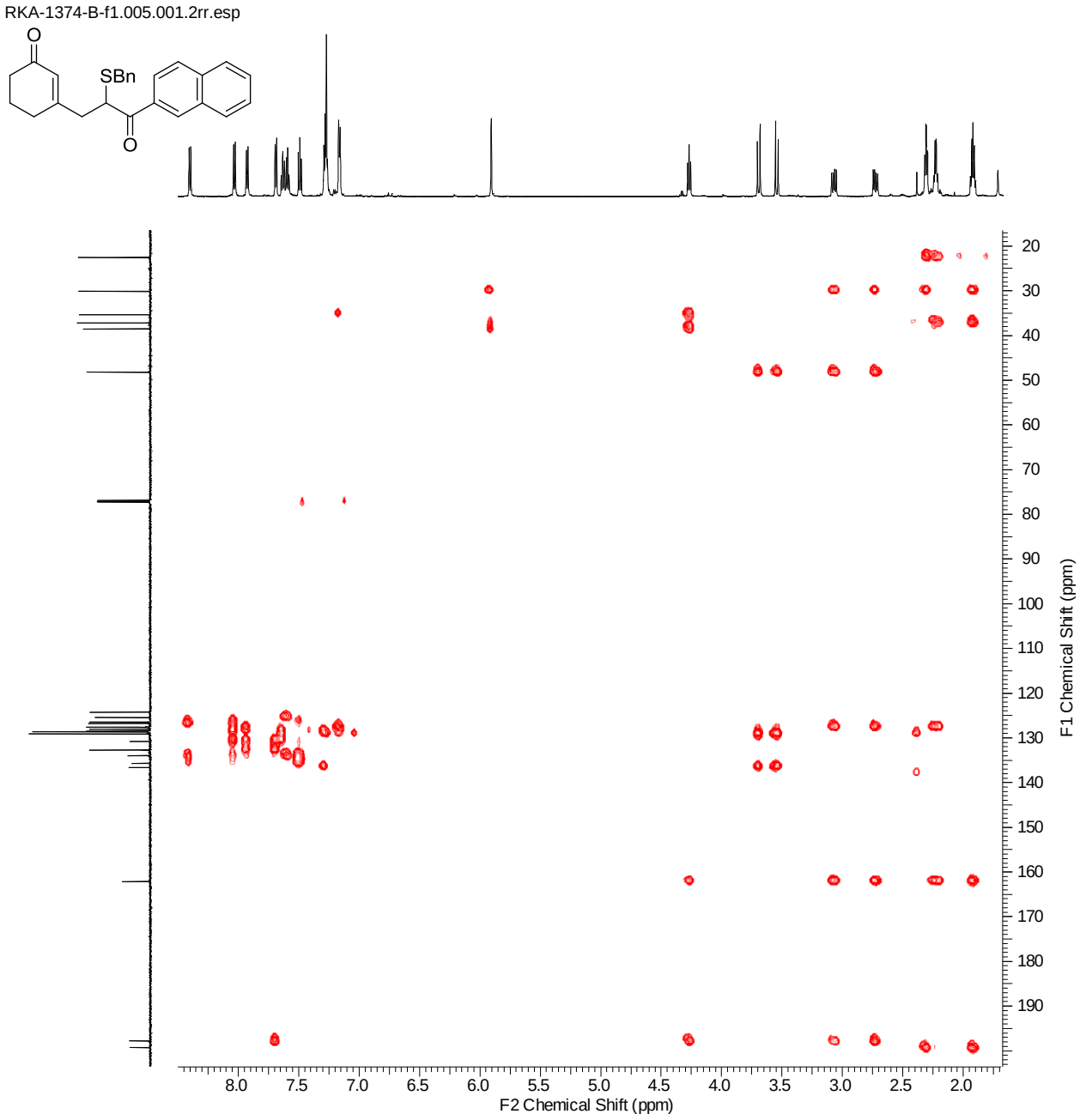


Figure S68. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6h**

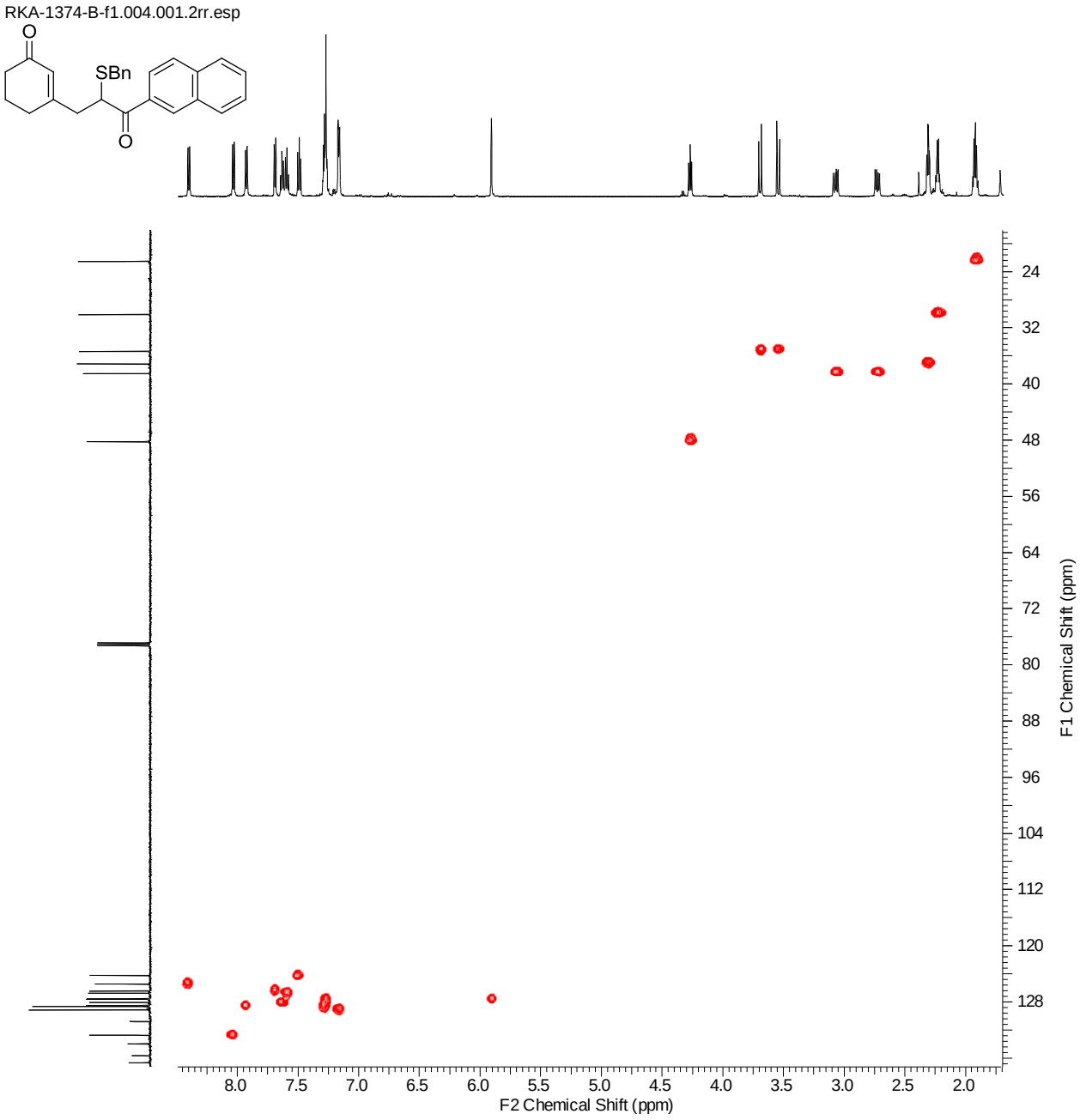


Figure S69. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **6h**

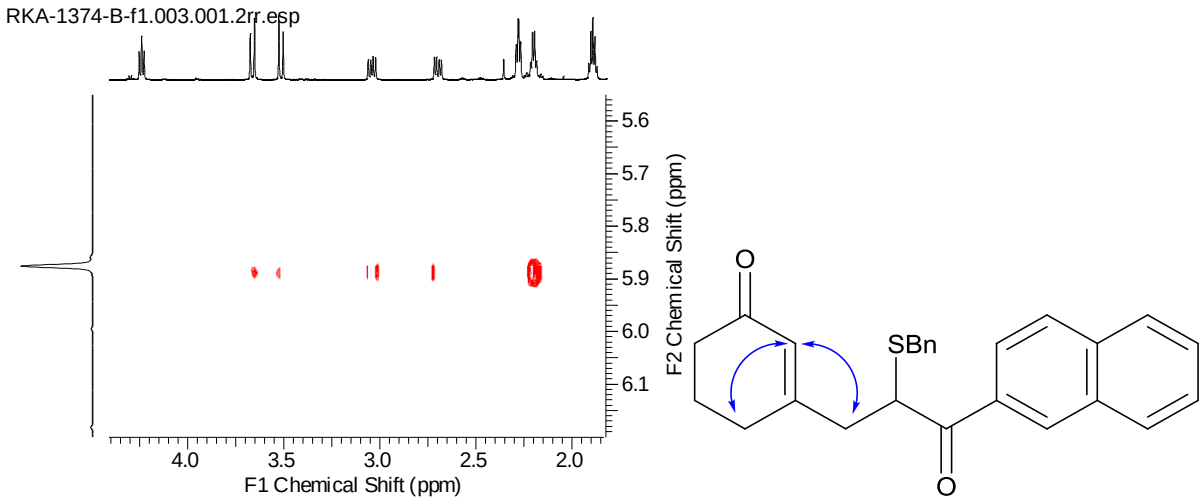


Figure S70. Section of COSY spectra for **6h** showing allylic ^{4}J couplings to 5.89 ppm resonance

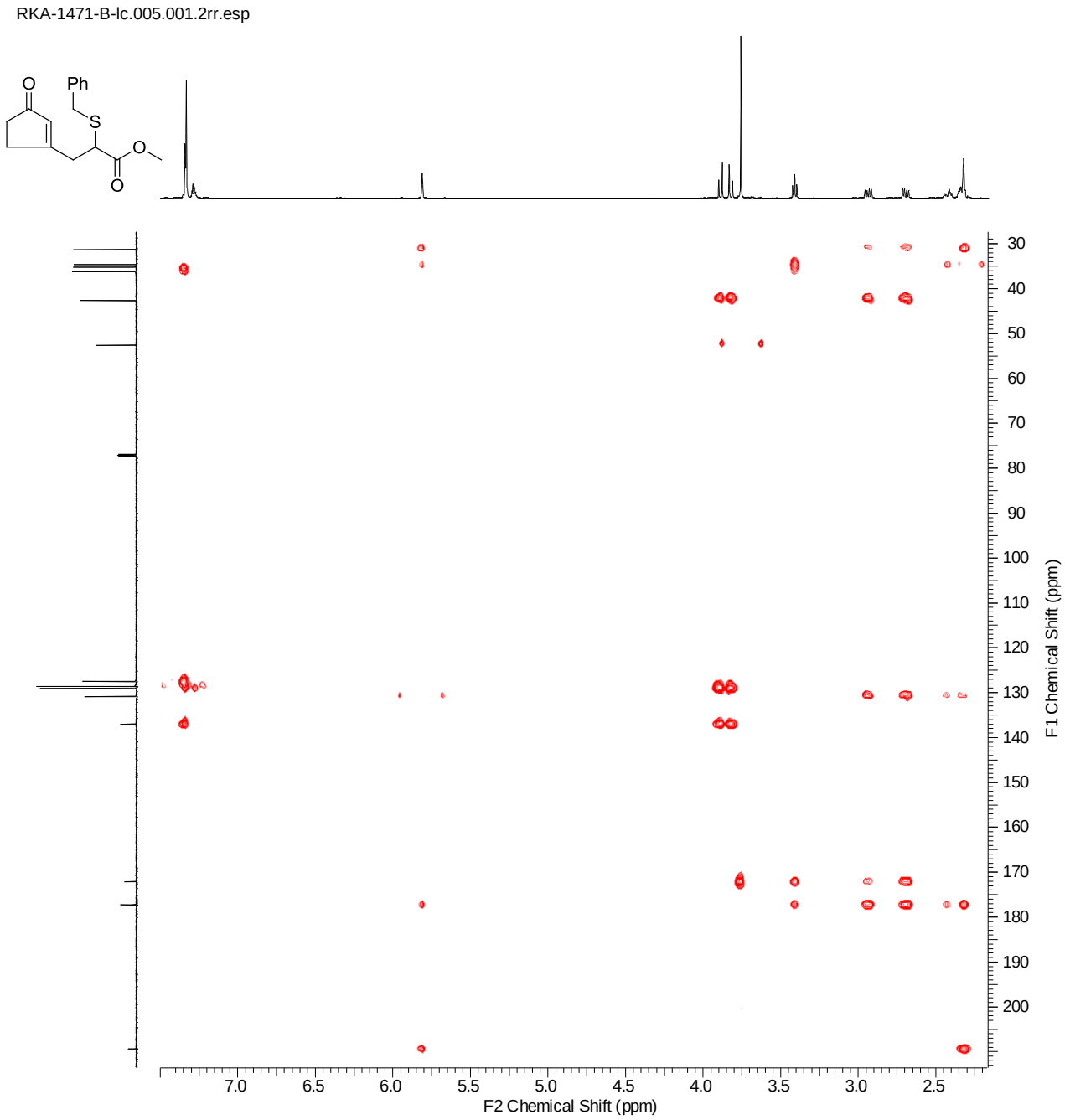


Figure S71. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **8**

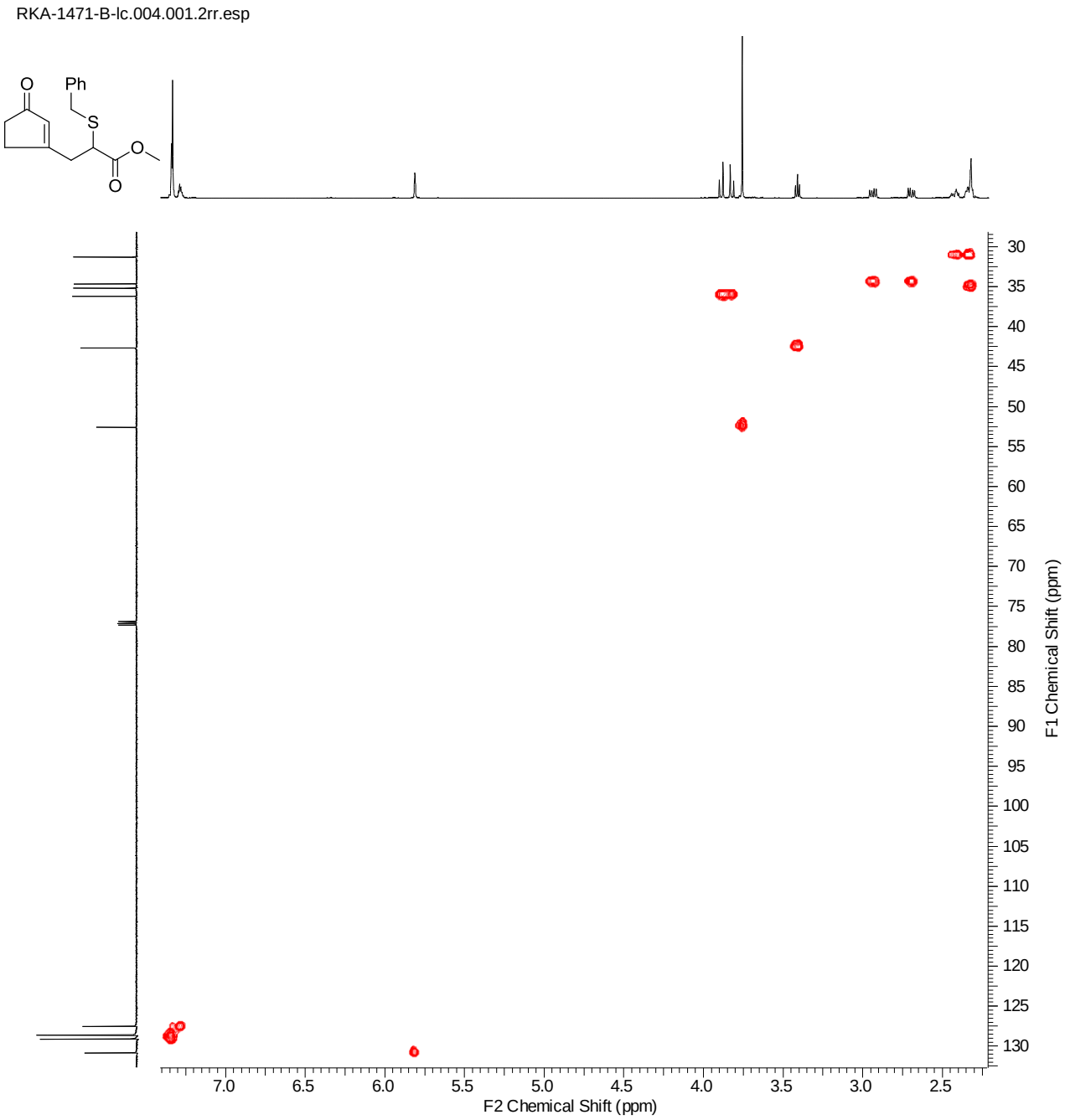


Figure S72. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **8**

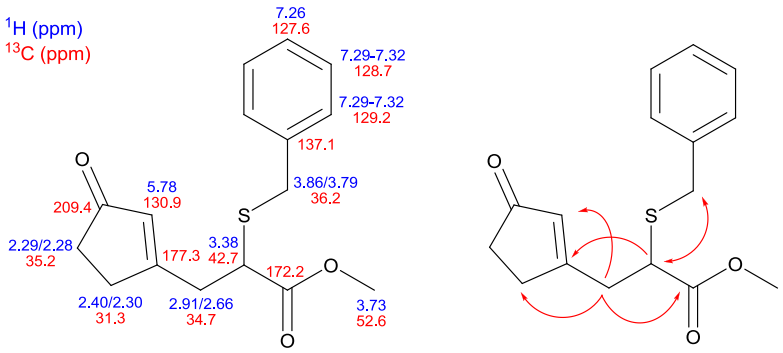


Figure S73. Spectral assignment and selected HMBC correlations for adduct **8**

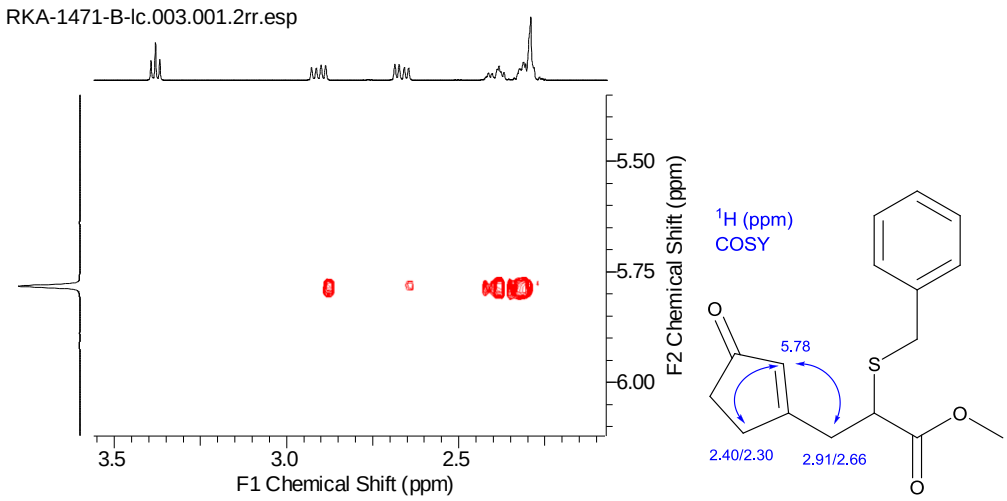


Figure S74. Section of COSY spectra for **8** showing allylic ^{4}J couplings to 5.78 ppm resonance

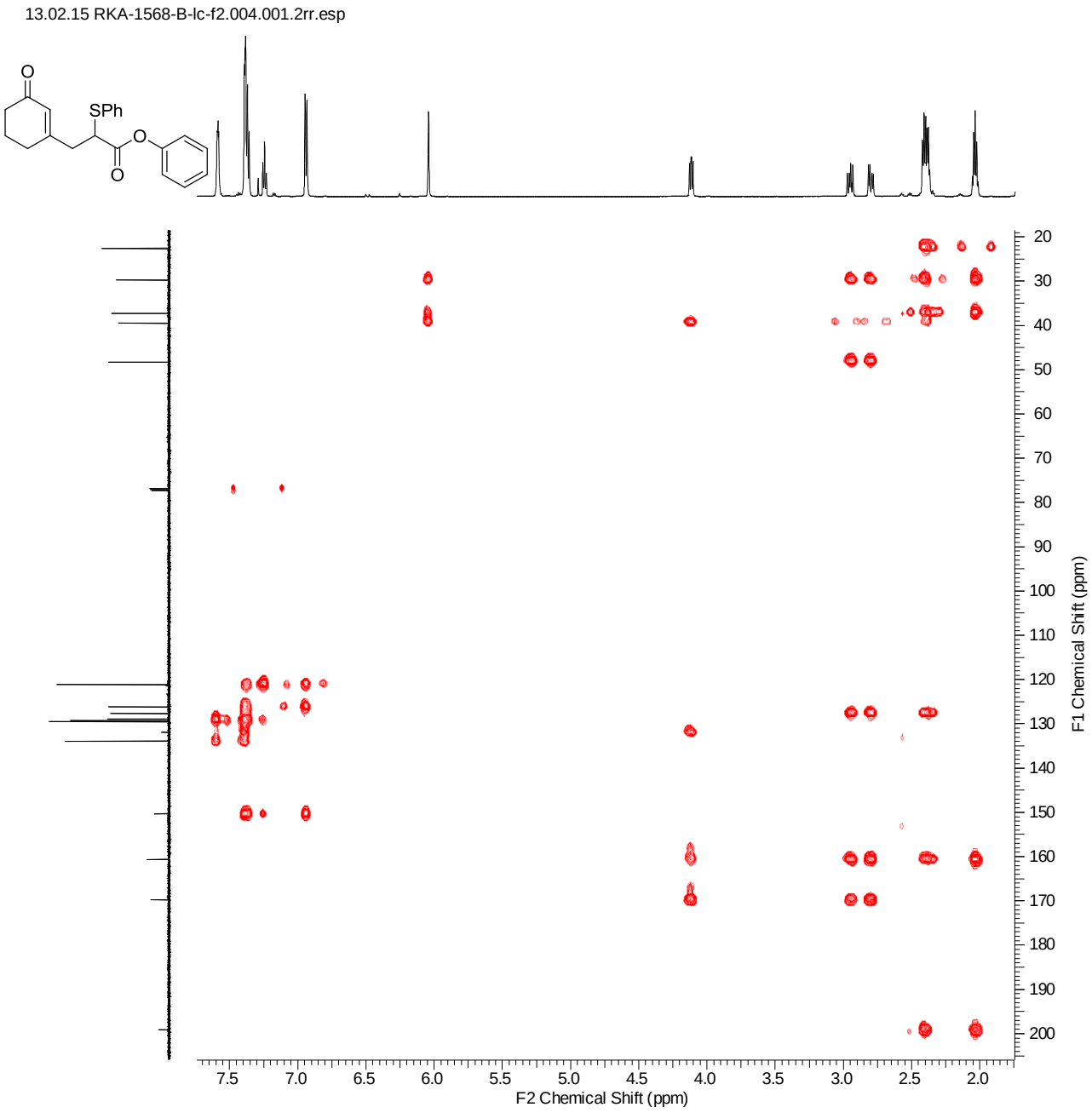


Figure S75. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **23**

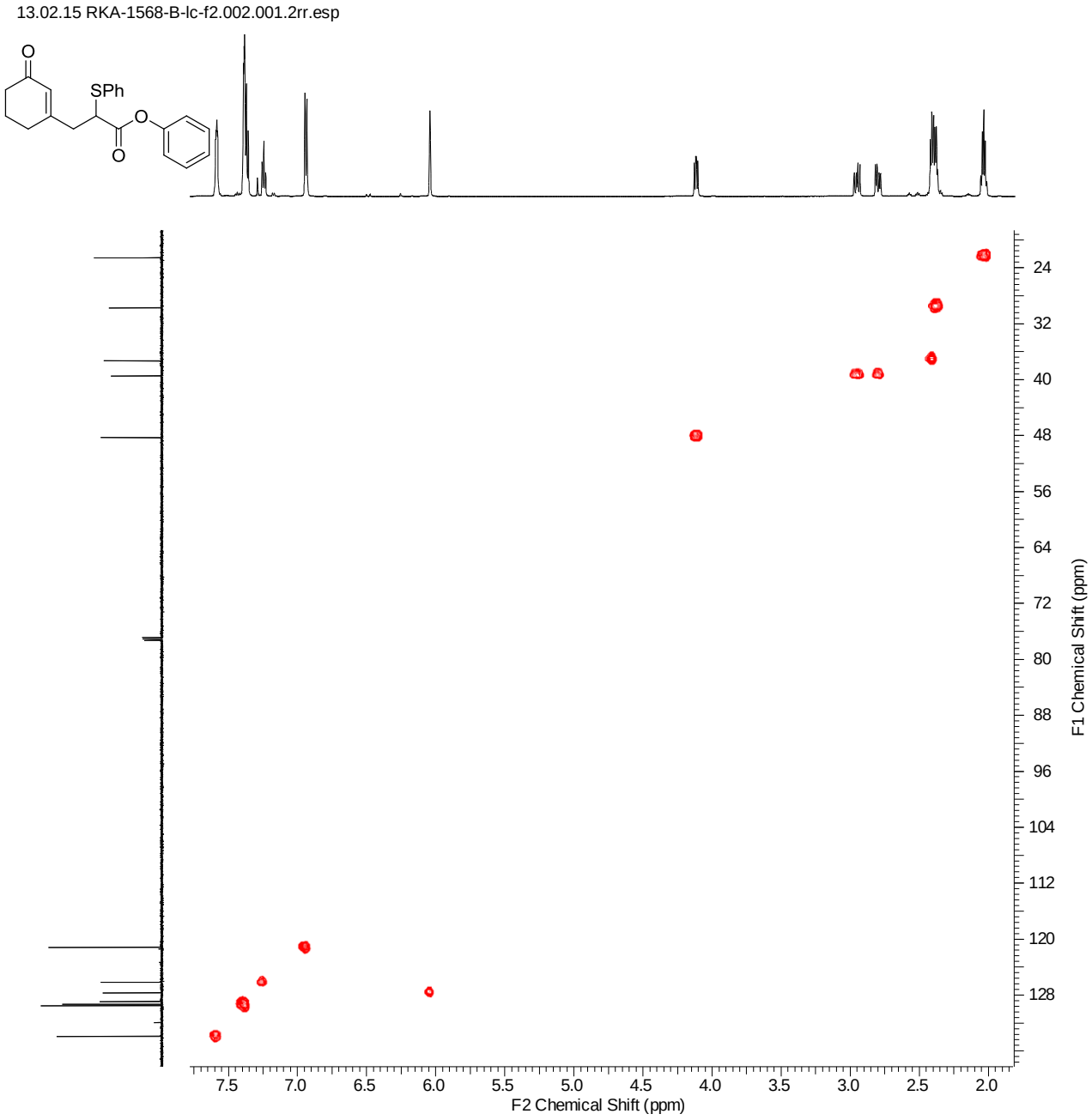


Figure S76. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **23**

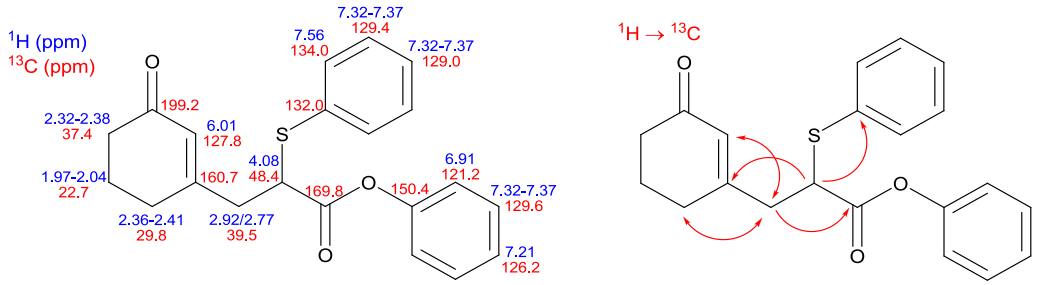


Figure S77. Spectral assignment and selected ^{1}H,^{13}C HMBC correlations for adduct **23**

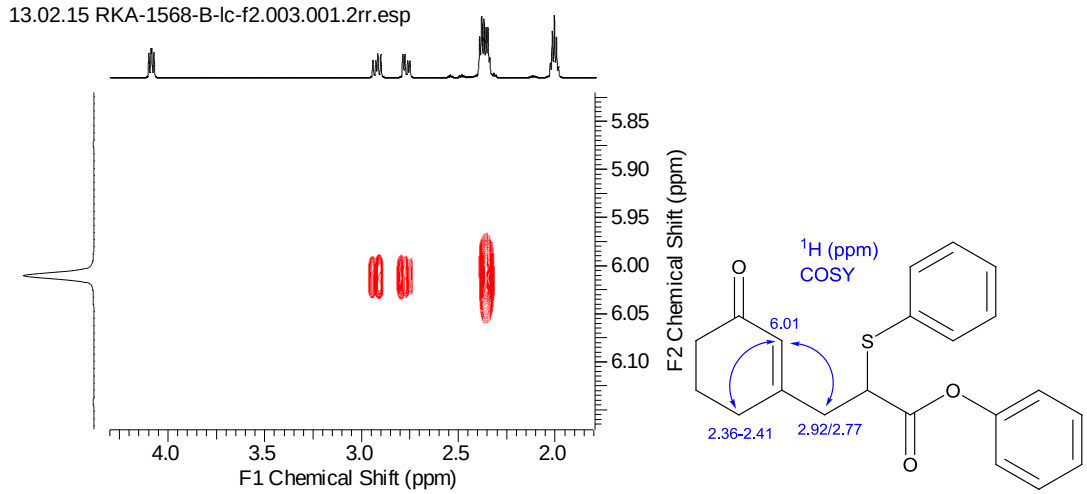


Figure S78. Section of COSY spectra for **23** showing allylic ^4J couplings to 6.01 ppm resonance

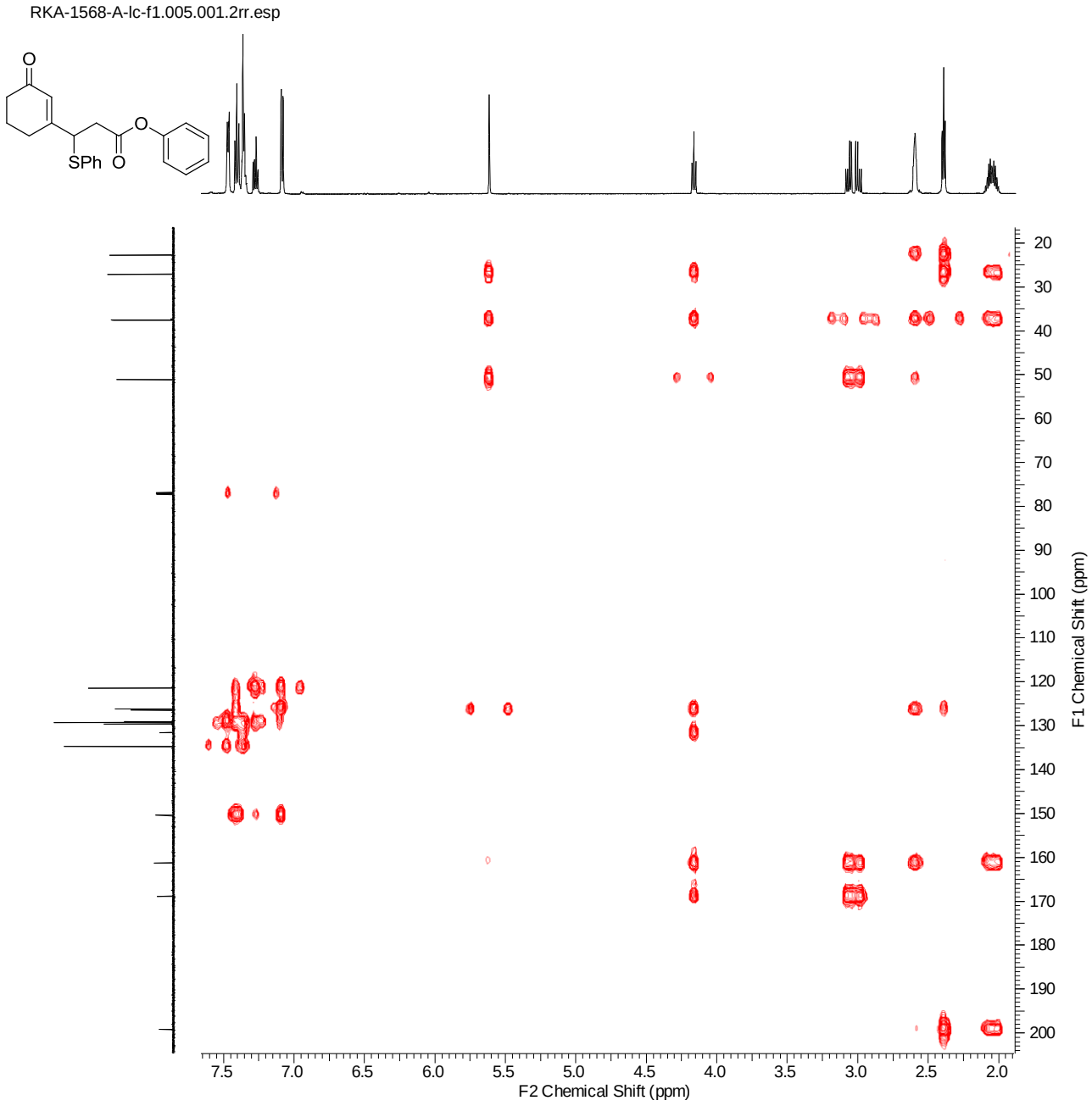


Figure S79. $^{1}H,^{13}C$ HMBC (600, 151 MHz, $CDCl_3$) spectrum for adduct **24**

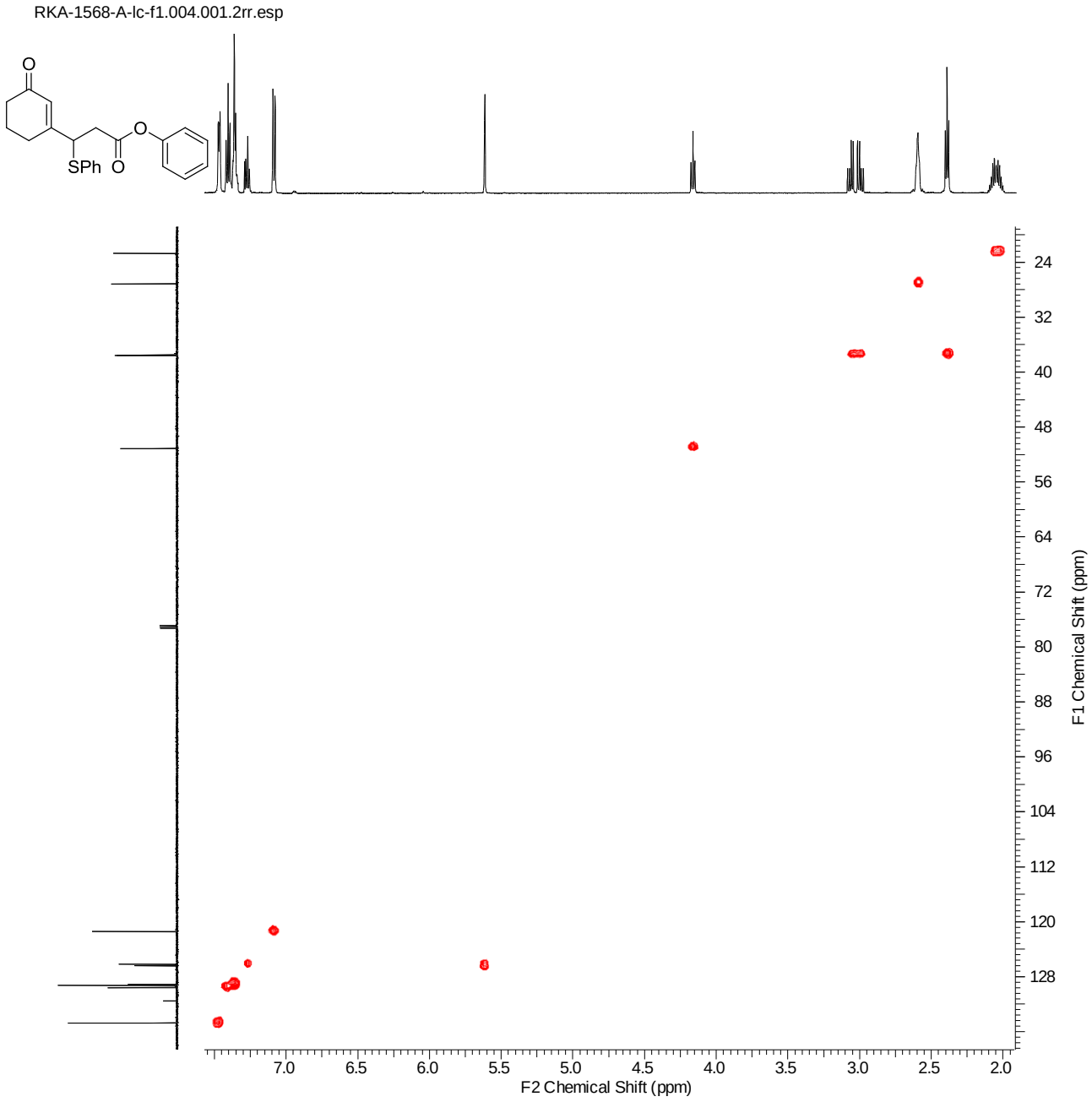


Figure S80. $^{1}H,^{13}C$ HSQC (600, 151 MHz, $CDCl_3$) spectrum for adduct **24**

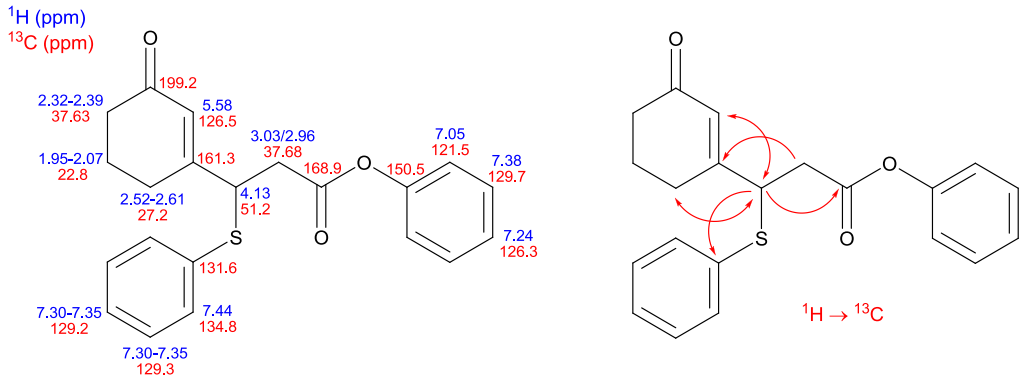


Figure S81. Spectral assignment and selected ^{1}H,^{13}C HMBC correlations for adduct **24**

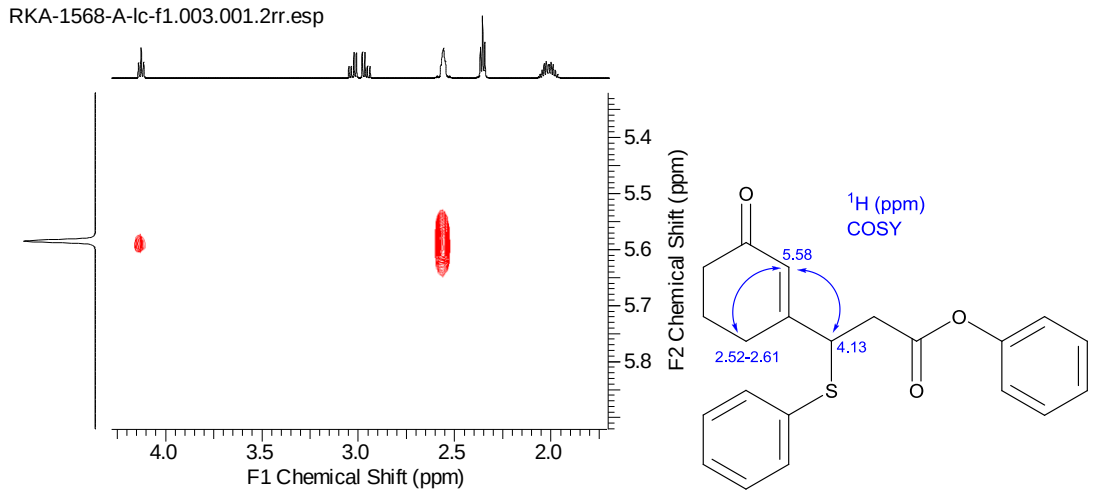
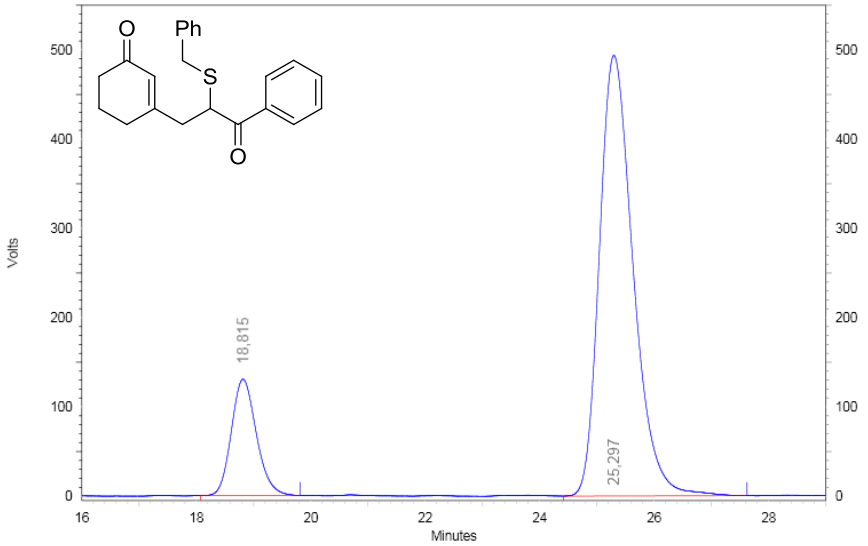


Figure S82. Section of COSY spectra for **24** showing allylic ^{4}J couplings to 5.58 ppm resonance

S10. Chiral HPLC chromatograms

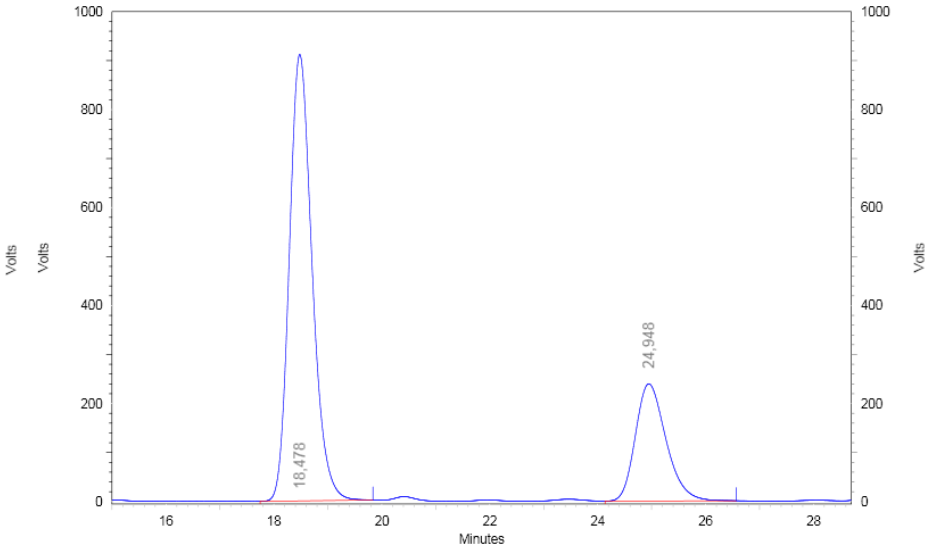
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1478-A-LC-FR3-9010.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-09 11:00:27
Printed: 2015-02-06 12:36:51



UV2000-220nm Results (System (2014-10-09 11:42:38) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
18,815	3965516	16,41	130399	20,89
25,297	20202400	83,59	493732	79,11
Totals	24167916	100,00	624131	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1478-B-LC-FR3-9010.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-09 10:28:46
Printed: 2015-02-06 12:39:37

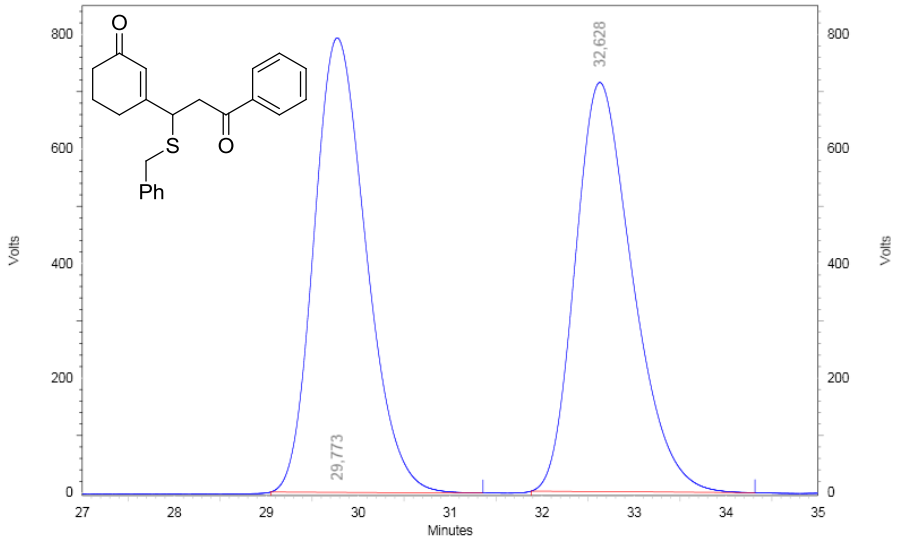


UV2000-220nm Results (System (2014-10-09 10:59:31) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
18,478	26728796	73,95	911057	79,20
24,948	9416024	26,05	239270	20,80
Totals	36144820	100,00	1150327	100,00

Figure S83. HPLC chromatogram (AD-H, hexane / IPA, 9:1, 1 mL/min) for **6b** obtained with catalysts **10a / 11b** (left) and **10d / 11b** (right)

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1114-A-rac-9010.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2013-07-28 10:51:07
Printed: 2015-02-06 13:00:11

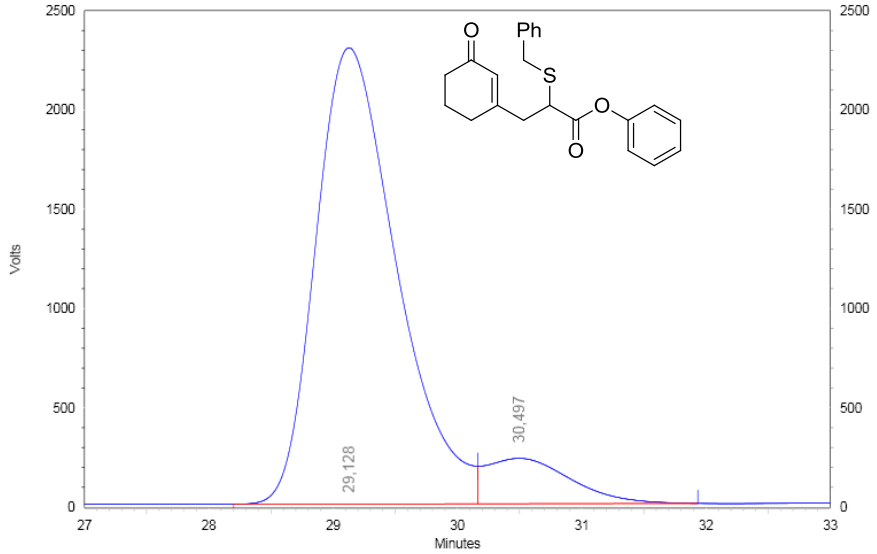


UV2000-220nm Results (System (2013-07-28 11:29:00) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
29,773	31228858	50,26	793099	52,62
32,628	30903237	49,74	714106	47,38
Totals	62132095	100,00	1507205	100,00

Figure S84. HPLC chromatogram (AD-H, hexane / IPA, 9:1, 1 mL/min) for racemic **7b**

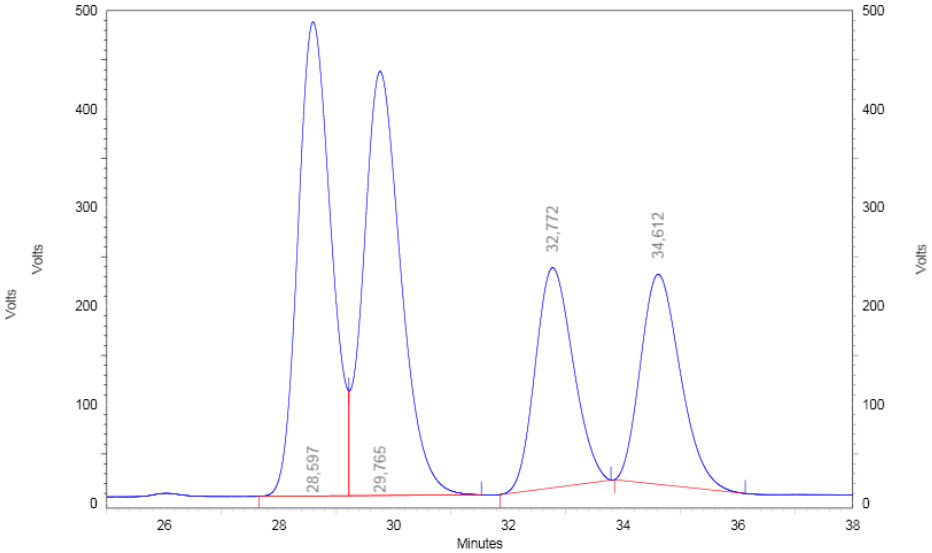
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1469-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-09 07:46:23
Printed: 2015-02-06 13:24:53



UV2000-220nm Results (System (2014-10-09 08:26:03) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
29,128	104051806	90,60	2297081	90,95
30,497	10799697	9,40	228444	9,05
Totals	114851503	100,00	2525525	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1469-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-01 09:35:35
Printed: 2015-02-06 13:22:44

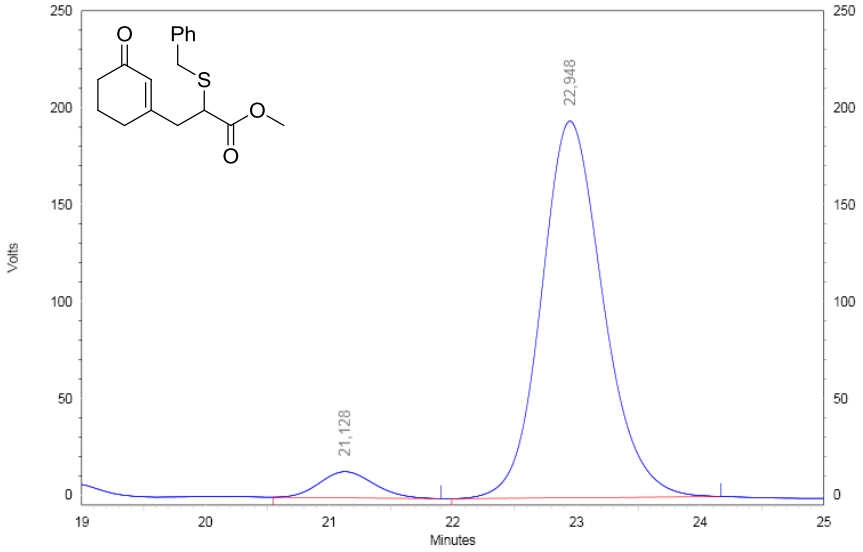


UV2000-220nm Results (System (2014-10-01 10:16:15) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
28,597	19236783	32,44	481179	35,69
29,765	19539631	32,95	430467	31,93
32,772	10232967	17,26	223322	16,56
34,612	10291731	17,36	213274	15,82
Totals	59301112	100,00	1348242	100,00

Figure S85. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **6c** obtained with **10f / 11b** (left), and a mixture of racemic **6c** with racemic **7c** obtained using DABCO (right)

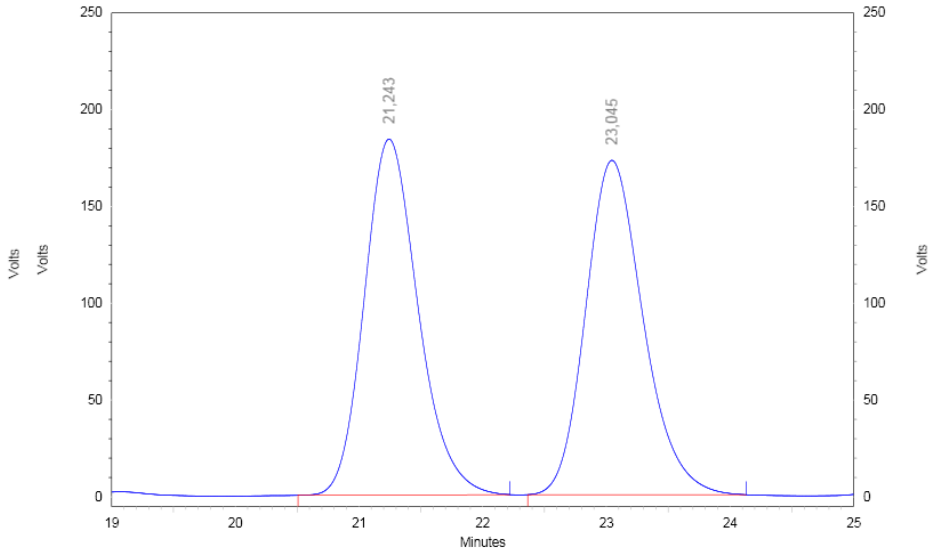
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1569-ADH-955-1-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-01-28 14:48:14
Printed: 2015-02-06 13:35:46



UV2000-220nm Results (System (2015-01-28 15:13:39) (Original))

Retention Time	Area	Area %	Height	Height %
21,128	411055	5,75	13474	6,48
22,948	6743744	94,25	194299	93,52
Totals	7154799	100,00	207773	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1569-ADH-955-1-RAC-TRUE.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-01-28 15:14:56
Printed: 2015-02-06 13:31:38

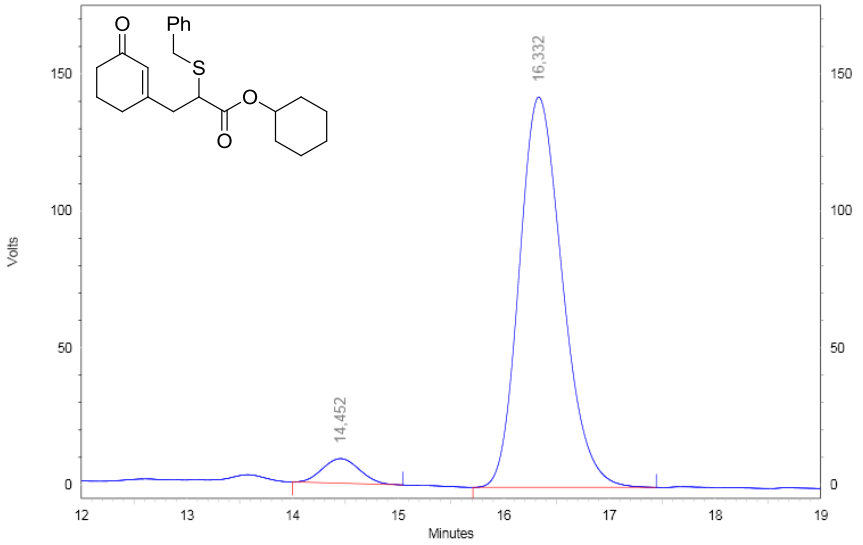


UV2000-220nm Results (System (2015-01-28 15:44:22) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
21,243	5558750	49,89	183784	51,57
23,045	5583044	50,11	172620	48,43
Totals	11141794	100,00	356404	100,00

Figure S86. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **6d** obtained with **10f / 11b** (left), and a racemic compound (right)

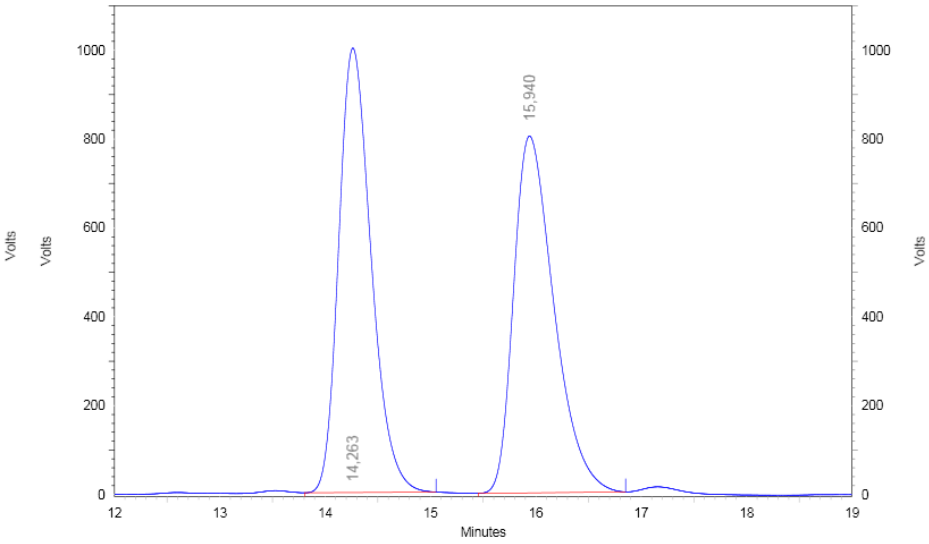
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1449-ADH-955-1-RECRYST.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-01-20 10:22:39
Printed: 2015-02-06 13:04:52



UV2000-220nm Results (System (2015-01-20 10:41:43) (Original))

Retention Time	Area	Area %	Height	Height %
14,452	218943	5,14	8982	5,93
16,332	4042289	94,86	142516	94,07
Totals	4261232	100,00	151498	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1449-ADH-955-1-RECRYST-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-01-20 10:43:28
Printed: 2015-02-06 13:03:12

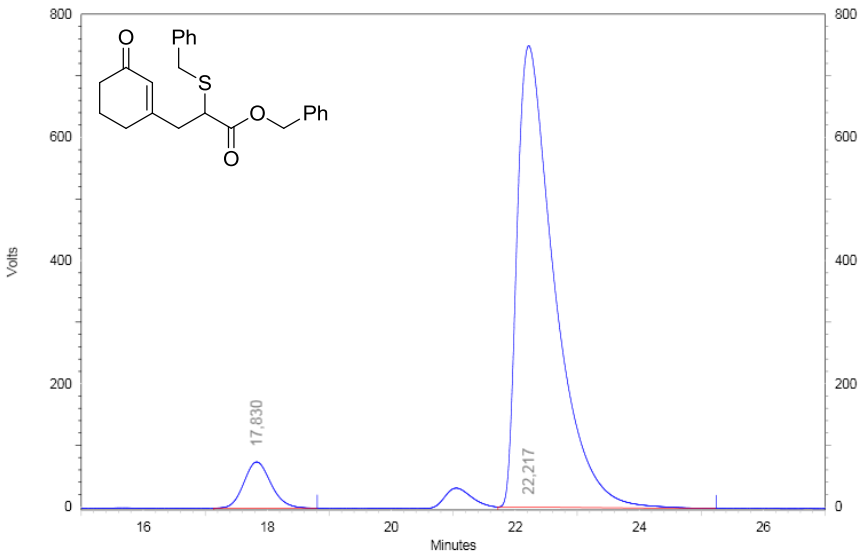


UV2000-220nm Results (System (2015-01-20 11:12:34) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
14,263	21434895	50,10	1000472	55,47
15,940	21348843	49,90	803164	44,53
Totals	42783738	100,00	1803636	100,00

Figure S87. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **6j** obtained with **10f / 11b** after single crystallization from DCM/cyclohexane (left), and a racemic compound (right)

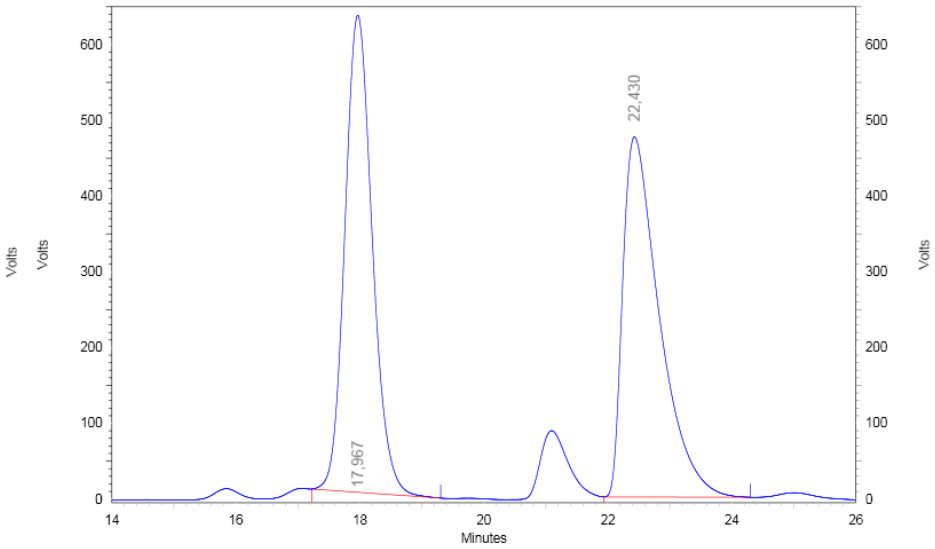
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1499-ADH-9010-1-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 13:36:28
Printed: 2015-02-06 12:57:31



UV2000-220nm Results (System (2014-11-17 14:12:54) (Original))

Retention Time	Area	Area %	Height	Height %
17,830	2272463	6,77	74959	9,10
22,217	31287454	93,23	749168	90,90
Totals	33559917	100,00	824127	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1499-ADH-9010-1-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 13:05:13
Printed: 2015-02-06 12:55:54

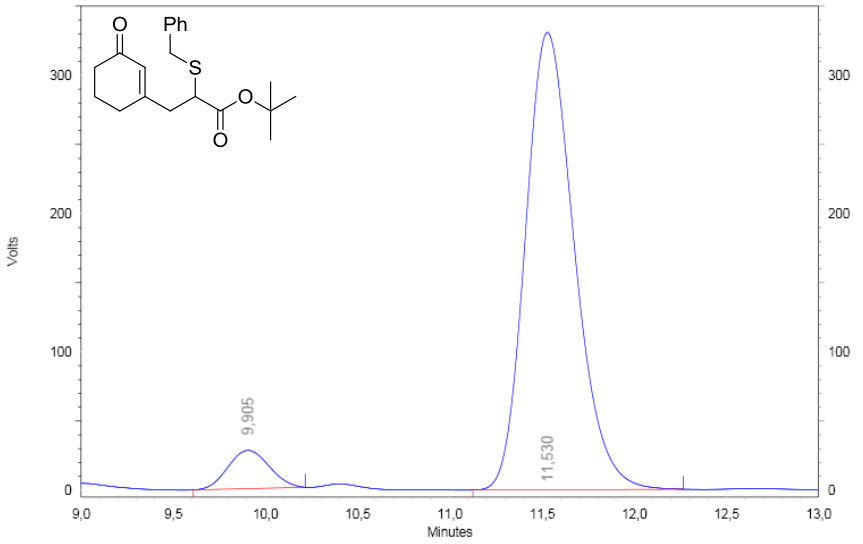


UV2000-220nm Results (System (2014-11-17 13:34:57) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
17,967	19358568	49,86	629936	56,98
22,430	19467878	50,14	475613	43,02
Totals	38826446	100,00	1105549	100,00

Figure S88. HPLC chromatograms (AD-H, hexane / IPA, 9:1, 1 mL/min) for **6k** obtained with **10f / 11b** (left), and a racemic compound (right)

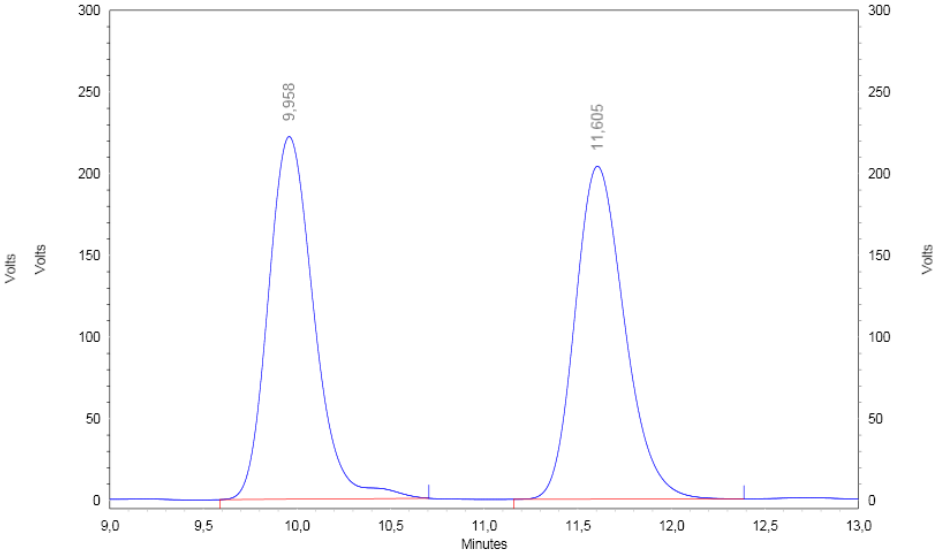
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1381-B.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-06-20 12:07:49
Printed: 2015-02-06 13:27:57



UV2000-220nm Results (System (2014-06-20 12:37:12)) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
9,905	430618	6,60	27661	7,72
11,530	6092157	93,40	330771	92,28
Totals	6522775	100,00	358432	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1381-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-06-20 11:45:52
Printed: 2015-02-06 13:29:42

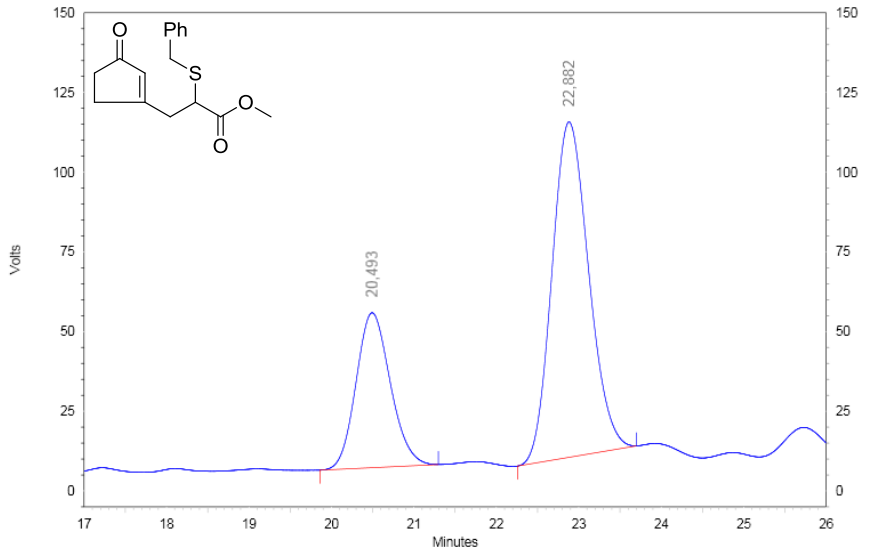


UV2000-220nm Results (System (2014-06-20 12:06:47)) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
9,958	3763252	50,11	221911	52,13
11,605	3747176	49,89	203813	47,87
Totals	7510428	100,00	425724	100,00

Figure S89. HPLC chromatograms (AD-H, hexane / IPA, 97:3, 1.0 mL/min) for **6l** obtained with **10f / 11b** (left), and a racemic compound (right)

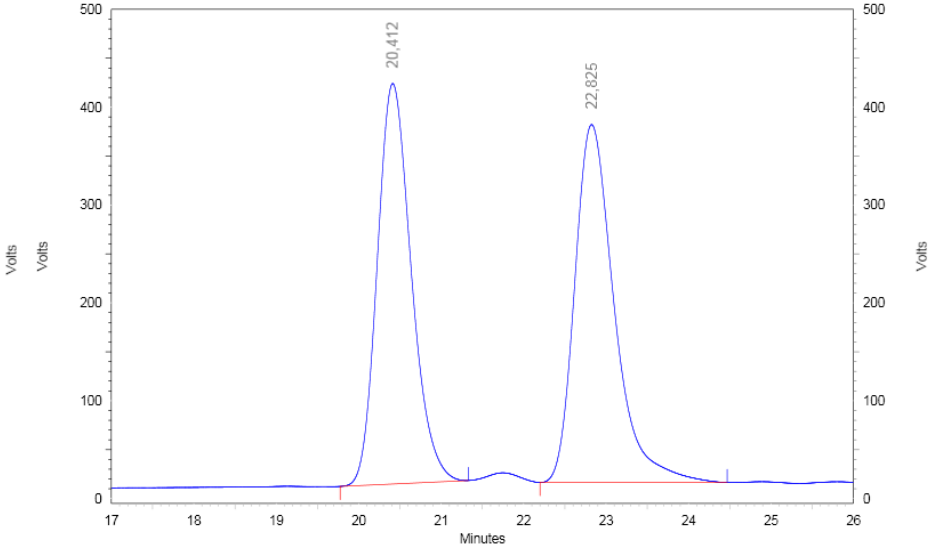
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1471-B-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-02 14:19:23
Printed: 2015-02-06 12:44:41



UV2000-220nm Results (System (2014-10-02 14:46:46) (Original))

Retention Time	Area	Area %	Height	Height %
20,493	1404484	30,16	48609	31,60
22,882	3252008	69,84	105198	68,40
Totals	4656492	100,00	153807	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1471-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-02 13:43:10
Printed: 2015-02-06 12:42:08

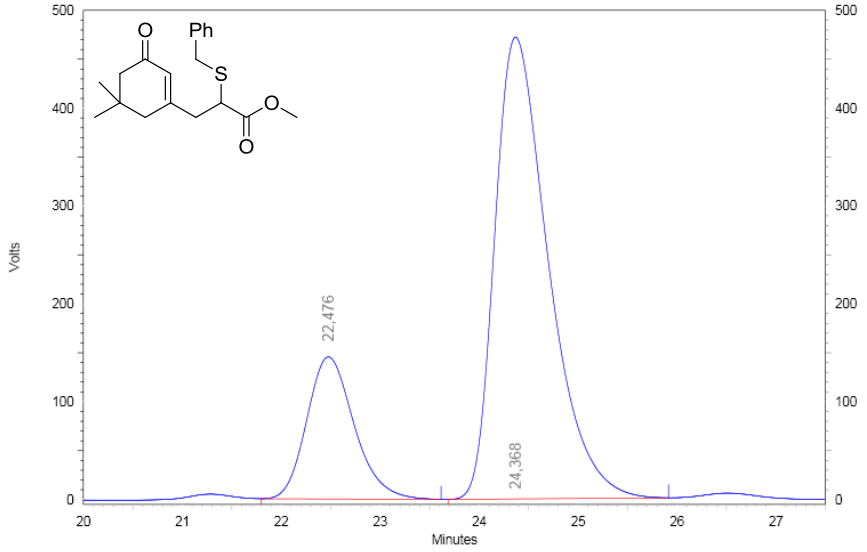


UV2000-220nm Results (System (2014-10-02 14:17:36) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
20,412	11713424	49,01	409321	52,80
22,825	12188890	50,99	365860	47,20
Totals	23902314	100,00	775181	100,00

Figure S90. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **8** obtained with **10f / 11b** (left), and a racemic compound (right)

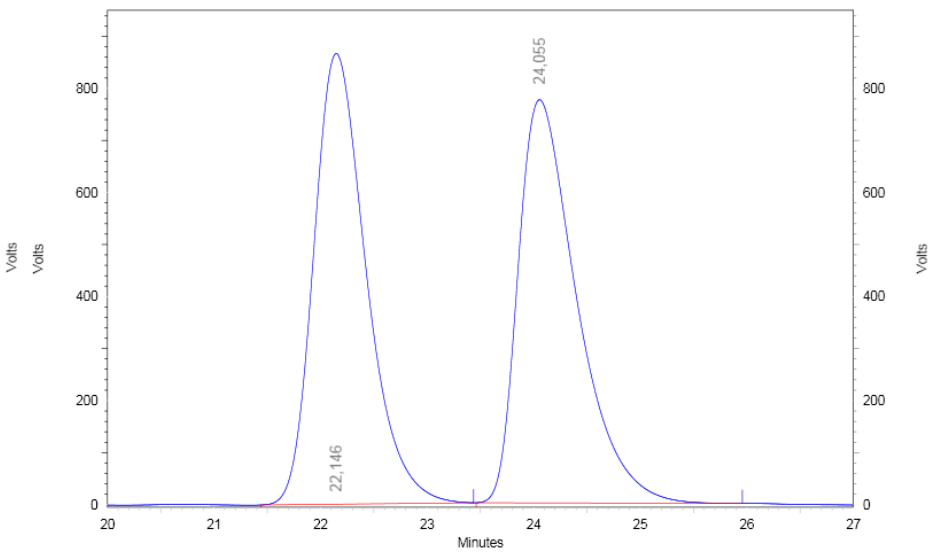
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1521-B-ADH-973-08-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 12:08:15
Printed: 2015-02-06 12:53:54



UV2000-220nm Results (System (2014-11-17 12:35:47) (Original))

Retention Time	Area	Area %	Height	Height %
22,476	4817314	21,35	145175	23,53
24,368	17742576	78,65	471902	76,47
Totals	22559890	100,00	617077	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1521-ADH-973-08-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 10:55:06
Printed: 2015-02-06 12:51:26

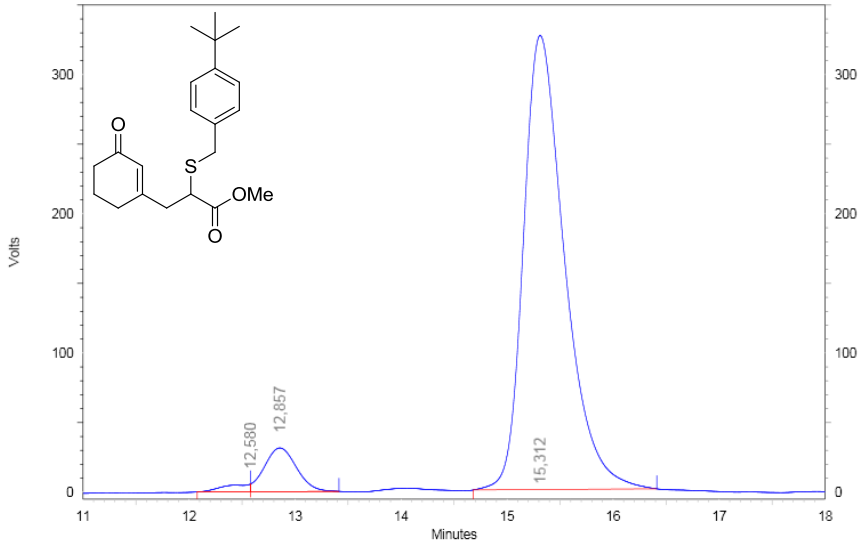


UV2000-220nm Results (System (2014-11-17 11:29:50) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
22,146	29617579	50,07	866352	52,78
24,055	29530936	49,93	774938	47,22
Totals	59148515	100,00	1641290	100,00

Figure S91. HPLC chromatograms (AD-H, hexane / IPA, 97:3, 0.8 mL/min) for **9** obtained with **10f / 11b** (left), and a racemic compound (right)

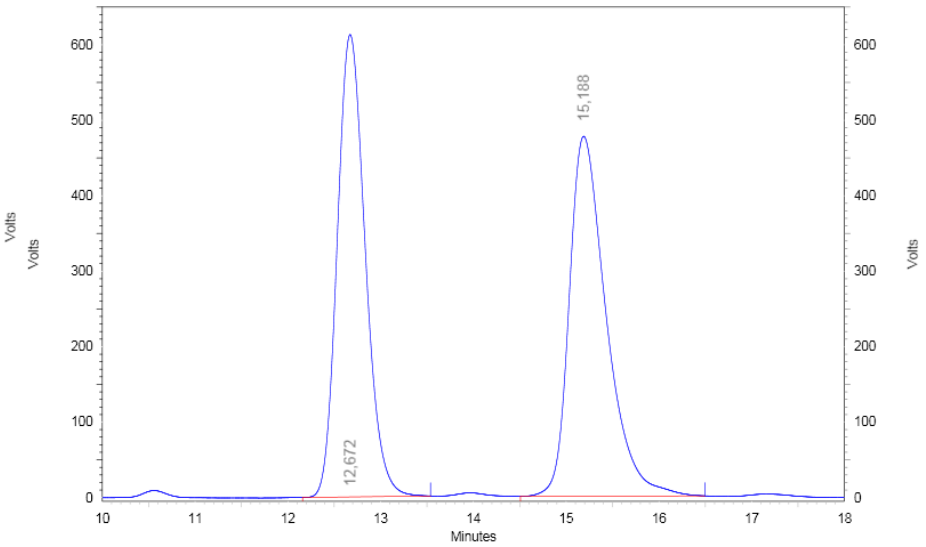
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1426-A-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-08-28 10:46:53
Printed: 2015-02-06 11:51:51



UV2000-220nm Results (System (2014-08-28 11:10:03) (Original))

Retention Time	Area	Area %	Height	Height %
12,580	94161	0,98	5572	1,53
12,857	660320	6,91	31396	8,64
15,312	8807010	92,11	326249	89,82
Totals	9561491	100,00	363217	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1426-A-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-08-28 10:21:42
Printed: 2015-02-06 11:50:10

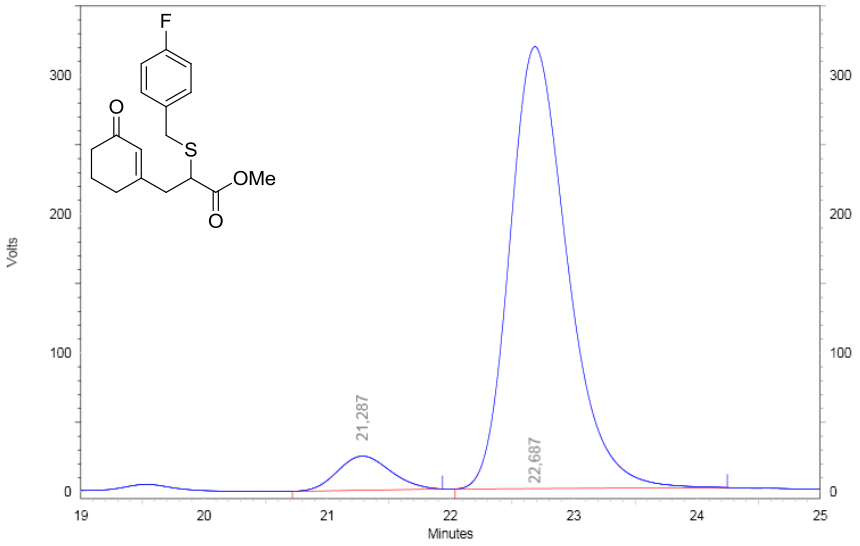


UV2000-220nm Results (System (2014-08-28 10:46:01) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
12,672	12853046	49,31	612699	56,23
15,188	13212612	50,69	476981	43,77
Totals	26065658	100,00	1089680	100,00

Figure S92. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **12** obtained with **10f / 11b** (left), and a racemic compound (right)

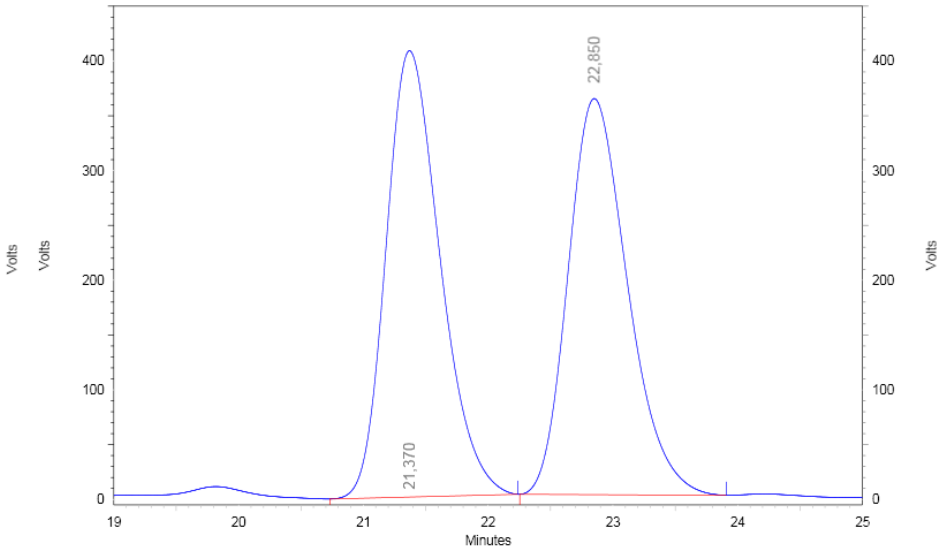
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1467-B-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-26 14:19:50
Printed: 2015-02-06 12:11:48



UV2000-220nm Results (System (2014-09-26 14:44:53) (Original))

Retention Time	Area	Area %	Height	Height %
21,287	734059	6,63	24581	7,17
22,687	10336272	93,37	318464	92,83
Totals	11070331	100,00	343045	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1467-B-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-26 13:44:29
Printed: 2015-02-06 12:08:49

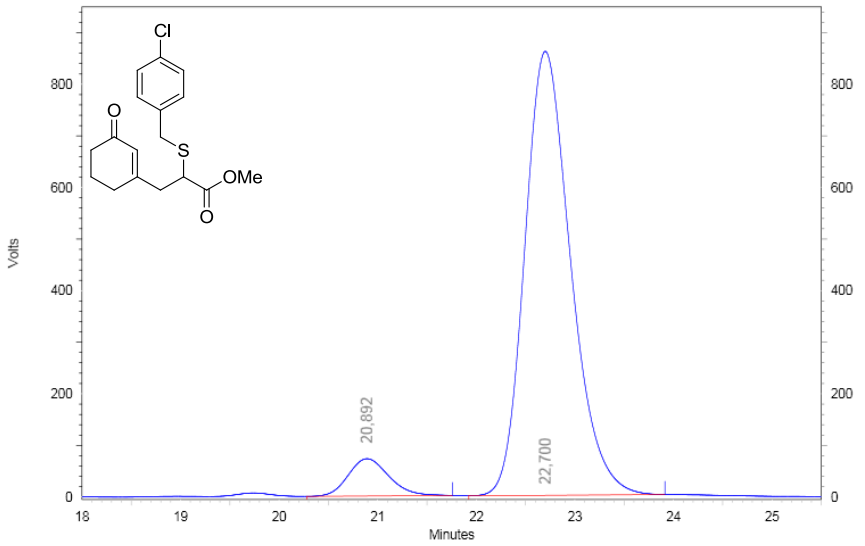


UV2000-220nm Results (System (2014-09-26 14:19:01) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
21,370	12243905	50,63	407128	52,98
22,850	11938820	49,37	361375	47,02
Totals	24182725	100,00	768503	100,00

Figure S93. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **13** obtained with **10f / 11b** (left), and a racemic compound (right)

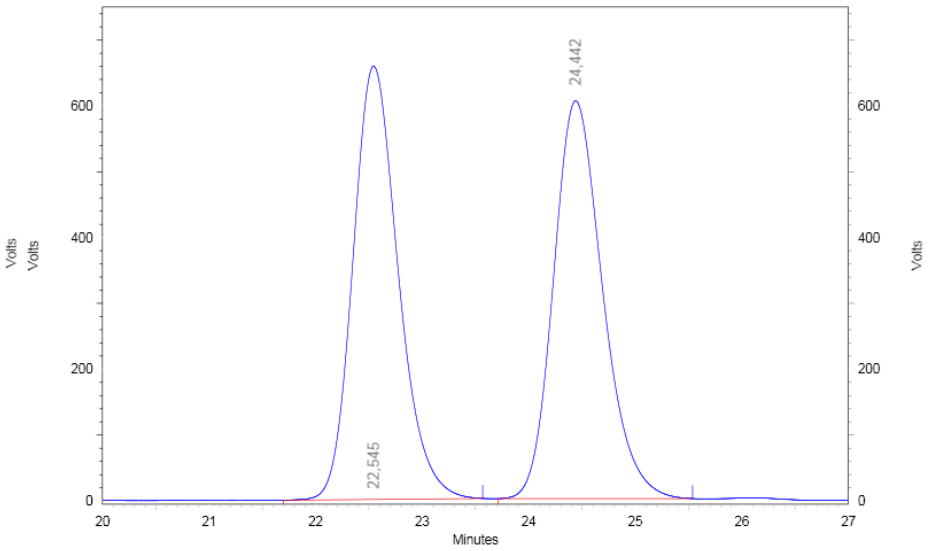
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1448-B-cr.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-17 14:11:52
Printed: 2015-02-06 11:56:48



UV2000-220nm Results (System (2014-09-17 14:37:44) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
20,892	2077643	6,94	72429	7,76
22,700	27878061	93,06	860712	92,24
Totals	29955704	100,00	933141	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1448-B-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-17 13:33:26
Printed: 2015-02-06 11:54:42

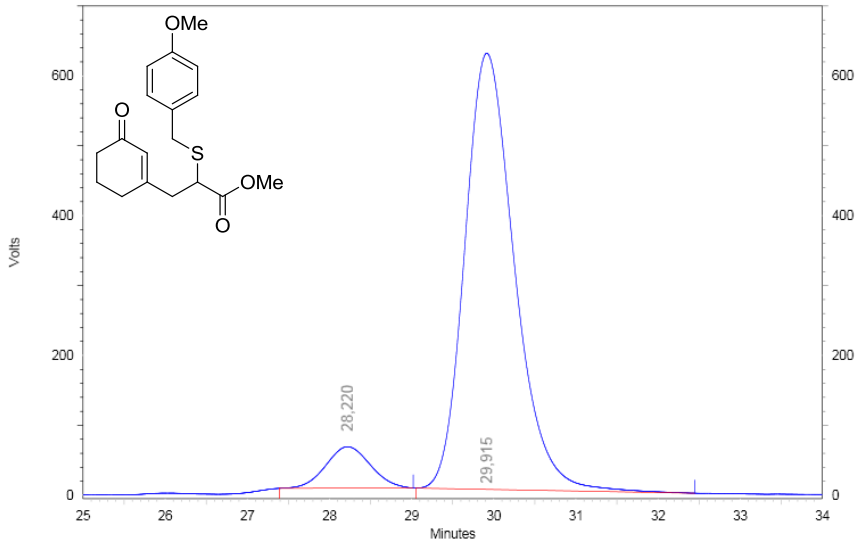


UV2000-220nm Results (System (2014-09-17 14:11:00) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
22,545	19441219	50,12	658052	52,14
24,442	19345372	49,88	604091	47,86
Totals	38786591	100,00	1262143	100,00

Figure S94. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **14** obtained with **10f / 11b** (left), and a racemic compound (right)

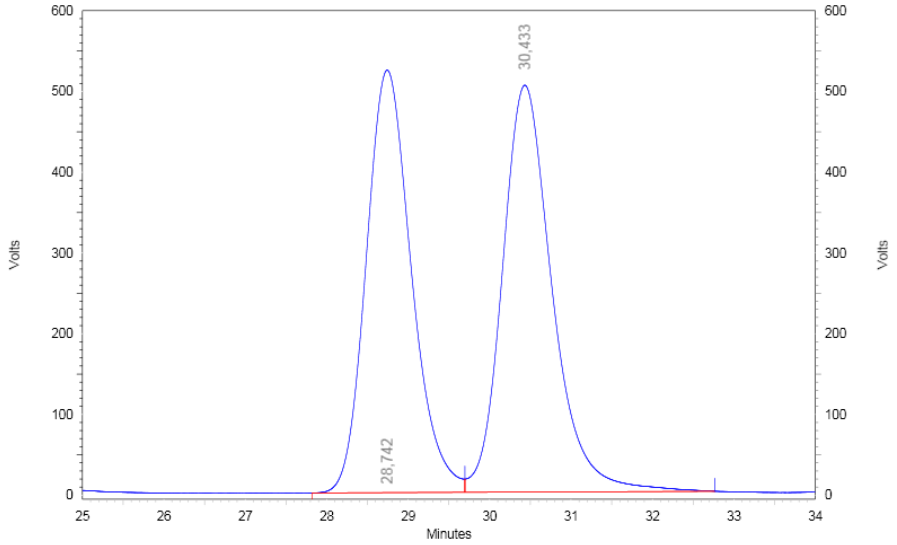
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1448-A.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-17 12:56:15
Printed: 2015-02-06 12:01:38



UV2000-220nm Results (System (2014-09-17 13:32:36) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
28,220	2238700	7,88	59322	8,68
29,915	26179708	92,12	624146	91,32
Totals	28418408	100,00	683468	100,00

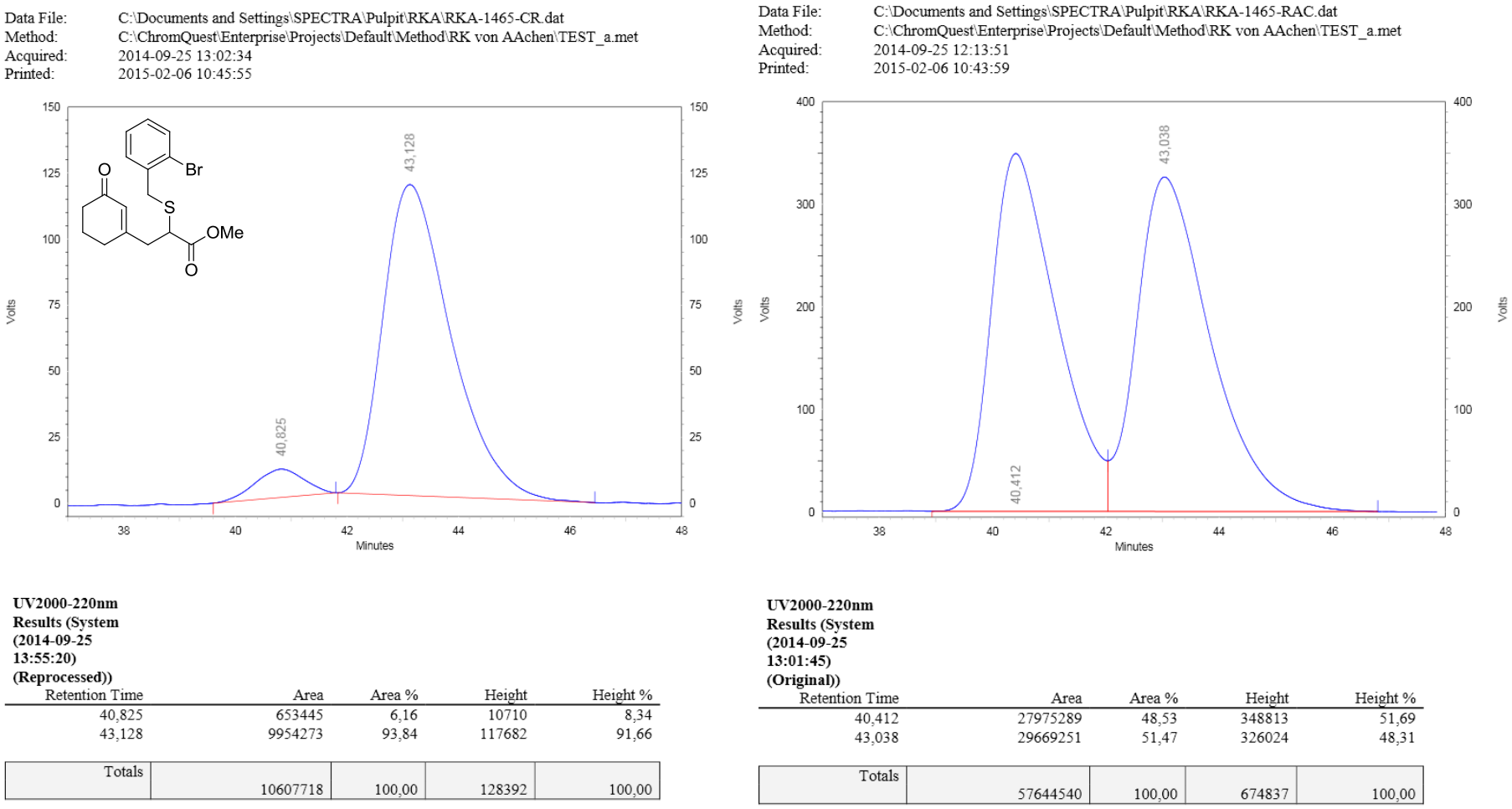
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1448-A-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-17 12:04:47
Printed: 2015-02-06 11:59:47



UV2000-220nm Results (System (2014-09-17 12:55:12) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
28,742	20150074	48,50	523218	50,95
30,433	21395206	51,50	503780	49,05
Totals	41545280	100,00	1026998	100,00

Figure S95. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **15** obtained with **10f / 11b** (left), and a racemic compound (right)



UV2000-220nm Results (System (2014-09-25 13:55:20) (Reprocessed))

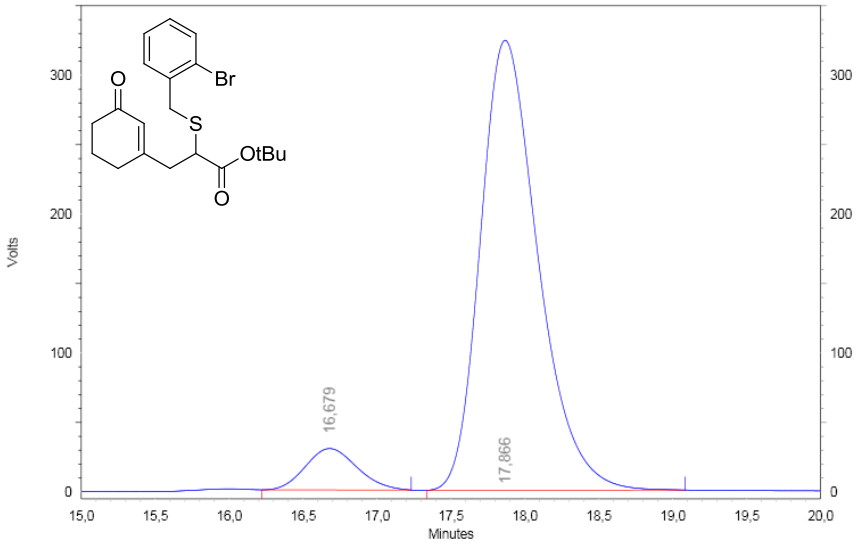
Retention Time	Area	Area %	Height	Height %
40,825	653445	6,16	10710	8,34
43,128	9954273	93,84	117682	91,66
Totals	10607718	100,00	128392	100,00

UV2000-220nm Results (System (2014-09-25 13:01:45) (Original))

Retention Time	Area	Area %	Height	Height %
40,412	27975289	48,53	348813	51,69
43,038	29669251	51,47	326024	48,31
Totals	57644540	100,00	674837	100,00

Figure S96. HPLC chromatograms (AD-H, hexane / IPA, 97:3, 1 mL/min) for **16** obtained with **10f / 11b** (left), and a racemic compound (right)

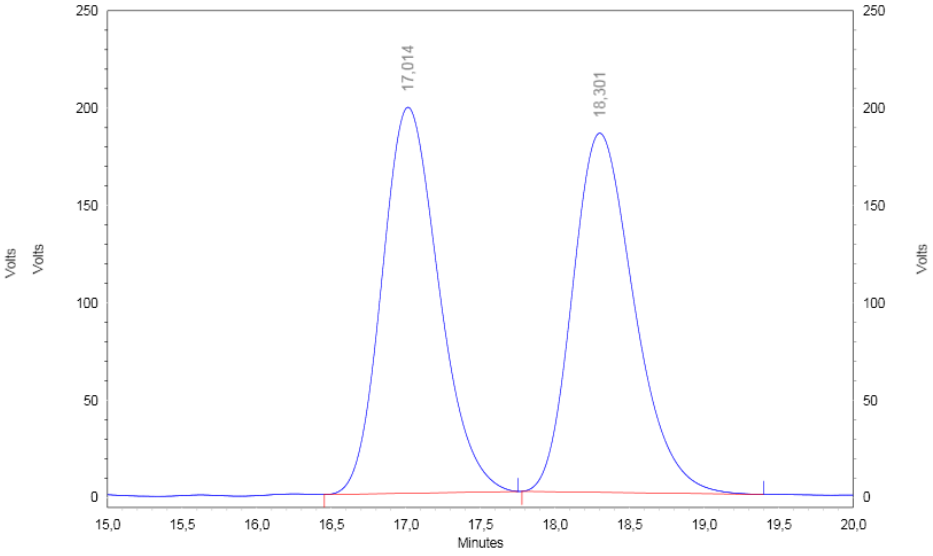
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1473-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-01 11:42:07
Printed: 2015-02-06 10:41:06



UV2000-220nm Results (System (2014-10-01 12:10:52) (Original))

Retention Time	Area	Area %	Height	Height %
16,679	722998	7,60	29803	8,42
17,866	8787130	92,40	323991	91,58
Totals	9510128	100,00	353794	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1473-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-01 11:20:36
Printed: 2015-02-06 10:39:35

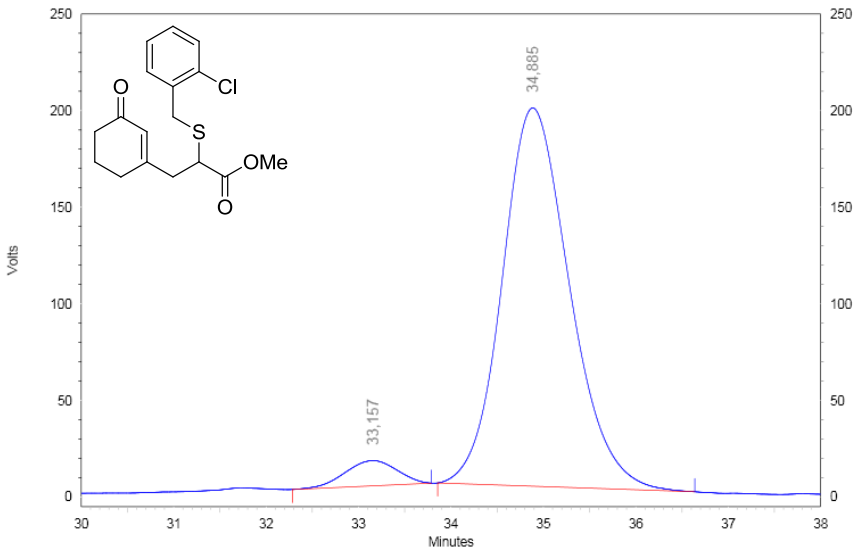


UV2000-220nm Results (System (2014-10-01 11:40:47) (Original))

Retention Time	Area	Area %	Height	Height %
17,014	5248988	49,80	198139	51,80
18,301	5291555	50,20	184349	48,20
Totals	10540543	100,00	382488	100,00

Figure S97. HPLC chromatograms (AD-H, hexane / IPA, 97:3, 1 mL/min) for **17** obtained with **10f / 11b** (left), and a racemic compound (right)

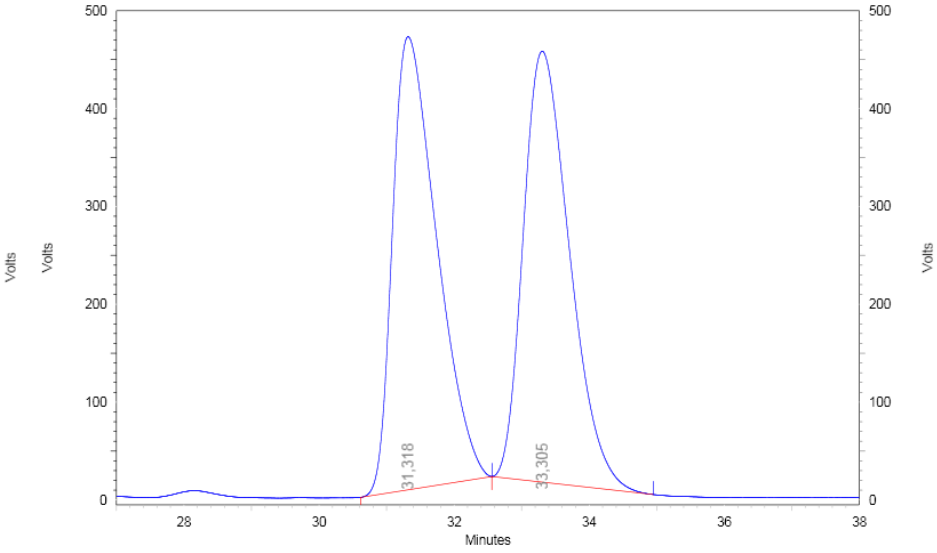
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1464-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-24 13:57:50
Printed: 2015-02-06 10:52:53



UV2000-220nm Results (System (2015-02-06 10:52:03) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
33,157	509421	4,89	13042	6,25
34,885	9908498	95,11	195765	93,75
Totals	10417919	100,00	208807	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1464-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-24 13:04:48
Printed: 2015-02-06 10:49:57

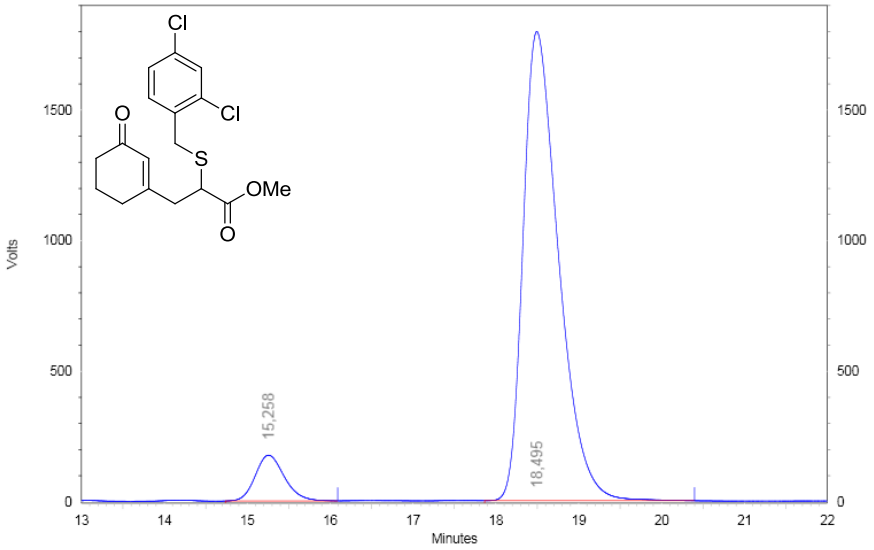


UV2000-220nm Results (System (2014-09-24 13:56:57) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
31,318	21023124	50,02	463140	51,26
33,305	21006165	49,98	440457	48,74
Totals	42029289	100,00	903597	100,00

Figure S98. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **18** obtained with **10f / 11b** (left), and a racemic compound (right)

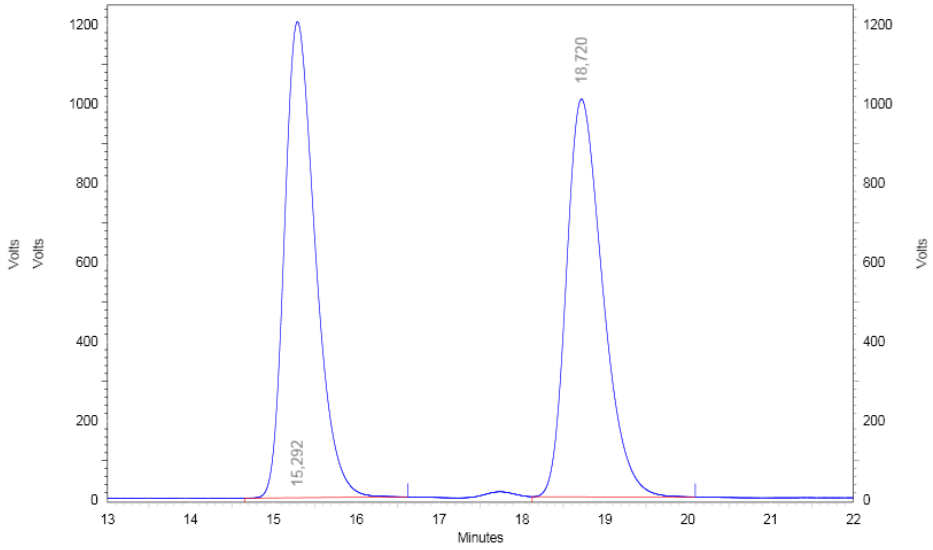
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1466-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-29 10:35:19
Printed: 2015-02-06 11:48:03



UV2000-220nm Results (System (2014-09-29 11:07:44) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
15,258	4264304	7,40	175122	8,88
18,495	53376691	92,60	1796262	91,12
Totals	57640995	100,00	1971384	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1466-LC-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-09-29 10:12:08
Printed: 2015-02-06 11:46:19

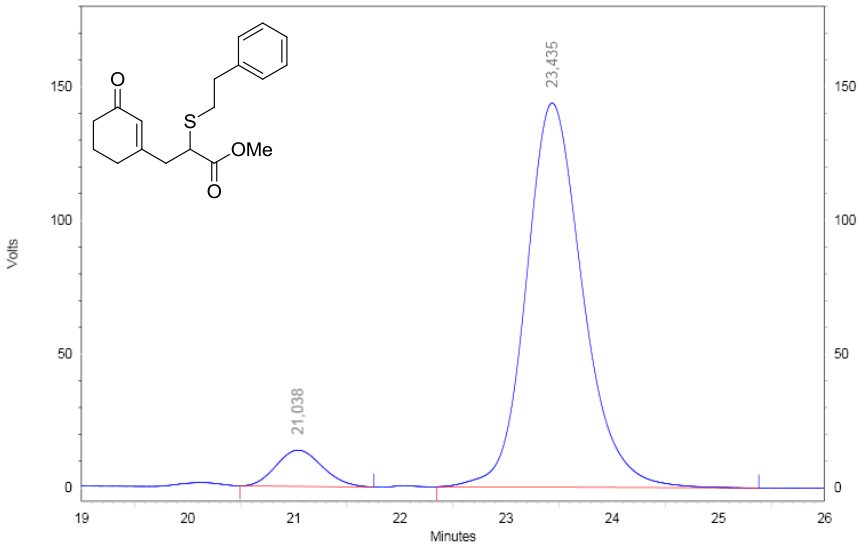


UV2000-220nm Results (System (2014-09-29 10:34:15) (Original))

Retention Time	Area	Area %	Height	Height %
15,292	31046678	50,43	1201669	54,48
18,720	30522550	49,57	1003979	45,52
Totals	61569228	100,00	2205648	100,00

Figure S99. HPLC chromatograms (AD-H, hexane / IPA, 9:1, 1 mL/min) for **19** obtained with **10f / 11b** (left), and a racemic compound (right)

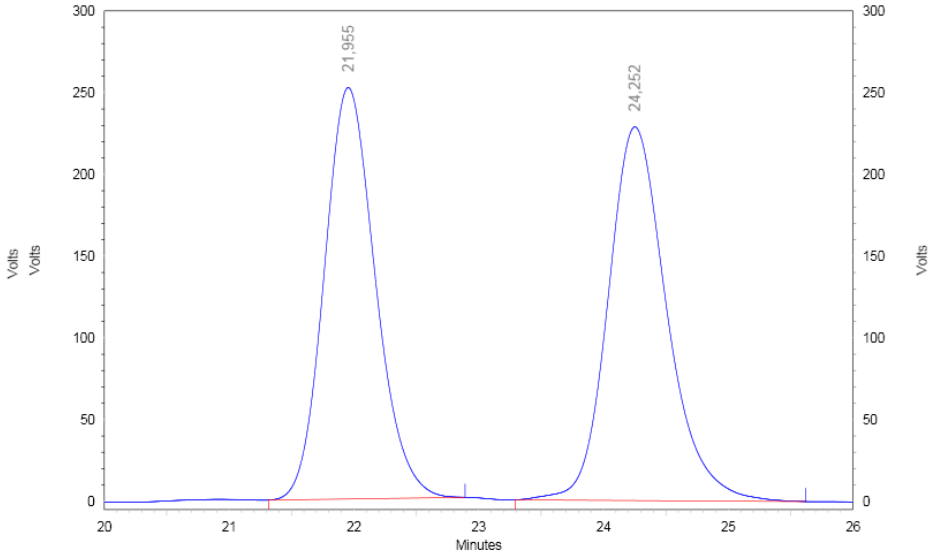
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1486-A-CR.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-24 09:16:37
Printed: 2015-02-06 10:37:30



UV2000-220nm Results (System (2014-10-24 09:43:09) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
21,038	408830	7,16	13546	8,62
23,435	5298942	92,84	143660	91,38
Totals	5707772	100,00	157206	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1486-A-955_RAC_ADH.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-10-24 08:32:23
Printed: 2015-02-06 10:35:37

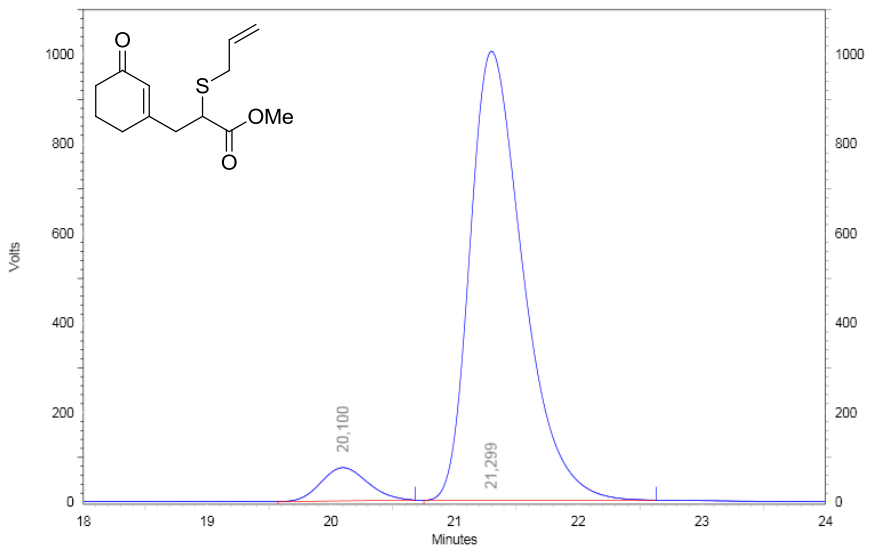


UV2000-220nm Results (System (2014-10-24 09:14:40) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
21,955	7160287	48,91	251624	52,41
24,252	7479276	51,09	228521	47,59
Totals	14639563	100,00	480145	100,00

Figure S100. HPLC chromatograms (AD-H, hexane / IPA, 95:5, 1 mL/min) for **20** obtained with **10f / 11b** (left), and a racemic compound (right)

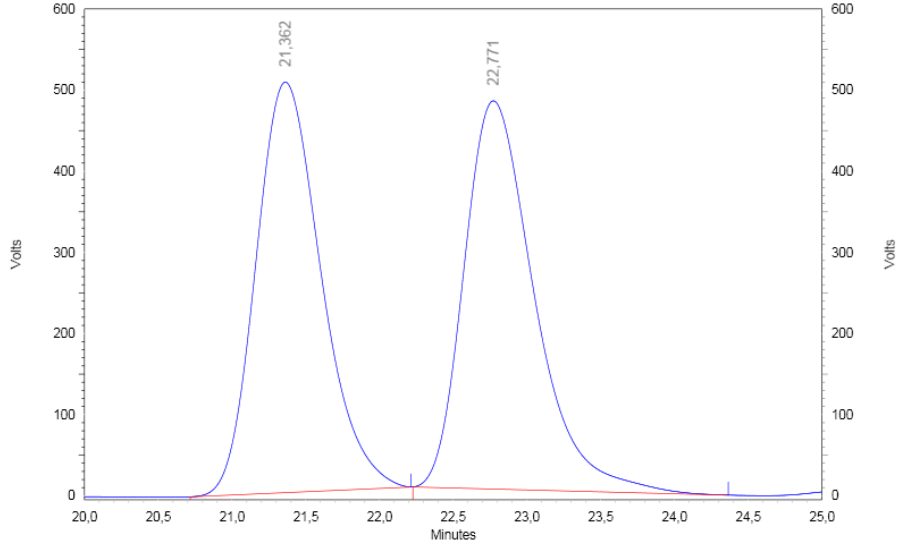
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1513-A-ADH-973-08-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 10:24:06
Printed: 2015-02-06 10:33:44



UV2000-220nm Results (System (2014-11-17 10:52:45) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
20,100	1946680	6,12	74289	6,89
21,299	29865002	93,88	1003535	93,11
Totals	31811682	100,00	1077824	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1513-A-ADH-973-08-RAC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 09:50:28
Printed: 2015-02-06 10:31:24

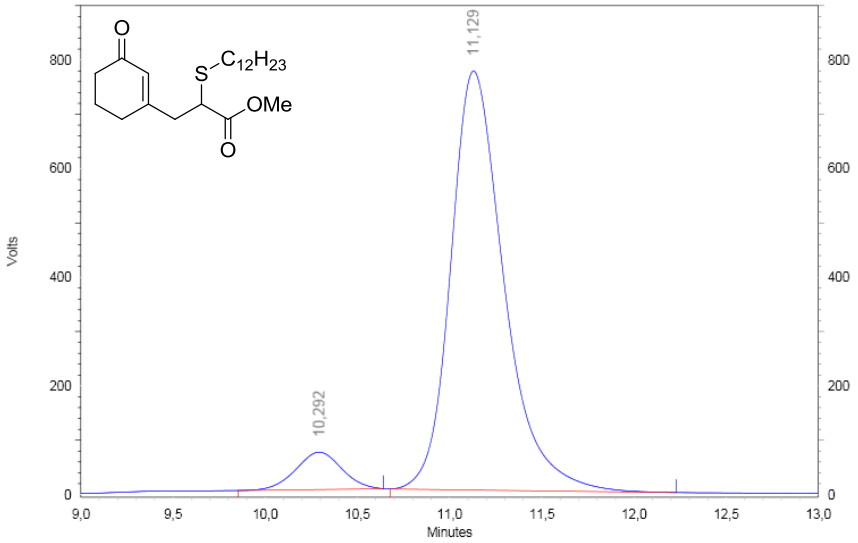


UV2000-220nm Results (System (2014-11-17 10:22:25) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
21,362	15507577	49,54	505916	51,39
22,771	15795228	50,46	478465	48,61
Totals	31302805	100,00	984381	100,00

Figure S101. HPLC chromatograms (AD-H, hexane / IPA, 97:3, 0.8 mL/min) for **21** obtained with **10f / 11b** (left), and a racemic compound (right)

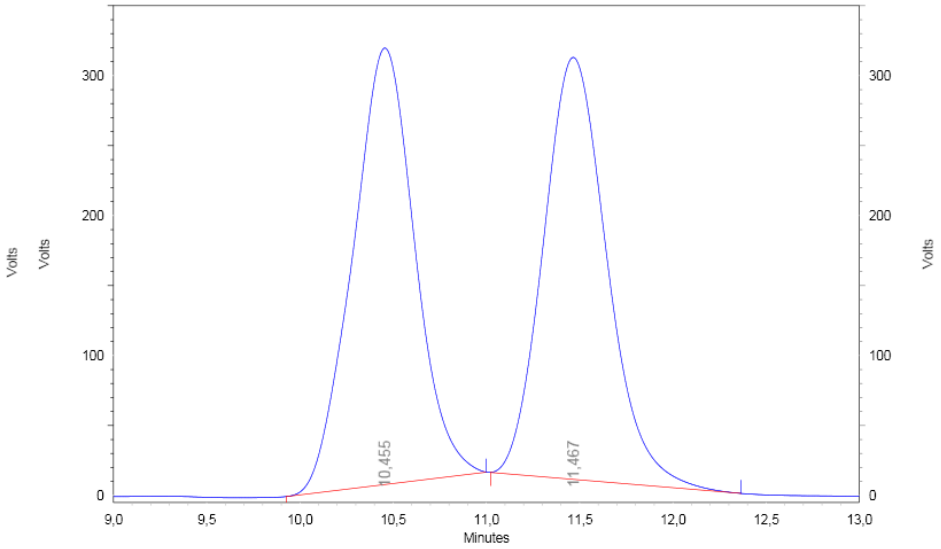
Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1513-B-ADH-973-08-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 09:27:41
Printed: 2015-02-06 10:19:11



UV2000-220nm Results (System (2014-11-17 09:48:47) (Original))

Retention Time	Area	Area %	Height	Height %
10,292	1191245	7,14	68820	8,19
11,129	15500114	92,86	771504	91,81
Totals	16691359	100,00	840324	100,00

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1513-B-RAC-ADH-973-08.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2014-11-17 09:11:19
Printed: 2015-02-06 10:15:01

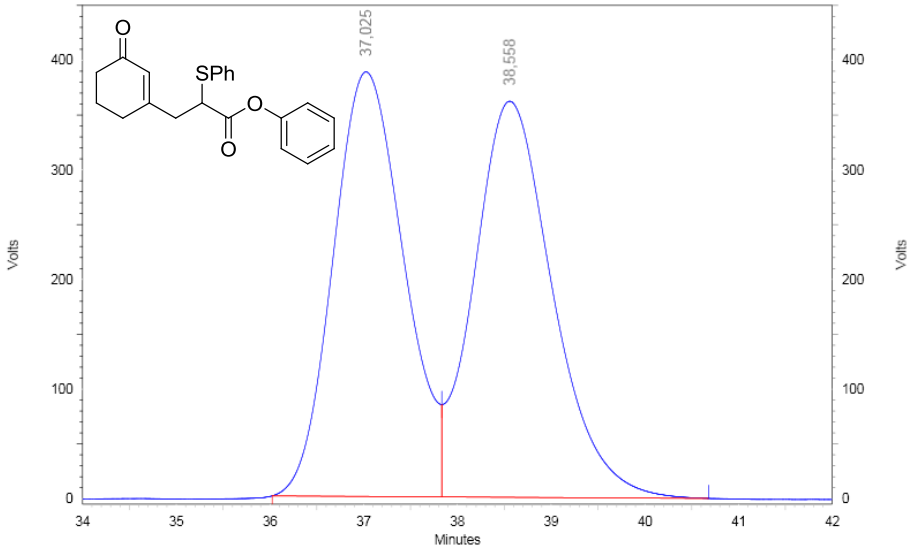


UV2000-220nm Results (System (2014-11-17 09:25:46) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
10,455	7201863	50,19	311907	50,85
11,467	7148186	49,81	301498	49,15
Totals	14350049	100,00	613405	100,00

Figure S102. HPLC chromatograms (AD-H, hexane / IPA, 97:3, 0.8 mL/min) for **22** obtained with **10f / 11b** (left), and a racemic compound (right)

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1568-ADH-955-1-B-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-02-16 14:10:57
Printed: 2015-02-17 11:39:16

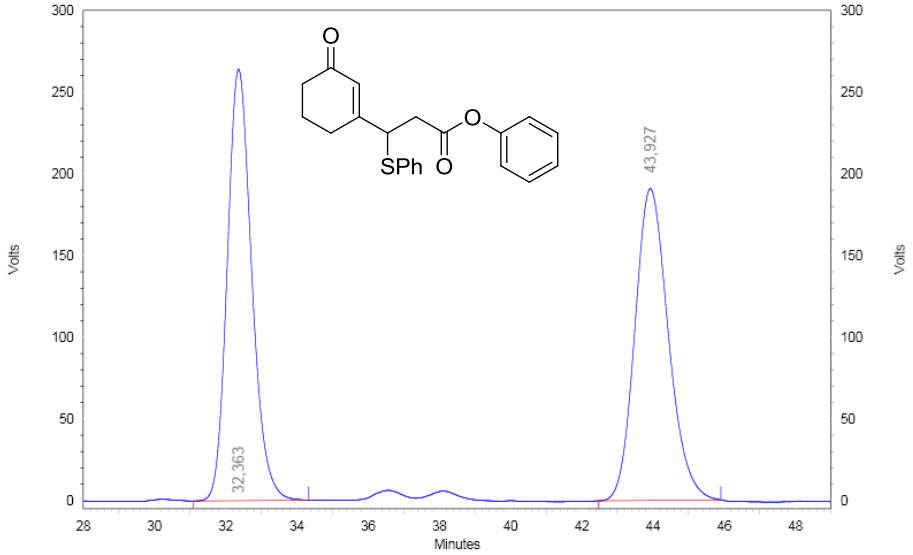


UV2000-220nm Results (System (2015-02-16 14:54:53) (Original))

Retention Time	Area	Area %	Height	Height %
37,025	20292643	48,96	387277	51,74
38,558	21155793	51,04	361281	48,26
Totals	41448436	100,00	748558	100,00

Figure S103. HPLC chromatogram (AD-H, hexane / IPA, 95:5, 1 mL/min) for **23** obtained with **10f / 11b**

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1568-ADH-955-1-A-LC-FR1.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-02-16 13:17:35
Printed: 2015-02-16 14:13:45

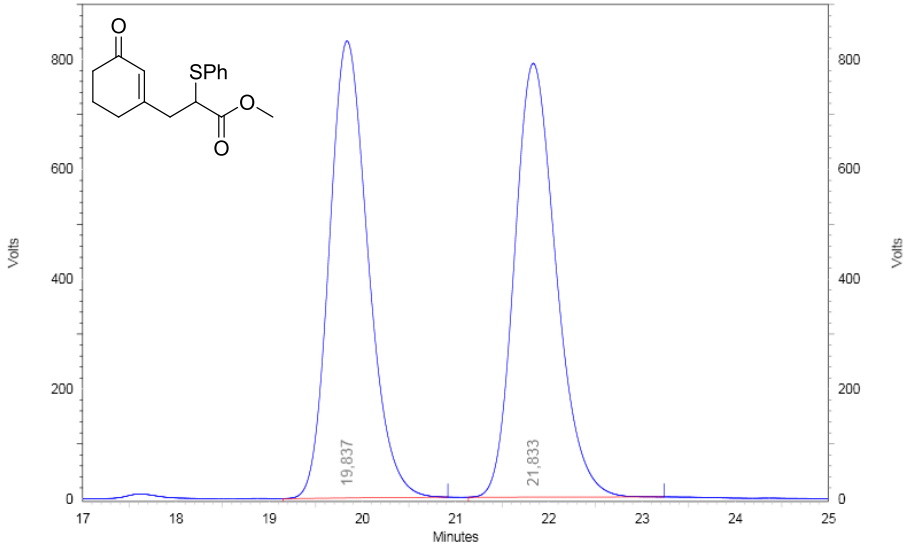


UV2000-220nm Results (System (2015-02-16 14:13:03) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
32,363	12611553	50,30	264154	58,06
43,927	12460560	49,70	190787	41,94
Totals	25072113	100,00	454941	100,00

Figure S104. HPLC chromatogram (AD-H, hexane / IPA, 95:5, 1 mL/min) for **24** obtained with **10f / 11b**

Data File: C:\Documents and Settings\SPECTRA\Pulpit\RKA\RKA-1448-ADH-955-1-C-LC.dat
Method: C:\ChromQuest\Enterprise\Projects\Default\Method\RK von AAchen\TEST_a.met
Acquired: 2015-02-16 14:59:46
Printed: 2015-02-16 15:34:08



UV2000-220nm Results (System (2015-02-16 15:31:58) (Reprocessed))

Retention Time	Area	Area %	Height	Height %
19,837	24006474	49,49	832268	51,30
21,833	24504362	50,51	789979	48,70
Totals	48510836	100,00	1622247	100,00

Figure S105. HPLC chromatogram (AD-H, hexane / IPA, 95:5, 1 mL/min) for **25** obtained with **10f / 11b**