Supporting Information

Experimental and computational insights into the unexpected Type I dyotropic rearrangement within *N*-Clovanylamides synthesised via Microwave-assisted Sn^{II}-catalysis

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Supporting Information

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EXPERIMENTAL SECTION

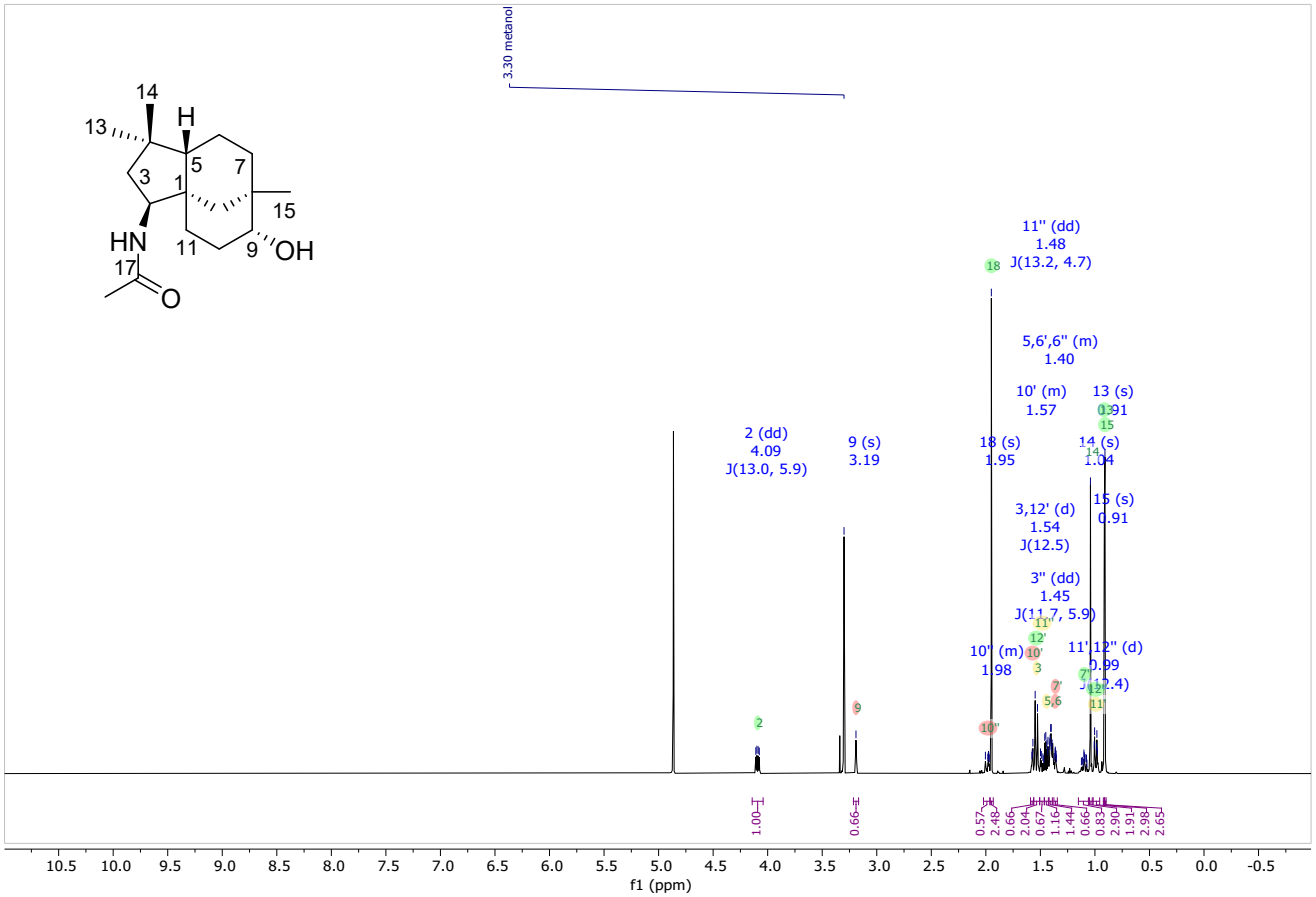

Figure S1a. ^{1}H NMR spectrum (600 MHz) of N-(9α-hydroxyclovan-2β-yl)acetamide (8) in CD_3OD.

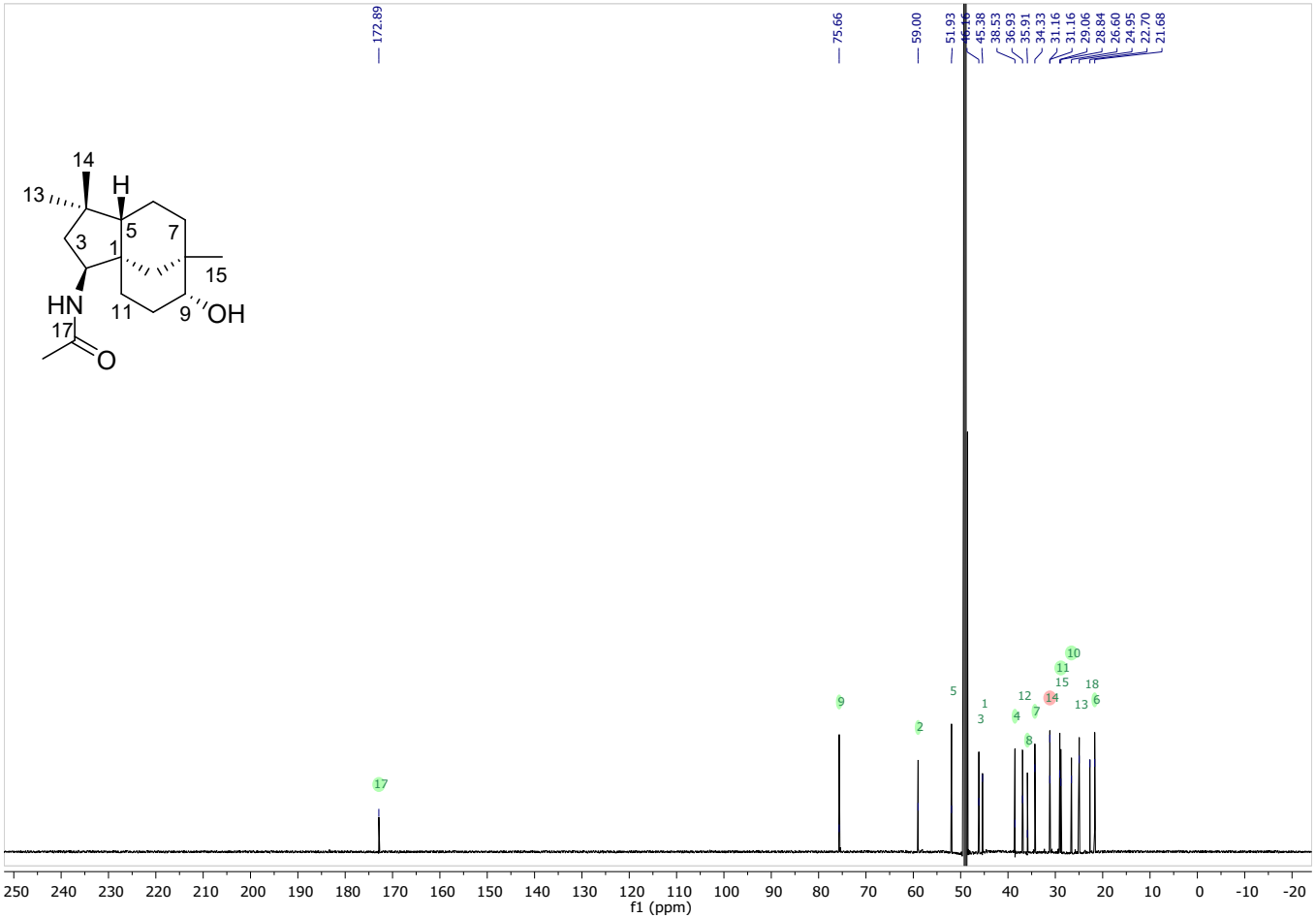

Figure S1b. ^{13}C NMR spectrum (150 MHz) of N-(9α-hydroxyclovan-2β-yl)acetamide (8) in CD_3OD.

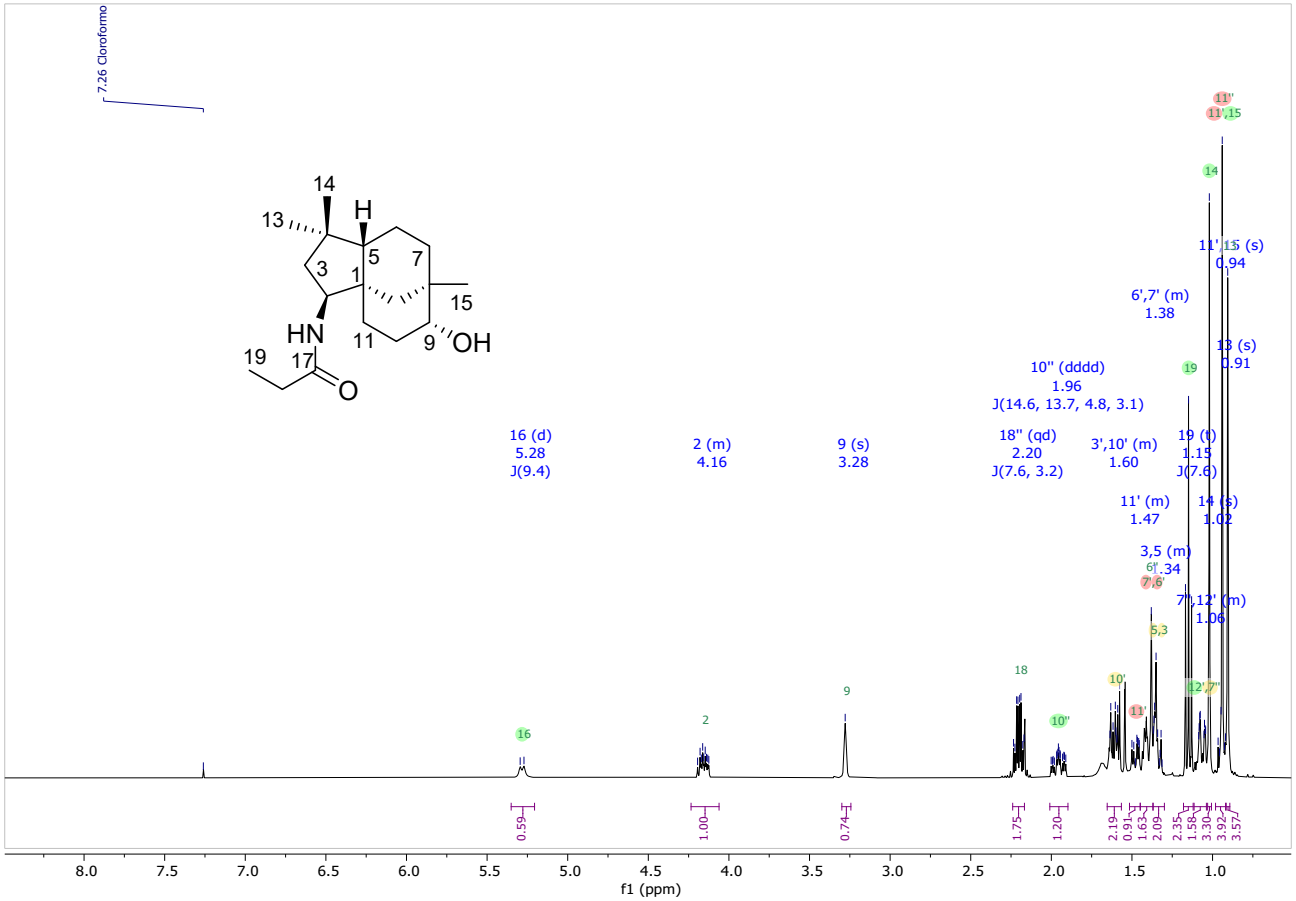

Figure S2a. ^{1}H-NMR spectrum (400 MHz) of N-(9α-hydroxyclovan-2β-yl)propionamide (9) in $CDCl_3$.

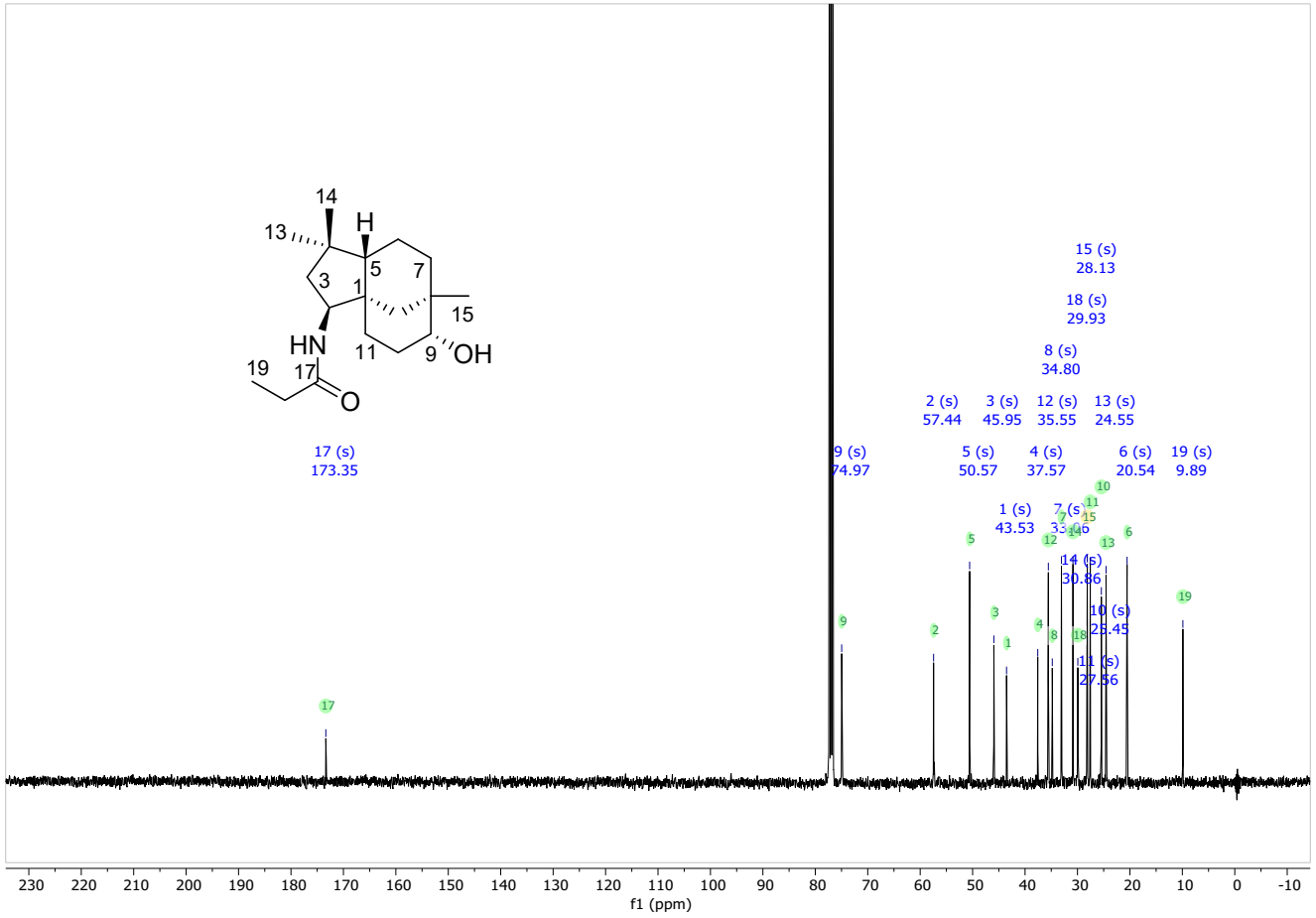

Figure S2b. ^{13}C-NMR spectrum (100 MHz) of N-(9α-hydroxyclovan-2β-yl)propionamide (9) in $CDCl_3$.

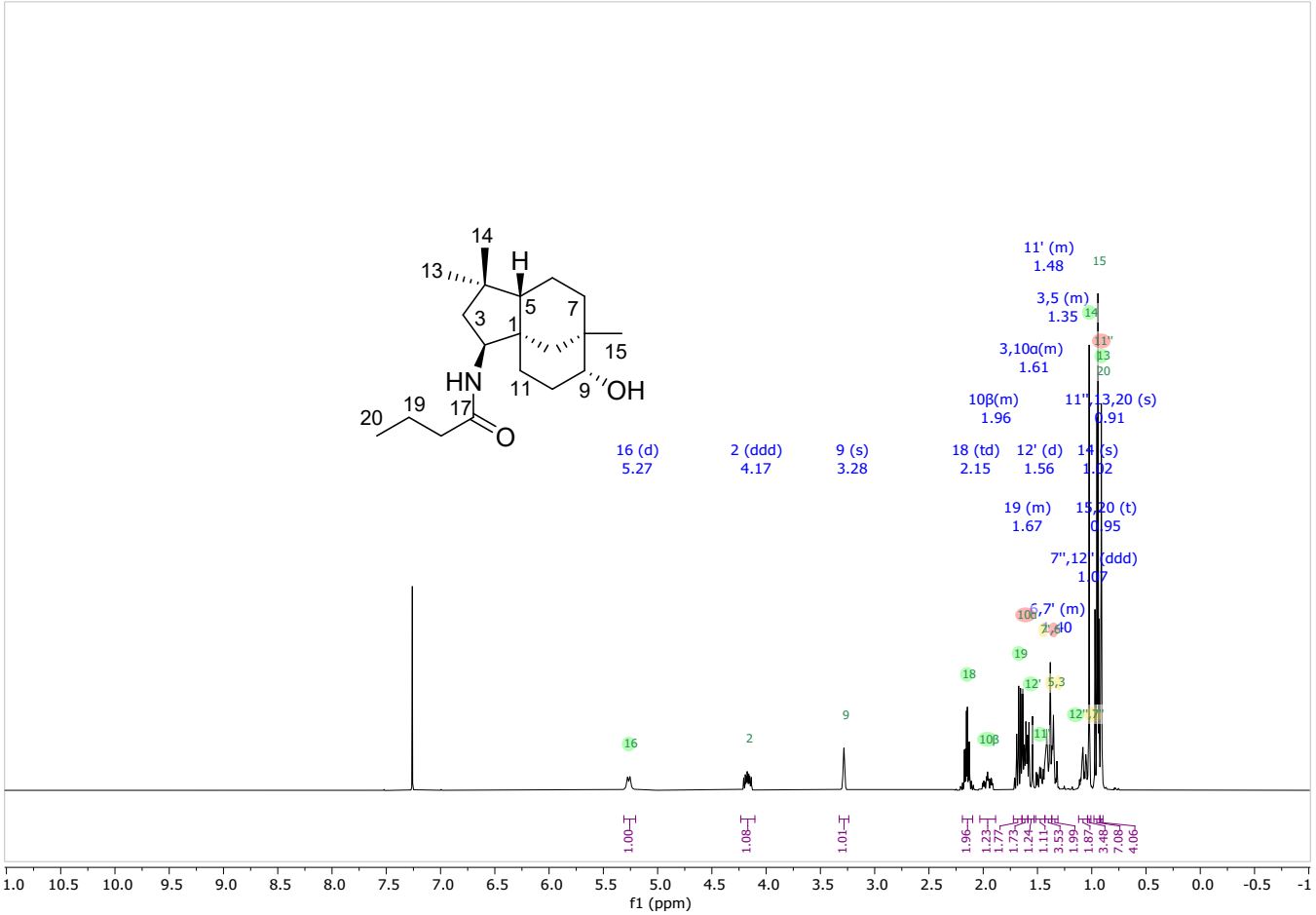

Figure S3a. [1]H-NMR spectrum (400 MHz) of N-(9α-hydroyiclovan-2β-yl)butyroamide (10) in CDCl3.

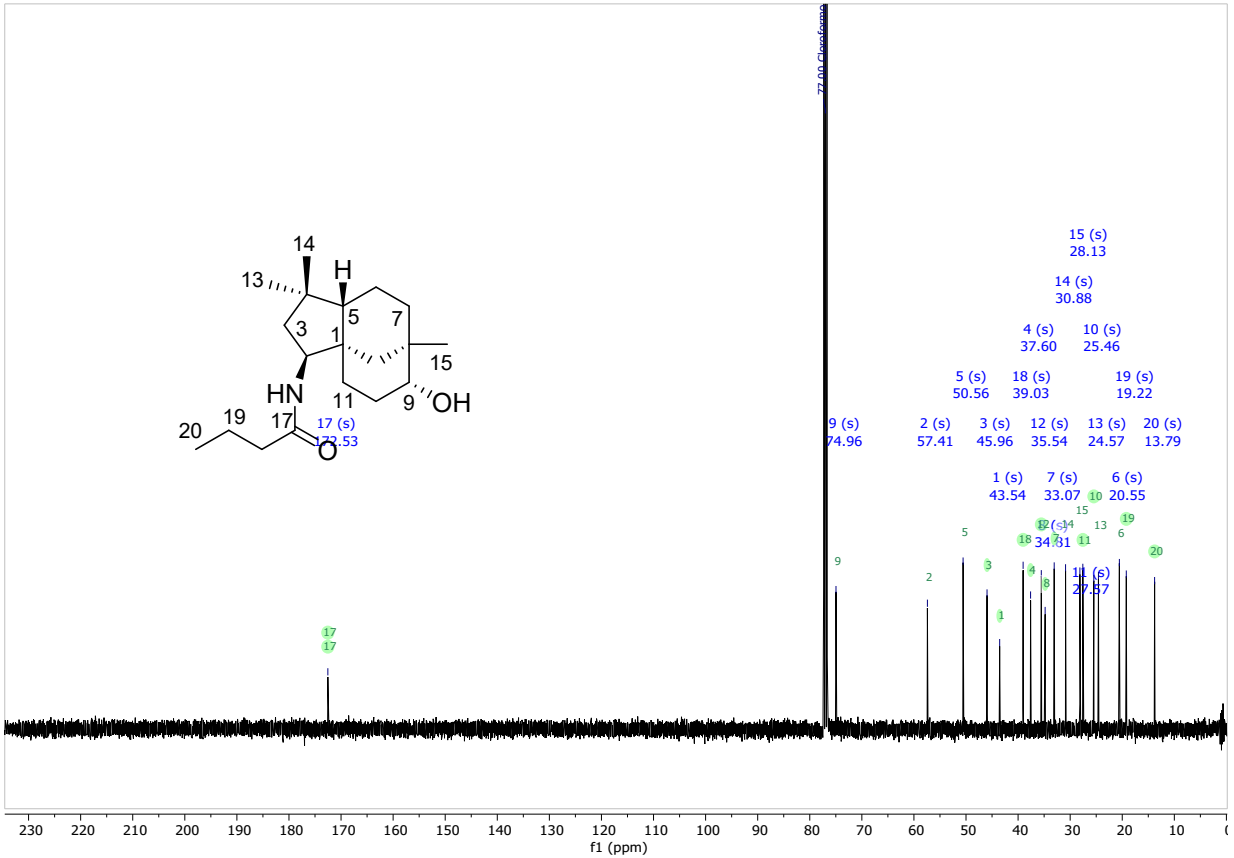

Figure S3b. ^{13}C-NMR spectrum (100 MHz) of N-(9α-hydroxyclovan-2β-yl)butyroamide (10) in $CDCl_3$.

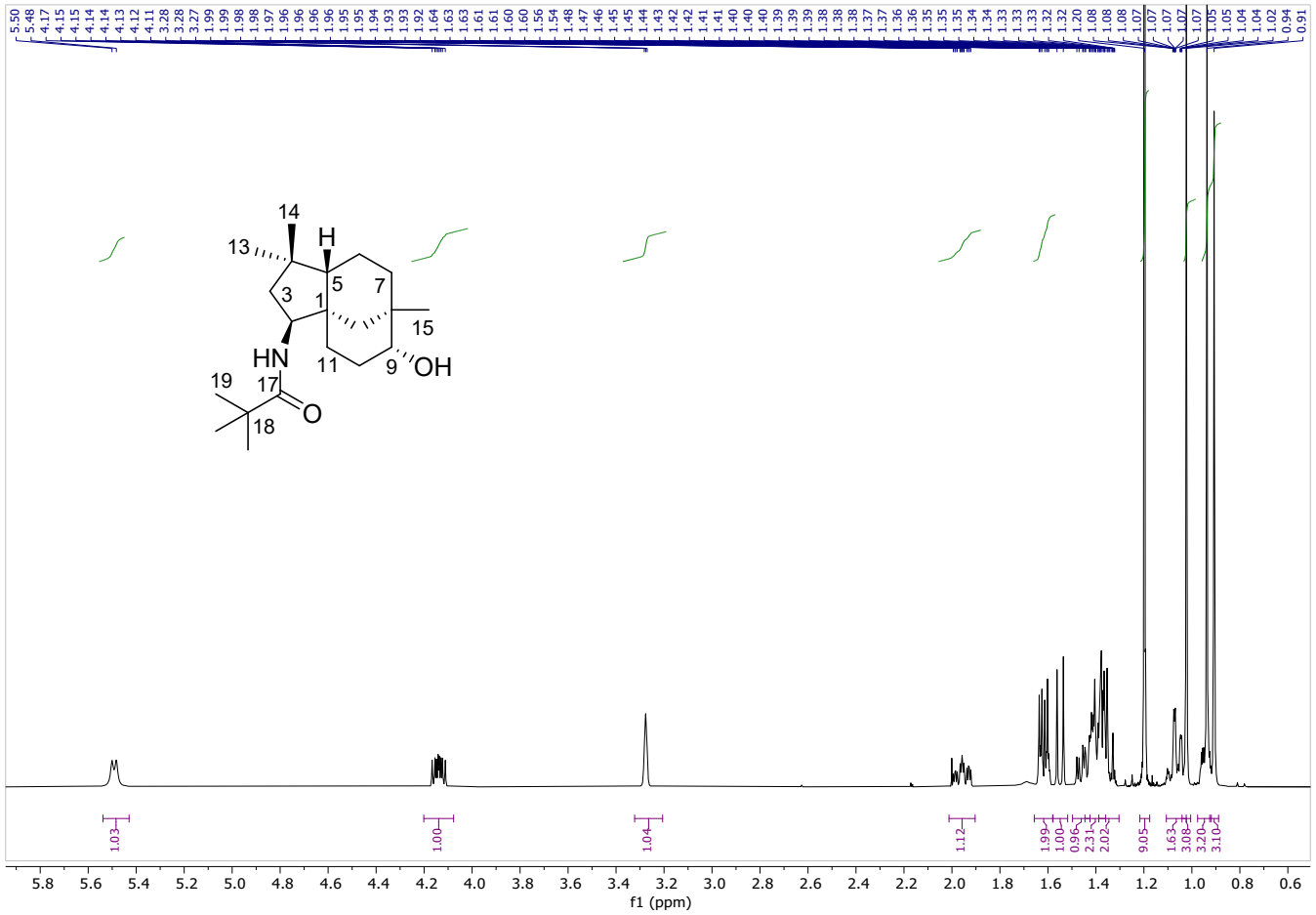

Figure S4a. ^{1}H NMR spectrum (500 MHz) of 2,2-dimethyl-N-(9α-hydroxyclovan-2β-yl)propionamide (11) in $CDCl_3$.

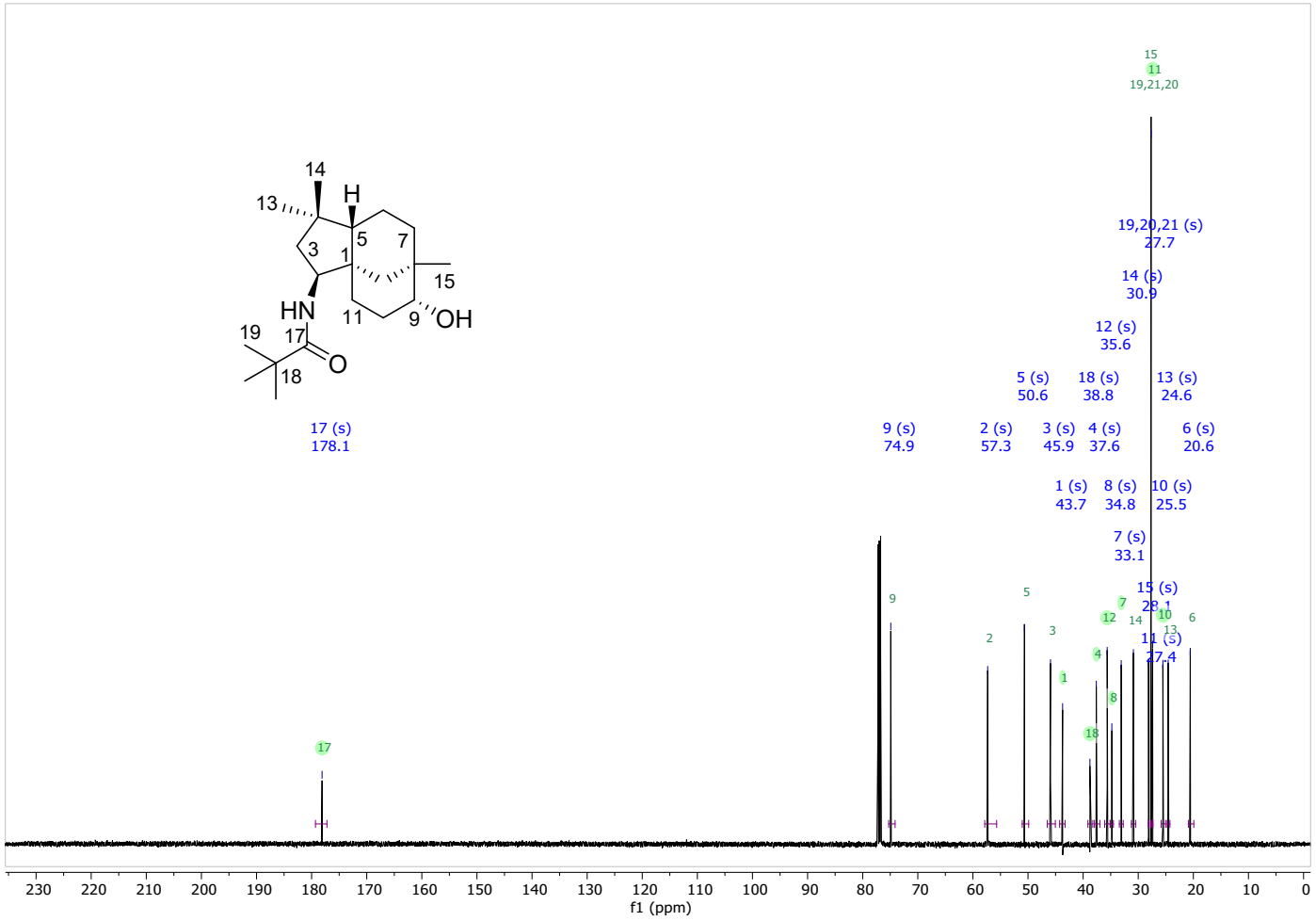

Figure S4b. ^{13}C NMR spectrum (125MHz) of 2,2-dimethyl-N-(9α-hydroxyclovan-2β-yl)propionamide (11) in $CDCl_3$.

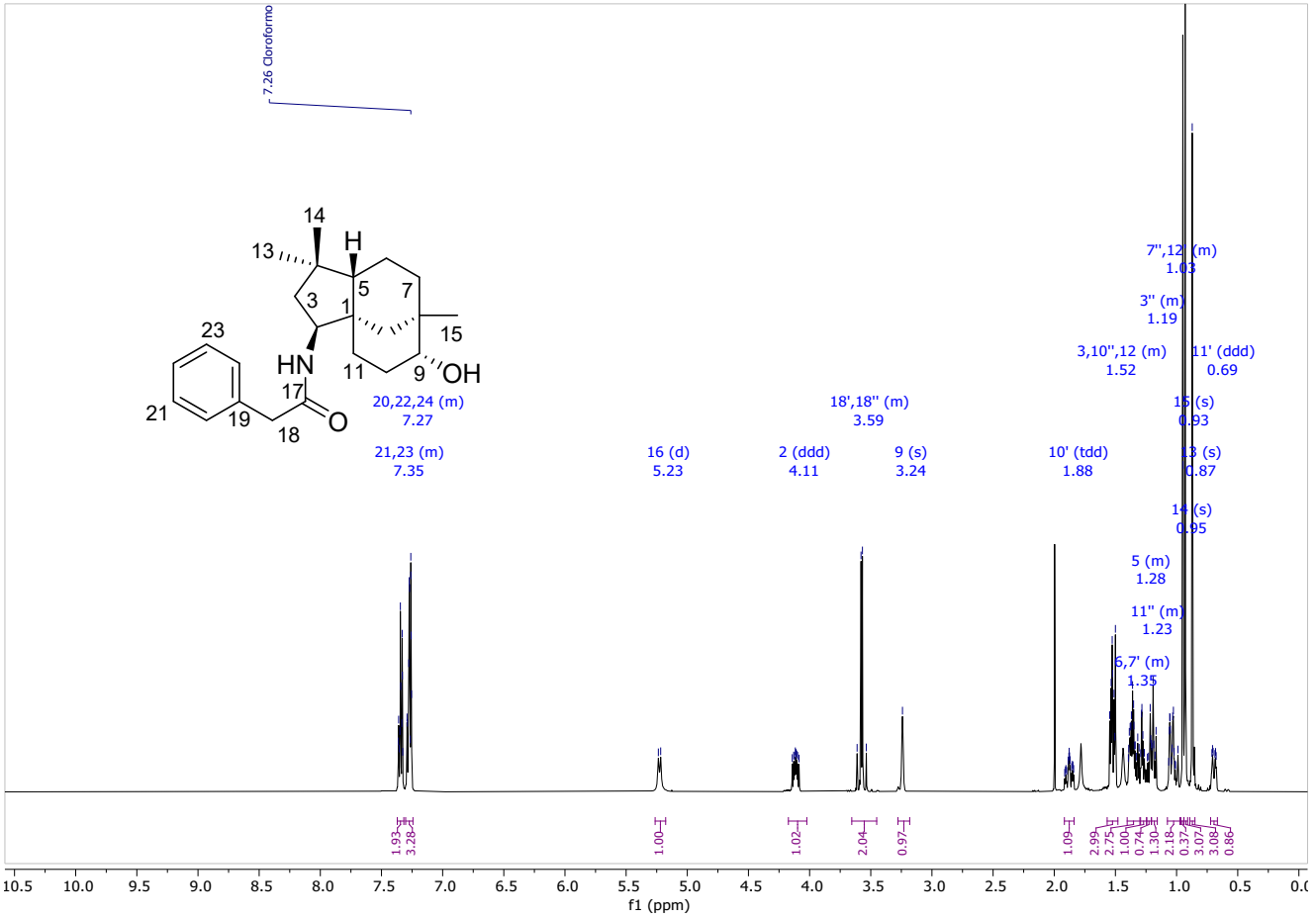

Figure S5a. ^{1}H NMR spectrum (500 MHz) of 2-phenyl-N-(9α-hydroxyclovan-2β-yl)acetamide (12) in $CDCl_3$.

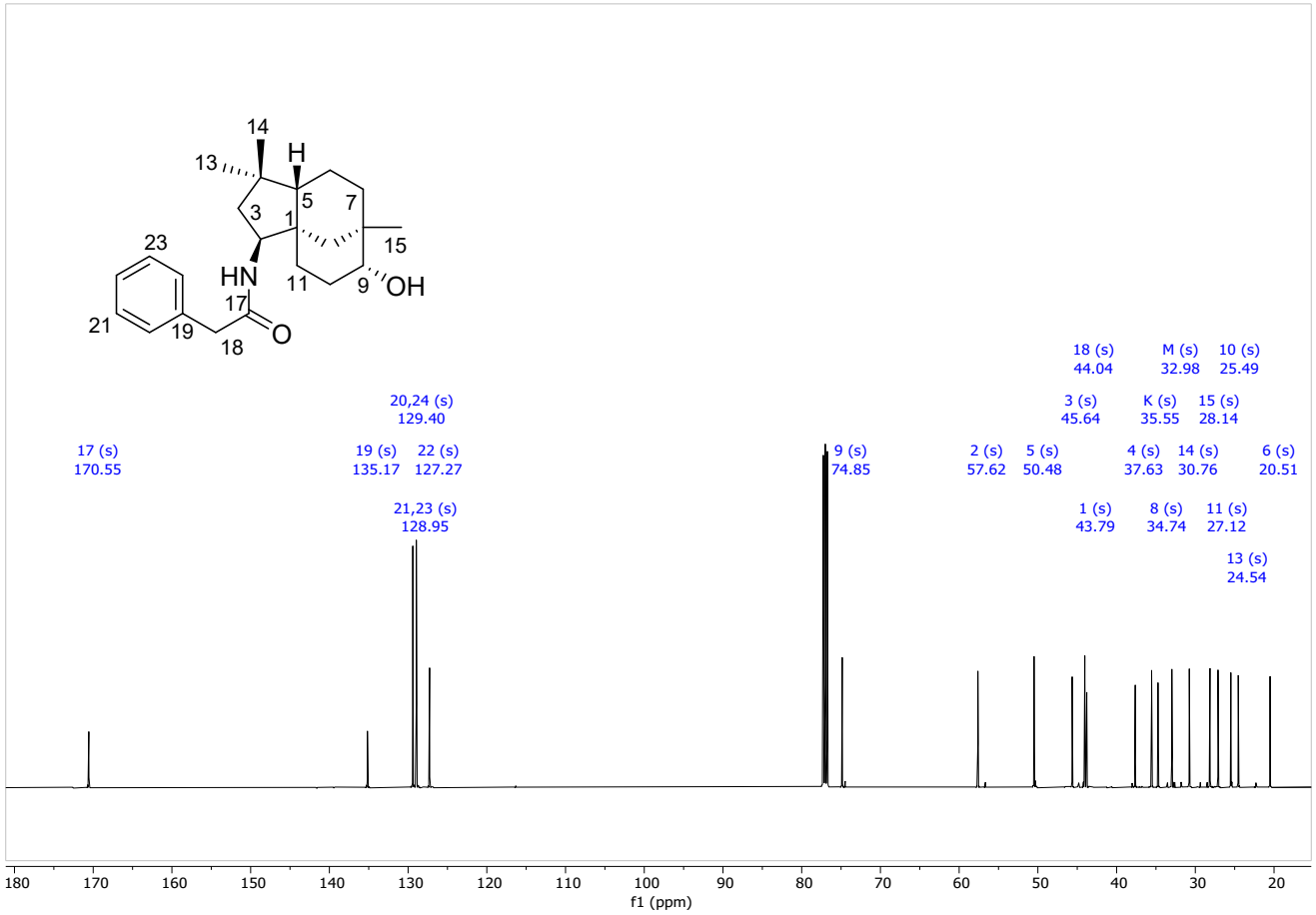

Figure S5b. ^{13}C NMR spectrum (125 MHz) of 2-phenyl-N-(9α-hydroxyclovan-2β-yl)acetamide (12) in $CDCl_3$.

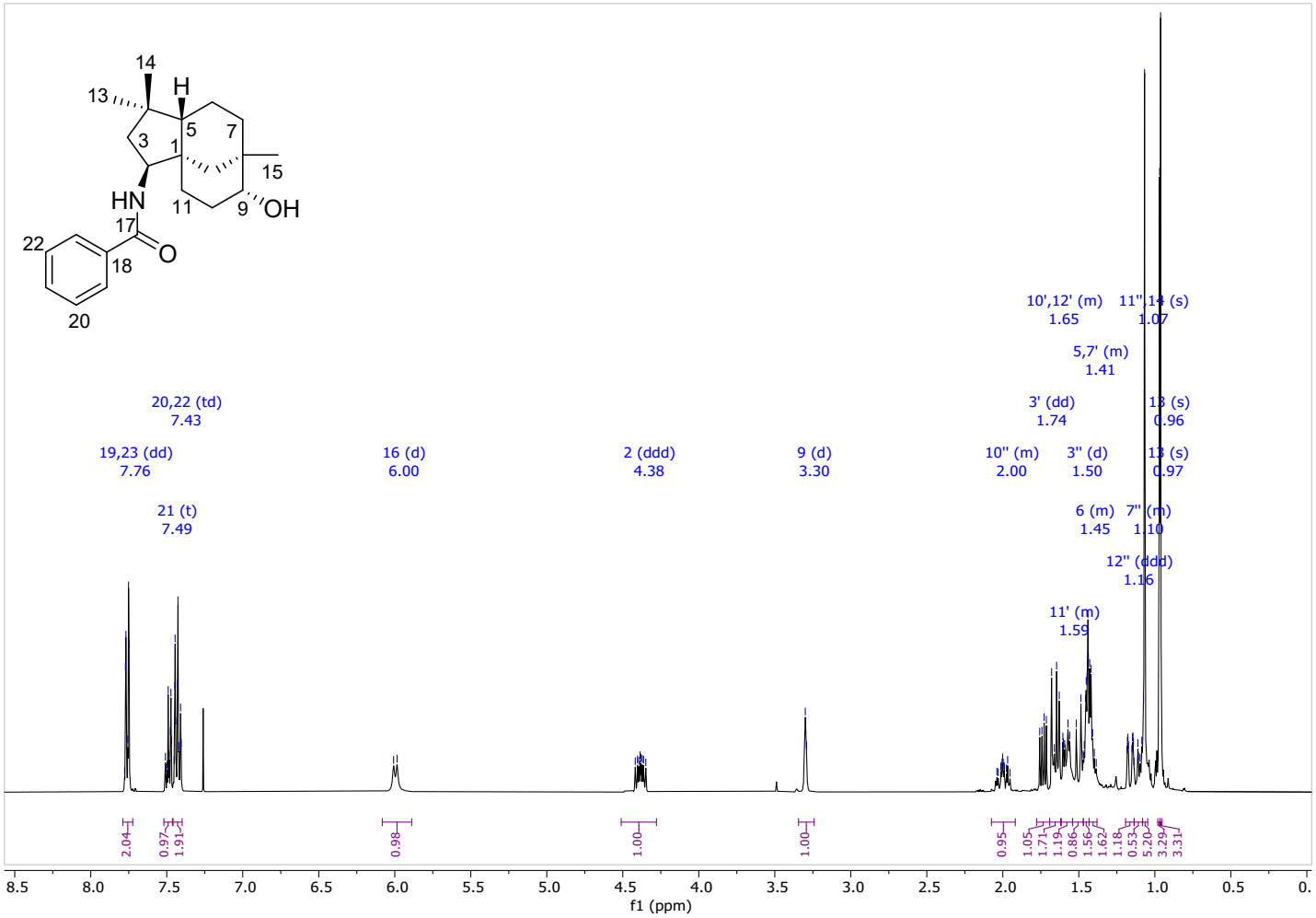

Figure S6a. ^{1}H NMR spectrum (400 MHz) of N-(9α-hydroxyclovan-2β-yl)benzamide (13) in $CDCl_3$.

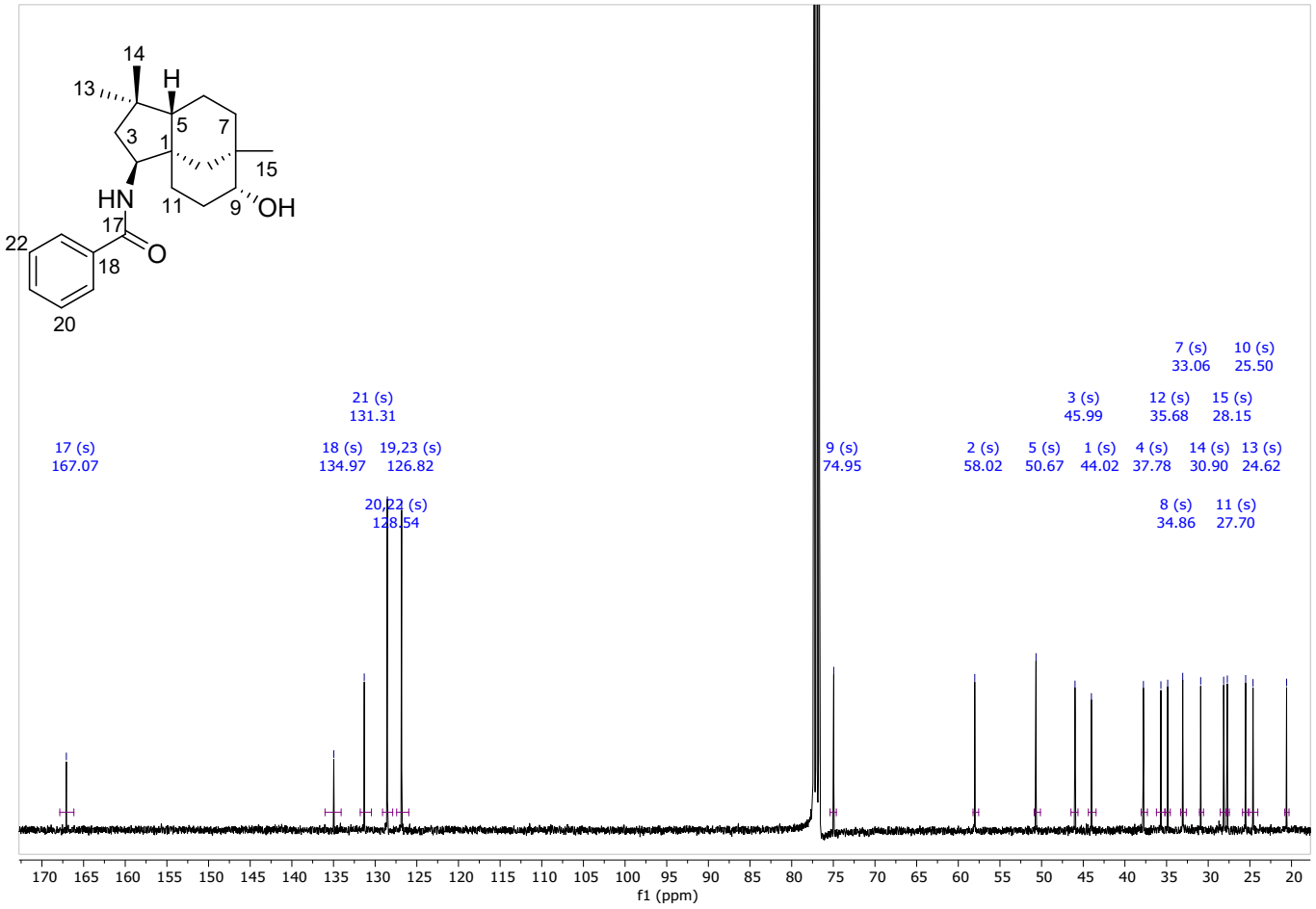

Figure S6b. ^{13}C NMR spectrum (100 MHz) of N-(9α-hydroxyclovan-2β-yl)benzamide (13) in $CDCl_3$.

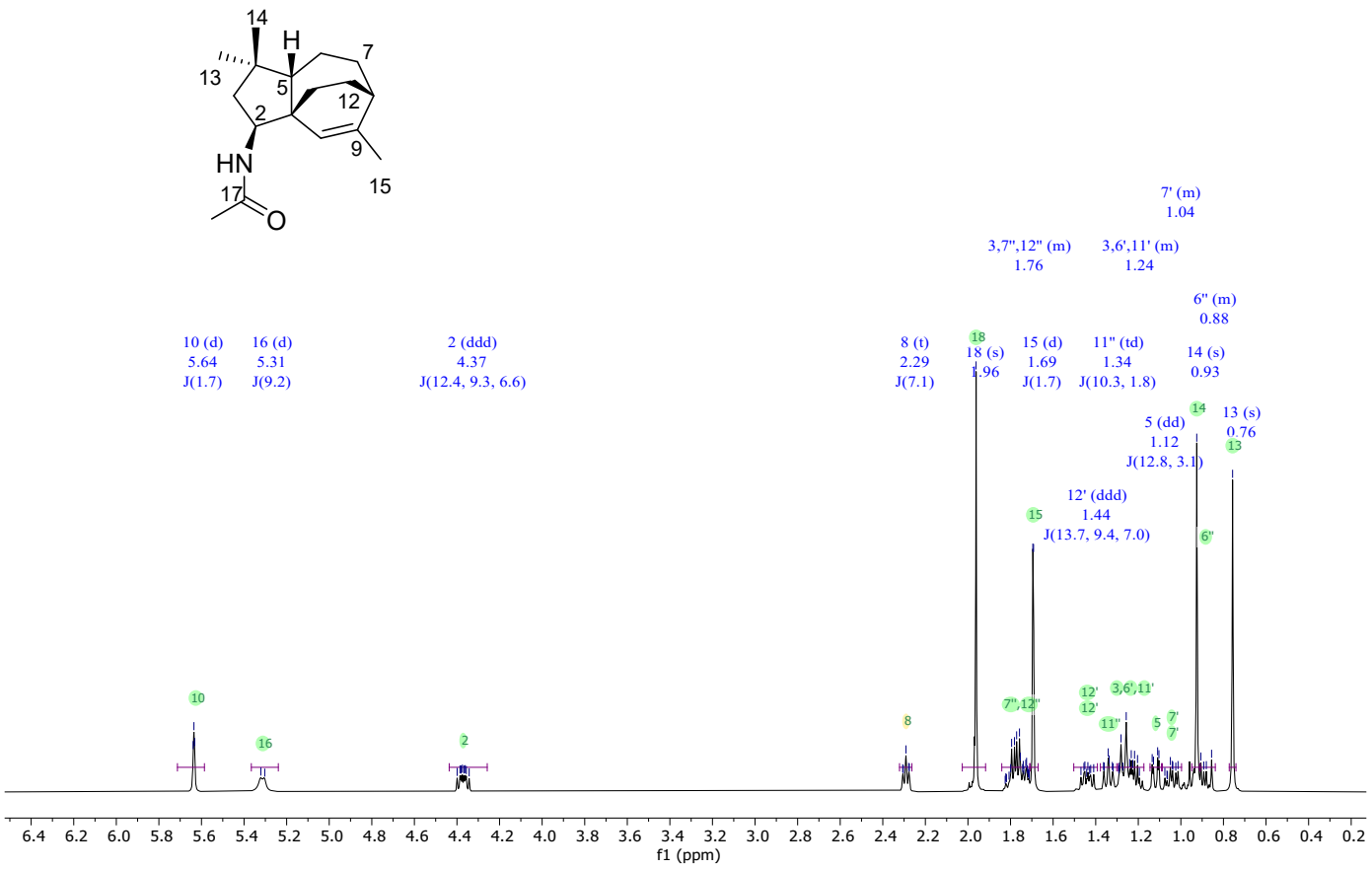

Figure S7a. ^{1}H NMR spectrum (500 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (14) in $CDCl_3$.

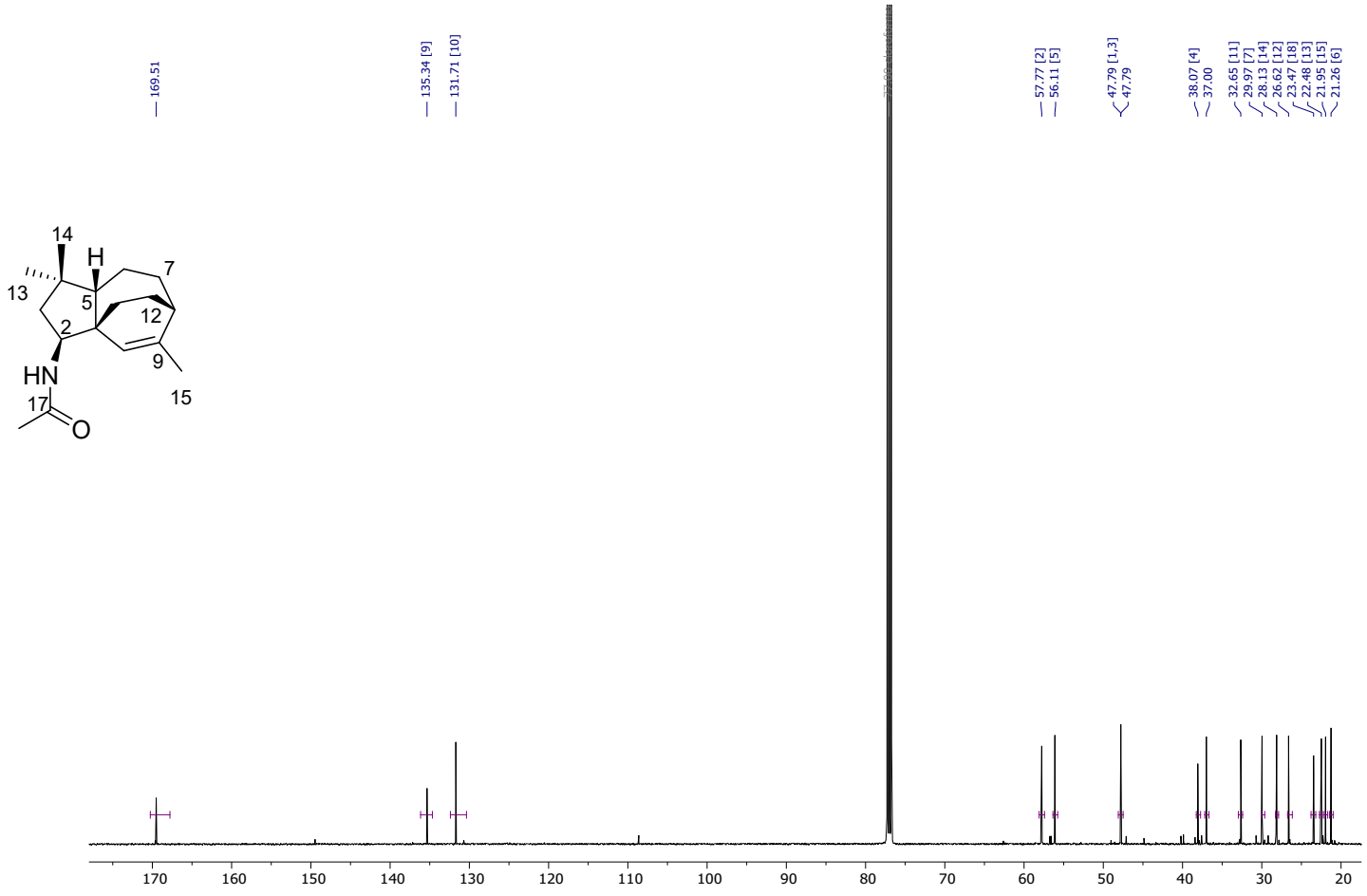

Figure S7b. ^{13}C NMR spectrum (125 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (14) in $CDCl_3$.

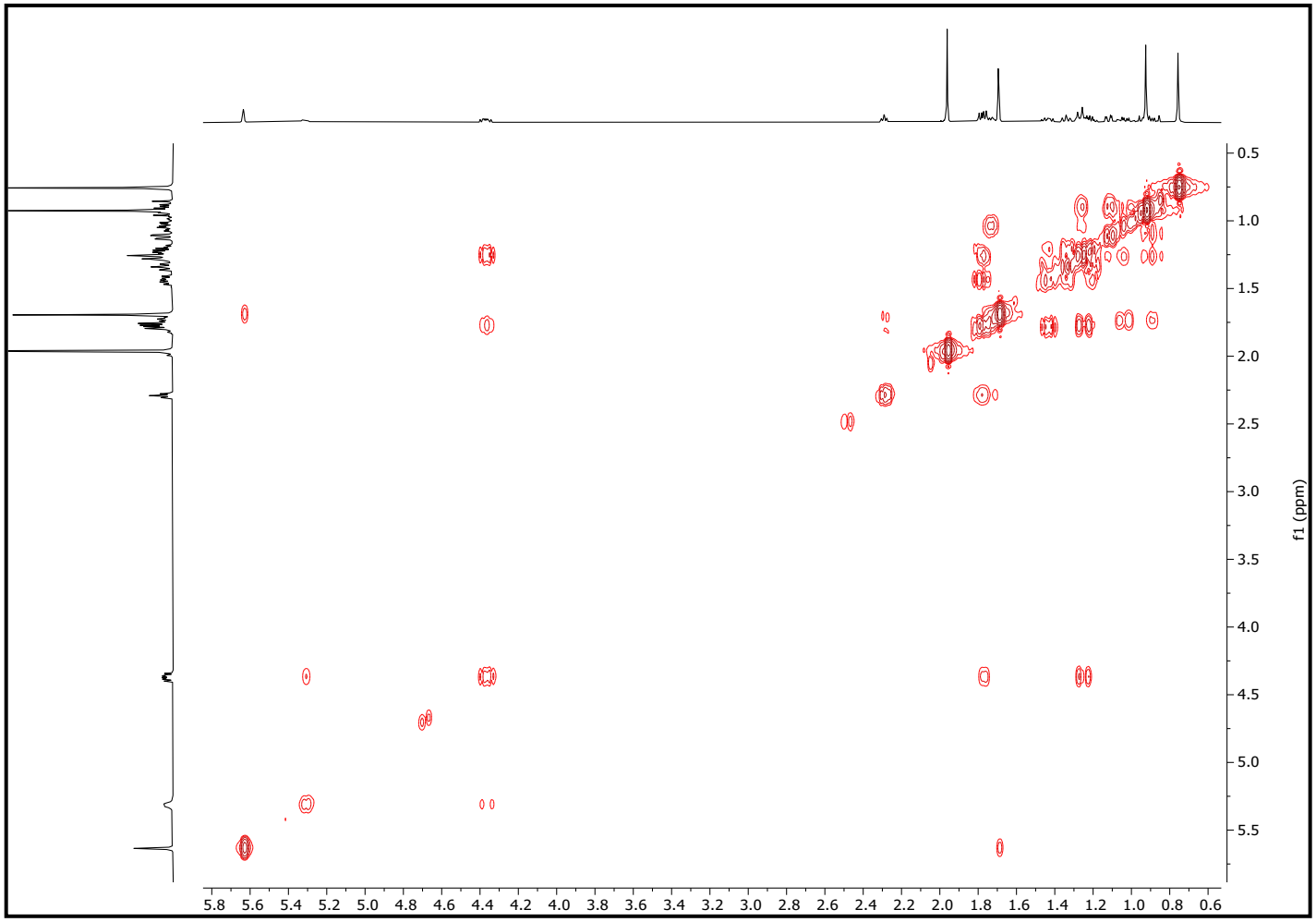

Figure S7c. $^{1}H,^{1}H$-COSY spectrum of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (14) in $CDCl_3$.

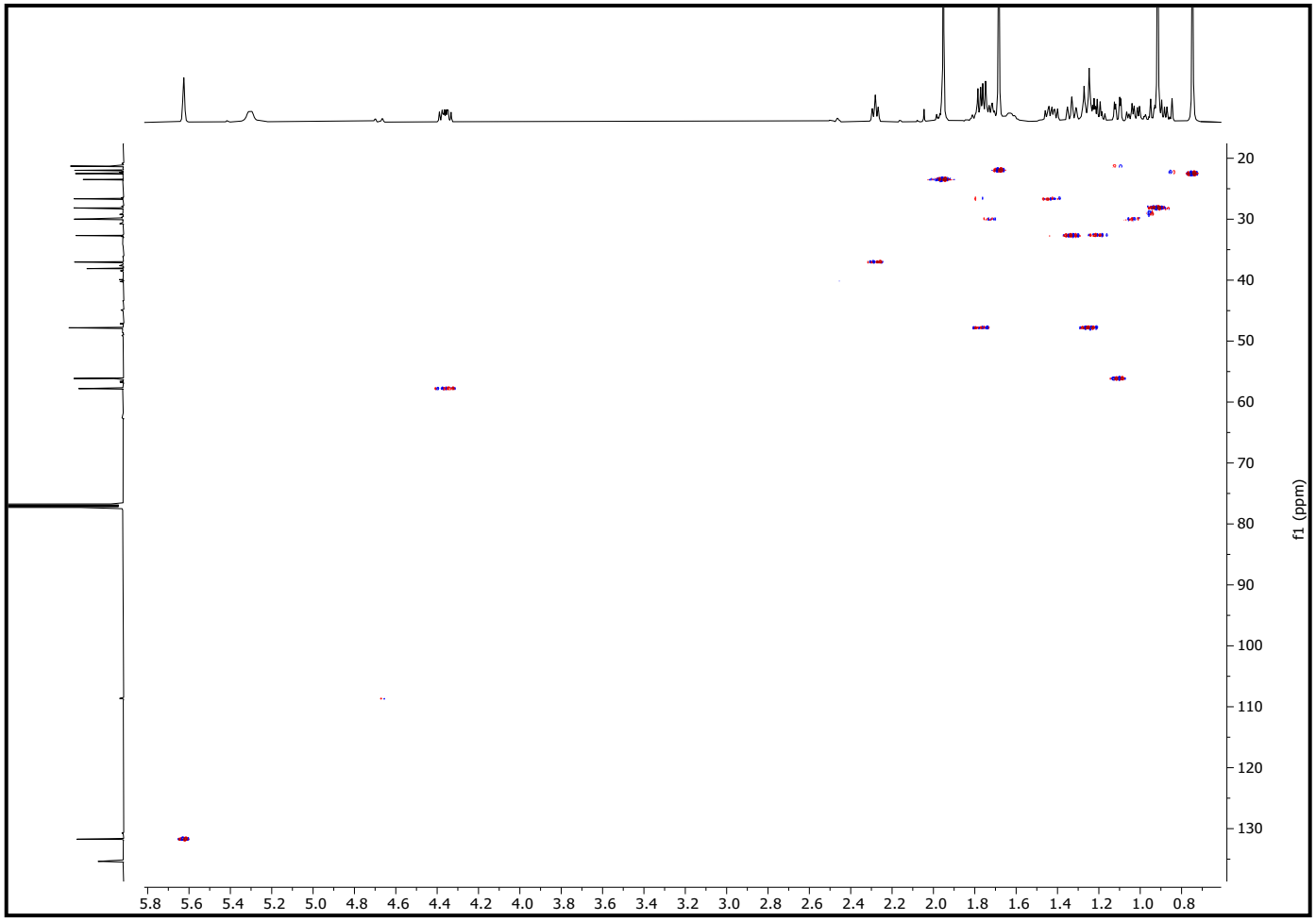

Figure S7d. HSQC spectrum of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (14) $CDCl_3$.

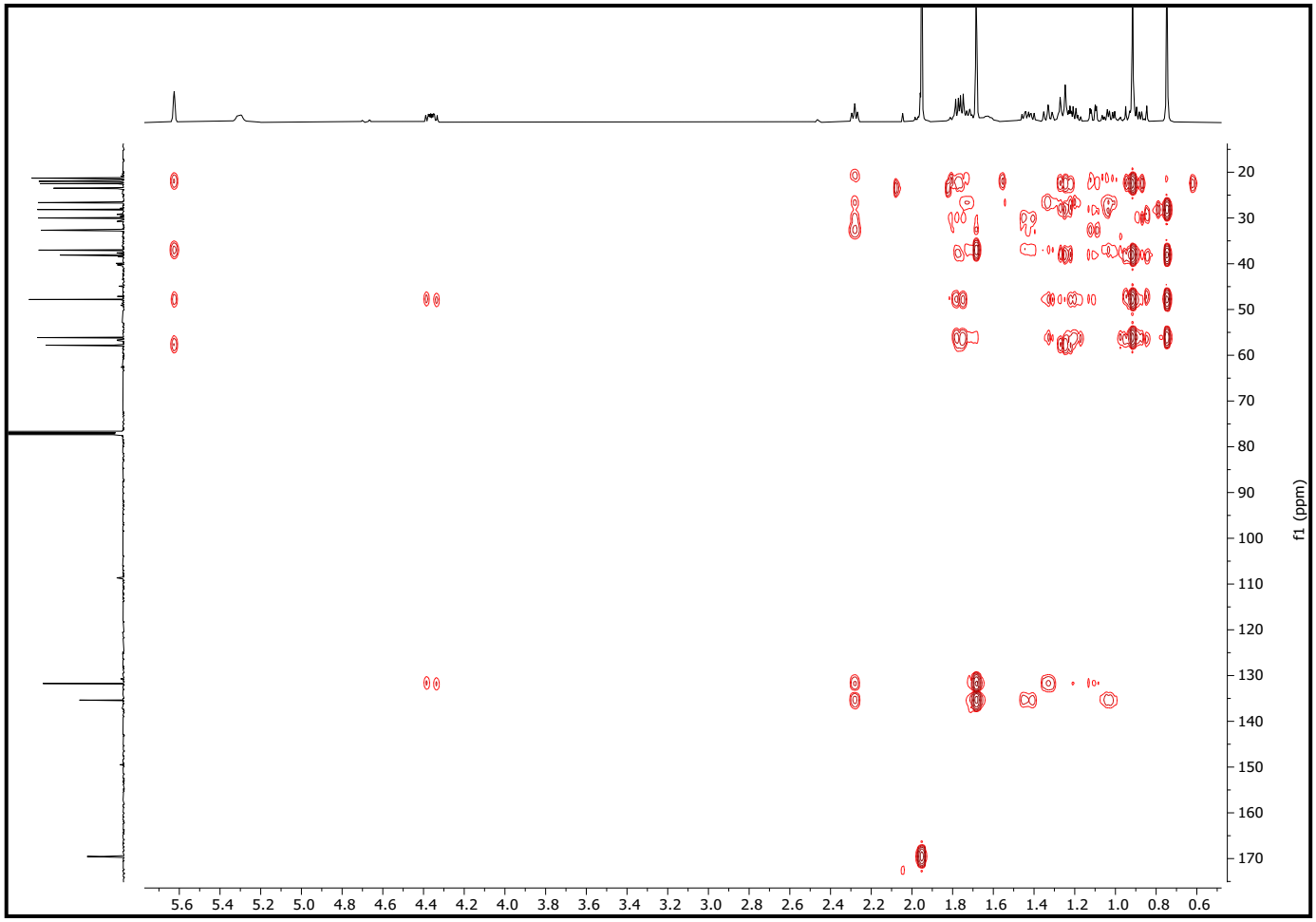

Figure S7e. HMBC spectrum of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (14) in $CDCl_3$.

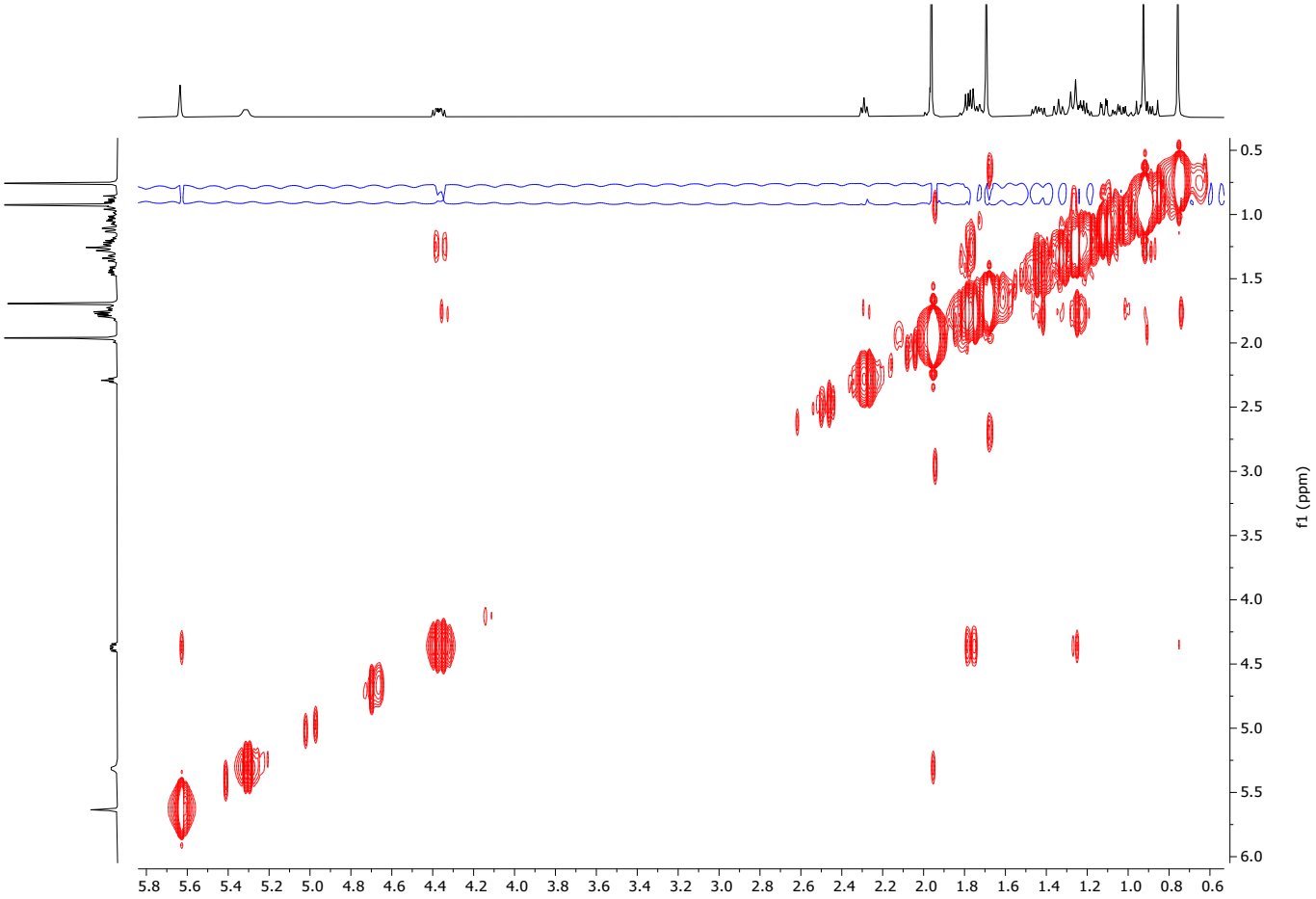

Figure S7f. NOESY2D spectrum of N-((1S,2S,5S,8S)-4,4,9-trimethyltricicle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (14) in $CDCl_3$.

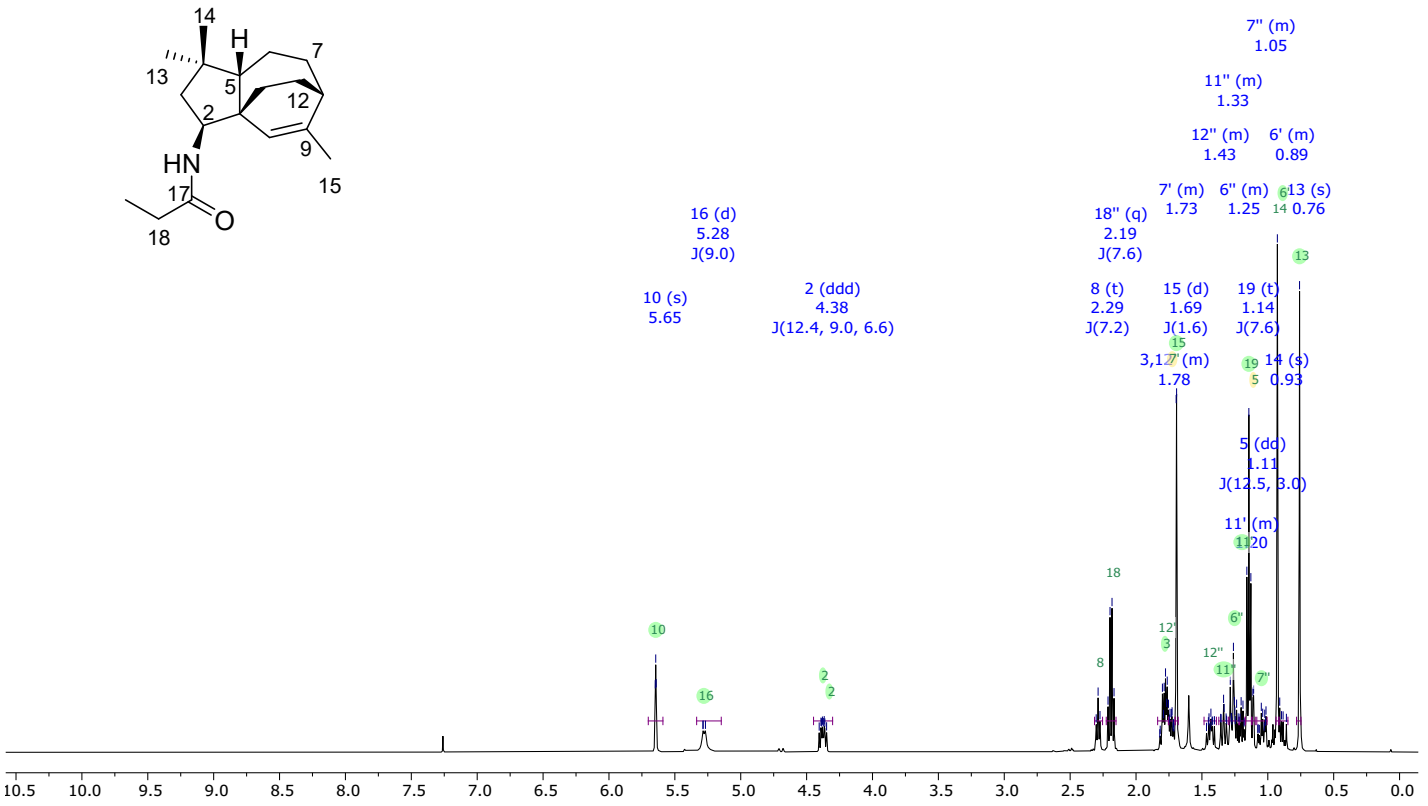

Figure S8a. ^{1}H-NMR spectrum (400 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)propionamide (15) in $CDCl_3$.

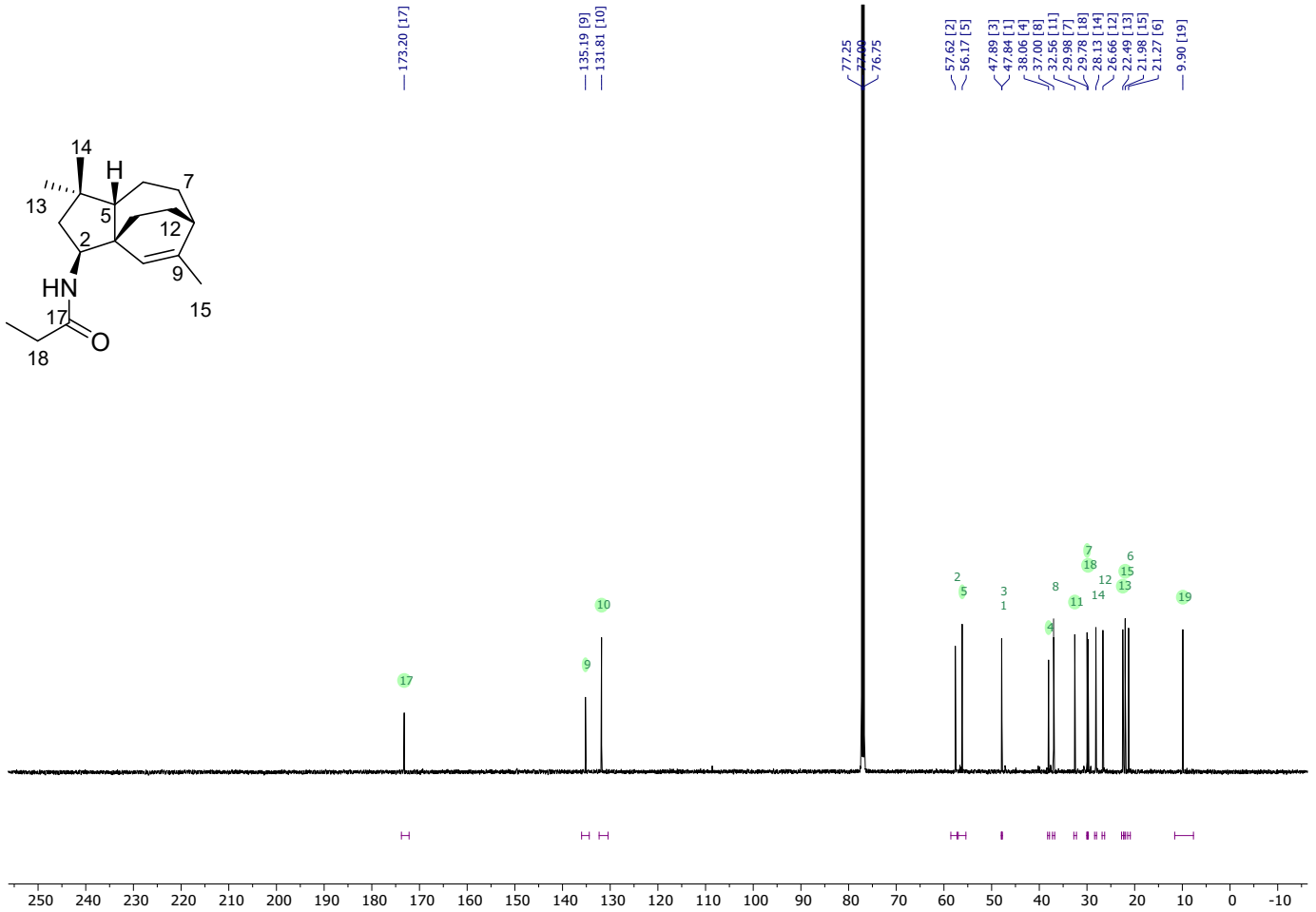

Figure S8b. ^{13}C-NMR spectrum (100 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)propionamida (15) in $CDCl_3$.

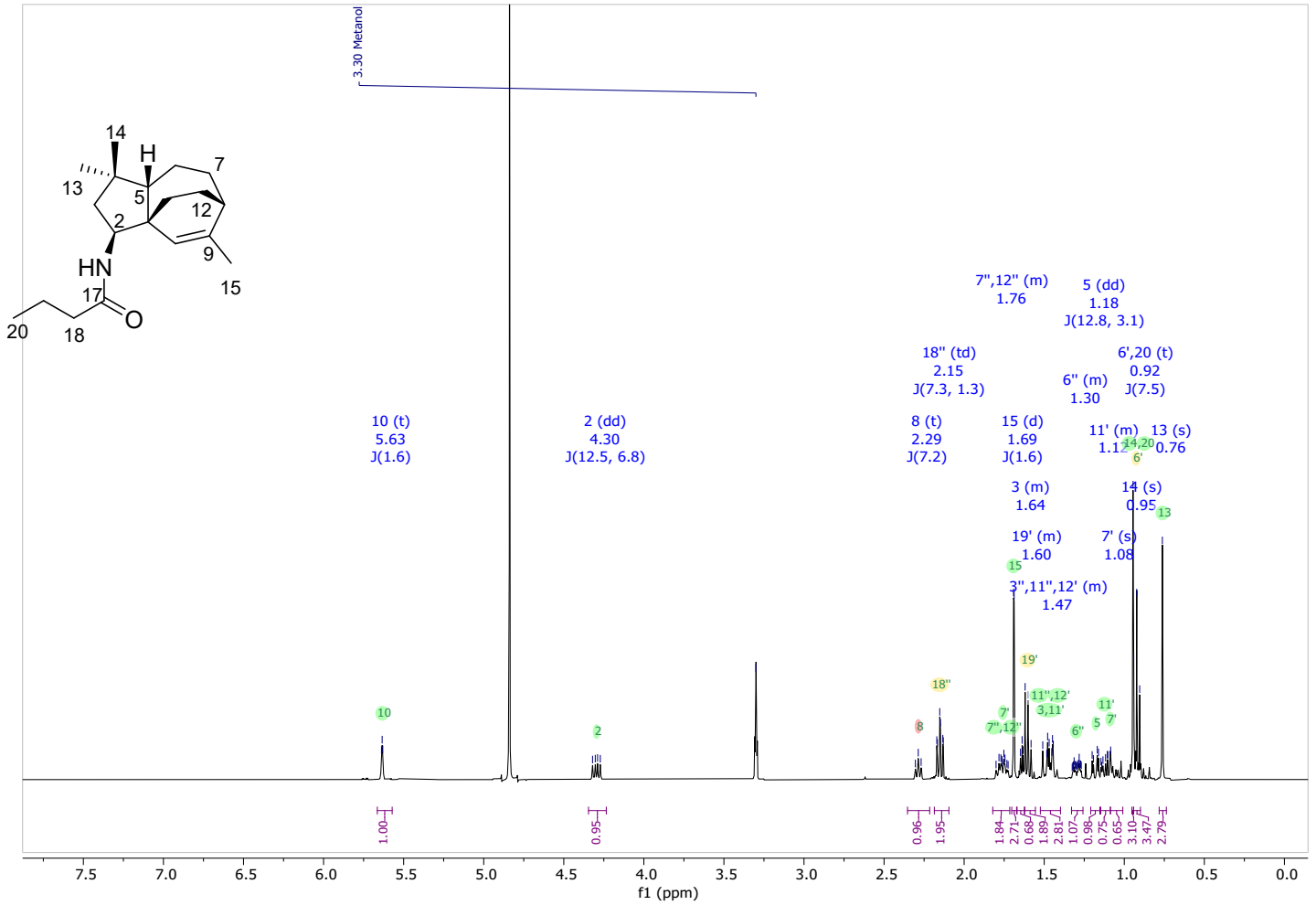

Figure S9a. ^{1}H-NMR spectrum (500 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)butiroamide (16) in CD_3OD.

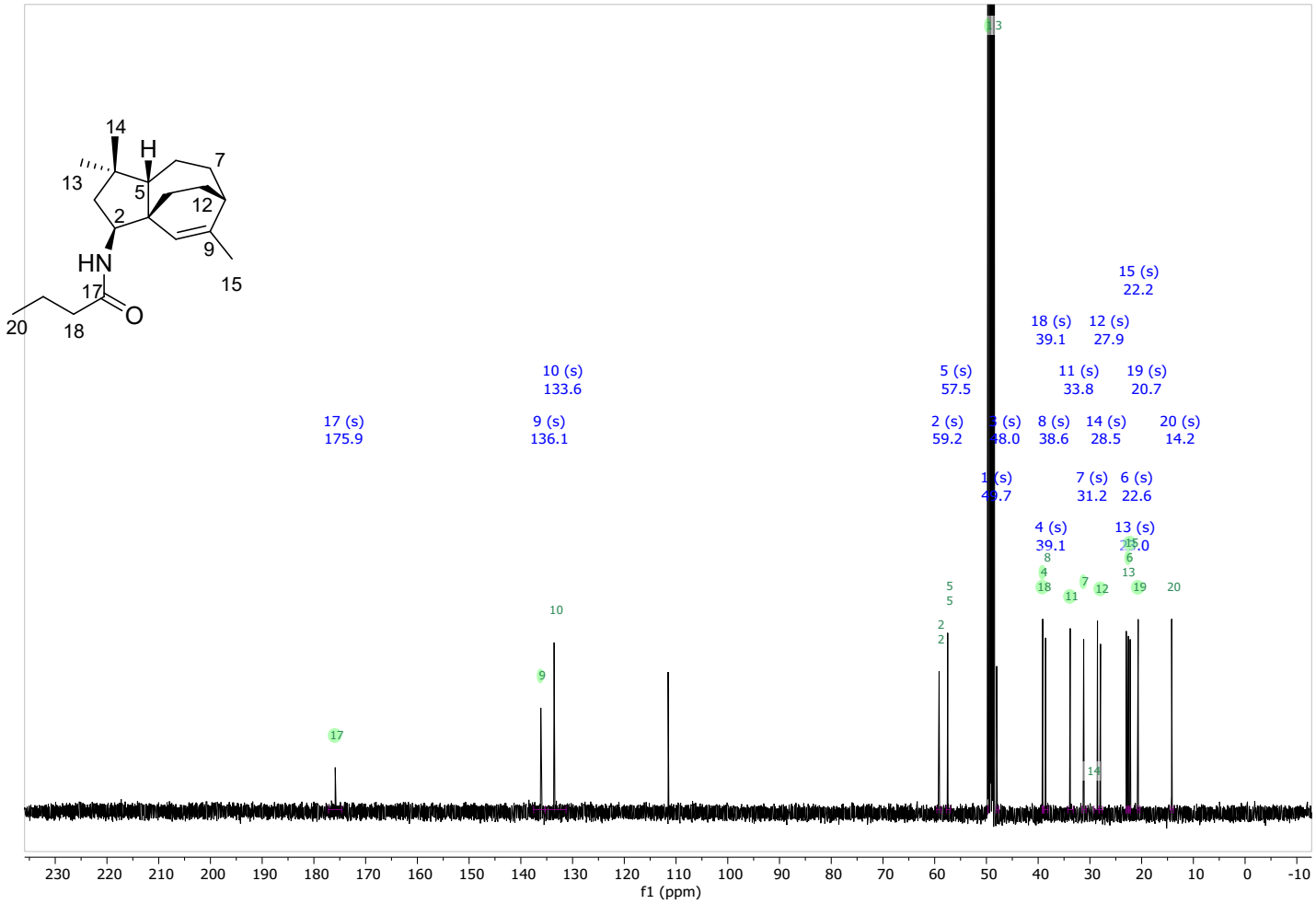

Figure S9b. ^{13}C-NMR spectrum (125 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)butiroamide (16) in CD_3OD.

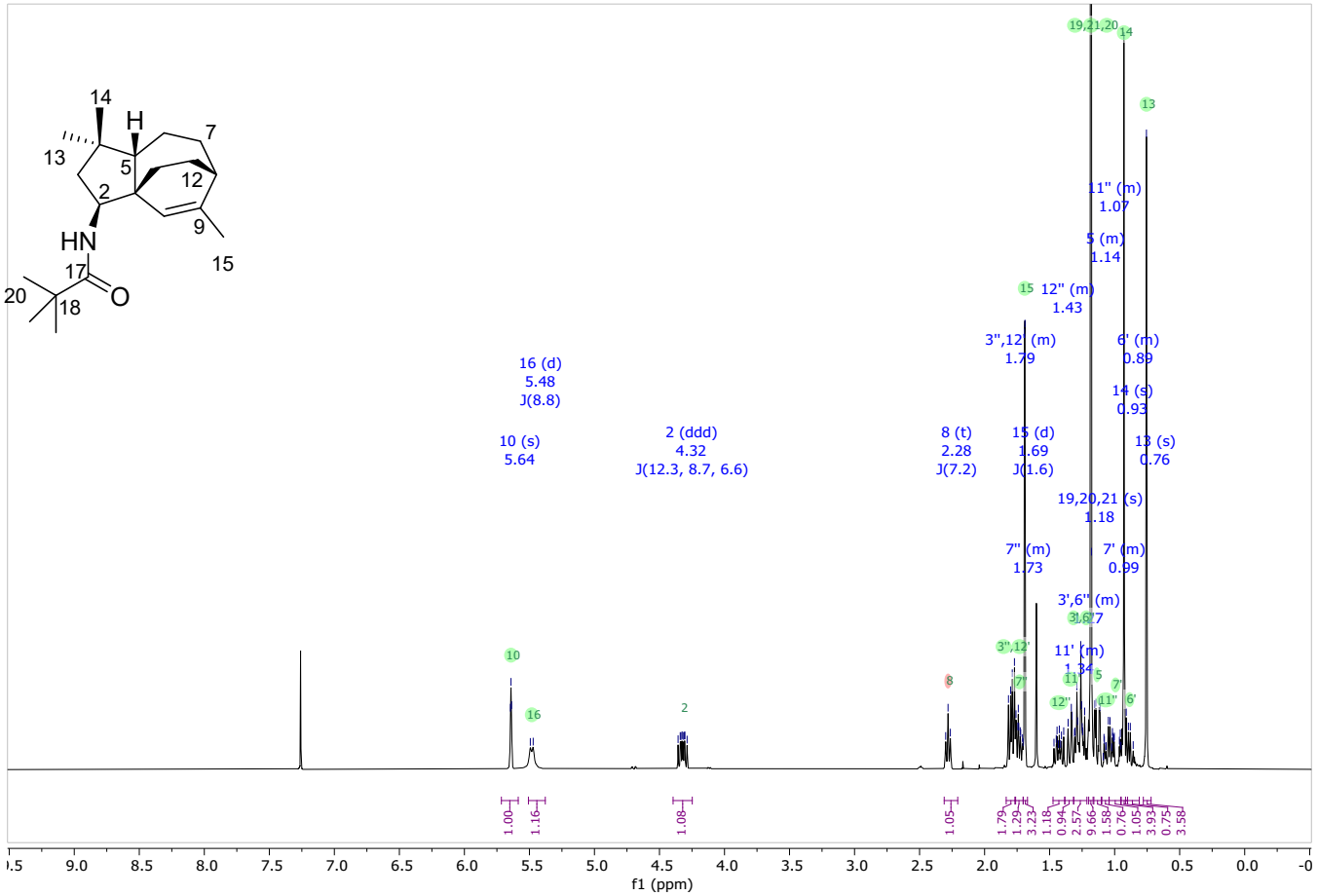

Figure S10a. ^{1}H-NMR spectrum (400 MHz) of 2,2-dimethyl-N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)propionamide (17) in $CDCl_3$.

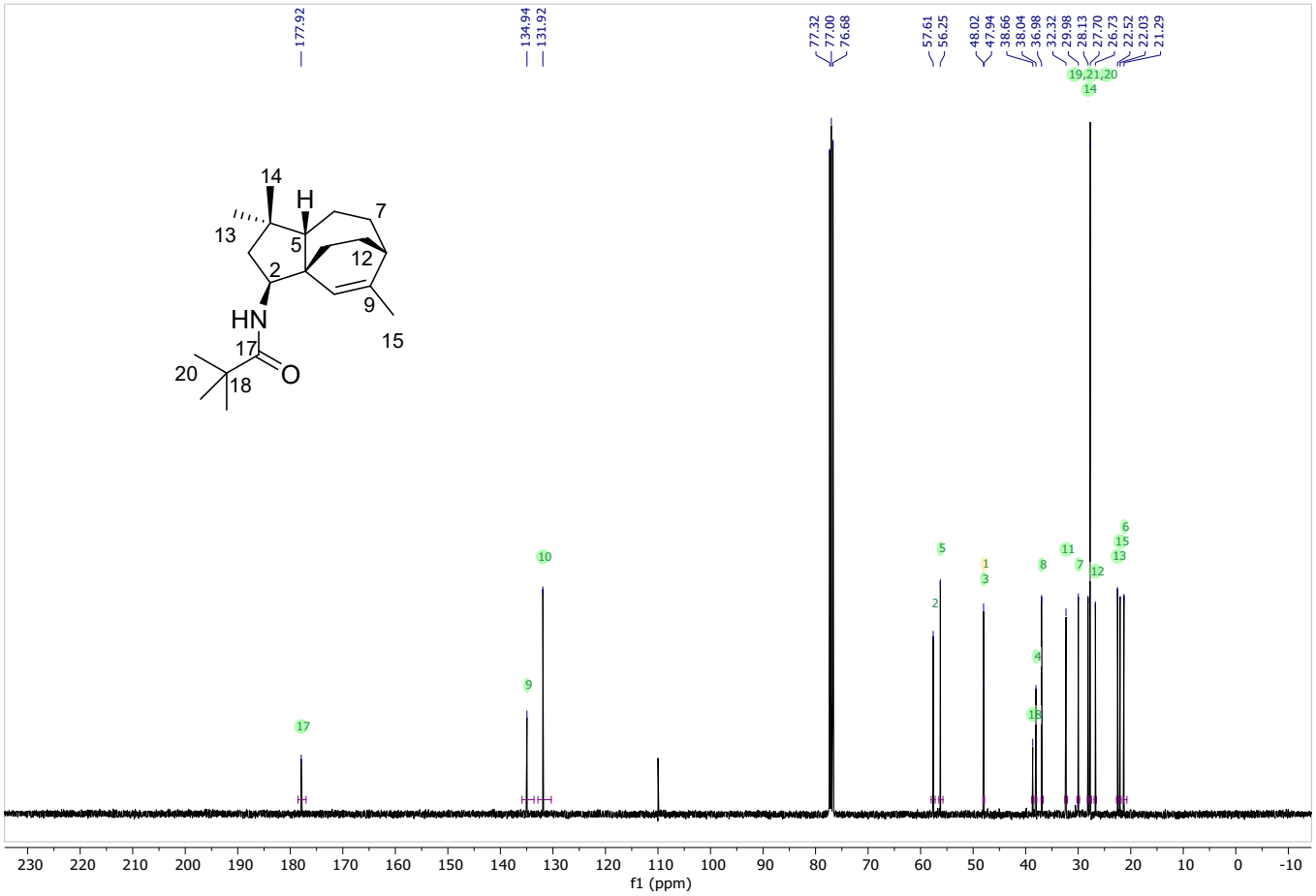

Figure S10b. ^{13}C-NMR spectrum (100 MHz) of 2,2-dimethyl-N-((1S,2S,5S,8S)-4,4,9-trimethylltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)propionamide (17) in $CDCl_3$.

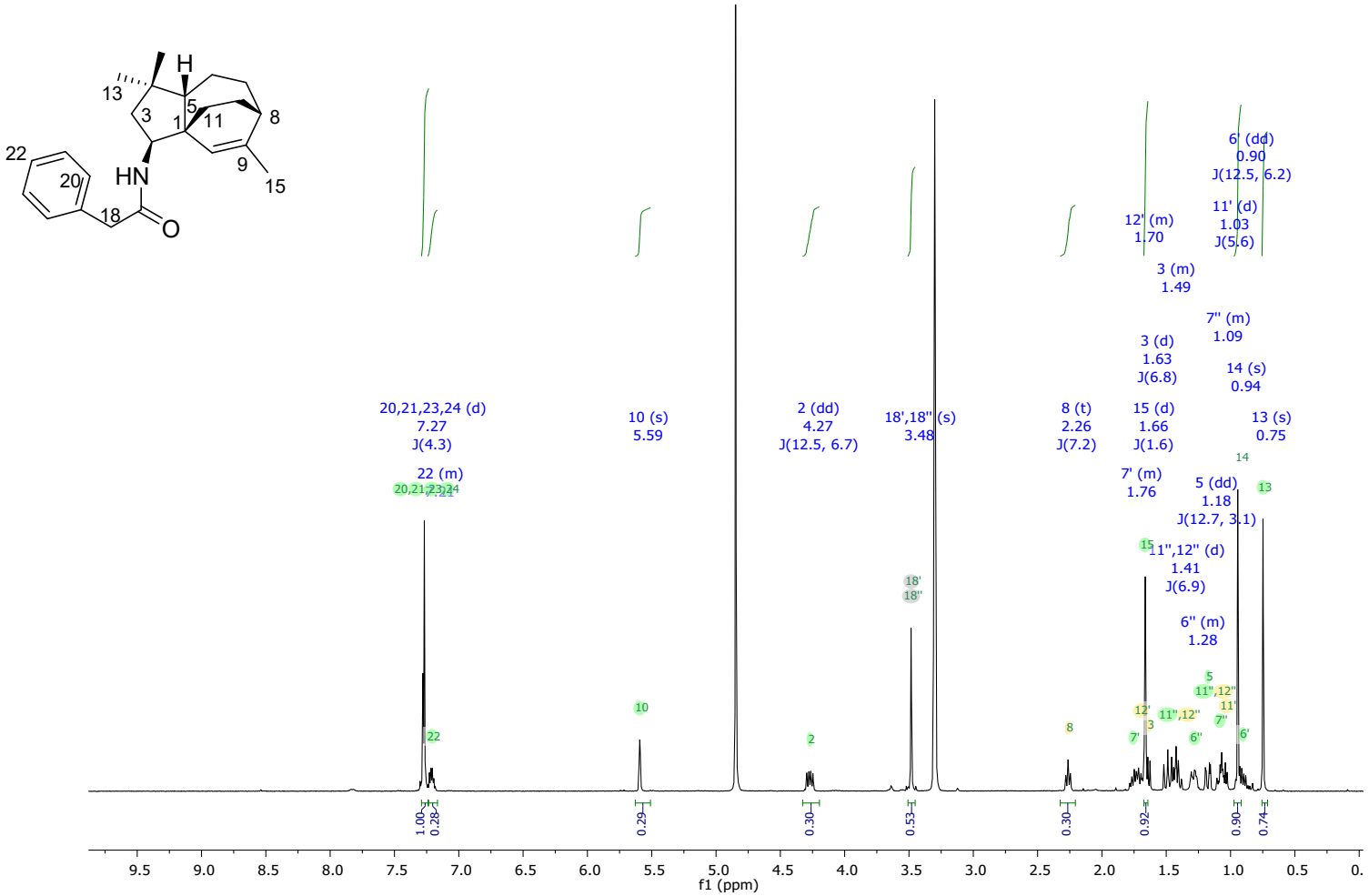

Figure S11a. ^{1}H-NMR spectrum(400 MHz) of 2-phenyl-N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (18) in CD_3OD.

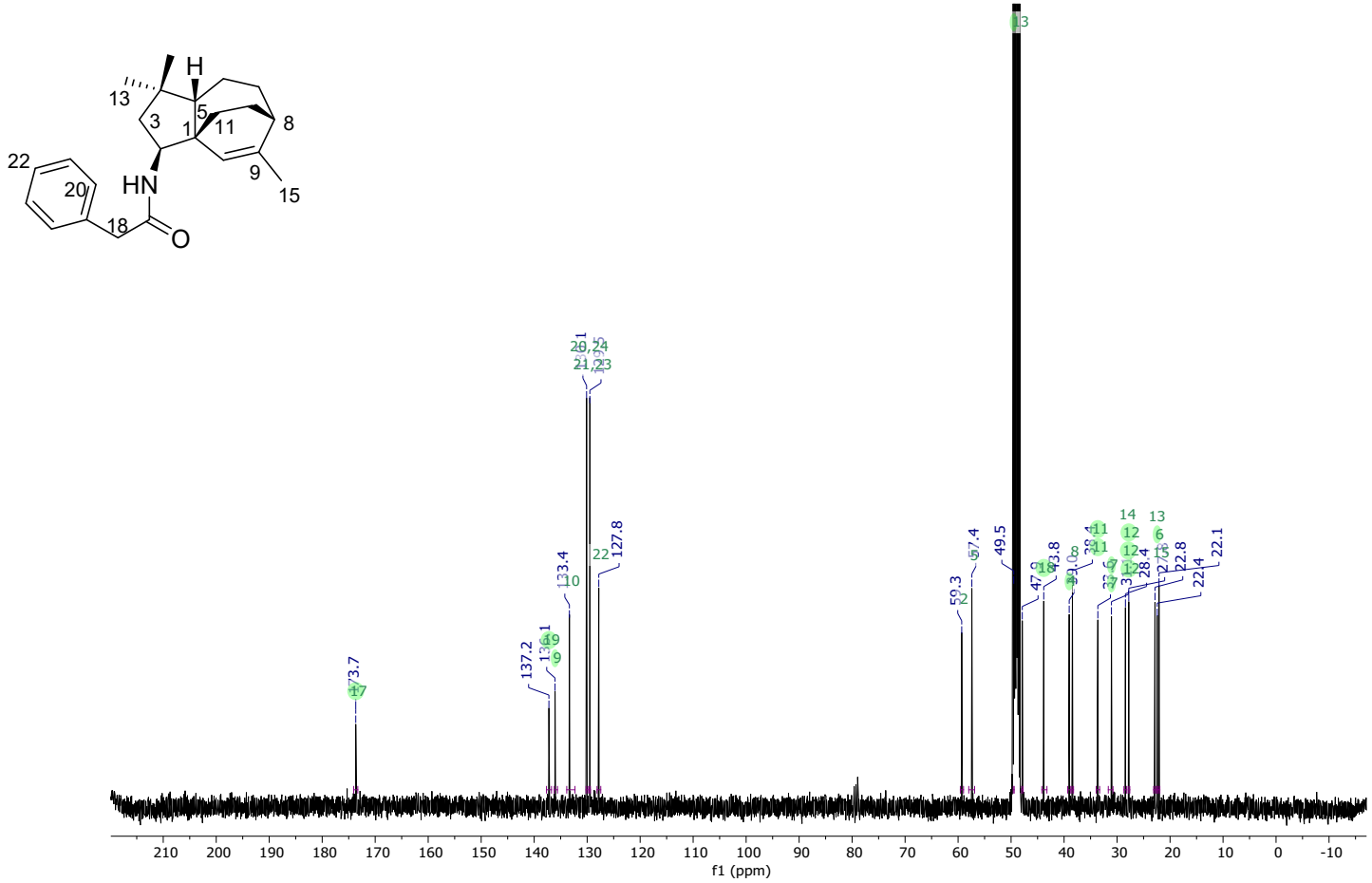

Figure S11b. ^{13}C-NMR spectrum(100 MHz) of 2-phenyl-N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)acetamide (18) in CD_3OD.

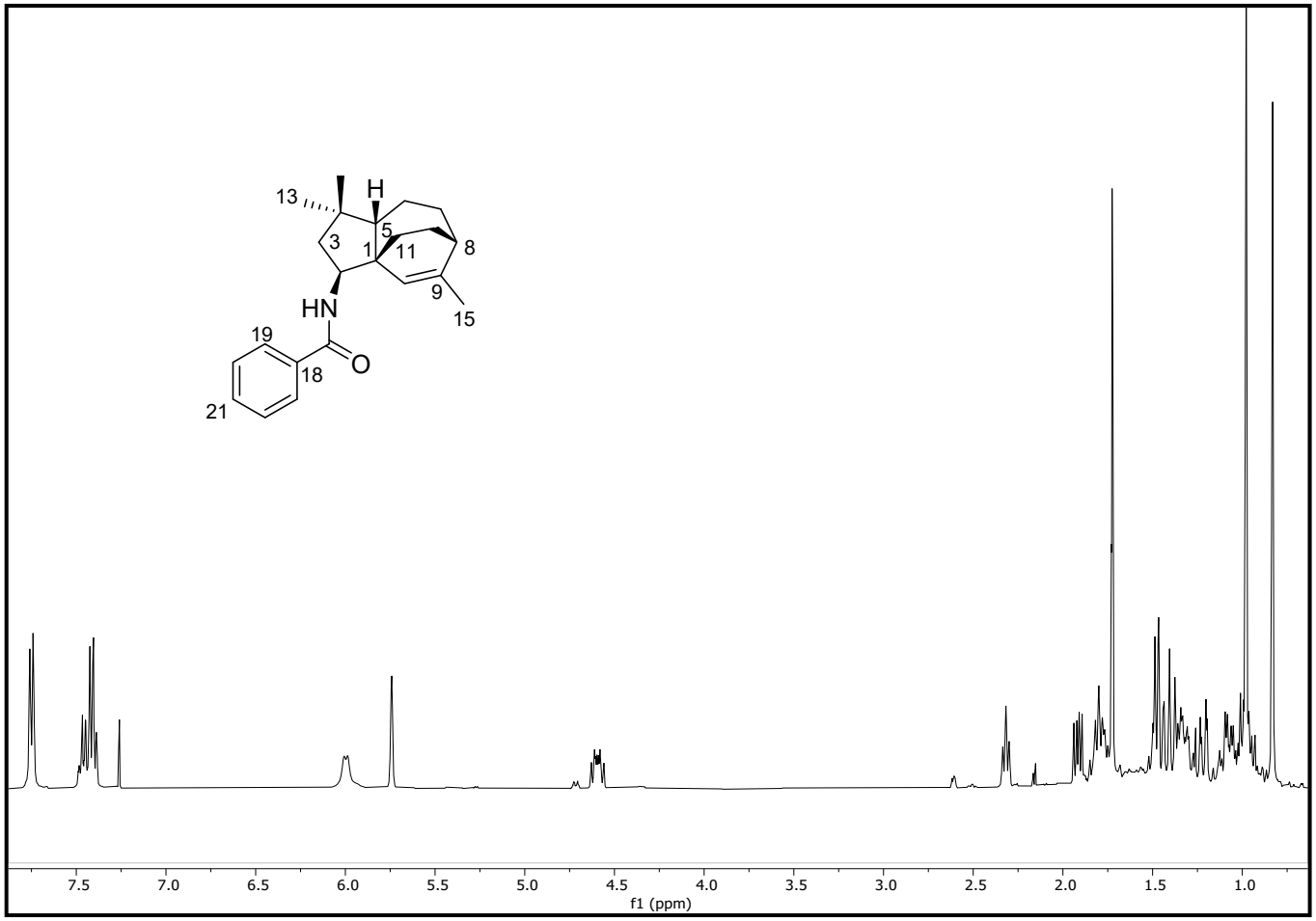

Figure S12a. ^{1}H- NMR spectrum (500 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)benzamide (19) in $CDCl_3$.

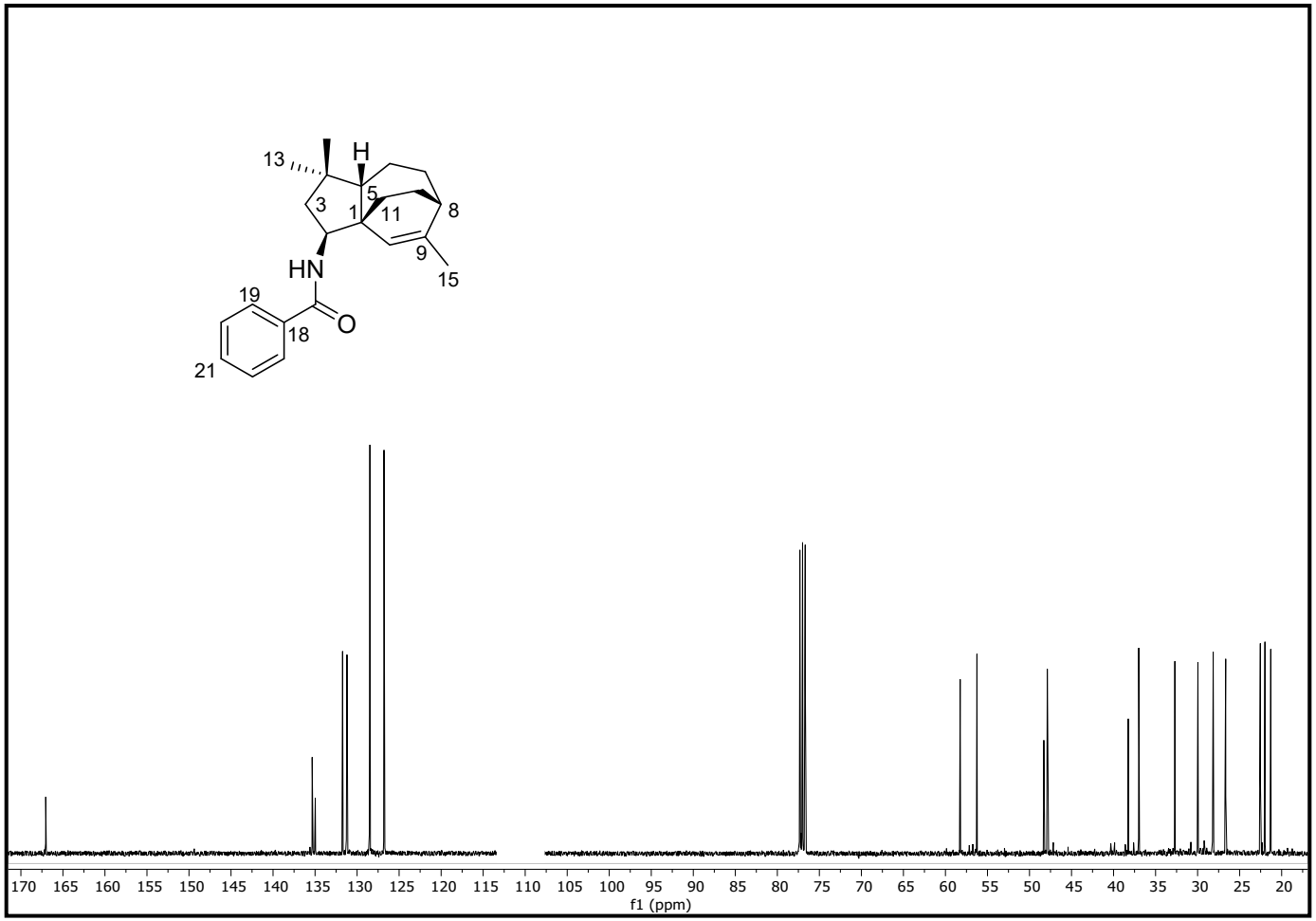

Figure S12b. ^{13}C-NMR spectrum (100 MHz) of N-((1S,2S,5S,8S)-4,4,9-trimethyltricycle(6.2.2.0^{1,5})dodec-9-en-2-yl)benzamide (19) in $CDCl_3$.

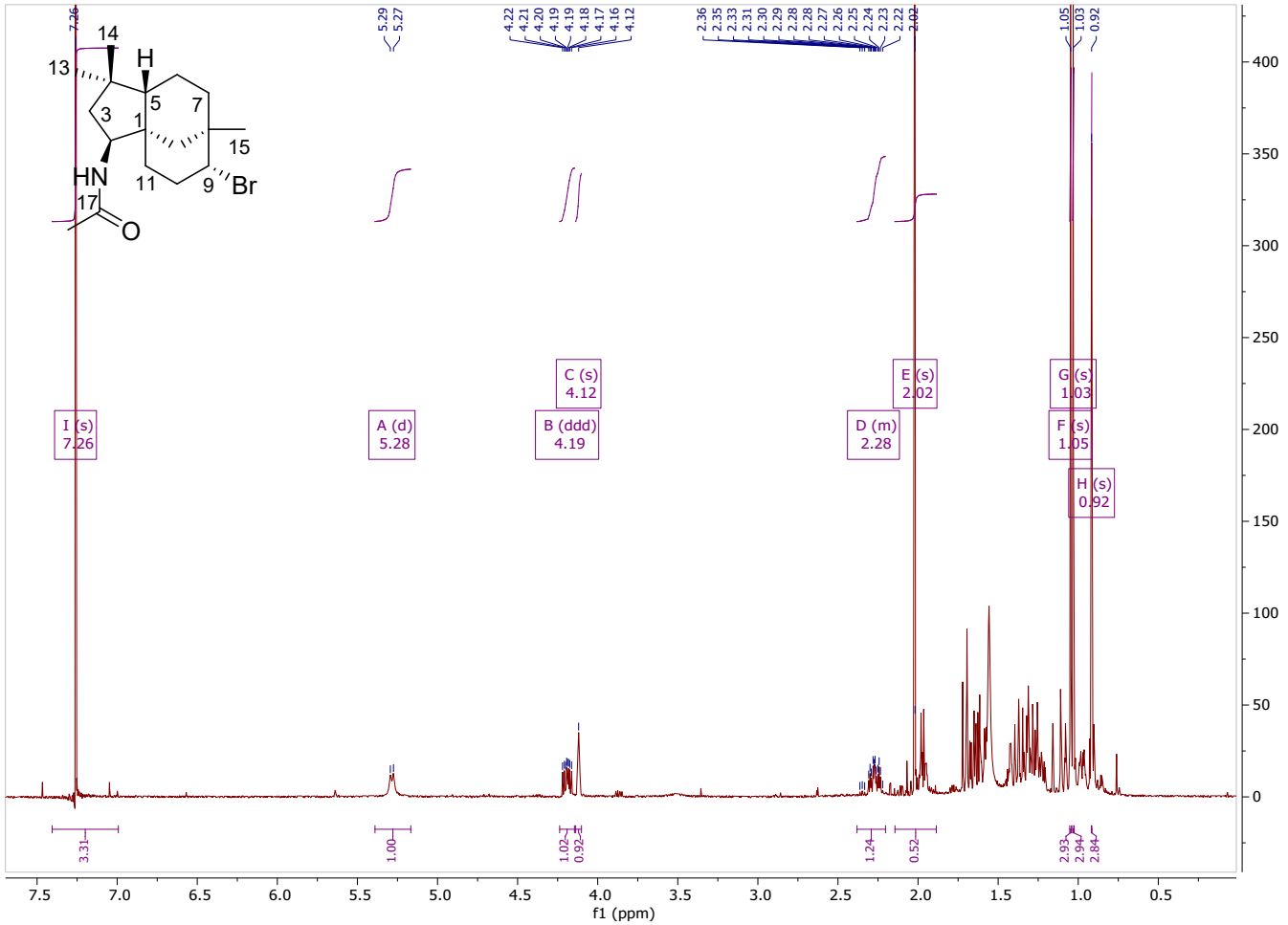

Figure S13a. ^{1}H NMR spectrum (500 MHz) of N-(9α-bromoclovan-2β-yl)acetamide (20)in $CDCl_3$.

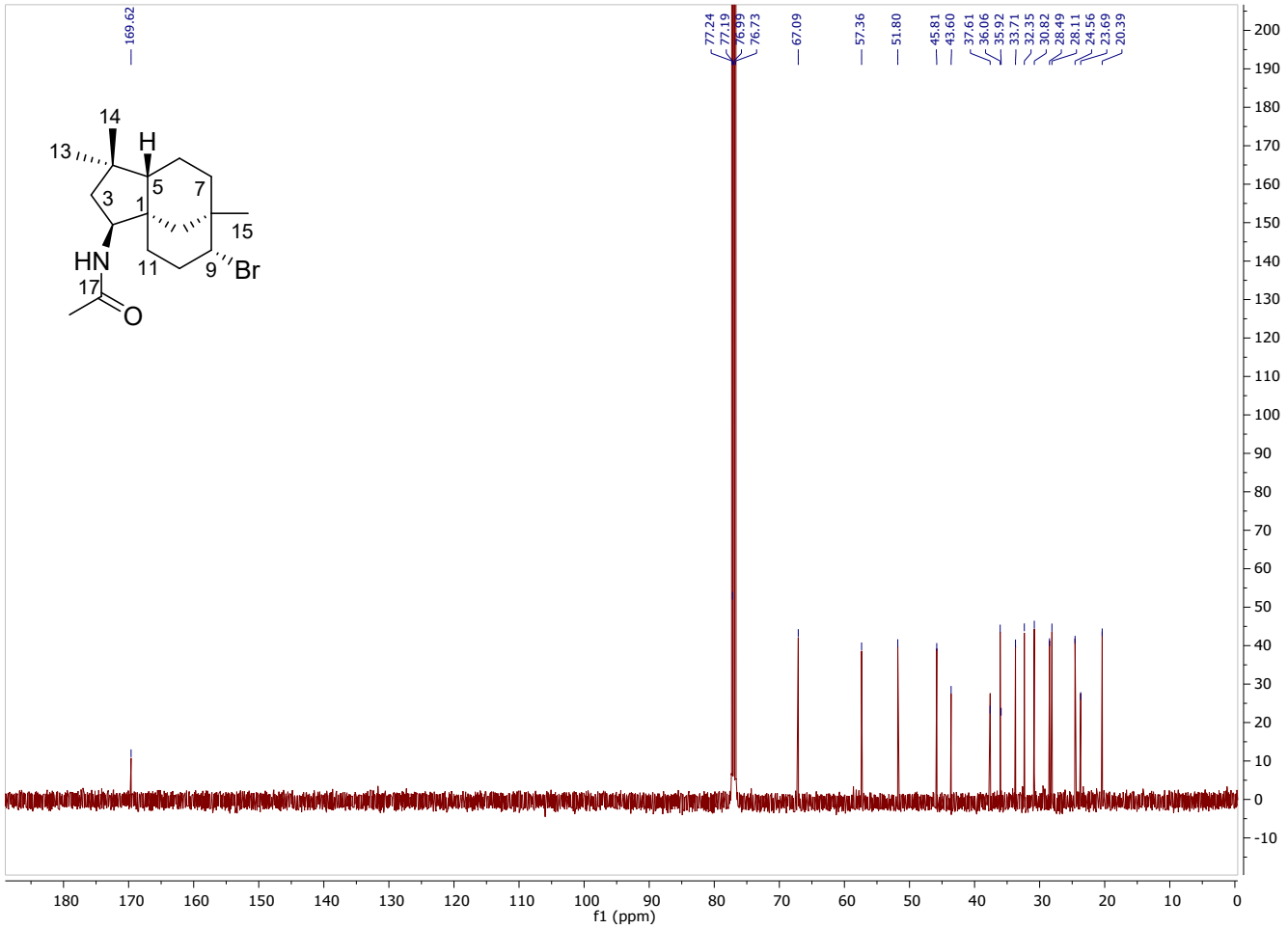

Figure S13b. ^{13}C NMR spectrum (125 MHz) of N-(9α-bromoclovan-2β-yl)acetamide (20) in $CDCl_3$.

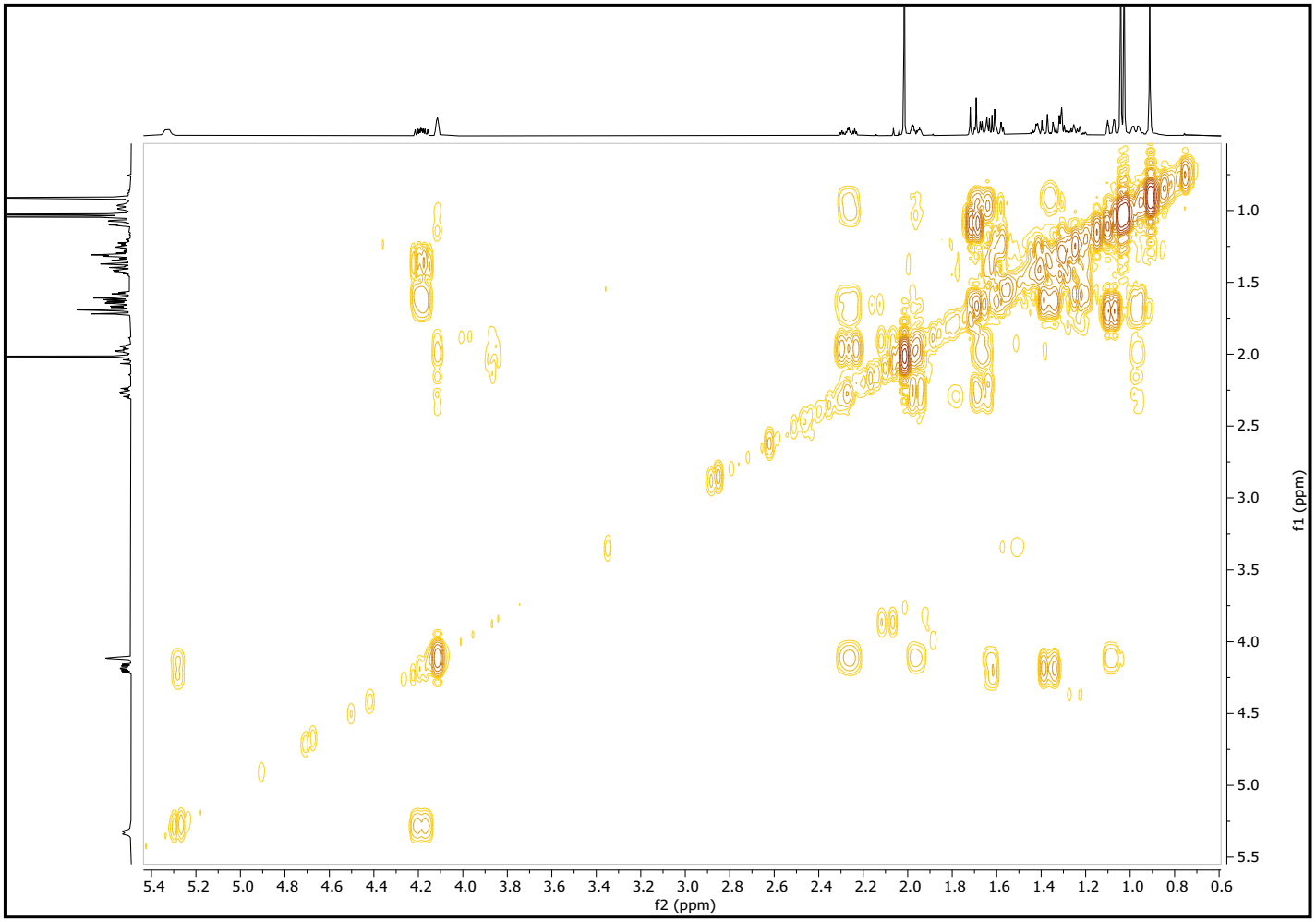

Figure S13c. $^{1}H,^{1}H$-COSY spectrum of N-(9α-bromoclovan-2β-yl)acetamide (20) in $CDCl_3$.

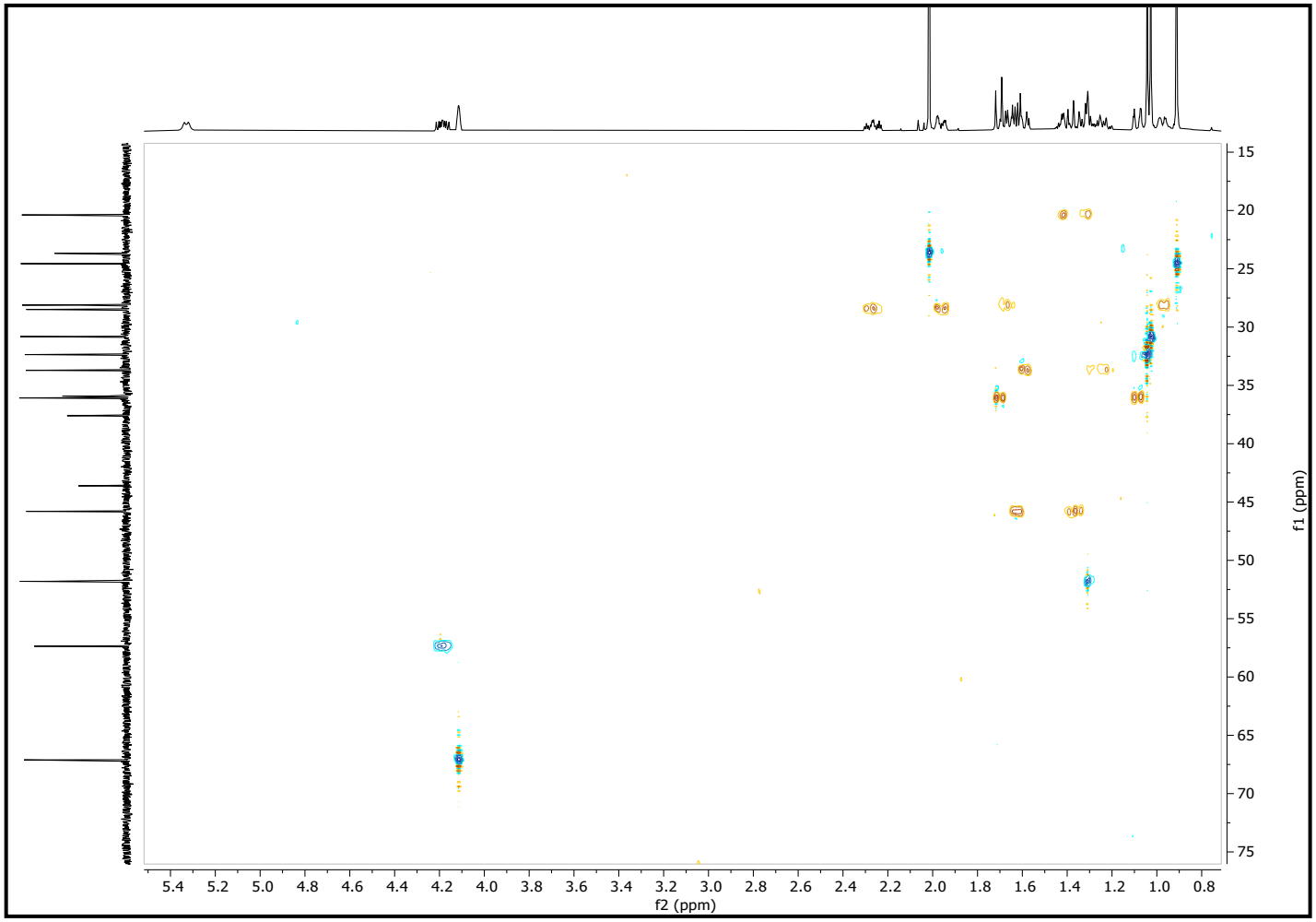

Figure S13d. HSQC spectrum of N-(9α-bromoclovan-2β-yl)acetamide (20) in $CDCl_3$.

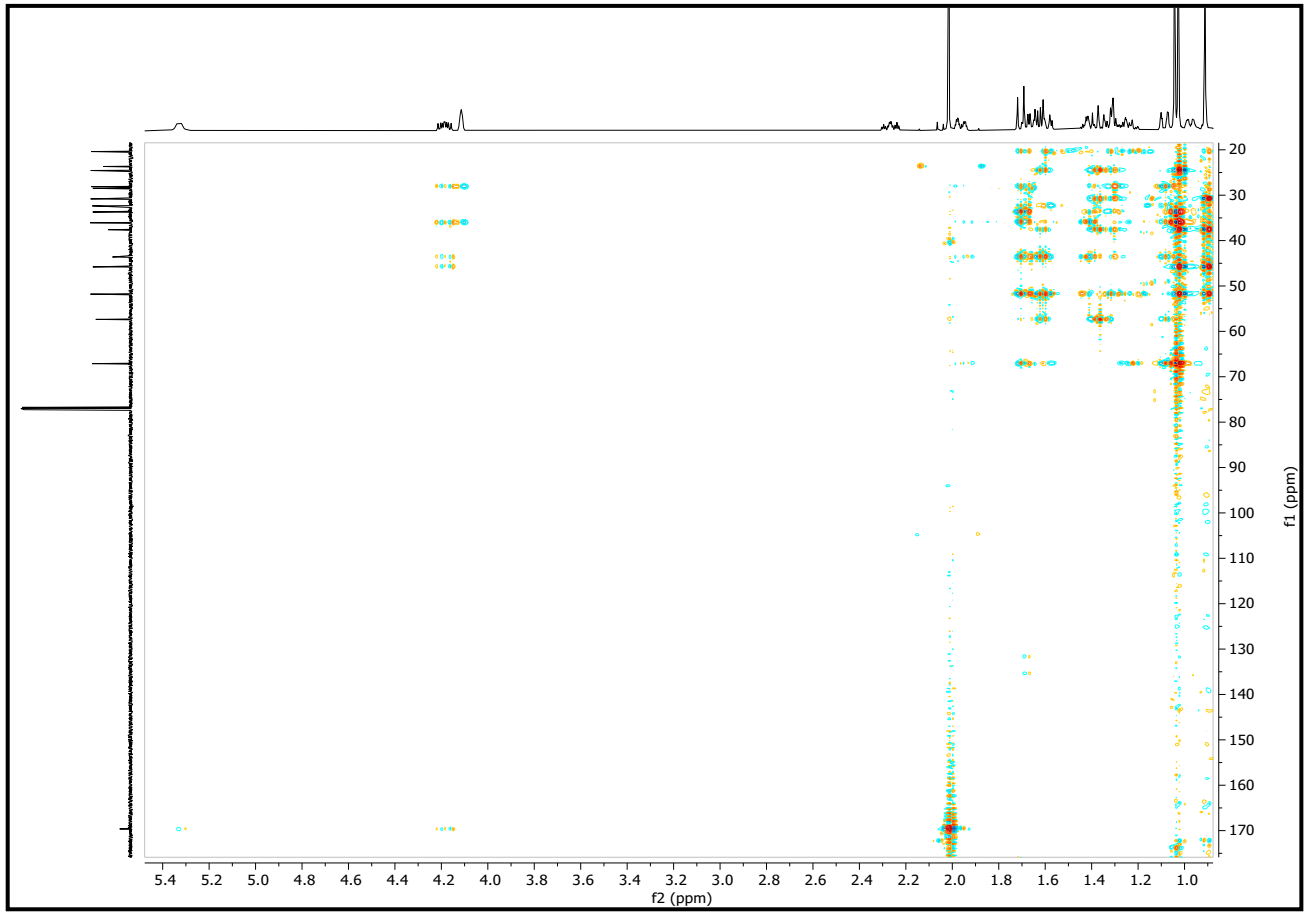

Figure S13e. HMBC spectrum of N-(9α-bromoclovan-2β-yl)acetamide (20) in $CDCl_3$.

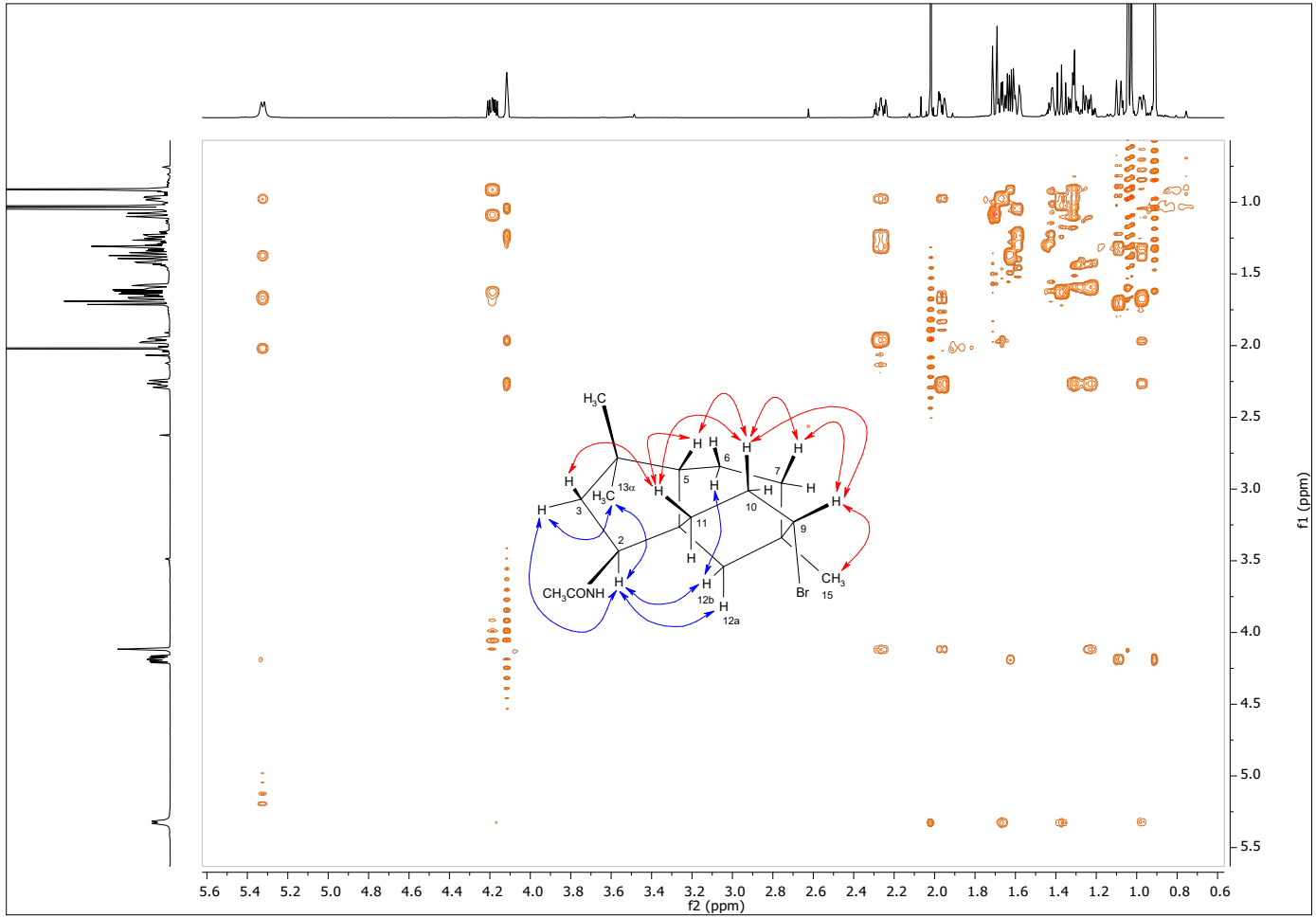

Figure S13f. NOESY2D spectrum of N-(9α-bromoclovan-2β-yl)acetamide (20) in $CDCl_3$. Selected NOESY2D correlations for compound 20.

Table S1. ^{1}H-NMR spectroscopic data of compounds 8-13.

	8	**9**	**10**	**11**	**12**	**13**
Position	δ_H[a], Mult. *J* (Hz)	δ_H[b], Mult. *J* (Hz)	δ_H[b], Mult. *J* (Hz)	δ_H[c], Mult. *J* (Hz)	δ_H[c], Mult. *J* (Hz)	δ_H[b], Mult *J* (Hz)
1	-	-	-	-	-	-
2	α: 4.09, dd (13.0, 6.0)	α: 4.16, m	α: 4.17, ddd (12.6, 9.4, 6.0)	α: 4.14, ddd (12.5,9.2, 6.0)	α: 4.11, ddd (12.4, 9.4, 6.0)	α: 4.38, ddd (12.6, 9.3, 6.0)
3	α: 1.45, dd (11.8, 6.0) β: 1.53, m	α: 1.32, m β: 1.61, m	a: 1.35, m b: 1.61, m	α: 1.35, m β: 1.62, m	α: 1.52, m β: 1.19, m	α: 1.74, dd (11.6, 6.0) m β: 1.5, m
4	-	-	-	-	-	-
5	β: 1.43, m	β: 1.34, m	β: 1.35, m	β: 1.35, m	β: 1.28, m	β: 1.41, m
6	a , b: 1.46, m	a, b: 1.35, m	a, b: 1.40, m	a, b: 1.40, m	a, b: 1.35, m	a, b: 1.45, m
7	α: 1.36, m β: 1.10, m	a: 1.40, m b: 1.06, m	a: 1.40, m b: 1.07, m	a: 1.40, m b: 1.06, m	a: 1.35, m b: 1.03, m	a: 1.41, m b: 1.10, m
8	-	-	-	-	-	-
9	β: 3.20, s	β: 3.28, s	β: 3.28, s	β: 3.28, d (3.1)	β: 3.24, s	β: 3.30, d (3.3)
10	α: 1.57, m β: 1.98, m	α: 1.61, m β: 1.96, tdd (14.6, 5.0, 3.0)	a: 1.60, m b: 1.96, m	a: 1.62, m b: 1.96, tdd (14.6, 5.0, 3.1)	α: 1.52, m β: 1.88, tdd (14.3, 5.0, 3.2)	α: 1.65, m β: 2.00, m
11	a: 1.50, m b: 1.00, m	a: 1.47, m b: 0.94, m	a: 1.48, m b: 0.91, m	a: 1.46, m b: 0.94, m	a: 1.23, m b: 0.69, ddd (10.0, 4.7, 2.4)	a: 1.59, m b: 1.07, m
12	a: 1.54, d (12,4) b: 0.99, d (12,4)	a: 1.58, d (12.6) b: 1.06, m	a:1.56, d (13.2) b: 1.07, m	a: 1.55, m b: 1.06, m	a: 1.52, m b: 1.03, m	a: 1.65, m b: 1.16, m
13	α: 0.91, s	α: 0.91, s	α: 0.91, s	α: 0.91, s	α: 0.87, s	α: 0.97, s
14	β: 1.04, s	β: 1.02, s	β: 1.02, s	β: 1.02, s	β: 0.95, s	β: 1.07, s
15	0.90, s	0.94, s	0.94, s	0.94, s	0.93, s	0.96, s
16	-	5.3, d (9.4)	5.3, d (9.4)	5.5, d (9.0)	5.23, d (9.4)	6.00, d (9.3)
17	-	-	-	-	-	-
18	1.95, s	a y b:2.20, m	a y b: 2.15, m	-	3.59, m	-
19	-	1.15, t (7.6)	a y b: 1.67, m	1.20, s	-	7.76, dd (6.7, 2.8)
20	-	-	0.95, t (7.5)	1.20, s	7.27, m	7.43, td (6.8, 2.9)
21	-	-	-	1.20, s	7.35, m	7.49, t (6.8)
22					7.27, m	7.43, td (6.8, 2.9)
23					7.35, m	7.76, dd (6.7, 2.8)
24					7.27, m	-

[a] CD_3OD (600 MHz); [b] $CDCl_3$ (400 MHz); [c] $CDCl_3$ (500 MHz).

Table S2. ^{13}C-NMR spectroscopic data of compounds 8-13.

	8	9	10	11	12	13
Position	δ_C[a]	δ_C[b]	δ_C[b]	δ_C[c]	δ_C[c]	δ_C[b]
1	45.4, C	43.5, C	43.5, C	43.7, C	43.8, C	44.0, C
2	59.0, CH	57.4, CH	57.4, CH	57.3, CH	57.6, CH	58.0, CH
3	46.2, CH_2	45.9, CH_2	46.0, CH_2	45.9, CH_2	45.6, CH_2	46.0, CH_2
4	38.5, C	37.6, C	37.6, C	37.6, C	37.6, C	37.8, C
5	51.9, CH	50.6, CH	50.6, CH	50.6, CH	50.5, CH	50.7, CH
6	21.7, CH_2	20.5, CH_2	20.6, CH_2	20.6, CH_2	20.5, CH_2	20.6, CH_2
7	34.3, CH_2	33.1, CH_2	33.1, CH_2	33.1, CH_2	33.0, CH_2	33.1, CH_2
8	35.9, C	34.8, C	34.8, C	34.8, C	34.7, C	34.9, C
9	75.7, CH	75.0, CH	75.0, CH	74.9, CH	74.8, CH	75.0, CH
10	26.6, CH_2	25.4, CH_2	25.5, CH_2	25.5, CH_2	25.5, CH_2	25.5, CH_2
11	28.8, CH_2	27.6, CH_2	27.6, CH_2	27.4, CH_2	27.1, CH_2	27.7, CH_2
12	37.0, CH_2	35.6, CH_2	35.5, CH_2	35.6, CH_2	35.6, CH_2	35.7, CH_2
13	25.0, CH_3	24.6, CH_3	24.6, CH_3	24.6, CH_3	24,5, CH_3	24.6, CH_3
14	31.2, CH_3	30.9, CH_3	30.9, CH_3	30.9, CH_3	30.8, CH_3	30.9, CH_3
15	29.1, CH_3	28.1, CH_3	28.1, CH_3	28.1, CH_3	28.1, CH_3	28.1, CH_3
16	-	-	-	-	-	-
17	172.9, C	173.4, C	172.5, C	178.1, C	170.6, C	167.1, C
18	22.7, CH_3	29.9, CH_2	39.0, CH_2	38.8, C	44.0 CH_2	135.0, C
19	-	9.9, CH_3	19.2, CH_2	27.7, CH_3	135.2, C	126.8, CH
20	-	-	13.8, CH_3	27.7, CH_3	129.4, CH	128.5, CH
21	-	-	-	27.7, CH_3	129.0, CH	131.3, CH
22					127.3, C	128.5, CH
23					129.0, C	126.8, CH
24					129.4, CH	

[a] CD_3OD (150 MHz); [b] $CDCl_3$ (100 MHz); [c] $CDCl_3$ (125 MHz).

Table S3. ^{1}H-NMR spectroscopic data of compounds 14-19.

	14	**15**	**16**	**17**	**18**	**19**
Position	δ_H[a], Mult. *J* (Hz)	δ_H[b], Mult. *J* (Hz)	δ_H[c], Mult. *J* (Hz)	δ_H[b], Mult. *J* (Hz)	δ_H[d], Mult. *J* (Hz)	δ_H[b], Mult. *J* (Hz)
1	-	-	-	-	-	-
2	α: 4.37, ddd (12.4, 9.2, 6.6)	α: 4.38, ddd (12.4, 9.0, 6.6)	α: 4.,30, dd (12.5, 6.8)	α: 4.32, ddd (12.3, 8.8, 6.6)	α: 4.27, dd (12.5, 6.7)	α: 4.59, ddd (12.1, 8.0, 6.7)
3	α:1.76 , m β: 1.24, m	α: 1.78, m β: 1.25, m	α: 1.64, m β: 1.47, m	α: 1.79, m β: 1.27, m	α: 1.63, m β: 1.49, m	α: 1.92, dd (11.7, 6.7) β: 1.36, m
4	-	-	-	-	-	-
5	β: 1.12, dd (12.8, 3.1)	β: 1.11, dd (12.5, 3.0)	β: 1.18 dd (12.8, 3.1)	β: 1.14, m	β: 1.18, dd (12.7, 3.1)	α: 1.21, dd (12.5, 2.9)
6	a: 1.24, m b: 0.88, m	a: 1.25, m b: 0.89, m	a: 1.30, m b: 0.92, m	a: 1.27, m b: 0.89, m	a: 1.28, m b: 0.90, m	a: 1.27, m b: 0.94, m
7	a: 1.76, m b: 1.04, m	a: 1.73, m b: 1.05, m	a: 1.76, m b: 1.08, m	a: 1.73, m b: 0.99, m	a: 1.76, m b: 1.09, m	a: 1.77, m b: 1.06, m
8	2.29, t (7.,1)	2.29, t (7.2)	2.29, t (7.2)	2.28, t (7.2)	2.26, t (7.2)	2.32, t (7.2)
9	,	-	-	-	-	-
10	5.64, s	5.65, s	5.63, t (1.6)	5.64, s	5.59, s	5.74, s
11	a: 1.34, m b: 1.24, m	a: 1.33, m b: 1.20, m	a: 1.,47, m b: 1.12, m	a: 1.34, m b: 1.07, m	a: 1.41, m b: 1.03, m	a: 1.48, d (8.4) b: 1.31, m
12	a: 1.,76, m b: 1.44, m	a: 1.78, m b: 1.43, m	a: 1.76, m b: 1.47, m	a: 1.79, m b: 1.43, m	a: 1.70, m b: 1.41, m	a: 1.82, m b: 1.42, m
13	α: 0.76, s	α: 0.76, s	α: 0.76, s	α: 0.76, s	α: 0.75, s	α: 0.83, s
14	β: 0.93, s	β: 0.93, s	β: 0.95, s	β: 0.93, s	β: 0.94, s	β: 0.98, s
15	1.69, d (1.7)	1.69, d (1.,6)	1.69, d (1.,6)	1.69, d (1.6)	1.66, d (1.6)	1.73, s
16	5.31, d (9.2)	5.28, d (9.0)	-	5.48, d (8.8)	-	6.00, d (8.0)
17	-	-	-	-	-	-
18	1.96, s	a, b: 2.19, q (7.6)	a, b: 2.15, td (7.3, 1.3)	-	a, b: 3.48, s	-
19	-	1.14, t (7.6)	a, b: 1.60, m	1.18, s	-	7.75, m
20	-	-	0.92, t (7.5)	1.18, s	7.27, m	7.40, m
21	-	-	-	1.18, s	7.27, m	7.46, m
22					7.21, m	7.40, m
23					7.27, m	7.75, m
24					7.27, m	-

[a] $CDCl_3$ (500 MHz); [b] $CDCl_3$ (400 MHz); [c] CD_3OD (500 MHz); [d] CD_3OD (400 MHz)

Table S4. ^{13}C-NMR spectroscopic data of compounds 14-19.

	14	**15**	**16**	**17**	**18**	**19**
Position	δ_C[a],	δ_C[b],	δ_C[d],	δ_C[b],	δ_C[d],	δ_C[b],
1	47.8, C	47.8, C	49.7, C	47.9, C	49.5, C	48.3, C
2	57.8, CH	57.6, CH	59.2, CH	57.6, CH	59.3, CH	58.3, CH
3	47.8, CH_2	47.9, CH_2	48.0, CH_2	48.0, CH_2	47.9, CH_2	47.9, CH_2
4	38.1, C	38.1, C	39.1, C	38.7, C	39.0, C	38.3, C
5	56.1, CH	56.2, CH	57.5, CH	56.2, CH	57.4, CH	56.3, CH
6	21.3, CH_2	21.3, CH_2	22.6, CH_2	21.3, CH_2	22.4, CH_2	21.3, CH_2
7	30.0, CH_2	30.0, CH_2	31.2, CH_2	30.0, CH_2	31.1, CH_2	30.0, CH_2
8	37.0, CH	37.0, CH	38.6, CH	37.0, CH	38.4, CH	37.0, CH
9	135.3, C	135.2, C	136.1, C	134.9, C	136.1, C	135.3, C
10	131.7, CH	131.8, CH	133.6, CH	131,9, CH	133.4, CH	131.7, CH
11	32.7, CH_2	32.6, CH_2	33.8, CH_2	32.3, CH_2	33.6, CH_2	32.7, CH_2
12	26.6, CH_2	26.7, CH_2	27.9, CH_2	26.7, CH_2	27.8, CH_2	26.7, CH_2
13	22.5, CH_3	22.5, CH_3	23.0, CH_3	22.5, CH_3	22.8, CH_3	22.5, CH_3
14	28.1, CH_3	28.1, CH_3	28.5, CH_3	28.1, CH_3	28.4, CH_3	28.1, CH_3
15	21.9, CH_3	22.0, CH_3	22.2, CH_3	22.0, CH_3	22.1, CH_3	22.0, CH_3
16	-	-	-	-	-	-
17	169.5, C	173.2, C	175.9, C	177.9, C	173.7, C	167.0, C
18	23.5, CH_3	29.8, CH_2	39.1. CH_2	38.7, CH_2	43.8, CH_2	135.0, C
19	-	9.9, CH_3	20.7, CH_2	27.7, CH_3	137.2, C	126.8, CH
20	-	-	14.2, CH_3	27.7, CH_3	130.1, CH	128.5, CH
21		-		27.7, CH_3	129.5, CH	131.2, CH
					127.8, C	128.5, CH
					129.5, CH	126.8, CH
					130.1, CH	-

[a] $CDCl_3$ (125 MHz); [b] $CDCl_3$ (100 MHz); [c] CD_3OD (125 MHz); [d] CD_3OD (100 MHz)

Table S5. Microwave methods for amide preparation.

Table S5.1. Method A

Nº	t	T1-vessel (ºC)	T2-vessel (ºC)	P (bar)	E (W)
1	0:00:10	60	50	30	1000
2	0:01:00	60	50	35	1000
3	0:00:20	60	50	40	1000

Table S5.2. Method B

Nº	t	T1-vessel (ºC)	T2-vessel (ºC)	P (bar)	E (W)
1	0:00:10	80	50	30	1000
2	0:01:00	80	50	35	1000
3	0:00:20	80	50	40	1000

Table S5.3. Method C

Nº	t	T1-vessel (ºC)	T2-vessel (ºC)	P (bar)	E (W)
1	0:00:10	120	50	30	1000
2	0:01:00	120	50	35	1000
3	0:00:20	120	50	40	1000

Table S5.4. Method D

Nº	t	T1-vessel (ºC)	T2-vessel (ºC)	P (bar)	E (W)
1	0:00:10	100	50	30	1000
2	0:01:00	120	50	35	1000
3	0:02:00	140	50	40	1000
4	0:00:20	140	50	45	1000

Table S5.5. Method E

Nº	t	T1-vessel (ºC)	T2-vessel (ºC)	P (bar)	E (W)
1	0:00:10	100	50	30	1000
2	0:01:00	120	50	35	1000
3	0:02:00	140	50	40	1000
4	0:01:10	140	50	45	1000

Table S5.6. Method F

Nº	t	T1-vessel (ºC)	T2-vessel (ºC)	P (bar)	E (W)
1	0:00:10	100	50	30	1000
2	0:01:00	120	50	35	1000
3	0:02:00	140	50	40	1000
4	0:00:50	160	50	45	1000

COMPUTATIONAL SECTION

Table S6. Results of the functional, basis set, and solvent tests on the relative free energy (kcal mol^{-1}) of the possible isomers of compound 20.

Entry	Functional [a]	Basis set system	Solvent model	ΔG [b]			
				20	**20a**	**20b**	**20c**
1	M06-2X (D3)	6-311g(d,p)	SMD(acetone)	0.0	-0.9	3.2	3.9
2	M06-2X (D3)	6-311g(d,p)	PCM(acetone)	0.0	-1.0	3.3	3.8
3	M06-2X (D3)	6-311g(d,p)	SMD(acetonitrile)	0.0	-1.0	3.2	3.9
4	M06-2X (D3)	6-311g(d,p)	None	0.0	-1.0	3.4	3.4
5	M06-2X (D3)	Def2TZVPP	SMD(acetone)	0.0	-1.2	3.6	4.1
6	wB97XD	6-311g(d,p)	SMD(acetone)	0.0	-1.6	3.0	3.9
7	PBE0 (D3)	6-311g(d,p)	SMD(acetone)	0.0	-1.0	3.8	4.1
8	B3LYP (D3)	6-311g(d,p)	SMD(acetone)	0.0	-1.3	3.1	4.1

[a] For those functionals including the label "(D3)", Grimme's D3 dispersion correction term was computed by means of a single-point calculation on the optimized species obtained at each level of theory. [b] The structures of the four isomers of **20** were fully optimized using the different methodologies described in the text. Relative free energies were obtained by combining the computed electronic energy, thermal and entropic corrections (298 K), and Grimme's D3 dispersion correction.

Table S6 summarizes the results of a number of tests on the effects of the functional, basis set system, and solvent model, on the relative free energies of the isomers of **20**. It shows that the stability of these species does not vary significantly when other functionals, basis sets, or solvent models are employed. Specifically, entries 1, 6, 7 and 8 of the table shows that changes on the functional only lead to minor energy changes. The effect of the basis set system, ie. 6-311g(d,p) vs. Def2-TZVPP, which can be analyzed by comparing entry 1 (level of theory used In the manuscript) with entry 5, again shows only minor energy differences. Finally, in relation to the solvent model and selected solvent, comparison of entries 1-4 shows that none of them leads to major energy changes. All in all, the computations suggest that **20a** is ca. 1 kcal/mol more stable than **20**, whereas isomer **20b** and **20c** are ca. 3-4 kcal/mol less stable than **20**.

Table S7. Computational analysis of the solvent effects on the relative free energy (kcal mol^{-1}) of the ion pair formed between 22^+ and Br^-.

Entry	Functional	Basis set system	Solvent model	ΔG [a]
1	M06-2X (D3)	6-311g(d,p)	SMD(acetone, ε=20.493)	+19.5
2	M06-2X (D3)	6-311g(d,p)	SMD(acetonitrile, ε=35.688)	+18.9
3	M06-2X (D3)	6-311g(d,p)	SMD(water, ε=78.3553)	+19.2

[a] The structures were fully optimized using the different methodologies shown in the table. Free energy values are given with respect to compound **20**.

Table S7 shows that the relative stability of the ion pair formed between **22**$^+$ and Br^- does not change significantly in solvents such as acetone, acetonitrile, and water.

Table S8. QTAIM topological properties of selected bond critical points (bcp) of TS_{dyo}.[a]

bcp	Label	ρ(r)	$\nabla^2\rho(r)$	*H*(r)	*G*(r)
Br-C9	bcp1	0.0102	0.0297	0.0012	0.0062
C8-C9	bcp2	0.3151	-0.9071	-0.3304	0.1037
C7-C8	bcp3	0.1238	0.0107	-0.0507	0.0534
C7-H	bcp4	0.2750	-0.9259	-0.2708	0.0393

[a] (ρ(r) = electron density, ∇2ρ(r) = Laplacian of electron density; H(r) local energy density; G(r)= local kinetic (Lagrangian) energy).

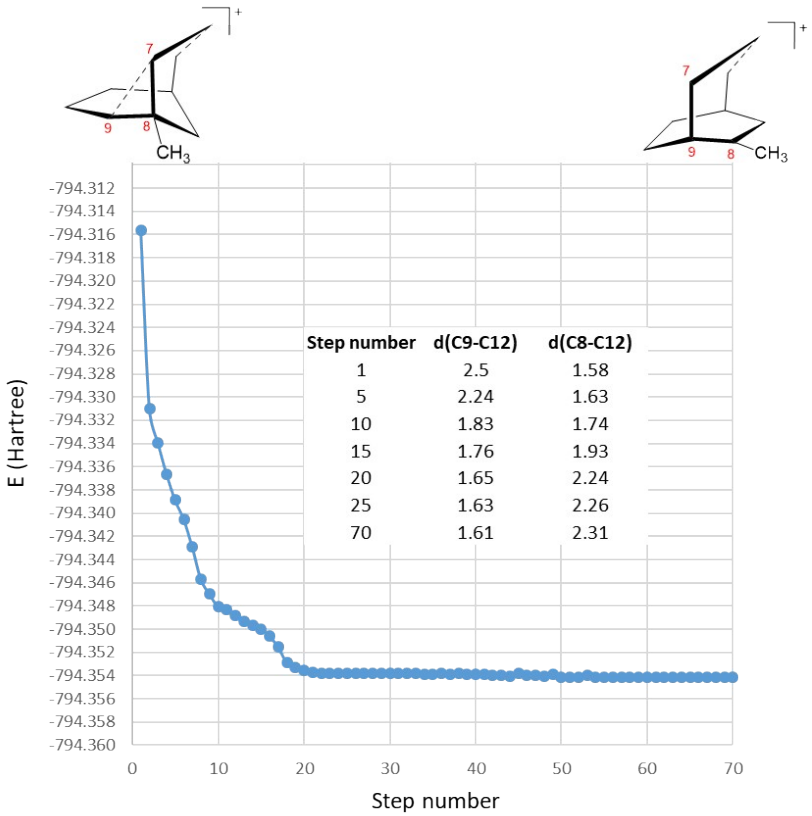

Figure S14. Optimisation (M06-2X/6-311g(d,p), SMD(acetone)) trajectory from the secondary carbocation guess structure labelled as 21^+ in Scheme 3, into the optimised structure of the tertiary carbocation 22^+. For simplicity, some of the substituents were removed in the representations.

The graph shows how the optimisation of an initial guess structure of the secondary carbocation evolves into $\mathbf{22}^+$ without any barrier. It is worth noting that our initial guess geometry was obtained by optimizing the structure resulting after removing the bromide atom in **20**, while keeping the C7···C9 distance fixed at a distance long enough (2.50 Å) to avoid bonding interactions between those centers. As expected, once such constraint is eliminated, the optimization trajectory in Figure S14 shows the cleavage of the C7-C8 bond and the formation of a new C7···C9 bond in the final structure. While the optimized structure of $\mathbf{22}^+$ is included in the Cartesian Coordinates section, those of the initial guess (step number 1) together with step numbers 5, 10, 15, 20 and 25 are included below.

Cartesian coordinates of the initial guess structure (step 1):

C	-0.24402200	-1.11563500	1.09769200
C	0.11163200	-0.17949700	-0.07021700
C	1.04935600	-0.93631000	-1.01472100
C	2.36004400	-1.30965900	-0.30230000
C	2.04525200	-2.21258800	0.90295300
C	0.99548500	-1.61973200	1.83619400
C	0.78557200	1.13926200	0.44430300
C	-0.14764500	2.32699700	0.04710000
C	-1.51407300	1.63728200	-0.10577400
C	-1.16218100	0.32360700	-0.80471400
C	3.04183400	-0.00710400	0.27632700

C	2.24182300	1.26034400	-0.01108600
C	0.26017600	3.00123200	-1.27003700
C	-0.17840800	3.39115100	1.14382400
C	3.32305600	-1.97432900	-1.28478800
H	1.47137200	-0.79186900	2.37097000
H	0.71742300	-2.35337200	2.59473900
H	-0.79626900	-1.97482700	0.70248100
H	-0.90896200	-0.60556200	1.79885300
H	2.70848900	-3.01166400	1.23360900
H	3.18821500	-0.10255700	1.35593100
H	4.04151900	0.08702700	-0.15504600
H	1.27943900	-0.32607200	-1.89429200
H	4.22368000	-2.32649400	-0.77150300
H	2.86132400	-2.82382600	-1.79129200
H	3.62729800	-1.24790200	-2.04368700
H	2.72175700	2.10999800	0.48509700
H	2.28449100	1.46258200	-1.08440000
H	-0.86453300	0.56429400	-1.82904400
H	-2.22890900	2.23633700	-0.67782500
H	-1.94480300	1.43143800	0.87478200
H	1.21187400	3.52895300	-1.16473700
H	0.36573500	2.29308900	-2.09597500
H	-0.49799500	3.73765500	-1.55301200
H	-0.51811400	2.96428800	2.09176200
H	0.81664800	3.82068800	1.29960100
H	-0.85635900	4.20788300	0.87586900
H	0.78873800	1.10200900	1.54018300
H	0.55716700	-1.84601200	-1.37767300
N	-2.23826700	-0.64819000	-0.96695600
H	-2.22686100	-1.17413400	-1.82815500
C	-3.21440900	-0.96649800	-0.08179300
O	-3.35156900	-0.44384700	1.01468000
C	-4.15035800	-2.06578200	-0.54077900
H	-4.07683000	-2.28045100	-1.60685700
H	-3.91188400	-2.97248000	0.02089100
H	-5.17202900	-1.77736000	-0.29315400

Cartesian coordinates at step 5:

C	-0.25199200	-1.10022000	1.09811900
C	0.10225100	-0.19420700	-0.08681700
C	1.01270100	-0.98111000	-1.02998600
C	2.34908900	-1.32404500	-0.33485400
C	2.17274000	-1.83825900	0.99506100
C	1.00715900	-1.60379000	1.81933400
C	0.79026200	1.12770200	0.39994300
C	-0.16604600	2.31331000	0.04383100
C	-1.52789700	1.61202000	-0.09251100
C	-1.17882300	0.30671000	-0.80986900
C	3.07844900	0.04124400	0.17607900
C	2.21623000	1.26151900	-0.13224900
C	0.20200500	3.01952700	-1.26869400
C	-0.17854500	3.35265600	1.16420500
C	3.30363900	-2.13865200	-1.20126500
H	1.41416200	-0.79932200	2.47822900
H	0.85296900	-2.43022800	2.51507500

H	-0.80487200	-1.97056400	0.73382400
H	-0.89295200	-0.58274500	1.81118700
H	3.01751300	-2.36192400	1.44931000
H	3.32316800	0.01130800	1.24378000
H	4.02716800	0.05260900	-0.36110800
H	1.22818700	-0.42069400	-1.94253000
H	4.23459900	-2.34391700	-0.66833800
H	2.84014600	-3.08450100	-1.48762200
H	3.53368400	-1.57367500	-2.10662600
H	2.70622300	2.13053600	0.31783200
H	2.20652600	1.42046700	-1.21103300
H	-0.88237100	0.55683800	-1.83141000
H	-2.25571300	2.20873900	-0.64922300
H	-1.94187500	1.39366200	0.89279000
H	1.15794900	3.54282300	-1.18228100
H	0.27344100	2.33491800	-2.11740300
H	-0.56365200	3.76470700	-1.50246900
H	-0.49184000	2.90276000	2.11040900
H	0.81644300	3.78750800	1.30387500
H	-0.86967700	4.16773500	0.92860800
H	0.84748900	1.09051600	1.49447600
H	0.53739900	-1.92135700	-1.32595500
N	-2.25031300	-0.66608200	-0.96581000
H	-2.29535300	-1.13720600	-1.85721300
C	-3.20107200	-0.99428100	-0.05435500
O	-3.26130100	-0.52067800	1.07023900
C	-4.19991300	-2.03160600	-0.52112100
H	-4.18295800	-2.19461400	-1.59840000
H	-3.97855600	-2.97425500	-0.01467100
H	-5.19605600	-1.71322400	-0.21347000

Cartesian coordinates at step 10:

C	-0.25210900	-1.21565900	0.99708500
C	0.07733500	-0.20805900	-0.11466600
C	1.01200400	-0.90112100	-1.10999100
C	2.28860400	-1.39212600	-0.44471600
C	2.23578500	-1.75016700	0.90871100
C	1.00604200	-1.69079600	1.74672400
C	0.74520400	1.07807000	0.47520600
C	-0.10894600	2.29573600	0.01523900
C	-1.49985400	1.65953600	-0.14178500
C	-1.20192100	0.32140600	-0.82428500
C	2.97266900	-0.11777700	0.51991800
C	2.23159800	1.15953000	0.13564400
C	0.37075600	2.89387500	-1.31394100
C	-0.11301100	3.39672200	1.07481900
C	3.34332900	-1.94988900	-1.36115400
H	1.20553000	-1.09363700	2.63880300
H	0.87141100	-2.71770000	2.10871900
H	-0.74233400	-2.08234700	0.54468600
H	-0.95942800	-0.77956600	1.70256000
H	3.10324800	-2.25249400	1.33263100
H	3.00695900	-0.18088400	1.61616400
H	4.01063900	-0.18682800	0.20430300
H	1.27508500	-0.24458300	-1.94418500

H	4.23041700	-2.26069100	-0.80793100
H	2.92027100	-2.81675800	-1.87348400
H	3.62043400	-1.20628800	-2.11024300
H	2.70923400	1.97606000	0.68366900
H	2.38541600	1.34319100	-0.92805300
H	-0.92739700	0.53882300	-1.85925100
H	-2.18169200	2.27986500	-0.73014700
H	-1.94444400	1.48834600	0.83897400
H	1.34062800	3.38456100	-1.19579400
H	0.47202300	2.14702500	-2.10594200
H	-0.34328800	3.64981200	-1.65264100
H	-0.48997300	3.01859200	2.02904400
H	0.89633200	3.78892500	1.23532000
H	-0.74927700	4.23036700	0.76259900
H	0.65843800	1.02658100	1.56709400
H	0.52288700	-1.78215300	-1.53951900
N	-2.30579900	-0.62414100	-0.94184500
H	-2.40870400	-1.07084200	-1.84085700
C	-3.24963900	-0.91847300	-0.01160600
O	-3.26932300	-0.45695700	1.12006200
C	-4.28357700	-1.93005400	-0.45622200
H	-4.27735900	-2.11126200	-1.53062800
H	-4.08816800	-2.87046000	0.06480400
H	-5.26732900	-1.57555000	-0.14814600

Cartesian coordinates at step 15:

C	-0.28964600	-1.28284000	0.92520300
C	0.05641500	-0.22799900	-0.12838600
C	0.99562500	-0.87740400	-1.14318500
C	2.22155200	-1.46147900	-0.51625300
C	2.21119600	-1.80244400	0.82509400
C	0.94421400	-1.79587800	1.66767900
C	0.73999800	1.01943800	0.51964000
C	-0.03423200	2.27165300	0.02190200
C	-1.44927500	1.70062400	-0.15676400
C	-1.20940300	0.35217300	-0.84178900
C	2.94524400	-0.21380700	0.77424500
C	2.24568600	1.04835200	0.26970000
C	0.50329000	2.80646100	-1.31354600
C	-0.00322900	3.39571500	1.05374100
C	3.35251000	-1.78019300	-1.43774400
H	1.14208300	-1.22220700	2.57618600
H	0.79040600	-2.82974100	1.97435600
H	-0.78590400	-2.11696200	0.42221900
H	-1.00087600	-0.86920700	1.64125300
H	3.03226100	-2.40857800	1.19103700
H	2.92290000	-0.20437400	1.86786900
H	3.97848000	-0.31364300	0.46303300
H	1.28218600	-0.18880400	-1.94228900
H	4.18332700	-2.26140400	-0.92342700
H	2.95773800	-2.46253000	-2.19662500
H	3.69486100	-0.88049300	-1.95432800
H	2.70526400	1.88156000	0.80756100
H	2.46517300	1.19414800	-0.78953900
H	-0.93136900	0.54535100	-1.88065200

H	-2.10041800	2.35229800	-0.74529100
H	-1.90911100	1.53619500	0.81859900
H	1.46839500	3.30279200	-1.17895400
H	0.63780800	2.01884900	-2.05844900
H	-0.19520900	3.54232000	-1.72220700
H	-0.43911700	3.06917700	2.00212100
H	1.02232500	3.72791800	1.24168600
H	-0.57247300	4.25976000	0.69711400
H	0.57745800	0.96276100	1.60341700
H	0.49430600	-1.72909400	-1.62439500
N	-2.35651800	-0.54102600	-0.94480200
H	-2.46940700	-1.01209500	-1.83011200
C	-3.28758500	-0.82222100	0.00161900
O	-3.28103300	-0.36512900	1.13528000
C	-4.34046000	-1.82323300	-0.42505500
H	-4.33136100	-2.03296500	-1.49427200
H	-4.16802800	-2.75293400	0.12226100
H	-5.31922500	-1.44138800	-0.13342600

Cartesian coordinates at step 20:

C	-0.27085600	-1.29928100	0.92747500
C	0.04538300	-0.25119000	-0.14541700
C	0.93917600	-0.95377800	-1.18101900
C	2.15627600	-1.53698400	-0.59880200
C	2.28385100	-1.60984200	0.82773500
C	1.01040600	-1.73551200	1.66182300
C	0.73474200	0.99991900	0.49467200
C	-0.01817900	2.24725800	-0.04443700
C	-1.44288000	1.69592200	-0.21480400
C	-1.22044200	0.32177300	-0.85088300
C	2.97423000	-0.13755500	0.98805700
C	2.25518000	1.03777500	0.32540800
C	0.54825800	2.74217500	-1.38151300
C	0.01617200	3.39553200	0.96251800
C	3.28625500	-1.87028600	-1.47186900
H	1.13580500	-1.15325700	2.57568700
H	0.91409700	-2.77898700	1.97263400
H	-0.73398000	-2.16434000	0.44309800
H	-0.99500800	-0.90226500	1.63880700
H	3.07321900	-2.29280700	1.13928200
H	2.96059300	-0.04140000	2.07372700
H	4.00327200	-0.21838300	0.63942900
H	1.20219600	-0.33738000	-2.04693400
H	4.12776700	-2.29912000	-0.93328300
H	2.92079000	-2.56639600	-2.23700600
H	3.58508800	-0.96658900	-2.01670700
H	2.64946800	1.95377900	0.77567100
H	2.51541100	1.08046300	-0.73608000
H	-0.96002000	0.48976300	-1.89852000
H	-2.07431100	2.33678500	-0.83645800
H	-1.91396600	1.58408000	0.76235700
H	1.53315800	3.19582100	-1.24250700
H	0.65492700	1.94289800	-2.12034600
H	-0.11154200	3.50627500	-1.80248700
H	-0.41846400	3.08865000	1.91791000

H	1.04267100	3.72961600	1.14341000
H	-0.55196200	4.25290900	0.58917000
H	0.52487400	0.95637500	1.57088100
H	0.39898200	-1.82887600	-1.58813500
N	-2.37029500	-0.57031900	-0.91141100
H	-2.48916400	-1.08199000	-1.77303900
C	-3.29027300	-0.80182300	0.05892000
O	-3.28275600	-0.26321200	1.15617700
C	-4.37326300	-1.79027900	-0.31534000
H	-4.35338900	-2.08130900	-1.36520400
H	-4.24918200	-2.68017800	0.30582700
H	-5.34143900	-1.34916300	-0.07586900

Cartesian coordinates at step 25:

C	-0.26183800	-1.29506900	0.93198800
C	0.05119100	-0.24735800	-0.14040300
C	0.95433400	-0.93717400	-1.17252700
C	2.17597000	-1.52033700	-0.60014400
C	2.30086200	-1.60235000	0.82680000
C	1.01672600	-1.75338800	1.65254900
C	0.72633400	1.01049100	0.50103900
C	-0.03140800	2.25121100	-0.04388700
C	-1.45125200	1.69029000	-0.21913300
C	-1.21939200	0.31571100	-0.85181400
C	2.96398100	-0.12354200	0.99480400
C	2.24454200	1.05415200	0.33362800
C	0.53521100	2.74318100	-1.38242900
C	-0.00584600	3.40371400	0.95775200
C	3.28769600	-1.87852900	-1.48726100
H	1.15383600	-1.20015600	2.58322300
H	0.92607900	-2.80642100	1.92417400
H	-0.74333200	-2.15121400	0.45051400
H	-0.97296900	-0.88857100	1.65086400
H	3.08896700	-2.28675600	1.13676900
H	2.94503700	-0.02037500	2.08191400
H	4.00130300	-0.18162700	0.66600700
H	1.21194300	-0.31748400	-2.03775500
H	4.14034800	-2.29308300	-0.95490900
H	2.90027600	-2.60656600	-2.21209100
H	3.57550900	-1.00092700	-2.07732300
H	2.63857600	1.96851300	0.78618000
H	2.50495300	1.10122300	-0.72806900
H	-0.95588100	0.47786500	-1.89953100
H	-2.08512200	2.32578700	-0.84355700
H	-1.92537400	1.57396800	0.75629100
H	1.51771000	3.20275100	-1.24488700
H	0.64608800	1.94138400	-2.11761500
H	-0.12886500	3.50115700	-1.80785100
H	-0.44178400	3.09966900	1.91351200
H	1.01810500	3.74459400	1.13955800
H	-0.57781200	4.25596000	0.57826600
H	0.51207600	0.96808400	1.57662900
H	0.42063900	-1.81282600	-1.58837800
N	-2.36766300	-0.57884900	-0.91189100
H	-2.50929800	-1.06011600	-1.78724500

C	-3.28655900	-0.81270700	0.05902200
O	-3.25681300	-0.30408900	1.17007200
C	-4.37842100	-1.78976900	-0.32080800
H	-4.37289300	-2.05898200	-1.37667100
H	-4.25137700	-2.69319500	0.27985800
H	-5.34137300	-1.34916700	-0.06026900

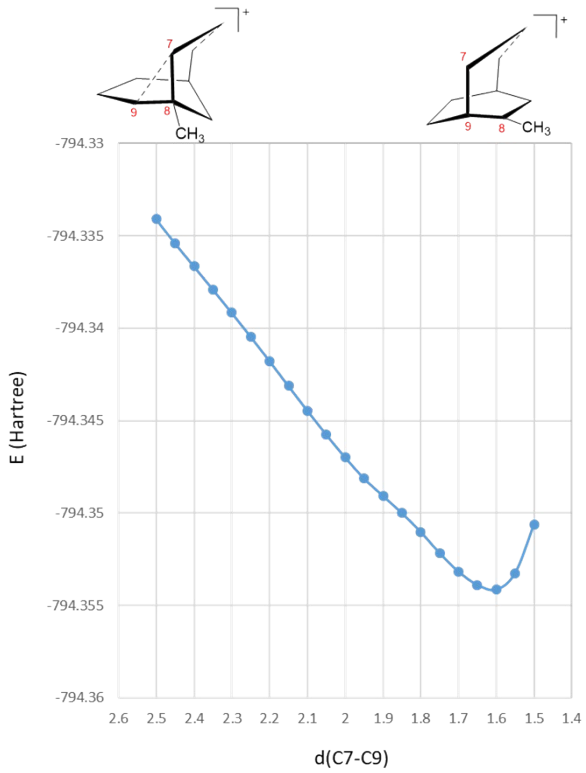

Figure S15. Relaxed scan (M06-2X/6-311g(d,p), SMD(acetone)) along the C7-C9 coordinate in carbocation 22^+. This graph is analogous to that included in Figure 2 of the manuscript, but herein absolute energies were employed. For simplicity, some of the substituents were removed in the representations.

Specifically, the graph shows how a relaxed scan along the C7-C9 coordinate, with distances shown in reverse order between 2.50 Å and 1.50 Å, in steps of 0.05 Å. This graph is also complementary to that in Figure S14, all in all showing that the hypothetical secondary carbocation $\mathbf{21}^+$ is not a stable structure that can be optimized, as it collapses into $\mathbf{22}^+$, with a C9-C12 distance of ca. 1.6 Å.
The Cartesian coordinates of a number of points along this relaxed scan, specifically those with d(C7-C9) distances of 2.40, 2.20, 2.00 and 1.80 Å are included below.

Cartesian coordinates of the optimized structure with C9-C12 distance constrained at 2.40 Å:

C	-0.23021900	-1.03708600	1.17125000
C	0.11476800	-0.19019800	-0.06122000
C	1.00184100	-1.03478600	-0.97875900
C	2.34801500	-1.32728800	-0.30134600
C	2.16975400	-1.83992800	1.04307400
C	1.01845100	-1.57322900	1.86789900
C	0.82709400	1.14353600	0.35394800
C	-0.17166900	2.31704600	0.06806700
C	-1.52711400	1.59940300	-0.06421000
C	-1.16320000	0.30164400	-0.78643300
C	3.11316900	0.10652400	0.00322700
C	2.19852700	1.28389500	-0.30594000
C	0.14451600	3.07877100	-1.22638200
C	-0.17636100	3.31299500	1.22742500

C	3.27567100	-2.20859400	-1.13890300
H	1.45950800	-0.83602400	2.57876700
H	0.84410600	-2.42947800	2.53031600
H	-0.83722000	-1.89066300	0.85928800
H	-0.82578600	-0.46547400	1.88361600
H	3.00766300	-2.36907400	1.49839100
H	3.46171900	0.15499400	1.03925500
H	3.99480800	0.07774300	-0.63656100
H	1.19245200	-0.52410500	-1.92573700
H	4.22963900	-2.36456900	-0.63070400
H	2.81307900	-3.17852600	-1.33226500
H	3.46419300	-1.71552800	-2.09465200
H	2.69661500	2.19044200	0.05195600
H	2.09379400	1.38402400	-1.38759900
H	-0.86033800	0.56487400	-1.80352700
H	-2.25964200	2.19024200	-0.62097300
H	-1.94142500	1.37659700	0.91923400
H	1.11044800	3.58678700	-1.16463500
H	0.16445400	2.42962700	-2.10558000
H	-0.62175200	3.84165600	-1.39049500
H	-0.44019600	2.81647300	2.16548700
H	0.80922200	3.77416800	1.34945400
H	-0.90134200	4.11313200	1.04934400
H	0.99029300	1.11825500	1.43775200
H	0.50709900	-1.98283600	-1.21472900
N	-2.22311100	-0.68240900	-0.96661600
H	-2.26905200	-1.12120100	-1.87424500
C	-3.19711200	-1.01321300	-0.08124700
O	-3.27622600	-0.55923600	1.05037200
C	-4.20147900	-2.02715400	-0.58561600
H	-4.11426100	-2.23325500	-1.65196400
H	-4.06131200	-2.95601800	-0.02828900
H	-5.20308800	-1.65552200	-0.36654600

Cartesian coordinates of the optimized structure with C9-C12 distance constrained at 2.20 Å:

C	-0.24259500	-1.11770100	1.09804900
C	0.09935600	-0.19853800	-0.08272700
C	1.00565200	-0.97735200	-1.03803400
C	2.31193500	-1.37856200	-0.35927800
C	2.18213400	-1.85151900	0.97345800
C	1.00601100	-1.63196200	1.81841800
C	0.79472900	1.11676400	0.41043800
C	-0.14229000	2.30971700	0.03966400
C	-1.51335100	1.62563200	-0.09475100
C	-1.17983500	0.31063400	-0.80153800
C	3.07209800	0.03335500	0.26975100
C	2.22796200	1.23741100	-0.10482500
C	0.24667400	2.99100100	-1.27946500
C	-0.14570300	3.36261500	1.14709100
C	3.30694200	-2.08808200	-1.25973400
H	1.33393400	-0.97545200	2.63851700
H	0.82994000	-2.59062700	2.32586300
H	-0.80476700	-1.97577600	0.72050900
H	-0.88734300	-0.60157300	1.80987200
H	3.04123600	-2.35018900	1.42071300

H	3.23826900	0.01056000	1.35213200
H	4.04725000	-0.02038400	-0.20923300
H	1.23600900	-0.39321500	-1.93233100
H	4.21413800	-2.35454100	-0.71442900
H	2.85279500	-2.99753700	-1.65862900
H	3.57222500	-1.43794500	-2.09568900
H	2.71432200	2.11364300	0.33621900
H	2.24643300	1.36796200	-1.18748200
H	-0.88851800	0.55214900	-1.82679200
H	-2.23029800	2.22829900	-0.65905800
H	-1.93306300	1.42252000	0.89115600
H	1.21182300	3.49736400	-1.19331700
H	0.31172900	2.29198200	-2.11724400
H	-0.50276200	3.74691400	-1.53059700
H	-0.46664700	2.92782500	2.09774600
H	0.85368100	3.78807300	1.28441800
H	-0.82686200	4.18248500	0.89957900
H	0.84505000	1.07818000	1.50524100
H	0.50399500	-1.89193000	-1.37244000
N	-2.26110900	-0.65462900	-0.95370100
H	-2.32142900	-1.11220500	-1.85120200
C	-3.22475800	-0.96481200	-0.04985900
O	-3.29047100	-0.48885100	1.07358900
C	-4.23347100	-1.98986400	-0.52225400
H	-4.18921800	-2.17977500	-1.59430700
H	-4.04853200	-2.92396300	0.01352800
H	-5.23077900	-1.64204900	-0.25197800

Cartesian coordinates of the optimized structure with C9-C12 distance constrained at 2.00 Å:

C	-0.25440100	-1.20759500	1.01277400
C	0.08334500	-0.21219400	-0.10516400
C	1.01340600	-0.91922900	-1.09302800
C	2.28289200	-1.41142300	-0.42920000
C	2.20706100	-1.83541900	0.90003200
C	0.99156400	-1.71248200	1.74906600
C	0.75791400	1.07897300	0.46762700
C	-0.11110700	2.29258000	0.02349100
C	-1.49825900	1.64895700	-0.13220800
C	-1.19477200	0.31670300	-0.82116700
C	3.01979800	-0.04755900	0.52186700
C	2.23534400	1.17681100	0.09150700
C	0.35537900	2.90309200	-1.30530900
C	-0.11478700	3.38636400	1.08988800
C	3.35111500	-1.93710200	-1.35195800
H	1.24079000	-1.09962700	2.62087700
H	0.82438400	-2.71804200	2.15163500
H	-0.77211000	-2.06118600	0.56681000
H	-0.94249400	-0.75316800	1.72606400
H	3.06898500	-2.34886700	1.32005100
H	3.05536700	-0.10632200	1.61356300
H	4.03681200	-0.12898400	0.15046600
H	1.27471800	-0.27251300	-1.93455100
H	4.22308500	-2.28823200	-0.79922100
H	2.93153900	-2.77042800	-1.92078800
H	3.65393300	-1.16140700	-2.05809300

H	2.69890700	2.02959700	0.59797500
H	2.36367700	1.32844000	-0.98091400
H	-0.91393800	0.53556000	-1.85424700
H	-2.18741500	2.26693400	-0.71422200
H	-1.93849600	1.46750200	0.84910500
H	1.31669500	3.41069500	-1.18830400
H	0.46792900	2.16003500	-2.09897800
H	-0.37323800	3.64663400	-1.64049600
H	-0.48982800	3.00191500	2.04240300
H	0.89422600	3.77903800	1.25112300
H	-0.75260700	4.22125900	0.78402500
H	0.69802500	1.02962600	1.56173500
H	0.51545300	-1.80125600	-1.51286800
N	-2.29946800	-0.62580200	-0.94566300
H	-2.38020800	-1.09669700	-1.83462700
C	-3.25062000	-0.91402000	-0.02173600
O	-3.29169100	-0.42610700	1.09808300
C	-4.28241400	-1.92830100	-0.46649300
H	-4.24017500	-2.15181600	-1.53206200
H	-4.12102000	-2.84927800	0.09856800
H	-5.27194300	-1.54887800	-0.20999200

Cartesian coordinates of the optimized structure with the C9-C12 distance constrained at 1.80 Å:

C	-0.26532200	-1.27762400	0.95105600
C	0.06161000	-0.23816900	-0.12682700
C	0.97684600	-0.91983500	-1.15011000
C	2.20288100	-1.50509400	-0.54206300
C	2.24619600	-1.74123700	0.83631300
C	0.99427100	-1.75392000	1.68811200
C	0.74077800	1.02482800	0.49737300
C	-0.05219400	2.26240200	-0.00762600
C	-1.46336400	1.67742400	-0.17562200
C	-1.20992400	0.32078000	-0.83707800
C	2.99410800	-0.10402200	0.82410100
C	2.24764900	1.08507200	0.24639700
C	0.48152800	2.79700900	-1.34369700
C	-0.03179000	3.39230000	1.01954900
C	3.33374100	-1.84347400	-1.43846400
H	1.17596300	-1.15913500	2.58615600
H	0.85824000	-2.78354300	2.02716400
H	-0.75009700	-2.13166100	0.46933600
H	-0.97828600	-0.86283800	1.66386300
H	3.08188900	-2.33518900	1.19612100
H	2.98845600	-0.08070100	1.91435300
H	4.01142500	-0.21477100	0.45987800
H	1.25314400	-0.26350100	-1.98052000
H	4.19025900	-2.24162300	-0.89716600
H	2.96309500	-2.59954800	-2.14009800
H	3.62034700	-0.97229500	-2.03353500
H	2.66862200	1.97158400	0.73185200
H	2.46315300	1.18040800	-0.81979700
H	-0.93850900	0.50836000	-1.87872400
H	-2.11655300	2.31317500	-0.77949600
H	-1.92399400	1.53283400	0.80248600
H	1.45202300	3.28286500	-1.21095400

H	0.60557800	2.01296700	-2.09548100
H	-0.21069300	3.54322800	-1.74403500
H	-0.45048300	3.06030500	1.97365400
H	0.98953500	3.74429400	1.19572000
H	-0.62116900	4.24403600	0.66653800
H	0.58591100	0.97596200	1.58246200
H	0.45086400	-1.77837700	-1.59661200
N	-2.34525200	-0.58842800	-0.92572400
H	-2.46518500	-1.06120200	-1.80901000
C	-3.28114500	-0.84012600	0.02410200
O	-3.27636200	-0.34578400	1.14204600
C	-4.36602700	-1.81103000	-0.39035600
H	-4.29302900	-2.13039200	-1.42945500
H	-4.30800700	-2.68557400	0.26078500
H	-5.33389300	-1.33610200	-0.22275800

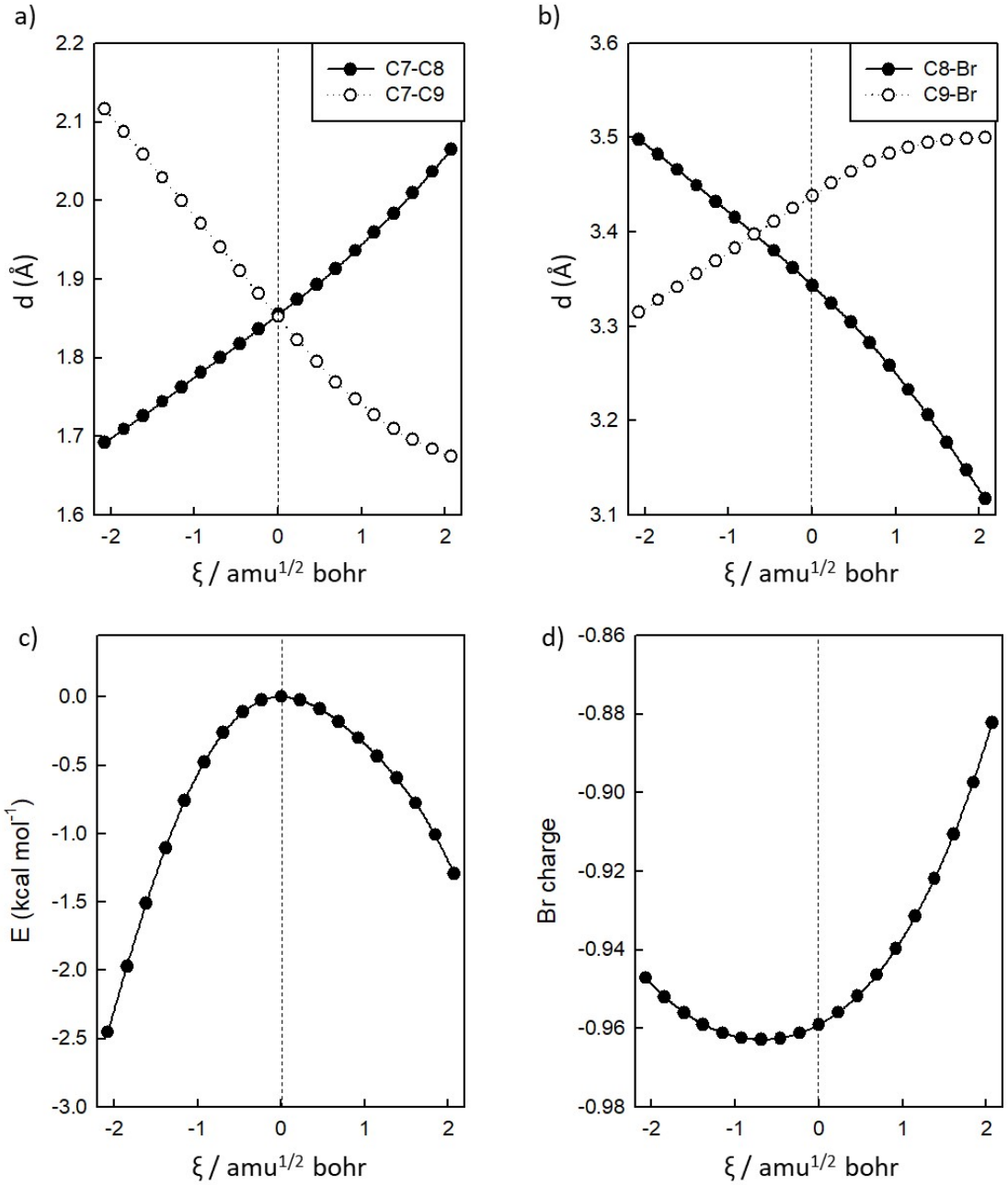

Figure S16. For transition state TS_{dyo} (reaction coordinate = 0) and the 9 previous and subsequents steps along the intrinsic reaction coordinate, evolution of (a) C7-C8 and C7-C9 distances, (b) Br-C8 and Br-C9 distances, (c) relative energy with respect to that of TS_{dyo}, (d) computed NBO charge of the bromide center.

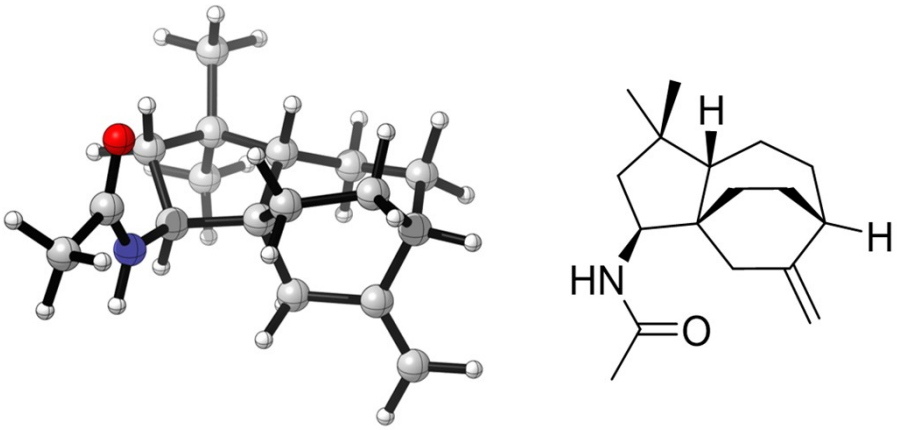

Figure S17. Optimized structure of the exocyclic isomer of 14.

Cartesian coordinates and energetic data (a.u.) of the optimized species.

Compound 14

E= -793.937755097
G correction = 0.371322
D3(0) correction = -0.00350286
C -0.699123 1.064494 -0.488847
C -0.087530 -0.233805 0.163660
C -1.025853 -0.914433 1.140181
C -2.125804 -1.516553 0.681620
C -2.945318 0.010902 -1.128666
C -2.220991 1.161306 -0.418313
C -2.393196 -1.401596 -0.804800
C -1.113551 -1.726102 -1.618203
C 0.194565 -1.267218 -0.943812
C 0.064700 2.262380 0.131826
C 1.472046 1.671650 0.299871
C 1.208019 0.277336 0.872970
C -3.135778 -2.214942 1.542144
C -0.521761 2.677666 1.487814
C 0.079119 3.473903 -0.798011
H -1.211945 -1.267690 -2.606246
H -1.069895 -2.805669 -1.781963
H 0.697939 -2.124232 -0.488028
H 0.884804 -0.842404 -1.675375
H -0.785819 -0.915574 2.202538
H -4.121531 -1.749342 1.431623
H -3.246466 -3.261446 1.238851
H -2.856216 -2.185556 2.597308
H -2.545010 2.110413 -0.858829
H -2.531349 1.181771 0.629341
H 0.964992 0.400839 1.930647
H 2.111288 2.270726 0.955360
H 1.953364 1.588205 -0.675311
H -1.486157 3.176465 1.359657
H -0.680002 1.825516 2.155255
H 0.152433 3.379811 1.987964
H 0.521202 3.217730 -1.765246
H -0.932957 3.851520 -0.972730
H 0.666161 4.288512 -0.361675
H -0.414409 1.039262 -1.549911
N 2.344580 -0.638216 0.881570
H 2.445668 -1.206751 1.709067
C 3.241977 -0.860357 -0.108896
O 3.240755 -0.283469 -1.187418
C 4.276205 -1.922641 0.202027
H 4.321448 -2.185340 1.258865
H 4.030266 -2.817165 -0.375606
H 5.251096 -1.566387 -0.131097
H -4.005284 0.049930 -0.857088
H -2.892997 0.152294 -2.213714
H -3.165077 -2.122110 -1.090694

Compound 14-exo
E= -793.935647992
G correction = 0.372632
D3(0) correction = -0.00356889
C -0.773258 1.054054 -0.426337
C -0.108243 -0.225321 0.186594
C -0.957155 -0.931166 1.258364
C -2.147909 -1.681636 0.679433
C -3.028086 -0.003001 -0.983080
C -2.287881 1.123181 -0.253143
C -2.438146 -1.418530 -0.781453
C -1.162762 -1.657452 -1.626592
C 0.147620 -1.262048 -0.913289
C 0.014194 2.276683 0.116890
C 1.432678 1.698217 0.234340
C 1.202157 0.314215 0.844076
C -2.879815 -2.518171 1.413342
C -0.505289 2.750699 1.480875
C -0.026686 3.451334 -0.858896
H -1.263401 -1.103646 -2.564198
H -1.113130 -2.715776 -1.895177
H 0.598462 -2.147267 -0.451326
H 0.872471 -0.876596 -1.632665
H -1.297941 -0.216030 2.013551
H -3.727647 -3.047638 0.988946
H -2.655551 -2.697725 2.461547
H -2.654209 2.085567 -0.626453
H -2.540573 1.093754 0.811096
H 0.987864 0.457731 1.906501
H 2.096076 2.314608 0.848518
H 1.871474 1.598055 -0.759275
H -1.495604 3.204128 1.384016
H -0.584892 1.940313 2.209694
H 0.168138 3.509125 1.892055
H 0.368527 3.160487 -1.836503
H -1.049698 3.814985 -0.997185
H 0.574217 4.286252 -0.484287
H -0.566187 1.025461 -1.505217
H -0.308477 -1.645880 1.779276
N 2.343222 -0.596171 0.839497
H 2.472743 -1.143301 1.677329
C 3.227092 -0.821624 -0.162342
O 3.202370 -0.259716 -1.248546
C 4.277782 -1.868372 0.146075
H 4.340908 -2.118346 1.205084
H 4.034393 -2.772211 -0.417935
H 5.243665 -1.504657 -0.204757
H -4.070127 -0.012114 -0.648154
H -3.040184 0.203657 -2.058876
H -3.200590 -2.128383 -1.112851

Compound 22^{+}
E= -794.354165340
G correction = 0.382037
D3(0) correction = -0.00365571

C 0.234420 -1.282796 -0.934419
C -0.057165 -0.235407 0.144992
C -0.968453 -0.916254 1.171909
C -2.183342 -1.507781 0.602834
C -2.340308 -1.525118 -0.832326
C -1.054464 -1.707551 -1.657945
C -0.712716 1.037806 -0.488080
C 0.060914 2.262309 0.070529
C 1.473177 1.681222 0.239971
C 1.224183 0.302589 0.857148
C -2.968165 -0.052392 -1.008103
C -2.230993 1.104881 -0.329376
C -0.500704 2.747211 1.413808
C 0.051724 3.426156 -0.918344
C -3.245158 -2.005389 1.474302
H -1.177544 -1.145671 -2.585287
H -0.987970 -2.761170 -1.933622
H 0.696538 -2.152464 -0.457779
H 0.954330 -0.887174 -1.650511
H -3.131588 -2.207877 -1.141484
H -2.952587 0.069045 -2.093442
H -4.006310 -0.089922 -0.677510
H -1.247013 -0.286516 2.024843
H -4.225893 -1.923312 1.001911
H -3.034598 -3.086098 1.556083
H -3.220836 -1.574047 2.473213
H -2.604385 2.033912 -0.769255
H -2.496626 1.141119 0.731604
H 0.967892 0.455736 1.908145
H 2.114990 2.301635 0.871418
H 1.945701 1.569927 -0.736769
H -1.477241 3.220414 1.280301
H -0.622547 1.939580 2.140923
H 0.172395 3.492316 1.847773
H 0.481617 3.126037 -1.878082
H -0.966937 3.785091 -1.094769
H 0.637420 4.265127 -0.530272
H -0.492757 1.000713 -1.562780
H -0.443230 -1.779765 1.624748
N 2.360281 -0.608758 0.900282
H 2.500030 -1.102688 1.768880
C 3.268317 -0.846889 -0.079849
O 3.240964 -0.323457 -1.184063
C 4.339331 -1.854393 0.278887
H 4.373366 -2.090031 1.342321
H 4.145856 -2.771262 -0.283111
H 5.304655 -1.462927 -0.042595

Compound (22+,Br-)
E= -3368.71037047
G correction = 0.375726
D3(0) correction = -0.00412601
C -0.078336 0.020401 1.585611
C -0.589696 -0.058343 0.142489
C -0.220879 1.277952 -0.508205

C -0.682668 2.448341 0.193298
C -1.348743 2.276170 1.480176
C -0.774463 1.148872 2.364548
C -2.129369 -0.337338 0.109798
C -2.349094 -1.470522 -0.928194
C -1.064555 -2.295559 -0.756339
C 0.041703 -1.241343 -0.662876
C -2.834293 1.959710 1.004462
C -2.987920 0.908996 -0.100830
C -2.473815 -0.938997 -2.361946
C -3.589769 -2.298353 -0.598880
C -0.532663 3.784788 -0.384850
Br 3.257480 1.056523 -0.790738
H -1.597882 0.753027 2.962042
H -0.066431 1.600150 3.061416
H 1.000427 0.202291 1.553881
H -0.233272 -0.936304 2.087073
H -1.399128 3.219634 2.024285
H -3.330506 1.625857 1.918624
H -3.295832 2.897279 0.690555
H -0.434091 1.368515 -1.580053
H 0.305766 4.243229 0.164470
H -0.301494 3.771989 -1.447948
H -1.406258 4.402927 -0.159154
H -4.043219 0.624572 -0.145675
H -2.752630 1.360718 -1.069458
H 0.238821 -0.873447 -1.674135
H -0.895636 -2.994778 -1.580211
H -1.113782 -2.861194 0.174122
H -3.411430 -0.393355 -2.498438
H -1.656253 -0.267761 -2.637809
H -2.471574 -1.776097 -3.066299
H -3.520511 -2.722153 0.406970
H -4.497237 -1.688982 -0.653374
H -3.700955 -3.123769 -1.308893
H -2.391132 -0.762139 1.088027
H 0.906621 1.398859 -0.487666
N 1.341251 -1.694185 -0.186980
H 2.113726 -1.097754 -0.478286
C 1.597858 -2.529621 0.847507
O 0.754608 -3.172637 1.460185
C 3.062046 -2.617858 1.226677
H 3.727030 -2.179237 0.482877
H 3.197498 -2.088747 2.173761
H 3.319867 -3.664996 1.387813

TS20b
E= -3368.70633493
G correction = 0.377262
D3(0) correction = -0.00411906
C -0.082755 0.233436 1.346116
C 0.641962 -0.049672 0.024819
C -0.274113 -0.982998 -0.770098
C -0.666192 -2.190667 -0.077564
C -0.270608 -2.353124 1.313464

C -0.282910 -1.059858 2.154807
C 2.055619 -0.662483 0.296416
C 3.058153 0.136852 -0.578505
C 2.412662 1.532831 -0.585245
C 0.927739 1.237851 -0.809429
C 1.201128 -2.934037 1.115568
C 2.115394 -2.181131 0.141053
C 3.171058 -0.426706 -2.001398
C 4.448837 0.169573 0.051753
C -1.452110 -3.209557 -0.761892
Br -3.641229 -0.065139 -0.444647
H 0.488848 -1.163150 2.920440
H -1.242284 -1.015179 2.673070
H -1.058432 0.670515 1.116302
H 0.481399 0.961353 1.930369
H -0.843807 -3.145166 1.795440
H 1.617293 -2.905817 2.125314
H 1.115442 -3.978950 0.813005
H 0.038332 -1.204383 -1.795983
H -2.483372 -2.822405 -0.625770
H -1.263605 -3.249895 -1.834201
H -1.396118 -4.184870 -0.279632
H 3.138651 -2.528744 0.310644
H 1.864628 -2.458830 -0.887388
H 0.803585 0.975536 -1.863021
H 2.823447 2.187487 -1.358990
H 2.554829 2.008467 0.385568
H 3.684307 -1.392176 -1.998483
H 2.198909 -0.571804 -2.480453
H 3.754595 0.257118 -2.624951
H 4.412079 0.601460 1.055864
H 4.871009 -0.837434 0.126141
H 5.132367 0.773032 -0.553586
H 2.303666 -0.425920 1.339476
H -1.287843 -0.499748 -0.881607
N -0.006380 2.337067 -0.606757
H -0.822143 2.328053 -1.202599
C -0.022823 3.237583 0.408395
O 0.839246 3.321484 1.271123
C -1.232941 4.147066 0.416227
H -1.694102 4.248739 -0.566467
H -1.970995 3.725816 1.104621
H -0.935581 5.125651 0.790920

TS20c
E= -3368.70363987
G correction = 0.378439
D3(0) correction = -0.00406803
C -1.493657 -1.307646 0.999929
C -0.794247 -0.238735 0.148834
C 0.371589 -0.958832 -0.536114
C 1.179820 -1.795381 0.342468
C 0.961002 -1.685531 1.781274
C -0.558076 -1.806835 2.111406
C -0.357231 0.960863 1.054230

C -0.819710 2.253089 0.328488
C -2.105835 1.773679 -0.361813
C -1.716343 0.408079 -0.931814
C 1.552071 -0.296821 2.236958
C 1.116624 0.942707 1.449645
C 0.207671 2.743257 -0.700906
C -1.106667 3.380076 1.318451
C 2.141196 -2.742184 -0.203129
Br 3.814577 0.194223 -1.110545
H -0.723148 -1.246675 3.033736
H -0.768214 -2.855194 2.327214
H -1.779335 -2.140365 0.348979
H -2.409643 -0.904336 1.431749
H 1.525197 -2.454477 2.309461
H 1.244522 -0.220948 3.283156
H 2.641286 -0.370997 2.209627
H 1.126592 -0.288392 -0.999527
H 3.034610 -2.801242 0.421536
H 1.624667 -3.714439 -0.093541
H 2.379565 -2.564360 -1.248266
H 1.336517 1.818451 2.069008
H 1.747974 1.030579 0.562330
H -1.097455 0.586568 -1.814476
H -2.452106 2.458453 -1.141015
H -2.899011 1.654797 0.377400
H 1.090722 3.155739 -0.205846
H 0.556158 1.949861 -1.367844
H -0.231910 3.535535 -1.314453
H -1.866864 3.078093 2.044629
H -0.202359 3.663753 1.865463
H -1.470557 4.269677 0.794807
H -0.961960 0.895679 1.968180
H 0.036636 -1.586403 -1.377000
N -2.803110 -0.429092 -1.426757
H -2.648889 -0.872681 -2.319596
C -4.011949 -0.640757 -0.849584
O -4.353352 -0.169585 0.225874
C -4.948492 -1.532348 -1.636940
H -4.541418 -1.858067 -2.593817
H -5.179943 -2.407373 -1.026461
H -5.879830 -0.988825 -1.804379

Compound 20
E= -3368.74958581
G correction = 0.383789
D3(0) correction = -0.00403291
C -0.050803 0.634514 1.020976
C 0.602249 -0.184276 -0.105949
C -0.494938 -0.587931 -1.094596
C -1.542055 -1.485545 -0.414397
C -2.190568 -0.718441 0.750933
C -1.171482 -0.132714 1.721918
C 1.332707 -1.449947 0.461994
C 2.851695 -1.301244 0.130423
C 3.005831 0.219784 -0.039636

C 1.740226 0.612549 -0.802568
C -0.838533 -2.738961 0.219172
C 0.677872 -2.752936 -0.002892
C 3.262479 -2.026677 -1.158284
C 3.717262 -1.826051 1.275651
C -2.573238 -1.960365 -1.436977
Br -3.364681 0.777286 0.101747
H -0.750659 -0.968572 2.289423
H -1.676570 0.505939 2.448516
H -0.463585 1.553849 0.592243
H 0.703354 0.935430 1.752169
H -2.906975 -1.357630 1.266624
H -1.045864 -2.794782 1.291544
H -1.273423 -3.641181 -0.218073
H -0.062976 -1.122049 -1.947298
H -3.374558 -2.525731 -0.950302
H -3.021157 -1.124481 -1.977399
H -2.088201 -2.617307 -2.164545
H 1.116669 -3.604455 0.527033
H 0.874138 -2.913852 -1.066052
H 1.830606 0.216305 -1.817752
H 3.919049 0.495356 -0.575540
H 3.017897 0.709254 0.934871
H 3.195153 -3.111343 -1.038815
H 2.645380 -1.750893 -2.017304
H 4.301810 -1.783249 -1.398596
H 3.495583 -1.296066 2.206335
H 3.541614 -2.894168 1.440514
H 4.780891 -1.693080 1.053210
H 1.250253 -1.415499 1.554864
H -0.983886 0.308100 -1.494098
N 1.501588 2.038541 -0.998202
H 1.090182 2.296110 -1.882970
C 1.714211 3.047665 -0.118346
O 2.179395 2.901873 1.002626
C 1.306459 4.418565 -0.617812
H 1.133919 4.454225 -1.693437
H 0.388311 4.709797 -0.101449
H 2.084354 5.132268 -0.346103

Compound 20a
E= -3368.75113304
G correction = 0.383770
D3(0) correction = -0.00396728
C 0.353567 -1.011804 -0.751561
C 0.762625 0.082911 0.245851
C -0.192029 0.003206 1.437505
C -1.645821 0.320347 1.010635
C -2.018935 -0.813802 0.044124
C -1.115163 -0.896762 -1.176331
C 0.714976 1.504991 -0.412321
C 2.173802 2.065644 -0.421116
C 3.024975 0.788502 -0.319068
C 2.246486 -0.066761 0.681459
C -1.701565 1.714464 0.316247

C -0.336643 2.407515 0.237690
C 2.469333 2.996622 0.763029
C 2.459414 2.826602 -1.715578
C -2.530703 0.297305 2.256019
Br -3.910987 -0.668642 -0.584475
H -1.262013 -0.012302 -1.801595
H -1.394285 -1.762674 -1.780022
H 0.507602 -1.988229 -0.278518
H 0.994060 -0.982166 -1.636238
H -2.020918 -1.760704 0.586575
H -2.109437 1.614104 -0.693380
H -2.400278 2.355911 0.860142
H 0.107005 0.709708 2.218385
H -3.567604 0.538857 2.013708
H -2.508727 -0.686983 2.734767
H -2.169828 1.036297 2.977225
H -0.431406 3.339605 -0.328610
H -0.021574 2.687342 1.246418
H 2.339191 0.407481 1.662316
H 4.048834 0.988143 0.010905
H 3.066651 0.283245 -1.284614
H 1.892428 3.922492 0.691337
H 2.240982 2.539541 1.729329
H 3.530110 3.264768 0.759854
H 2.313711 2.181817 -2.586894
H 1.794262 3.690660 -1.815033
H 3.490236 3.194778 -1.732696
H 0.424010 1.373327 -1.461448
H -0.152712 -0.999782 1.881248
N 2.722832 -1.428798 0.899080
H 2.694779 -1.757574 1.852575
C 3.201236 -2.298332 -0.024445
O 3.293426 -2.055829 -1.218938
C 3.618635 -3.646512 0.525912
H 3.615670 -3.693611 1.614589
H 2.934019 -4.401472 0.132918
H 4.617419 -3.876693 0.153005

Compound 20b
E= -3368.74479806
G correction = 0.384219
D3(0) correction= -0.00407620
C 0.066691 0.718931 1.122471
C 0.508777 -0.132637 -0.071326
C -0.694783 -0.247528 -1.026286
C -2.033236 -0.575588 -0.327681
C -1.832217 -1.037821 1.121455
C -1.022682 -0.005546 1.937539
C 1.059145 -1.508146 0.438636
C 2.426150 -1.738727 -0.260715
C 2.945611 -0.298931 -0.394823
C 1.712833 0.480601 -0.855836
C -1.200055 -2.451597 1.170005
C 0.067268 -2.662097 0.331494
C 2.282564 -2.404852 -1.635752

C 3.359742 -2.588234 0.599862
C -2.888372 -1.525326 -1.150256
Br -3.137190 1.140007 -0.222749
H -0.571827 -0.525177 2.786605
H -1.706771 0.735944 2.354834
H -0.319474 1.672720 0.749770
H 0.926600 0.946659 1.754862
H -2.821675 -1.133064 1.577511
H -0.971863 -2.650767 2.221614
H -1.950044 -3.189825 0.872028
H -0.505945 -1.020966 -1.776942
H -3.842493 -1.727077 -0.659463
H -3.080570 -1.111168 -2.141709
H -2.354930 -2.471258 -1.278605
H 0.550423 -3.588650 0.659371
H -0.202541 -2.818806 -0.716561
H 1.556420 0.245750 -1.912118
H 3.777593 -0.208561 -1.099651
H 3.273704 0.066045 0.579258
H 1.955714 -3.443349 -1.533995
H 1.563938 -1.895220 -2.282456
H 3.249939 -2.410621 -2.147449
H 3.519713 -2.124128 1.577314
H 2.947463 -3.589491 0.759485
H 4.334354 -2.704066 0.114971
H 1.293274 -1.372494 1.503114
H -0.787494 0.692709 -1.575263
N 1.814708 1.936016 -0.832004
H 1.402218 2.418666 -1.616471
C 2.355270 2.717230 0.135135
O 2.877139 2.293061 1.156530
C 2.249957 4.206179 -0.122138
H 2.023802 4.450276 -1.159979
H 1.457961 4.606734 0.515825
H 3.188108 4.676887 0.171389

Compound 20c
E= -3368.74403229
G correction = 0.384430
D3(0) correction= -0.00406571
C -0.813154 -1.015697 1.191609
C -0.607439 -0.035578 0.033882
C 0.598308 -0.536322 -0.791430
C 1.788608 -1.005297 0.078516
C 1.711091 -0.468624 1.515374
C 0.397009 -1.001941 2.149454
C -0.442622 1.418474 0.592126
C -1.396108 2.330781 -0.225805
C -2.554791 1.368067 -0.527525
C -1.844361 0.069954 -0.915820
C 1.847079 1.060366 1.651062
C 1.002124 1.896313 0.685568
C -0.753660 2.846208 -1.520675
C -1.868001 3.528610 0.596545
C 1.927177 -2.523720 0.068467

Br 3.506091 -0.333779 -0.765600
H 0.177285 -0.377874 3.018707
H 0.565778 -2.011567 2.530909
H -0.957892 -2.019018 0.777808
H -1.727952 -0.766120 1.731473
H 2.543375 -0.909749 2.072003
H 1.577466 1.314848 2.681172
H 2.897376 1.334663 1.525836
H 0.903524 0.234528 -1.497853
H 2.767086 -2.848513 0.685429
H 1.012076 -2.974826 0.461723
H 2.071036 -2.891953 -0.948421
H 1.020266 2.939918 1.017877
H 1.464824 1.884346 -0.305243
H -1.453991 0.204355 -1.927897
H -3.214570 1.729126 -1.322144
H -3.148317 1.212312 0.374343
H 0.048240 3.556659 -1.302022
H -0.327553 2.046654 -2.131620
H -1.503278 3.367175 -2.124331
H -2.363966 3.201081 1.514767
H -1.027829 4.173667 0.872112
H -2.577781 4.134679 0.024446
H -0.851072 1.405563 1.612001
H 0.263447 -1.392360 -1.389137
N -2.677717 -1.123330 -1.018804
H -2.493181 -1.722027 -1.809467
C -3.661188 -1.525054 -0.177387
O -3.998746 -0.919942 0.830463
C -4.341926 -2.821797 -0.564330
H -4.020182 -3.215321 -1.528387
H -4.132667 -3.560244 0.212581
H -5.419636 -2.653359 -0.580515

TS_{dyo}
E= -3368.70064385
G correction = 0.376690
D3(0) correction = -0.00407564
C -0.107175 0.517698 1.067845
C 0.681274 -0.123673 -0.080847
C -0.329793 -0.763601 -1.033194
C -1.209267 -1.772264 -0.345891
C -1.456347 -1.634473 1.013446
C -0.921440 -0.512797 1.855817
C 1.693841 -1.187693 0.455354
C 3.096562 -0.803560 -0.097131
C 2.968561 0.722779 -0.233662
C 1.573430 0.906851 -0.834636
C -0.157670 -2.912499 0.666042
C 1.247338 -2.617087 0.152510
C 3.393456 -1.447278 -1.407726
N 1.056465 2.267683 -0.900632
H 0.503935 2.485647 -1.716961
C 1.143507 3.240362 0.041613
O 1.741195 3.122909 447278 -1.458177

C 4.203764 -1.189162 0.881802
C -2.088072 -2.609061 -1.222574
Br -3.751530 0.528969 -0.094707
H -0.358438 -0.930892 2.694704
H -1.810036 -0.035026 2.275806
H -0.803143 1.246930 0.645194
H 0.571846 1.046235 1.738865
H -2.239671 -2.251039 1.444140
H -0.144364 -2.952821 1.758341
H -0.588846 -3.845238 0.315668
H 0.157089 -1.225939 -1.896571
H -2.670627 -3.328334 -0.646028
H -2.777600 -1.914771 -1.711579
H -1.500010 -3.126826 -1.983312
H 1.916670 -3.334159 0.637186
H 1.283758 -2.817029 -0.919418
H 1.620033 0.589002 -1.879100
H 3.751268 1.158844 -0.860776
H 3.012498 1.189146 0.751234
H 3.548267 -2.525003 -1.357312
H 2.589588 -1.295125 -2.183139
H 4.309604 -1.018559 -1.874617
H 4.053073 -0.706070 1.851250
H 4.229161 -2.272311 1.038185
H 5.182396 -0.884791 0.497900
H 1.744520 -1.077233 1.545489
H -1.026752 -0.002583 1.101282
C 0.401107 4.514221 -0.303658
H 0.278504 4.656811 -1.377634
H -0.589752 4.467545 0.156654
H 0.937323 5.360028 0.124497