

Supplementary Information

Cellulose-reinforced poly(ethylene-co-vinyl acetate)-supported
Ag nanoparticles with excellent catalytic properties: Synthesis
of thioamides using the Willgerodt–Kindler reaction

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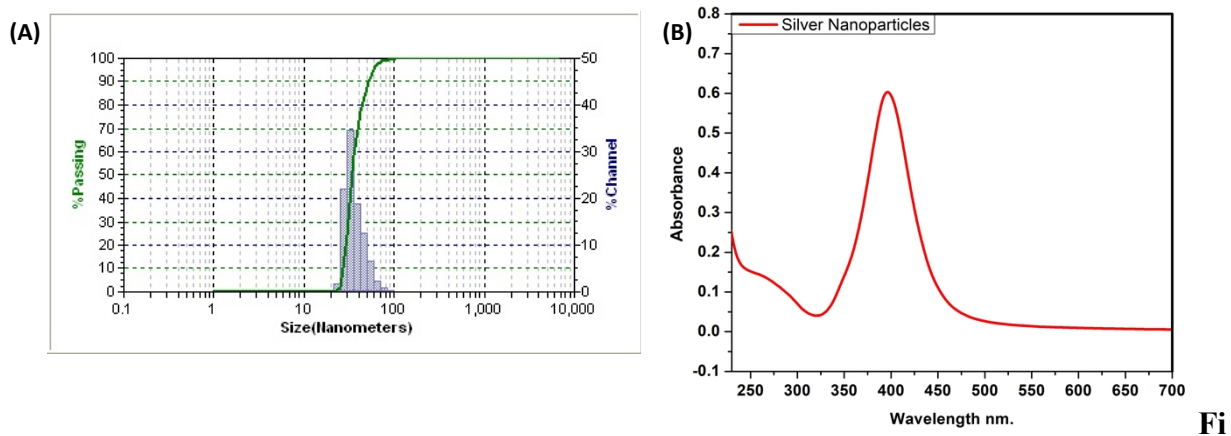


Figure S1. (A) Dynamic light scattering and (B) ultraviolet-visible spectra of Ag nanoparticles.

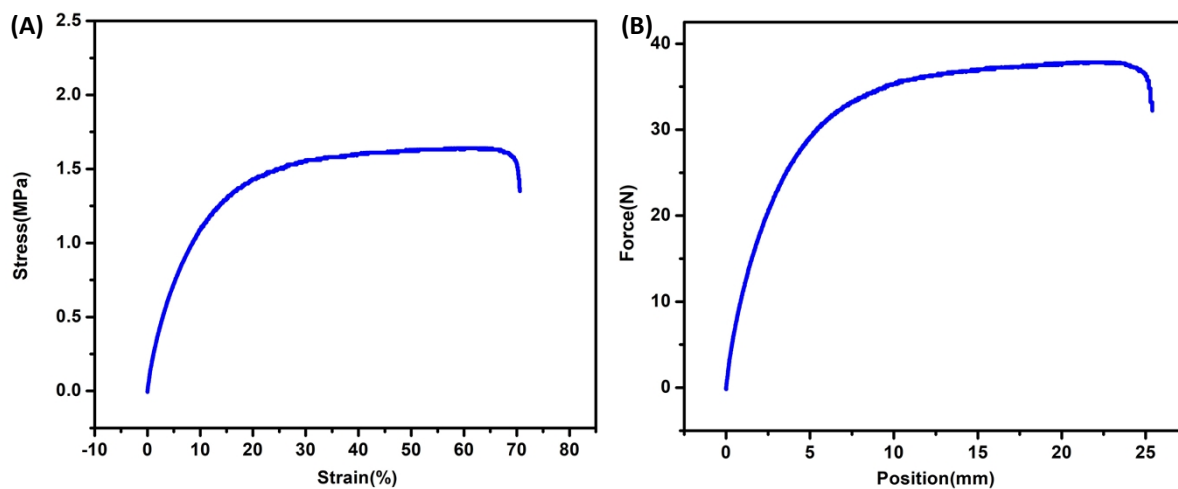


Figure S2. (A) Stress-strain and (B) force-position curves of poly(ethylene-co-vinyl acetate).

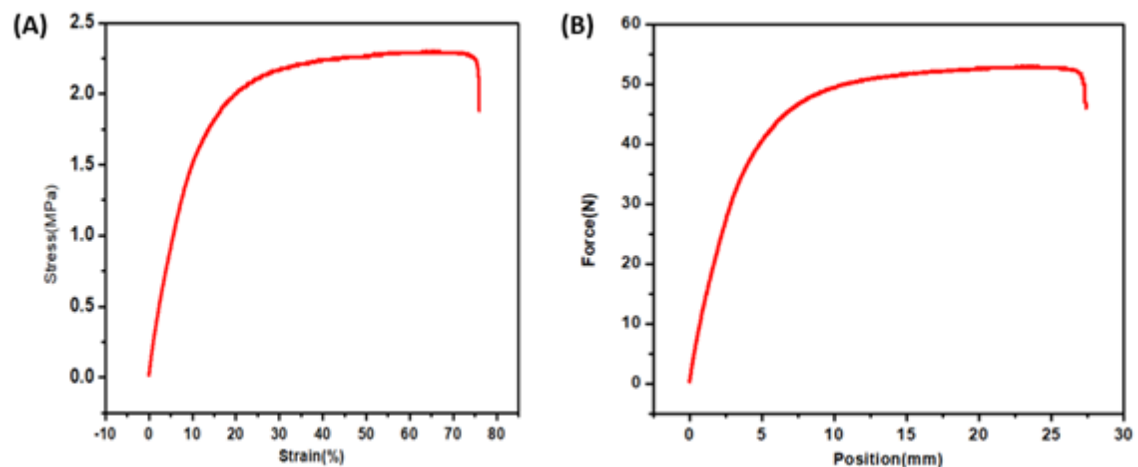


Figure S3. (A) Stress–strain and (B) force–position curves of the cellulose–poly(ethylene-co-vinyl acetate) composite.

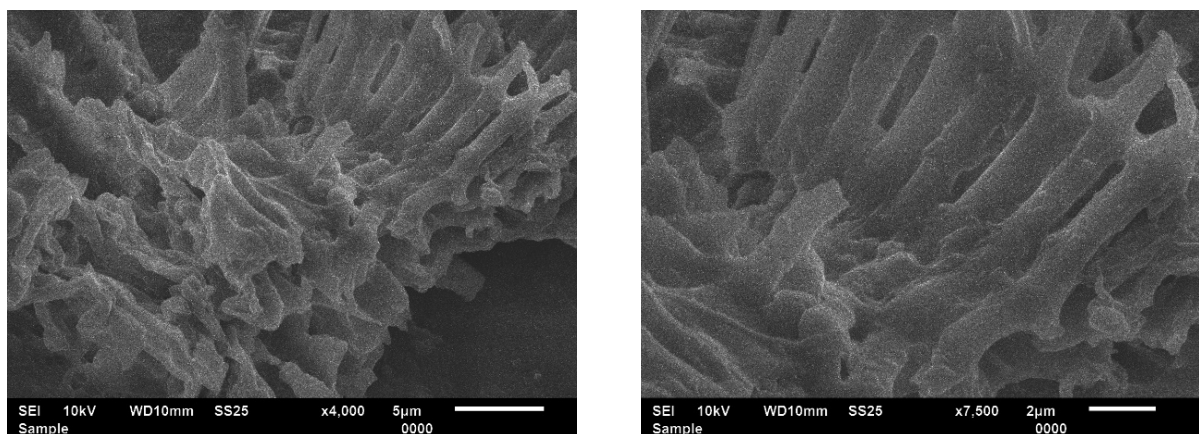


Figure S4. Scanning electron micrographs of the AgNPs@cellulose–PEVA after five catalytic cycles at different magnifications. Here, AgNPs and PEVA denote Ag nanoparticles and poly(ethylene-co-vinyl acetate), respectively.

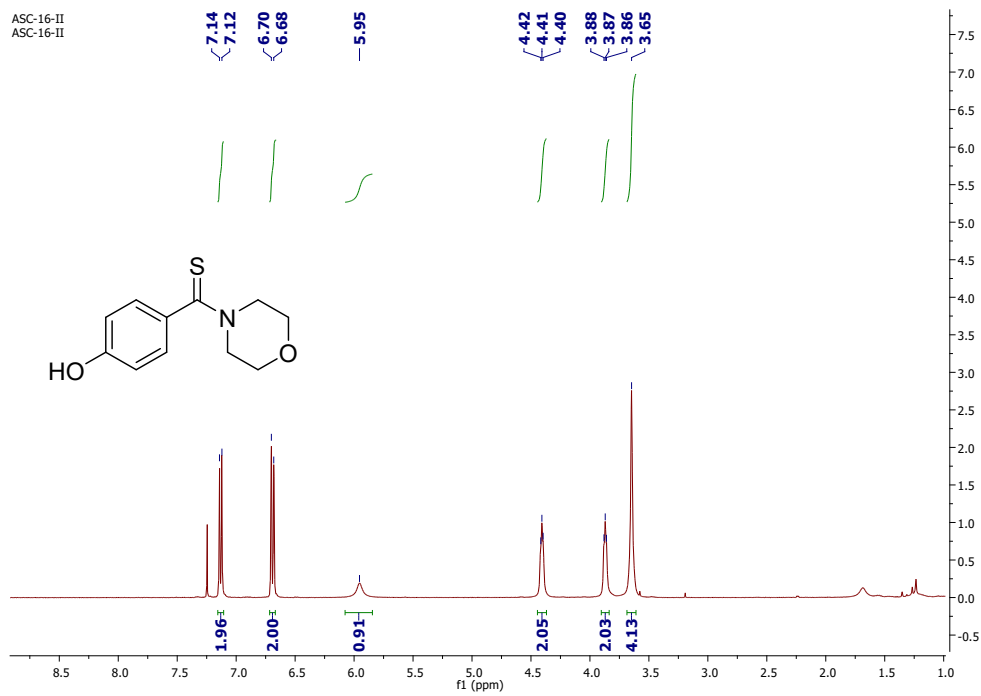


Figure S5. ^1H NMR (CDCl_3) of 1.

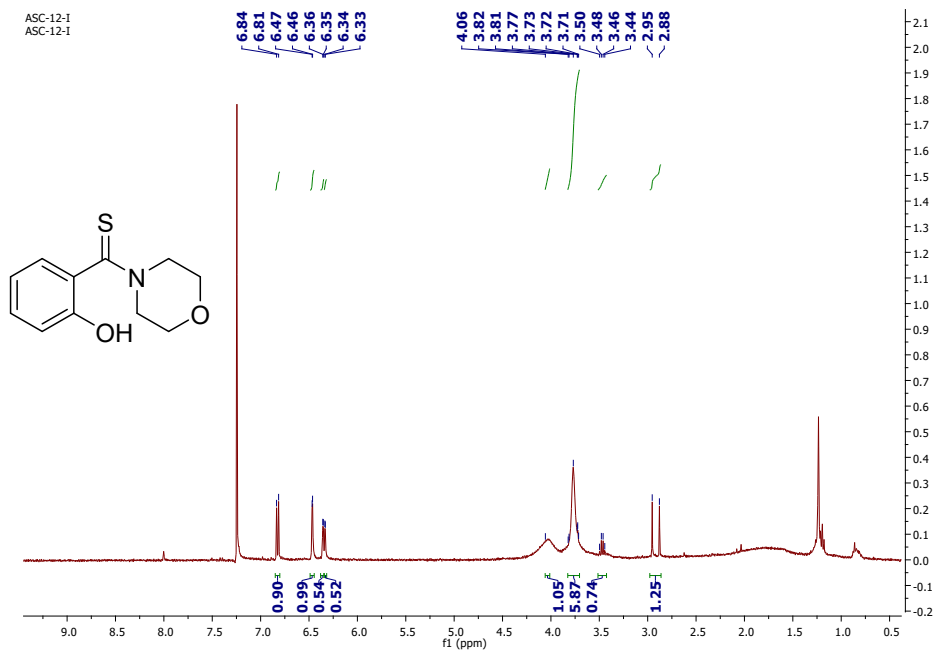


Figure S6. ^1H NMR (CDCl_3) of 2.

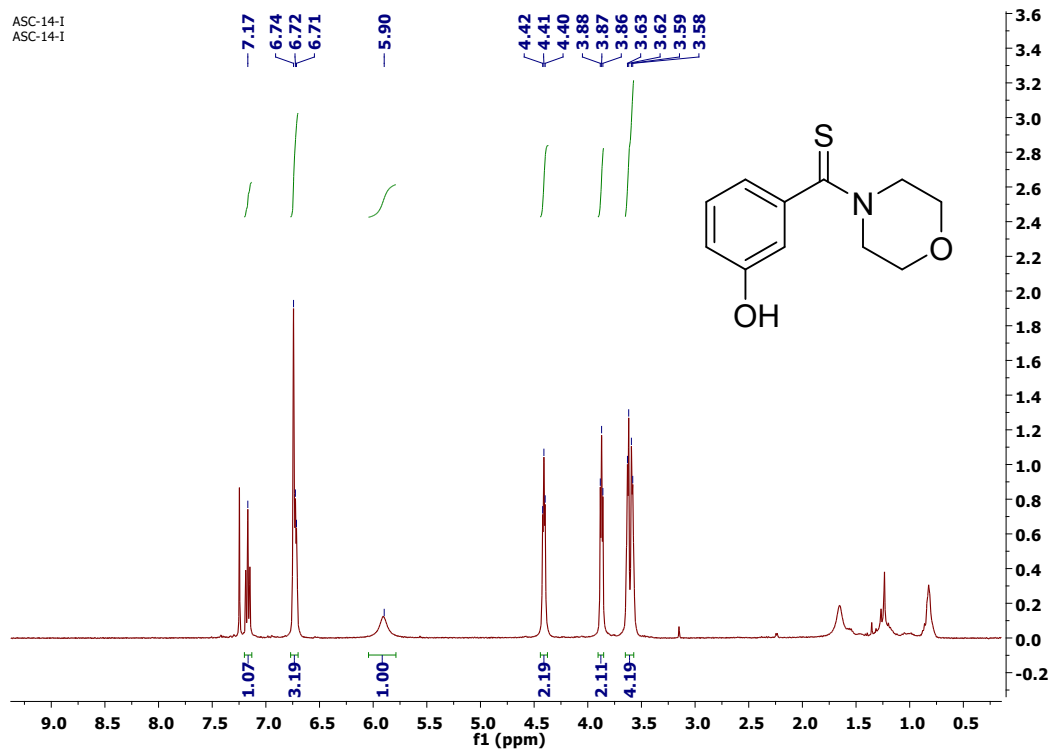


Figure S7. ^1H NMR (CDCl_3) of 3.

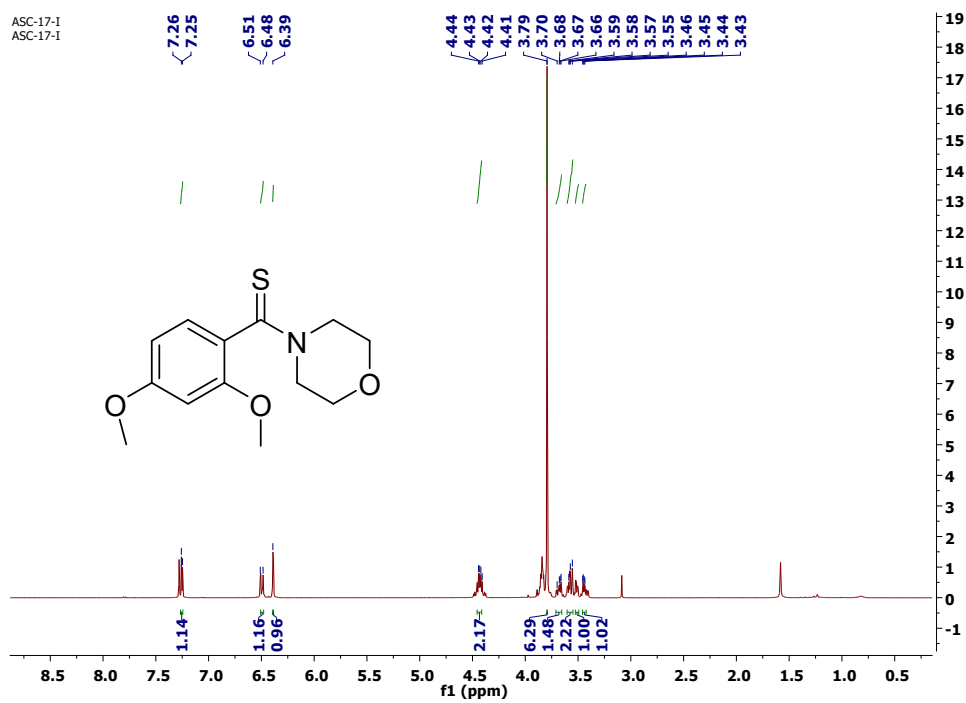


Figure S8. ^1H NMR (CDCl_3) of 4.

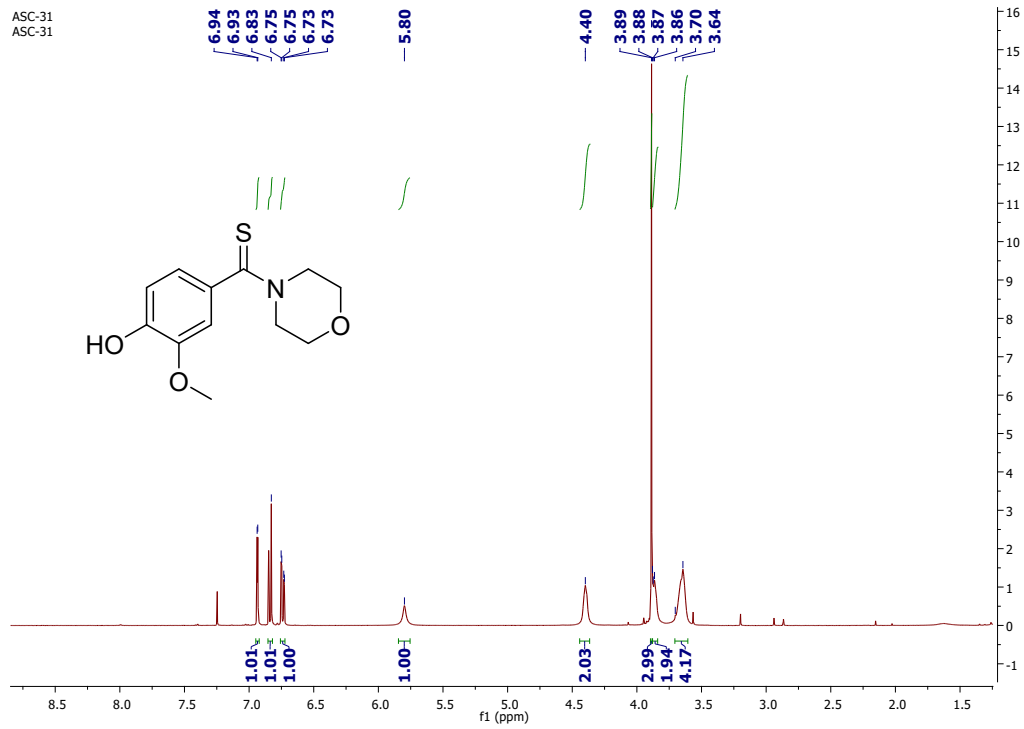


Figure S9. ^1H NMR (CDCl_3) of 5.

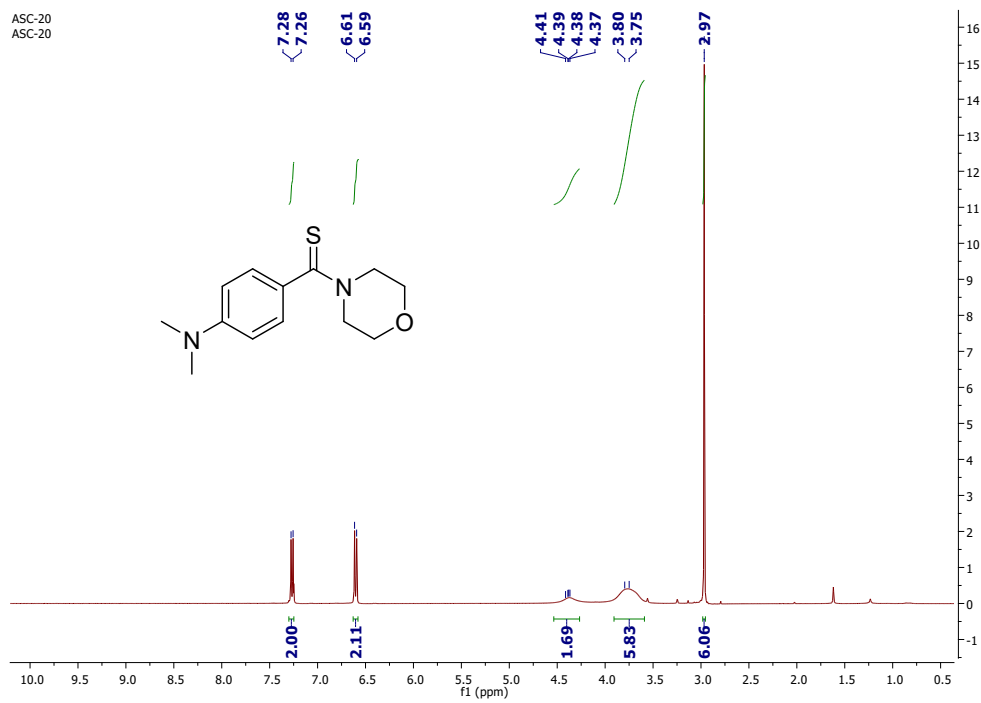


Figure S10. ^1H NMR (CDCl_3) of 6.

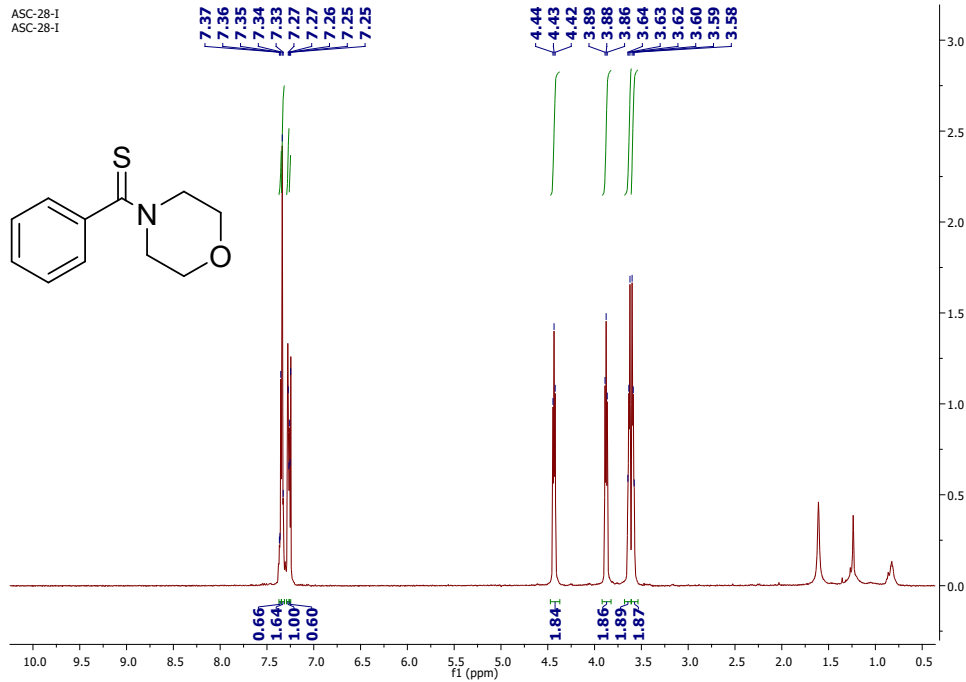


Figure S11. ^1H NMR (CDCl_3) of **7**.

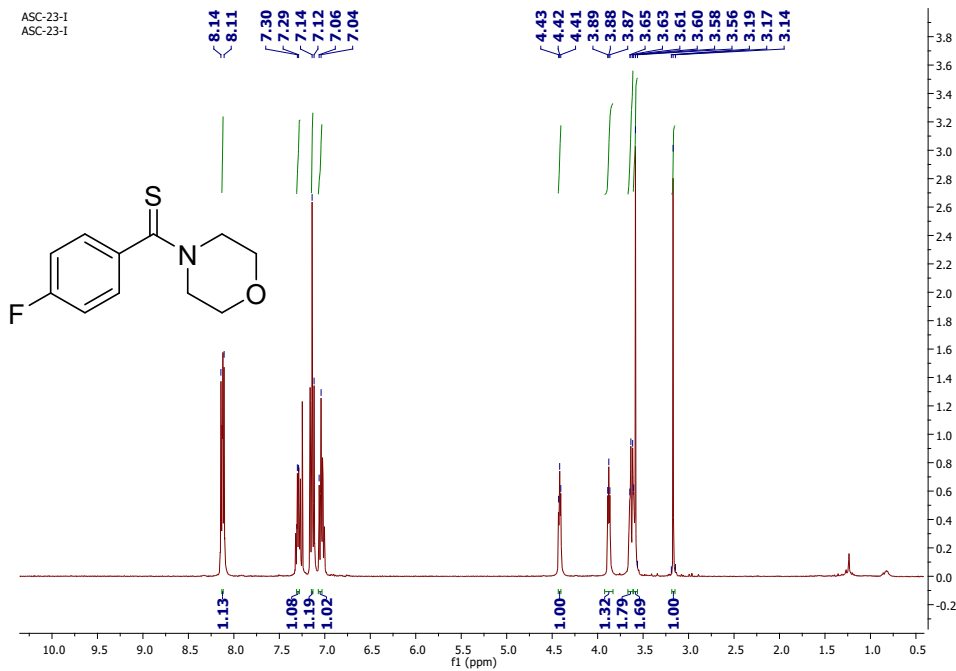


Figure S12. ^1H NMR (CDCl_3) of **8**.

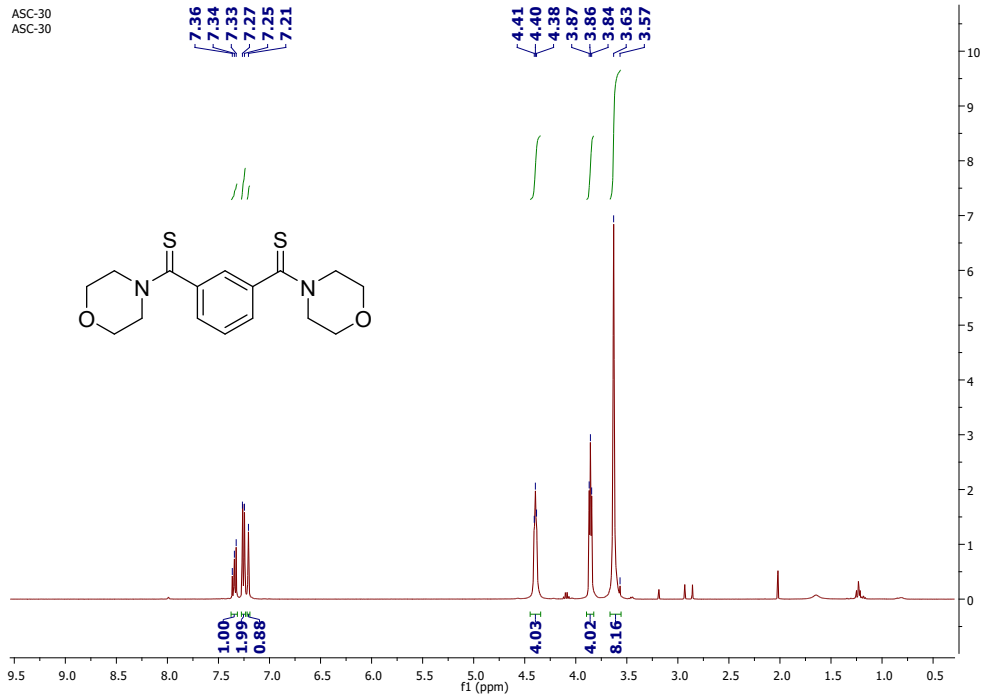


Figure S13. ^1H NMR (CDCl_3) of **9**.

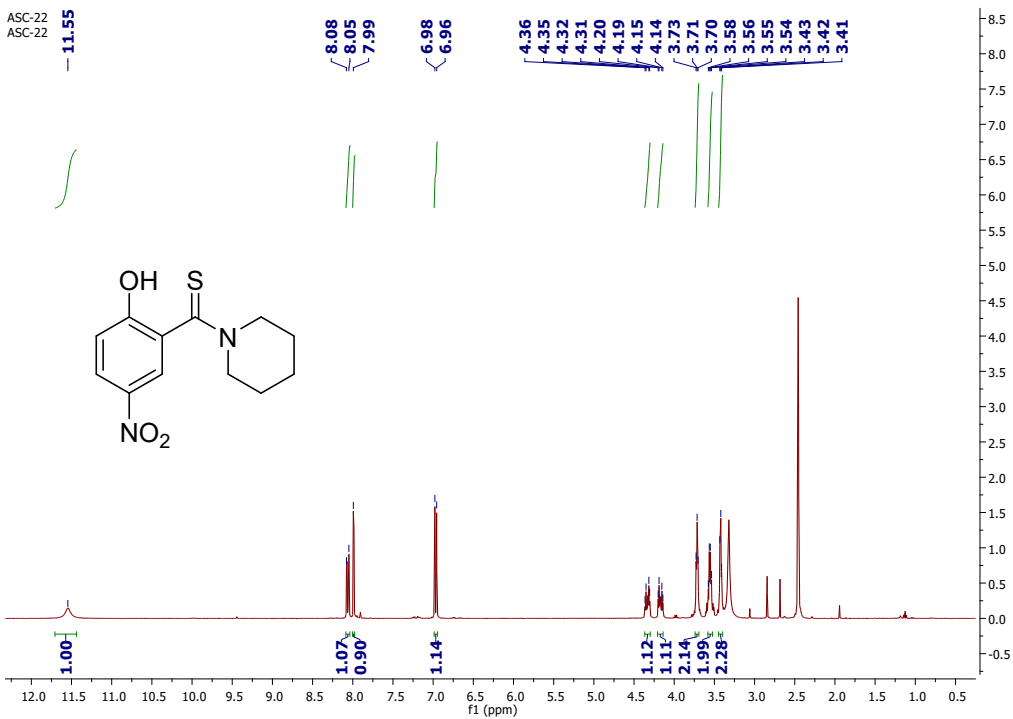


Figure S14. ^1H NMR (CDCl_3) of **10**.

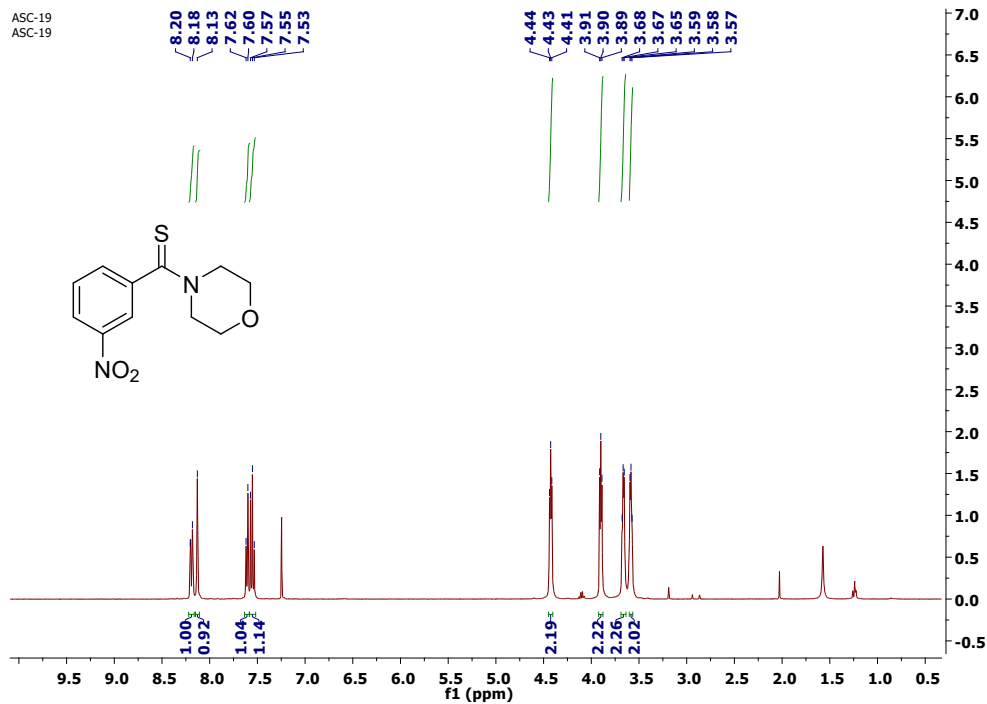


Figure S15. ^1H NMR (CDCl_3) of 11.

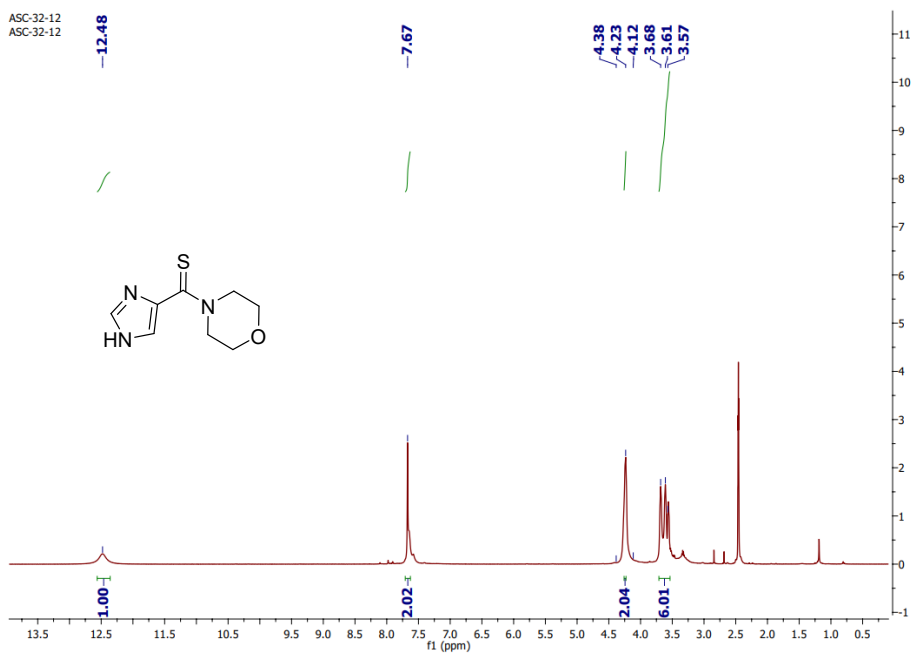


Figure S16. ^1H NMR (CDCl_3) of 12.

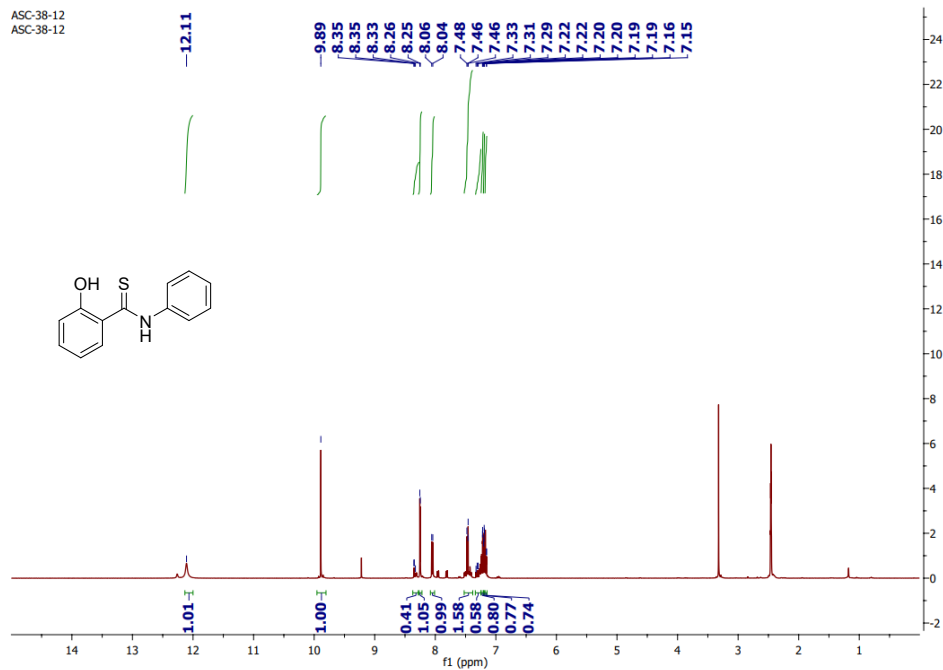


Figure S17. ^1H NMR (CDCl_3) of 13.

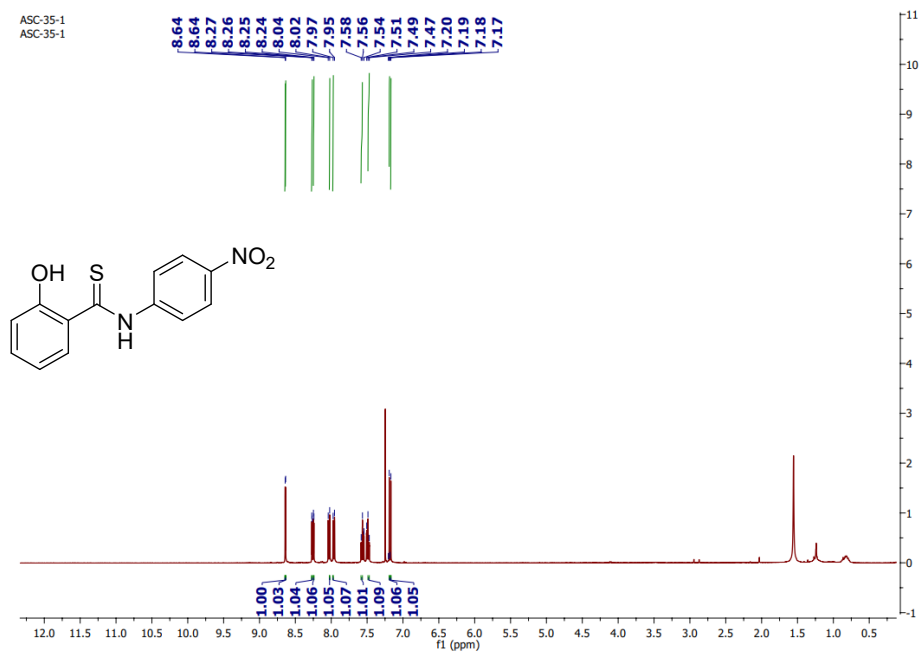


Figure S18. ^1H NMR (CDCl_3) of 14.

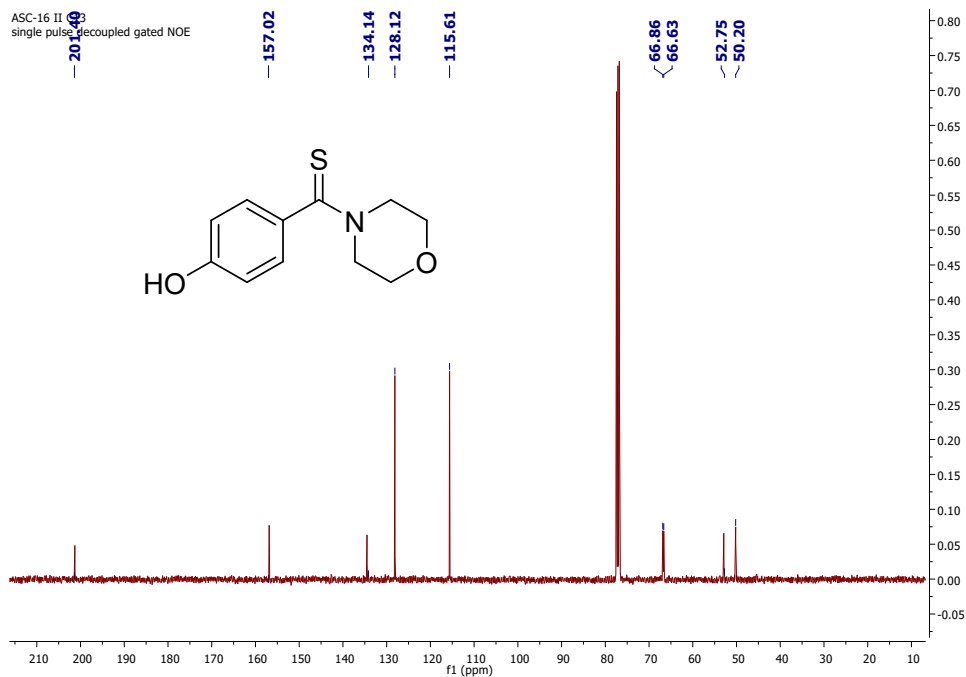


Figure S19. ^{13}C NMR (CDCl_3) of 1.

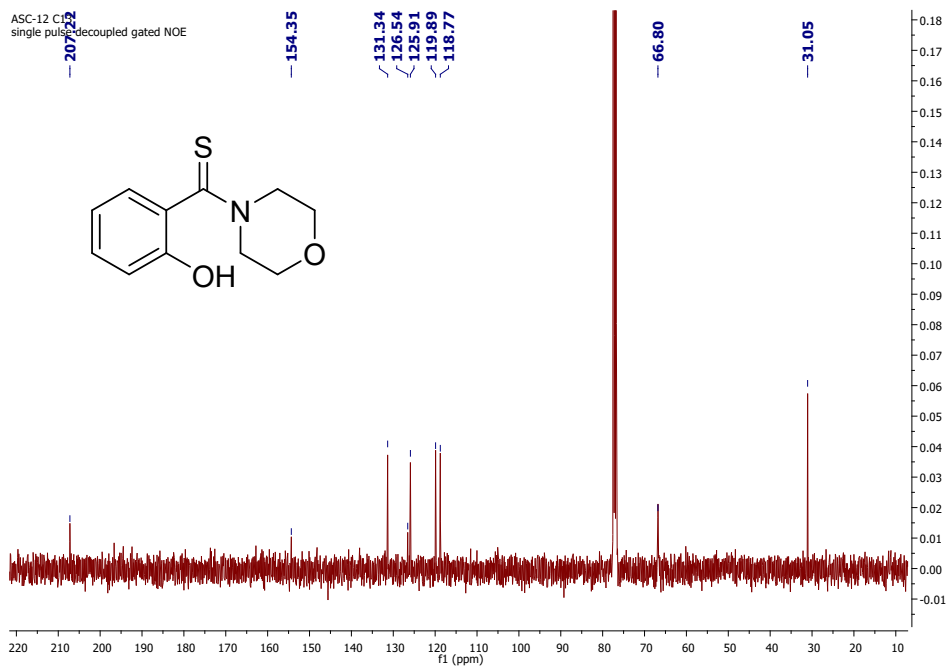


Figure S20. ^{13}C NMR (CDCl_3) of 2.

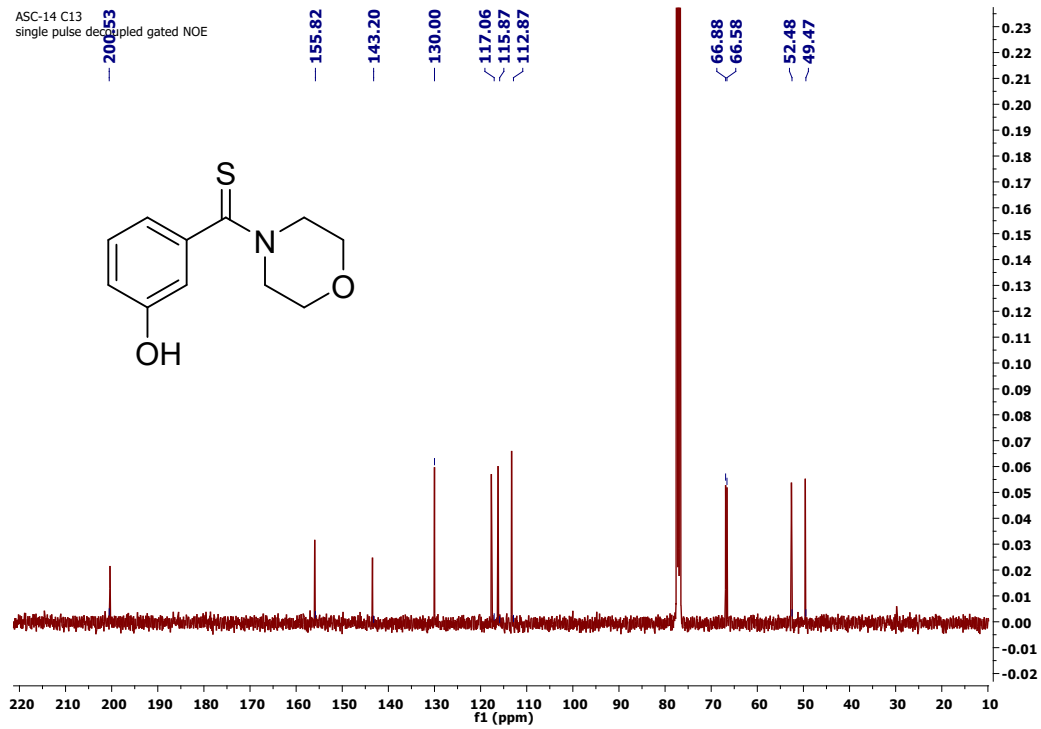


Figure S21. ^{13}C NMR (CDCl_3) of 3.

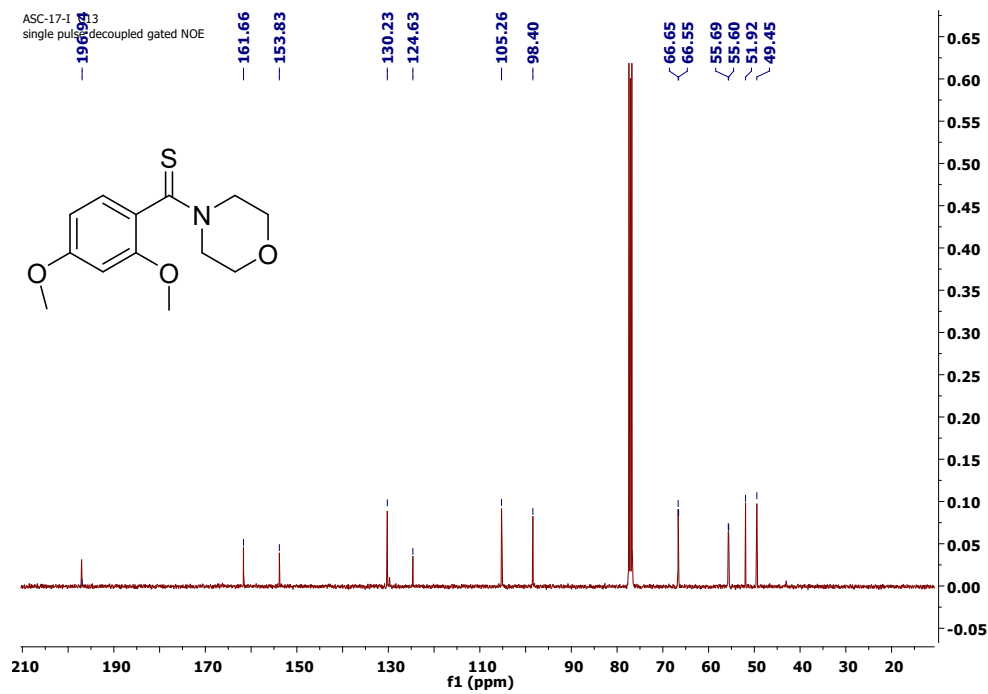


Figure S22. ^{13}C NMR (CDCl_3) of 4.

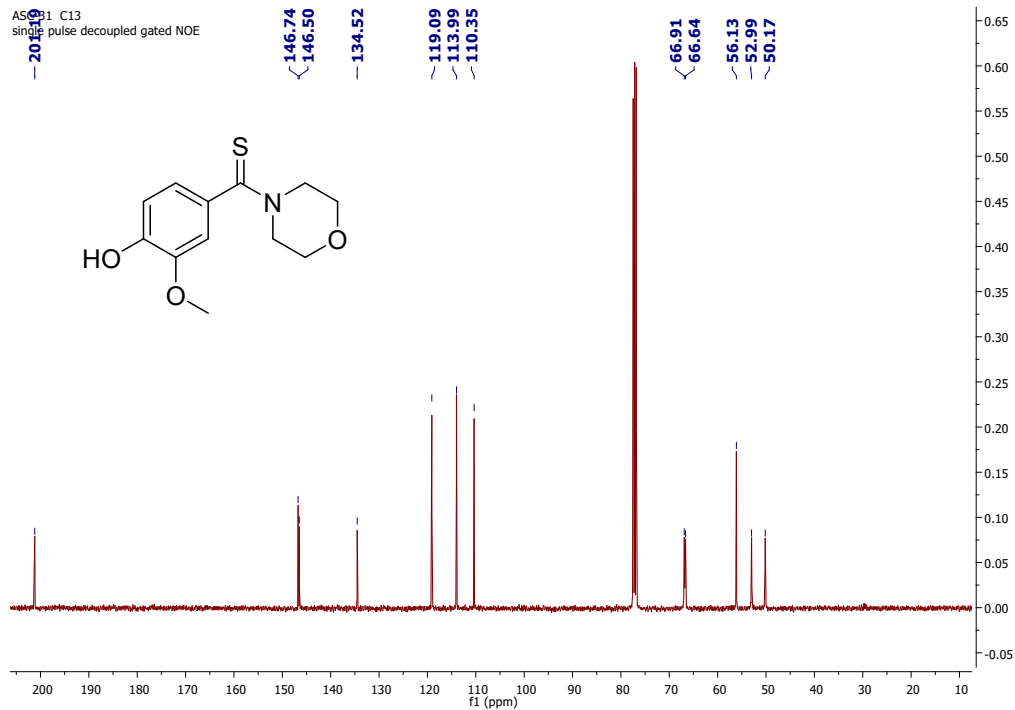


Figure S23. ^{13}C NMR (CDCl_3) of 5.

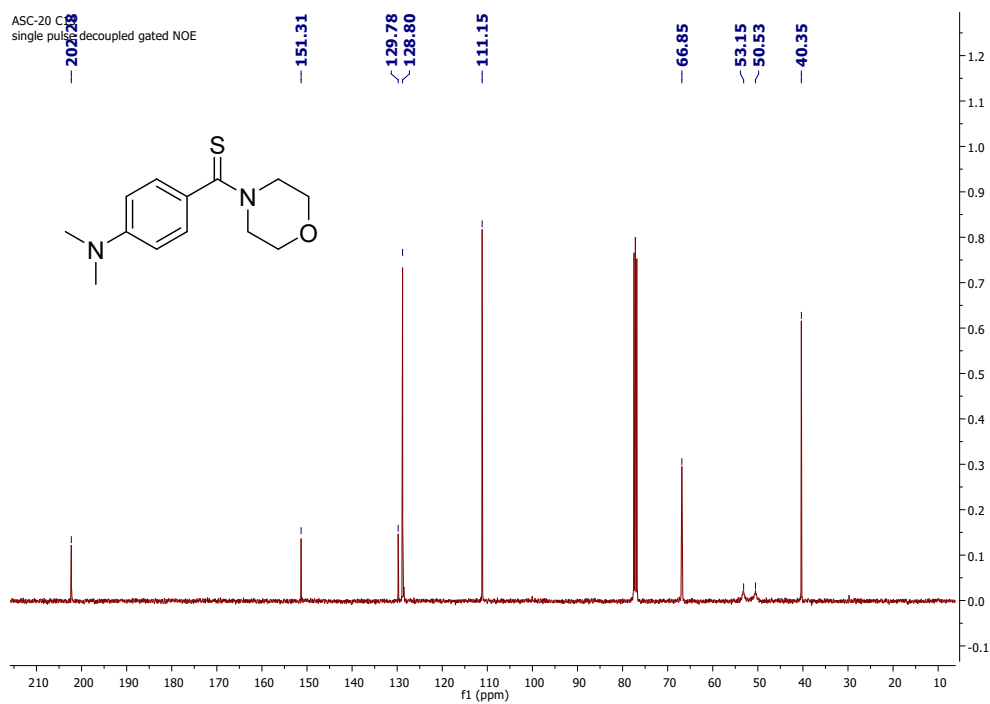


Figure S24. ^{13}C NMR (CDCl_3) of 6.

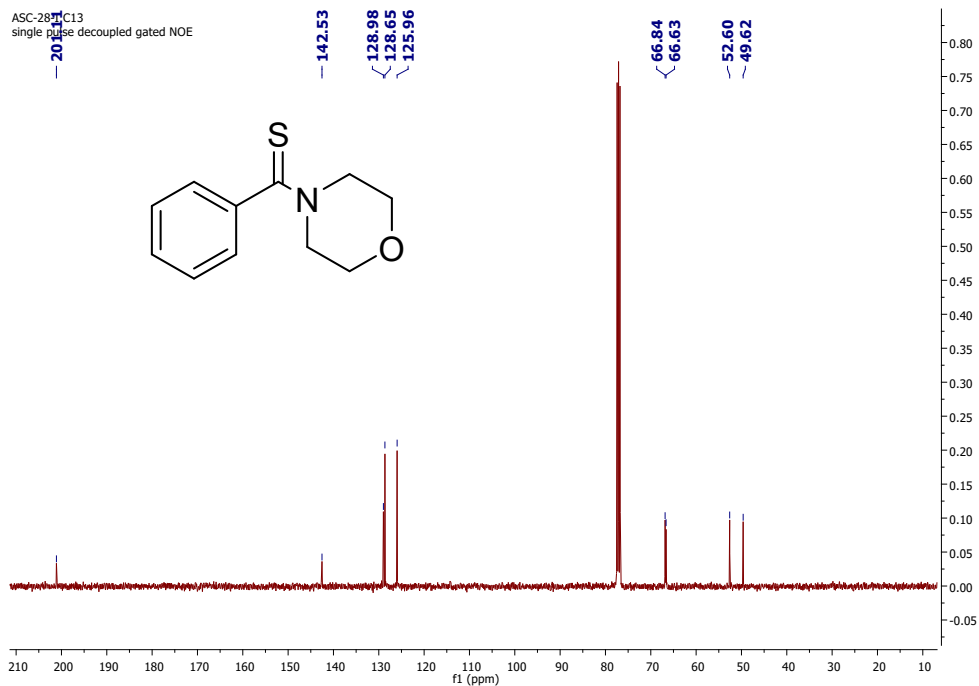


Figure S25. ^{13}C NMR (CDCl_3) of 7.

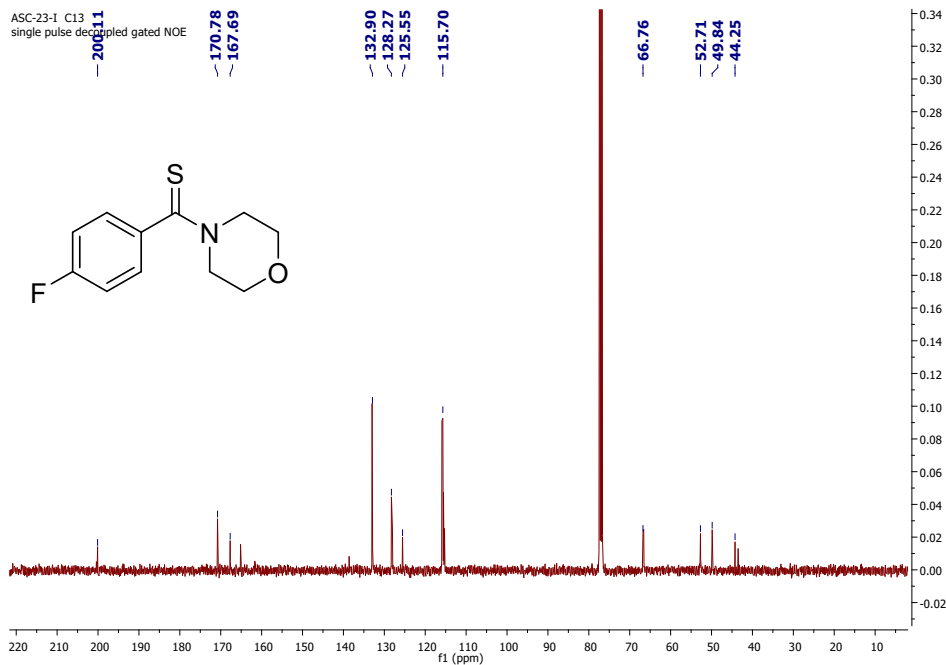


Figure S26. ^{13}C NMR (CDCl_3) of 8.

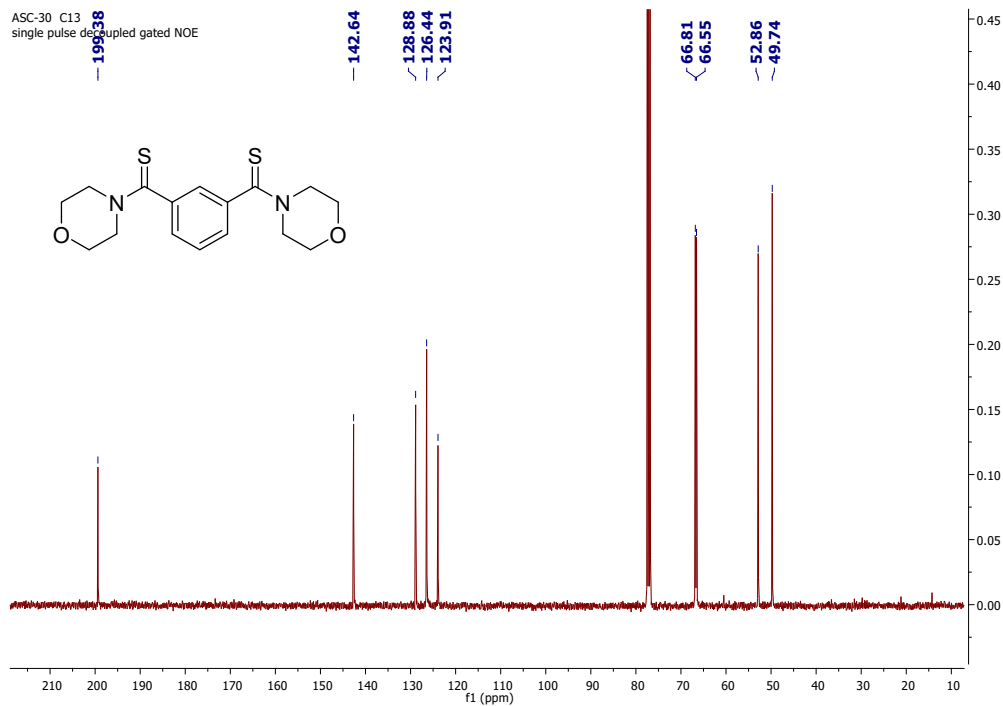


Figure S27. ^{13}C NMR (CDCl_3) of **9**.

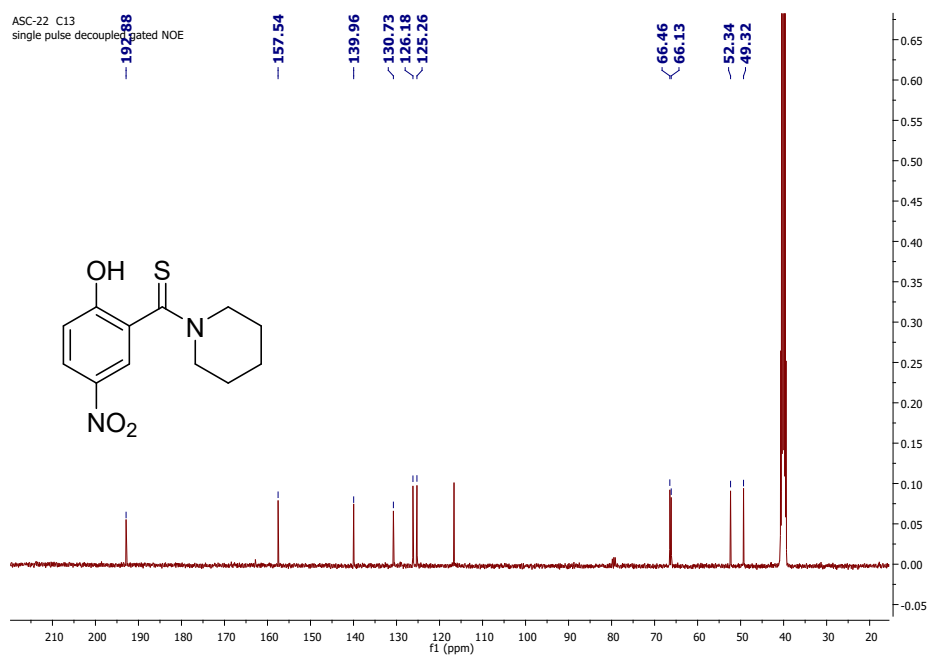


Figure S28. ^{13}C NMR (CDCl_3) of **10**.

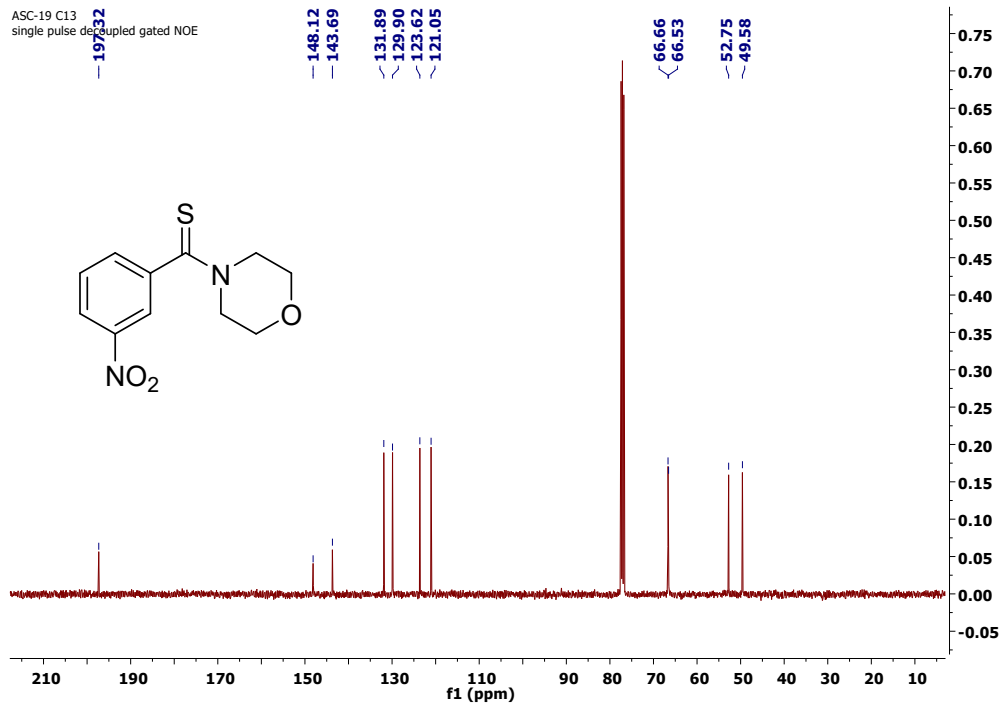


Figure S29. ^{13}C NMR (CDCl_3) of 11.

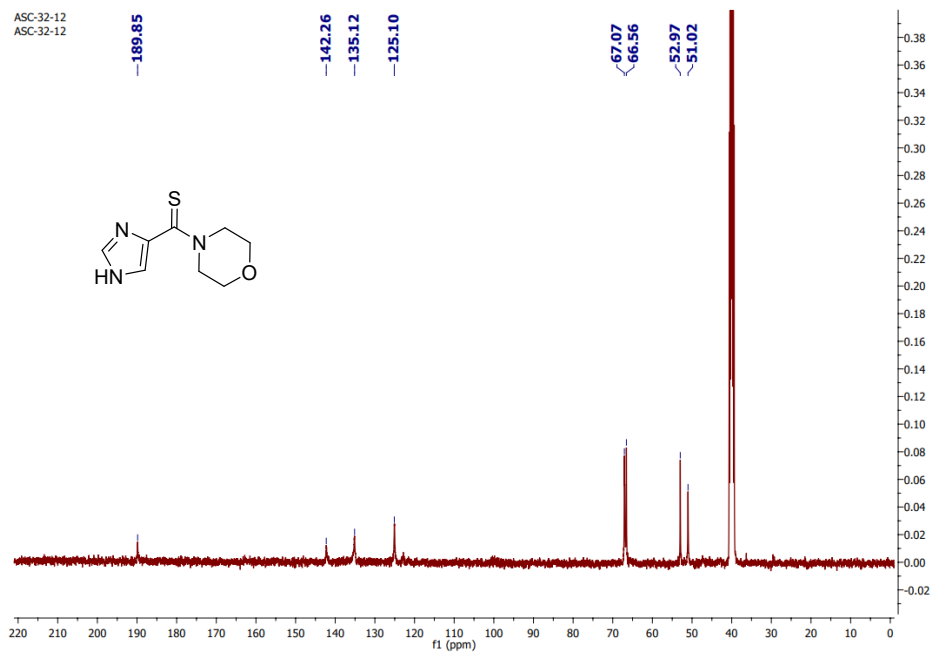


Figure S30. ^{13}C NMR (CDCl_3) of 12.

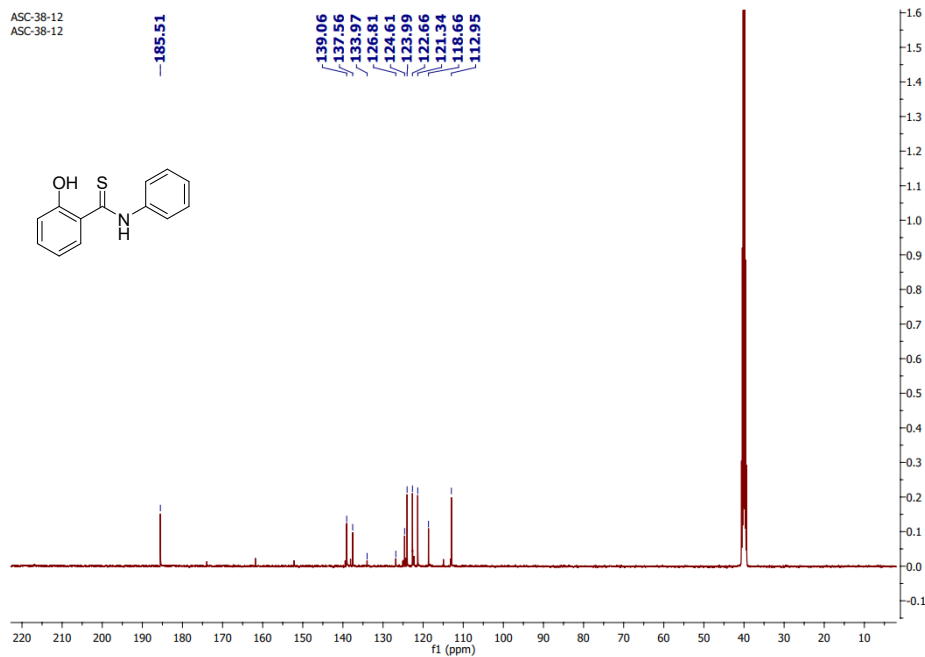


Figure S31. ^{13}C NMR (CDCl_3) of 13.

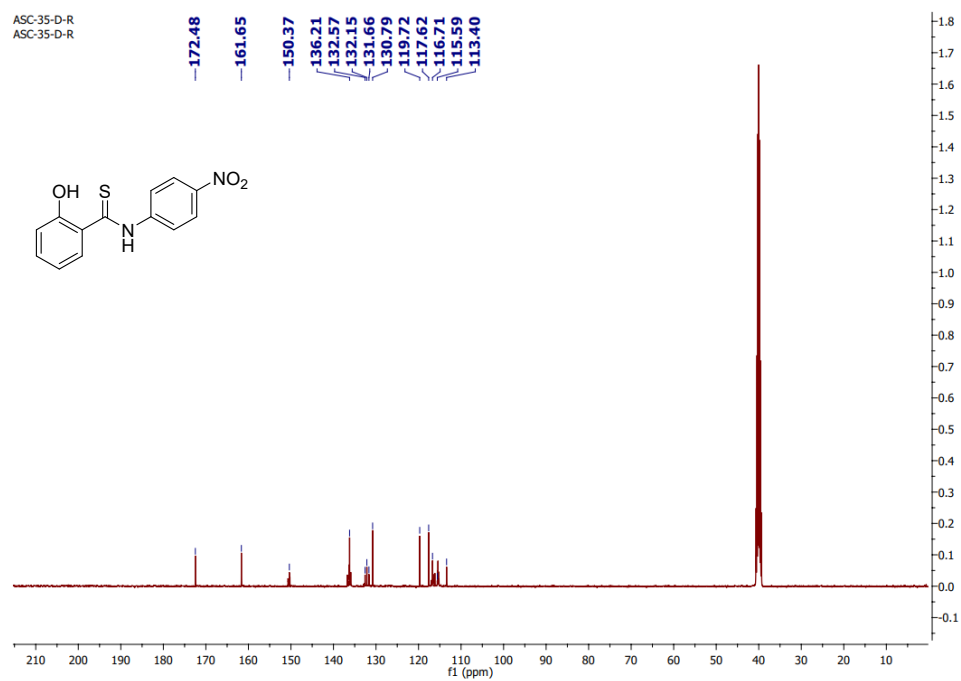


Figure S32. ^{13}C NMR (CDCl_3) of 14.

Monoisotopic Mass, Even Electron Ions

47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 8-25 H: 11-30 N: 0-2 O: 0-4 S: 0-1

Sample Name : ASC-16

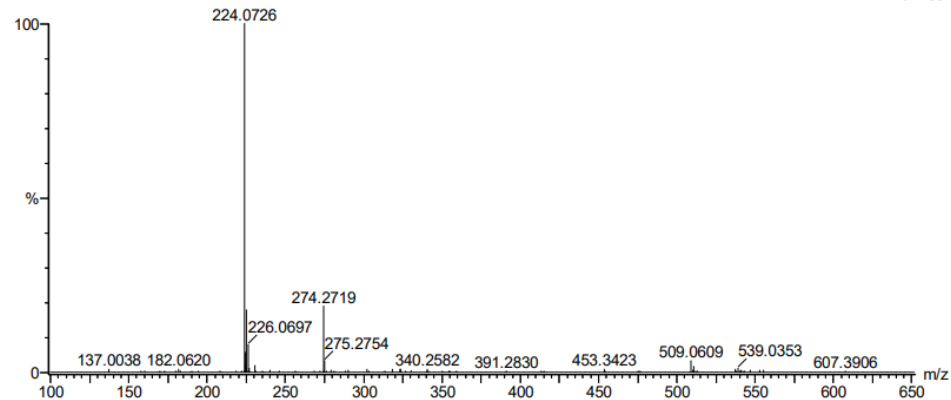
IITRPR

XEVO G2-XS QTOF

Test Name : HRMS-1

101219-ASC-16- 18 (0.183) AM2 (Ar,22000.0,0.00,0.00); Cm (18:20)

1: TOF MS ES+
2.10e+007



Minimum: -1.5
Maximum: 5.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
224.0726	224.0745	-1.9	-8.5	5.5	1078.6	n/a	n/a	C11 H14 N O2 S

Figure S33. HRMS of 1.

Monoisotopic Mass, Even Electron Ions

53 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 9-45 H: 7-50 N: 0-3 O: 1-3 S: 0-1

Sample Name : SS-ASC-12

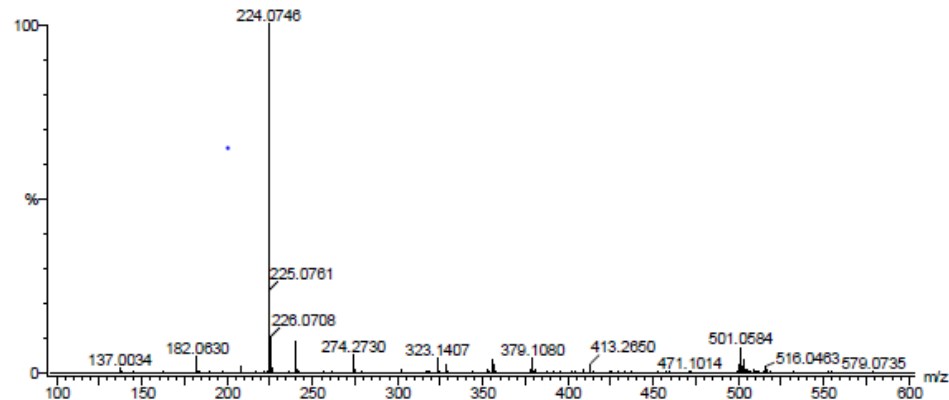
IITRPR

XEVO G2-XS QTOF

Test Name : HRMS-1

221119-SS-ASC-12- 12 (0.131) AM2 (Ar,22000.0,0.00,0.00); Cm (8:18)

1: TOF MS ES+
1.33e+008



Minimum: -1.5
Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
224.0746	224.0745	0.1	0.4	5.5	1294.6	n/a	n/a	C11 H14 N O2 S

Figure S34. HRMS of 2.

Monoisotopic Mass, Even Electron Ions

84 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 11-20 H: 11-35 N: 0-4 O: 1-4 Na: 0-1 S: 0-1

Sample Name : ASC-14 IITRPR

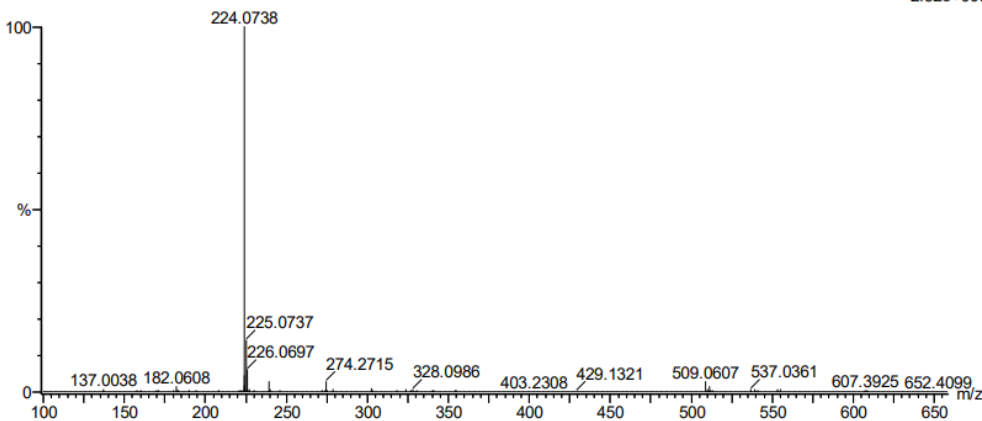
XEVO G2-XS QTOF

Test Name : HRMS-1

1: TOF MS ES+

051219-ASC-14- 20 (0.211) AM (Top,4, Ar,10000.0,0.00,0.00); Cm (20:23)

2.52e+007



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
224.0738	224.0745	-0.7	-3.1	5.5	937.6	n/a	n/a	C11 H14 N O2 S

Figure S35. HRMS of 3.

Monoisotopic Mass, Even Electron Ions

51 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 8-25 H: 11-30 N: 0-2 O: 0-4 S: 0-1

Sample Name : ASC-17 IITRPR

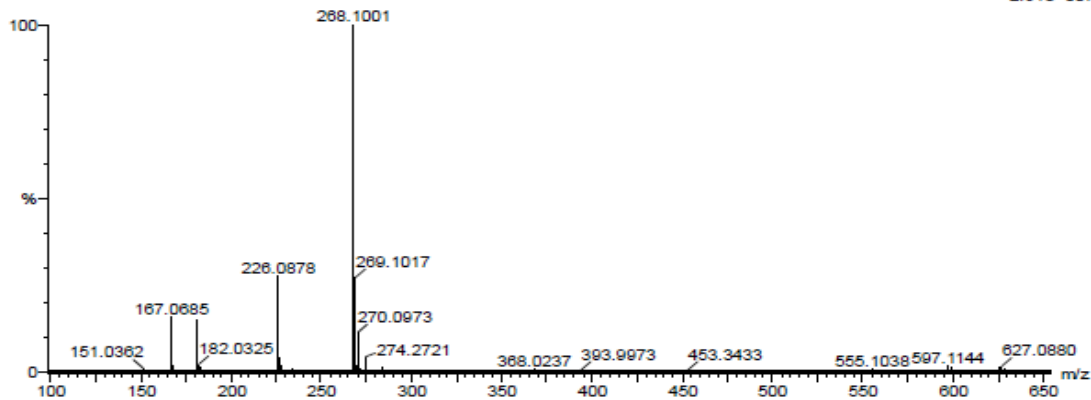
XEVO G2-XS QTOF

Test Name : HRMS-1

1: TOF MS ES+

101219-ASC-17- 19 (0.203) AM2 (Ar,22000.0,0.00,0.00); Cm (19:20)

2.91e+007



Minimum: -1.5
Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
268.1001	268.1007	-0.6	-2.2	5.5	1109.0	n/a	n/a	C13 H18 N O3 S

Figure S36. HRMS of 4.

Monoisotopic Mass, Even Electron Ions

35 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 9-25 H: 13-25 N: 0-2 O: 0-3 S: 0-2

Sample Name : ASC-31

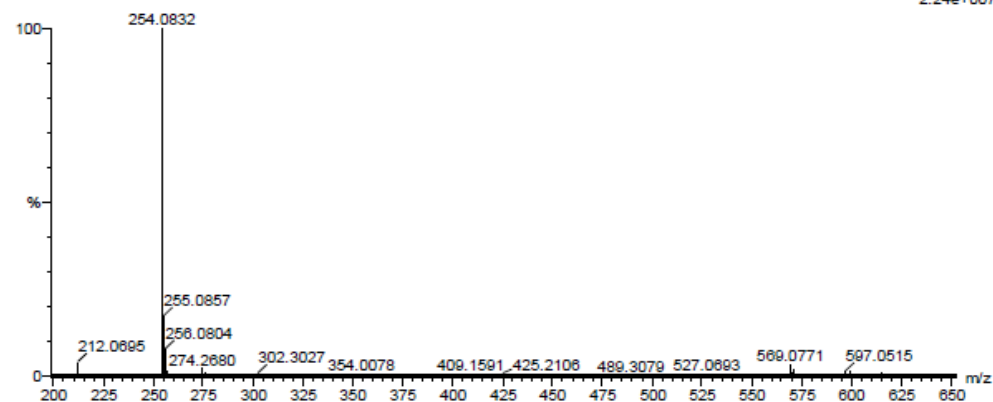
IITRPR

XEVO G2-XS QTOF

Test Name : HRMS-1

210120-ASC-31- 17 (0.174)

1: TOF MS ES+
2.24e+007



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
254.0832	254.0851	-1.9	-7.5	5.5	1739.1	n/a	n/a	C12 H16 N O3 S

Figure S37. HRMS of 5.

Monoisotopic Mass, Even Electron Ions

83 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 11-30 H: 11-35 N: 0-3 O: 0-5 S: 0-1

Sample Name : ASC-20

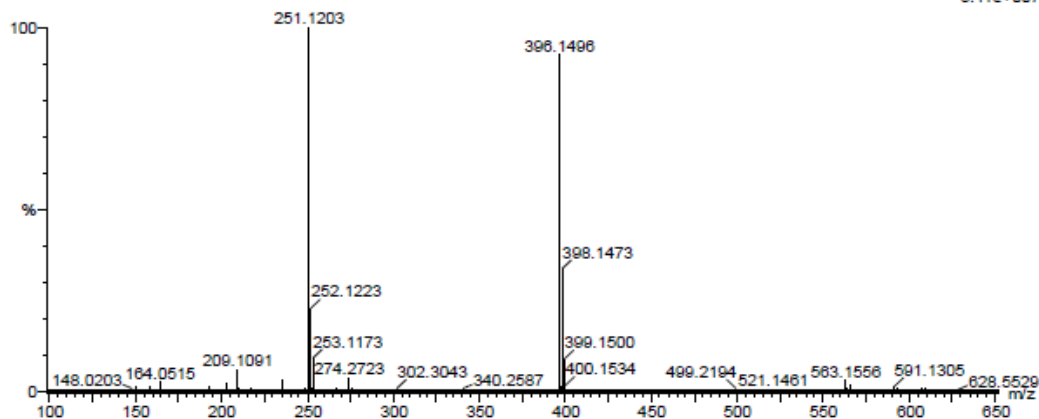
IITRPR

XEVO G2-XS QTOF

Test Name : HRMS-1

171219-ASC-20- 18 (0.183) AM2 (Ar,22000.0,0.00,0.00); Cm (18:21)

1: TOF MS ES+
3.11e+007

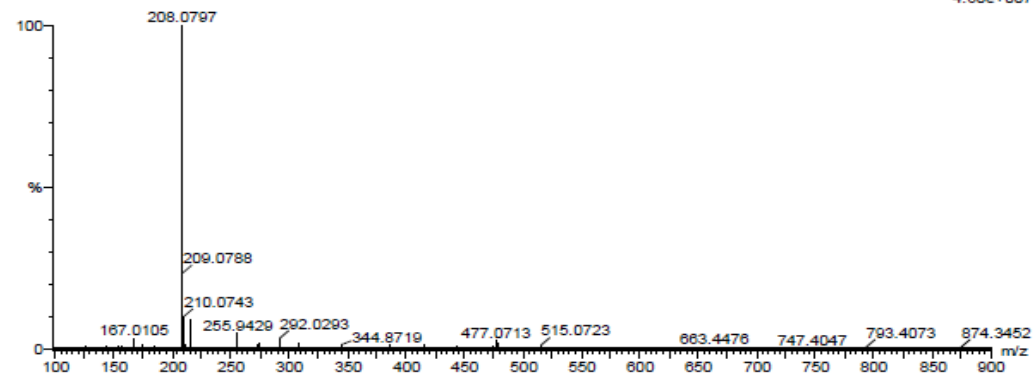


Minimum: -1.5
Maximum: 5.0 7.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
251.1203	251.1218	-1.5	-6.0	5.5	1080.2	n/a	n/a	C13 H19 N2 O S

Figure S38. HRMS of 6.

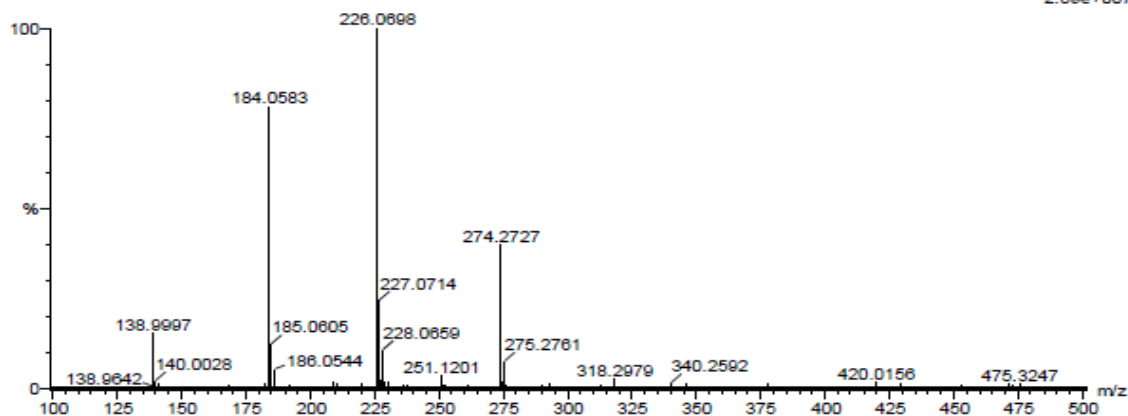
Monoisotopic Mass, Even Electron Ions
 47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 10-30 H: 11-35 N: 0-3 O: 0-2 S: 0-2
 Sample Name : ASC-28 IITRPR XEVO G2-XS QTOF
 Test Name : HRMS-1 1: TOF MS ES+
 070120-ASC-28 16 (0.165) 4.60e+007



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
208.0797	208.0796	0.1	0.5	5.5	2682.5	n/a	n/a	C11 H14 N O S

Figure S39. HRMS of 7.

Monoisotopic Mass, Odd and Even Electron Ions
 350 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 11-30 H: 11-35 N: 0-2 O: 0-5 F: 0-4 S: 0-3
 Sample Name : ASC-23 IITRPR XEVO G2-XS QTOF
 Test Name : HRMS-1 1: TOF MS ES+
 261219-ASC-23- 17 (0.174) 2.89e+007



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
226.0698	226.0702	-0.4	-1.8	5.5	1950.2	n/a	n/a	C11 H13 N O F S

Figure S40. HRMS of 8.

Monoisotopic Mass, Even Electron Ions
 47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 9-25 H: 18-30 N: 0-3 O: 0-3 S: 0-2
 Sample Name : ASC-30 IITRPR XEVO G2-XS QTOF
 Test Name : HRMS-1
 170120-ASC-30- 18 (0.183) 1: TOF MS ES+
 3.24e+007

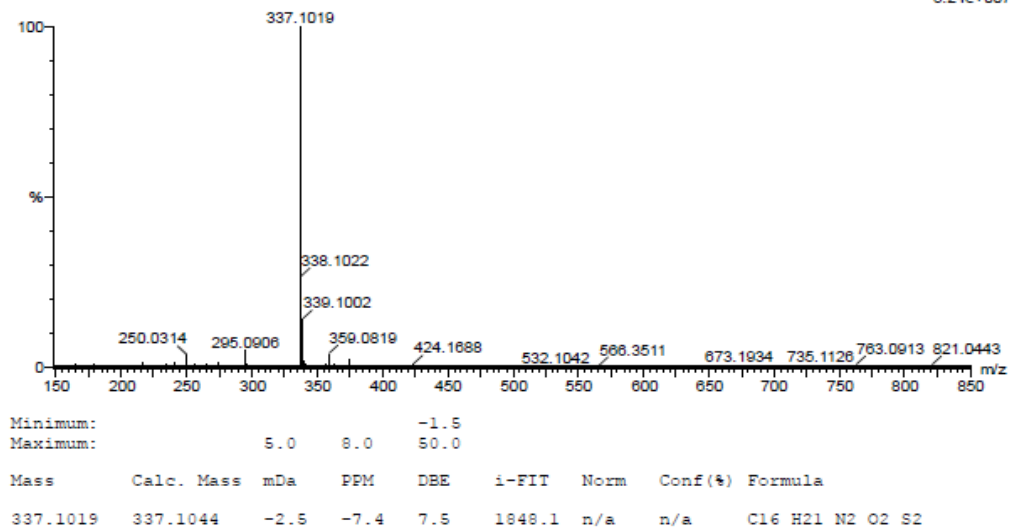


Figure S41. HRMS of 9.

Monoisotopic Mass, Even Electron Ions
 93 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 11-30 H: 10-35 N: 0-3 O: 0-5 S: 0-1
 Sample Name : ASC-22 IITRPR XEVO G2-XS QTOF
 Test Name : HRMS-1
 201219-ASC-22 14 (0.148) 1: TOF MS ES+
 4.00e+007

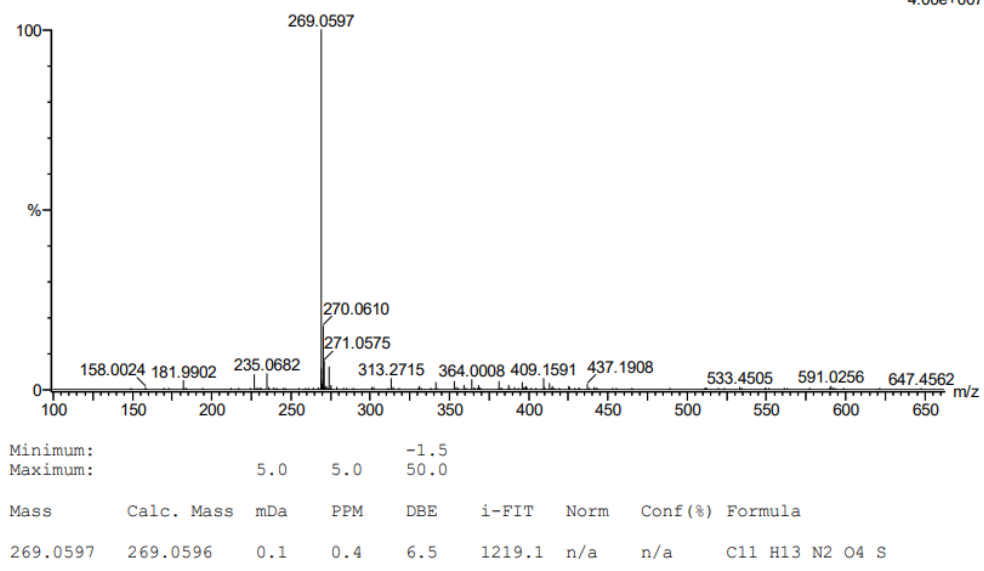


Figure S42. HRMS of 10.

Monoisotopic Mass, Even Electron Ions
 78 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
 Elements Used:
 C: 8-35 H: 10-45 N: 0-2 O: 0-4 S: 0-1
 Sample Name : ASC-19 IITRPR XEVO G2-XS QTOF
 Test Name : HRMS-1
 121219-ASC-19 16 (0.165) AM2 (Ar,22000.0,0.00,0.00); Cm (16:21) 1: TOF MS ES+
 2.38e+007

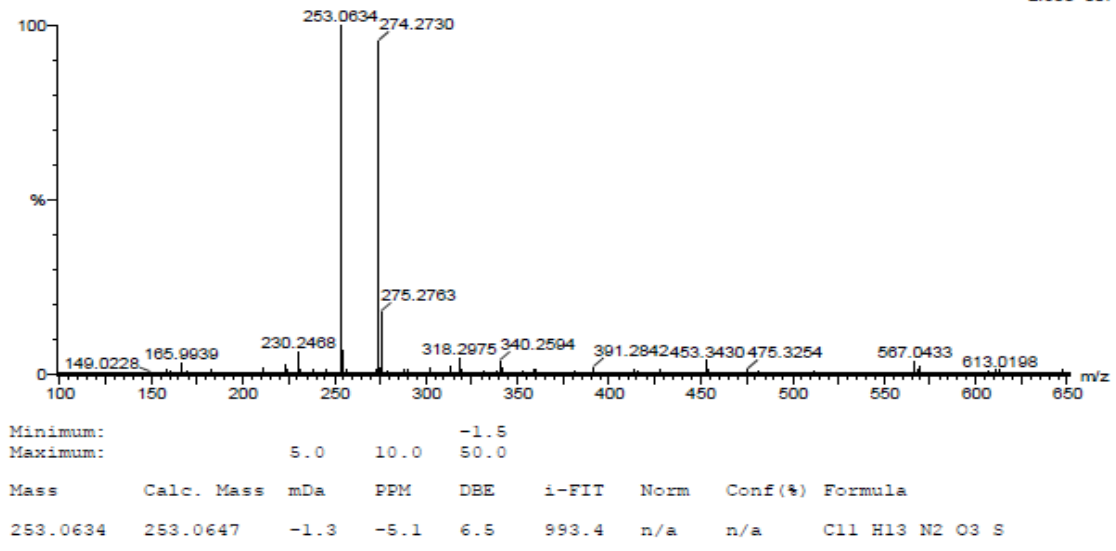


Figure S43. HRMS of 11.

Monoisotopic Mass, Odd and Even Electron Ions
 43 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
 Elements Used:
 C: 8-25 H: 11-25 N: 0-3 O: 0-3 S: 0-2
 Sample Name : ASC-32 IITRPR XEVO G2-XS QTOF
 Test Name : HRMS-1
 210120-ASC-32- 16 (0.165) 1: TOF MS ES+
 2.68e+007

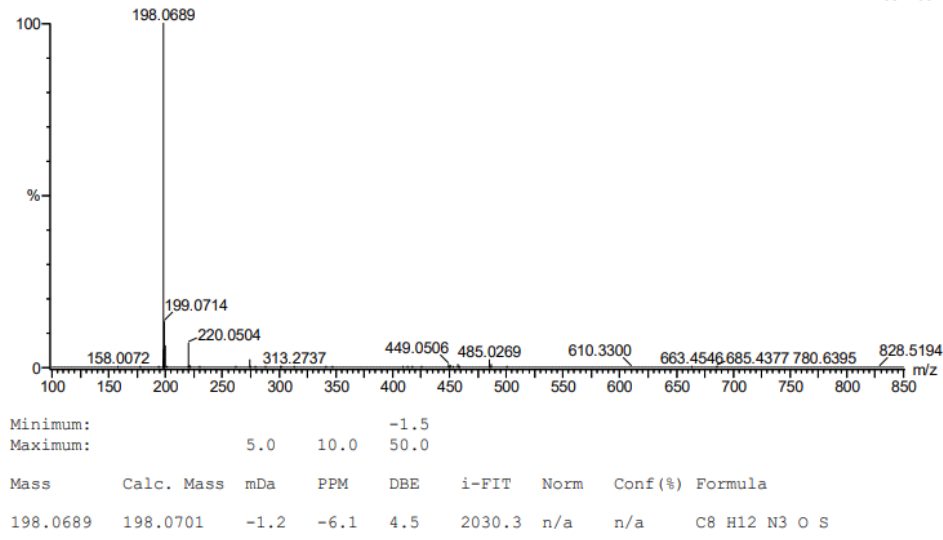


Figure S44. HRMS of 12.

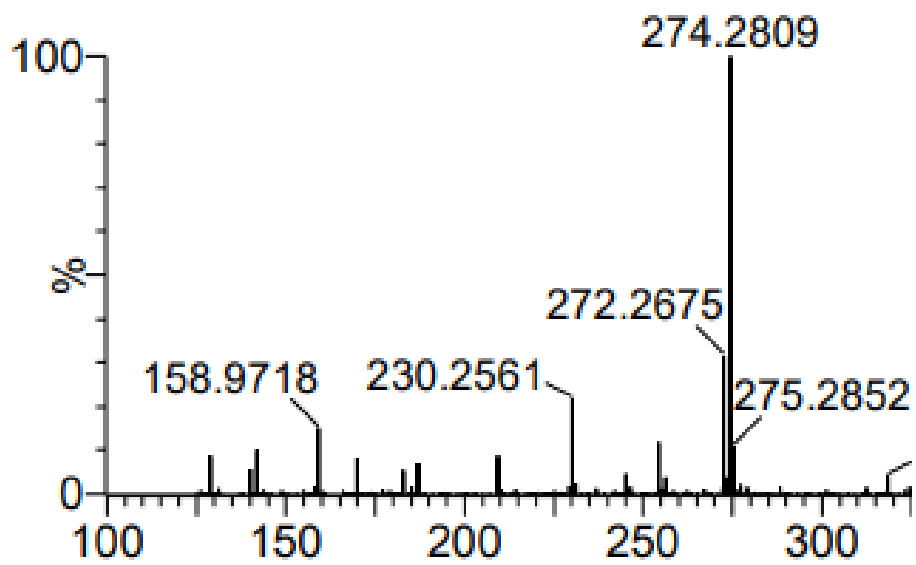


Figure S45. HRMS of 13.

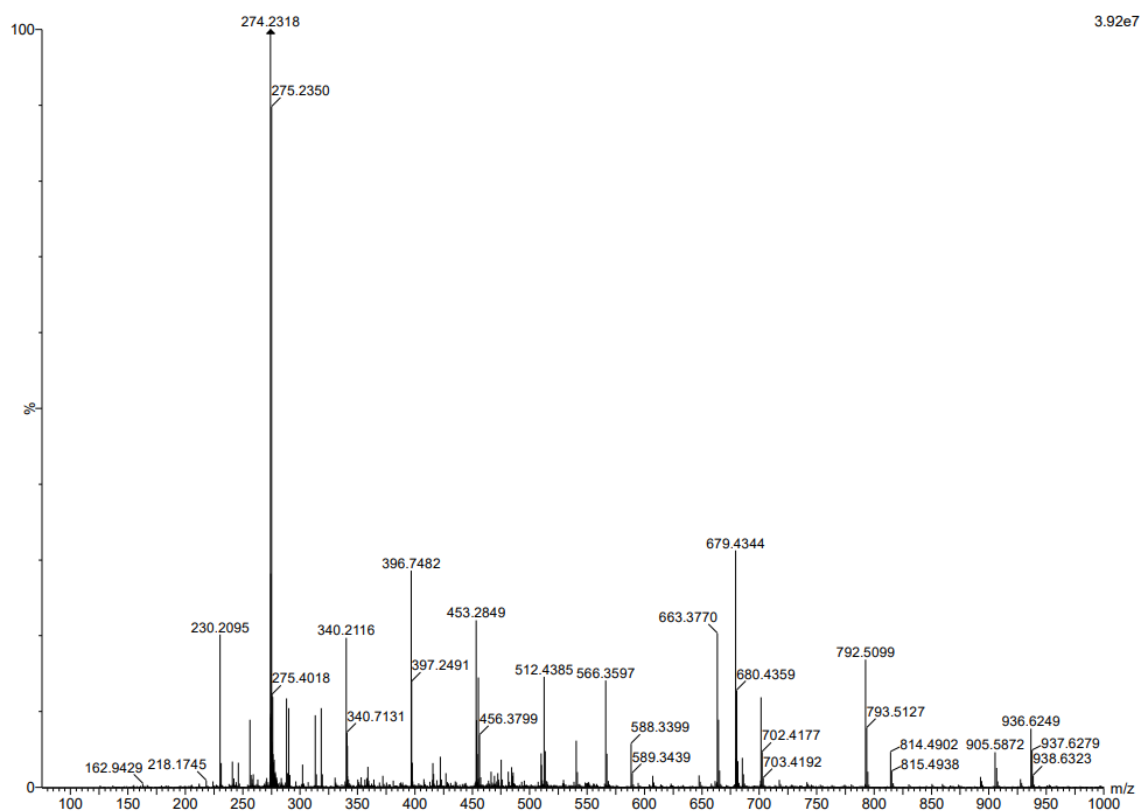


Figure S46. HRMS of 14.

Table S1. Impact energies of the AgNPs@cellulose–PEVA hybrid catalyst in the Izod and Charpy modes. Here, AgNPs and PEVA denote Ag nanoparticles and poly(ethylene-co-vinyl acetate), respectively.

Entry	Mode	Energy (kJ/m)	Degree
1	Izod	1.865	123
2	Charpy	5.939	81

Table S2. Yields of several reported catalysts for the synthesis of thioamides. Here, AgNPs and PEVA denote Ag nanoparticles and poly(ethylene-co-vinyl acetate), respectively.

Entry	Catalyst	Time (h)	Yield (%)	Reference
1	Pyridine	24	86	1
2	-	70	68	2
3	Metal complex	18	82	3
4	K ₂ S ₂ O ₈	4	51	4
5	AgNPs@cellulose–PEVA	2.5	98	This study

References

1. T. B. Nguyen, M. Q. Tran, L. Ermolenko, A. Al-Mourabit, , *Org. Lett.*, 2014, **16**, 310–313. DOI:[10.1021/ol403345e](https://doi.org/10.1021/ol403345e).
2. M. Patra, J. Hess, S. Konatschnig, B. Spingler, G. Gasser, , *Organometallics*, 2013, **32**, 6098–6105. DOI:[10.1021/om400715m](https://doi.org/10.1021/om400715m).
3. X. Wang, M. Ji, S. Lim, H. Y. Jang, , *J. Org. Chem.*, 2014, **79**, 7256–7260. DOI:[10.1021/jo501378v](https://doi.org/10.1021/jo501378v).
4. J. Wei, Y. Li, X. Jiang, , *Org. Lett.*, 2016, **18**, 340–343. DOI:[10.1021/acs.orglett.5b03541](https://doi.org/10.1021/acs.orglett.5b03541).