Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rational design of arsine catalysts for arsa-Wittig reaction

Junya Yukiyasu,[a] Ryoto Inaba,[a] Takashi Yumura,[b] Hiroaki Imoto,*[a] and Kensuke Naka*[a,c]

[a] Faculty of Molecular Chemistry and Engineering, Graduate School of Science and Technology, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.
[b] Faculty of Material Science and Technology, Graduate School of Science and Technology, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.
[c] Materials Innovation Lab, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.

Contents:

1. Synthesis

Products of the catalytic arsa-Wittig reactions using 5

*(E)-Ethyl cinnamate (**8**).*[1] Product: 112 mg, 0.640 mmol, 67%. Benzaldehyde (107 mg, 1.01 mmol), ethyl bromoacetate (201 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (234 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 45 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.69 (d, J = 16.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.38 (t, J = 4.0 Hz, 3H), 6.44 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 6.7 Hz, 2H), 1.34 (t, J = 8.0 Hz, 3H) ppm.

*Ethyl (2E)-3-(4-cyanophenyl)-2-propenoate (**9**).*[2] Product: 145 mg, 0.721 mmol, 72%. 4-Cyanobenzaldehyde (130 mg, 0.991 mmol), ethyl bromoacetate (201 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.70-7.60 (m, 5H), 6.52 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 6.7 Hz, 2H), 1.35 (t, J = 8.0 Hz, 3H) ppm.

*Ethyl (2E)-3-(2-fluorophenyl)-2-propenoate (**10**).*[3] Product: 134 mg, 0.690 mmol, 69%. 2-Fluorobenzaldehyde (124 mg, 0.999 mmol), ethyl bromoacetate (201 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 43 mg, 0.099 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.81 (d, 1H, J = 16.2 Hz), 7.53 (td, 1H, J = 7.6, 1.6 Hz), 7.38-7.34 (m, 1H), 7.16 (td, 1H, J = 7.6, 1.0), 7.09 (ddd, J = 10.7, 8.3, 1.1), 6.53 (d, 1H, J = 16.2 Hz), 4.27 (q, 2H, J = 7.2 Hz), 1.34 (t, 3H, J = 7.2 Hz) ppm.

*(E)-Ethyl 3-(2-chlorophenyl)prop-2-enoate (**11**).*[2] Product: 138 mg, 0.655 mmol, 65%. 2-Chlorobenzaldehyde (141 mg, 1.00 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (198 mg, 1.21 mmol), Cy_2MeN (236 mg, 1.21 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 45 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 8.09 (d, J = 16.0 Hz, 1H), 7.63-7.60 (m, 1H), 7.42-7.40 (m, 1H), 7.32-7.27 (m, 2H), 6.43 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 8.0 Hz, 2H), 1.35 (t, J = 8.0 Hz, 3H) ppm.

*Ethyl (2E)-3-(2-bromophenyl)-2-propenoate (**12**).*[4] Product: 161 mg, 0.631 mmol, 63%. 2-Bromobenzaldehyde (185 mg, 1.00 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 45 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400

MHz): δ= 8.05 (d, J = 16.0 Hz, 1H), 7.62-7.59 (m, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.22 (td, J = 8.0, 1.6 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H) ppm.

*(E)-Ethyl 3-(4-fluorophenyl)prop-2-enoate (**13**)*.[5] Product: 113 mg, 0.582 mmol, 58%. 2-Fluorobenzaldehyde (125 mg, 1.01 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (196 mg, 1.19 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.65 (d, J = 16.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.10-7.05 (t, J = 10.0 Hz, 2H), 6.36 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 4.0 Hz, 2H), 1.34 (t, J = 8.0 Hz, 3H) ppm.

*(E)-Ethyl 3-(4-chlorophenyl)prop-2-enoate (**14**)*.[6] Product: 148 mg, 0.703 mmol, 70%. 4-Chlorobenzaldehyde (141 mg, 1.00 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (234 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.63 (d, J = 16.0 Hz, 1H), 7.45 (d, J = 12.0 Hz, 2H), 7.35 (d, J = 12.0 Hz, 2H), 6.40 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 6.7 Hz, 2H), 1.34 (t, J = 8.0 Hz, 3H) ppm.

*(E)-Ethyl 3-(4-bromophenyl)prop-2-enoate (**15**)*.[7] Product: 187 mg, 0.733 mmol, 74%. 4-Bromobenzaldehyde (184 mg, 0.994 mmol), ethyl bromoacetate (201 mg, 1.20 mmol), $(EtO)_3SiH$ (198 mg, 1.21 mmol), Cy_2MeN (234 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 45 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.61 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.42(d, J = 16.0 Hz, 1H), 4.26 (q, J = 4.0 Hz, 2H), 1.34 (t, J = 6.0 Hz, 3H) ppm.

*Ethyl cinnamylideneacetate (**16**)*.[8] Product: 86 mg, 0.43 mmol, 43%. *trans*-Cinnamaldehyde (132 mg, 0.999 mmol), ethyl bromoacetate (201 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (234 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.48-7.28 (m, 6H), 6.93-6.87 (m, 2H), 5.99 (d, J = 16.0 Hz, 1H), 4.23 (q, J = 6.7 Hz, 2H), 1.32 (t, J = 8.0 Hz, 3H) ppm.

*(E)-Ethyl 3-(naphthalene-2-yl)prop-2-enoate (**17**)*.[9] Product: 117 mg, 0.517 mmol, 52%. 1-Naphthaldehyde (157 mg, 1.01 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (198 mg, 1.21 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 43 mg, 0.099 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400

MHz): δ= 8.52 (d, J = 16.0 Hz, 1H), 8.18 (d, J = 12.0 Hz, 1H), 7.86 (t, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.58-7.44 (m, 3H), 6.52 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 5.3 Hz, 2H), 1.37 (t, J = 6.0 Hz, 3H) ppm.

*(E)-Ethyl 3-(2-thienyl)-2-propenoate (**18**)*.[8] Product: 114 mg, 0.626 mmol, 62%. 2-Thiophenecarboxyaldehyde (112 mg, 0.999 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.78 (d, J = 16.0 Hz, 1H),7.37 (d, J = 4.0 Hz, 1H),7.25 (d, J = 4.0 Hz, 1H), 7.06-7.04 (m, 1H), 6.24 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 6.7 Hz, 2H), 1.33 (t, J = 6.0 Hz, 3H) ppm.

*(E)-Ethyl 3-[4-(N,N-dimethylamino)phenyl]prop-2-enoate (**19**)*.[8] NMR yield: 3%. *p*-Dimethylaminobenzaldehyde (149 mg, 0.999 mmol), ethyl bromoacetate (202 mg, 1.21 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (234 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.62 (d, J = 16.0 Hz, 1H), 7.44-7.36 (m, 2H), 6.67 (d, J = 12.0 Hz, 2H), 6.22 (d, J = 16.0 Hz, 1H), 4.23 (q, J = 4.0 Hz, 2H), 3.01 (s, 6H), 1.33 (t, J = 6.0 Hz, 3H) ppm.

*(E)-Ethyl 3-(4-methylphenyl)prop-2-enoate (**20**)*.[9] Product: 75 mg, 0.39 mmol, 39%. *p*-Tolualdehyde (120 mg, 0.999 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (198 mg, 1.21 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.66 (d, J = 16.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.26 (q, J = 8.0 Hz, 2H), 2.37 (s, 3H), 1.33 (t, J = 8.0 Hz, 3H) ppm.

*(E)-Ethyl 3-(4-methoxyphenyl)prop-2-enoate (**21**)*.[9] Product: 51 mg, 0.25 mmol, 25%. *p*-Anisaldehyde (137 mg, 1.01 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 43 mg, 0.099 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.64 (d, J = 16.0 Hz, 1H), 7.44-7.36 (m, 2H), 6.67 (d, J = 12.0 Hz, 2H), 6.22 (d, J = 16.0 Hz, 1H), 4.23 (q, J = 4.0 Hz, 2H), 3.01 (s, 6H), 1.33 (t, J = 6.0 Hz, 3H) ppm.

*Ethyl (2E)-cyclohexylprop-2-enoate (**22**)*.[2] NMR yield: 33%. Cyclohexanecarboxaldehyde (112 mg, 0.998 mmol), ethyl bromoacetate (201 mg, 1.20

mmol), $(EtO)_3SiH$ (197 mg, 1.20 mmol), Cy_2MeN (234 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 6.92 (dd, J = 16.0 Hz, 1H), 5.76 (d, J = 16.0 Hz, 1H), 4.19 (q, J = 6.7 Hz, 2H), 1.29 (t, J = 8.0 Hz, 3H), 1.26-1.10 (m, 5H) ppm.

(*E*)-Methyl cinnamate (**23**).[1] Product: 90 mg, 0.55 mmol, 55%. Benzaldehyde (107 mg, 1.01 mmol), methyl bromoacetate (184 mg, 1.20 mmol), $(EtO)_3SiH$ (198 mg, 1.21 mmol), Cy_2MeN (235 mg, 1.20 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 45 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.70 (d, J = 16.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.38 (t, J = 6.0 Hz, 3H), 6.45 (d, J = 16.0 Hz, 1H), 3.81 (s, 3H) ppm.

(*E*)-Cinnamonitrile (**25**).[10] NMR yield: 11%. Benzaldehyde (106 mg, 0.999 mmol), bromoacetonitrile (144 mg, 1.20 mmol), $(EtO)_3SiH$ (198 mg, 1.21 mmol), Cy_2MeN (236 mg, 1.21 mmol) and tris(*p*-(dimethylamino)phenyl)arsine (**5**, 44 mg, 0.10 mmol) were used. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ= 7.46-7.39 (m, 6H), 5.88 (d, J = 16.0 Hz, 1H) ppm.

2. NMR Spectra

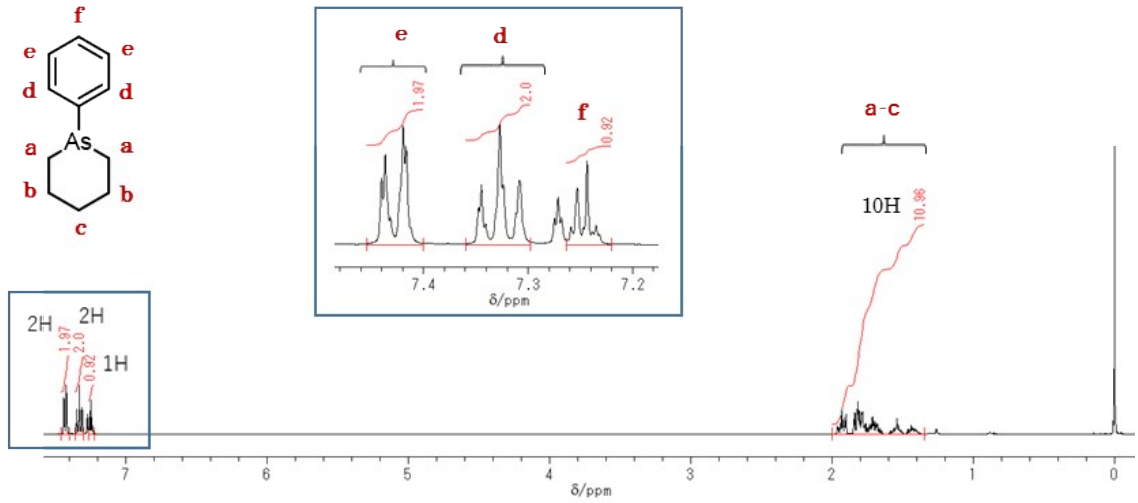


Figure S1. ^{1}H-NMR spectrum (400 MHz) of **2** in $CDCl_3$.

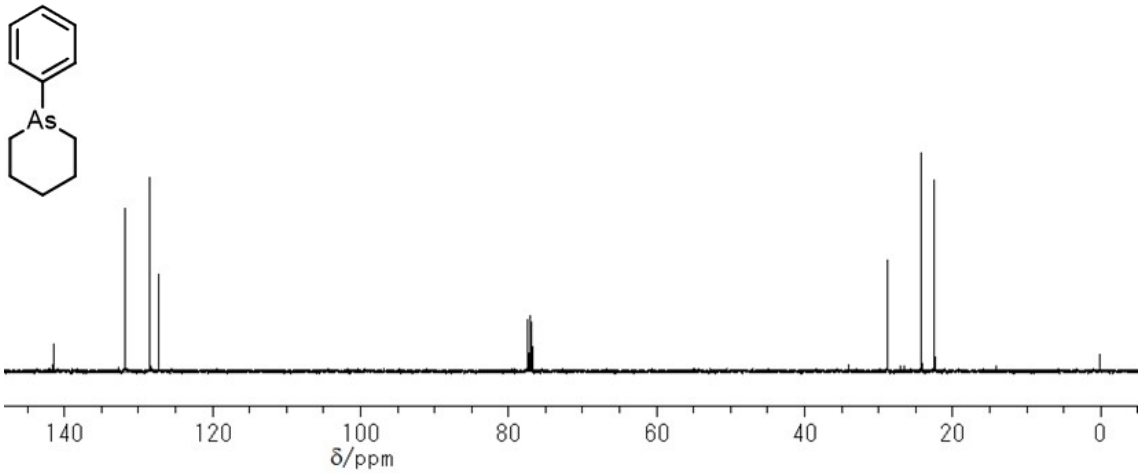


Figure S2. ^{13}C-NMR spectrum (100 MHz) of **2** in $CDCl_3$.

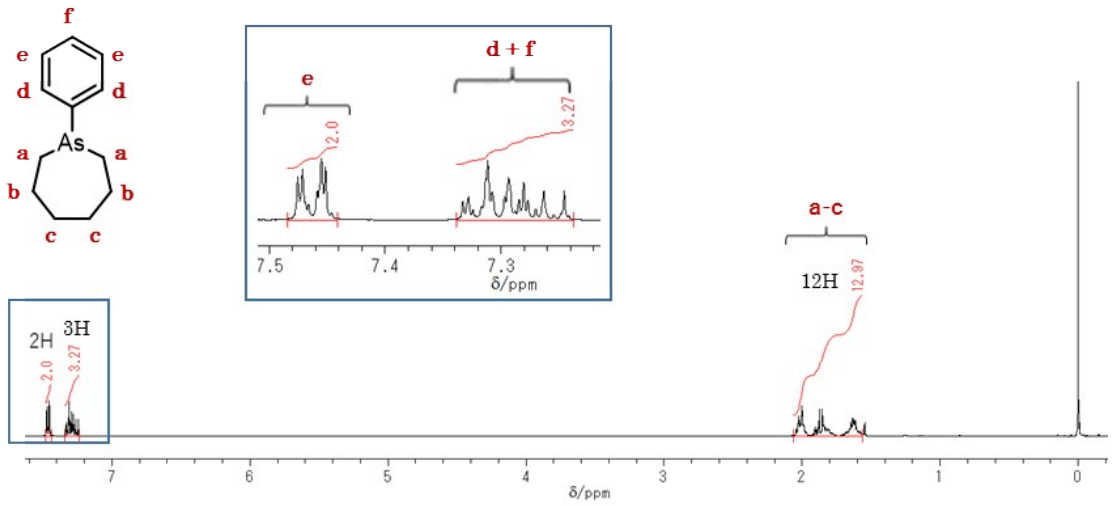


Figure S3. ^{1}H-NMR spectrum (400 MHz) of **3** in $CDCl_3$.

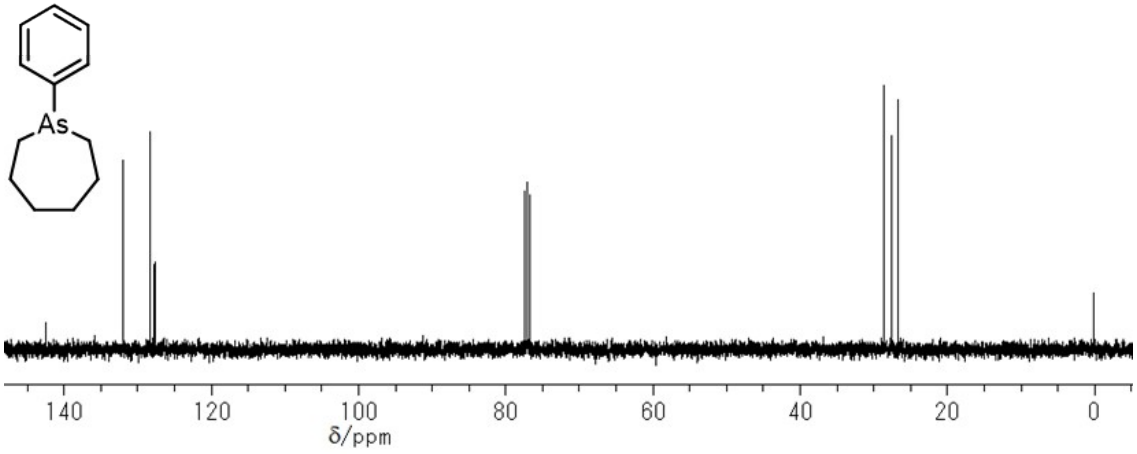


Figure S4. ^{13}C-NMR spectrum (100 MHz) of **3** in $CDCl_3$.

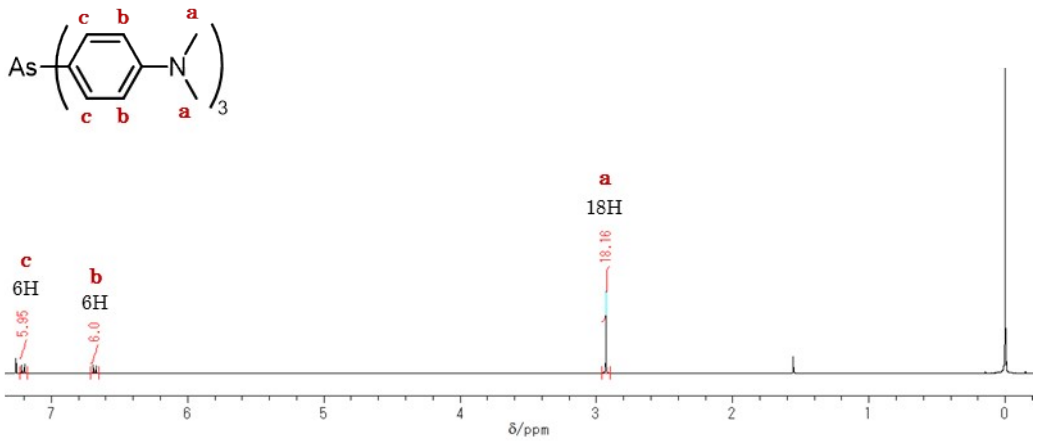


Figure S5. ^{1}H-NMR spectrum (400 MHz) of **5** in $CDCl_3$.

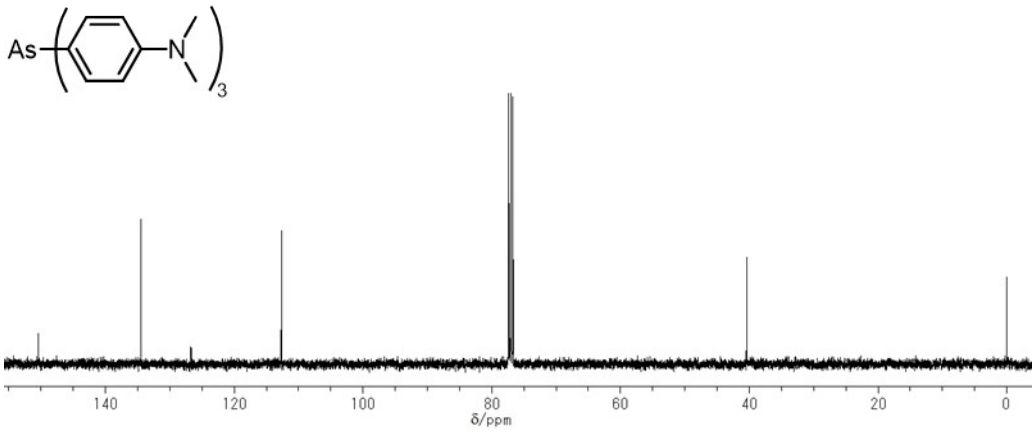


Figure S6. ^{13}C-NMR spectrum (100 MHz) of **5** in $CDCl_3$.

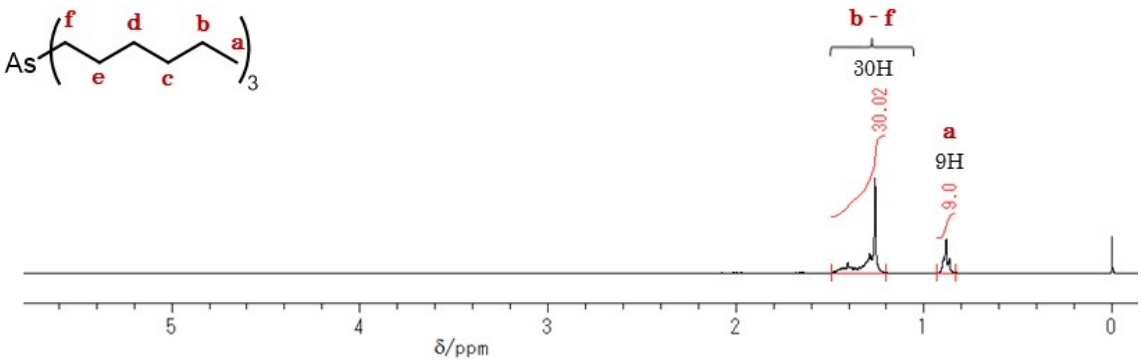


Figure S7. ^{1}H-NMR spectrum (400 MHz) of **6** in $CDCl_3$.

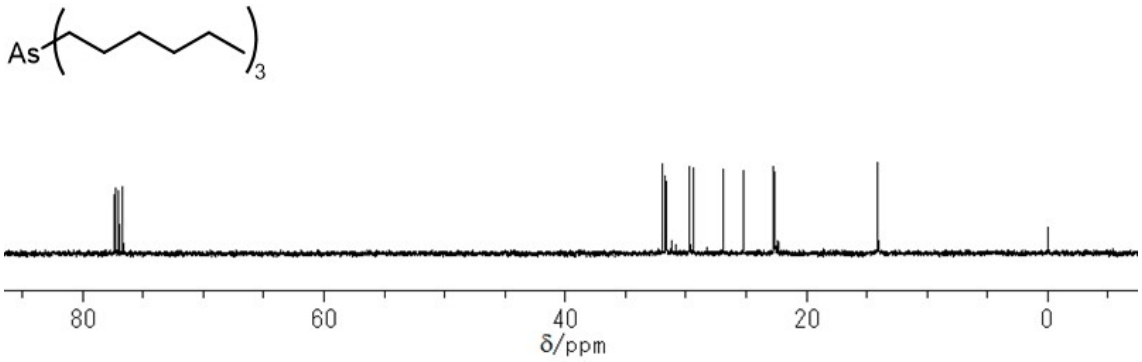


Figure S8. ^{13}C-NMR spectrum (100 MHz) of **6** in $CDCl_3$.

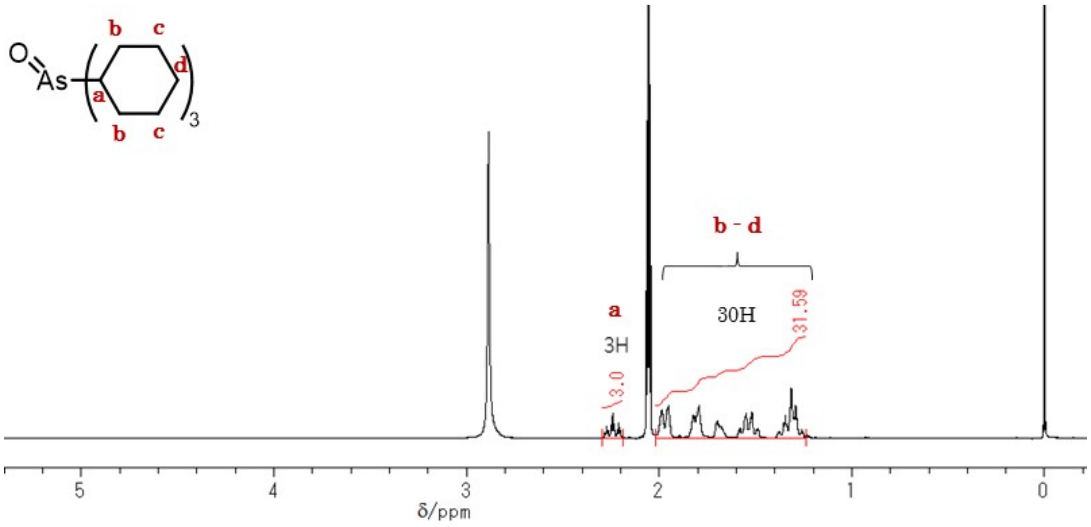


Figure S9. ^{1}H-NMR spectrum (400 MHz) of **7** in $CDCl_3$.

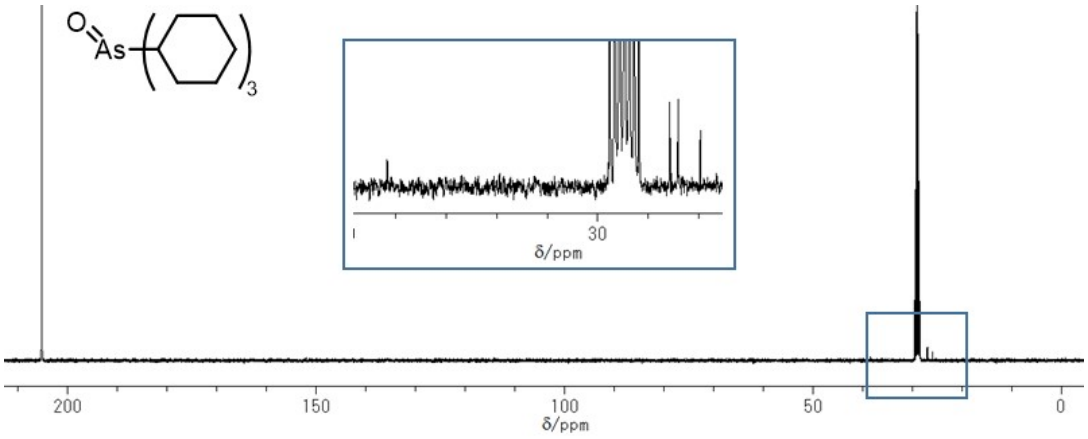


Figure S10. ^{13}C-NMR spectrum (100 MHz) of **7** in $CDCl_3$.

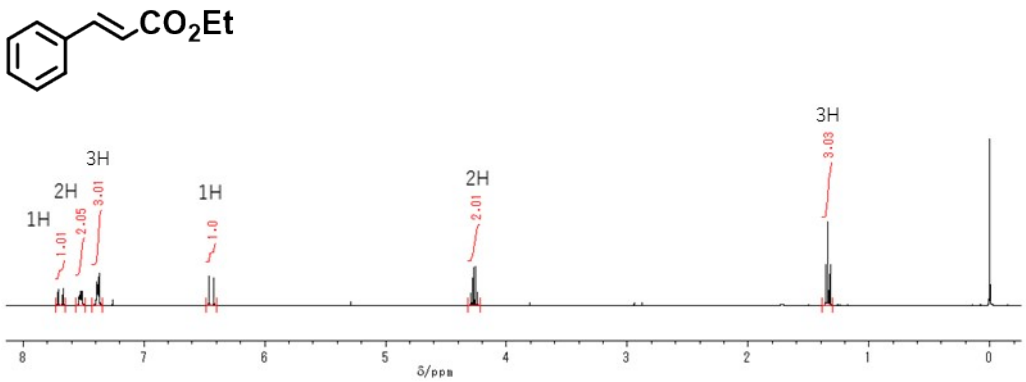


Figure S11. ^{1}H-NMR spectrum (400 MHz) of **8** in $CDCl_3$.

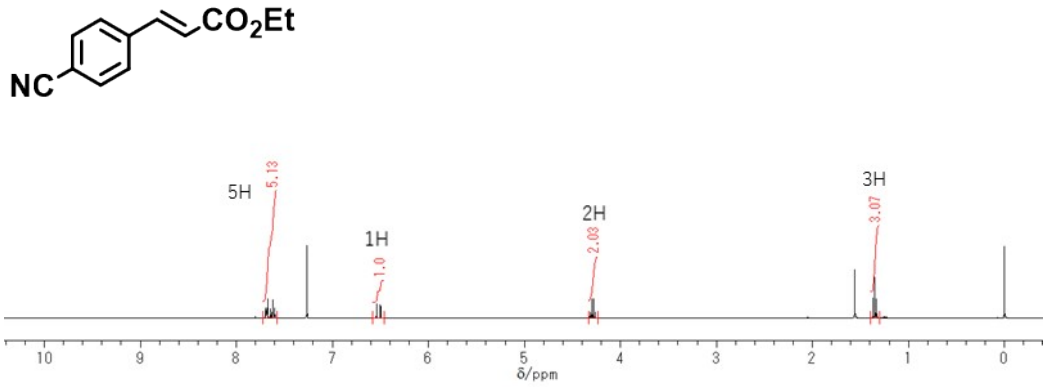


Figure S12. ^{1}H-NMR spectrum (400 MHz) of **9** in $CDCl_3$.

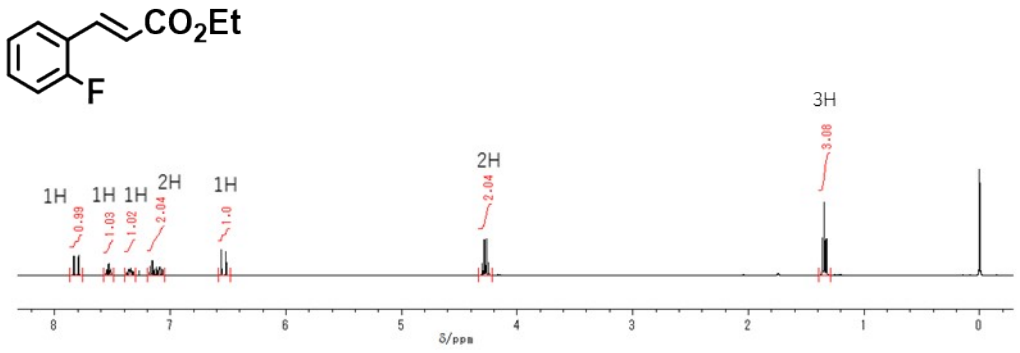


Figure S13. ^{1}H-NMR spectrum (400 MHz) of **10** in $CDCl_3$.

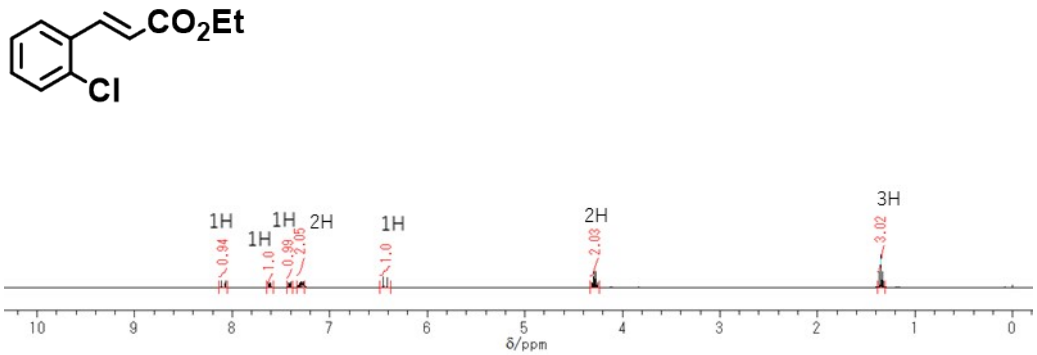


Figure S14. ^{1}H-NMR spectrum (400 MHz) of **11** in $CDCl_3$.

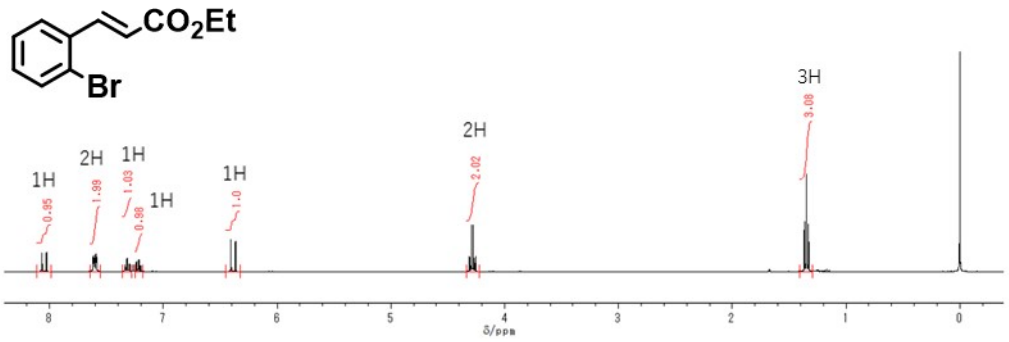


Figure S15. ^{1}H-NMR spectrum (400 MHz) of **12** in $CDCl_3$.

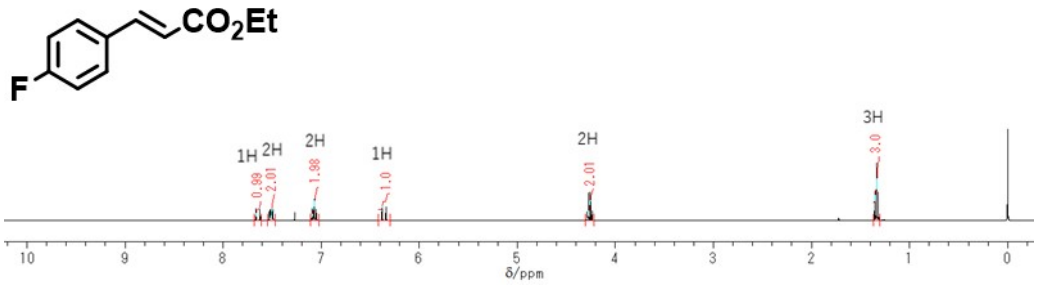


Figure S16. ^{1}H-NMR spectrum (400 MHz) of **13** in $CDCl_3$.

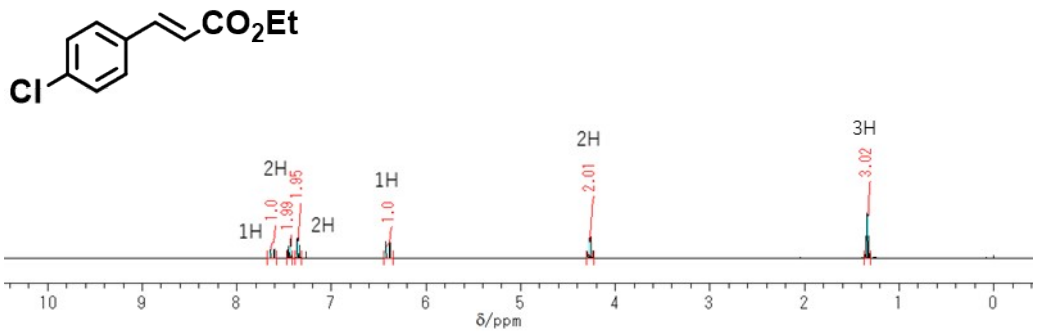


Figure S17. ^{1}H-NMR spectrum (400 MHz) of **14** in $CDCl_3$.

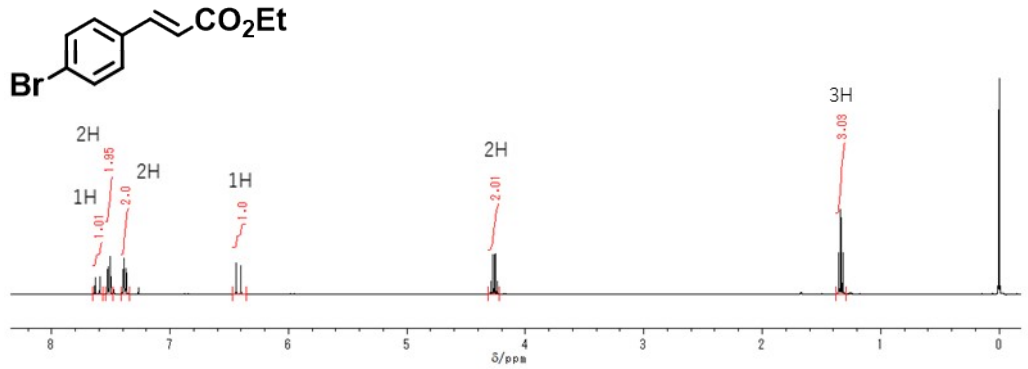


Figure S18. ^{1}H-NMR spectrum (400 MHz) of **15** in $CDCl_3$.

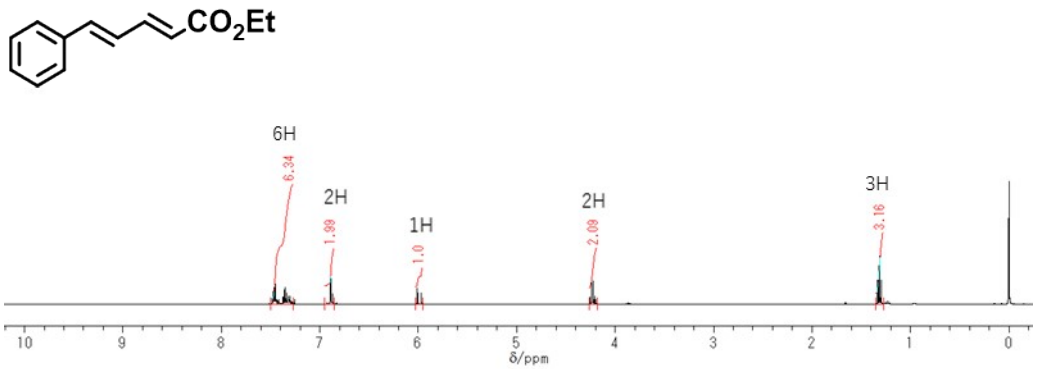


Figure S19. ^{1}H-NMR spectrum (400 MHz) of **16** in $CDCl_3$.

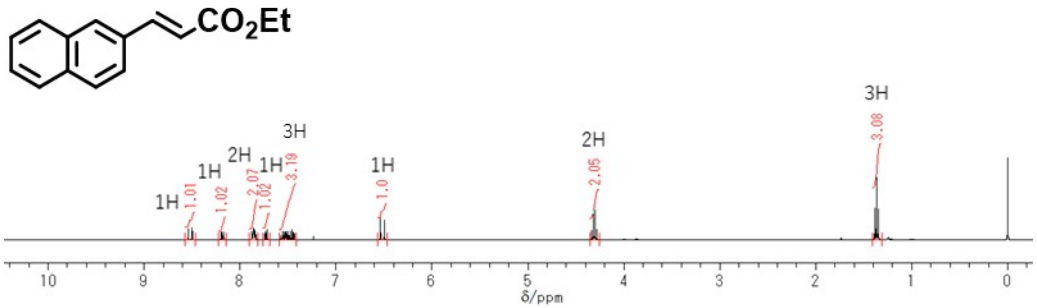


Figure S20. ^{1}H-NMR spectrum (400 MHz) of **17** in $CDCl_3$.

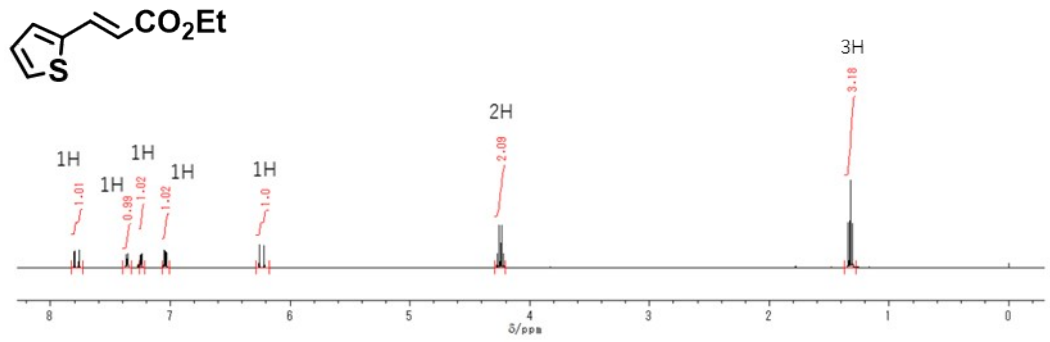


Figure S21. ^{1}H-NMR spectrum (400 MHz) of **18** in $CDCl_3$.

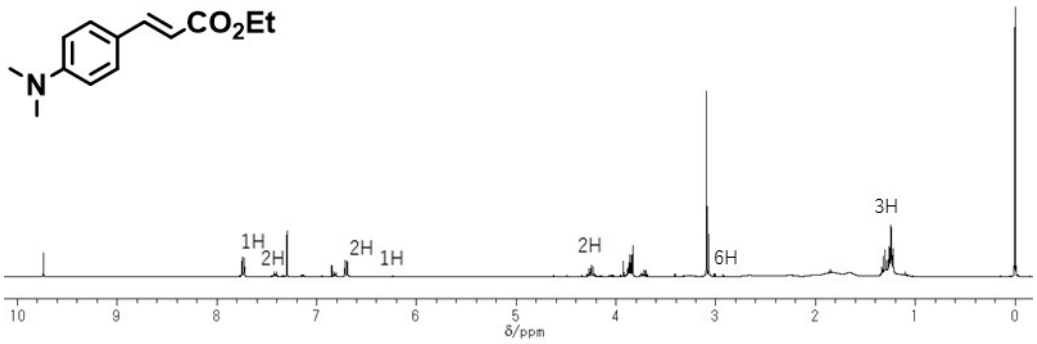


Figure S22. ^{1}H-NMR spectrum (400 MHz) of **19** (crude) in $CDCl_3$.

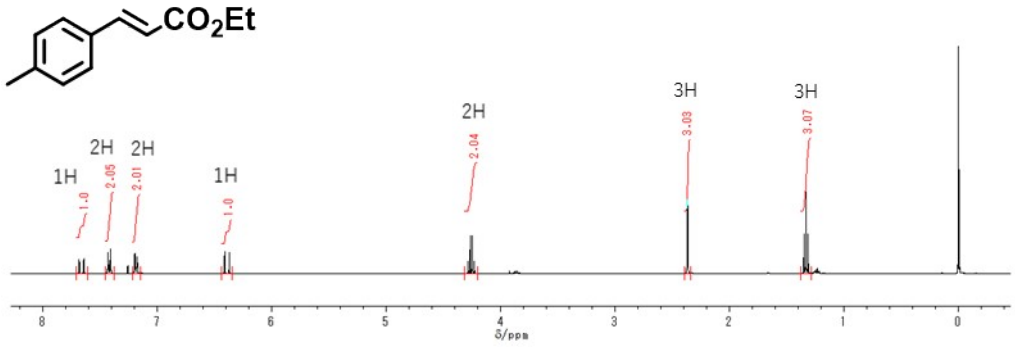


Figure S23. ^{1}H-NMR spectrum (400 MHz) of **20** in $CDCl_3$.

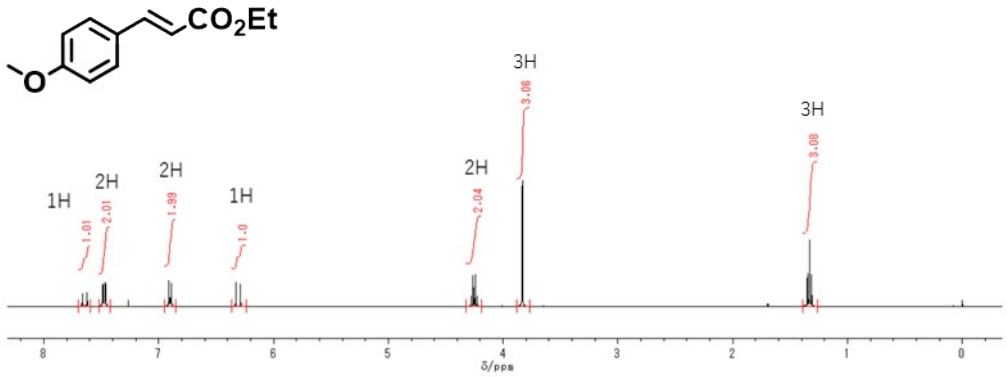


Figure S24. ^{1}H-NMR spectrum (400 MHz) of **21** in $CDCl_3$.

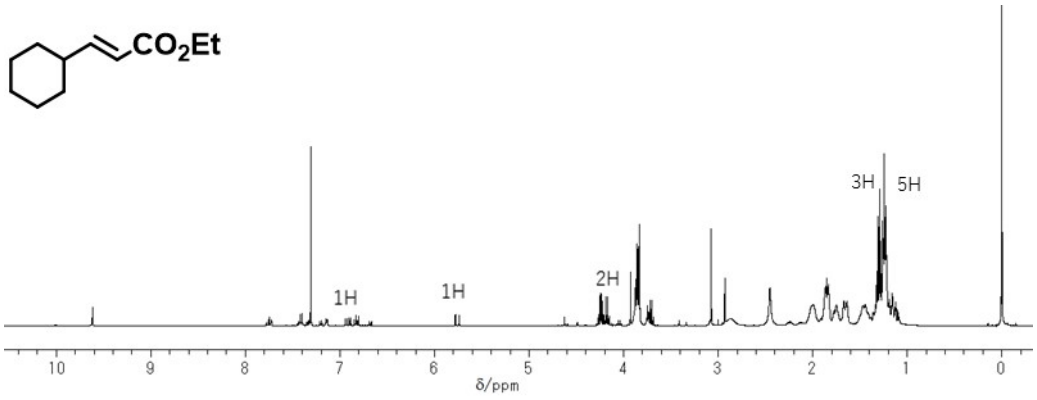


Figure S25. ^{1}H-NMR spectrum (400 MHz) of **22** (crude) in $CDCl_3$.

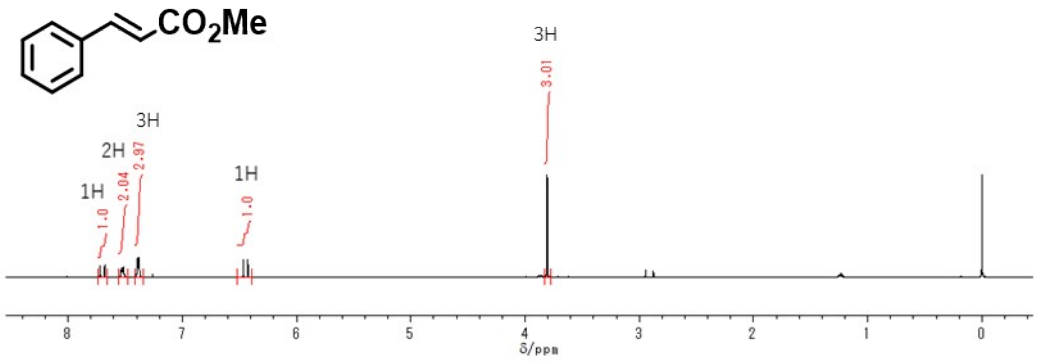


Figure S26. ^{1}H-NMR spectrum (400 MHz) of **23** in $CDCl_3$.

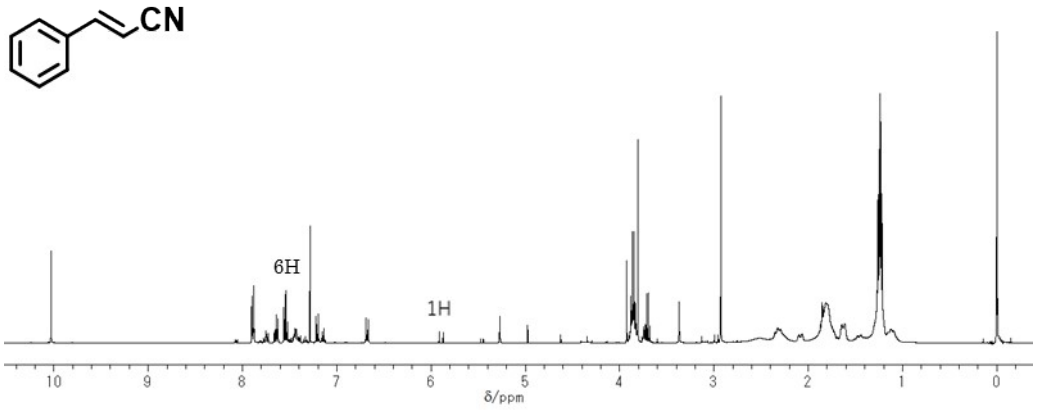


Figure S27. ^{1}H-NMR spectrum (400 MHz) of **25** (crude) in $CDCl_3$.

3. Test of nucleophilicity

The nucleophilicities of **1** and **5** were compared by the reaction with ethyl bromoacetate. A toluene solution (1 mL) of **1** (88.6 mg, 0.43 mmol) or **5** (84.8 mg, 0.42 mmol) and ethyl bromoacetate (84.8 mg, 0.51 mmol for **1**, 85.6 mg, 0.51 mmol for **5**) was stirred at 25 °C for 24 h. The reaction yield was estimated by ^{1}H-NMR spectrum with 1,3,5-trimethoxybenzene as an internal standard.

Arsonium salt of **1**: Yield 43%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.01-7.98 (m, 2H), 7.65-7.60 (m, 3H), 5.01 (s, 2H), 4.16(q, J = 8.0 Hz, 2H), 3.30(m, 2H), 2.77(m, 2H), 2.49(m, 2H), 2.06(m, 2H), 1.23(t, J = 8.0 Hz, 3H) ppm.

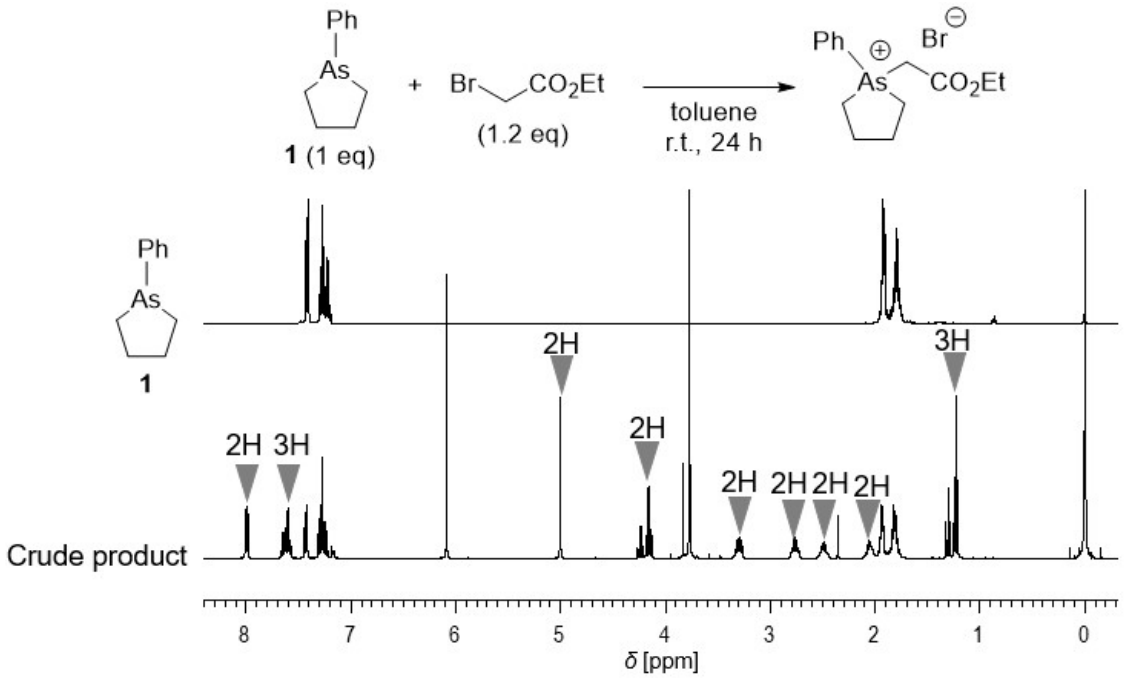


Figure S28. ^{1}H-NMR spectra (400 MHz in $CDCl_3$) of **1** and the crude product. Inverted triangles indicate the product signals.

Arsonium salt of **5**: Yield 72%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.43 (d, J = 8.0Hz, 6H), 6.81 (d, J = 8.0Hz, 6H), 4.33 (s, 2H), 4.03(q, J = 8.0 Hz, 2H), 3.05(s, 18H), 1.09(t, J = 4.0 Hz 3H) ppm.

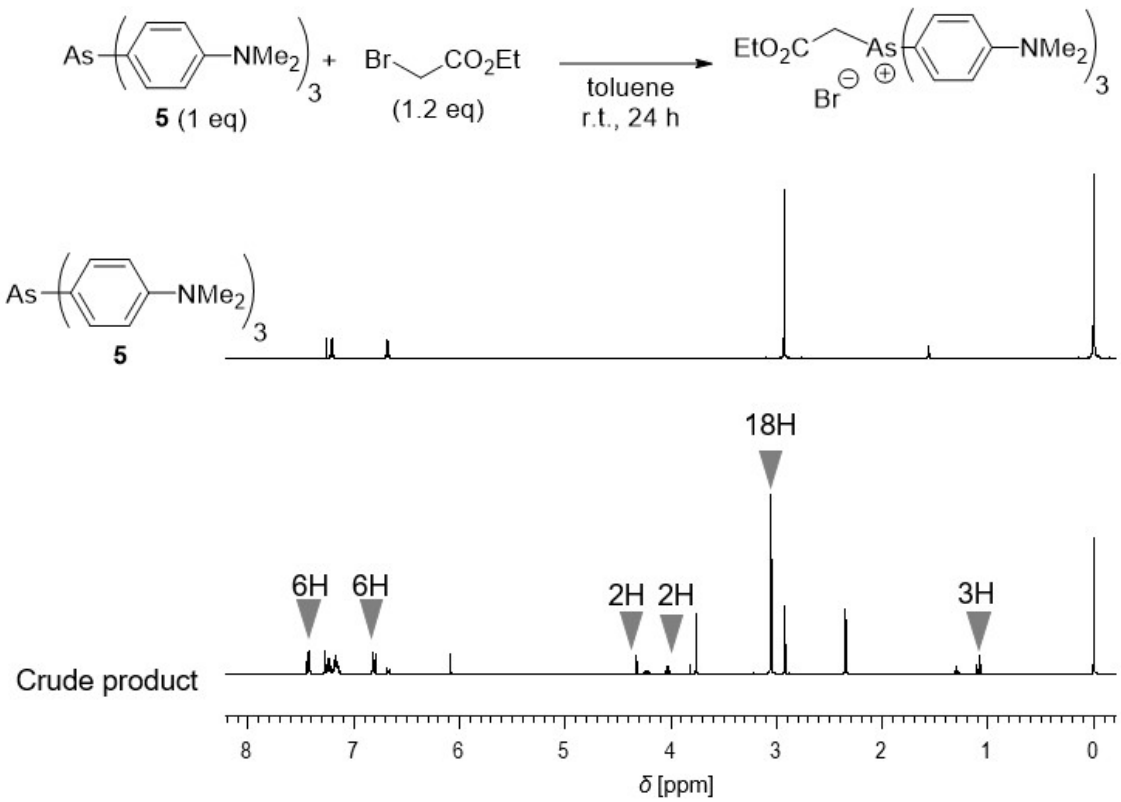
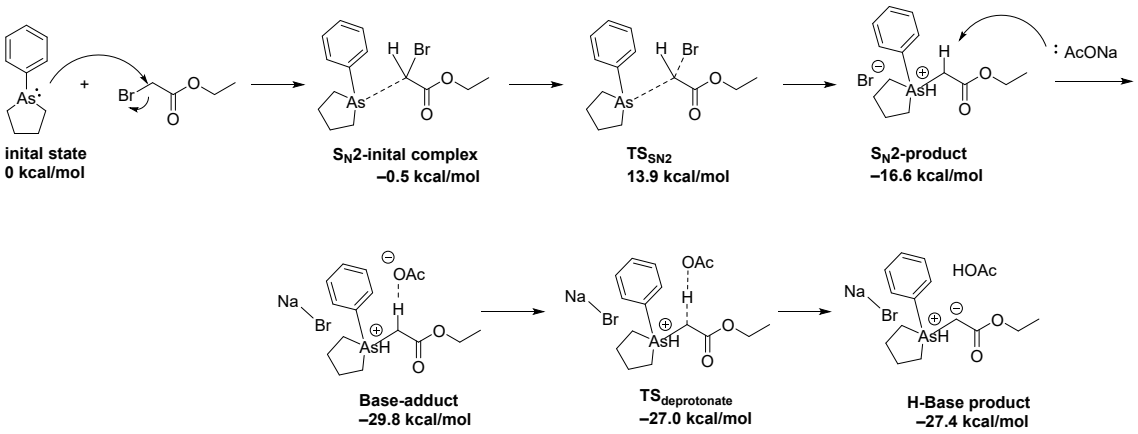


Figure S29. ^{1}H-NMR spectra (400 MHz in $CDCl_3$) of **5** and the crude product. Inverted triangles indicate the product signals.

4. DFT calculations



Scheme S1. Plausible mechanism of generation of arsonium ylide between bromoacetate and **1**.

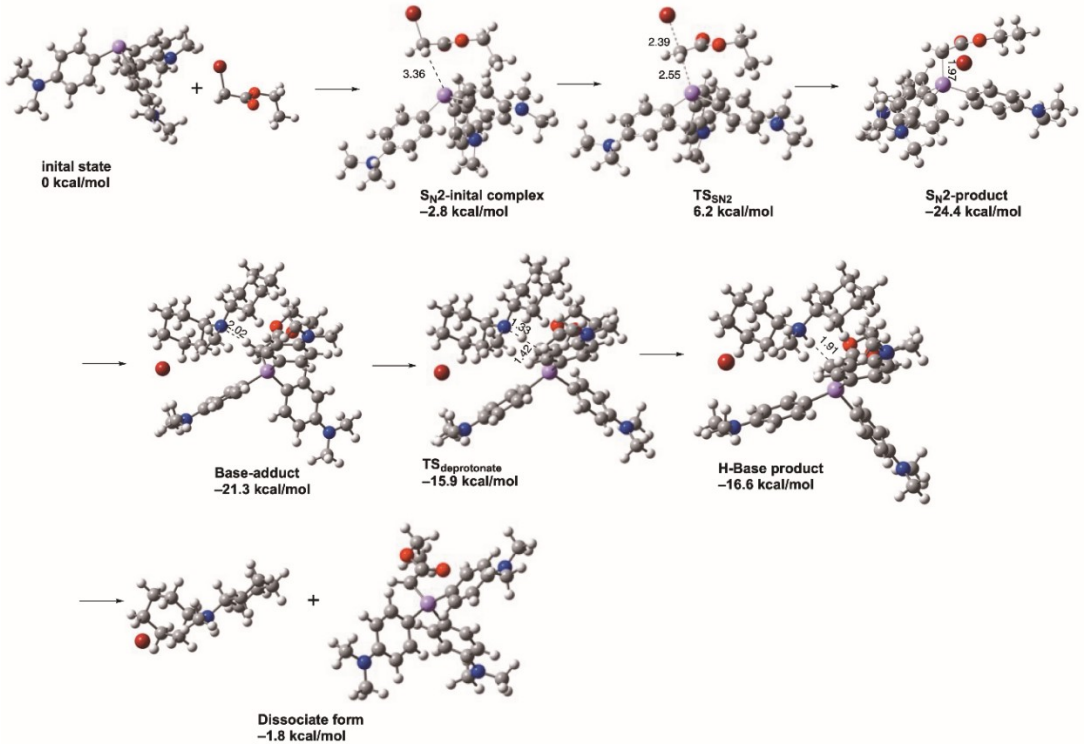


Figure S30. Optimized geometries for local minima and transition state during the S_N2 reaction with ethyl bromoacetate and tris(*p*-(dimethylamino)phenyl)arsine (**5**) to form an arsonium salt, and the deprotationa of the resultant arsonium salt by the Cy_2MeN base to form an arsonium ylide. Their geometries were obtained at the B3LYP-D3 calculations using the polarizable continuum model to include solvent effects of THF. The energy values in kcal/mol are their free energies obtained at 25 ºC.

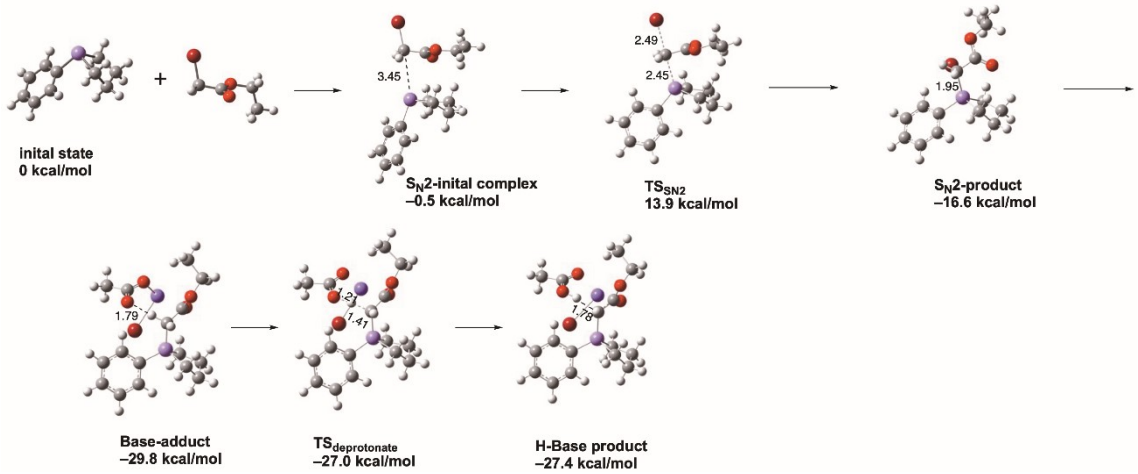


Figure S31. Optimized geometries for local minima and transition state during the S_N2 reaction with ethyl bromoacetate and 1-phenylaroslane (**1**) to form an arsonium salt, and the deprotationa of the resultant arsonium salt by the sodium acetate base to form an arsonium ylide. Their geometries were obtained at the B3LYP-D3 calculations using the polarizable continuum model to include solvent effects of toluene. The energy values in kcal/mol are their free energies obtained at 25 ºC.

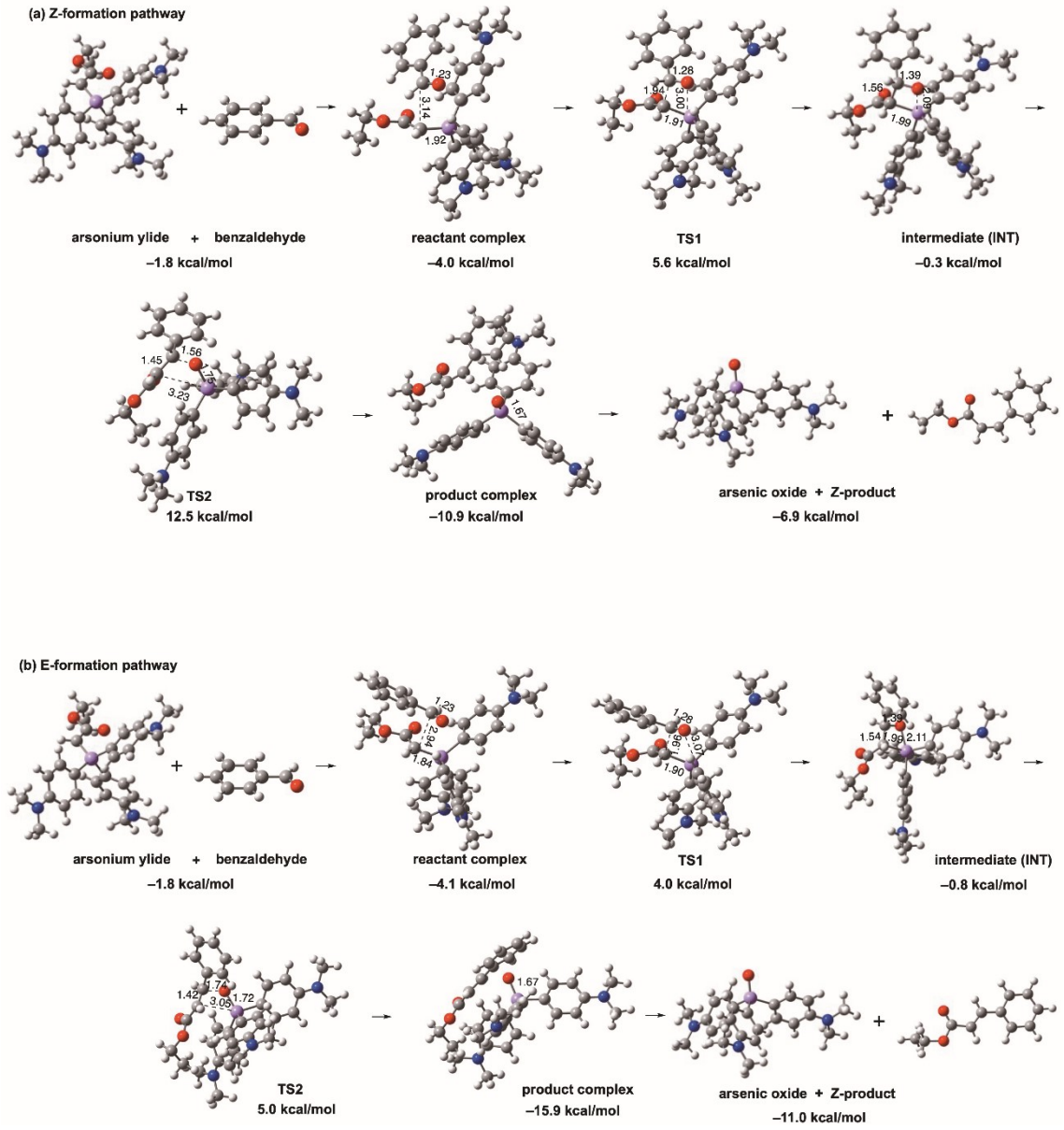


Figure S32. Optimized geometries for local minima and transition state during the reaction between benzaldehyde and the arsonium ylide formed from the first half reactions between ethyl bromoacetate, **5**, and the Cy_2MeN base. Their geometries were obtained at the B3LYP-D3 calculations using the polarizable continuum model to include solvent effects of THF. The energy values in kcal/mol are their free energies obtained at 25 ºC. There are two reaction pathways to from *Z*- and *E*-ethyl cinnamate, given in (a) and (b), respectively.

Cartesian coordinates of optimized geometries formed during the arsa-Wittig reactions discussed in the main text

[A] S_N2 reaction between ethyl bromoacetate and tris(*p*-(dimethylamino)phenyl)arsine (**5**) to form an arsonium salt, and the deprotationa of the resultant arsonium salt by the Cy_2MeN base to form an arsonium ylide. Their total energies were obtained at the B3LYP-D3 calculations using the polarizable continuum model to include solvent effects of THF. Their free energies were also obtained at 25 ºC.
(Scheme 3 & Figure S28)

(1) ethyl bromoacetate
Total energy: -3137.63060367 Hartree
Free energy: = -3137.290010 Hartree

Br	-3.54925700	-1.37689800	-0.09007700
N	0.82534600	-0.34163400	-0.43012400
C	0.14399600	-1.63207900	-0.06018700
H	0.20804700	-1.76671300	1.01756000
H	-0.90730900	-1.59010000	-0.35396500
H	0.64817800	-2.44964500	-0.57071600
H	0.91105100	-0.35135300	-1.45084000
C	2.25930000	-0.19499700	0.11064000
C	3.00809100	-1.53017300	0.20676700
C	3.03328400	0.78949300	-0.77994900
H	2.13559800	0.21837100	1.11658400
C	4.42954600	-1.29931700	0.75205700
H	3.06743500	-1.98888400	-0.78884200
H	2.48461500	-2.22863400	0.86293700
C	4.45259900	1.01991900	-0.23716500
H	3.09690600	0.36543200	-1.79190000
H	2.51119800	1.74649700	-0.86434900
C	5.21817100	-0.30159300	-0.10376100
H	4.94906900	-2.26149000	0.80443200
H	4.35933500	-0.92235900	1.78127800
H	4.98210700	1.71195300	-0.89984700
H	4.38670700	1.50840400	0.74404000
H	6.20697500	-0.12574700	0.33333400

H	5.38208100	-0.72858000	-1.10244900
C	-0.03382000	0.90110800	-0.10340600
C	-1.03487400	1.15686300	-1.23351500
C	-0.70951200	0.80022600	1.26643300
H	0.67978000	1.72813900	-0.08007100
C	-1.82485200	2.44522000	-0.94111300
H	-1.73850000	0.32042000	-1.30317400
H	-0.50122300	1.25002100	-2.18847700
C	-1.47982600	2.10501900	1.54135900
H	-1.42786200	-0.02510800	1.26612400
H	0.03275400	0.62074400	2.05271200
C	-2.50761500	2.37518500	0.43260300
H	-2.56653000	2.59657300	-1.73255700
H	-1.14469500	3.30819600	-0.97356400
H	-1.97575700	2.02621800	2.51458000
H	-0.77523000	2.94589600	1.61094000
H	-3.04661200	3.30788200	0.63452000
H	-3.23846400	1.55747400	0.42069100

(2) tris(*p*-(dimethylamino)phenyl)arsine (**5**)

Total energy: -3330.73281405 Hartree

Free energy: = -3330.304011 Hartree

As	0.00035500	0.00075100	-1.80285000
C	-0.70566900	-4.21700600	0.39968300
C	-1.33182500	-3.04278700	0.88285200
C	-1.13586900	-1.81430100	0.25840900
C	-0.32960800	-1.68619300	-0.87852100
C	0.27670900	-2.85082500	-1.36911100
C	0.10111200	-4.08731000	-0.75714400
H	-1.97434100	-3.08253000	1.75376600
H	-1.62810300	-0.93869700	0.67080400
H	0.90554100	-2.79689800	-2.25561500
H	0.59119400	-4.95238800	-1.18603800
C	1.62583900	0.55836700	-0.87794500
C	2.13955800	-0.07577400	0.25913600

C	2.33155000	1.66561800	-1.36843500
C	3.30162100	0.36831500	0.88351100
H	1.62696600	-0.93948300	0.67179200
C	3.49033400	2.13142700	-0.75650500
H	1.97070200	2.18323600	-2.25504300
C	4.00594100	1.49730300	0.40020300
H	3.65699400	-0.16833700	1.75450600
H	3.99475000	2.98811900	-1.18561300
C	-1.29585000	1.12922700	-0.87815200
C	-2.60845100	1.18311000	-1.36688200
C	-1.00321000	1.89449000	0.25663000
C	-3.59197900	1.95272200	-0.75488600
H	-2.87645300	0.60921800	-2.25178500
C	-1.96967100	2.67783300	0.88105000
H	0.00182300	1.88560100	0.66759000
C	-3.30046400	2.71922900	0.39988700
H	-4.58691000	1.95799800	-1.18214700
H	-1.68252800	3.25656700	1.75025600
N	5.14512300	1.96696900	1.03564500
N	-4.27743700	3.47017300	1.03528000
N	-0.86781300	-5.43839800	1.03530100
C	5.76750600	1.15282600	2.06970700
H	6.64494300	1.67254500	2.45547300
H	5.08325700	0.99389700	2.91027600
H	6.08512100	0.16630000	1.69933400
C	5.96135000	2.97641100	0.37666500
H	6.35306400	2.63821900	-0.59469300
H	5.39010400	3.89596200	0.20916200
H	6.80648300	3.22842600	1.01780100
C	-1.88357500	-5.57060800	2.06981000
H	-1.87130000	-6.59015500	2.45602600
H	-1.67924200	-4.89800600	2.90996700
H	-2.89704500	-5.35333800	1.69972800
C	-0.40129300	-6.64984800	0.37637200
H	-0.88974700	-6.82002700	-0.59511200
H	0.68072300	-6.61462800	0.20913000

H	-0.60559800	-7.50785700	1.01739100
C	-3.88417100	4.41821900	2.06773500
H	-4.77358000	4.91649900	2.45433600
H	-3.40199900	3.90705100	2.90809600
H	-3.19092900	5.18776100	1.69554800
C	-5.56096800	3.66878700	0.37755100
H	-5.46585100	4.17417500	-0.59551700
H	-6.07093800	2.71321400	0.21371400
H	-6.20143500	4.27617600	1.01763300

(3) S_N2-intial complex

Total energy: -6209.58803732 Hartree

Free energy: = -6209.063773 Hartree

C	2.24946700	1.61644300	-2.33991600
As	0.03101400	0.17091900	-0.27341300
H	1.34164400	1.91249300	-2.85672500
C	-3.28137200	3.46190800	0.89935100
C	-3.07096700	3.03262500	-0.43430000
C	-2.11008900	2.07343400	-0.73206800
C	-1.30619700	1.49282000	0.25938700
C	-1.50604400	1.92318400	1.57444600
C	-2.45871800	2.88751000	1.89607000
H	-3.65746300	3.44711400	-1.24475700
H	-1.98689700	1.77243400	-1.77081500
H	-0.90492600	1.50554600	2.37691500
H	-2.56117700	3.18616500	2.93200000
C	2.41568300	0.11251400	-2.38022700
O	3.27205900	-0.29508400	-1.43326200
O	1.87348400	-0.60240300	-3.20049700
C	3.55981600	-1.72036600	-1.35889800
H	3.39066800	-2.16320800	-2.34204800
H	4.62358500	-1.77434800	-1.11744600
C	2.70908400	-2.37883300	-0.28744700
H	2.92566900	-3.45131300	-0.26101300
H	2.92036700	-1.95222400	0.69484600

H	1.64605800	-2.24304900	-0.49133200
H	2.29258700	2.01300500	-1.32992800
Br	3.76749900	2.44307600	-3.33415100
C	-1.16735700	-1.30200000	-0.70140200
C	-2.37011600	-1.53126200	-0.01829900
C	-0.86522900	-2.14539700	-1.77944400
C	-3.21489400	-2.58101700	-0.35741100
H	-2.66128000	-0.87104500	0.79403500
C	-1.69805200	-3.20263600	-2.13502000
H	0.03831900	-1.97641400	-2.35932800
C	-2.89233300	-3.46252900	-1.42027400
H	-4.13283800	-2.70934100	0.20259200
H	-1.41824600	-3.81946500	-2.97981300
C	0.74247500	-0.33261400	1.46373600
C	0.29361500	-1.41049500	2.23351800
C	1.85340800	0.37886900	1.93653400
C	0.91549400	-1.76447200	3.42696300
H	-0.55012500	-2.00382300	1.89471100
C	2.48436000	0.04932500	3.13098100
H	2.25356000	1.20319300	1.35059800
C	2.02502600	-1.03471100	3.91898400
H	0.53324200	-2.61655100	3.97511600
H	3.34247600	0.63171100	3.44201900
N	-3.71106900	-4.53031100	-1.74410500
N	-4.25831700	4.39648100	1.21288100
N	2.63234900	-1.36308800	5.12028500
C	-4.89883700	5.13953500	0.13696100
H	-5.43353200	4.46620700	-0.54159700
H	-5.63250600	5.82500100	0.56225300
H	-4.18349700	5.72564000	-0.46004000
C	-4.27388000	4.98147300	2.54585400
H	-4.43176500	4.21279900	3.31004800
H	-3.34133600	5.51407800	2.78770900
H	-5.10090500	5.68849300	2.61747900
C	-5.02747500	-4.63406900	-1.13096900
H	-5.52076100	-5.53675000	-1.49205600

H	-4.94901900	-4.71478700	-0.04127800
H	-5.67166100	-3.77265700	-1.36261200
C	-3.46137200	-5.27526300	-2.96977900
H	-3.53417600	-4.64616800	-3.86951800
H	-2.46592200	-5.73253400	-2.95627300
H	-4.19150500	-6.08034900	-3.05511600
C	3.90532800	-0.74542000	5.46435800
H	3.80610700	0.34265200	5.54135800
H	4.23090500	-1.11416800	6.43735600
H	4.69501000	-0.96385800	4.72957400
C	2.28566900	-2.61885200	5.77084600
H	1.22256100	-2.64516700	6.03314800
H	2.50285600	-3.49593700	5.14259000
H	2.85396600	-2.71127100	6.69669500

(4) T_{SN2}

Total energy: -6209.57459652 Hartree

Free energy: = -6209.049413 Hartree

Imaginary frequency: 394.2 *i*cm^{-1}

C	0.03266200	-1.54446400	2.31405900
As	-0.10954400	-0.06061500	0.24694600
H	-0.93754400	-1.17506900	2.60156900
C	-4.03078400	-1.84643300	-1.82054100
C	-4.08352500	-1.12548600	-0.59975300
C	-2.93074000	-0.60274800	-0.03063700
C	-1.67388900	-0.76376500	-0.63286100
C	-1.61487900	-1.47797100	-1.83443100
C	-2.75707200	-2.01439500	-2.41802000
H	-5.02703100	-0.97156400	-0.09191500
H	-3.01994400	-0.04933100	0.90138900
H	-0.66104000	-1.62715500	-2.33143400
H	-2.65397000	-2.56126000	-3.34666000
C	1.22062800	-0.75320100	2.72123900
O	2.33911600	-1.23247500	2.14653400
O	1.17263100	0.22051400	3.45262700

C	3.53426000	-0.42089200	2.30412500
H	3.53971300	0.00420500	3.30971600
H	4.36100600	-1.12682500	2.20733000
C	3.58704100	0.65996500	1.23454600
H	4.42494800	1.33466300	1.43494700
H	3.71543000	0.22332200	0.24283200
H	2.66462600	1.24544500	1.23055700
H	0.11142800	-2.33737700	1.58939900
Br	0.10784300	-3.10040000	4.12905400
C	-0.46763900	1.82821700	0.31135800
C	-1.22069500	2.45947000	-0.68979000
C	-0.00321600	2.61032600	1.37825800
C	-1.47596800	3.82296800	-0.65137600
H	-1.62350400	1.87748800	-1.51339600
C	-0.24975200	3.97663600	1.43205100
H	0.55941200	2.15107100	2.18540200
C	-0.98557600	4.62799100	0.40978600
H	-2.06307200	4.26201100	-1.44800000
H	0.12661600	4.53556700	2.27921600
C	1.29539100	-0.28726100	-1.04395600
C	1.75479700	0.76321300	-1.84682300
C	1.96129100	-1.51840900	-1.12644900
C	2.82956600	0.59600700	-2.71049000
H	1.27754900	1.73682100	-1.79334500
C	3.03181600	-1.70694800	-1.99006200
H	1.66020900	-2.34711300	-0.49243500
C	3.49660800	-0.65125400	-2.81601500
H	3.15104800	1.44214800	-3.30421900
H	3.51410900	-2.67566100	-2.01171400
N	-1.21754800	5.98445600	0.44502600
N	-5.17248900	-2.35501400	-2.40319000
N	4.55114600	-0.83125000	-3.68467300
C	-6.43830400	-2.29596500	-1.68629900
H	-6.72876900	-1.25966600	-1.47816100
H	-7.22002300	-2.74058200	-2.30187200
H	-6.40335900	-2.83824000	-0.73056000

C	-5.06364500	-3.21595300	-3.57195400
H	-4.59257400	-2.68959700	-4.41028100
H	-4.47843800	-4.12434000	-3.36886500
H	-6.06153400	-3.51735100	-3.88984200
C	-2.08516200	6.59901600	-0.54970000
H	-2.14054000	7.67135400	-0.36414800
H	-1.69262200	6.45597700	-1.56332700
H	-3.10595800	6.19277100	-0.51926300
C	-0.81097900	6.76022900	1.60818300
H	-1.31179000	6.42554700	2.52749700
H	0.27160200	6.69735000	1.76898600
H	-1.06161100	7.80823300	1.44606400
C	5.31988500	-2.06756100	-3.64002200
H	4.68765700	-2.93492800	-3.86099200
H	6.10403400	-2.02950400	-4.39583500
H	5.79278100	-2.23038500	-2.66094900
C	5.10592300	0.31394300	-4.39296800
H	4.35103500	0.78821000	-5.03013200
H	5.50293400	1.07714700	-3.70827700
H	5.91766800	-0.02235400	-5.03761400

(5) S_N2-product

Total energy: -6209.62463353 Hartree

Free energy: = -6209.098256 Hartree

C	0.24999400	0.01168500	-2.40153600
As	-0.25396700	-0.14729000	-0.50804100
H	-0.45068200	-0.61322200	-2.95412700
C	-3.51177700	2.95047100	0.92403700
C	-3.68728800	2.18427800	-0.25902700
C	-2.72178200	1.28002000	-0.67126200
C	-1.54622600	1.09997500	0.06721600
C	-1.35559000	1.84856700	1.23221200
C	-2.31524000	2.75152200	1.66112300
H	-4.57863300	2.29846700	-0.86170100
H	-2.89675600	0.71312700	-1.58152200

H	-0.44290400	1.73828100	1.80870900
H	-2.12737800	3.31248400	2.56709200
C	1.65333400	-0.53137100	-2.49830000
O	2.55415900	0.44687500	-2.40190400
O	1.93182700	-1.71646000	-2.57211400
C	3.93972900	0.04291400	-2.23152700
H	3.99970700	-0.58560000	-1.33769600
H	4.24409400	-0.55376200	-3.09609200
C	4.74969600	1.31408700	-2.08714100
H	5.80384700	1.06430100	-1.93500800
H	4.66423700	1.93476500	-2.98324700
H	4.39912700	1.89049200	-1.22762300
H	0.19222800	1.07421800	-2.64508800
Br	0.55258900	3.35670900	-1.46798800
C	-1.09013000	-1.85154400	-0.34223000
C	-2.06859700	-2.03969700	0.64525700
C	-0.74337400	-2.94363500	-1.15115500
C	-2.69191700	-3.26554300	0.81794900
H	-2.36148100	-1.21344900	1.28579700
C	-1.35919000	-4.17596200	-0.99124000
H	0.02519900	-2.84290200	-1.91061600
C	-2.35709800	-4.37586000	-0.00125200
H	-3.44479200	-3.35804100	1.58982900
H	-1.06112600	-4.98815200	-1.64149400
C	1.31898600	-0.16982400	0.55903000
C	1.70596100	-1.37338100	1.16619100
C	2.16305300	0.94642000	0.67094500
C	2.89432200	-1.46633600	1.87463700
H	1.08162300	-2.25665900	1.08158200
C	3.34807500	0.86497400	1.38424600
H	1.89431900	1.87984100	0.18271300
C	3.75532200	-0.34526000	2.00660600
H	3.15584200	-2.41715100	2.32019300
H	3.96899600	1.74931900	1.44543800
N	-2.97227500	-5.59126900	0.15781000
N	-4.46648700	3.84485400	1.34122800

N	4.93352200	-0.42641900	2.70467400
C	5.85336900	0.70408700	2.71326100
H	5.39159500	1.59081300	3.16261800
H	6.73029800	0.44805400	3.30673200
H	6.18844000	0.96856400	1.70114100
C	5.37207600	-1.70489500	3.24861300
H	4.64287100	-2.10387800	3.96315800
H	5.52767400	-2.45636700	2.46252000
H	6.31416600	-1.56537000	3.77765000
C	-3.99148200	-5.76747800	1.18332700
H	-4.35734400	-6.79307800	1.15327500
H	-3.59246100	-5.57945700	2.18823400
H	-4.84644000	-5.09786400	1.02472200
C	-2.61122100	-6.71253400	-0.69905900
H	-2.80163400	-6.49177200	-1.75702800
H	-1.55254700	-6.98100000	-0.59154600
H	-3.20822100	-7.58116500	-0.42395200
C	-4.21885500	4.68393900	2.50591500
H	-5.08388100	5.32357400	2.67772400
H	-4.06407400	4.07975600	3.40788300
H	-3.33892500	5.32699300	2.37003800
C	-5.64136500	4.09534300	0.51745500
H	-5.37410300	4.48863800	-0.47263000
H	-6.23108300	3.18198100	0.37434900
H	-6.27744200	4.82769300	1.01333900

(6) Cy_2MeN

Total energy: -565.274314871 Hartree

Free energy: = -564.946655 Hartree

N	-0.02487800	0.74149200	-0.57219800
C	0.13560200	2.19226700	-0.48768100
H	0.13095800	2.59857600	0.53855900
H	1.08598900	2.47543300	-0.94642800
H	-0.65167500	2.69813700	-1.05114400
C	-1.24271700	0.19439500	0.07160600

C	-2.44113400	1.16090400	0.04336200
C	-1.65454200	-1.12214000	-0.62200900
H	-1.04471500	-0.02752800	1.13918900
C	-3.68597100	0.53523000	0.69369000
H	-2.66594800	1.42141100	-1.00044100
H	-2.20054500	2.09297700	0.56288200
C	-2.89035800	-1.76181700	0.02588900
H	-1.86250900	-0.89023800	-1.67525200
H	-0.82603500	-1.83775300	-0.61871000
C	-4.07726100	-0.79054500	0.02974800
H	-4.51872500	1.24705400	0.65065700
H	-3.48107600	0.35743300	1.75893500
H	-3.15157200	-2.68784600	-0.49975700
H	-2.65135500	-2.04550300	1.06076900
H	-4.93950300	-1.23502800	0.54106000
H	-4.38793300	-0.59735900	-1.00680800
C	1.19733100	0.00531800	-0.17702100
C	2.25406100	0.01608800	-1.29546400
C	1.82900900	0.44089300	1.16392800
H	0.89771500	-1.04153800	-0.05260700
C	3.45968400	-0.86639700	-0.93374300
H	2.60433000	1.04261000	-1.46847000
H	1.78829100	-0.32218400	-2.22775000
C	3.02334000	-0.45520200	1.52794600
H	2.17723300	1.47892700	1.08718400
H	1.07545000	0.41739900	1.96021300
C	4.07709900	-0.45358300	0.41060000
H	4.21207100	-0.82161100	-1.73008900
H	3.13202700	-1.91400100	-0.87072500
H	3.46918400	-0.12627100	2.47431500
H	2.66959400	-1.48374100	1.68842700
H	4.90910300	-1.11968600	0.66868400
H	4.49894100	0.55741100	0.31758900

(7) Base-adduct

Total energy: -6774.92341087 Hartree

Free energy: = -6774.039873 Hartree

C	0.55505600	0.28771500	-1.48669100
As	1.20875200	-0.54203400	0.14560900
C	-2.42350300	-3.19760500	1.62373800
C	-1.65023700	-2.44454300	2.54824100
C	-0.56714500	-1.68687700	2.13320600
C	-0.20860800	-1.61482300	0.77974100
C	-0.96495800	-2.35617400	-0.14449300
C	-2.03506200	-3.13217100	0.25839100
H	-1.90027500	-2.44714500	3.60056600
H	-0.00220900	-1.14133000	2.88160900
H	-0.73097900	-2.32891700	-1.20410000
H	-2.59830700	-3.66104200	-0.49774500
C	1.53174200	1.28266400	-2.04645300
O	1.30493300	1.48809500	-3.35001000
O	2.40065100	1.84393800	-1.39888400
C	2.16991800	2.44516400	-4.03241500
H	1.59625900	2.73201400	-4.91457600
H	2.30420200	3.31791000	-3.38993200
C	3.49828700	1.80695700	-4.40030600
H	4.09170400	2.51104500	-4.99141600
H	4.06418000	1.54945700	-3.50189600
H	3.34034000	0.90259900	-4.99430000
Br	-5.42387800	-1.10833900	1.09165000
N	-2.14255000	1.72211400	-0.77933800
C	-2.40812700	1.19918400	0.56998000
H	-2.88614400	1.93775800	1.23148800
H	-3.06743300	0.33294700	0.54036800
H	-1.47373900	0.87368900	1.03073300
H	0.38638000	-0.52495600	-2.19511900
C	-1.70683100	3.14355500	-0.75176500
C	-0.54214700	3.30800500	0.24850600
C	-1.29422100	3.63618600	-2.15427100
H	-2.53087700	3.79157900	-0.39487900
C	0.09572800	4.70158500	0.22912400

H	0.22737200	2.55765600	0.04081700
H	-0.89652300	3.10719300	1.26160000
C	-0.63639400	5.02460400	-2.14246200
H	-0.60351100	2.90708200	-2.59274500
H	-2.16553100	3.67352300	-2.81431500
C	0.55287900	5.08892500	-1.17905500
H	0.93492900	4.71897900	0.93475100
H	-0.63378300	5.44162200	0.58764100
H	-0.32669800	5.28453100	-3.16165800
H	-1.37955800	5.77611500	-1.84056200
H	0.99736800	6.09123300	-1.18222400
H	1.33447800	4.38907700	-1.50466300
C	-3.23002000	1.40581600	-1.73961500
C	-3.27196500	-0.10161200	-2.05144500
C	-4.62378200	1.91737100	-1.32061400
H	-2.96465900	1.89730300	-2.68072900
C	-4.32772800	-0.41367600	-3.12375800
H	-3.52466400	-0.66815600	-1.15013000
H	-2.27838800	-0.42694300	-2.38232600
C	-5.67864000	1.59204300	-2.39071600
H	-4.91594700	1.43124100	-0.38264200
H	-4.58690500	2.99928600	-1.14129200
C	-5.71369900	0.08591800	-2.68986100
H	-4.35327800	-1.49387800	-3.31403700
H	-4.04587900	0.06619200	-4.07317900
H	-6.66556600	1.93887300	-2.06028700
H	-5.44637600	2.14222400	-3.31519900
H	-6.45996600	-0.13330400	-3.46401600
H	-6.00913300	-0.44858600	-1.77795500
C	1.88312400	0.63187100	1.47761200
C	1.05859500	1.33186000	2.36898300
C	3.26876000	0.83889300	1.55392100
C	1.58687000	2.21349000	3.29826300
H	-0.01530300	1.19504100	2.34917600
C	3.81261800	1.71845400	2.47440500
H	3.93889600	0.31261700	0.88294200

C	2.98592500	2.44276600	3.37495300
H	0.90505500	2.72690200	3.96295700
H	4.88704500	1.84545800	2.49224700
C	2.60793200	-1.71881700	-0.39203200
C	3.57271000	-1.36357000	-1.34658200
C	2.68588700	-2.99767100	0.17797300
C	4.57553200	-2.24454000	-1.72119900
H	3.56511000	-0.38034400	-1.80292600
C	3.68026700	-3.89214100	-0.18573800
H	1.95206600	-3.31047100	0.91460900
C	4.65949300	-3.54287000	-1.15255100
H	5.29458400	-1.92063200	-2.46215200
H	3.69160700	-4.86828400	0.28117600
N	-3.47341600	-3.97696100	2.03191900
N	3.51586600	3.32019600	4.28272900
N	5.64465800	-4.42152300	-1.52108800
C	4.95215600	3.56523900	4.31261100
H	5.17620000	4.28728800	5.09671800
H	5.51164900	2.64718900	4.52945300
H	5.31605400	3.97194300	3.36020500
C	2.63742100	4.08704200	5.15711200
H	1.94979800	4.72356200	4.58526900
H	2.04067700	3.43132300	5.80265900
H	3.24054700	4.72923200	5.79753500
C	-4.05913300	-3.73724900	3.34899900
H	-4.46598800	-2.72017200	3.41225800
H	-4.86986200	-4.44866700	3.50807300
H	-3.32345700	-3.89700300	4.14290900
C	-4.34656100	-4.57795300	1.02532700
H	-4.87618600	-3.80270600	0.45760000
H	-3.77304100	-5.21791900	0.34799900
H	-5.07890100	-5.20934800	1.52976300
C	5.70495500	-5.74764800	-0.92067100
H	6.54997600	-6.29287100	-1.33912000
H	5.84114300	-5.69395100	0.16685100
H	4.79455700	-6.32589700	-1.12326300

C	6.63381500	-4.03641700	-2.51887400
H	6.16588900	-3.79809300	-3.48248400
H	7.21620100	-3.16402000	-2.19633900
H	7.32557600	-4.86297900	-2.67610900
H	-0.42588800	0.76816800	-1.26404100

(8) $TS_{deprotonate}$

Total energy: -6774.91164418 Hartree

Free energy: = -6774.031384 Hartree

Imaginary frequency: 1410.7 $i$cm^{-1}

C	-0.37273400	-0.23658900	-1.44190400
As	-1.04375000	0.58998600	0.14427300
C	2.59233800	3.30666000	1.55352400
C	1.75881100	2.66662000	2.50727300
C	0.66238600	1.91175700	2.11784000
C	0.34598400	1.73480500	0.76412800
C	1.12963800	2.41311100	-0.18312700
C	2.21544600	3.18439900	0.19144200
H	1.97718700	2.74424900	3.56401200
H	0.05836400	1.45164700	2.89187200
H	0.91325200	2.33131900	-1.24296400
H	2.80263900	3.65337500	-0.58588100
C	-1.40555800	-1.03294500	-2.10887100
O	-1.19729100	-1.09682200	-3.45113600
O	-2.32855700	-1.62596200	-1.55488800
C	-2.16358000	-1.85722800	-4.22136800
H	-1.63808400	-2.10452900	-5.14587600
H	-2.40184800	-2.77996200	-3.68681900
C	-3.41209700	-1.03054800	-4.48722800
H	-4.11055600	-1.59640900	-5.11165800
H	-3.90893800	-0.78125400	-3.54657000
H	-3.15583700	-0.10309400	-5.00794200
Br	5.33110800	0.86947100	1.07120500
N	1.87372100	-1.68175000	-0.80537800
C	2.20354400	-1.19336700	0.55911000

H	2.61801600	-1.99110800	1.18050500
H	2.92838900	-0.38231600	0.52943900
H	1.29406800	-0.81349800	1.01752800
H	0.01653600	0.54432200	-2.09408600
C	1.38733700	-3.11521400	-0.77565800
C	0.20570200	-3.22656800	0.21062900
C	1.01227600	-3.60557600	-2.18730800
H	2.20655500	-3.74277700	-0.39731200
C	-0.48331000	-4.59547800	0.17499800
H	-0.53099900	-2.45353800	-0.01133500
H	0.55336400	-3.03604600	1.22800900
C	0.29977600	-4.96716300	-2.17140800
H	0.36783900	-2.86497200	-2.67190200
H	1.91089400	-3.69150900	-2.80475200
C	-0.92017900	-4.96269800	-1.24542400
H	-1.34039500	-4.57311900	0.85784400
H	0.20396600	-5.36546200	0.55340200
H	0.01337400	-5.22882500	-3.19637400
H	1.00340100	-5.74149600	-1.83490700
H	-1.41423900	-5.94117700	-1.25823200
H	-1.64953600	-4.22162100	-1.59848800
C	2.97695000	-1.40715000	-1.79536200
C	3.14671700	0.10110000	-2.04772700
C	4.31105900	-2.05846500	-1.39513000
H	2.64180200	-1.84329700	-2.73964600
C	4.22702000	0.34766600	-3.11389400
H	3.44773400	0.61435600	-1.12984400
H	2.19583500	0.52855000	-2.37756000
C	5.38978400	-1.79267100	-2.45809800
H	4.64586100	-1.63036600	-0.44342900
H	4.18049600	-3.13767700	-1.25498300
C	5.56265300	-0.28732900	-2.70401800
H	4.34512700	1.42727300	-3.26399800
H	3.89956000	-0.07080200	-4.07705200
H	6.33718500	-2.24139200	-2.13742600
H	5.10847800	-2.28888700	-3.39866500

H	6.32278800	-0.11123400	-3.47489600
H	5.90653200	0.18772900	-1.77663900
C	-1.67581000	-0.58930400	1.50425800
C	-0.90492900	-1.05941900	2.57588300
C	-2.98188200	-1.08412900	1.36057900
C	-1.41096200	-1.98531400	3.47595300
H	0.11597500	-0.72579900	2.71525100
C	-3.50096800	-2.00946000	2.25001200
H	-3.59223600	-0.75584300	0.52813200
C	-2.72905900	-2.49300700	3.34013600
H	-0.77138800	-2.31827100	4.28251700
H	-4.51047400	-2.36533700	2.09119300
C	-2.55255500	1.67856400	-0.30210500
C	-2.97141700	1.87204600	-1.62231300
C	-3.24943500	2.34387500	0.71630900
C	-4.05250500	2.68865700	-1.92575200
H	-2.45764100	1.37997400	-2.44213400
C	-4.33184100	3.16243300	0.43546900
H	-2.95329400	2.21580500	1.75408500
C	-4.76867400	3.36008200	-0.90178900
H	-4.33971200	2.80038700	-2.96313900
H	-4.83941300	3.65042800	1.25739400
N	3.69479700	4.03519200	1.93370400
N	-3.23687900	-3.41015200	4.22472500
N	-5.84109900	4.16706700	-1.18974600
C	-4.54712200	-4.00233900	3.98697200
H	-4.77732400	-4.69783900	4.79319800
H	-5.33195000	-3.23754700	3.97071500
H	-4.58461300	-4.55264600	3.03697800
C	-2.37996300	-3.97383700	5.26004500
H	-1.52153900	-4.51263700	4.83620900
H	-1.99818100	-3.19340100	5.92812500
H	-2.95831500	-4.67343600	5.86243600
C	4.27055000	3.78318100	3.25387500
H	4.59228100	2.73740900	3.34481800
H	5.13764400	4.43059700	3.38911800

H	3.55843800	4.02350000	4.04859700
C	4.62861800	4.48328300	0.90150600
H	5.09144000	3.62704100	0.39397100
H	4.12201200	5.12264500	0.17255200
H	5.40927800	5.08245400	1.37226400
C	-6.55677500	4.84450900	-0.11764100
H	-7.36822400	5.43323500	-0.54388900
H	-6.99332000	4.13123200	0.59327700
H	-5.90187600	5.52535800	0.44111500
C	-6.26745100	4.35071300	-2.56981000
H	-5.47425300	4.79623700	-3.18394100
H	-6.56362700	3.40061300	-3.03286200
H	-7.12725200	5.01918700	-2.59423500
H	0.79002300	-0.98705300	-1.13730100

(9) H-Base product

Total energy: -6774.91730832 Hartree

Free energy: = -6774.032388 Hartree

C	0.49032500	0.22840600	-1.52593100
As	1.09849400	-0.63133600	0.02371600
C	-2.47498300	-3.55606000	1.19708300
C	-1.57963900	-3.06914100	2.18377200
C	-0.50413300	-2.25950000	1.84770600
C	-0.27164300	-1.86459800	0.52212900
C	-1.12502600	-2.38505300	-0.46368900
C	-2.18684800	-3.21487800	-0.14760900
H	-1.72908900	-3.31487500	3.22696500
H	0.15150400	-1.92824900	2.64581800
H	-0.98205300	-2.13250400	-1.50782200
H	-2.82777800	-3.55246100	-0.95016600
C	1.43732000	1.11905300	-2.11980100
O	1.15937200	1.35473000	-3.44782800
O	2.37838000	1.68844100	-1.55073800
C	2.09214600	2.19763200	-4.15748100
H	1.53743100	2.54668000	-5.03197200

H	2.35315900	3.05883800	-3.53685200
C	3.33531200	1.41757200	-4.56125100
H	4.00999600	2.05267900	-5.14452100
H	3.86469400	1.07069800	-3.67050500
H	3.06377800	0.54989900	-5.17026200
H	-1.13313200	1.14197700	-1.10666900
Br	-5.21831500	-1.10232000	1.03788100
N	-1.97120500	1.69005600	-0.73398400
C	-2.23961800	1.08736400	0.61390700
H	-2.63844100	1.84333900	1.28864500
H	-2.95427400	0.26921700	0.54382100
H	-1.29847200	0.70190600	0.98760100
H	-0.01370100	-0.44565400	-2.21040000
C	-1.45159400	3.13054900	-0.62760700
C	-0.25474600	3.15442600	0.34075000
C	-1.08422100	3.67076000	-2.02084700
H	-2.27234700	3.72089600	-0.20717100
C	0.45710500	4.51225500	0.36983800
H	0.45934700	2.38470500	0.04431100
H	-0.58148200	2.90633400	1.35234200
C	-0.34035600	5.01480000	-1.94762800
H	-0.45652200	2.93673400	-2.53719300
H	-1.98537700	3.80612600	-2.62498100
C	0.88730400	4.94112700	-1.03482500
H	1.32021400	4.43234600	1.03981400
H	-0.21080000	5.27310500	0.79781300
H	-0.05760300	5.31261800	-2.96333200
H	-1.02405600	5.78857500	-1.57172200
H	1.39810200	5.91036300	-1.00462400
H	1.59900800	4.20347300	-1.42768100
C	-3.13127900	1.48914400	-1.70286300
C	-3.25547300	0.01070600	-2.09853500
C	-4.44479800	2.05186200	-1.14887900
H	-2.85382000	2.04220700	-2.60167300
C	-4.39129300	-0.16332700	-3.12061800
H	-3.48237700	-0.60468600	-1.22304500

H	-2.30749300	-0.33385800	-2.52386900
C	-5.57442900	1.85744700	-2.17550300
H	-4.71389600	1.51479600	-0.23292300
H	-4.33511800	3.11463400	-0.90588300
C	-5.71604300	0.37948200	-2.56691700
H	-4.48544000	-1.22562200	-3.37237800
H	-4.13524200	0.36162900	-4.05219100
H	-6.51226300	2.23536100	-1.75363200
H	-5.36525400	2.45927300	-3.07160000
H	-6.51652300	0.25749200	-3.30611000
H	-5.98740200	-0.19969600	-1.67549900
C	1.56405300	0.49967600	1.49884000
C	0.74737400	0.74205200	2.61054000
C	2.78365300	1.18912300	1.41169100
C	1.11761700	1.64879200	3.59441900
H	-0.20611900	0.23978900	2.72111100
C	3.16688200	2.09739300	2.38496700
H	3.42419900	1.03304500	0.55285700
C	2.34165200	2.35984600	3.51040900
H	0.44581900	1.80297300	4.42848400
H	4.11173000	2.61142200	2.26525700
C	2.72262300	-1.59332000	-0.33111200
C	3.18307700	-1.76683000	-1.63979800
C	3.47286100	-2.15162700	0.71145800
C	4.34853100	-2.47163500	-1.91037300
H	2.62918900	-1.33922000	-2.47055700
C	4.63969200	-2.85991900	0.46423400
H	3.15510000	-2.02247600	1.74267600
C	5.11127100	-3.04654500	-0.86189100
H	4.66725000	-2.56861700	-2.94017000
H	5.18808500	-3.26548600	1.30471400
N	-3.55346300	-4.34612700	1.52724700
N	2.71561400	3.26058000	4.47816500
N	6.26163400	-3.75522600	-1.11857400
C	3.89990600	4.08611600	4.27985900
H	4.03194900	4.73676900	5.14375100

H	4.80157700	3.47059300	4.18539900
H	3.81986900	4.71618600	3.38298700
C	1.78348100	3.60792200	5.54278400
H	0.85861100	4.05667100	5.15407700
H	1.51272700	2.72667200	6.13508400
H	2.25598600	4.32503100	6.21328000
C	-4.08598800	-4.25634800	2.88622400
H	-4.42533500	-3.23517500	3.10543400
H	-4.93422700	-4.93593800	2.97753200
H	-3.34232700	-4.56563000	3.62581500
C	-4.52305500	-4.67682000	0.48412100
H	-5.02602200	-3.77515300	0.11132100
H	-4.03399100	-5.19966100	-0.34318100
H	-5.26890000	-5.35452200	0.90234700
C	7.07036800	-4.25669000	-0.01672400
H	7.92769900	-4.79661000	-0.41755800
H	7.44545300	-3.44630800	0.62351100
H	6.50177900	-4.95176600	0.61273000
C	6.77245200	-3.84520000	-2.47893500
H	6.04994000	-4.33028500	-3.14640300
H	7.01171800	-2.85748400	-2.89654100
H	7.68255200	-4.44423000	-2.48181000

(10) arsonium ylide

Total energy: -3637.23331986 Hartree

Free energy: = -3636.718835 Hartree

C	-0.41873000	-0.25655800	2.51116600
As	0.06756100	-0.05926400	0.75651900
C	4.25051000	-2.20876500	0.07880600
C	3.16684100	-2.40357700	-0.81489000
C	1.94631800	-1.77568100	-0.60408000
C	1.73771600	-0.93591000	0.49603100
C	2.80405200	-0.73602300	1.38439700
C	4.03005400	-1.35658200	1.19246100
H	3.27446900	-3.04889500	-1.67717400

H	1.14161500	-1.95222400	-1.31173100
H	2.67782300	-0.08959500	2.24860000
H	4.81881900	-1.17620400	1.91131400
C	-1.70364500	0.18068100	2.86417900
O	-2.02361700	-0.09576500	4.18433000
O	-2.52488100	0.75318900	2.11614800
C	-3.36133800	0.23277800	4.59141000
H	-3.31442500	0.30671800	5.68213300
H	-3.64353500	1.20782900	4.18314000
C	-4.35645100	-0.83612300	4.15694700
H	-5.35962600	-0.60044500	4.52850400
H	-4.38987300	-0.88681400	3.06597400
H	-4.06455600	-1.81627200	4.54710300
H	0.24454500	-0.75173100	3.20529700
C	0.30515600	1.72975000	0.09396000
C	1.39529500	2.05027800	-0.72340600
C	-0.63566700	2.73141500	0.37540400
C	1.56056900	3.33214800	-1.23478500
H	2.13968600	1.29580700	-0.96032500
C	-0.48218800	4.01631200	-0.12691900
H	-1.49073900	2.49639000	1.00183600
C	0.61929600	4.35449300	-0.95552400
H	2.42529500	3.53479800	-1.85373200
H	-1.22680800	4.76084700	0.12487600
C	-1.20214200	-0.84859700	-0.43353400
C	-1.87738500	-2.01014700	-0.04251500
C	-1.46332000	-0.31712400	-1.69975800
C	-2.79160400	-2.62748500	-0.88353300
H	-1.69755200	-2.41863300	0.94859600
C	-2.37158800	-0.92439200	-2.55831000
H	-0.95996100	0.58914300	-2.02333700
C	-3.05922800	-2.10455700	-2.17608900
H	-3.30184300	-3.51573400	-0.53364300
H	-2.55093900	-0.47321800	-3.52577300
N	5.46693400	-2.81661300	-0.12605600
N	0.76439700	5.62403600	-1.47209400

N	-3.95103600	-2.72147300	-3.02620500
C	-0.14430700	6.68373500	-1.05880700
H	0.12333600	7.60643900	-1.57326100
H	-1.18117400	6.44436800	-1.32241000
H	-0.10314300	6.86988200	0.02378200
C	1.97132000	5.97301000	-2.20692700
H	2.87803800	5.86478400	-1.59475800
H	2.08882300	5.34763700	-3.09986000
H	1.90450400	7.00994000	-2.53543500
C	5.63868200	-3.74661000	-1.23274000
H	5.45893000	-3.25837700	-2.19840800
H	6.66260200	-4.11908100	-1.23345300
H	4.96178700	-4.60856000	-1.15614300
C	6.53425400	-2.66155300	0.85184200
H	6.82017300	-1.60922900	0.97006800
H	6.24915900	-3.04984800	1.83920300
H	7.41336400	-3.20914700	0.51357900
C	-4.30303200	-2.08955400	-4.28946900
H	-5.00847500	-2.72498700	-4.82437500
H	-4.76823400	-1.10373100	-4.14740700
H	-3.42147200	-1.95972100	-4.92817800
C	-4.74439700	-3.84680400	-2.55288800
H	-4.10537900	-4.68303400	-2.24585100
H	-5.38404500	-3.57662700	-1.70079900
H	-5.38504000	-4.19915100	-3.36098600

(11) Br·HNCy$_2$Me

Total energy: -3137.63060367 Hartree

Free energy: = -3137.290010 Hartree

Br	-3.54925700	-1.37689800	-0.09007700
N	0.82534600	-0.34163400	-0.43012400
C	0.14399600	-1.63207900	-0.06018700
H	0.20804700	-1.76671300	1.01756000
H	-0.90730900	-1.59010000	-0.35396500
H	0.64817800	-2.44964500	-0.57071600

H	0.91105100	-0.35135300	-1.45084000
C	2.25930000	-0.19499700	0.11064000
C	3.00809100	-1.53017300	0.20676700
C	3.03328400	0.78949300	-0.77994900
H	2.13559800	0.21837100	1.11658400
C	4.42954600	-1.29931700	0.75205700
H	3.06743500	-1.98888400	-0.78884200
H	2.48461500	-2.22863400	0.86293700
C	4.45259900	1.01991900	-0.23716500
H	3.09690600	0.36543200	-1.79190000
H	2.51119800	1.74649700	-0.86434900
C	5.21817100	-0.30159300	-0.10376100
H	4.94906900	-2.26149000	0.80443200
H	4.35933500	-0.92235900	1.78127800
H	4.98210700	1.71195300	-0.89984700
H	4.38670700	1.50840400	0.74404000
H	6.20697500	-0.12574700	0.33333400
H	5.38208100	-0.72858000	-1.10244900
C	-0.03382000	0.90110800	-0.10340600
C	-1.03487400	1.15686300	-1.23351500
C	-0.70951200	0.80022600	1.26643300
H	0.67978000	1.72813900	-0.08007100
C	-1.82485200	2.44522000	-0.94111300
H	-1.73850000	0.32042000	-1.30317400
H	-0.50122300	1.25002100	-2.18847700
C	-1.47982600	2.10501900	1.54135900
H	-1.42786200	-0.02510800	1.26612400
H	0.03275400	0.62074400	2.05271200
C	-2.50761500	2.37518500	0.43260300
H	-2.56653000	2.59657300	-1.73255700
H	-1.14469500	3.30819600	-0.97356400
H	-1.97575700	2.02621800	2.51458000
H	-0.77523000	2.94589600	1.61094000
H	-3.04661200	3.30788200	0.63452000
H	-3.23846400	1.55747400	0.42069100

[B] S_N2 reaction between ethyl bromoacetate and 1-phenylaroslane (**1**) to form an arsonium salt, and the deprotationa of the resultant arsonium salt by the sodium acetate base to form an arsonium ylide. Their total energies were obtained at the B3LYP-D3 calculations using the polarizable continuum model to include solvent effects of toluene. Their free energies were also obtained at 25 ºC.
(Scheme S1 & Figure S29)

(1) ethyl bromoacetate
Total energy: -2878.82757761 Hartree
Free energy: = -2878.753224 Hartree

C	-0.63465800	0.86563500	0.72787500
H	-0.56092600	0.56600400	1.77231300
C	0.68352200	0.68099900	0.00501000
O	1.18892400	-0.54081900	0.22408600
O	1.20399400	1.54645500	-0.66751300
C	2.45315800	-0.84993900	-0.42642900
H	2.46771300	-1.94020900	-0.47407900
H	2.43411100	-0.44283200	-1.44039300
C	3.62428700	-0.30196300	0.37197300
H	4.56513000	-0.60662000	-0.09688200
H	3.58886100	0.78949300	0.40011900
H	3.60741100	-0.68622500	1.39574300
H	-0.97321300	1.89245300	0.62222400
Br	-2.02943700	-0.28530100	-0.07720600

(2) 1-phenylaroslane (**1**)
Total energy: -2622.70460450 Hartree
Free energy: = -2622.538101 Hartree

As	0.93331800	-0.63120800	-0.78173500
C	1.79621200	1.15702500	-0.71584000
C	1.61275800	-0.97255200	1.07912900
C	-3.58001300	0.36174200	0.43820900
C	-2.78259000	1.38218300	-0.08163900
C	-1.45334000	1.12898500	-0.43084900
C	-0.89677000	-0.14486700	-0.26505500

C	-1.71587700	-1.16546300	0.24305800
C	-3.04133700	-0.91721200	0.59961900
H	-4.61251500	0.55890300	0.71113400
H	-3.19240300	2.37986600	-0.21293600
H	-0.85599200	1.94295300	-0.82948800
H	-1.30911300	-2.16709100	0.36671700
H	-3.65356200	-1.72129200	0.99828900
C	2.48903100	0.23498400	1.46646000
C	1.95001100	1.49560100	0.77099600
H	2.16577000	-1.91374500	1.09489100
H	0.74019800	-1.07079600	1.72876100
H	3.51934500	0.06129400	1.12997200
H	2.52706700	0.36328600	2.55456000
H	2.61677100	2.35241900	0.92879000
H	0.97059300	1.75836200	1.18963800
H	2.77527300	1.02801400	-1.18934100
H	1.24056500	1.89513300	-1.29824500

(3) S_N2-inital complex

Total energy: -5501.55147535 Hartree

Free energy: = -5501.292047 Hartree

C	-2.16074300	-1.22376000	0.07637100
As	1.14008800	-0.23840100	-0.07107100
H	-1.62178200	-1.86085800	-0.61778700
C	0.90494300	1.52165500	0.81565200
C	1.31904300	0.69415300	-1.83141000
C	5.80240800	-1.09978600	0.56524500
C	5.16868700	-0.17653500	1.39750900
C	3.80992400	0.10437300	1.23140200
C	3.05756500	-0.53093300	0.23657600
C	3.70748900	-1.46557600	-0.58528200
C	5.06515800	-1.74558900	-0.43009800
H	6.85886100	-1.31716000	0.69192600
H	5.73177800	0.33237800	2.17496000
H	3.34859600	0.83198000	1.89159900

H	3.14755900	-1.98060500	-1.36335100
H	5.54535300	-2.46889200	-1.08314000
C	-2.19465600	0.19678400	-0.44356200
O	-2.67541600	1.04323200	0.47726400
O	-1.82394700	0.52279200	-1.55303200
C	-2.84487100	2.42533400	0.05876500
H	-1.86837700	2.82877900	-0.22412200
H	-3.48648000	2.44164900	-0.82705700
C	1.04168500	2.18726700	-1.57085800
C	1.50316700	2.55283800	-0.14936600
H	0.60976000	0.25260600	-2.53143100
H	2.33673000	0.52133700	-2.18814000
H	-0.03564300	2.36450300	-1.65833300
H	1.53553100	2.81674800	-2.32048500
H	1.20691000	3.57652900	0.11225100
H	2.59777300	2.50428100	-0.09427800
H	-0.17223200	1.66114300	0.94180000
H	1.35190700	1.52466700	1.81199100
C	-3.45169000	3.17138100	1.22848700
H	-3.60472000	4.21983000	0.95677100
H	-4.41709400	2.73921200	1.50515300
H	-2.79001800	3.13216800	2.09836300
H	-1.73970000	-1.27726000	1.07791700
Br	-4.01518200	-1.91924700	0.20000800

(4) TS_{SN2}

Total energy: -5501.52845809 Hartree

Free energy: =-5501.269126 Hartree

Imaginary frequency: 379.9 *i*cm^{-1}

C	-1.19113400	-0.99153900	-0.04174800
As	0.91509500	0.25437700	-0.12734300
H	-0.87446800	-1.58770100	-0.88019100
C	0.92519700	2.07444500	0.62543900
C	1.13528800	0.94105200	-1.96194900
C	5.14009000	-1.72616500	0.70509900

C	4.94007800	-0.38263700	1.02751800
C	3.69845900	0.21417200	0.80448900
C	2.64015300	-0.52821300	0.26544700
C	2.85041200	-1.87637900	-0.05572100
C	4.09297000	-2.47246600	0.16156500
H	6.10633300	-2.18981700	0.87852200
H	5.75068300	0.20433700	1.44878900
H	3.56885000	1.26050400	1.06143200
H	2.04296000	-2.47424400	-0.47000700
H	4.23965400	-3.51819100	-0.09061900
C	-1.89194900	0.29013600	-0.32047400
O	-2.28573100	0.88183400	0.82066200
O	-2.00302800	0.78442500	-1.42825800
C	-3.06226300	2.09733700	0.66867100
H	-2.50431900	2.80162000	0.04372400
H	-3.99089400	1.84615700	0.14700000
C	0.86894400	2.45295800	-1.84142900
C	1.45884200	2.96141900	-0.51210000
H	0.43309300	0.43382300	-2.62327400
H	2.16288600	0.72189700	-2.26000200
H	-0.21332000	2.62173700	-1.84882400
H	1.29514800	2.99245800	-2.69383400
H	1.20146100	4.01269400	-0.34217500
H	2.55331800	2.89433100	-0.54719300
H	-0.11644400	2.29836200	0.86671300
H	1.50715600	2.11107600	1.54756500
C	-3.31507300	2.63975700	2.06017600
H	-3.91454900	3.55261600	1.99796800
H	-3.85607500	1.90905100	2.66721500
H	-2.37248900	2.87861200	2.56185000
H	-1.04702700	-1.33595900	0.96765200
Br	-3.36000300	-2.20917600	-0.08226100

(5) S_N2-product

Total energy: -5501.58256008 Hartree

Free energy: = -5501.317751 Hartree

C	0.74638300	0.17721900	-1.51929000
As	-0.54513200	0.68338600	-0.15591000
H	0.72431100	-0.89551200	-1.68819900
C	-0.88559900	2.56887900	-0.55222600
C	-0.06317600	1.07603800	1.69522800
C	-4.64596900	-1.62760900	-0.50333600
C	-4.61336100	-0.23397500	-0.57064600
C	-3.39607700	0.44062800	-0.47819900
C	-2.20103800	-0.27550400	-0.31939100
C	-2.23944800	-1.67328500	-0.23456400
C	-3.45922500	-2.34255500	-0.33465400
H	-5.59344600	-2.15278500	-0.57767900
H	-5.53160300	0.33149800	-0.69487900
H	-3.39772600	1.52341000	-0.53745800
H	-1.32098100	-2.22697900	-0.06401300
H	-3.47800100	-3.42612000	-0.27176200
C	2.09457400	0.63864600	-1.01066800
O	3.08877400	-0.06138000	-1.54580800
O	2.21606300	1.57283400	-0.23252500
C	4.42455500	0.13427500	-0.99016700
H	5.09648800	0.04600600	-1.84633800
H	4.49096900	1.14363500	-0.58019100
C	-0.07586900	2.60940400	1.79760200
C	-1.13105300	3.18743200	0.83184900
H	0.87757900	0.58580500	1.92473000
H	-0.87328900	0.60603300	2.25756200
H	0.91185400	2.98778900	1.51994300
H	-0.27871900	2.91366200	2.82931400
H	-1.07287200	4.27972100	0.79324300
H	-2.13821900	2.92694600	1.18218600
H	0.05283000	2.92700600	-0.98288000
H	-1.69599400	2.71062300	-1.26723600
C	4.68288500	-0.93129700	0.06099300
H	5.66339900	-0.76753500	0.51947600
H	3.90759000	-0.90445500	0.83068600

H	4.66594300	-1.92800900	-0.38744000
H	0.46281900	0.73937300	-2.41605700
Br	1.10435000	-1.95866400	0.90267200

(6) AcONa

Total energy: -390.871302572 Hartree

Free energy: = -390.849976 Hartree

C	0.53679100	0.00113600	-0.01693400
O	-0.05677100	1.12422900	-0.00937200
O	-0.05546800	-1.12283800	-0.00944200
Na	-2.00301100	-0.00096800	0.01012100
C	2.06466100	0.00006800	0.00664400
H	2.46204900	0.91300700	-0.44159100
H	2.40161200	-0.04075900	1.04892100
H	2.45865600	-0.87994700	-0.50641500

(7) Base-adduct

Total energy: -5892.49622210 Hartree

Free energy: = -5892.188795 Hartree

C	-0.78899000	-0.72407500	-1.14468800
As	0.86212000	-1.12187000	-0.23003600
C	1.39789600	-2.87254000	-0.95826200
C	0.84438800	-1.80680400	1.59640700
C	4.36041300	1.80975200	-1.30102200
C	3.04318200	2.19877600	-1.55469300
C	1.97979500	1.35364800	-1.23820300
C	2.25382100	0.10099100	-0.67967100
C	3.57044900	-0.29380900	-0.41828600
C	4.62528000	0.56363600	-0.73001200
H	5.18043100	2.47862600	-1.54429700
H	2.83600700	3.17081400	-1.99111500
H	0.95901800	1.68618100	-1.40690100
H	3.78701300	-1.26327600	0.02163400
H	5.64663000	0.25869300	-0.52485200

C	-2.01008100	-1.22350400	-0.43685700
O	-2.94382300	-1.59523900	-1.30879300
O	-2.15041200	-1.24416400	0.78284500
C	-4.30477900	-1.78773200	-0.81719600
H	-4.68606800	-2.64132600	-1.38115700
H	-4.26440100	-2.04329300	0.24289000
C	0.85885400	-3.33099800	1.42386700
C	1.81306400	-3.69697100	0.27114500
H	-0.01058300	-1.40672700	2.13001300
H	1.76660100	-1.41180600	2.02853100
H	-0.15496300	-3.67047100	1.17785700
H	1.15299200	-3.81670800	2.35941800
H	1.78324100	-4.76919900	0.05430300
H	2.84361800	-3.45493200	0.55883500
H	0.50698800	-3.29312400	-1.43303100
H	2.17830700	-2.73825500	-1.70782300
C	-5.10002500	-0.51867900	-1.07493300
H	-6.10942100	-0.62454300	-0.66451400
H	-4.60230900	0.33881800	-0.61363200
H	-5.18042700	-0.32764100	-2.14870200
H	-0.69183100	-1.17043500	-2.13579800
Br	0.44874200	1.50659000	1.84751500
O	-1.16768900	2.09475700	-1.72588700
C	-1.87713500	2.51166100	-0.77051100
O	-2.72158800	1.80308500	-0.12992700
Na	-2.15589200	0.90273400	1.77517900
C	-1.64886300	3.94508600	-0.29780600
H	-0.83204100	3.89815800	0.43245600
H	-1.33700500	4.58871000	-1.12371200
H	-2.53432000	4.35419500	0.19459500
H	-0.91409000	0.38041800	-1.28536800

(8) $TS_{deprotonate}$

Total energy: -5892.48803609 Hartree

Free energy: = -5892.184363 Hartree

Imaginary frequency: 1266.3 *i*cm^{-1}

C	0.83047400	0.70657900	-1.13789400
As	-0.79120000	1.13059100	-0.24419900
H	1.02183000	-0.67500900	-1.32201300
C	-1.30402600	2.92915600	-0.88082500
C	-0.76597200	1.72157900	1.61314800
C	-4.51087000	-1.56022500	-1.25063700
C	-3.23313900	-2.01547900	-1.58271000
C	-2.10899300	-1.24378300	-1.28950000
C	-2.27210200	0.00018400	-0.67383400
C	-3.55091900	0.45778300	-0.33623700
C	-4.67021500	-0.32277000	-0.62439000
H	-5.38082700	-2.16976300	-1.47579300
H	-3.10636700	-2.98125300	-2.06207000
H	-1.11911000	-1.62200600	-1.51728900
H	-3.68864000	1.42058500	0.14772600
H	-5.66008000	0.03459000	-0.35805200
C	2.01918500	1.19454700	-0.45426000
O	2.97536100	1.58166000	-1.32276500
O	2.19873000	1.19425100	0.77336600
C	4.32490500	1.74168200	-0.81454600
H	4.75289000	2.55423800	-1.40631300
H	4.28076400	2.04598700	0.23293100
C	-0.68939200	3.25032900	1.50903300
C	-1.63913300	3.72399700	0.39233800
H	0.05851900	1.26112000	2.14459600
H	-1.71384800	1.36531100	2.02307200
H	0.34018700	3.53267500	1.25592600
H	-0.93516100	3.71363100	2.46982400
H	-1.54478400	4.80109200	0.22095100
H	-2.67736500	3.53697400	0.69334300
H	-0.41462500	3.32680900	-1.37639900
H	-2.11869400	2.85363100	-1.60186800
C	5.09405000	0.44191400	-0.99515600
H	6.10742100	0.54644000	-0.59368300
H	4.58377200	-0.37673200	-0.48062800

H	5.16675000	0.18321200	-2.05554600
H	0.73544500	1.08963900	-2.15508800
Br	-0.48193000	-1.66475300	1.75867200
O	1.09541000	-1.85918500	-1.58290900
C	1.83677800	-2.50005800	-0.73705000
O	2.70963000	-1.96291900	-0.02385900
Na	2.07553200	-0.86070400	1.80271600
C	1.52929700	-3.97392400	-0.60493400
H	0.68374400	-4.03493700	0.09059600
H	1.22381800	-4.40573600	-1.56013300
H	2.37806800	-4.51543500	-0.18485000

(9) Base-adduct

Total energy: -5892.49060333 Hartree

Free energy: = -5892.185035 Hartree

C	0.77384100	0.82575500	-1.13738600
As	-0.85431900	1.13885900	-0.26434300
C	-1.51130500	2.90655600	-0.86402400
C	-0.86787400	1.69330200	1.60294200
C	-4.42094400	-1.76830100	-1.24939700
C	-3.12558000	-2.12951800	-1.62550200
C	-2.04825100	-1.29164800	-1.33832200
C	-2.27202400	-0.07822800	-0.68359700
C	-3.56939600	0.28390700	-0.30363600
C	-4.64305100	-0.56042600	-0.58545500
H	-5.25508400	-2.42759000	-1.46984300
H	-2.94878500	-3.07201600	-2.13454400
H	-1.04393200	-1.59835700	-1.60179600
H	-3.75603000	1.22284700	0.20996000
H	-5.64677500	-0.27579000	-0.28524700
C	1.94021100	1.31862200	-0.47921600
O	2.90949600	1.69438400	-1.35890100
O	2.13342700	1.36252700	0.75588100
C	4.24927500	1.87544700	-0.84925100
H	4.67290400	2.68919100	-1.44400100

H	4.20099500	2.18742900	0.19608800
C	-0.88197300	3.22546700	1.52394900
C	-1.87220700	3.66069500	0.42676100
H	-0.01514700	1.28025100	2.12826500
H	-1.79079400	1.27499700	2.01112900
H	0.12677100	3.56828100	1.26175600
H	-1.14083200	3.65966700	2.49492400
H	-1.84221000	4.74430300	0.27280000
H	-2.89376300	3.40973400	0.73852300
H	-0.65706100	3.36366200	-1.36950900
H	-2.33365400	2.78785600	-1.57053200
C	5.04718200	0.59005200	-1.01394300
H	6.06503100	0.72556200	-0.63291300
H	4.56844600	-0.22918500	-0.47105400
H	5.10820800	0.30859200	-2.06956400
H	0.67927500	1.08836500	-2.18938700
Br	-0.38462700	-1.71100300	1.72415600
O	1.23439500	-1.89957800	-1.51160700
C	2.01547700	-2.49838400	-0.63394200
O	2.81371600	-1.89894100	0.09094500
Na	2.07513700	-0.63676600	1.81539400
C	1.80005200	-3.98353200	-0.55745300
H	0.93501100	-4.11757300	0.10301700
H	1.55917200	-4.40534700	-1.53489000
H	2.66805500	-4.47557200	-0.11873200
H	1.15926300	-0.88784100	-1.32161700

[C] The reaction between benzaldehyde and the arsonium ylide formed from the first half reactions between ethyl bromoacetate, **5**, and the Cy_2MeN base. Their total energies were obtained at the B3LYP-D3 calculations using the polarizable continuum model to include solvent effects of THF. Their free energies were also obtained at 25 ºC.
(Scheme 4 & Figure S30)

(1) benzaldehyde
Total energy: -345.595969703 Hartree
Free energy: = -345.516407 Hartree

C	1.98862700	0.47163600	0.00014700
H	2.27107500	1.54599300	0.00007100
O	2.84677700	-0.39719100	0.00009100
C	0.53424800	0.21521700	0.00005600
C	0.04645100	-1.10194500	0.00002800
C	-0.36085700	1.29451000	-0.00000100
C	-1.32475500	-1.33324300	-0.00004900
H	0.75821000	-1.92117200	0.00008400
C	-1.73558600	1.06071800	-0.00012300
H	0.02291900	2.31159400	0.00001400
C	-2.21548500	-0.25174700	-0.00013100
H	-1.70613600	-2.34959000	-0.00006400
H	-2.43028500	1.89465100	-0.00018600
H	-3.28586000	-0.43482400	-0.00020300

(2) Z-reactant complex
Total energy: -3982.85788793 Hartree
Free energy: = -3982.238712 Hartree

C	0.21690200	0.34724100	-2.22454600
As	0.64007000	-0.01610800	-0.47451900
C	3.31899100	-3.94558600	-0.36434000
C	3.68543500	-2.77806800	0.35196200
C	2.89500800	-1.63744900	0.30939800
C	1.71005600	-1.59501900	-0.43586100
C	1.33083000	-2.74993200	-1.13632800
C	2.10933400	-3.89914100	-1.10360500

H	4.59122300	-2.75742300	0.94425200
H	3.21603700	-0.76571900	0.87162000
H	0.40398800	-2.76630600	-1.70106500
H	1.77015600	-4.76600200	-1.65629400
C	-0.58470700	1.47189200	-2.46639000
O	-0.97841900	1.57256900	-3.79751400
O	-0.95069600	2.32516200	-1.63514400
C	-1.62895500	2.79959100	-4.17075900
H	-2.13854300	2.57071900	-5.11117000
H	-2.37888600	3.06408100	-3.41890300
C	-0.62804300	3.93383400	-4.34848900
H	-1.13517100	4.84082500	-4.69464400
H	-0.13995500	4.14902400	-3.39485200
H	0.13615200	3.66237600	-5.08341900
H	0.47484800	-0.36428700	-2.99499100
C	-0.77873000	-0.24777700	0.79420900
C	-0.96755500	-1.46080600	1.46148200
C	-1.63771200	0.82249300	1.08559400
C	-2.00281500	-1.62050200	2.37557800
H	-0.31353500	-2.30283900	1.25784500
C	-2.66152200	0.68164600	2.00822700
H	-1.51029300	1.76364500	0.56339000
C	-2.88526000	-0.55205600	2.66959500
H	-2.12470500	-2.58279500	2.85626300
H	-3.31517500	1.52548000	2.18605300
C	1.69247800	1.39777000	0.27024100
C	2.44956900	2.22103200	-0.56928100
C	1.73717000	1.63681100	1.64794000
C	3.23213500	3.24778600	-0.06040800
H	2.40767400	2.06208600	-1.64361200
C	2.51851700	2.65521200	2.17886000
H	1.14500800	1.02702600	2.32416300
C	3.29691700	3.48945200	1.33644300
H	3.78947000	3.86695500	-0.75165800
H	2.51491600	2.80626200	3.25071600
N	4.10434000	-5.07576100	-0.34423400

N	-3.92767800	-0.70644400	3.55972600
N	4.08688500	4.49318400	1.85387700
C	-4.88787000	0.37280400	3.74251500
H	-5.62898000	0.07169100	4.48281800
H	-4.39751700	1.28036700	4.11314800
H	-5.41260500	0.62517400	2.81080900
C	-4.25307800	-2.03280000	4.06261600
H	-4.48963400	-2.73700900	3.25189000
H	-3.42536700	-2.45408200	4.64542700
H	-5.11974500	-1.96593200	4.71999300
C	5.27970500	-5.12839800	0.51296800
H	5.02458500	-5.01161500	1.57562700
H	5.77376900	-6.09130200	0.38605300
H	6.00096100	-4.34574100	0.24916300
C	3.64256100	-6.29362700	-0.99482300
H	2.70096100	-6.66268200	-0.56479600
H	3.48702100	-6.13767900	-2.06893300
H	4.39708700	-7.07112400	-0.87804500
C	4.02231000	4.80557100	3.27424900
H	4.71671800	5.61577300	3.49562200
H	3.01650500	5.12030300	3.58709100
H	4.31273900	3.94241000	3.88452400
C	4.76021900	5.42085100	0.95624400
H	5.45567000	4.89584600	0.29110600
H	4.05297600	5.98531900	0.33205100
H	5.33880000	6.13291000	1.54433300
C	-2.31117800	-1.51183400	-2.06384700
O	-1.86001700	-2.57998600	-1.66595200
H	-1.90055900	-1.01909800	-2.96053900
C	-3.44387700	-0.81178000	-1.43047200
C	-3.83996900	0.44284900	-1.91601900
C	-4.14933900	-1.41177100	-0.37700600
C	-4.92604500	1.10008400	-1.34094900
H	-3.28542400	0.89680800	-2.73104300
C	-5.24240800	-0.76185200	0.18480500
H	-3.81685500	-2.37629300	-0.01088000

C	-5.62817200	0.49596100	-0.29363200
H	-5.22747400	2.07652000	-1.70753600
H	-5.78771400	-1.22268500	1.00267300
H	-6.47862100	1.00485100	0.15114000

(2) *Z*-TS1

Total energy: -3982.84422186 Hartree

Free energy: = -3982.223535 Hartree

Imaginary frequency: 305.2 *i*cm^{-1}

C	-0.23570200	0.35808600	-2.03322000
As	0.39452000	-0.16459800	-0.30797300
C	3.99449400	-3.25593400	-0.62271000
C	4.00035400	-2.18749700	0.31082800
C	2.93784800	-1.29858600	0.38446800
C	1.82016900	-1.42735700	-0.45379100
C	1.79479400	-2.48911400	-1.36962000
C	2.85317600	-3.38267200	-1.45592600
H	4.83838200	-2.04656100	0.98125600
H	2.99148300	-0.49075900	1.10746600
H	0.91280800	-2.61713800	-1.99254700
H	2.78765600	-4.18867800	-2.17587800
C	-0.77236100	1.71430100	-2.00406000
O	-0.65479800	2.33710500	-3.20893400
O	-1.33679200	2.23511800	-1.04353900
C	-1.19517100	3.67858700	-3.28801100
H	-1.36053600	3.84511000	-4.35479400
H	-2.15576700	3.70778200	-2.76752800
C	-0.21830200	4.69072100	-2.70758400
H	-0.61847500	5.70402200	-2.81508400
H	-0.05149200	4.48997300	-1.64670000
H	0.74210400	4.64060000	-3.22935700
H	0.57061500	0.20210100	-2.74688700
C	-0.94597000	-0.80904900	0.87091200
C	-0.90740800	-2.12317600	1.34333400
C	-1.99701600	0.02529200	1.26743900

C	-1.89579900	-2.60288800	2.19124400
H	-0.10811600	-2.78884500	1.03399300
C	-2.97819300	-0.43497400	2.13287900
H	-2.05749800	1.03602100	0.87983200
C	-2.96250600	-1.76792000	2.61399500
H	-1.83870000	-3.63201000	2.52133000
H	-3.78189100	0.23739600	2.40248900
C	1.17932800	1.35389100	0.54470500
C	1.94724500	2.25647900	-0.20236100
C	1.02331500	1.59581900	1.91263500
C	2.52740800	3.37094400	0.38413800
H	2.08173900	2.10517300	-1.27005200
C	1.60261500	2.70250700	2.52118700
H	0.42832000	0.92054700	2.51965100
C	2.37443100	3.62599700	1.77236600
H	3.09785000	4.04614300	-0.24036600
H	1.44393000	2.85059900	3.58153000
N	5.05163400	-4.12991800	-0.71527100
N	-3.94463000	-2.23372700	3.46409800
N	2.95625200	4.72315100	2.36574600
C	-5.13450900	-1.42443100	3.69199100
H	-5.80190600	-1.95223000	4.37306700
H	-4.87760800	-0.46615800	4.15635200
H	-5.68327700	-1.21627300	2.76173700
C	-4.00266100	-3.65368500	3.78391000
H	-4.15094400	-4.27954700	2.89179900
H	-3.08413700	-3.98281200	4.28168000
H	-4.83062900	-3.83273300	4.46975700
C	6.16686600	-4.02663400	0.21484400
H	5.84855300	-4.16151000	1.25767700
H	6.90107900	-4.79740200	-0.01753100
H	6.66622100	-3.05330100	0.13535600
C	4.98333100	-5.26287000	-1.62734200
H	4.15577100	-5.94215500	-1.38113000
H	4.85483100	-4.93339600	-2.66539100
H	5.91377800	-5.82696700	-1.56961700

C	2.67662500	5.02444000	3.76254500
H	3.22555100	5.91962100	4.05349100
H	1.60732700	5.20332400	3.94306700
H	2.99985500	4.20721000	4.41793800
C	3.62845000	5.72093400	1.54534600
H	4.47228200	5.28410700	0.99853300
H	2.95047500	6.18261000	0.81380800
H	4.02213900	6.50766300	2.18832000
C	-1.48799700	-1.03877000	-2.54111900
O	-1.10528900	-2.13736300	-2.00394600
H	-1.30246200	-0.87952300	-3.62680800
C	-2.86155300	-0.50406600	-2.17841200
C	-3.44788300	0.54946900	-2.89372800
C	-3.60443700	-1.13368900	-1.17630300
C	-4.73500200	0.99053100	-2.58821500
H	-2.88426400	1.03086800	-3.68912100
C	-4.89383300	-0.69774500	-0.86733500
H	-3.14424600	-1.95649600	-0.64114300
C	-5.46318000	0.36773000	-1.56852200
H	-5.17334400	1.81341900	-3.14656000
H	-5.45294500	-1.18869000	-0.07497800
H	-6.46725100	0.70715700	-1.32925600

(3) Z-INT

Total energy: -3982.85693942 Hartree

Free energy: = -3982.232849 Hartree

C	-0.44029200	0.78431400	-2.08866800
As	0.16212600	-0.30709200	-0.53699900
C	4.04445000	-3.07012000	-0.82002700
C	3.79275900	-2.23424600	0.29793300
C	2.66393500	-1.42929200	0.34645300
C	1.71515700	-1.42955400	-0.68694000
C	1.94542100	-2.26999800	-1.78209500
C	3.07906100	-3.06902900	-1.85776300
H	4.48328300	-2.20731700	1.13122800

H	2.52697900	-0.78959300	1.21229500
H	1.20331800	-2.31130400	-2.57025200
H	3.20802200	-3.69997100	-2.72807600
C	-1.03586300	2.09285200	-1.66007100
O	-0.50818400	3.13159300	-2.33310800
O	-1.88121000	2.21175600	-0.79043100
C	-0.94064800	4.45851100	-1.91855400
H	-0.72752100	5.09179300	-2.78174600
H	-2.01893800	4.43745400	-1.74353400
C	-0.17982600	4.90973400	-0.68219100
H	-0.48694000	5.92468300	-0.41033900
H	-0.38099800	4.24296700	0.15908500
H	0.89696400	4.90569200	-0.86710400
H	0.44875800	0.94300800	-2.70252500
C	-1.03718600	-0.99087000	0.79445400
C	-0.82444200	-2.27959700	1.29381600
C	-2.15655500	-0.28111800	1.24079100
C	-1.68708800	-2.84176400	2.22788300
H	0.02316300	-2.86480900	0.94973700
C	-3.02399800	-0.82872700	2.17852900
H	-2.36732400	0.70378000	0.84206600
C	-2.81110900	-2.12510700	2.70709000
H	-1.48237200	-3.84476400	2.58004300
H	-3.88219500	-0.24458300	2.48543700
C	1.02102200	1.18320100	0.45320000
C	2.06224900	1.87306400	-0.18434400
C	0.65136900	1.62322000	1.72630300
C	2.69291400	2.96433400	0.39875800
H	2.40876900	1.54601200	-1.16269900
C	1.26257300	2.72023200	2.33034000
H	-0.13742100	1.11217700	2.26948000
C	2.28914000	3.43783600	1.67187000
H	3.49599900	3.45097900	-0.14039700
H	0.93382600	3.01569600	3.31896200
N	5.17976200	-3.84715600	-0.89321100
N	-3.66217700	-2.66647100	3.65480900

N	2.86991800	4.55748100	2.24154000
C	-4.92615000	-2.00064300	3.93737400
H	-5.46576500	-2.56455100	4.69849700
H	-4.76053400	-0.99154200	4.33000700
H	-5.56816900	-1.91829400	3.04753500
C	-3.53458300	-4.07369900	4.00642500
H	-3.68929100	-4.74122300	3.14547000
H	-2.54524100	-4.28557200	4.42615700
H	-4.27388300	-4.32067100	4.76865300
C	6.07246400	-3.93515200	0.25354800
H	5.57188400	-4.34616300	1.14180600
H	6.91251300	-4.58361000	0.00561800
H	6.47823100	-2.95162800	0.51741000
C	5.33840600	-4.79582500	-1.98620000
H	4.54369800	-5.55529700	-1.99818100
H	5.33558400	-4.28675600	-2.95692400
H	6.29587200	-5.30602500	-1.88271500
C	2.57296900	4.89097800	3.62631500
H	3.10984400	5.79947200	3.90007100
H	1.50317000	5.08462500	3.76456600
H	2.86610000	4.09349700	4.32541300
C	4.04322300	5.15133100	1.61897900
H	4.89488500	4.45630600	1.57010800
H	3.82125900	5.48578900	0.59918600
H	4.34953700	6.02644600	2.19246100
C	-1.31300200	-0.37504000	-2.65878900
O	-0.81591200	-1.48102000	-1.97076600
H	-1.10889900	-0.44329600	-3.74381100
C	-2.81623800	-0.16842700	-2.50305600
C	-3.48937600	0.80196800	-3.25653800
C	-3.54620700	-0.97014100	-1.62429300
C	-4.86598500	0.98012700	-3.12084100
H	-2.92824600	1.42807500	-3.94789000
C	-4.92543600	-0.79658800	-1.48556800
H	-3.00998000	-1.71699800	-1.05259900
C	-5.58996400	0.17987500	-2.23040000

H	-5.37492400	1.73981100	-3.70786700
H	-5.47979600	-1.42183900	-0.79049100
H	-6.66242100	0.31614100	-2.12302500

(4) *Z*-TS2

Total energy: -3982.83652299 Hartree

Free energy: = -3982.212433 Hartree

Imaginary frequency: 13.7 *i*cm^{-1}

C	-1.96734800	0.77589400	-2.39450900
As	0.54841400	0.02202200	-0.52032900
C	5.27945400	-0.20388700	-0.39494600
C	4.55292300	0.66154800	0.46463000
C	3.16916900	0.72896400	0.40260400
C	2.44270100	-0.05001200	-0.50725600
C	3.14926400	-0.90909000	-1.35931900
C	4.53290800	-0.98908100	-1.31298300
H	5.07009800	1.28700700	1.18053200
H	2.65176000	1.41032500	1.07202200
H	2.60987100	-1.51957300	-2.07608500
H	5.03477900	-1.66379700	-1.99428000
C	-2.98516000	0.81003500	-1.43597700
O	-3.47109200	2.11885400	-1.26967100
O	-3.50694300	-0.11494200	-0.77522700
C	-4.56667600	2.27534300	-0.36388100
H	-5.07002600	3.19643600	-0.67825200
H	-5.26667800	1.44080800	-0.47406000
C	-4.10286300	2.38471800	1.08376400
H	-4.95504600	2.56375100	1.74948800
H	-3.60913500	1.45726200	1.38300800
H	-3.38864400	3.20458300	1.19953600
H	-1.68234500	1.72509400	-2.83371100
C	-0.06319200	-1.23965800	0.75765400
C	0.87280300	-2.02552600	1.44675900
C	-1.42998300	-1.41842700	1.02166000

C	0.46187100	-2.96602300	2.37932200
H	1.93439700	-1.91107000	1.25473900
C	-1.84717300	-2.35236500	1.95582400
H	-2.17999500	-0.85244000	0.47273700
C	-0.91566800	-3.15535600	2.66673200
H	1.21606800	-3.55376700	2.88634600
H	-2.91045400	-2.46659000	2.12427400
C	0.06844600	1.77093600	0.01325800
C	0.26735500	2.86100500	-0.84529200
C	-0.38519100	2.01049500	1.31397600
C	-0.00504800	4.15195000	-0.42944000
H	0.61272300	2.69476800	-1.86096400
C	-0.65136000	3.30235500	1.74931600
H	-0.54643300	1.18399200	1.99858200
C	-0.47581800	4.41292100	0.88710400
H	0.14289100	4.96280800	-1.13053800
H	-1.01375000	3.44046900	2.75925900
N	6.64892600	-0.27758300	-0.34172300
N	-1.33052000	-4.07807400	3.59380200
N	-0.74718600	5.69377500	1.30544200
C	-2.75298500	-4.30518300	3.81277000
H	-2.88048600	-5.06437100	4.58366900
H	-3.25654400	-3.39243000	4.15294700
H	-3.25755400	-4.65419400	2.90211900
C	-0.35828000	-4.93514400	4.25800300
H	0.18921700	-5.56532700	3.54431900
H	0.37369500	-4.34651200	4.82420200
H	-0.87557100	-5.58855800	4.95962800
C	7.38801000	0.52849600	0.61979000
H	7.09793500	0.29557800	1.65241600
H	8.45315500	0.32499300	0.51599600
H	7.23082300	1.60227800	0.45554500
C	7.36947700	-1.17060600	-1.23849100
H	7.08548900	-2.21945300	-1.08294200
H	7.18727200	-0.92070900	-2.29141900
H	8.43902600	-1.08028800	-1.05238300

C	-1.35488400	5.91449400	2.61069200
H	-1.49580200	6.98378200	2.76476900
H	-2.33327900	5.42211100	2.69978300
H	-0.71152200	5.54291000	3.41670400
C	-0.68095900	6.79896400	0.35838700
H	0.32724000	6.90602300	-0.05812100
H	-1.38458600	6.67238700	-0.47588000
H	-0.92685400	7.72700000	0.87357100
C	-1.17815900	-0.37868300	-2.79329500
O	0.26665000	-0.37209900	-2.19764600
H	-0.86446500	-0.28261400	-3.84050300
C	-1.76758400	-1.76802900	-2.61626100
C	-3.03924400	-2.02620100	-3.14860600
C	-1.06202600	-2.82493300	-2.03454600
C	-3.59353000	-3.30264100	-3.09166700
H	-3.59356000	-1.20652300	-3.59439500
C	-1.62043400	-4.10462600	-1.96324800
H	-0.08552400	-2.63945500	-1.60938300
C	-2.88629500	-4.35128200	-2.49308300
H	-4.58191500	-3.47973700	-3.50699400
H	-1.05881700	-4.90711300	-1.49265600
H	-3.31969200	-5.34609700	-2.44175700

(5) Z-product complex

Total energy: -3982.87316031 Hartree

Free energy: = -3982.249727 Hartree

C	-2.77109400	0.73827300	-1.81686000
As	1.07725800	0.06852900	-0.83001600
C	5.75230000	0.17730200	0.06744100
C	4.80816100	0.32837500	1.11626700
C	3.44504200	0.29360400	0.85643100
C	2.95264700	0.12048500	-0.44238500
C	3.87621600	-0.02449100	-1.48185600
C	5.24527500	0.00594600	-1.24528300
H	5.13931400	0.47094900	2.13701500

H	2.76014300	0.40654500	1.69309400
H	3.50698300	-0.15940800	-2.49459300
H	5.91951300	-0.10561000	-2.08489000
C	-3.69818700	0.88973900	-0.68266900
O	-4.20829200	2.14863100	-0.68043300
O	-3.96529000	0.06661000	0.18158300
C	-5.06747000	2.50465900	0.42991100
H	-5.70340200	3.30229200	0.03939700
H	-5.68930000	1.64510300	0.69160600
C	-4.24316400	2.97863700	1.61661600
H	-4.90562300	3.27726000	2.43548500
H	-3.59128700	2.17618700	1.97041100
H	-3.62369200	3.83359500	1.33444000
H	-2.47138800	1.68291700	-2.25618000
C	0.37720300	-1.27706000	0.33035500
C	1.10509200	-2.45296000	0.55246600
C	-0.92968300	-1.19994400	0.82622700
C	0.54267200	-3.52866700	1.22512600
H	2.12204300	-2.53736900	0.17858300
C	-1.50180000	-2.26036700	1.50955600
H	-1.53398400	-0.31927600	0.64511600
C	-0.79068900	-3.46894200	1.70584200
H	1.13514500	-4.42493400	1.35675200
H	-2.52725700	-2.15956100	1.83776100
C	0.28740500	1.71781400	-0.26625300
C	-0.07613800	2.66728900	-1.22544600
C	0.06136000	2.01644500	1.08225700
C	-0.66388900	3.87202700	-0.86190900
H	0.09382800	2.44676000	-2.27550200
C	-0.52306200	3.21598100	1.46677200
H	0.32337300	1.29573400	1.85191600
C	-0.92123300	4.17243400	0.49941900
H	-0.92963900	4.57559200	-1.64030300
H	-0.68707300	3.39940800	2.52070000
N	7.10826200	0.18905500	0.31789900
N	-1.37632200	-4.54945600	2.33776600

N	-1.55438100	5.34209000	0.87229800
C	-2.81515800	-4.53059200	2.57814200
H	-3.10835300	-5.46245900	3.06207400
H	-3.08927400	-3.71026200	3.24961900
H	-3.38985300	-4.42124500	1.64775300
C	-0.71754500	-5.84752400	2.27580400
H	-0.57647200	-6.19709800	1.24207600
H	0.26344600	-5.81530400	2.76126200
H	-1.32217800	-6.58198200	2.80819000
C	7.59563900	0.51034600	1.65136200
H	7.23191800	-0.21099400	2.39250600
H	8.68460300	0.46742200	1.65536600
H	7.29060300	1.51518200	1.97699300
C	8.04903100	0.17209200	-0.79277100
H	7.93263200	-0.73431900	-1.39833100
H	7.92869800	1.04112300	-1.45538400
H	9.06622300	0.18015800	-0.40163300
C	-1.57576600	5.73083300	2.27655200
H	-2.07417000	6.69512100	2.37331200
H	-2.13500600	5.00729700	2.88046200
H	-0.56502400	5.82048800	2.69879100
C	-1.86119700	6.34819300	-0.13478200
H	-0.95858200	6.76222800	-0.60741100
H	-2.49745100	5.92958400	-0.92177500
H	-2.40939100	7.16614600	0.33253800
C	-2.18499700	-0.38423600	-2.28531500
O	0.89499000	-0.15806600	-2.47447800
H	-1.39211300	-0.21555600	-3.00861500
C	-2.39293900	-1.80087100	-1.96074900
C	-3.62802100	-2.33760400	-1.56067300
C	-1.28634100	-2.66364300	-2.08556000
C	-3.74632800	-3.69413300	-1.26621100
H	-4.49034800	-1.68851500	-1.47592400
C	-1.40319200	-4.01379700	-1.76649800
H	-0.32776700	-2.24078400	-2.37077000
C	-2.63292100	-4.53507400	-1.35679500

H	-4.70849100	-4.09718100	-0.96293400
H	-0.53329900	-4.65995400	-1.83308700
H	-2.72509900	-5.58935600	-1.11166500

(6) *Z*-ethyl cinnamate

Total energy: -576.884360941 Hartree

Free energy: = -576.719611 Hartree

C	-0.76721900	1.27121500	0.00038600
C	-1.60019300	0.05563200	-0.00051200
O	-2.90697400	0.41441600	-0.00013900
O	-1.25130700	-1.11668000	-0.00165800
C	-3.86717000	-0.66861100	-0.00085000
H	-3.69800400	-1.29112000	-0.88545100
H	-1.35953500	2.18082700	0.00080300
C	0.57798400	1.43600600	0.00060600
H	-3.69666800	-1.29340400	0.88182000
C	-5.24865500	-0.04476900	0.00100400
H	-6.00893700	-0.83129400	0.00060700
H	-5.39349600	0.57586800	0.88983500
H	-5.39493200	0.57817000	-0.88598700
C	1.75020100	0.55666000	0.00039300
C	1.72539500	-0.85361800	0.00123900
C	3.00912000	1.19822100	-0.00055800
C	2.91427700	-1.57969100	0.00103800
H	0.77144300	-1.36190400	0.00197900
C	4.19421900	0.46858000	-0.00085500
H	3.05167100	2.28418900	-0.00109900
C	4.15068300	-0.92773900	-0.00004600
H	2.87519000	-2.66511400	0.00172600
H	5.14829900	0.98679600	-0.00167700
H	5.07195300	-1.50270800	-0.00025700
H	0.86742500	2.48648900	0.00101900

(7) arsenic oxide

Total energy: -3405.95221103 Hartree

Free energy: = -3405.523705 Hartree

As	0.01655100	-0.00079700	1.44597600
C	-2.31707300	-3.71727600	-0.39694700
C	-1.13600700	-3.22328700	-1.00692500
C	-0.44409300	-2.15083700	-0.45733700
C	-0.88846000	-1.51897500	0.70969800
C	-2.06131100	-1.99219300	1.31212500
C	-2.76486400	-3.06426000	0.78104800
H	-0.75374600	-3.67851600	-1.91168200
H	0.45996000	-1.80581700	-0.95109000
H	-2.42610800	-1.51966300	2.22040300
H	-3.66488300	-3.39477800	1.28357000
C	1.77405900	-0.03111600	0.68674000
C	2.08767700	0.66900800	-0.48372000
C	2.77776900	-0.80565100	1.28266100
C	3.35655800	0.60445600	-1.04658700
H	1.33455000	1.28548100	-0.96637500
C	4.05203700	-0.88107200	0.73763100
H	2.56351200	-1.34761600	2.20011000
C	4.37651600	-0.18315500	-0.45486800
H	3.55369300	1.17158100	-1.94736100
H	4.79724300	-1.48329800	1.24142700
C	-0.69307000	2.78704700	1.29556200
C	-1.60740100	1.45178600	-0.48022300
C	-1.27415600	3.92548200	0.75433700
H	-0.12068400	2.87271300	2.21555300
C	-2.19469500	2.58013000	-1.03951900
H	-1.75428300	0.49204200	-0.96768000
C	-2.03660800	3.85592100	-0.44075600
H	-1.13620300	4.87087700	1.26326800
H	-2.78038800	2.46630600	-1.94279200
N	-2.99985100	-4.79218600	-0.92270900
N	5.63224800	-0.27003700	-1.01584700
N	-2.59915400	4.98382300	-0.99740300
C	6.69555300	-0.96977600	-0.30914900

H	6.44162600	-2.02456200	-0.15163000
H	7.60667100	-0.93431900	-0.90597700
H	6.90991400	-0.52135100	0.67129900
C	5.97191800	0.55995900	-2.16244300
H	5.31712100	0.34657900	-3.01546100
H	5.89795100	1.63343900	-1.93720100
H	6.99544600	0.34633100	-2.46963900
C	-2.58781700	-5.35852500	-2.19871900
H	-1.56058400	-5.73936100	-2.15290300
H	-3.24039800	-6.19487700	-2.44810700
H	-2.64223300	-4.62570300	-3.01622100
C	-4.27127500	-5.19959800	-0.34254000
H	-4.15513700	-5.48815600	0.70879800
H	-5.02746400	-4.40357700	-0.39525700
H	-4.65137700	-6.06584800	-0.88350200
C	-3.48072100	4.86083400	-2.14910800
H	-3.82124400	5.85193400	-2.44795000
H	-2.95873400	4.41586300	-3.00453600
H	-4.36528100	4.24502600	-1.93295500
C	-2.53031700	6.25433800	-0.29001800
H	-3.02505300	6.21268300	0.69067100
H	-1.49123500	6.56678700	-0.13283700
H	-3.02086100	7.02366100	-0.88592000
C	-0.84807200	1.53218100	0.69265400
O	0.02530500	0.01109200	3.10561400

(8) *E*-reactant complex

Total energy: -3982.85490656 Hartree

Free energy: = -3982.238880 Hartree

C	0.84335600	-0.55115300	-1.53343700
As	-0.30519900	0.08406200	-0.24543900
C	-1.31973300	4.60974600	-1.29620100
C	-2.33620400	3.68466700	-0.94688400
C	-2.02717100	2.36508500	-0.64580600
C	-0.70677800	1.89924300	-0.67207900

C	0.30789400	2.81039800	-0.99995100
C	0.01630700	4.13257600	-1.30588800
H	-3.37292900	3.99388700	-0.91130900
H	-2.83735200	1.68979900	-0.38751400
H	1.34479200	2.49187100	-1.00271900
H	0.83494300	4.79740400	-1.55003200
C	1.19055300	-1.90925500	-1.47733700
O	1.90897500	-2.32388900	-2.58338200
O	0.91695400	-2.70895800	-0.55816600
C	2.26051500	-3.71526900	-2.63111400
H	3.11273500	-3.76609500	-3.31479600
H	2.58577100	-4.05082300	-1.64215100
C	1.09777500	-4.56436100	-3.12806900
H	1.39874400	-5.61389500	-3.21575700
H	0.26496200	-4.49606500	-2.42391200
H	0.75909800	-4.21833500	-4.10967000
H	1.15198300	0.10373000	-2.33464000
C	0.16725300	0.02589400	1.61345300
C	0.21323500	1.19630400	2.37629200
C	0.44118400	-1.19899800	2.23854800
C	0.52341800	1.15593700	3.72991900
H	0.01403800	2.15655400	1.91180900
C	0.75433700	-1.25272700	3.58980900
H	0.42737400	-2.11017200	1.65003300
C	0.79728000	-0.07429600	4.37945600
H	0.55375600	2.08705900	4.28114500
H	0.96906600	-2.21733400	4.03181600
C	-1.95860100	-0.88143700	-0.31118900
C	-2.37245800	-1.47088300	-1.51071600
C	-2.78939500	-1.00961900	0.80712700
C	-3.57005900	-2.16566900	-1.60123400
H	-1.73104400	-1.39941800	-2.38523300
C	-3.99553900	-1.69519400	0.73736700
H	-2.49222400	-0.57729500	1.75806400
C	-4.42529600	-2.29076300	-0.47576800
H	-3.83827400	-2.61595400	-2.54838500

H	-4.59920400	-1.77378300	1.63242500
N	-1.61654200	5.91524100	-1.61363600
N	1.08817300	-0.12495700	5.72601700
N	-5.62599200	-2.96119300	-0.55937100
C	1.50952700	-1.38150900	6.32883400
H	1.68972600	-1.22640200	7.39240800
H	0.73289300	-2.14896400	6.23175000
H	2.43247700	-1.77259900	5.87742400
C	1.26744300	1.11109900	6.47387700
H	2.09352800	1.72088200	6.08093500
H	0.35708900	1.72153000	6.45592000
H	1.48511200	0.87252800	7.51474700
C	-2.98448100	6.39914600	-1.49739700
H	-3.36452300	6.32487500	-0.46896100
H	-3.02186200	7.44577000	-1.79821200
H	-3.66345700	5.83887200	-2.15143200
C	-0.54261500	6.86491800	-1.86727000
H	0.11717400	6.98633600	-0.99699600
H	0.07332800	6.55352100	-2.71946200
H	-0.97238700	7.83746900	-2.10554400
C	-6.41412400	-3.18795300	0.64336500
H	-7.32539000	-3.72420800	0.37956900
H	-5.87086400	-3.78195400	1.39198800
H	-6.70850400	-2.24073600	1.11035100
C	-5.97377100	-3.67692800	-1.77857400
H	-6.02516400	-2.99761300	-2.63744800
H	-5.25234000	-4.47161900	-2.01588000
H	-6.95597900	-4.13355800	-1.65863900
C	3.09618700	0.26017600	0.17789900
H	2.56556200	-0.52979400	0.73644700
O	2.85433600	1.44493400	0.38230600
C	4.13819600	-0.22594100	-0.74906600
C	4.89433400	0.67503800	-1.51410100
C	4.38785200	-1.60158000	-0.84160400
C	5.88624600	0.20091700	-2.36688600
H	4.68604200	1.73646800	-1.42366000

C	5.38434200	-2.07623700	-1.69277900
H	3.78082000	-2.29109000	-0.26152200
C	6.13230500	-1.17545900	-2.45568000
H	6.47076100	0.89559400	-2.96263900
H	5.57228900	-3.14273500	-1.76804000
H	6.90751100	-1.54355100	-3.12140000

(8) *E*-TS1

Total energy: -3982.84538892 Hartree

Free energy: = -3982.226020 Hartree

Imaginary frequency: 319.7 *i*cm^{-1}

C	0.57754300	-1.12517600	-1.16317200
As	-0.04902900	0.25640600	-0.01550400
C	1.05651100	4.52082400	-1.77484300
C	-0.22449500	4.25348300	-1.22584300
C	-0.53420300	3.00027800	-0.71748600
C	0.40567500	1.96052800	-0.72749000
C	1.68107200	2.21437900	-1.25336900
C	2.00217800	3.46211900	-1.76746800
H	-0.98290400	5.02512600	-1.19609900
H	-1.52815700	2.83546400	-0.31274600
H	2.42509200	1.42151700	-1.23952500
H	2.99802600	3.61492600	-2.16356000
C	-0.26568100	-2.30618500	-1.09414400
O	-0.37909700	-2.94114300	-2.28868700
O	-0.76633200	-2.74594000	-0.05587600
C	-1.13461600	-4.17477600	-2.29460600
H	-0.76878800	-4.71746600	-3.16915000
H	-0.89707100	-4.74667200	-1.39403800
C	-2.62660800	-3.89162800	-2.39097200
H	-3.18655000	-4.83117500	-2.43813700
H	-2.96056700	-3.32684900	-1.51729200
H	-2.85034000	-3.30947500	-3.28995200
H	0.77896900	-0.72887500	-2.15481100
C	0.58590600	0.12159900	1.76959700

C	1.24452800	1.19526800	2.37530400
C	0.39833800	-1.06080200	2.49695400
C	1.69911200	1.10450000	3.68328400
H	1.41316500	2.11303300	1.82077200
C	0.85044200	-1.16449400	3.80536300
H	-0.09977700	-1.90544500	2.03250100
C	1.51079300	-0.08092400	4.44050500
H	2.20855100	1.95676600	4.11399300
H	0.69334100	-2.09644700	4.33300100
C	-1.95204000	0.18988200	0.06525400
C	-2.69166500	-0.04000200	-1.10256000
C	-2.64754300	0.34380000	1.26808100
C	-4.07521200	-0.12317400	-1.07687800
H	-2.18087900	-0.18223600	-2.05124600
C	-4.03382700	0.27162800	1.31411800
H	-2.10427400	0.51141300	2.19299500
C	-4.79133000	0.03510600	0.13902800
H	-4.59903100	-0.31701300	-2.00379200
H	-4.52566200	0.38828500	2.27108600
N	1.36787700	5.75476700	-2.29309500
N	1.94758200	-0.17401300	5.74287900
N	-6.16464800	-0.03608700	0.17293300
C	1.85257900	-1.44256300	6.45116800
H	2.24237200	-1.31966000	7.46132000
H	0.81128600	-1.77574100	6.53366500
H	2.42660500	-2.23862500	5.95662800
C	2.72898400	0.90740300	6.32565200
H	3.66720100	1.08285100	5.78080600
H	2.16266200	1.84616900	6.33794300
H	2.97632900	0.65612700	7.35671300
C	0.39829000	6.83896000	-2.23106100
H	0.12788100	7.08994700	-1.19646900
H	0.82359400	7.72853900	-2.69460100
H	-0.52255300	6.58627400	-2.77118400
C	2.70878800	6.01884300	-2.79561100
H	3.47092100	5.90433800	-2.01313500

H	2.96752300	5.34667600	-3.62295800
H	2.75760200	7.04146800	-3.16826900
C	-6.86182100	0.00995100	1.45058700
H	-7.93554000	-0.05248000	1.27605300
H	-6.57260600	-0.81922300	2.11129700
H	-6.66353100	0.95031000	1.97811500
C	-6.90258400	-0.40884700	-1.02604700
H	-6.73195700	0.30786600	-1.83789000
H	-6.62577100	-1.40836800	-1.38944000
H	-7.96942300	-0.41080900	-0.80447600
C	2.35512400	-1.47967200	-0.40921900
H	1.95628500	-2.00971200	0.48278200
O	2.95180500	-0.36416800	-0.24130000
C	2.89058000	-2.46879300	-1.42382200
C	3.76034400	-2.03183100	-2.42829800
C	2.53561100	-3.82282900	-1.37258600
C	4.25535100	-2.92750300	-3.37671700
H	4.04047600	-0.98299100	-2.43731100
C	3.02961200	-4.72299300	-2.31736500
H	1.86421100	-4.16716800	-0.58901500
C	3.88946100	-4.27640100	-3.32564900
H	4.92982700	-2.57786200	-4.15398600
H	2.74724500	-5.77111000	-2.26743400
H	4.27630900	-4.97548400	-4.06174700

(9) *E*-INT

Total energy: -3982.85717497 Hartree

Free energy: = -3982.233719 Hartree

C	-1.10900400	0.58091300	-1.67977100
As	-0.29397900	-0.09538100	0.01389300
C	-0.04787300	-4.71362900	1.18460800
C	1.02036700	-3.81520900	1.43861800
C	0.93048000	-2.47948700	1.07486900
C	-0.22482000	-1.95861900	0.47274300
C	-1.28844400	-2.83643400	0.23291700

C	-1.20939000	-4.18053600	0.57042600
H	1.92806400	-4.16090600	1.91661200
H	1.78381100	-1.83745900	1.26761600
H	-2.19555200	-2.44535400	-0.21014900
H	-2.05983100	-4.81634900	0.35914600
C	-0.45008900	1.79673300	-2.24958800
O	0.43970500	1.47936900	-3.20392300
O	-0.68397200	2.94236500	-1.89643800
C	1.20645400	2.57485600	-3.77673800
H	1.59010200	2.16589700	-4.71324200
H	0.52447200	3.40012700	-3.99695300
C	2.33053800	3.00746200	-2.85013100
H	2.92959800	3.78254300	-3.33886000
H	1.92594500	3.41364700	-1.92111800
H	2.97592500	2.16113400	-2.60764300
H	-1.06872300	-0.26061500	-2.37548700
C	-0.46142200	1.05151000	1.53653000
C	-0.69203100	0.49603800	2.79791800
C	-0.40819100	2.44380700	1.41648900
C	-0.84209500	1.30135800	3.92003700
H	-0.75746500	-0.58211200	2.91308000
C	-0.56256300	3.26218300	2.53093400
H	-0.25444600	2.90887800	0.44842900
C	-0.77107800	2.71348600	3.81974200
H	-1.01971600	0.82624400	4.87640000
H	-0.52379600	4.33488000	2.39038600
C	1.61904700	0.13981800	-0.41979900
C	2.15782300	-0.56463500	-1.50547000
C	2.49763800	0.92461000	0.33218100
C	3.50243200	-0.48661200	-1.84163500
H	1.51710300	-1.20499000	-2.10740900
C	3.85019700	1.02321800	0.01382600
H	2.13287600	1.47602800	1.19303800
C	4.39096400	0.32757000	-1.09338500
H	3.86143500	-1.05865500	-2.68793000
H	4.48389700	1.64342300	0.63525100

N	0.04229200	-6.04563900	1.51668100
N	-0.89284700	3.52135800	4.93627900
N	5.72592600	0.43949300	-1.43659300
C	-1.02489600	4.96106500	4.76450500
H	-1.10946300	5.43265700	5.74368100
H	-0.14199300	5.38184900	4.27061600
H	-1.90972600	5.23614400	4.17147400
C	-1.31101900	2.93450700	6.20134400
H	-2.30360100	2.46383300	6.14128300
H	-0.59626800	2.17603700	6.53948100
H	-1.34748000	3.71362000	6.96293400
C	1.20773600	-6.53982100	2.23538800
H	1.32937200	-6.05159200	3.21223800
H	1.09900400	-7.61100300	2.40297200
H	2.12851100	-6.38288600	1.66063300
C	-1.10429300	-6.92221900	1.32624400
H	-1.97421100	-6.59938300	1.91479100
H	-1.40464600	-6.96440300	0.27235700
H	-0.83985700	-7.93243200	1.63756800
C	6.63948900	1.13265600	-0.54086300
H	7.63914900	1.13092500	-0.97562000
H	6.33997500	2.17790100	-0.40358000
H	6.69466000	0.66247800	0.45224300
C	6.28056300	-0.43554500	-2.45868800
H	6.19662100	-1.50005100	-2.19412900
H	5.77906600	-0.28582000	-3.42159700
H	7.33597700	-0.20076200	-2.59758900
C	-2.49211300	0.71808200	-1.01301800
H	-2.58435700	1.76553400	-0.66371300
O	-2.40490400	-0.19143800	0.03957400
C	-3.63090200	0.46134500	-1.98702300
C	-4.41203900	-0.69285500	-1.89070200
C	-3.89924000	1.38182700	-3.01041900
C	-5.43961200	-0.93187600	-2.80775000
H	-4.20806900	-1.38523000	-1.08123200
C	-4.92038800	1.14342200	-3.93007000

H	-3.30080600	2.28747700	-3.08165100
C	-5.69494400	-0.01750000	-3.83180400
H	-6.04287900	-1.83166800	-2.72061600
H	-5.11606400	1.86297100	-4.72041600
H	-6.49322200	-0.20275600	-4.54486400

(10) *E*-TS2

Total energy: -3982.84583890 Hartree

Free energy: = -3982.223714 Hartree

Imaginary frequency: 304.7 *i*cm^{-1}

C	0.97177000	-2.30264300	-1.51437700
As	-0.21540800	0.29587300	-0.44488700
C	-3.52176500	3.67753000	0.02262400
C	-2.34176100	3.68828900	0.81123300
C	-1.37253800	2.70764600	0.65573700
C	-1.51343500	1.68551300	-0.29038300
C	-2.67185800	1.66875200	-1.07687400
C	-3.65570900	2.63797300	-0.93333000
H	-2.17967600	4.46462400	1.54780300
H	-0.48320100	2.75948700	1.27803100
H	-2.79849200	0.88994900	-1.82176600
H	-4.52925600	2.58590900	-1.57040000
C	2.35906000	-2.01518100	-1.50338400
O	2.98828500	-2.61497800	-0.41335300
O	3.00549300	-1.34400000	-2.31821300
C	4.41228300	-2.45382300	-0.32529600
H	4.75753400	-3.30429900	0.27124100
H	4.85116300	-2.52502900	-1.32528400
C	4.78841400	-1.13242700	0.32800600
H	5.87617400	-1.05296300	0.43608700
H	4.43150100	-0.30366300	-0.28399900
H	4.33532300	-1.04556900	1.32026200
H	0.56871800	-2.98331100	-0.77744300
C	1.49951300	1.06147600	-0.20621200
C	2.00682300	1.31303500	1.07562900
C	2.24892600	1.46700800	-1.31601800

C	3.21439800	1.97223700	1.25114900
H	1.45912600	0.98567400	1.95436800
C	3.45787700	2.12723600	-1.15675600
H	1.88997500	1.24481800	-2.31451300
C	3.97479200	2.40617700	0.13485100
H	3.57250500	2.13488700	2.25908800
H	4.01256300	2.40685500	-2.04270900
C	-0.57256600	-0.84421000	1.04264000
C	-1.84074600	-0.82575100	1.63957000
C	0.42165300	-1.66389900	1.59894100
C	-2.12560800	-1.62146700	2.74035300
H	-2.62202800	-0.18784400	1.23873600
C	0.15774800	-2.44400800	2.71205800
H	1.40900200	-1.70055200	1.15228700
C	-1.13070400	-2.45554200	3.31338800
H	-3.12148800	-1.58292100	3.16222300
H	0.95529700	-3.05707400	3.11160600
N	-4.49557200	4.63587700	0.18006300
N	5.17294300	3.06599300	0.29942400
N	-1.39885800	-3.23971700	4.40658800
C	6.01813000	3.32167400	-0.85973800
H	6.91083600	3.85881300	-0.54000100
H	6.33236700	2.39466700	-1.36051400
H	5.50008200	3.94758800	-1.59415000
C	5.77156400	3.14786200	1.62529600
H	5.11830200	3.68565400	2.32101800
H	5.98182900	2.15573500	2.05016400
H	6.70957600	3.69892200	1.56119600
C	-4.28922800	5.73959000	1.10659200
H	-3.41195500	6.34459100	0.83933400
H	-5.16461900	6.38819800	1.09313700
H	-4.15400800	5.38063800	2.13421700
C	-5.65598700	4.64660000	-0.69892000
H	-5.37490800	4.78101500	-1.75247100
H	-6.22934800	3.71523200	-0.61653200
H	-6.31322400	5.46824800	-0.41588800

C	-0.36232800	-4.09632200	4.96665600
H	-0.76687400	-4.63658700	5.82175300
H	-0.00617700	-4.83413900	4.23633400
H	0.50111000	-3.51399200	5.31217200
C	-2.73175800	-3.24552700	4.99315900
H	-3.01940600	-2.24989000	5.35425000
H	-3.49061500	-3.57973400	4.27396500
H	-2.74787000	-3.92827800	5.84185800
C	0.12705700	-1.75883700	-2.51433600
H	0.65227300	-1.40877800	-3.40144400
O	-0.49616900	-0.18880900	-2.07442100
C	-1.14618100	-2.48747900	-2.80224100
C	-2.14414500	-2.59701000	-1.82204600
C	-1.34129400	-3.11397400	-4.03881400
C	-3.29632000	-3.34158000	-2.06372100
H	-2.01274700	-2.08077600	-0.87917000
C	-2.49876500	-3.85758600	-4.28404500
H	-0.57974200	-3.02563100	-4.80935600
C	-3.47879900	-3.97707800	-3.29656100
H	-4.05837100	-3.41910400	-1.29302700
H	-2.63500800	-4.33979500	-5.24796000
H	-4.37930700	-4.55369900	-3.48686300

(11) *E*-Product complex

Total energy: -3982.87892140 Hartree

Free energy: = -3982.257775 Hartree

C	3.12541200	-1.64280700	-1.11812900
As	-0.89422000	0.37639900	-0.75310700
C	-5.44474600	-0.23718100	0.46570100
C	-4.44676400	-0.04381500	1.45596000
C	-3.11588500	0.12822700	1.09988500
C	-2.71519700	0.13464100	-0.24200500
C	-3.69172700	-0.06237900	-1.22469600
C	-5.02701600	-0.24173800	-0.89068700
H	-4.70850000	-0.03768700	2.50628000
H	-2.37783200	0.25032000	1.88823700

H	-3.39241000	-0.08327000	-2.26885800
H	-5.74601400	-0.39024500	-1.68617800
C	3.60417900	-0.25394400	-1.14934900
O	4.65324800	-0.07571300	-0.30730200
O	3.14224000	0.64901000	-1.83312400
C	5.21356800	1.25951800	-0.25111600
H	6.20676600	1.11537600	0.17949300
H	5.31730000	1.64326400	-1.26975500
C	4.36957400	2.19839500	0.59891500
H	4.86969900	3.16923400	0.67937800
H	3.38907900	2.35260100	0.14413300
H	4.23911800	1.79703500	1.60803700
H	3.72960700	-2.35598000	-0.56826900
C	-0.40515500	2.21590300	-0.56180700
C	-1.01942100	3.07177800	0.35828200
C	0.68508300	2.70246300	-1.29437300
C	-0.57341100	4.37464200	0.54323700
H	-1.86378800	2.72482700	0.94817400
C	1.15215300	3.99832700	-1.11464600
H	1.19517800	2.05054000	-1.99508100
C	0.53089300	4.87701900	-0.19123500
H	-1.08080200	4.99818300	1.26819500
H	2.00689200	4.32289300	-1.69416500
C	0.12732000	-0.51759600	0.59571500
C	-0.15209900	-1.85101100	0.92151600
C	1.25101500	0.08434100	1.17263700
C	0.69883900	-2.58830200	1.73028300
H	-1.03091500	-2.33450800	0.50605500
C	2.11418500	-0.63816100	1.98263500
H	1.48196200	1.12174100	0.95693600
C	1.88699700	-2.01222500	2.24528800
H	0.46053300	-3.62632700	1.92192000
H	2.98903800	-0.14152100	2.37910600
N	-6.76484500	-0.42375800	0.80822800
N	0.98247800	6.16945500	-0.01738500
N	2.79340300	-2.76074800	2.97137400

C	2.23906400	6.57803000	-0.62993800
H	2.44274100	7.61708100	-0.37159500
H	3.08759300	5.96552100	-0.29157200
H	2.18756700	6.51165700	-1.72250200
C	0.43063700	6.98691800	1.05358500
H	-0.64938300	7.12305200	0.92912000
H	0.60666900	6.55194500	2.04838400
H	0.89214200	7.97395800	1.02533000
C	-7.17782000	-0.31254500	2.19959800
H	-6.96468100	0.68161700	2.61648600
H	-8.25100000	-0.48723200	2.27094300
H	-6.67551200	-1.05849000	2.82742100
C	-7.77885800	-0.52598400	-0.23125500
H	-7.82794800	0.37905800	-0.85258800
H	-7.58992300	-1.38092000	-0.89158600
H	-8.75419400	-0.67328000	0.23173500
C	4.11517700	-2.19967800	3.22942300
H	4.72737300	-2.94402100	3.73842500
H	4.62659000	-1.89725800	2.30385600
H	4.05038700	-1.32278300	3.88267400
C	2.65399400	-4.21206300	2.98430200
H	1.71595900	-4.51278500	3.46258000
H	2.67376200	-4.64260600	1.97170300
H	3.47039500	-4.64560600	3.56192300
C	1.94521100	-1.95722200	-1.68483200
H	1.36218900	-1.15057700	-2.12472800
O	-0.66119500	-0.13354100	-2.32590500
C	1.31117600	-3.27614700	-1.69156700
C	1.99911500	-4.45938100	-1.36276700
C	-0.06023000	-3.35533700	-2.00361000
C	1.33301300	-5.68197300	-1.33204600
H	3.06106900	-4.42404700	-1.13946100
C	-0.72382500	-4.58088300	-1.96875400
H	-0.59682700	-2.43380200	-2.21679900
C	-0.03213500	-5.74755000	-1.63266500
H	1.87777700	-6.58662900	-1.07801000

H	-1.78441100	-4.62569400	-2.19954600
H	-0.54949300	-6.70217300	-1.60708700

(11) *E*-ethyl cinnamate

Total energy: -576.891977801 Hartree

Free energy: = -576.726324 Hartree

C	-0.63075800	-0.30360400	0.18335400
C	-2.00466600	0.22536800	0.26324500
O	-2.90055300	-0.78690900	0.33375300
O	-2.31655800	1.40711900	0.26971600
C	-4.30051900	-0.41508500	0.39978500
H	-4.79084000	-1.28418300	0.84317100
H	-0.52489100	-1.38283500	0.19092300
C	0.41686900	0.53839400	0.10469400
H	-4.40999100	0.44087400	1.07059200
C	-4.85121800	-0.10639300	-0.98378200
H	-5.92296900	0.10575100	-0.91798900
H	-4.34914500	0.76709500	-1.40610700
H	-4.70723800	-0.95772300	-1.65523800
H	0.18521800	1.60247000	0.10469500
C	1.83540700	0.19395000	0.01898700
C	2.77743500	1.23708200	-0.05788100
C	2.30575300	-1.13478800	0.00925200
C	4.14230700	0.96669000	-0.14188000
H	2.42998300	2.26662900	-0.05117900
C	3.66788700	-1.40372100	-0.07464400
H	1.60365800	-1.96010500	0.06768000
C	4.59193000	-0.35497600	-0.15063100
H	4.85277500	1.78553700	-0.20033600
H	4.01353600	-2.43298700	-0.08103200
H	5.65422800	-0.56970200	-0.21593000

5. References

[1] S. Omar, R. Abu-Rezig, *J. Phys. Chem. C*. **2014**, *118*, 30045–30056.

[2] P. Wang, C-R. Liu, X-L. Sun, S-S. Chen, J-F. Li, Z. Xie, Y. Tang, *Chem. Commun.* **2012**, *48*, 290–292.

[3] G. Obi, F. R. V. Heerden, *Synth*. *Commun*. **2018**, *12*, 1482–1486.

[4] H. Zhang, X. Huang, *Adv*. *Synth*. *Catal*. **2016**, *358*, 3736–3742.

[5] P. S-W. Leung, Y. Teng, P. H. Toy, *Org. Lett.*, **2010**, *12*, 4996–4999.

[6] H. Zhang, X. Huang, *Adv*. *Synth*. *Catal*. **2016**, *358*, 3736–3742.

[7] N. K. Jobson, R. Spike, A. R. Crawford, D. Dewar, S. L. Pimlott, A. Sutherland, *Org. Biomol. Chem.* **2008**, *6*, 2369–2376.

[8] H. Lebel, M. Davi, *Adv, Synth, Catal*. **2008**, *350*, 2352–2358.

[9] R. Inaba, I. Kawashima, T. Fujii, T. Yumura, H. Imoto, K. Naka, *Chem. Eur. J*. **2020**, *26*, 13400–13407.

[10] M. Hyotanishi, Y. Isomura, H. Yamamoto, H. Kawasaki, Y. Obora, *Chem. Commun.* **2011**, *47*, 5750–5752.

[11] J. Ruan, X. Li, O. Saidi, J. Xiao, *J. Am. Chem. Soc.* **2008**, *130*, 2424–2425.